THE METHOD OF VOLUME AVERAGING

Theory and Applications of Transport in Porous Media

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The Method of Volume Averaging

by

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For

Suzanne

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PREFACE

This monograph is based on a graduate course that has been taught at UC Davis since 1976, and the subjects have been selected primarily for their pedagogical value. Most of the material can be covered in 28 one-hour lectures; however, shorter versions of a course can be developed by omitting several sections that are especially time consuming or by omitting one or more of the five chapters. The problems at the end of each chapter represent an integral part of the monograph and the solutions are available from the author.

Chapter 1 deals with bulk diffusion and heterogeneous reaction in porous media, and it serves to present the key elements of the method of volume averaging. In an abbreviated treatment, one can omit Sec. 1.1 and begin with Sec. 1.2 where the boundary value problem for diffusion and reaction is analyzed. Section 1.2 is crucial to all that follows. The origins of many of the length-scale constraints that appear in the method of volume averaging are discussed in Sec. 1.3. If one is willing to accept those constraints without proof, this section can be omitted. The closure problem that is developed in Sec. 1.4 is also crucial to all that follows, while the material on symmetric unit cells that is presented in Sec. 1.5 can be accepted without proof if one is inclined to do so. Section 1.6 deals with the comparison between theory and experiment and this is an essential part of Chapter 1.

Chapter 2 represents a study of transient heat conduction in two-phase systems, and one of the dominant concepts in this chapter is the *principle of local thermal equilibrium*. All multiphase transport processes should be considered both in terms of a theory for the *separate dependent variables* associated with each phase, and in terms of a *single dependent variable* that might accurately describe the multiphase transport process. Section 2.3 deals with this specific problem.

Chapter 3 has a single objective which is to examine the phenomena of spatial dispersion. Since both spatial and temporal dispersion occur in many processes of interest to engineers, it is important to clearly identify the physics associated with spatial dispersion and this is best done in a study of *passive* dispersion. Here the word passive refers to the *absence* of adsorption, heterogeneous reaction, and interphase mass transport. These phenomena are of great importance to many engineers and scientists, and dispersion in *active* systems is examined in several of the problems at the end of the chapter.

Chapter 4 is devoted to the derivation of Darcy's law. This result is the key to understanding a wide variety of processes involving flow in porous media, and it also serves as an excellent example of the role of the closure problem in the determination of the final form of the volume averaged transport equation.

Chapter 5 represents a study of single-phase flow in heterogeneous porous media. Since most real systems are heterogeneous at some scale of interest, it is this last short chapter that provides a theoretical foundation for many important problems of transport in porous media.

Several colleagues have played key roles in the development of this monograph. Discussions with John Slattery (Texas A&M University) in 1962 led to an effort to prove Darcy's law, and this motivated much of the early work on volume averaging. Studies with Ruben Carbonell (North Carolina State University), beginning in 1973, resulted in closure problems that allowed us to predict effective diffusivities, effective thermal conductivities, and dispersion coefficients. In this same period, discussions with Bill Gray (Notre Dame University) provided an improved understanding of the spatial deviation transport equation and the closure problem. In 1984 an extensive analysis of diffusive transport in two-phase systems was initiated with Alberto Ochoa-Tapia (Universidad Autónoma Metropolitana) and parts of that work are found in Chapters 1 and 2. During a sabbatical in 1985, work began with Michel Quintard (Institut de Mécanique des Fluides de Toulouse) on the material presented in Chapter 5, and a series of studies followed that dealt with the problem of transport in heterogeneous porous media. In the summer of 1991, the general problem of local and large-scale equilibrium was explored and some of the results of that work are found in Chapter 2.

Many other colleagues and students have contributed to the completion of this monograph. In addition to the regular presentation of the graduate course at UC Davis, abbreviated versions have been taught at Universidad Nacional del Sur, Universidad Nacional del Litoral, Universidad Simón Bolívar, Tsing Hua University, and Centro de Investigación Energía (UNAM), while the complete course has been presented at Université de Bordeaux I, Technische Universiteit of Eindhoven, Wageningen Agricultural University, and the Center for Nonlinear Studies at Los Alamos. The contributions of students and faculty in Argentina, Venezuela, Taiwan, México, The Netherlands, France, New Mexico, and Davis are greatly appreciated.

Stephen Whitaker

OVERVIEW

The method of volume averaging is a technique that can be used to rigorously derive continuum equations for multiphase systems. This means that equations which are *valid within a particular phase* can be spatially smoothed to produce equations that are *valid everywhere*. For example, in the process of drying a porous medium, one needs to know how water is transported *through the pores* to the external surface where it is removed by warm, dry air. The direct analysis of this process, in terms of transport equations that are valid within the pores, is essentially impossible because of the complex structure of the typical porous medium. Rather than attack this problem in terms of equations and boundary conditions that are *valid in the pores*, we can use the pore-scale information to derive local volume averaged equations that are *valid everywhere*. Given these latter equations, the moisture transport problem can be solved using classical methods.

Single-phase flow in porous media represents a well known process in which volume averaged transport equations, suggested by Darcy in 1856, are used to analyze the flow. In this case, the velocity field in the pore space is determined by Stokes' equations, the continuity equation, and the no-slip boundary condition given by

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta, \quad \text{in the } \beta\text{-phase} \tag{1}$$

$$\nabla \cdot \mathbf{v}_\beta = 0, \quad \text{in the } \beta\text{-phase} \tag{2}$$

B.C. $$\mathbf{v}_\beta = 0, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

The *change of scale* that can be accomplished by the method of volume averaging leads to Darcy's law and the volume averaged continuity equation which we express as

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta} \cdot \left(\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g} \right), \quad \text{in the porous medium} \tag{4}$$

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle = 0, \quad \text{in the porous medium} \tag{5}$$

This change of scale is illustrated in Figure 1 where we have indicated that Stokes' equations are valid in the β-phase that occupies the pores, and that Darcy's law is valid *everywhere* in the porous medium. To obtain Eq. 4 from Eqs. 1 and 3, one first forms the *local volume average* of Stokes' equations. This leads to an averaged equation that contains *spatial deviations* of the pressure and velocity for which one must develop a *closure problem*. In the case of Darcy's law, the closure problem controls the form of the macroscopic equation and it provides a means of *predicting* the permeability tensor, $\mathbf{K}_\beta$. The continuity equation given by Eq. 5 is obtained directly from Eq. 2 without the use of a closure problem.

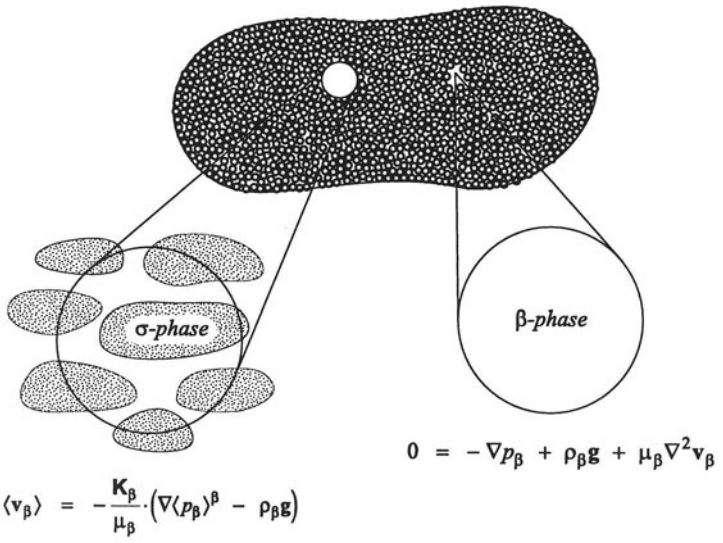


Figure 1. Change of scale

Most porous media of practical importance are hierarchical in nature, i.e., they are characterized by more than one length scale. When these length scales are disparate, the hierarchical structure can be analyzed by the method of volume averaging. There is a tendency to think of hierarchical systems as geological in origin; however, an example of a different type is the packed bed catalytic reactor shown in Figure 2. The essential

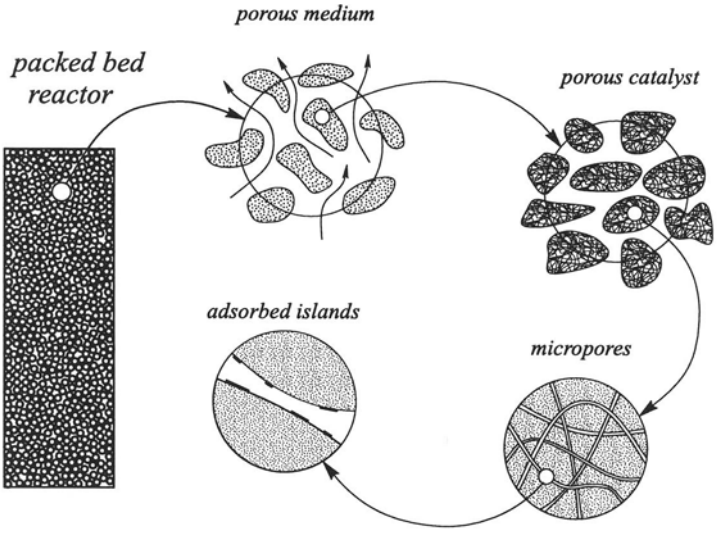


Figure 2. Length scales and averaging volumes for a catalytic reactor

macroscopic characteristic of the reactor is the change in the concentration that occurs from the inlet to the outlet, and this change is determined by the heterogeneous chemical reaction that takes place at the non-uniform catalytic surface suggested by the absorbed islands in Figure 2. The efficient design of a catalytic reactor requires that information about the rate of reaction at the catalytic surface be accurately transported through several length scales to the *design length-scale.*

Often the hierarchical system illustrated in Figure 2 is studied experimentally at the level of the porous medium in order to extract a rate expression for the conversion of a particular chemical species. Such experiments are usually carried out in the absence of concentration gradients in order to facilitate the interpretation of the data. If the concentration gradients in the porous catalyst are also negligible in the design application, one proceeds *up* the hierarchy of length scales to derive a volume averaged transport equation for the packed bed. This allows one to predict the rate of chemical reaction *per unit volume of the reactor.* On the other hand, if the concentration gradients in the porous catalyst are not negligible in the design application, one must proceed *down* the hierarchy of length scales in order to accurately describe the coupled process of diffusion and reaction. In a complete study, this procedure would descend to the level of the heterogeneous catalytic surface.

In geological transport problems, one also encounters hierarchical systems such as the stratified aquifer illustrated in Figure 3. Large-scale averaged equations are required to describe chemical transport within the aquifer, and these are derived on the basis of Darcy-scale transport equations. At the Darcy scale, we have illustrated clusters of microbes that may metabolize chemical contaminants which are transported by the flowing fluid, and this process is represented by the well known equations of continuum physics. The particles that make up the porous medium are often porous themselves, and significant adsorption of chemical species may take place within the particles. This means that volume averaged transport equations must be derived for diffusion and adsorption in the porous particles. In order to develop equations that accurately predict the fate of chemicals within the aquifer, one must *transport information* over several length scales. When the length scales are disparate, this can be accomplished by the method of volume averaging.

At each level of averaging there are three principle objectives. The first objective is the development of the *spatially smoothed equations* and the identification of the constraints that must be satisfied in order for these equations to be valid. The second objective is the derivation of the *closure problems* that are necessary to predict the effective transport coefficients that appear in the spatially smoothed transport equations. The third objective is the successful *comparison between theory and experiment,* and this represents a serious challenge for hierarchical systems.

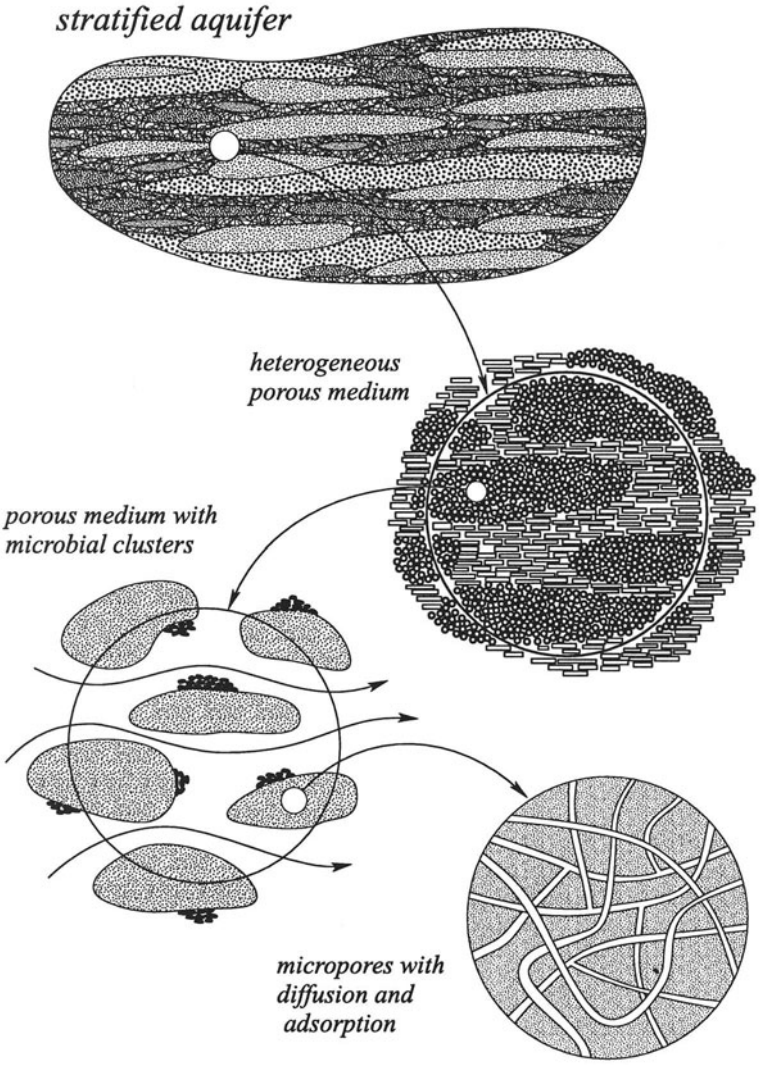


Figure 3. Length scales and averaging volumes in a geological system

Chapter 1

Diffusion and Heterogeneous Reaction in Porous Media

In this chapter we consider the process of bulk diffusion in a porous catalyst with heterogeneous, first order, irreversible reaction. Simultaneous diffusion and reaction occurs in such diverse systems as porous catalysts, (Jackson, 1977), soil aggregates (Rappoldt, 1990), and biofilms (Wood and Whitaker, 1998), and our objective in this chapter is to illustrate a general procedure by which governing point equations and boundary conditions for diffusion and reaction can be spatially smoothed to produce continuum models for multiphase systems. Our specific objectives in this chapter are four in number and we list them as:

1. To illustrate the process of *spatial smoothing* which leads to the governing equation for the local volume averaged concentration, $\langle c_{A\gamma} \rangle^{\gamma}$.
2. To develop the *closure problem* for the spatial deviation concentration $\tilde{c}_{A\gamma}$ that appears in the spatially smoothed equation for $\langle c_{A\gamma} \rangle^{\gamma}$.
3. To solve the closure problem in order to *predict* values of the effective diffusivity tensor, $\mathbf{D}_{eff}$.
4. To compare theory and experiment in the *absence of adjustable parameters.*

The process of *spatial smoothing* and the development of the *closure problem* are especially important aspects of this first chapter since these developments will be repeated with only minor variations in each of the remaining four chapters.

1.1 Governing Equations and Boundary Conditions

The governing equation for the concentration of species A in an N-component system can be expressed as

$$\underbrace{\frac{\partial c_A}{\partial t}}_{\substack{\text{bulk}\\ \text{accumulation}}} + \underbrace{\nabla\cdot(c_A \mathbf{v}_A)}_{\substack{\text{bulk}\\ \text{transport}}} = \underbrace{R_A}_{\substack{\text{homogeneous}\\ \text{reaction}}}, \quad A = 1, 2, \ldots, N \tag{1.1-1}$$

in which c_A is the molar concentration, and R_A is the molar rate of production per unit volume owing to *homogeneous* chemical reaction. The velocity of species A is represented by $\mathbf{v}_A$ and this must be determined by the laws of mechanics for multicomponent systems. At the interface in a fluid-fluid system, such as the β-γ system, the jump condition *associated with* Eq. 1.1-1 can be expressed as (Whitaker, 1992)

$$\underbrace{\left.\frac{dc_{As}}{dt}\right|_{\mathbf{n}_{\beta\gamma}(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}}_{\substack{\text{surface}\\ \text{accumulation}}} + \underbrace{\nabla_s\cdot(c_{As}\mathbf{v}_{As})}_{\substack{\text{surface}\\ \text{transport}}} + \underbrace{c_{As}(\nabla_s\cdot\mathbf{n}_{\beta\gamma})(\mathbf{w}\cdot\mathbf{n}_{\beta\gamma})}_{\substack{\text{effect of changing}\\ \text{surface area}}}$$

$$= \underbrace{\left[c_{A\beta}(\mathbf{v}_{A\beta}-\mathbf{w})\cdot\mathbf{n}_{\beta\gamma} + c_{A\gamma}(\mathbf{v}_{A\gamma}-\mathbf{w})\cdot\mathbf{n}_{\gamma\beta}\right]}_{\substack{\text{interfacial flux from the}\\ \text{bulk phases to the surface}}} + \underbrace{R_{As}}_{\substack{\text{heterogeneous}\\ \text{reaction}}} \tag{1.1-2}$$

Here we have used a subscript s to identify all surface quantities, thus c_{As} represents the *surface concentration* of species A having units of moles *per unit area* and R_{As} represents the *heterogeneous* rate of reaction having units of moles per unit time *per unit area*. The accumulation term in Eq. 1.1-2 is given in terms of the time rate of change of the surface concentration measured by an observer moving normal to the surface at the *speed of displacement* of the surface, $\mathbf{w}\cdot\mathbf{n}_{\beta\gamma}$, and the surface transport is represented in terms of the surface concentration c_{As} and the surface velocity $\mathbf{v}_{As}$ (Slattery,1990). In Eq. 1.1-2 we have used ∇_s to represent the *surface gradient operator* (Ochoa-Tapia *et al*, 1993), while ∇ is the traditional three-space gradient operator that appears in Eq. 1.1-1. The third term on the left hand side of Eq. 1.1-2 represents the rate of change of the surface concentration owing to the rate of change of surface area per unit area, and this term is important, for example, in the analysis of a growing soap bubble. Often the flux of a chemical species from a bulk phase to an interface represents the most important aspect of a mass transfer process. In the jump condition given by Eq. 1.1-2, the flux of species A *from* the β-phase *to the surface* is given by $c_{A\beta}(\mathbf{v}_{A\beta}-\mathbf{w})\cdot\mathbf{n}_{\beta\gamma}$, while the flux of species A *from* the γ-phase *to the surface* is given a similar expression, $c_{A\gamma}(\mathbf{v}_{A\gamma}-\mathbf{w})\cdot\mathbf{n}_{\gamma\beta}$. The unit normal vectors have the characteristic that $\mathbf{n}_{\beta\gamma}$ is directed from the β-phase toward the γ-phase and $\mathbf{n}_{\gamma\beta}$ is directed from the γ-phase toward the β-phase.

In this chapter, we are concerned with the system illustrated in Figure 1.1 where the κ-phase represents a rigid solid in contact with a fluid phase which is identified as the γ-phase. The γ-κ interface is a catalytic surface at which chemical reactions can take place, and in general both the κ-phase and the γ-phase will be continuous. The governing equation for the concentration of species A can be expressed as

$$\frac{\partial c_{A\gamma}}{\partial t} + \nabla \cdot \mathbf{N}_{A\gamma} = R_{A\gamma}, \quad \text{in the } \gamma\text{-phase} \tag{1.1-3}$$

in which $\mathbf{N}_{A\gamma}$ is the molar flux of species A given by

$$\mathbf{N}_{A\gamma} = c_{A\gamma}\mathbf{v}_{A\gamma} \tag{1.1-4}$$

The jump condition for species A at the γ-κ interface is a simplified version of Eq. 1.1-2 that can be expressed as

$$\underbrace{\frac{\partial c_{As}}{\partial t}}_{\substack{\text{surface}\\ \text{accumulation}}} + \underbrace{\nabla_s \cdot \mathbf{N}_{As}}_{\substack{\text{surface}\\ \text{transport}}} = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}}_{\substack{\text{exchange with}\\ \text{bulk phase}}} + \underbrace{R_{As}}_{\substack{\text{heterogeneous}\\ \text{reaction}}}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1.1-5}$$

Here $\mathbf{n}_{\gamma\kappa}$ represents the unit normal vector pointing *from* the γ-phase *toward* the κ-phase, thus $\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}$ represents the molar flux of species A from the fluid phase to the catalytic surface. In the absence of surface accumulation and surface transport, $\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}$ is balanced by the molar rate of production of species A owing to *heterogeneous* chemical reaction, R_{As}.

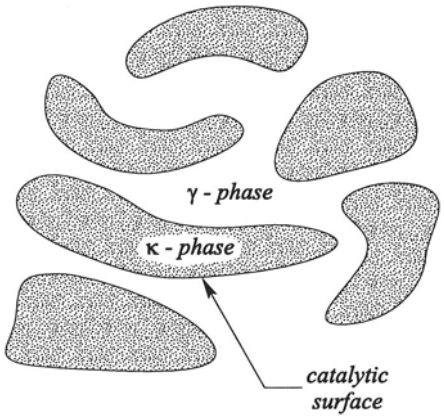


Figure 1.1. Catalytic porous medium

The surface and bulk concentrations are connected by an *interfacial flux constitutive equation*, and the simplest model available is the linear relation given by

$$\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma} = k_1 c_{A\gamma} - k_{-1} c_{As}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1.1-6}$$

Here k_1 is referred to as the adsorption rate constant and k_{-1} is known as the desorption rate constant. Use of Eq. 1.1-6 leads to a linear adsorption isotherm and this imposes a significant simplification on the process under consideration.

In order to evaluate the molar flux, $\mathbf{N}_{A\gamma}$, we require the species velocity, $\mathbf{v}_{A\gamma}$, that is determined by the *species momentum equation* (Whitaker, 1986a and 1987a). In the absence of Knudsen diffusion effects and electrical forces, the mechanical problem associated with the determination of $\mathbf{v}_{A\gamma}$ can be described by the Stefan-Maxwell equations

$$0 = -\nabla x_{A\gamma} + \sum_{B=1}^{B=N} \frac{x_{A\gamma}\mathbf{N}_{B\gamma} - x_{B\gamma}\mathbf{N}_{A\gamma}}{c_\gamma \mathscr{D}_{AB}}, \quad A = 1, 2, \ldots, N-1 \tag{1.1-7}$$

and the Navier-Stokes equations

$$\rho_\gamma \left(\frac{\partial \mathbf{v}_\gamma}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \mathbf{v}_\gamma\right) = -\nabla p_\gamma + \rho_\gamma \mathbf{g} + \mu_\gamma \nabla^2 \mathbf{v}_\gamma \tag{1.1-8}$$

Here $x_{A\gamma}$ is the mole fraction of species A given by

$$x_{A\gamma} = c_{A\gamma} \Big/ \sum_{B=1}^{B=N} c_{B\gamma} \tag{1.1-9}$$

and $\mathbf{v}_\gamma$ represents the mass average velocity defined by

$$\mathbf{v}_\gamma = \sum_{B=1}^{B=N} \omega_{B\gamma} \mathbf{v}_{B\gamma} \tag{1.1-10}$$

The mass fraction, $\omega_{A\gamma}$, can be expressed in terms of the species densities according to

$$\omega_{A\gamma} = \rho_{A\gamma} \Big/ \sum_{B=1}^{B=N} \rho_{B\gamma} \tag{1.1-11}$$

The N–1 independent Stefan-Maxwell equations given by Eq. 1.1-7 represent a simplified form of the *species momentum equations,* while the Navier-Stokes equations given by Eq. 1.1-8 represent the *sum* of the N species momentum equations for the incompressible flow of a Newtonian fluid (Whitaker, 1991a).

One must think of Eqs. 1.1-7 and 1.1-8 as the N equations that are normally used to determine the N species velocities that appear explicitly in Eqs. 1.1-1 and 1.1-2. When N is greater than two, the problem of determining the concentration in an N-component system represents a challenging task. Often the complexity associated with Eqs. 1.1-7 and 1.1-8 is avoided by imposing two constraints on the system of governing equations. These are given by

I. $$x_{A\gamma} << 1 \tag{1.1-12}$$

II. $$\mathbf{N}_{B\gamma} = \mathbf{O}\left(\mathbf{N}_{A\gamma}\right), \quad B = 1, 2, \ldots, N \tag{1.1-13}$$

When these two constraints are used with the Stefan-Maxwell equation for species A, we obtain,

$$\mathbf{N}_{A\gamma} = -c_\gamma \mathscr{D}_{Am} \nabla x_{A\gamma} \tag{1.1-14}$$

in which $\mathscr{D}_{Am}$ is the mixture diffusivity for species A given by

$$\frac{1}{\mathscr{D}_{Am}} = \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_{B\gamma}}{\mathscr{D}_{AB}} \tag{1.1-15}$$

For a system constrained by Eqs. 1.1-12 and 1.1-13, one can usually neglect variations in the total molar concentration so that the molar flux given by Eq. 1.1-14 takes the form

$$\mathbf{N}_{A\gamma} = -\mathscr{D}_{Am} \nabla c_{A\gamma} \tag{1.1-16}$$

Substitution of this result into Eq. 1.1-3 leads to the classic governing equation for diffusion and reaction of species A in the absence of convective transport.

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla \cdot \left(\mathscr{D}_{Am} \nabla c_{A\gamma}\right) + R_{A\gamma} \tag{1.1-17}$$

While this result is ubiquitous in the chemical engineering literature, one must remember that it was obtained on the basis of the severe constraints represented by Eqs. 1.1-12 and 1.1-13 along with the plausible intuitive hypothesis that small causes give rise to small effects (Birkhoff, 1960).

1.1.1 BOUNDARY CONDITION

To develop the boundary condition at the γ-κ interface, we consider a first order, irreversible, heterogeneous reaction in which species A is being consumed. For this case R_{As} is given by

$$R_{As} = -k_s c_{As}, \quad \text{at the } \gamma - \kappa \text{ interface} \tag{1.1-18}$$

and when surface transport is negligible we can use this result in Eq. 1.1-5 to obtain

$$\underbrace{\frac{\partial c_{As}}{\partial t}}_{\substack{\text{surface} \\ \text{accumulation}}} = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}}_{\substack{\text{exchange with} \\ \text{bulk phase}}} - \underbrace{k_s c_{As}}_{\substack{\text{heterogeneous} \\ \text{reaction}}} \tag{1.1-19}$$

For processes in which the rate of accumulation is negligible, Eq. 1.1-19 reduces to (see Problem 1-1)

$$0 = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}}_{\substack{\text{exchange with} \\ \text{bulk phase}}} - \underbrace{k_s c_{AS}}_{\substack{\text{heterogeneous} \\ \text{reaction}}} \tag{1.1-20}$$

and one can use Eq. 1.1-6 to obtain

$$0 = \underbrace{k_1 c_{A\gamma}}_{\text{adsorption}} - \underbrace{k_{-1} c_{AS}}_{\text{desorption}} - \underbrace{k_s c_{AS}}_{\substack{\text{heterogeneous} \\ \text{reaction}}} \tag{1.1-21}$$

This result allows us to solve for c_{AS} in terms of $c_{A\gamma}$ leading to

$$c_{AS} = \left(\frac{k_1}{k_s + k_{-1}}\right) c_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1.1-22}$$

Substitution of this expression into Eq. 1.1-18 provides the following representation for the heterogeneous reaction rate in terms of the bulk concentration:

$$R_{AS} = -k_s c_{AS} = -\left(\frac{k_s k_1}{k_s + k_{-1}}\right) c_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1.1-23}$$

If a Langmuir adsorption model is used in place of Eq. 1.1-6, one finds a nonlinear representation for the heterogeneous reaction rate (see Problems 1-2 and 1-24) instead of the linear relation given by Eq. 1.1-23. We can use Eq. 1.1-23, along with Eqs. 1.1-16 and 1.1-20 to express the diffusive flux at the catalytic surface as

$$-\mathbf{n}_{\gamma\kappa} \cdot \mathscr{D}_{Am} \nabla c_{A\gamma} = k c_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1.1-24}$$

in which the *pseudo reaction rate constant*, k, is given by

$$k = \left(\frac{k_s k_1}{k_s + k_{-1}}\right) \tag{1.1-25}$$

The boundary condition given by Eq. 1.1-24 can be used to study the process of *diffusion and reaction* in a porous catalyst provided that the catalytic surface is quasi-steady. When the rate of accumulation in Eq. 1.1-19 is significant and the rate of heterogeneous reaction is negligible, we have the important case of *diffusion and adsorption* (see Problems 1-3 and 1-23). When both surface accumulation and heterogeneous reaction are important, the problem becomes more difficult and the analysis is given elsewhere (Whitaker, 1986b).

1.2 Spatial Smoothing

In most problems of diffusion and reaction in porous media, homogeneous reactions can be ignored and we will do so in this study. This means that our boundary value problem can be expressed as

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot\left(\mathscr{D}_{\gamma}\nabla c_{A\gamma}\right), \quad \text{in the } \gamma\text{-phase} \tag{1.2-1}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_{\gamma}\nabla c_{A\gamma} = k\,c_{A\gamma}, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.2-2}$$

B.C.2 $$c_{A\gamma} = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\gamma e} \tag{1.2-3}$$

I.C. $$c_{A\gamma} = \mathscr{G}(\mathbf{r}), \quad \text{at } t=0 \tag{1.2-4}$$

in which $\mathscr{D}_{\gamma}$ is the mixture diffusivity defined by Eq. 1.1-15. In this formulation, we have used $\mathscr{A}_{\gamma e}$ to represent the entrances and exits of the γ-phase at the boundary of the macroscopic region illustrated in Figure 1.2, and we have used $\mathscr{A}_{\gamma\kappa}$ to represent the

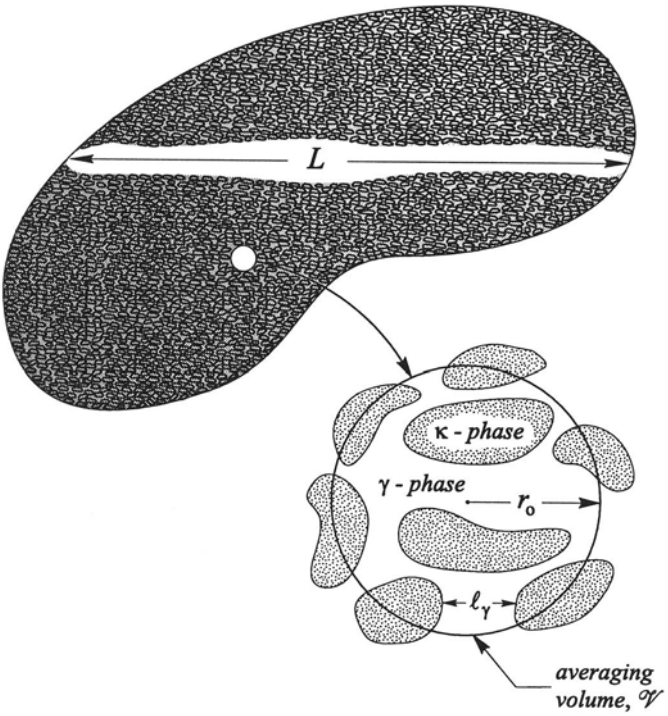


Figure 1.2. Macroscopic region and averaging volume

entire interfacial area within that region. It should be clear that, in general, the point concentration will not be known at $\mathscr{A}_{\gamma e}$ and Eq. 1.2-3 serves primarily as a reminder of what we *do not know* about $c_{A\gamma}$ at $\mathscr{A}_{\gamma e}$ rather than what we do know. The same can be said about the initial condition for $c_{A\gamma}$ since we will usually know something about the

average concentration at $t = 0$, but we will rarely know anything about the details of the *point concentration.*

If the information represented by Eqs. 1.2-3 and 1.2-4 were available to us, and if we knew the position of the γ-κ interface, we could solve the boundary value problem in order to determine $c_{A\gamma}$ as a function of position and time (see Problem 1-4). We could then calculate the rate of reaction of species A per unit volume of the porous medium and make use of this quantity in the design of a catalytic reactor. Even if we could solve this boundary value problem exactly, we would not do so since the solution would yield more information than we need. For design purposes, it is sufficient to determine the *average concentration* and the *average rate of reaction* associated with the averaging volume $\mathscr{V}$ illustrated in Figure 1.2. The details of this averaging volume are presented in Figure 1.3 where we have used the position vector $\mathbf{r}_\gamma$ to locate any point in the γ-phase. The position vector $\mathbf{x}$ locates the centroid of the averaging volume which may lie in either the γ-phase or the κ-phase. The *relative position vector* $\mathbf{y}_\gamma$ is used to locate points in the γ-phase relative to the centroid of $\mathscr{V}$.

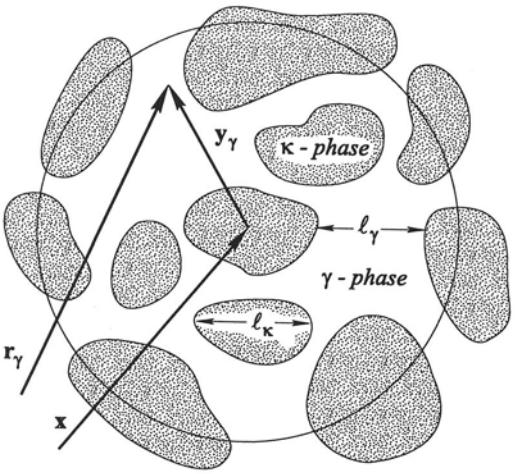


Figure 1.3. Averaging volume for the γ-κ system

The process of spatial smoothing begins by associating with *every* point in space an averaging volume which is invariant with respect to time and space. For the two-phase system under consideration we can express the averaging volume as

$$\mathscr{V} = V_\gamma(\mathbf{x}) + V_\kappa(\mathbf{x}) \tag{1.2-5}$$

Here $V_\gamma(\mathbf{x})$ represents the volume of the γ-phase contained within the averaging volume, and the volume fraction of the γ-phase (usually identified as the *porosity*) is given by

$$\varepsilon_\gamma = V_\gamma(\mathbf{x})/\mathscr{V} \tag{1.2-6}$$

In the method of volume averaging one encounters many *measures of concentration* and it is necessary to identify each of them in some precise manner. We begin by defining the *superficial average* of $c_{A\gamma}$ according to

$$\langle c_{A\gamma}\rangle\big|_{\mathbf{x}} = \frac{1}{\mathscr{V}}\int_{V_\gamma(\mathbf{x})} c_{A\gamma}\big|_{\mathbf{x}+\mathbf{y}_\gamma}\, dV \tag{1.2-7}$$

This definition clearly indicates that the average concentration is associated with the centroid of the averaging volume, indicated by the position vector $\mathbf{x}$ in Figure 1.3, while integration over $V_\gamma(\mathbf{x})$ is performed in terms of the components of the relative position vector $\mathbf{y}_\gamma$. In general, we will avoid the precise notation used in Eq. 1.2-7 and simply express the superficial average as

$$\langle c_{A\gamma}\rangle = \frac{1}{\mathscr{V}}\int_{V_\gamma} c_{A\gamma}\, dV \tag{1.2-8}$$

The superficial average concentration is not the *preferred dependent variable* since it is not a good representation of the concentration in the γ-phase. For example, if $c_{A\gamma}$ were a constant given by $c^\circ_{A\gamma}$, the superficial average concentration would not be equal to $c^\circ_{A\gamma}$. Because of this, the preferred dependent variable is the *intrinsic average concentration* which is defined by

$$\langle c_{A\gamma}\rangle^\gamma\big|_{\mathbf{x}} = \frac{1}{V_\gamma(\mathbf{x})}\int_{V_\gamma(\mathbf{x})} c_{A\gamma}\big|_{\mathbf{x}+\mathbf{y}_\gamma}\, dV \tag{1.2-9}$$

The relation between these two concentrations is given by

$$\langle c_{A\gamma}\rangle = \varepsilon_\gamma\langle c_{A\gamma}\rangle^\gamma \tag{1.2-10}$$

where it is understood that both are evaluated at $\mathbf{x}$. If one is not careful about defining average values, it is possible to make errors on the order of ε_γ.

Even though $\langle c_{A\gamma}\rangle^\gamma$ is the preferred dependent variable, it is convenient to begin the process of spatial smoothing with the superficial average. Thus we integrate Eq. 1.2-1 over the domain V_γ associated with the point located by $\mathbf{x}$ and divide by $\mathscr{V}$ to obtain

$$\frac{1}{\mathscr{V}}\int_{V_\gamma}\frac{\partial c_{A\gamma}}{\partial t}dV = \frac{1}{\mathscr{V}}\int_{V_\gamma}\nabla\cdot\left(\mathscr{D}_\gamma\nabla c_{A\gamma}\right)dV \tag{1.2-11}$$

Since V_γ is not a function of time, we can use the general transport theorem (Whitaker, 1981) to express the left hand side of this result as

$$\frac{1}{\mathscr{V}}\int_{V_\gamma(\mathbf{x})}\left.\frac{\partial c_{A\gamma}}{\partial t}\right|_{\mathbf{x}+\mathbf{y}_\gamma} dV = \frac{d}{dt}\left\{\frac{1}{\mathscr{V}}\int_{V_\gamma(\mathbf{x})} c_{A\gamma}\big|_{\mathbf{x}+\mathbf{y}_\gamma} dV\right\} = \frac{d}{dt}\langle c_{A\gamma}\rangle\big|_{\mathbf{x}} \tag{1.2-12}$$

Because the superficial average concentration is associated the fixed point **x**, it is appropriate to make use of the partial derivative and express Eq. 1.2-11 as

$$\frac{\partial\langle c_{A\gamma}\rangle}{\partial t} = \langle\nabla\cdot(\mathscr{D}_\gamma\nabla c_{A\gamma})\rangle \tag{1.2-13}$$

Given that V_γ is independent of time, Eq. 1.2-6 indicates that ε_γ is also independent of time and we can use Eq. 1.2-10 in Eq. 1.2-13 to obtain

$$\varepsilon_\gamma\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \langle\nabla\cdot(\mathscr{D}_\gamma\nabla c_{A\gamma})\rangle \tag{1.2-14}$$

Obviously the left hand side of this result is in its final form, i.e., the accumulation of species A is expressed in terms of the intrinsic average concentration. It is of some importance to understand that Eq. 1.2-14 is a *superficial average* transport equation, i.e., the term on the left hand side represents the accumulation of species A *per unit volume of the porous medium* and not per unit volume of the fluid phase.

1.2.1 SPATIAL AVERAGING THEOREM

It should be clear that we need to interchange differentiation and integration on the right hand side of Eq. 1. 2-14 in order to express the diffusive flux in terms of $\langle c_{A\gamma}\rangle^\gamma$. This will be accomplished by means of the spatial averaging theorem (see Problems 1-5 through 1-7). Given some quantity ψ_γ associated with the γ-phase, we can express the spatial averaging theorem for the γ-κ system as

$$\langle\nabla\psi_\gamma\rangle = \nabla\langle\psi_\gamma\rangle + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\psi_\gamma dA \tag{1.2-15}$$

in which $A_{\gamma\kappa}$ represents the area of the γ-κ interface contained within $\mathscr{V}$. This theorem represents a three-dimensional version of the Leibniz rule for interchanging differentiation and integration. It was derived independently by Marle (1967) in a study of single-phase flow in porous media, by Anderson and Jackson (1967) in a study of fluidized beds, by Slattery (1967) in a study of two-phase flow in porous media, and by Whitaker (1967) in a study of dispersion in porous media. Since 1967 other derivations have been presented by Whitaker (1969), Drew (1971), Bachmat (1972), Gray and Lee (1977), Whitaker (1985), Howes and Whitaker (1985), Gray *et al.* (1993), and Quintard and Whitaker (1994b). When the macroscopic process is one-dimensional, a special form of Eq. 1.2-15 is appropriate (see Problem 1-8). The averaging theorem can be

extended to include systems with many phases (see Problem 1-9) and the form for three-phase systems is essential for the study of drying (see Problem 1-10).

While we will repeatedly use the spatial averaging theorem in the form given by Eq. 1. 2-15, it is of some value to list a more explicit form of this theorem given by

$$\langle \nabla \psi_\gamma \rangle = \nabla \langle \psi_\gamma \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \psi_\gamma \Big|_{\mathbf{x}+\mathbf{y}_\gamma} dA \tag{1.2-16}$$

Here we have used the notation illustrated in Figure 1.3 in order to be precise about the area integral, and in order to complete our understanding of this theorem we also need to be precise about the definitions of the two gradient operators. To be clear about those operators, we consider the curve, $\mathbf{r}_\gamma(s)$, that lies entirely in the γ-phase as illustrated in Figure 1.4. The *directional derivative* of ψ_γ associated with that curve is defined by (Stein and Barcellos, 1992)

$$\frac{d\psi_\gamma}{ds} = \lim_{\Delta s \to 0} \left\{ \frac{\psi_\gamma[\mathbf{r}_\gamma(s+\Delta s)] - \psi_\gamma[\mathbf{r}_\gamma(s)]}{\Delta s} \right\} \tag{1.2-17}$$

and the unit tangent to the curve is expressed as

$$\lambda = \frac{d\mathbf{r}_\gamma}{ds} \tag{1.2-18}$$

On the basis of Eqs. 1.2-17 and 1.2-18 we *define* the gradient of ψ_γ according to (Hildebrand, 1976)

$$\frac{d\psi_\gamma}{ds} = \frac{d\mathbf{r}_\gamma}{ds} \cdot \nabla \psi_\gamma \tag{1.2-19}$$

In order to be clear about the gradient of the average, we consider the curve, $\mathbf{x}(s)$, illustrated in Figure 1.5 that locates points in both the γ and κ-phases. For that curve, the directional derivative of $\langle \psi_\gamma \rangle$ is given by

$$\frac{d\langle \psi_\gamma \rangle}{ds} = \lim_{\Delta s \to 0} \left\{ \frac{\langle \psi_\gamma \rangle[\mathbf{x}(s+\Delta s)] - \langle \psi_\gamma \rangle[\mathbf{x}(s)]}{\Delta s} \right\} \tag{1.2-20}$$

with the unit tangent vector taking the form

$$\lambda = \frac{d\mathbf{x}}{ds} \tag{1.2-21}$$

On the basis of Eqs. 1.2-20 and 1.2-21 we *define* the gradient of $\langle \psi_\gamma \rangle$ according to

$$\frac{d\langle \psi_\gamma \rangle}{ds} = \frac{d\mathbf{x}}{ds} \cdot \nabla \langle \psi_\gamma \rangle \tag{1.2-22}$$

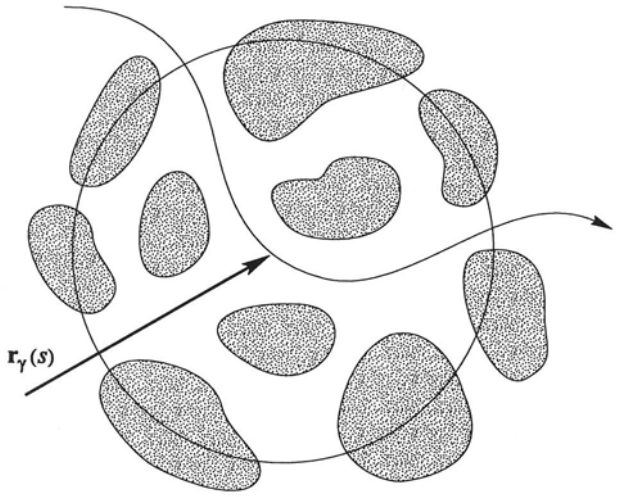


Figure 1.4. Arbitrary curve in the γ-phase

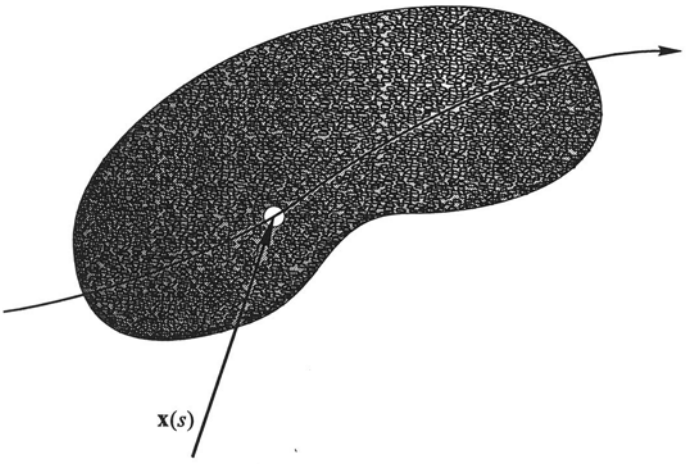


Figure 1.5. Arbitrary curve in the porous medium

In the averaging theorem the symbol for the two gradient operators is the same; however, the significance is different as indicated by Eqs. 1. 2-19 and 1.2-22.

The vector form of the spatial averaging theorem is given by

$$\langle \nabla \cdot \mathbf{a}_\gamma \rangle = \nabla \cdot \langle \mathbf{a}_\gamma \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \mathbf{a}_\gamma \, dA \tag{1.2-23}$$

and we can use this result with the right hand side of Eq. 1.2-14 to obtain

$$\langle \nabla\cdot(\mathscr{D}_\gamma \nabla c_{A\gamma})\rangle = \nabla\cdot\langle \mathscr{D}_\gamma \nabla c_{A\gamma}\rangle + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma \nabla c_{A\gamma}\, dA \tag{1.2-24}$$

Substitution of this result into Eq. 2-14 allows us to express the spatially smoothed transport equation as

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\langle \mathscr{D}_\gamma \nabla c_{A\gamma}\rangle + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma \nabla c_{A\gamma}\, dA \tag{1.2-25}$$

Clearly a second application of the averaging theorem is required to complete our analysis of the diffusive flux, but before doing that we want to use the boundary condition given by Eq. 1.2-2 to express Eq. 1.2-25 as

$$\underbrace{\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot\langle \mathscr{D}_\gamma \nabla c_{A\gamma}\rangle}_{\text{diffusion}} - \underbrace{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} k\, c_{A\gamma} dA}_{\substack{\text{heterogeneous}\\ \text{reaction}}} \tag{1.2-26}$$

This form illustrates a key aspect of the process of spatial smoothing, i.e., the interfacial boundary condition given by Eq. 1.2-2 is *joined* to the governing equation given by Eq. 1.2-1. This is a general characteristic of the governing equations for multiphase transport phenomena, and because of its importance we state this characteristic as:

> The form of a spatially smoothed transport equation depends *both* on the form of the governing point equation *and* on the form of the interfacial boundary conditions.

When spatially smoothed transport equations are generated intuitively, this characteristic is sometimes ignored. Later it will become clear that the interfacial boundary conditions influence the form of the averaged equation at two levels. The first level is illustrated by Eq 1.2-26 while the second level occurs in the *closure problem* described in Sec. 1.4.

Returning to Eq. 1.2-26, we note that the molecular diffusivity changes slowly with pressure, temperature, and concentration, thus it is appealing to ignore variations of $\mathscr{D}_\gamma$ within the averaging volume and express Eq. 1.2-26 as (see Problem 1-11)

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\mathscr{D}_\gamma \langle \nabla c_{A\gamma}\rangle\right) - \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} k\, c_{A\gamma}\, dA \tag{1.2-27}$$

In this study we will also ignore variations in the reaction rate constant within the averaging volume and express Eq. 1.2-27 as

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} = \nabla \cdot \left(\mathscr{D}_\gamma \langle \nabla c_{A\gamma} \rangle \right) - a_v k \langle c_{A\gamma} \rangle_{\gamma\kappa} \tag{1.2-28}$$

Here a_v represents the surface area per unit volume which is given explicitly by

$$a_v = A_{\gamma\kappa} / \mathscr{V} \tag{1.2-29}$$

and the area averaged concentration is defined by

$$\langle c_{A\gamma} \rangle_{\gamma\kappa} = \frac{1}{A_{\gamma\kappa}} \int_{A_{\gamma\kappa}} c_{A\gamma} \, dA \tag{1.2-30}$$

If we accept Eq. 1.2-28, our next step is a second application of the averaging theorem and this leads to

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} = \nabla \cdot \left[\mathscr{D}_\gamma \left(\nabla \langle c_{A\gamma} \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} dA \right) \right] - a_v k \langle c_{A\gamma} \rangle_{\gamma\kappa} \tag{1.2-31}$$

Here we find ourselves confronted with four different concentrations; however, one of these can be eliminated by the use of Eq. 1.2-10 which yields

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} = \nabla \cdot \left[\mathscr{D}_\gamma \left(\varepsilon_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma + \langle c_{A\gamma} \rangle^\gamma \nabla \varepsilon_\gamma + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} \, dA \right) \right] - a_v k \langle c_{A\gamma} \rangle_{\gamma\kappa} \tag{1.2-32}$$

One might assume that the area averaged concentration, $\langle c_{A\gamma} \rangle_{\gamma\kappa}$, is essentially equal to the volume averaged concentration, $\langle c_{A\gamma} \rangle^\gamma$, and under these circumstances the last term in Eq. 1.2-32 does not present a problem. However, the presence of the point concentration in Eq. 1.2-32 does present a problem since $c_{A\gamma}$ is only available to us in terms of the solution of the boundary value problem given by Eqs. 1.2-1 through 1.2-4. We attack this difficulty in terms of a *spatial decomposition* that is analogous to the *temporal decomposition* used in the study of turbulent transport phenomena.

1.2.2 SPATIAL DECOMPOSITION

Since the intrinsic average concentration is the quantity of interest, we decompose the point concentration according to (Gray, 1975)

$$c_{A\gamma} = \langle c_{A\gamma} \rangle^\gamma + \tilde{c}_{A\gamma} \tag{1.2-33}$$

in which $\tilde{c}_{A\gamma}$ is referred to as the *spatial deviation concentration.* In some respects one could think of Eq. 1.2-33 as decomposing the point concentration into what we want and whatever else remains. This is indeed true; however, the important characteristic of Eq. 1.2-33 is that it represents a *decomposition of length scales.* By this we mean that the average concentration undergoes significant changes *only* over the large length-scale, L. In Sec. 1.4 we will see that the spatial deviation concentration $\tilde{c}_{A\gamma}$ is dominated by the small length-scale ℓ_γ and it is for this reason that we refer to Eq. 1.2-33 as a decomposition of length scales. When Eq. 1.2-33 is used in Eq. 1.2-32 we obtain

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left[\mathscr{D}_\gamma\left(\varepsilon_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma + \langle c_{A\gamma}\rangle^\gamma\nabla\varepsilon_\gamma + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^\gamma dA + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}dA\right)\right] - a_v k\langle c_{A\gamma}\rangle_{\gamma\kappa} \tag{1.2-34}$$

Here we are confronted with three distinct problems that appear in essentially every application of the method of volume averaging. For this study of diffusion and reaction in porous media, these three problems take the form:

1. The presence of the volume averaged concentration, $\langle c_{A\gamma}\rangle^\gamma$, *inside* the integral over the area $A_{\gamma\kappa}$.
2. The presence of the *area averaged concentration*, $\langle c_{A\gamma}\rangle_{\gamma\kappa}$, in the heterogeneous reaction rate term.
3. The presence of the *spatial deviation concentration* $\tilde{c}_{A\gamma}$ in the governing equation for $\langle c_{A\gamma}\rangle^\gamma$.

We will consider the first two problems in the next section and then move on to the determination of $\tilde{c}_{A\gamma}$ in Sec. 1.4 where we will present the closure problem.

1.3 Length-Scale Constraints

In thinking about the area integral of $\mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^\gamma$ in Eq. 1.2-34, we must remember that under the integral sign $\langle c_{A\gamma}\rangle^\gamma$ is evaluated at points in the γ-phase indicated by the position vector $\mathbf{y}_\gamma$ illustrated in Figure 1.3. We make this point clear by writing

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^{\gamma} dA = \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}+\mathbf{y}_{\gamma}} dA \tag{1.3-1}$$

This clearly indicates that Eq. 1.2-34 is a *non-local* transport equation since the dependent variable $\langle c_{A\gamma}\rangle^{\gamma}$ is evaluated at points other than the centroid, $\mathbf{x}$. Non-local problems have been studied by Cushman (1983), Koch and Brady (1987), Quintard and Whitaker (1990a-b), Cushman and Ginn (1993), Goyeau *et al.* (1997) and many others. The analysis of non-local phenomena, or evolving heterogeneities (Cushman, 1990), is extremely complex, thus there is a great deal of motivation for avoiding a non-local problem whenever possible. From Eq. 1.2-34 we can extract a *local theory* provided certain length-scale constraints are satisfied, and in order to develop these constraints we need to represent $\langle c_{A\gamma}\rangle^{\gamma}$ in terms of a Taylor series.

1.3.1 TAYLOR SERIES EXPANSION

In order to remove the volume averaged concentration from the area integral in Eq. 1.2-34, we use a Taylor series expansion about the centroid of the averaging volume to obtain

$$\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}+\mathbf{y}_{\gamma}} = \langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \mathbf{y}_{\gamma}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \tfrac{1}{2}\mathbf{y}_{\gamma}\mathbf{y}_{\gamma}:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \ldots \tag{1.3-2}$$

Substitution of this result into Eq. 1.3-1 leads to

$$\begin{aligned}\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^{\gamma} dA = {} & \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} dA + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{y}_{\gamma}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} dA \\ & + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tfrac{1}{2}\mathbf{y}_{\gamma}\mathbf{y}_{\gamma}:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} dA + \ldots.\end{aligned} \tag{1.3-3}$$

Since all terms evaluated at the centroid can be removed from the integrals, we have

$$\begin{aligned}\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\langle c_{A\gamma}\rangle^{\gamma} dA = {} & \left\{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} dA\right\}\langle c_{A\gamma}\rangle^{\gamma} + \left\{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{y}_{\gamma} dA\right\}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} \\ & + \left\{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tfrac{1}{2}\mathbf{y}_{\gamma}\mathbf{y}_{\gamma} dA\right\}:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} + \ldots.\end{aligned} \tag{1.3-4}$$

The terms in braces represent a series of *geometrical integrals* that are related to the structure of the porous medium. In their present form the integrals are difficult to

interpret; however, Quintard and Whitaker (1994b) have developed a set of geometrical theorems that relate these integrals to the spatial moments of the porous medium. These are given by (see Problems 1-12 and 1-13)

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} dA = -\nabla\langle 1\rangle \tag{1.3-5a}$$

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{y}_{\gamma} dA = -\nabla\langle \mathbf{y}_{\gamma}\rangle \tag{1.3-5b}$$

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{y}_{\gamma}\mathbf{y}_{\gamma} dA = -\nabla\langle \mathbf{y}_{\gamma}\mathbf{y}_{\gamma}\rangle \tag{1.3-5c}$$

$$\cdots\cdots\cdots\cdots\cdots \tag{1.3-5d}$$

in which $\langle 1\rangle$, $\langle \mathbf{y}_{\gamma}\rangle$, $\langle \mathbf{y}_{\gamma}\mathbf{y}_{\gamma}\rangle$, etc., should be thought of as the zeroeth, first, second, etc., superficial spatial moments of the γ-phase contained in the averaging volume. If we recognize that

$$\langle 1\rangle = \frac{1}{\mathscr{V}}\int_{V_{\gamma}} 1 dV = \varepsilon_{\gamma} \tag{1.3-6}$$

we see that Eq. 1.3-5a leads to the well-known result given by

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} dA = -\nabla\varepsilon_{\gamma} \tag{1.3-7}$$

When Eqs. 1.3-7, 1.3-5b, and 1.3-5c are used in Eq. 1.3-3, the volume averaged transport equation given by Eq. 1.2-34 takes the form

$$\varepsilon_{\gamma}\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} =$$

$$\nabla\cdot\left[\mathscr{D}_{\gamma}\left(\varepsilon_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma} - \nabla\langle \mathbf{y}_{\gamma}\rangle\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} - \tfrac{1}{2}\nabla\langle \mathbf{y}_{\gamma}\mathbf{y}_{\gamma}\rangle : \nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} - \cdots + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma} dA\right)\right]$$

$$- a_{v}k\langle c_{A\gamma}\rangle_{\gamma\kappa} \tag{1.3-8}$$

Here we can see a major problem resulting from the use of the expansion given by Eq. 1.3-2. If the higher order terms are not negligible, the volume averaged transport

equation will contain a third order derivative of $\langle c_{A\gamma}\rangle^{\gamma}$ and this leads to a mathematically ill-posed problem.

If the γ-phase is uniformly distributed about the centroid, and the radius of the averaging volume is large compared to the characteristic length scale for the γ-phase,

$$\ell_{\gamma} \ll r_{o} \tag{1.3-9}$$

it is intuitively appealing to think of $\langle \mathbf{y}_{\gamma}\rangle$ as being zero. In a study of transport in ordered and disordered porous media, Quintard and Whitaker (1994a-e) considered the characteristics of the spatial moments in some detail, and they suggested the following *definition* of a disordered porous medium.

> A porous medium is disordered *with respect to* an averaging volume $\mathscr{V}$ when $\nabla\langle \mathbf{y}_{\gamma}\rangle << \mathbf{I}$

This definition of *disordered* is obviously well-suited for the method of volume averaging; however, it appears to be consistent with the concepts encountered in other studies of disordered systems (Strieder and Aris, 1973; Torquato, 1986; Shah and Ottino, 1987; Rubinstein and Torquato, 1989, Dagan, 1989).

Goyeau *et al.* (1997) examined the geometrical characteristics of dendritic systems that appeared to be *ordered* and *non-homogeneous*; nevertheless, they found that suitable averaging volumes could be found such that $\nabla\langle \mathbf{y}_{\gamma}\rangle << \mathbf{I}$ and we will make use of this inequality to impose the restriction

$$\nabla\langle \mathbf{y}_{\gamma}\rangle\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} \ll \varepsilon_{\gamma}\nabla\langle c_{A}\rangle^{\gamma} \tag{1.3-10}$$

Under these circumstances Eq. 1.3-8 simplifies to

$$\varepsilon_{\gamma}\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} =$$

$$= \nabla\cdot\left[\mathscr{D}_{\gamma}\left(\varepsilon_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma} - \tfrac{1}{2}\nabla\langle \mathbf{y}_{\gamma}\mathbf{y}_{\gamma}\rangle:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} - \ldots. + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}dA\right)\right]$$

$$- a_{v}k\langle c_{A\gamma}\rangle_{\gamma\kappa} \tag{1.3-11}$$

and we now need to direct our attention to the term involving $\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}$.

1.3.2 ORDER OF MAGNITUDE ESTIMATES

In this development, and elsewhere, we need *estimates* of terms such as $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ and $\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}$ (see Problems 1-14 through 1-16). We could estimate the first derivative of the average concentration as

$$\nabla\langle c_{A\gamma}\rangle^{\gamma} = \mathbf{O}\left(\Delta\langle c_{A\gamma}\rangle^{\gamma}/\Delta L\right) \tag{1.3-12}$$

where $\Delta\langle c_{A\gamma}\rangle^{\gamma}$ represents the change of the average concentration that occurs over a distance ΔL. The estimate of the gradient of the average concentration could *also* be expressed as

$$\nabla\langle c_{A\gamma}\rangle^{\gamma} = \mathbf{O}\left(\Delta\langle c_{A\gamma}\rangle^{\gamma}/L_c\right) \tag{1.3-13}$$

in which L_c represents a characteristic length associated with the average concentration. The estimate of the second derivative of the average concentration takes the form

$$\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} = \mathbf{O}\left[\Delta\left(\nabla\langle c_{A\gamma}\rangle^{\gamma}\right)/\Delta L\right] \tag{1.3-14}$$

in which $\Delta(\nabla\langle c_{A\gamma}\rangle^{\gamma})$ represents the change of the gradient of the average concentration that takes place over the distance ΔL. Alternatively, one could follow the type of nomenclature used in Eq. 1.3-13 in order to estimate the second derivative of the average concentration as

$$\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} = \mathbf{O}\left[\Delta\left(\nabla\langle c_{A\gamma}\rangle^{\gamma}\right)/L_{c1}\right] \tag{1.3-15}$$

Here L_{c1} represents a characteristic length associated with the *first derivative* of $\langle c_{A\gamma}\rangle^{\gamma}$ in the same sense that L_c represents a characteristic length associated with the average concentration. Both L_c and L_{c1} will be *functions of time* for a transient process, and both may be significantly different than the generic large length-scale, L, that is illustrated in Figure 1.2. Rather than use Eq. 1.3-15 as our representation of the order of magnitude of the second derivative, we will simplify the nomenclature to

$$\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} = \mathbf{O}\left[\nabla\langle c_{A\gamma}\rangle^{\gamma}/L_{c1}\right] \tag{1.3-16}$$

In this form, L_{c1} accounts for *both* the change in $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ and the distance over which this change takes place, and when the gradient of the average concentration is a constant one must remember that L_{c1} is infinite. The conventions represented by Eqs. 1.3-13 and 1.3-16 will be used throughout this monograph.

It will be left as an exercise for the reader to demonstrate the order of magnitude estimate (see Problem 1-17)

$$\langle \mathbf{y}_{\gamma}\mathbf{y}_{\gamma}\rangle = \mathbf{O}\left(\varepsilon_{\gamma}r_o^2\right) \tag{1.3-17}$$

which immediately leads to

$$\nabla\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle = \mathbf{O}\left(\Delta\varepsilon_\gamma r_o^2 / L_\varepsilon\right) \tag{1.3-18}$$

Here we have followed the convention indicated by Eq. 1.3-13 and *defined* L_ε by the estimate

$$\nabla\varepsilon_\gamma = \mathbf{O}\left(\Delta\varepsilon_\gamma / L_\varepsilon\right) \tag{1.3-19}$$

We now return to Eq. 1.3-11 and note that the term involving $\nabla\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle : \nabla\nabla\langle c_{A\gamma} \rangle^\gamma$ can be estimated as

$$\nabla\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle : \nabla\nabla\langle c_{A\gamma} \rangle^\gamma = \mathbf{O}\left[\left(\frac{r_o^2}{L_\varepsilon L_{c1}}\right)\Delta\varepsilon_\gamma \nabla\langle c_{A\gamma} \rangle^\gamma\right] \tag{1.3-20}$$

This provides the important inequality

$$\nabla\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle : \nabla\nabla\langle c_{A\gamma} \rangle^\gamma << \Delta\varepsilon_\gamma \nabla\langle c_{A\gamma} \rangle^\gamma \tag{1.3-21}$$

when the following length-scale constraint is satisfied.

$$r_o^2 << L_\varepsilon L_{c1} \tag{1.3-22}$$

Once again we note that neither L_ε nor L_{c1} is necessarily equal to the generic large length-scale, L, illustrated in Figure 1.2. One must make a judgment about L_ε and L_{c1} for every problem, and one must not think of the length scales as being unique for any given problem. For example, in the center of the region illustrated in Figure 1.2, one might think of L_ε as being infinite since the porosity is uniform. On the other hand, *at the surface of a catalyst pellet* it is appropriate to use $L_\varepsilon \approx r_o$ because the volume fraction of the γ-phase changes significantly over the distance r_o in this particular region. Sometimes one represents Eq. 1.3-22 as

$$r_o^2 << L^2 \tag{1.3-23}$$

with the idea that L represents the *smallest* large length-scale associated with the problem under consideration. On the basis of either Eqs. 1.3-22 or 1.3-23 we simplify Eq. 1.3-11 to

$$\varepsilon_\gamma \frac{\partial\langle c_{A\gamma} \rangle^\gamma}{\partial t} = \nabla\cdot\left[\mathscr{D}_\gamma\left(\varepsilon_\gamma \nabla\langle c_{A\gamma} \rangle^\gamma + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\, dA\right)\right] - a_v k \langle c_{A\gamma} \rangle_{\gamma\kappa} \tag{1.3-24}$$

and we are now confronted with only two problems: The presence of the spatial deviation concentration $\tilde{c}_{A\gamma}$ in the area integral, and the area averaged concentration

$\langle c_{A\gamma}\rangle_{\gamma\kappa}$ in the heterogeneous reaction rate term. We will deal with the area averaged concentration first and then move on to the determination of $\tilde{c}_{A\gamma}$ in the next section.

1.3.3 AREA AVERAGED CONCENTRATION

We begin our analysis of the area averaged concentration with the decomposition given by Eq. 1.2-33 which allows us to express $\langle c_{A\gamma}\rangle_{\gamma\kappa}$ as

$$\langle c_A\rangle_{\gamma\kappa} = \frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\left(\langle c_{A\gamma}\rangle^{\gamma}\Big|_{x+y_\gamma} + \tilde{c}_{A\gamma}\Big|_{x+y_\gamma}\right)dA \tag{1.3-25}$$

In the next section, we will show that for all practical problems of diffusion and reaction in porous media the spatial deviation concentration is small compared to the volume averaged concentration, i.e.,

$$\tilde{c}_{A\gamma} << \langle c_{A\gamma}\rangle^{\gamma} \tag{1.3-26}$$

This means that Eq. 1.3-25 takes the form

$$\langle c_{A\gamma}\rangle_{\gamma\kappa} = \frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\langle c_{A\gamma}\rangle^{\gamma}\Big|_{x+y_\gamma} dA \tag{1.3-27}$$

and we can use a Taylor series expansion of $\langle c_{A\gamma}\rangle^{\gamma}$ around the centroid of the averaging volume to express this result as

$$\langle c_{A\gamma}\rangle_{\gamma\kappa} = \langle c_{A\gamma}\rangle^{\gamma} + \langle \mathbf{y}_\gamma\rangle_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} + \tfrac{1}{2}\langle \mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} + \ldots \tag{1.3-28}$$

No precise estimates of $\langle \mathbf{y}_\gamma\rangle_{\gamma\kappa}$ are available; however, one can easily generate arguments in favor of

$$\langle \mathbf{y}_\gamma\rangle_{\gamma\kappa} << r_o \tag{1.3-29}$$

On the basis of Eq. 1.3-13 this result leads to

$$\langle \mathbf{y}_\gamma\rangle_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} << \Delta\langle c_{A\gamma}\rangle^{\gamma}(r_o/L_c) <<< \langle c_{A\gamma}\rangle^{\gamma} \tag{1.3-30}$$

when $r_o << L_c$. This allows us to simplify Eq. 1.3-28 in the obvious manner, and we move on to the next term involving $\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}$. We can draw upon the same type of arguments that led to the estimate given by Eq. 1.3-17 in order to obtain

$$\langle \mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa} = \mathbf{O}\left(r_o^2\right) \tag{1.3-31}$$

and this result, along with our estimate of $\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}$ given by Eq. 1.3-16, leads to

$$\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle_{\gamma\kappa} : \nabla\nabla\langle c_{A\gamma}\rangle^\gamma = \mathbf{O}\left[\left(\frac{r_o^2}{L_{c1}L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right] \tag{1.3-32}$$

On the basis of this estimate, and the restriction given by Eq. 1.3-30, we can express Eq. 1.3-28 as

$$\langle c_{A\gamma}\rangle_{\gamma\kappa} = \langle c_{A\gamma}\rangle^\gamma + \mathbf{O}\left[\left(\frac{r_o^2}{L_{c1}L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right] + \ldots \tag{1.3-33}$$

This indicates that when the following two length-scale constraints

$$r_o \ll L_c\,, \qquad r_o^2 \ll L_{c1}L_c \tag{1.3-34}$$

are valid, the rate of reaction can be expressed in terms of the volume average concentration according to

$$a_v k\langle c_{A\gamma}\rangle_{\gamma\kappa} = a_v k\langle c_{A\gamma}\rangle^\gamma \tag{1.3-35}$$

Under these circumstances the volume averaged diffusion equation given by Eq. 1.3-24 takes the form

$$\varepsilon_\gamma \frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left[\mathscr{D}_\gamma\left(\varepsilon_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right)\right] - a_v k\langle c_{A\gamma}\rangle^\gamma \tag{1.3-36}$$

and we are left with the problem of determining the spatial deviation concentration, $\tilde{c}_{A\gamma}$.

1.3.4 THE FILTER

Before moving on to the closure problem and the determination of $\tilde{c}_{A\gamma}$, we should think about the role that the term

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}dA = \left\{\begin{matrix} spatial \\ deviation \\ filter \end{matrix}\right\} \tag{1.3-37}$$

plays in the transport equation for $\langle c_{A\gamma}\rangle^\gamma$. Let us consider the possibility that the original boundary value problem given by Eqs. 1.2-1 through 1.2-4 could be solved for some arbitrarily complex porous medium. Knowing $c_{A\gamma}$, we could compute $\langle c_{A\gamma}\rangle^\gamma$ and from Eq. 1.2-33 we could determine the spatial deviation concentration according to

$$\tilde{c}_{A\gamma} = c_{A\gamma} - \langle c_{A\gamma}\rangle^\gamma \tag{1.3-38}$$

Given an *exact* representation for $\tilde{c}_{A\gamma}$, one can wonder how much of the information is lost in the area integral in Eq. 1.3-37. A little thought will indicate that the area integral

acts as a filter which allows some information to pass from the original point equation and boundary conditions for $c_{A\gamma}$ to the local volume average transport equation for $\langle c_{A\gamma}\rangle^{\gamma}$. Knowledge of how this filter operates on the $\tilde{c}_{A\gamma}$-field is of crucial importance in the closure problem, and we will learn more about this in the following sections.

1.4 The Closure Problem

In Sec 1.2 we introduced the problem of diffusion and heterogeneous reaction in terms of the following boundary value problem

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot\left(\mathscr{D}_{\gamma}\nabla c_{A\gamma}\right), \quad \text{in the } \gamma\text{-phase} \tag{1.4-1}$$

B.C.1
$$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_{\gamma}\nabla c_{A\gamma} = k\,c_{A\gamma}, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.4-2}$$

B.C.2
$$c_{A\gamma} = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\gamma e} \tag{1.4-3}$$

I.C.
$$c_{A\gamma} = \mathscr{G}(\mathbf{r}), \quad \text{at } t=0 \tag{1.4-4}$$

and we showed that the volume averaged form of Eq. 1.4-1 could be expressed as

$$\underbrace{\varepsilon_{\gamma}\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot\left[\mathscr{D}_{\gamma}\left(\varepsilon_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma} + \frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right)\right]}_{\text{diffusion}} - \underbrace{a_{v}k\langle c_{A\gamma}\rangle^{\gamma}}_{\substack{\text{heterogeneous}\\ \text{reaction}}} \tag{1.4-5}$$

Our objective in this section is to obtain a *closed form* of this result and this means that we must develop a representation for the spatial deviation concentration, $\tilde{c}_{A\gamma}$. This representation will be based on the boundary value problem for $\tilde{c}_{A\gamma}$, and in order to develop the governing differential equation for the spatial deviation concentration we require the *intrinsic form* of Eq. 1.4-5. Thus we divide that result by ε_{γ} to obtain

$$\begin{aligned}\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} &= \nabla\cdot\left(\mathscr{D}_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}\right) + \varepsilon_{\gamma}^{-1}\nabla\varepsilon_{\gamma}\cdot\mathscr{D}_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}\\ &+ \varepsilon_{\gamma}^{-1}\nabla\cdot\left[\frac{\mathscr{D}_{\gamma}}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\,\tilde{c}_{A\gamma}\,dA\right] - \varepsilon_{\gamma}^{-1}a_{v}k\langle c_{A\gamma}\rangle^{\gamma}\end{aligned} \tag{1.4-6}$$

We now recall that the spatial deviation concentration is defined by

$$\tilde{c}_{A\gamma} = c_{A\gamma} - \langle c_{A\gamma}\rangle^{\gamma} \tag{1.4-7}$$

and this leads us to subtract Eq. 1.4-6 from the point diffusion equation given by Eq. 1.4-1 in order to obtain

$$\underbrace{\frac{\partial \tilde{c}_{A\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot\left(\mathscr{D}_{\gamma}\nabla\tilde{c}_{A\gamma}\right)}_{\text{diffusion}} - \underbrace{\varepsilon_{\gamma}^{-1}\nabla\varepsilon_{\gamma}\cdot\mathscr{D}_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}}_{\text{diffusive source}} - \underbrace{\varepsilon_{\gamma}^{-1}\nabla\cdot\left[\frac{\mathscr{D}_{\gamma}}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right]}_{\text{non-local diffusion}}$$

$$+ \underbrace{\varepsilon_{\gamma}^{-1}a_{v}k\langle c_{A\gamma}\rangle^{\gamma}}_{\text{reactive source}} \tag{1.4-8}$$

From Eq. 1.4-2 and the decomposition represented by Eq. 1.4-7 we obtain the interfacial boundary condition for $\tilde{c}_{A\gamma}$ which we express as

$$\text{B.C.1}\quad -\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_{\gamma}\nabla\tilde{c}_{A\gamma} - k\tilde{c}_{A\gamma} = \underbrace{\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}}_{\text{diffusive source}} + \underbrace{k\langle c_{A\gamma}\rangle^{\gamma}}_{\substack{\text{reactive}\\ \text{source}}},\quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.4-9}$$

while the second boundary condition and the initial condition are given by

$$\text{B.C.2}\qquad \tilde{c}_{A\gamma} = \mathscr{H}(\mathbf{r},t),\quad \text{at } \mathscr{A}_{\gamma e} \tag{1.4-10}$$

$$\text{I.C.}\qquad \tilde{c}_{A\gamma} = \mathscr{I}(\mathbf{r}),\quad \text{at } t=0 \tag{1.4-11}$$

It should be clear that the spatial deviation concentration will not, in general, be known at the entrances and exits of the macroscopic system, thus Eq. 1.4-10 serves as a reminder of what we *do not know* about $\tilde{c}_{A\gamma}$ rather that what we do know. The same comment can be made about the initial condition given by Eq. 1.4-11; however, there may be some processes for which $\tilde{c}_{A\gamma}$ could be specified as zero at $t=0$.

1.4.1 SOURCES

The key to the successful development of the closure problem is to understand the role of the *sources* that have been identified in Eqs. 1.4-8 and 1.4-9. These sources represent non-homogeneous terms in the boundary value problem for $\tilde{c}_{A\gamma}$, as do the functions $\mathscr{H}(\mathbf{r},t)$ and $\mathscr{I}(\mathbf{r})$. If all the non-homogeneous terms were zero, one could prove that $\tilde{c}_{A\gamma}=0$, thus we must think of $\mathscr{D}_{\gamma}\nabla\langle c_A\rangle^{\gamma}$ and $k\langle c_A\rangle^{\gamma}$, along with $\mathscr{H}(\mathbf{r},t)$ and $\mathscr{I}(\mathbf{r})$, as the *generators* of the $\tilde{c}_{A\gamma}$-field. Since the characteristic length-scale for $\tilde{c}_{A\gamma}$ is the small length scale, ℓ_{γ}, the function $\mathscr{H}(\mathbf{r},t)$ will influence the $\tilde{c}_{A\gamma}$-field only in a thin layer near the boundary of the macroscopic region. Because of this, the contribution of

$\mathscr{H}(\mathbf{r},t)$ to the closure problem can be ignored. Subsequently we will argue that the boundary value problem for $\tilde{c}_{A\gamma}$ is quasi-steady and this means that the function $\mathscr{I}(\mathbf{r})$ will have no influence on the $\tilde{c}_{A\gamma}$-field; thus, the dominant sources are $\mathscr{D}_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma$ and $k\langle c_{A\gamma}\rangle^\gamma$, and we will make use of this idea after we develop a simplified form of Eqs. 1.4-8 through 1.4-11.

1.4.2 SIMPLIFICATIONS

We begin the process of simplifying Eq. 1.4-8 by examining the non-local diffusion term, and noting that the estimate

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA \;=\; \mathbf{O}\left(a_v\tilde{c}_{A\gamma}\right) \tag{1.4-12}$$

is reasonable when $\mathbf{n}_{\gamma\kappa}$ and $\tilde{c}_{A\gamma}$ are *strongly correlated.* Since we are dealing with an average quantity, we express our estimate of the divergence as

$$\nabla\cdot\left\{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right\} \;=\; \mathbf{O}\left(\frac{a_v\tilde{c}_{A\gamma}}{L}\right) \tag{1.4-13}$$

Here one should think of L as the characteristic length associated with the term on the left hand side of Eq. 1.4-12, and on the basis of Eq. 1.4-13 we estimate the non-local diffusion term in Eq. 1.4-8 as

$$\underbrace{\varepsilon_\gamma^{-1}\nabla\cdot\left[\frac{\mathscr{D}_\gamma}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right]}_{\text{non-local diffusion}} \;=\; \mathbf{O}\left(\frac{\varepsilon_\gamma^{-1}a_v\mathscr{D}_\gamma\tilde{c}_{A\gamma}}{L}\right) \tag{1.4-14}$$

For most porous media, a reasonable representation of the interfacial area per unit volume is given by (see Problem 1-18)

$$a_v \;\approx\; \ell_\gamma^{-1} \tag{1.4-15}$$

This leads to the following form of our estimate for the non-local term

$$\underbrace{\varepsilon_\gamma^{-1}\nabla\cdot\left[\frac{\mathscr{D}_\gamma}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right]}_{\text{non-local diffusion}} \;=\; \mathbf{O}\left(\frac{\varepsilon_\gamma^{-1}\mathscr{D}_\gamma\tilde{c}_{A\gamma}}{\ell_\gamma L}\right) \tag{1.4-16}$$

while our estimate of the diffusion term in Eq. 1.4-8 is given by

$$\underbrace{\nabla\cdot\left(\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma}\right)}_{\text{diffusion}} = \mathbf{O}\left(\frac{\mathscr{D}_\gamma\tilde{c}_{A\gamma}}{\ell_\gamma^2}\right) \tag{1.4-17}$$

At this point we need only recognize that $\ell_\gamma << L$ in order to conclude that

$$\underbrace{\varepsilon_\gamma^{-1}\nabla\cdot\left[\frac{\mathscr{D}_\gamma}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right]}_{\text{non-local diffusion}} << \underbrace{\nabla\cdot\left(\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma}\right)}_{\text{diffusion}} \tag{1.4-18}$$

and the governing differential equation for $\tilde{c}_{A\gamma}$ can be simplified in the obvious manner. In addition, we can treat the closure problem as *quasi-steady* (Whitaker, 1988a) when

$$\underbrace{\frac{\partial\tilde{c}_{A\gamma}}{\partial t}}_{\text{accumulation}} << \underbrace{\nabla\cdot\left(\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma}\right)}_{\text{diffusion}} \tag{1.4-19}$$

and this condition will be satisfied whenever the characteristic time is *large enough* so that the following time-scale constraint is valid (Moyne, 1997):

$$\frac{\mathscr{D}_\gamma t^*}{\ell_\gamma^2} >> 1\,, \quad \text{closure process is quasi-steady} \tag{1.4-20}$$

When the macroscopic process is *transient*, one can argue that t^* must be constrained by

$$\frac{\mathscr{D}_\gamma t^*}{L_c L_{c1}} = \mathbf{O}(1)\,, \quad \text{macroscopic process is transient} \tag{1.4-21}$$

however, both these conditions can often be satisfied because ℓ_γ is generally very small compared to the characteristic lengths associated with $\langle c_{A\gamma}\rangle^\gamma$ and $\nabla\langle c_{A\gamma}\rangle^\gamma$.

On the basis of Eqs. 1.4-18 and 1.4-19, we can express the quasi-steady closure problem as

$$0 = \underbrace{\nabla\cdot\left(\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma}\right)}_{\text{diffusion}} - \underbrace{\varepsilon_\gamma^{-1}\nabla\varepsilon_\gamma\cdot\mathscr{D}_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma}_{\text{diffusive source}} + \underbrace{\varepsilon_\gamma^{-1}a_v k\langle c_{A\gamma}\rangle^\gamma}_{\text{reactive source}} \tag{1.4-22}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma} - k\tilde{c}_{A\gamma} = \underbrace{\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma}_{\text{diffusive source}} + \underbrace{k\langle c_{A\gamma}\rangle^\gamma}_{\text{reactive source}}\,, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.4-23}$$

$$\text{B.C.2} \quad \tilde{c}_{A\gamma} = \mathscr{H}(\mathbf{r},t)\,, \quad \text{at } \mathscr{A}_{\gamma e} \tag{1.4-24}$$

Here it becomes apparent that there are *volume sources* involving $\mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma$ and $k \langle c_{A\gamma} \rangle^\gamma$, and there are *surface sources* involving these same two parameters. A little thought will indicate that the term $k \langle c_{A\gamma} \rangle^\gamma$ in the boundary condition given by Eq. 1.4-23 represents a *sink* since it creates a flux of $\tilde{c}_{A\gamma}$ *from* the γ-phase *to* the κ-phase. In addition, one can show that this *surface sink* is exactly balanced by the *volume source*, $\varepsilon_\gamma^{-1} a_v k \langle c_{A\gamma} \rangle^\gamma$, in Eq. 1.4-22. This means that the *average* reactive source is zero, and the terms involving $k \langle c_{A\gamma} \rangle^\gamma$ only influence the manner in which $\tilde{c}_{A\gamma}$ is distributed in the γ-phase. The diffusive source in Eq. 1.4-23 has the same characteristic, i.e., the average surface diffusive source is zero; however, it changes sign over a distance ℓ_γ and it dominates the manner in which $\tilde{c}_{A\gamma}$ is distributed in the γ-phase.

The order of magnitude of the *surface* diffusive source per unit volume can be estimated as

$$\left\{ \begin{matrix} \textit{order of magnitude} \\ \textit{of the surface} \\ \textit{diffusive source} \end{matrix} \right\} = \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \left| \mathbf{n}_{\gamma\kappa} \cdot \mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma \right| dA = \mathbf{O}\left(a_v \mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma \right) \tag{1.4-25}$$

while the estimate of the *volume* diffusive source per unit volume takes the form

$$\left\{ \begin{matrix} \textit{order of magnitude} \\ \textit{of the volume} \\ \textit{diffusive source} \end{matrix} \right\} = \frac{1}{\mathscr{V}} \int_{V_\gamma} \left| \varepsilon_\gamma^{-1} \nabla \varepsilon_\gamma \cdot \mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma \right| dA = \mathbf{O}\left(\nabla \varepsilon_\gamma \, \mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma \right) \tag{1.4-26}$$

These two results allow us to estimate the ratio of the volume source to the surface source according to

$$\frac{\textit{volume source}}{\textit{surface source}} = \mathbf{O}\left(\frac{\nabla \varepsilon_\gamma}{a_v} \right) \tag{1.4-27}$$

For the typical porous medium $a_v \sim \ell_\gamma^{-1}$ and we obtain

$$\frac{\textit{volume source}}{\textit{surface source}} = \mathbf{O}\left(\frac{\ell_\gamma}{L_\varepsilon} \Delta \varepsilon_\gamma \right) << 1 \tag{1.4-28}$$

and the *volume diffusive source* in Eq. 1.4-22 can be discarded.

Further simplification of the closure problem can be achieved if we can demonstrate that $\tilde{c}_{A\gamma}$ is small compared to $\langle c_{A\gamma} \rangle^\gamma$. Directing our attention to the boundary condition given by Eq. 1.4-23, we use the estimates

$$\mathbf{n}_{\gamma\kappa} \cdot \mathscr{D}_\gamma \nabla \tilde{c}_{A\gamma} = \mathbf{O}\left(\mathscr{D}_\gamma \tilde{c}_{A\gamma} / \ell_\gamma\right) \tag{1.4-29a}$$

$$\mathbf{n}_{\gamma\kappa} \cdot \mathscr{D}_\gamma \nabla \langle c_{A\gamma} \rangle^\gamma = \mathbf{O}\left(\mathscr{D}_\gamma \Delta \langle c_{A\gamma} \rangle^\gamma / L_c\right) \tag{1.4-29b}$$

to obtain

B.C.1
$$\mathbf{O}\left(\frac{\mathscr{D}_\gamma \tilde{c}_{A\gamma}}{\ell_\gamma}\right) + \mathbf{O}\left(k\tilde{c}_{A\gamma}\right) = \mathbf{O}\left(\frac{\mathscr{D}_\gamma \Delta \langle c_{A\gamma} \rangle^\gamma}{L_c}\right) + \mathbf{O}\left(k\langle c_{A\gamma} \rangle^\gamma\right) \tag{1.4-30}$$

This can be arranged in the form of an estimate for $\tilde{c}_{A\gamma}$

$$\tilde{c}_{A\gamma} = \mathbf{O}\left\{\frac{\left(\ell_\gamma / L_c\right)\Delta \langle c_{A\gamma} \rangle^\gamma}{\left[1 + \mathbf{O}\left(k\ell_\gamma / \mathscr{D}_\gamma\right)\right]}, \frac{\left(k\ell_\gamma / \mathscr{D}_\gamma\right)\langle c_{A\gamma} \rangle^\gamma}{\left[1 + \mathbf{O}\left(k\ell_\gamma / \mathscr{D}_\gamma\right)\right]}\right\} \tag{1.4-31}$$

originally given by Ryan *et al.* (1981). In order to simplify this result we need to express the parameter $k\ell_\gamma / \mathscr{D}_\gamma$ in terms of the particle Thiele modulus which leads us to

$$\frac{k\ell_\gamma}{\mathscr{D}_\gamma} = \phi^2 \left(\ell_\gamma / L\right)^2 \tag{1.4-32}$$

Here ϕ represents the particle Thiele modulus which is given explicitly by

$$\phi = L\sqrt{a_v k / \mathscr{D}_\gamma} \tag{1.4-33}$$

In this representation the characteristic macroscopic length, L, is usually taken to the effective particle diameter (Carberry, 1976), and the small length scale ℓ_γ is related to a_v by

$$\ell_\gamma \approx a_v^{-1} \tag{1.4-34}$$

For practical reactor design problems, the particle Thiele modulus is usually less than ten ($\phi^2 \leq 100$) while ℓ_γ is typically many orders of magnitude smaller than L, thus Eq. 1.4-32 indicates that $k\ell_\gamma / \mathscr{D}_\gamma$ is very small compared to one.

$$\frac{k\ell_\gamma}{\mathscr{D}_\gamma} \lll 1 \tag{1.4-35}$$

Use of this result with Eq. 1.4-31 leads to the following estimate for the spatial deviation concentration:

$$\tilde{c}_{A\gamma} = \mathbf{O}\left[\left(\frac{\ell_\gamma}{L_c}\right)\Delta \langle c_{A\gamma} \rangle^\gamma\right] + \mathbf{O}\left[\left(\frac{k\ell_\gamma}{\mathscr{D}_\gamma}\right)\langle c_{A\gamma} \rangle^\gamma\right] \tag{1.4-36}$$

On the basis of Eq. 1.4-35, and because $\ell_\gamma << L_c$, this estimate leads us to conclude that

$$\tilde{c}_{A\gamma} << \langle c_{A\gamma}\rangle^\gamma \tag{1.4-37}$$

and we can discard $k\tilde{c}_{A\gamma}$ relative to $k\langle c_{A\gamma}\rangle^\gamma$ in Eq. 1.4-23. This allows us to express the boundary value problem for $\tilde{c}_{A\gamma}$ as

$$\nabla^2\tilde{c}_{A\gamma} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma \tag{1.4-38}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla\tilde{c}_{A\gamma} = \mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma + k\langle c_{A\gamma}\rangle^\gamma, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.4-39}$$

B.C.2 $$\tilde{c}_{A\gamma} = \mathscr{H}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\gamma e} \tag{1.4-40}$$

While Eq. 1.4-37 represents a reliable estimate of $\tilde{c}_{A\gamma}$ relative to $\langle c_{A\gamma}\rangle^\gamma$, one must be careful to remember that the length scales associated with $\tilde{c}_{A\gamma}$ and $\langle c_{A\gamma}\rangle^\gamma$ are very different and a similar inequality *does not exist* for the gradients of $\tilde{c}_{A\gamma}$ and $\langle c_{A\gamma}\rangle^\gamma$. In the absence of any chemical reaction, Eq. 1.4-39 immediately leads to the estimate

$$\nabla\tilde{c}_{A\gamma} = \mathbf{O}\left(\nabla\langle c_{A\gamma}\rangle^\gamma\right) \tag{1.4-41}$$

This relation between the gradient of $\tilde{c}_{A\gamma}$ and the gradient of $\langle c_{A\gamma}\rangle^\gamma$ must be kept in mind whenever simplifications are made in the volume averaged transport equation for $\langle c_{A\gamma}\rangle^\gamma$ or in the governing equation for $\tilde{c}_{A\gamma}$.

1.4.3 THE LOCAL PROBLEM

It should be clear that we have no intention of solving Eqs. 1.4-38 through 1.4-40 over the entire macroscopic region illustrated in Figure 1.2. Instead, we want to solve for $\tilde{c}_{A\gamma}$ in some *representative region* and use the computed results in Eq. 1.4-5 to affect the closure. Such a region is illustrated in Figure 1.6, and if we want to solve for $\tilde{c}_{A\gamma}$ in that region we must be willing to abandon the boundary condition given by Eq. 1.4-40. Since the source, $\mathscr{H}(\mathbf{r},t)$, only influences the $\tilde{c}_{A\gamma}$-field over a distance on the order of ℓ_γ, the loss of the boundary condition at $\mathscr{A}_{\gamma e}$ is of no consequence. If we treat the representative region shown in Figure 1.6 as a unit cell in a spatially periodic porous medium, we can replace the boundary condition imposed at $\mathscr{A}_{\gamma e}$ with a *spatially periodic condition* on $\tilde{c}_{A\gamma}$.

If we accept the model of a spatially periodic porous medium in order to solve the closure problem, we know that the unit normal vector must satisfy the condition

$$\mathbf{n}_{\gamma\kappa}(\mathbf{r}+\ell_i) = \mathbf{n}_{\gamma\kappa}(\mathbf{r}), \quad i=1,2,3 \tag{1.4-42}$$

Here ℓ_i represents the three non-unique lattice vectors that are required to describe a spatially periodic porous medium (Bensoussan, *et al*, 1978; Brenner, 1980; Sanchez-Palencia, 1980). While the geometry of our representative region may be invariant to a transformation of the type, $\mathbf{r} \rightarrow \bar{\mathbf{r}}+\ell_i$, the governing equation and boundary condition given by Eqs. 1.4-38 and 1.4-39 will not be unless we can treat $\langle c_{A\gamma}\rangle^{\gamma}$ and $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ as constants. Since $\langle c_{A\gamma}\rangle^{\gamma}$ cannot be a constant unless $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ is zero, there are some approximations to be made before we can impose a spatially periodic condition on $\tilde{c}_{A\gamma}$.

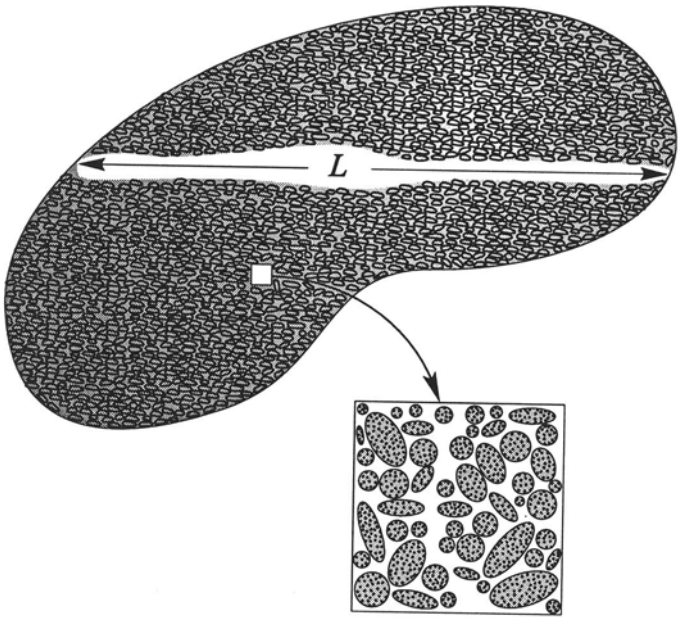


Figure 1.6. Representative region

In order to identify these approximations, we need to express $\langle c_{A\gamma}\rangle^{\gamma}$ and $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ in terms of Taylor series expansions about the centroid of the representative region. These expansions are given by

$$\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}+\mathbf{y}_\gamma} = \langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \mathbf{y}_\gamma\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \tfrac{1}{2}\mathbf{y}_\gamma\mathbf{y}_\gamma:\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \ldots \tag{1.4-43}$$

$$\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}+\mathbf{y}_\gamma} = \nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \mathbf{y}_\gamma\cdot\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\Big|_{\mathbf{x}} + \ldots \tag{1.4-44}$$

in which $\mathbf{x}$ represents the centroid of the representative region shown in Figure 1.6, and $\mathbf{y}_\gamma$ locates points in the γ-phase relative to the centroid. We can estimate the higher order terms in Eq. 1.4-43 and use the resulting representation in Eq. 1.4-38 to obtain

$$\nabla^2 \tilde{c}_{A\gamma} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} + \mathbf{O}\left[\left(\frac{r_0}{L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right]\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \tag{1.4-45}$$

Using both Eqs. 1.4-43 and 1.4-44 in the boundary condition given by Eq. 1.4-39 leads to the following form:

B.C.1

$$\begin{aligned} -\mathbf{n}_{\gamma\kappa}\cdot\nabla\tilde{c}_{A\gamma} &= \mathbf{n}_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} + \mathbf{O}\left[\left(\frac{r_0}{L_{c1}}\right)\nabla\langle c_{A\gamma}\rangle^\gamma\right] \\ &+ \left(\frac{k}{\mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} + \mathbf{O}\left[\left(\frac{k r_0}{\mathscr{D}_\gamma L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right], \quad \text{at } \mathscr{A}_{\gamma\kappa} \end{aligned} \tag{1.4-46}$$

Here we have used the estimates given by

$$\mathbf{y}_\gamma\cdot\nabla\langle c_{A\gamma}\rangle^\gamma = \mathbf{O}\left(\frac{r_0\Delta\langle c_{A\gamma}\rangle^\gamma}{L_c}\right) \tag{1.4-47a}$$

$$\mathbf{y}_\gamma\cdot\nabla\nabla\langle c_{A\gamma}\rangle^\gamma = \mathbf{O}\left(\frac{r_0\nabla\langle c_{A\gamma}\rangle^\gamma}{L_{c1}}\right) \tag{1.4-47b}$$

in which $\mathbf{y}_\gamma$ is on the order of r_0 and the length scales, L_c and L_{c1}, are defined by Eqs. 1.3-13 and 1.3-16. The estimate for $\mathbf{y}_\gamma$ is based on the idea that the representative region will never be larger than the averaging volume. In order to discard the higher term in the governing equation for $\tilde{c}_{A\gamma}$ we require the restriction

$$\mathbf{O}\left[\left(\frac{r_0}{L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right]\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \ll \left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} \tag{1.4-48}$$

while the boundary condition given by Eq. 1.4-46 can be simplified on the basis of

$$\mathbf{O}\left[\left(\frac{r_0}{L_{c1}}\right)\nabla\langle c_{A\gamma}\rangle^\gamma\right] \ll \mathbf{n}_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} \tag{1.4-49a}$$

$$\mathbf{O}\left[\left(\frac{k\,r_0}{\mathscr{D}_\gamma L_c}\right)\Delta\langle c_{A\gamma}\rangle^\gamma\right] \;<<\; \left(\frac{k}{\mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} \tag{1.4-49b}$$

These restrictions lead to the following constraints

$$r_0 \;<<\; L_c\,, \qquad r_0 \;<<\; L_{c1} \tag{1.4-50}$$

and when these constraints are satisfied, the closure problem can be expressed as

$$\nabla^2\tilde{c}_{A\gamma} \;=\; -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} \tag{1.4-51}$$

$$\text{B.C.1} \qquad -\mathbf{n}_{\gamma\kappa}\cdot\nabla\tilde{c}_{A\gamma} \;=\; \mathbf{n}_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}} + \left(\frac{k}{\mathscr{D}_\gamma}\right)\langle c_{A\gamma}\rangle^\gamma\Big|_{\mathbf{x}}\,, \quad \text{at } A_{\gamma\kappa} \tag{1.4-52}$$

$$\text{Periodicity:} \qquad \tilde{c}_{A\gamma}(\mathbf{r}+\ell_i) \;=\; \tilde{c}_{A\gamma}(\mathbf{r})\,, \quad i=1,2,3 \tag{1.4-53}$$

in which $A_{\gamma\kappa}$ represents the interfacial area contained within the representative region. Here we have discarded the boundary condition at $\mathscr{A}_{\gamma e}$ given by Eq. 1.4-40 and replaced it with the periodicity condition on $\tilde{c}_{A\gamma}$ (see Problem 1-19). This periodicity condition is *consistent with* Eqs. 1.4-51 and 1.4-52 only if the geometry of the representative region is spatially periodic and the source terms are either constant or spatially periodic. By imposing the constraints indicated by Eqs. 1.4-50 we have been able to treat the *reactive sources*, $(a_v k/\varepsilon_\gamma\mathscr{D}_\gamma)\langle c_{A\gamma}\rangle^\gamma$ and $(k/\mathscr{D}_\gamma)\langle c_{A\gamma}\rangle^\gamma$, as constants while the *diffusive source*, $\mathbf{n}_{\gamma\kappa}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma$, is spatially periodic because of the nature of the unit normal vector $\mathbf{n}_{\gamma\kappa}$.

It is important to understand that Eqs. 1.4-51 through 1.4-53 represent an *approximation* of the boundary value problem given by Eqs. 1.4-38 through 1.4-40 and the validity of this approximation is an important issue. It should be clear that the $\tilde{c}_{A\gamma}$-field will be dominated by the governing differential equation and the flux boundary condition, both of which contain source terms that generate the $\tilde{c}_{A\gamma}$-field. Neither the boundary condition given by Eq. 1.4-40 nor the periodicity condition given by Eq. 1.4-53 will have an important influence on the $\tilde{c}_{A\gamma}$-field. This is especially true for the values of $\tilde{c}_{A\gamma}$ evaluated at the γ-κ interface, and it is this value that *enters* the filter identified by Eq. 1.3-37. The role of this filter for diffusive transport processes has been explored in some detail by Ochoa-Tapia *et al.* (1994) for spatially periodic models and Maxwell's (1881) model, and their numerical calculations indicate why Maxwell's model provides good results for effective diffusivities and effective thermal conductivities even when the constraints inherent in the model are not satisfied.

One should keep in mind that the representative region shown in Figure 1.6 can be *arbitrarily complex.* In their study of two-phase flow in heterogeneous porous media, Ahmadi and Quintard (1996) used a log-normal distribution of permeabilities (Dagan, 1989) to construct large unit cells that were representative of complex, disordered systems. In a study of dispersion, Noble *et al.* (1998) made use of unit cells in which 80 octagonal cylinders were randomly distributed in order to determine the influence of disorder on longitudinal and lateral dispersion coefficients. It is clear from these initial studies of disordered systems that unit cells can indeed be constructed that are representative of real, disordered systems.

It is of some importance to note that Eqs. 1.4-51 through 1.4-53 determine $\tilde{c}_{A\gamma}$ only to within an arbitrary, additive constant. Sometimes this indeterminacy is removed by imposing the condition

$$\langle \tilde{c}_{A\gamma} \rangle^{\gamma} = 0 \tag{1.4-54}$$

While this constraint is quite plausible, it is not necessary since any additive constant associated with $\tilde{c}_{A\gamma}$ will not pass through the filter represented by Eq. 1.3-37. It is important to remember that in the development of the local volume averaged equation given by Eq. 1.3-36, we made repeated use of Eq. 1.3-7 which can be used to write

$$\frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} (constant) dA = -\left(\nabla \varepsilon_{\gamma}\right)(constant) \tag{1.4-55}$$

However, when the area integral in Eq. 1.3-36 is evaluated on the basis of the closure problem given by Eqs. 1.4-51 through 1.4-53, we find that

$$\frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} (constant) dA = 0, \quad \begin{cases} for\ a\ spatially \\ periodic\ porous \\ medium \end{cases} \tag{1.4-56}$$

Under these circumstances, the additive constant associated with $\tilde{c}_{A\gamma}$ plays no role in the evaluation of the area integral in Eq. 1.4-5. However, this is not true for all processes, and in Chapter 4 we will see that a condition of the type indicated by Eq. 1.4-54 plays a crucial role in the closure problem.

1.4.4 CLOSURE VARIABLES

Given the linear nature of the boundary value problem for $\tilde{c}_{A\gamma}$, we propose a solution *in terms of the sources* which we express as (see Problem 1-20)

$$\tilde{c}_{A\gamma} = \mathbf{b}_{\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} \Big|_{\mathbf{x}} + s_{\gamma} \langle c_{A\gamma} \rangle^{\gamma} \Big|_{\mathbf{x}} + \psi_{\gamma} \tag{1.4-57}$$

This approach to solving the boundary value problem for $\tilde{c}_{A\gamma}$ is known as the method of superposition, and we refer to the vector $\mathbf{b}_\gamma$ and the scalar s_γ as the *closure variables.* We can think of ψ_γ as an arbitrary function and this allows us to specify $\mathbf{b}_\gamma$ and s_γ in any way we wish, and we choose to determine these closure variables by means of the following two boundary value problems:

Problem I

$$\nabla^2 \mathbf{b}_\gamma = 0 \tag{1.4-58a}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \mathbf{b}_\gamma = \mathbf{n}_{\gamma\kappa}, \quad \text{at } A_{\gamma\kappa} \tag{1.4-58b}$$

Periodicity: $$\mathbf{b}_\gamma(\mathbf{r}+\ell_i) = \mathbf{b}_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.4-58c}$$

Problem II

$$\nabla^2 s_\gamma = -\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma} \tag{1.4-59a}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa} \cdot \nabla s_\gamma = k / \mathscr{D}_\gamma, \quad \text{at } A_{\gamma\kappa} \tag{1.4-59b}$$

Periodicity: $$s_\gamma(\mathbf{r}+\ell_i) = s_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.4-59c}$$

We can now develop the boundary value problem for ψ_γ by substituting the representation given by Eq. 1.4-57 into the closure problem given by Eqs. 1.4-51 through 1.4-53 and imposing the conditions on $\mathbf{b}_\gamma$ and s_γ required by Eqs.1.4-58 and 1.4-59. This leads to our third closure problem given by

Problem III

$$\nabla^2 \psi_\gamma = 0 \tag{1.4-60a}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \psi_\gamma = 0, \quad \text{at } A_{\gamma\kappa} \tag{1.4-60b}$$

Periodicity: $$\psi_\gamma(\mathbf{r}+\ell_i) = \psi_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.4-60c}$$

Certainly $\psi_\gamma = \textit{constant}$ is one solution to Eqs. 1.4-60 and it will be left as an exercise to prove that this is the only solution (see Problem 1-21). Since this additive constant will not pass through the filter in Eq. 1.4-5, as we have indicated by Eq. 1.4-56, the value of ψ_γ plays no role in the closed form of the volume averaged diffusion equation.

1.4.5 CLOSED FORM

Substitution of Eq. 1.4-57 into Eq. 1.4-5 leads to the closed form of the governing differential equation for $\langle c_{A\gamma} \rangle^\gamma$. Since $\langle c_{A\gamma} \rangle^\gamma$ and $\nabla \langle c_{A\gamma} \rangle^\gamma$ are evaluated at the

centroid of the representative unit cell, these terms can be removed from the area integral in Eq. 1.4-5 and this leads to

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left\{\varepsilon_\gamma \mathscr{D}_\gamma\left[\nabla\langle c_{A\gamma}\rangle^\gamma + \left(\frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{b}_\gamma\, dA\right)\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\right]\right\} + \nabla\cdot\left[\left(\frac{\varepsilon_\gamma \mathscr{D}_\gamma}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} s_\gamma\, dA\right)\langle c_{A\gamma}\rangle^\gamma\right] - a_v k\langle c_{A\gamma}\rangle^\gamma \tag{1.4-61}$$

The effective diffusivity tensor is defined by

$$\mathbf{D}_{eff} = \mathscr{D}_\gamma\left(\mathbf{I} + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\mathbf{b}_\gamma\, dA\right) \tag{1.4-62}$$

and we represent the *vector* associated with the chemical reaction as

$$\mathbf{u} = \frac{\varepsilon_\gamma \mathscr{D}_\gamma}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\, s_\gamma\, dA \tag{1.4-63}$$

Use of these two definitions in Eq. 1.4-61 leads to the following form of the closed equation

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma \mathbf{D}_{eff}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\right) + \nabla\cdot\left(\mathbf{u}\langle c_{A\gamma}\rangle^\gamma\right) - a_v k\langle c_{A\gamma}\rangle^\gamma \tag{1.4-64}$$

Since $\mathbf{u}$ has the units of velocity and is directly proportional to k, one can think of $\mathbf{u}\langle c_{A\gamma}\rangle^\gamma$ as a *convective transport term* that is generated by the heterogeneous reaction. Paine *et al.* (1983) have shown that this contribution to convective transport can be important when convection itself is important; however, we will demonstrate in the following paragraphs that this term is negligible for the case of diffusion in porous catalysts.

At this point in our analysis, we should think about how the interfacial boundary condition given by Eq. 1.2-2 has influenced the volume averaged transport equation. For the process of diffusion and reaction, we found that the interfacial boundary condition entered into the analysis in two ways:

1. In the process of *spatial smoothing*, the interfacial flux was incorporated directly into the volume averaged transport equation. That gave rise to the reaction rate term in Eq. 1.2-26.

2. In the *closure problem* we found that the heterogeneous reaction rate term acted as a source for the $\tilde{c}_{A\gamma}$-field. That gave rise to the convective-like term in Eq. 1.4-64.

Although the second contribution will be negligible in this case, one should always keep in mind that boundary conditions influence the final form of a volume averaged transport equation *both* in the spatial smoothing process *and* in the closure problem. This is particularly clear in the case of the chromatographic equation and Forchheimer's equation (Whitaker, 1997).

Turning our attention to the convective-like transport term, we can use Eqs. 1.4-59 to develop the estimate given by (see Problem 1-22)

$$\mathscr{D}_\gamma s_\gamma = \mathbf{O}\left(\ell_\gamma k\right) \tag{1.4-65}$$

and this can be used with Eq. 1.4-63 to conclude that

$$\mathbf{u} = \mathbf{O}(k) \tag{1.4-66}$$

From this result, and the fact that $a_v \approx \ell_\gamma^{-1}$, we can see that the last two terms in Eq. 1.4-64 are restricted by

$$a_v k \langle c_{A\gamma}\rangle^\gamma >> \nabla\cdot\left(\mathbf{u}\langle c_{A\gamma}\rangle^\gamma\right) \tag{1.4-67}$$

and under these circumstances Eq. 1.4-64 simplifies to

$$\varepsilon_\gamma \frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma \mathbf{D}_{eff}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\right) - a_v k\langle c_{A\gamma}\rangle^\gamma \tag{1.4-68}$$

In this particular case, we see from Eqs. 1.4-62 and 1. 4-58 that the effective diffusivity is a linear function of the molecular diffusivity and that it depends on the geometry of the porous medium through the $\mathbf{b}_\gamma$-field. The boundary value problem for the $\mathbf{b}_\gamma$-field is purely geometrical in nature and we will examine solutions of this problem in Sec. 1.6 in order to compare theory with experiment for the effective diffusivity. In addition to using the closure problem given by Eqs. 1. 4-58 to determine the effective diffusivity tensor, one can also use it to prove that $\mathbf{D}_{eff}$ is symmetric (see Problem 1-23).

1.5 Symmetric Unit Cells

In this section we develop some symmetry properties for the s_γ and $\mathbf{b}_\gamma$-fields that occur when symmetric unit cells are used to solve the two closure problems given by Eqs. 1. 4-58 and 1.4-59. Although the unit cell illustrated in Figure 1.6 is not symmetric, most calculations are carried out using relatively simple unit cells that are completely symmetric. Under these circumstances one can prove that $\mathbf{u} = 0$, and in the following paragraphs we present Ryan's (1983) proof. We begin with an explicit representation of Eqs. 1.4-59 for the x, y, z-coordinate system so that the closure problem takes the form

Problem II

$$\frac{\partial^2 s_\gamma}{\partial x^2} + \frac{\partial^2 s_\gamma}{\partial y^2} + \frac{\partial^2 s_\gamma}{\partial z^2} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \tag{1.5-1a}$$

B.C.1 $$-n_x \frac{\partial s_\gamma}{\partial x} - n_y \frac{\partial s_\gamma}{\partial y} - n_z \frac{\partial s_\gamma}{\partial z} = k/\mathscr{D}_\gamma, \quad \text{at } A_{\gamma\kappa} \tag{1.5-1b}$$

Periodicity: $$s_\gamma(\mathbf{r}+\ell_i) = s_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.5-1c}$$

Here we have used n_x, n_y, and n_z to represent the components of the unit normal vector $\mathbf{n}_{\gamma\kappa}$ in order to simplify the nomenclature.

Since Eqs. 1.5-1 are valid in any coordinate system, we consider the transformation $x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z}$ and express the closure problem in this new coordinate system as

Problem II′

$$\frac{\partial^2 \bar{s}_\gamma}{\partial \bar{x}^2} + \frac{\partial^2 \bar{s}_\gamma}{\partial \bar{y}^2} + \frac{\partial^2 \bar{s}_\gamma}{\partial \bar{z}^2} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \tag{1.5-2a}$$

B.C.1 $$-\bar{n}_x \frac{\partial \bar{s}_\gamma}{\partial \bar{x}} - \bar{n}_y \frac{\partial \bar{s}_\gamma}{\partial \bar{y}} - \bar{n}_z \frac{\partial \bar{s}_\gamma}{\partial \bar{z}} = k/\mathscr{D}_\gamma, \quad \text{at } A_{\gamma\kappa} \tag{1.5-2b}$$

Periodicity: $$\bar{s}_\gamma(\mathbf{r}+\ell_i) = \bar{s}_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.5-2c}$$

In Eqs. 1.5-2 we have used $\bar{s}_\gamma$ to mean

$$\bar{s}_\gamma = s_\gamma(\bar{x}, \bar{y}, \bar{z}) \tag{1.5-3}$$

We now consider a particular coordinate transformation given by

$$\bar{x} = -x, \quad \bar{y} = y, \quad \bar{z} = z \tag{1.5-4}$$

and for this case we see that Eq. 1.5-2a takes the form

$$\frac{\partial^2 \bar{s}}{\partial x^2} + \frac{\partial^2 \bar{s}}{\partial y^2} + \frac{\partial^2 \bar{s}}{\partial z^2} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \tag{1.5-5}$$

In the boundary condition given by Eq. 1.5-2b, the transformation specified by Eq. 1.5-4 leads to the following relations for the components of the normal vector

$$\bar{n}_x = n_x(\bar{x}, \bar{y}, \bar{z}) = n_x(-x, y, z) = -n_x(x, y, z) \tag{1.5-6a}$$

In addition, the symmetry of the unit cell also leads to

$$\bar{n}_y = n_y(\bar{x}, \bar{y}, \bar{z}) = n_y(-x, y, z) = n_y(x, y, z) \tag{1.5-6b}$$

$$\bar{n}_z = n_z(\bar{x}, \bar{y}, \bar{z}) = n_z(-x, y, z) = n_z(x, y, z) \tag{1.5-6c}$$

The derivatives in the boundary condition given by Eq. 1.5-2b can now be expressed as

$$\frac{\partial \bar{s}_\gamma}{\partial \bar{x}} = -\frac{\partial \bar{s}_\gamma}{\partial x}, \quad \frac{\partial \bar{s}_\gamma}{\partial \bar{y}} = \frac{\partial \bar{s}_\gamma}{\partial y}, \quad \frac{\partial \bar{s}_\gamma}{\partial \bar{z}} = \frac{\partial \bar{s}_\gamma}{\partial z} \tag{1.5-7}$$

and this allows us to write that boundary condition as

B.C.1 $$-n_x \frac{\partial \bar{s}_\gamma}{\partial x} - n_y \frac{\partial \bar{s}_\gamma}{\partial y} - n_z \frac{\partial \bar{s}_\gamma}{\partial z} = k/\mathscr{D}_\gamma, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{1.5-8}$$

To be absolutely clear about the form of Problem II′, we summarize these results to express this part of the closure problem as

Problem II′

$$\frac{\partial^2 \bar{s}_\gamma}{\partial x^2} + \frac{\partial^2 \bar{s}_\gamma}{\partial y^2} + \frac{\partial^2 \bar{s}_\gamma}{\partial y^2} = -\left(\frac{a_v k}{\varepsilon_\gamma \mathscr{D}_\gamma}\right) \tag{1.5-9a}$$

B.C.1 $$-n_x \frac{\partial \bar{s}_\gamma}{\partial x} - n_y \frac{\partial \bar{s}_\gamma}{\partial y} - n_z \frac{\partial \bar{s}_\gamma}{\partial z} = k/\mathscr{D}_\gamma, \quad \text{at } A_{\gamma\kappa} \tag{1.5-9b}$$

Periodicity: $$\bar{s}_\gamma(\mathbf{r}+\ell_i) = \bar{s}_\gamma(\mathbf{r}), \quad i = 1, 2, 3 \tag{1.5-9c}$$

When this boundary value problem is compared with that given by Eqs. 1.5-1, we conclude that

$$\bar{s}_\gamma = s_\gamma \tag{1.5-10}$$

for the coordinate transformation given by Eq. 1.5-4. We can also write Eq. 1.5-10 as

$$s_\gamma(-x, y, z) = s_\gamma(x, y, z) \tag{1.5-11}$$

and from this we see that s_γ is symmetric in x for a unit cell that is symmetric in x. One can repeat this proof of Ryan (1983) for cells that are *completely symmetric* to show that s_γ is *completely symmetric*. For this case we can prove that the vector $\mathbf{u}$ is equal to zero.

Because of the periodic nature of s_γ, we can express the area integral of s_γ over the entrances and exits of *any unit cell* as

$$\frac{1}{V_\gamma} \int_{A_{\gamma e}} \mathbf{n}_{\gamma e} s_\gamma \, dA = 0 \tag{1.5-12}$$

When this condition is used with Eq. 1.4-63, and the divergence theorem is applied in order to convert the area integral to a volume integral, we obtain the following expression for the vector $\mathbf{u}$:

$$\mathbf{u} = \varepsilon_\gamma \mathscr{D}_\gamma \left\{ \frac{1}{V_\gamma} \int_{V_\gamma} \nabla s_\gamma \, dV \right\} \tag{1.5-13}$$

The x-component of the this vector is given by

$$u_x = \varepsilon_\gamma \mathscr{D}_\gamma \left\{ \frac{1}{V_\gamma} \int_{V_\gamma} \frac{\partial s_\gamma}{\partial x} dV \right\} \tag{1.5-14}$$

and since s_γ is symmetric in x we know that $\partial s_\gamma / \partial x$ is skew-symmetric, i.e.,

$$\left. \frac{\partial s_\gamma}{\partial x} \right|_x = - \left. \frac{\partial s_\gamma}{\partial x} \right|_{-x} \tag{1.5-15}$$

This leads to the condition

$$u_x = 0 \tag{1.5-16}$$

and for a completely symmetric unit cell we have

$$\mathbf{u} = 0, \quad \text{completely symmetric unit cell} \tag{1.5-17}$$

Given that the convective transport term in Eq. 1.4-64 is *negligible*, as indicated in Eq. 1.4-67, this result for completely symmetric unit cells is not particularly important; however, the characteristics of symmetric unit cells are important and the analysis leading to Eq. 1.5-17 will prove to be useful in other studies.

Turning our attention to Problem I, we examine the x-component of the vector $\mathbf{b}_\gamma$ for the transformation given by Eq. 1.5-4. We designate $\mathbf{i} \cdot \mathbf{b}_\gamma$ as b_γ and express the closure problem for this component as

Problem I

$$\frac{\partial^2 b_\gamma}{\partial x^2} + \frac{\partial^2 b_\gamma}{\partial y^2} + \frac{\partial^2 b_\gamma}{\partial z^2} = 0 \tag{1.5-18a}$$

B.C.1
$$- n_x \frac{\partial b_\gamma}{\partial x} - n_y \frac{\partial b_\gamma}{\partial y} - n_z \frac{\partial b_\gamma}{\partial z} = n_x, \quad \text{at } A_{\gamma\kappa} \tag{1.5-18b}$$

Periodicity:
$$b_\gamma(\mathbf{r} + \ell_i) = b_\gamma(\mathbf{r}), \quad i = 1, 2, 3 \tag{1.5-18c}$$

In the $\bar{x}, \bar{y}, \bar{z}$ coordinate system we express this problem as

Problem I′

$$\frac{\partial^2 \bar{b}_\gamma}{\partial \bar{x}^2} + \frac{\partial^2 \bar{b}_\gamma}{\partial \bar{y}^2} + \frac{\partial^2 \bar{b}_\gamma}{\partial \bar{z}^2} = 0 \tag{1.5-19a}$$

B.C.1
$$-\bar{n}_x \frac{\partial \bar{b}_\gamma}{\partial \bar{x}} - \bar{n}_y \frac{\partial \bar{b}_\gamma}{\partial \bar{y}} - \bar{n}_z \frac{\partial \bar{b}_\gamma}{\partial \bar{z}} = \bar{n}_x, \quad \text{at } A_{\gamma\kappa} \tag{1.5-19b}$$

Periodicity:
$$\bar{b}_\gamma(\mathbf{r}+\ell_i) = \bar{b}_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.5-19c}$$

Here we have used $\bar{b}_\gamma$ to mean

$$\bar{b}_\gamma = b_\gamma(\bar{x},\bar{y},\bar{z}) \tag{1.5-20}$$

For the specific transformation given by Eq. 1.5-4, we can repeat the analysis given by Eqs. 1.5-2 through 1.5-9 to obtain

Problem I′

$$\frac{\partial^2 \bar{b}_\gamma}{\partial x^2} + \frac{\partial^2 \bar{b}_\gamma}{\partial y^2} + \frac{\partial^2 \bar{b}_\gamma}{\partial z^2} = 0 \tag{1.5-21a}$$

B.C.1
$$-n_x \frac{\partial \bar{b}_\gamma}{\partial x} - n_y \frac{\partial \bar{b}_\gamma}{\partial y} - n_z \frac{\partial \bar{b}_\gamma}{\partial z} = -n_x, \quad \text{at } A_{\gamma\kappa} \tag{1.5-21b}$$

Periodicity:
$$\bar{b}_\gamma(\mathbf{r}+\ell_i) = \bar{b}_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{1.5-21c}$$

The key idea here is that the x-component of the unit normal vector on the right hand side of Eq. 1.5-18b controls the behavior of the $\mathbf{b}_\gamma$-field and n_x is skew-symmetric in x. By comparing Eqs. 1.5-18 with Eqs. 1.5-21, we see that

$$b_\gamma = -\bar{b}_\gamma \tag{1.5-22}$$

and we can be more explicit by expressing this result as

$$b_{\gamma x}(x,y,z) = -b_{\gamma x}(-x,y,z) \tag{1.5-23a}$$

For a completely symmetric unit cell, the above proof can be repeated for the y and z-components of the vector $\mathbf{b}_\gamma$, and this leads to

$$b_{\gamma y}(x,y,z) = -b_{\gamma y}(x,-y,z) \tag{1.5-23b}$$

$$b_{\gamma z}(x,y,z) = -b_{\gamma z}(x,y,-z) \tag{1.5-23c}$$

These conditions can be used to reduce the computational domain, and in the original numerical studies (Ryan, 1983) this reduction was of considerable importance.

1.6 Comparison Between Theory and Experiment

Our objective in this section is to compare the theory that led to Eq. 1.4-68 with experiment; however, since the effective diffusivity is independent of the reaction rate it is sufficient to consider only the case of passive diffusion in porous media. The comparison between theory and experiment will be restricted to systems for which ε_γ and $\mathbf{D}_{eff}$ can be treated as constants, thus Eq. 1.4-68 can be simplified to

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} = \varepsilon_\gamma \mathbf{D}_{eff} : \nabla\nabla \langle c_{A\gamma} \rangle^\gamma \tag{1.6-1}$$

It is of some interest to note that we have retained the porosity in this result rather than canceling ε_γ from each side of Eq. 1.6-1. This has been done in an effort to avoid errors on the order of ε_γ, since numerous errors of this type have made their way into the literature.

It is important to remember at this point that our formulation of the diffusion problem was based on the restrictions given by Eqs. 1.1-12 and 1.1-13 and on the definition of the mixture diffusivity given by Eq. 1.1-15. This led to the molar flux being represented by

$$\mathbf{N}_{A\gamma} = - \mathscr{D}_\gamma \nabla c_{A\gamma} \tag{1.6-2}$$

and one can quickly draw upon the developments in Secs. 1.2 and 1.4 to demonstrate that the *superficial volume average* molar flux takes the form

$$\langle \mathbf{N}_{A\gamma} \rangle = - \varepsilon_\gamma \mathbf{D}_{eff} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \tag{1.6-3}$$

In many problems of practical importance, one is only interested in the transport of species A between a porous medium and the adjoining homogeneous fluid. We have shown this system in Figure 1.7 in which the ω-region represents the porous medium and the η-region represents the homogenous fluid. The molar flux associated with the ω-η interface can be expressed as

$$\left\{ \begin{matrix} \textit{moles of species A} \\ \textit{transferred per unit} \\ \textit{time and area} \end{matrix} \right\} = - \mathbf{n}_{\omega\eta} \cdot \varepsilon_\gamma \mathbf{D}_{eff} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \tag{1.6-4}$$

however, this is often written in the form

$$\left\{ \begin{matrix} \textit{moles of species A} \\ \textit{transferred per unit} \\ \textit{time and area} \end{matrix} \right\} = - \mathbf{n}_{\omega\eta} \cdot \mathbf{D}'_{eff} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \tag{1.6-5}$$

In this case the porosity has been incorporated into the effective diffusivity tensor, and this is entirely a matter of choice; however, one is less likely to commit an algebraic error if the porosity is retained as a separate factor as we have done in Eqs. 1.6-1 and

1.6-4. The general problem of constructing conditions at the boundary between a porous medium and a homogeneous fluid has been discussed by Ochoa-Tapia and Whitaker (1995a, 1995b, 1997, 1998a, 1998b).

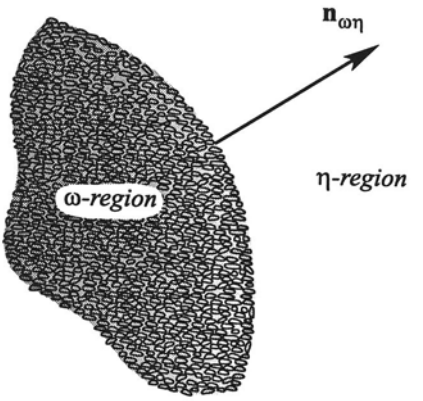


Figure 1.7. Boundary between a porous medium and a homogeneous fluid

1.6.1 EXPERIMENTAL STUDIES

Experimental studies that are consistent with Eqs. 1.1-12 and 1.1-13 are very difficult to carry out, especially in the presence of a chemical reaction. On the other hand, one can perform experiments with passive systems at high molar concentrations that are consistent with the theory leading to Eq. 1.6-1 and the closure problem that is used to determine the effective diffusivity defined by Eq. 1.4-62. These experiments are done with binary systems at constant temperature and pressure, and for these systems the single Stefan-Maxwell equation takes the form

$$\mathbf{N}_{A\gamma} = x_{A\gamma}\left(\mathbf{N}_{A\gamma} + \mathbf{N}_{B\gamma}\right) - \mathscr{D}_{AB}\nabla c_{A\gamma} \tag{1.6-6}$$

since the total molar concentration, c_γ, can be treated as a constant. In experimental systems that are set up to provide transient, one-dimensional molar fluxes, one can argue that

$$\langle \mathbf{N}_{A\gamma} \rangle = -\langle \mathbf{N}_{B\gamma} \rangle \tag{1.6-7}$$

If one is willing to assume that the average of spatial deviations is zero, one can make use of Eq. 1.6-7 in conjunction with Eq. 1.6-6 to obtain the following representation for the intrinsic volume average molar flux of species *A*

$$\langle \mathbf{N}_{A\gamma} \rangle = \left\langle \tilde{x}_{A\gamma}\left(\tilde{\mathbf{N}}_{A\gamma} + \tilde{\mathbf{N}}_{B\gamma}\right)\right\rangle - \left\langle \mathscr{D}_{AB}\nabla c_{A\gamma}\right\rangle \tag{1.6-8}$$

On the basis of the result given by Eq. 1.4-37, one can make use of the inequality

$$\left\langle \tilde{x}_{A\gamma}\left(\tilde{\mathbf{N}}_{A\gamma}+\tilde{\mathbf{N}}_{B\gamma}\right)\right\rangle \;<<\; \langle \mathbf{N}_{A\gamma}\rangle \tag{1.6-9}$$

and this allows us to express the superficial average molar flux as

$$\langle \mathbf{N}_{A\gamma}\rangle \;=\; -\langle \mathscr{D}_{AB}\nabla c_{A\gamma}\rangle \tag{1.6-10}$$

From here one can obtain Eq. 1.6-3 where $\mathscr{D}_{AB}$ replaces $\mathscr{D}_{\gamma}$ in the expression for the effective diffusivity tensor given by Eq. 1.4-62. Since all of the experiments that we wish to compare with the theory were obtained under conditions that led to Eq. 1.6-7, the justification of Eq. 1.6-10 is an important matter.

1.6.2 ISOTROPIC SYSTEMS

It is worthwhile to note that there are no homogeneous, isotropic porous media. By isotropic one means *invariant to any coordinate rotation* and by homogeneous one means *invariant to any coordinate translation*, and a little thought will indicate that there are no porous media that could satisfy these geometrical requirements. On the other hand, there exist porous media for which the diffusion process is isotropic and for which the effective diffusivity tensor and the porosity can be treated as constants. We think of these porous media as being *homogeneous and isotropic with respect to the diffusion process.*

As an example, we note that the representative porous medium illustrated in Figure 1.6 is invariant to coordinate translations of the type $\mathbf{r}=\bar{\mathbf{r}}+\ell_i$, but it is *not invariant* to an arbitrary translation and thus it is not homogeneous. Directing our attention of a simpler system, we note that the two-dimensional, square array illustrated in Figure 1.8 is only invariant to 90° rotations about certain points, but it is not invariant to arbitrary coordinate rotations about any point. Thus the porous medium is neither homogeneous nor isotropic. On the other hand, the system illustrated in Figure 1.8 can be used to solve the closure problem given by Eqs. 1.4-58, and this has been done by Ryan (1983) to obtain

$$D_{xx} \;=\; D_{yy}\,, \qquad D_{xy} \;=\; D_{yx} \;=\; 0 \tag{1.6-11}$$

Here we have used D_{xx}, D_{xy}, etc., to represent the components of $\mathbf{D}_{eff}$, and Eqs. 1.6-11 indicate that the system illustrated in Figure 1.8 is *homogeneous and transversely isotropic with respect to the diffusion process.* Ryan also solved the closure problem for the system shown in Figure 1.9, and for that array one might expect to find values of D_{yy} that are larger than the values for D_{xx} since diffusion in the x-direction would follow a more "tortuous path". However, the computed values of D_{xx} and D_{yy} differed by less that 1% while the off-diagonal components were zero. This indicates that for practical purposes the system shown in Figure 1.9 is also homogeneous and transversely isotropic *with respect to the diffusion process.* In a more recent study of diffusion in cellular systems, Ochoa (1989) repeated the original work of Ryan (1983) using several different numerical techniques, all of which gave good agreement with Ryan's calculations.

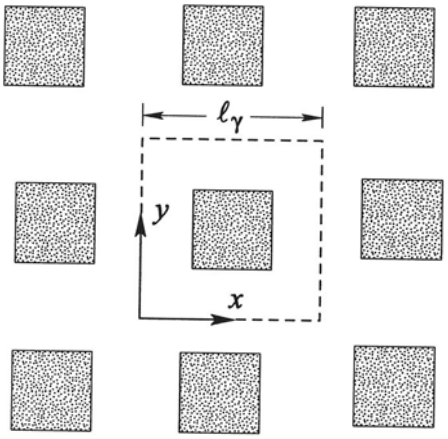


Figure 1.8. Two-dimensional square array as a model of a spatially periodic porous medium

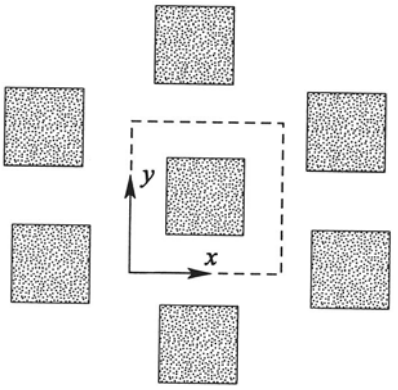


Figure 1.9. Two-dimensional array as a model of a spatially periodic porous medium

There are a number of unconsolidated porous media that appear to be isotropic with respect to the diffusion process and in Figure 1.10 we have compared the experimental data for these systems with several theories. The curve identified as Ryan *et al.* (1981) represents the solution of Eqs. 1.4-58 with the single distinct component of the effective diffusivity tensor being predicted by Eq. 1.4-62. The theoretical results for the models illustrated in Figures 1.8 and 1.9 are essentially identical and are in good agreement with the experimental data shown in Figure 1.10. The curve identified by Quintard represents a solution for the three-dimensional array of spheres illustrated in Figure 1.11. The results of Quintard (1993) are slightly higher than those of Ryan *et al.* (1981) and are in excellent agreement with the experimental data. The curve identified by Weissberg (1963) in Figure 1.10 is an upper bound determined by means of a variational principle which yields the following analytical representation:

$$\varepsilon_\gamma D_{eff}/\mathscr{D}_\gamma = \frac{\varepsilon_\gamma}{1 - \frac{1}{2}\ln\varepsilon_\gamma}, \quad \textit{Weissberg} \tag{1.6-12}$$

This result is also in reasonably good agreement with the experimental data, and as an upper bound it is appropriate that it always predicts values that are greater than either those of Ryan *et al.* or Quintard. The first attempt at a theoretical prediction of the effective diffusivity is due to Maxwell (1881) who analyzed a dilute suspension of spheres to obtain the result

$$\varepsilon_\gamma D_{eff}/\mathscr{D}_\gamma = \frac{2\varepsilon_\gamma}{3 - \varepsilon_\gamma}, \quad \textit{Maxwell} \tag{1.6-13}$$

Although Eq. 1.6-13 was originally considered to be restricted to values of ε_γ close to one, Hashin and Shtrikman (1962) have shown that it is an upper bound for any value of ε_γ and the comparison shown in Figure 1.10 verifies their analysis.

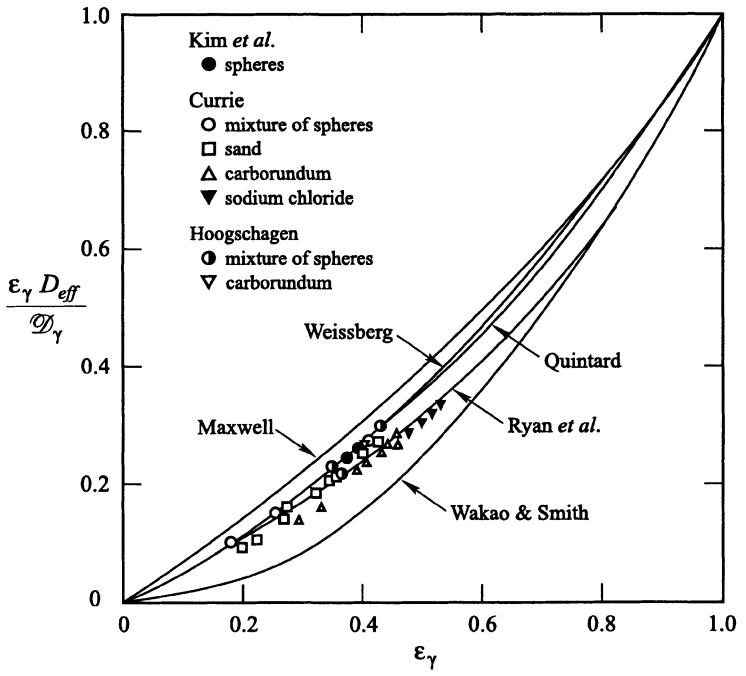


Figure 1.10. Comparison between theory and experiment for isotropic systems

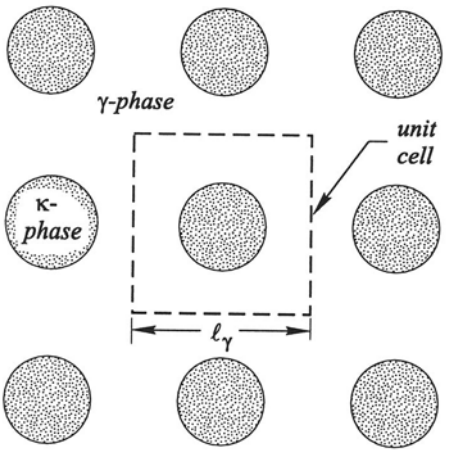


Figure 1.11. Three-dimensional array of spheres as a model of a spatially periodic porous medium

The micropore-macropore model of Wakao and Smith (1962) can be used to predict effective diffusivities for macropore systems and for the constraints associated with Eq. 1.2-1 their expression reduces to

$$\varepsilon_\gamma D_{eff} / \mathscr{D}_\gamma = \varepsilon_\gamma^2, \quad \textit{Wakao and Smith} \tag{1.6-14}$$

This result is illustrated in Figure 1.10 and one can see that it significantly under-predicts the effective diffusivity for values of the porosity in the range of practical importance. The problem of diffusion and reaction in a macropore-micropore model of a porous catalyst has been examined in some detail by Whitaker (1983a), and a comparison between theory and experiment is available in terms of effective diffusivities for packed beds of porous particles (Whitaker, 1988c).

1.6.3 MAXWELL'S CLOSURE PROBLEM

Equation 1.6-13 is of particular interest when viewed in terms of the closure problem given by Eqs. 1.4-58. Rather than solve that boundary value problem subject to the periodicity condition associated with the unit cell shown in Figure 1.11, Chang (1982, 1983) proposed a solution subject to a Dirichlet condition imposed at the spherical surface illustrated in Figure 1.12. This special form of Eqs. 1.4-58 is given by

$$\nabla^2 \mathbf{b}_\gamma = 0 \tag{1.6-15a}$$

B.C.1
$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \mathbf{b}_\gamma = \mathbf{n}_{\gamma\kappa}, \quad r = r_0 \tag{1.6-15b}$$

B.C.2
$$\mathbf{b}_\gamma = 0, \quad r = r_1 \tag{1.6-15c}$$

and in order to develop a precise correspondence with the spatially periodic model shown in Figure 1.11, we require that the porosity and the area per unit volume for the

two models be equal (Quintard and Whitaker, 1995a). The solution to Eqs. 1.6-15 produces the expression for the effective diffusivity given by Eq. 1.6-13, thus this form of the closure problem gives reasonable agreement with experimental data as one can see from the curve identified by Maxwell in Figure 1.10.

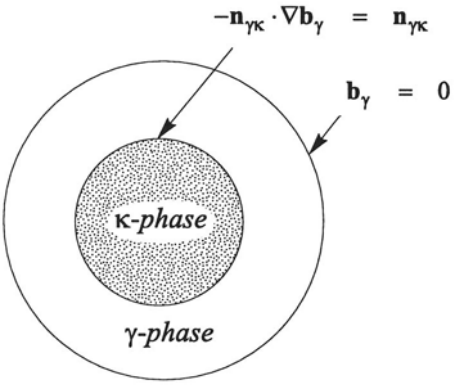


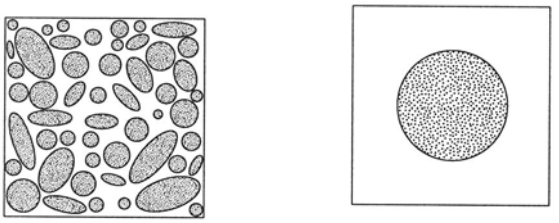
Figure 1.12. Chang's unit cell

Since the space occupied by the unit cell associated with Eqs. 1.6-15 does not fill the space occupied by the porous medium, it is surprising that Maxwell's closure problem gives such good agreement with experiment. A detailed study of Eqs. 1.4-58 and the special form given by Eqs. 1.6-15 has been carried out by Ochoa-Tapia *et al.* (1994), and their work indicates that there are significant differences between the $\mathbf{b}_\gamma$-field determined by Eqs. 1.4-58 and Eqs. 1.6-15. However, it is the area integral of $\mathbf{b}_\gamma \mathbf{n}_{\gamma\kappa}$ that determines the effective diffusivity tensor, and this area integral is not strongly influenced by either the periodicity condition given by Eq. 1.4-58c or the Dirichlet condition given by Eq. 1.6-15c.

1.6.4 ROLE OF THE FILTER

At this point we are in a position to learn something about the filtering characteristics of the area integral in Eq. 1.3-37 or in Eq. 1.4-62. To do so we consider the experimental data for sand (Currie, 1960) that are illustrated in Figure 1.10. We imagine that photomicrographs of the sand are available and that from them we can construct a detailed three-dimensional model of the sand. A two-dimensional rendering of the experimental system is illustrated in Figure 1.13, along with a theoretical model having the same porosity as the experimental system. Imagine that the boundary value problem represented by Eqs. 1.4-58 is solved for the experimental system shown in Figure 1.13 and the results are used in Eq. 1.4-62 to determine the effective diffusivity tensor. We expect that the computed values for D_{eff} would be in excellent agreement with the experimental values illustrated in Figure 1.10, and this means that the *experimental system* illustrated in Figure 1.13 would provide essentially the same result as the

theoretical model shown in that figure. This leads us to the question: "What gets through the filter for the process of diffusion in an isotropic system?", and the answer is most certainly, "Not much more than the porosity."



Experimental system *Theoretical model*

Figure 1.13. Experimental system and theoretical model for sand

1.6.5 ANISOTROPIC SYSTEMS

While many systems that are *isotropic with respect to diffusion* are available in the laboratory, most natural systems and many processed materials are anisotropic. The process of extrusion may be the cause of anisotropy in catalyst pellets (Satterfield, 1970, Sec. 1.8.2), and the experimental results of Currie (1960) for kaolin suggest that any kaolin-based catalyst will exhibit anisotropic behavior. Natural minerals such as clay and sandstone tend to be anisotropic (Muskat, Sec. 6.7, 1949) as do most cellular systems (Crapiste *et al.*, 1988a-b). Wood is a classic example of an anisotropic organic material and this has important consequences for the drying process (Bonneau and Puiggali, 1993; Turner, 1996). Although there are numerous anisotropic systems of practical importance, no experimental studies exist prior to those of Kim *et al.* (1987). Using a system similar to that employed by Currie (1960), Kim *et al.* (1987) measured the components of the effective diffusivity tensor parallel and perpendicular to the bedding plane. Three systems composed of mica particles were studied and measurements were also made for an artificial porous medium composed of mylar disks. Kim *et al.* (1987) described the properties of the mica and mylar particles in terms of the following three parameters:

1. The average projected area, A.
2. The average thickness, b.
3. An effective length, $a = \sqrt{A}$

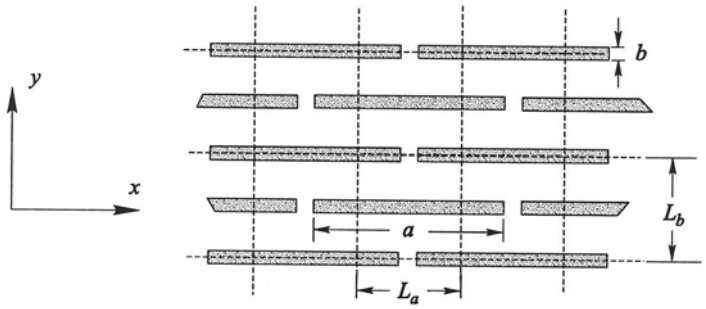
The properties of the four systems studied by Kim *et al.* (1987) are listed in Table 1.1 and the degree of anisotropy can be thought of as characterized by the ratio, a/b.

Given the success of the simple two-dimensional models illustrated in Figures 1.8 and 1.9, it would seem reasonable to begin a study of anisotropic systems with similar models such as those shown in Figures 1.14. From those figures it becomes immediately apparent that anisotropic systems are much more complicated than isotropic systems.

TABLE 1.1. Geometrical characteristics of porous media particles

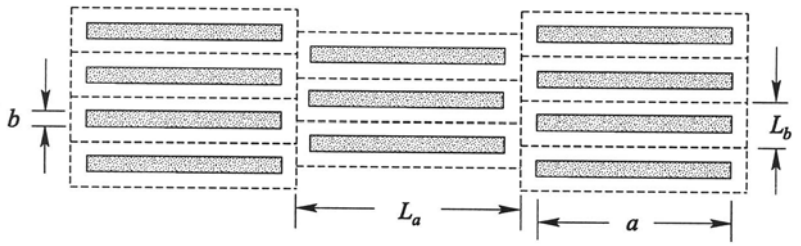
material	projected area A (mm^2)	average thickness b (mm)	effective length a (mm)	a/b
mica A	1.076	0.072	1.037	14.4
mica B	0.481	0.043	0.694	16.1
mica C	0.235	0.033	0.485	14.7
mylar disks	2.483	0.076	1.576	20.7

In the theoretical analysis of Kim *et al.* (1987), the particles were all parallel to the x-axis and the influence of the lattice vectors was accounted for by the ratio of the lengths of the sides of the unit cell, L_a / L_b, where L_a and L_b are illustrated in Figures 1.14.



$\varepsilon_\gamma = 0.85 \qquad L_a/L_b = 1 \qquad a/b = 15$

Figure 1.14a. Geometrical model of anisotropic porous media



$\varepsilon_\gamma = 0.75 \qquad L_a/L_b = 5 \qquad a/b = 15$

Figure 1.14b. Geometrical model of anisotropic porous media

The expectation of Kim *et al.* (1987) was that anisotropic porous media could be modeled in terms of the porosity, ε_γ, the particle geometry, a/b, and some choice of L_a / L_b (or the lattice vectors, ℓ_i). It was further assumed that a two-dimensional model would be acceptable and that the *mean orientation* of the particles was sufficient to characterize the porous medium. That these assumptions were *incorrect* is clearly demonstrated in Figures 1.15 and 1.16. There we have shown calculated and measured

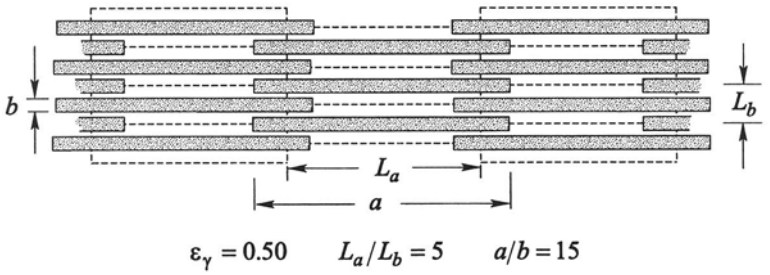


Figure 1.14c. Geometrical model of anisotropic porous media

values of $\varepsilon_\gamma D_{yy} / \mathscr{D}_\gamma$ and $\varepsilon_\gamma D_{xx} / \mathscr{D}_\gamma$ as a function of the porosity for several values of L_a / L_b and we see no choice of L_a / L_b that provides good agreement between theory and experiment. The value of $a/b = 15$ used in the calculations is in the proper range for both the mica and the mylar disks studied by Kim *et al.* (1987); however, there is no geometrical information available for the vermiculite and the mica used by Currie (1960).

While the presentation of theoretical results in Figures 1.15 and 1.16 is not exhaustive, it does indicate that one cannot find a *single value* of L_a / L_b that gives good agreement between theory and experiment. More extensive calculations are available in Kim *et al.* (1987) and in Ochoa (1989), and they all lead to the same conclusion that the two-dimensional models illustrated in Figure 1.14 are insufficient to capture the important characteristics of diffusion in anisotropic porous media. One of the interesting characteristics of the more extensive calculations is that *under all circumstances* the theory over-predicts the value of D_{xx}. The reason for this seems clear from the in situ photographs of the mica and mylar disk systems that were taken by Kim *et al.* (1987), and a sketch of the structure seen in the photographs is presented in Figure 1.17. It would appear that the *average orientation* of the particles was parallel to the x-axis or the bedding plane; however, the particles were arranged in groups that were inclined to the bedding plane at angles in the range of $\theta = \pm 20^\circ$. It seems clear that the orientation of the particles *around the bedding plane* is responsible for the experimental values of $\varepsilon_\gamma D_{xx} / \mathscr{D}_\gamma$ shown in Figure 1.16 being smaller than the theoretical values based on the models shown in Figure 1.14. In addition, it would appear that the *effective value* of a/b is less than the value listed in Table 1.1 because of the manner in which the particles align themselves in groups.

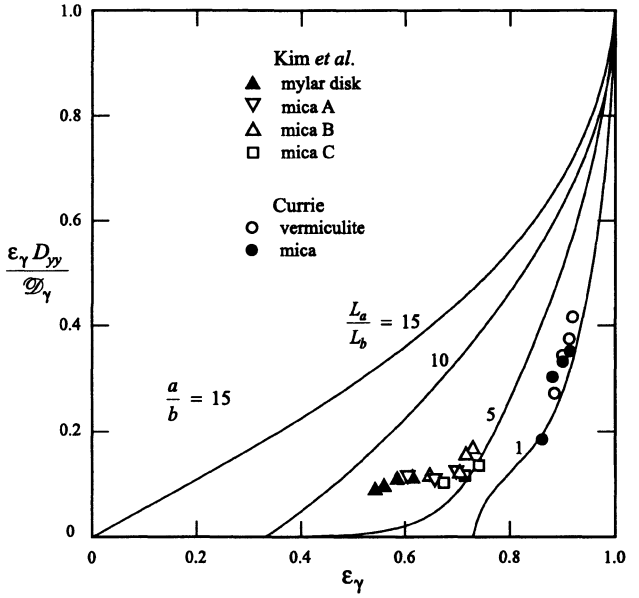


Figure 1.15. Effective diffusivities normal to the bedding plane

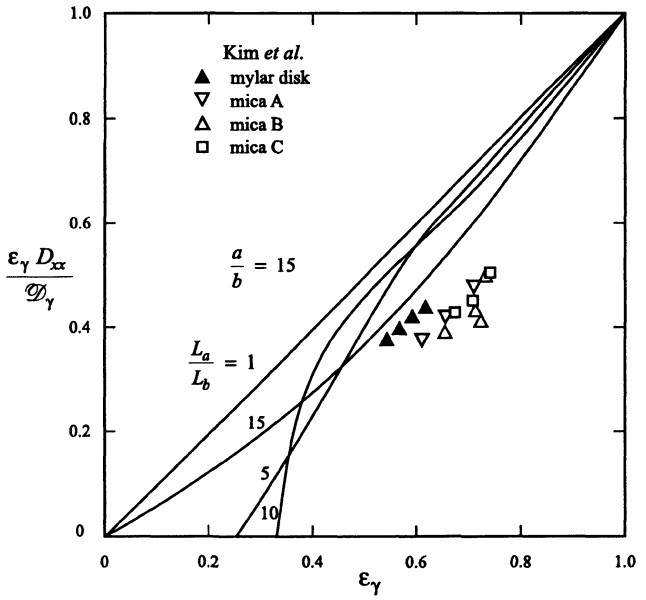


Figure 1.16. Effective diffusivities parallel to the bedding plane

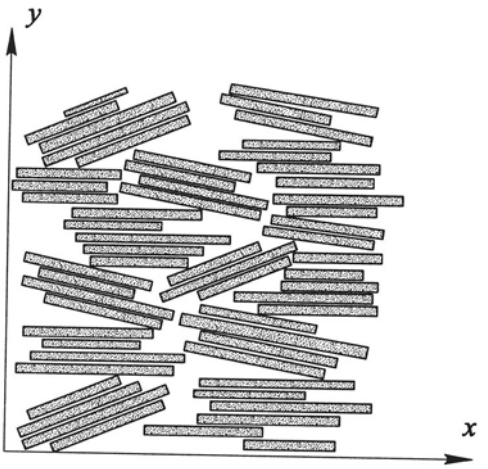


Figure 1.17. Observed particle orientation for anisotropic systems

On the basis of the results presented in Figures 1.15 and 1.16, we conclude that successful geometrical models will be based on knowledge of the porosity, ε_γ, the particle geometry perhaps described by a/b, the mean orientation represented by $\langle\theta\rangle$, and the mean of the square of the orientation, $\langle\theta^2\rangle$. The key to understanding what geometrical information passes through the filter represented by Eq. 1.3-37 is the closure problem given by Eqs. 1.4-58, however, at this time we do not know how to extract this information directly and for the present we rely on intuition and comparison between theory and experiment.

The first improvement on the calculations of Kim *et al.* (1987) was made by Sáez *et al.* (1991) who used a three-dimensional model of parallelepipeds in a planar configuration. This led to theoretical results which provided non-zero values of $\varepsilon_\gamma D_{yy}/\mathscr{D}_\gamma$ over a wider range of porosities than the two-dimensional models of Kim *et al.* (1987). In addition, Sáez *et al.* (1991) were able to obtain reasonably good agreement between the theory and the experimental results of Kim *et al.* for $\varepsilon_\gamma D_{yy}/\mathscr{D}_\gamma$ using $L_a/L_b = 8$ and $a/b = 15$. Not surprisingly, their calculations for the effective diffusivity parallel to the bedding plane, $\varepsilon_\gamma D_{xx}/\mathscr{D}_\gamma$, were uniformly too large since the particles in their model were all parallel to the bedding plane.

The calculations of Sáez *et al.* (1991) were followed by those of Quintard (1993) who used a three-dimensional array of spheres to produce the results shown in Figure 1.10. In addition, Quintard (1993) studied the problem of anisotropic systems using a three-dimensional model of cylindrical particles that *were not* arranged in a planar configuration. With this model, Quintard was able to reproduce some of the experimental data for $\varepsilon_\gamma D_{xx}/\mathscr{D}_\gamma$ shown in Figure 1.16; however, the calculations were rather limited in nature because of the computational cost. Quintard's (1993) study clearly established that the mean orientation, $\langle\theta\rangle$, of the particles is not sufficient for the

determination of effective diffusivities parallel to the bedding plane and that one must know something about how the particles are distributed about the mean.

The most recent study of diffusion in anisotropic systems is the work of Ochoa-Tapia *et al.* (1994) who made use of Maxwell's closure problem in conjunction with an ellipsoidal unit cell. The closure problem has the same general form as Eqs. 1.6-15, but ellipsoidal coordinates are used to achieve an anisotropic system. Values of the effective diffusivity orthogonal to the bedding plane are represented by $\varepsilon_\gamma D_{zz}/\mathscr{D}_\gamma$ in order to be consistent with the nomenclature of Ochoa-Tapia *et al.* (1994), and the comparison between theory and experiment for *oblate particles* is shown in Figure 1.18 for various

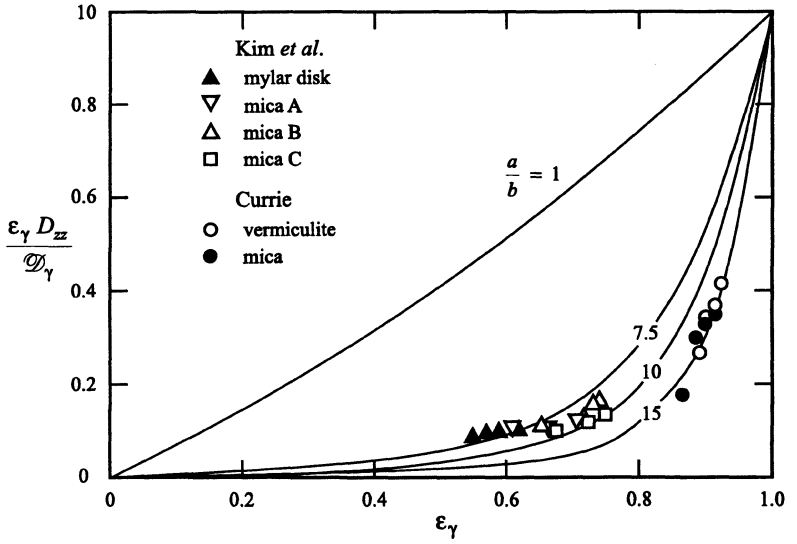
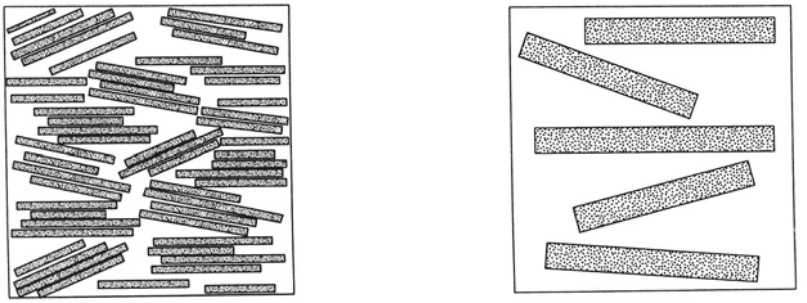


Figure 1.18. Experimental effective diffusivities normal to the bedding plane and theoretical effective diffusivities normal to the major axis of oblate particles

values of a/b. The parameter a/b represents the ratio of the major axis to the minor axis and thus has very nearly the same significance as the parameter listed in Table 1.1. In this case we see good agreement between theory and the experimental results of Kim *et al.* (1987) for a value of $a/b \sim 9$, while the experimental data of Currie (1960) would be better fit by a value of $a/b \sim 15$. The value of $a/b \sim 9$ is consistent with the results listed in Table 1.1 and the idea that the particles tend to align themselves in groups as suggested in Figure 1.17. The predictions for effective diffusivities parallel to the bedding plane are similar to those shown in Figure 1.16, i.e., the ellipsoidal unit cell predicts values of $\varepsilon_\gamma D_{xx}/\mathscr{D}_\gamma$ that are *too large*. The use of Maxwell's closure problem with ellipsoidal unit cells has the attractive feature that it produces analytical solutions with a minimum of effort and the results can be used to determine some properties of anisotropic systems. However, a general theory identifying the geometrical

characteristics that pass through the filter represented by Eq. 1.3-37 still remains to be developed, and the relation between an *experimental system* and a *theoretical model*, illustrated in Figure 1.13 for isotropic systems, needs to be altered for anisotropic systems. The idea that more information passes through the filter for anisotropic systems is illustrated in Figure 1.19 where we see that the unit cell used for theoretical calculations must incorporate more information about the structure of the system.



Experimental system *Theoretical model*

Figure 1.19. Experimental system and theoretical model for anisotropic porous media

1.7 Conclusions

In this chapter we have developed the closed form of the volume averaged transport equation for bulk diffusion with heterogeneous chemical reaction in porous media. We have used this process to set up much of the mathematical apparatus associated with the method of volume averaging, and we have illustrated the general framework of this procedure which consists of:

1. Spatial smoothing in which the governing equations and boundary conditions are joined.
2. Simplification of the spatially smoothed transport equation on the basis of the disparate length scales that often exist for multiphase systems.
3. Development of a closure problem, first in terms of the spatial deviation concentration and then in terms of the closure variables.
4. Comparison between theory and experiment in the absence of adjustable parameters.

For systems that are isotropic with respect to diffusion, all four of these objectives have been accomplished, while in the case of anisotropic systems we are still confronted with the problem of adjusting geometrical parameters in order to obtain agreement between theory and experiment.

1.8 Problems*

1-1. Show that the surface transport equation given by Eq. 1.1-19 can be treated as quasi-steady when $k_s t^* >> 1$.

1-2. The interfacial flux constitutive equation given by Eq. 1.1-6 expresses the *net* rate of adsorption as

$$\mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma} = k_1 c_{A\gamma} - k_{-1} c_{As}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1}$$

while the rate of adsorption is represented by

$$\left\{ \begin{matrix} \textit{rate of} \\ \textit{adsorption} \end{matrix} \right\} = k_1 c_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{2}$$

in which k_1 is a constant. If one thinks of the surface as consisting of adsorption sites, the rate of adsorption should depend on the number of *vacant sites.* If the dependence of the adsorption rate on vacant sites is linear, Eq. 2 should be written as

$$\left\{ \begin{matrix} \textit{rate of} \\ \textit{adsorption} \end{matrix} \right\} = k_1(1-\theta) c_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{3}$$

in which θ represents the fraction of *occupied sites.* Assume that θ is proportional to the surface concentration and use the chemical kinetic constitutive equation given by Eq. 1.1-18 in order to develop the following heterogeneous reaction rate equation:

$$R_{AS} = -\frac{k c_{A\gamma}}{1 + K c_{A\gamma}}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{4}$$

This is generally known as the Langmuir-Hinshelwood formulation.

1-3. For the process of pure adsorption in the absence of heterogeneous reaction and surface transport, Eq. 1.1-19 takes the form

$$\frac{\partial c_{AS}}{\partial t} = \mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{1}$$

When the linear interfacial flux constitutive equation given by Eq. 1.1-6 is applicable, this reduces to

$$\frac{\partial c_{AS}}{\partial t} = k_1 c_A - k_{-1} c_{AS}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{2}$$

---

* Solutions to all problems are available from the author.

Under equilibrium conditions, one can use Eq. 2 to conclude that

$$c_{A\sigma}^{eq} = K_{eq} c_{A\gamma} \tag{3}$$

in which the equilibrium constant is defined by

$$K_{eq} = \frac{k_1}{k_{-1}} \tag{4}$$

In order to analyze the adsorption process, Eq. 1 is typically written as

$$K_{eq} \frac{\partial c_{A\gamma}}{\partial t} = \mathbf{n}_{\gamma\kappa} \cdot \mathbf{N}_{A\gamma}, \quad \text{at the } \gamma\text{-}\kappa \text{ interface} \tag{5}$$

which makes use of Eq. 3 *even though* the surface is not at equilibrium. The condition illustrated by Eq. 5 is known as *local adsorption equilibrium* and it occurs when the departure from the equilibrium condition is *small enough* so that it can be neglected. In order to find the constraint associated with Eq. 5, decompose the surface concentration according to

$$c_{A\sigma} = c_{A\sigma}^{eq} + c_{A\sigma}^{*} \tag{6}$$

and then show that Eq. 5 is a valid approximation when the following constraint is satisfied:

$$k_{-1} t^{*} >> 1 \tag{7}$$

Here t^{*} represents the characteristic process time.

1-4. A model of diffusion and heterogeneous reaction in porous media can be constructed in terms of a single cylindrical pore in which the process is described by the following boundary value problem

$$\frac{\partial c_{A\gamma}}{\partial t} = \mathscr{D}_{\gamma}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_{A\gamma}}{\partial r}\right) + \frac{\partial^2 c_{A\gamma}}{\partial z^2}\right], \quad \text{in the } \gamma - \text{phase} \tag{1}$$

B.C.1 $$c_{A\gamma} = c_{A\gamma}^{o}, \quad z = 0 \tag{2}$$

B.C.2 $$-\mathscr{D}_{\gamma}\frac{\partial c_{A\gamma}}{\partial r} = k\, c_{A\gamma}, \quad r = r_o \tag{3}$$

B.C.3 $$\frac{\partial c_{A\gamma}}{\partial z} = 0, \quad z = L \tag{4}$$

I.C. unspecified (5)

Here we have assumed that the catalytic surface at $r = r_o$ is quasi-steady even though the diffusion process in the pore may be transient (Whitaker, 1986b).

The steady-state form of the boundary value problem for $c_{A\gamma}$ could be solved by classical means; however, in this problem you are asked to develop the area-averaged form of Eq. 1 and determine under what circumstances the concentration at $r = r_o$ can be replaced by the area-averaged concentration, $\langle c_{A\gamma} \rangle^{\gamma}$. This is defined by

$$\langle c_{A\gamma} \rangle^{\gamma} = \frac{1}{\pi r_o^2} \int_{r=0}^{r=r_o} 2\pi r c_{A\gamma} \, dr \tag{6}$$

thus you are seeking a constraint that will allow you to use the *approximation*

$$c_{A\gamma}\Big|_{r=r_o} = \langle c_{A\gamma} \rangle^{\gamma} \tag{7}$$

In your analysis of this problem, you should *not* use the formalism of the method of volume averaging, but instead you should apply the definition given by Eq. 6 directly to the governing differential equation given by Eq. 1. This will lead to the form

$$\frac{1}{\pi r_o^2} \int_{r=0}^{r=r_o} \frac{\partial c_{A\gamma}}{\partial t} 2\pi r dr = \frac{1}{\pi r_o^2} \int_{r=0}^{r=r_o} \mathscr{D}_{\gamma} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_{A\gamma}}{\partial r} \right) + \frac{\partial^2 c_{A\gamma}}{\partial z^2} \right] 2\pi r dr \tag{8}$$

Since the limits of integration are independent of t and z, one can interchange differentiation and integration to obtain

$$\frac{\partial \langle c_{A\gamma} \rangle^{\gamma}}{\partial t} = \frac{2\mathscr{D}_{\gamma}}{r_o^2} \int_{r=0}^{r=r_o} \frac{\partial}{\partial r} \left(r \frac{\partial c_{A\gamma}}{\partial r} \right) dr + \mathscr{D}_{\gamma} \frac{\partial^2 \langle c_{A\gamma} \rangle^{\gamma}}{\partial z^2} \tag{9}$$

Direct integration and imposition of the approximation indicated by Eq. 7 will lead to a useful form of the area-averaged transport equation.

After you have developed the area-averaged diffusion-reaction equation, solve the steady-state problem and determine the effectiveness factor defined by

$$\eta = \frac{\left\{ \begin{matrix} \textit{total rate of reaction} \\ \textit{in the pore} \end{matrix} \right\}}{\left\{ \begin{matrix} \textit{total rate of reaction} \\ \textit{in the pore if the} \\ \textit{concentration were } c_A^{\circ} \end{matrix} \right\}} \tag{10}$$

and indicate how η depends on the Thiele modulus.

1-5. If the function $\varphi(t)$ is defined by

$$\varphi(t) = \int_{\eta=a(t)}^{\eta=b(t)} f(t,\eta)d\eta \tag{1}$$

the one-dimensional Leibniz rule can be used to obtain

$$\frac{d\varphi}{dt} = \int_{\eta=a(t)}^{\eta=b(t)} \frac{\partial f}{\partial t}d\eta + f[t,b(t)]\frac{db}{dt} - f[t,a(t)]\frac{da}{dt} \tag{2}$$

Derive this result beginning with the definition

$$\frac{d\varphi}{dt} = \lim_{\Delta t\to 0}\left[\frac{\varphi(t+\Delta t)-\varphi(t)}{\Delta t}\right] \tag{3}$$

and express the integral between $a(t+\Delta t)$ and $b(t+\Delta t)$ in terms of three appropriately chosen integrals. Then use a simple geometrical interpretation of the integrals between $a(t)$ and $a(t+\Delta t)$ and between $b(t)$ and $b(t+\Delta t)$ to complete the derivation. If the integrand in Eq. 1 depends *only* on the dummy variable of integration, η, we have the *special case*

$$\varphi(t) = \int_{\eta=a(t)}^{\eta=b(t)} f(\eta)d\eta \tag{4}$$

and the special form of the Leibniz rule is given by

$$\frac{d\varphi}{dt} = f[b(t)]\frac{db}{dt} - f[a(t)]\frac{da}{dt} \tag{5}$$

The three-dimensional version of this result is encountered in the next problem in which time is replaced by the arclength along a line.

1-6. Derive the spatial averaging theorem using an approach analogous to the derivation of the Leibniz rule in one dimension (Whitaker, 1985). Begin the derivation by considering the derivative

$$\frac{d\varphi}{ds} = \lim_{\Delta s\to 0}\left[\frac{\varphi(s+\Delta s)-\varphi(s)}{\Delta s}\right] \tag{1}$$

in which $\varphi(s)$ is the integral defined by

$$\varphi(s) = \int_{V_\gamma(s)} \psi_\gamma dV \tag{2}$$

Here s is the distance along any line imbedded in the γ-κ system illustrated in Figure 1-6a, and ψ_γ is any function associated with the γ-phase. On the basis of

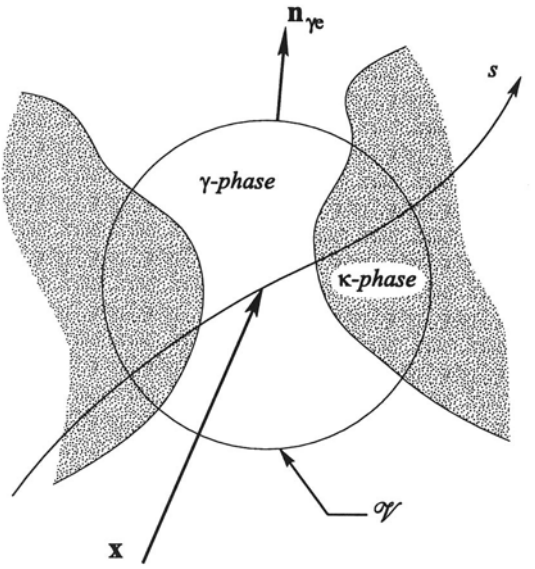


Figure 1-6a. Averaging volume and a two-phase system

Eq. 2, the derivative given by Eq. 1 takes the form

$$\frac{d}{ds}\int_{V_\gamma(s)} \psi_\gamma \, dV = \lim_{\Delta s \to 0} \left[\frac{\int_{V_\gamma(s+\Delta s)} \psi_\gamma \, dV - \int_{V_\gamma(s)} \psi_\gamma \, dV}{\Delta s} \right] \tag{3}$$

The two averaging volumes, $\mathscr{V}(s+\Delta s)$ and $\mathscr{V}(s)$, are illustrated in Figure 1-6b, and a little thought will indicate that the *intersection* of $V_\gamma(s+\Delta s)$ and $V_\gamma(s)$ will contribute nothing to the right hand side of Eq. 3. Once the intersection is removed, you should make use of the projected area theorem (Stein and Barcellos, 1992, Sec. 17.1) in the form

$$\Delta V = \pm \lambda \cdot \mathbf{n}_{\gamma e} \, dA \, \Delta s \tag{4}$$

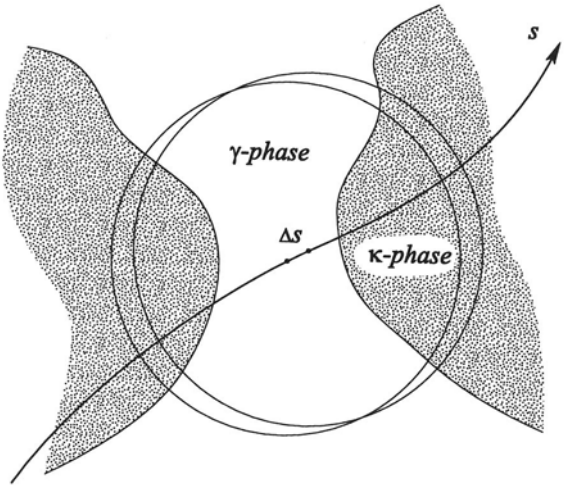


Figure 1-6b. Differential displacement of the averaging volume

Here dA represents a differential portion of the surface of the sphere located in the γ-phase, and $\mathbf{n}_{\gamma e}$ represents the outwardly directed unit normal vector illustrated in Figure 1-6a. Use of Eq. 4 will allow you to transform the two volume integrals to area integrals over the entrances and exits of the γ-phase contained within the averaging volume, $\mathscr{V}$. Make use of the fact that the derivative with respect to s can be expressed as (Stein and Barcellos, 1992, Sec. 14.7)

$$\frac{d}{ds} = \lambda \cdot \nabla \tag{5}$$

where λ is a unit vector tangent to the line illustrated in Figures 1-6a and 1-6b. Finally, you should use the divergence theorem

$$\int_{V_\gamma} \nabla \psi_\gamma \, dV = \int_{A_{\gamma e}} \mathbf{n}_{\gamma e} \psi_\gamma \, dA + \int_{A_{\gamma \kappa}} \mathbf{n}_{\gamma \kappa} \psi_\gamma \, dA \tag{6}$$

in order to obtain the traditional form of the averaging theorem.

1-7. In order to derive the averaging theorem for the divergence of a vector, replace ψ_γ in Problem 1-6 with the vector $\mathbf{a}_\gamma$ in order to prove that

$$\langle \nabla \mathbf{a}_\gamma \rangle = \nabla \langle \mathbf{a}_\gamma \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \mathbf{a}_\gamma dA \tag{1}$$

Form the double contraction of this result with the unit tensor **I** in order to obtain the desired result given by

$$\langle \nabla \cdot \mathbf{a}_\gamma \rangle = \nabla \cdot \langle \mathbf{a}_\gamma \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \mathbf{a}_\gamma dA \tag{2}$$

1-8. For multiphase transport problems that are one-dimensional *at the macroscopic level*, one would like to use an averaging volume in the shape of a disk or a slab such as we have illustrated in Figure 1-8. To derive the averaging theorem associated with this special averaging volume, one can follow the solution of Problem 1-6 to obtain

$$\lambda \cdot \nabla \left[\int_{V_\gamma} \psi_\gamma dV \right] - \lambda \cdot \int_{A_{\gamma e}} \psi_\gamma \mathbf{n}_{\gamma e} dA = 0 \tag{1}$$

however, λ *cannot be cancelled* in this result en route to the traditional averaging theorem. Instead we multiply by λ and divide by $\mathscr{V}$ so that Eq. 1 takes the form

$$\mathbf{N} \cdot \nabla \langle \psi_\gamma \rangle - \mathbf{N} \cdot \left[\frac{1}{\mathscr{V}} \int_{A_{\gamma e}} \psi_\gamma \mathbf{n}_{\gamma e} dA \right] = 0 \tag{2}$$

in which **N** is the *normal tensor* defined according to

$$\mathbf{N} = \lambda\lambda \tag{3}$$

This is related to the unit tensor and the *projection tensor* by

$$\mathbf{I} = \mathbf{N} + \mathbf{P} \tag{4}$$

in which **P** is the projection tensor for the plane that is orthogonal to the unit vector λ. When the thickness of the slab illustrated in Figure 1-8 tends to zero, show that Eq. 2 can be used to derive the form given by

$$\langle \nabla \psi_\gamma \rangle = \mathbf{N} \cdot \nabla \langle \psi_\gamma \rangle + \frac{1}{\mathscr{V}} \int_{A_{\gamma\kappa}} \psi_\gamma \mathbf{n}_{\gamma\kappa} dA, \quad A_{\gamma e} = 0 \tag{5}$$

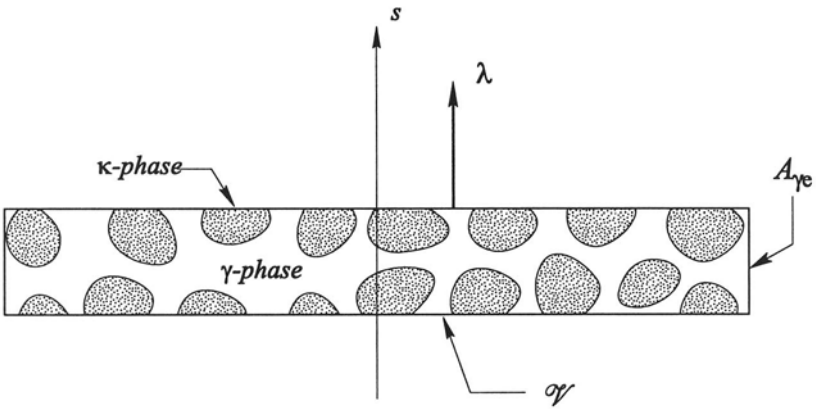


Figure 1-8. Averaging volume in the shape of a slab or a disk

1-9. Develop an extension of the averaging theorem for the γ-phase in the three-phase system illustrated in Figure 1-9. This can be done by considering the κ-phase shown in Figure 1-6a to be made up of the σ-phase and the β-phase.

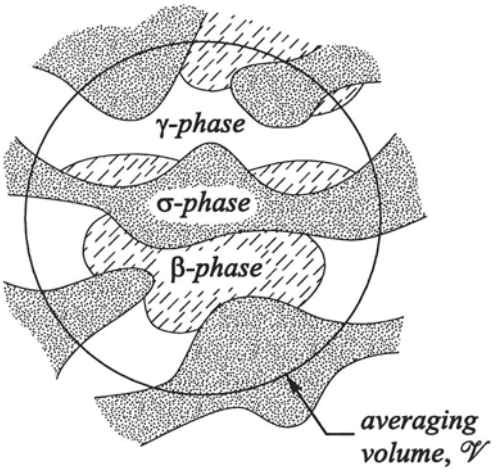


Figure 1-9. Three-phase system

1-10. In the process of drying a wet porous medium (Whitaker, 1998), one encounters the three-phase system illustrated in Figure 1-9 in which the γ-phase represents humid air and the β-phase represents pure water. The continuity equation for the β-phase is given by

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot \left(\rho_\beta \mathbf{v}_\beta \right) = 0 \tag{1}$$

and the volume averaged form of this equation is an essential feature of the theory of drying. Since the volume of the β-phase contained within the averaging volume is a function of time, one needs to make use of the general transport theorem in order to complete the averaging process. The general form of this theorem is given by

$$\frac{d}{dt} \int_{\mathscr{V}_a(t)} \psi_\beta \, dV = \int_{\mathscr{V}_a(t)} \frac{\partial \psi_\beta}{\partial t} dV + \int_{\mathscr{A}_a(t)} \psi_\beta \, \mathbf{w} \cdot \mathbf{n} \, dA \tag{2}$$

in which $\mathscr{V}_a(t)$ represents an *arbitrary*, time-dependent volume and $\mathscr{A}_a(t)$ identifies the bounding surface of this volume. The speed of displacement of the bounding surface is given by $\mathbf{w} \cdot \mathbf{n}$ in which $\mathbf{n}$ is the outwardly directed unit normal vector. Since $\mathscr{V}_a(t)$ is arbitrary, it can be set equal to $V_\beta(t)$ in order to obtain the special form that is needed in the analysis of Eq. 1. A key quantity of interest in the drying process is the mass rate of evaporation per unit volume that is defined by

$$\langle \dot{m} \rangle = \frac{1}{\mathscr{V}} \int_{A_{\beta\gamma}(t)} \rho_\beta (\mathbf{v}_\beta - \mathbf{w}) \cdot \mathbf{n}_{\beta\gamma} dA \tag{3}$$

In this problem you are asked to develop the volume averaged form of Eq. 1 in order to illustrate how the mass rate of evaporation, $\langle \dot{m} \rangle$, is related to the time rate of change of the volume fraction of the β-phase, ε_β, and the superficial average velocity, $\langle \mathbf{v}_\beta \rangle$. Begin your analysis with Eq. 1 and consider the density to be constant to obtain the final form of the volume averaged continuity equation. If the σ-phase is *impermeable*, the mass transfer boundary condition that can be extracted from Eq. 1.1-2 is given by

B.C.1 $$\rho_\beta (\mathbf{v}_\beta - \mathbf{w}) \cdot \mathbf{n}_{\beta\sigma} = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{4}$$

and if the porous medium is *rigid*, we have

$$\mathbf{v}_\beta \cdot \mathbf{n}_{\beta\sigma} = \mathbf{w} \cdot \mathbf{n}_{\beta\sigma} = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{5}$$

At the β–γ interface, Eq. 1.1-2 leads to the following boundary condition

B.C.2 $$\rho_\beta (\mathbf{v}_\beta - \mathbf{w}) \cdot \mathbf{n}_{\beta\gamma} = \rho_{A\gamma} (\mathbf{v}_{A\gamma} - \mathbf{w}) \cdot \mathbf{n}_{\beta\gamma}, \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{6}$$

1-11. In the method of volume averaging, one often uses the approximation

$$\langle \mathscr{D}_\gamma \nabla c_{A\gamma} \rangle = \mathscr{D}_\gamma \langle \nabla c_{A\gamma} \rangle \tag{1}$$

even though $\mathscr{D}_\gamma$ may vary significantly over the *macroscopic region* of interest. In general, the molecular diffusivity will depend on both the concentration and the temperature; however, in this problem we consider only the functional dependence of $\mathscr{D}_\gamma$ on the concentration $c_{A\gamma}$. The objective of this problem is to determine the constraint associated with Eq. 1 when $\mathscr{D}_\gamma$ on the right hand side is evaluated at the average concentration, $\langle c_{A\gamma}\rangle^\gamma$. Begin by representing $\mathscr{D}_\gamma$ in a Taylor series expansion about the concentration $\langle c_{A\gamma}\rangle^\gamma$ to show that (Whitaker, 1998, Sec. VIII)

$$\mathscr{D}_\gamma\Big|_{c_{A\gamma}} = \mathscr{D}_\gamma\Big|_{\langle c_{A\gamma}\rangle^\gamma} + \tilde{c}_{A\gamma}\left.\frac{\partial\mathscr{D}_\gamma}{\partial c_{A\gamma}}\right|_{\langle c_{A\gamma}\rangle^\gamma} + \frac{1}{2}\left(\tilde{c}_{A\gamma}\right)^2\left.\frac{\partial^2\mathscr{D}_\gamma}{\partial c_{A\gamma}^2}\right|_{\langle c_{A\gamma}\rangle^\gamma} + \ldots \tag{2}$$

Consider only the linear term in $\tilde{c}_{A\gamma}$ and make use of the over-estimate

$$\langle\tilde{c}_{A\gamma}\nabla c_{A\gamma}\rangle = \mathbf{O}\left(\tilde{c}_{A\gamma}\langle\nabla c_{A\gamma}\rangle\right) \tag{3}$$

to demonstrate that Eq. 1 is valid when the following constraint is imposed:

$$\frac{\ell_\gamma}{\mathscr{D}_\gamma}\frac{\partial\mathscr{D}_\gamma}{\partial c_{A\gamma}}\nabla\langle c_{A\gamma}\rangle^\gamma << 1 \tag{4}$$

Here we have made use of the estimate for $\tilde{c}_{A\gamma}$ given by

$$\tilde{c}_{A\gamma} = \mathbf{O}\left(\ell_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma\right) \tag{5}$$

on the basis of the analysis presented in Sec. 1.4.

1-12. Use the averaging theorem for the γ-κ system to prove that

$$\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}dA = -\nabla\varepsilon_\gamma$$

Begin by letting ψ_γ in Eq. 1.2-15 be a constant.

1-13. Use the averaging theorem for the γ-κ system to prove that

$$\left\{\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\mathbf{y}_\gamma dA\right\} = -\nabla\langle\mathbf{y}_\gamma\rangle$$

Begin by letting ψ_γ in Eq. 1.2-15 be equal to the position vector $\mathbf{r}_\gamma$ that locates points in the γ-phase. Then let $\mathbf{r}_\gamma = \mathbf{x} + \mathbf{y}_\gamma$ in order to prove the above result.

1-14. Given some function, $f(x)$, that has an *estimated* magnitude of A in the domain $0 \le x \le L$, we can construct the order of magnitude estimates given by

$$f = \mathbf{O}(A) \tag{1a}$$

$$\frac{df}{dx} = \mathbf{O}\left(\frac{\Delta f}{\Delta L}\right) = \mathbf{O}\left(\frac{A}{L}\right) \tag{1b}$$

$$\frac{d^2 f}{dx^2} = \mathbf{O}\left(\frac{\Delta(df/dx)}{\Delta L}\right) = \mathbf{O}\left(\frac{df/dx}{L}\right) = \mathbf{O}\left(\frac{A}{L^2}\right) \tag{1c}$$

One can define the *magnitude* of some function as

$$\mathcal{OM}[f(x)] = \frac{1}{L}\int_{x=0}^{x=L} |f(x)|dx = \left\{\begin{matrix}\textit{magnitude of the} \\ \textit{function, } f(x)\end{matrix}\right\} \tag{2}$$

and when we construct an *order of magnitude estimate* of the function, we are attempting to *estimate* $\mathcal{OM}[f(x)]$. In the same manner, we can define the magnitudes of the first and second derivatives of this function according to

$$\mathcal{OM}[(df/dx)] = \frac{1}{L}\int_{x=0}^{x=L} |(df/dx)|dx\,, \quad \mathcal{OM}\left[(d^2 f/dx^2)\right] = \frac{1}{L}\int_{x=0}^{x=L} \left|(d^2 f/dx^2)\right|dx \tag{3}$$

When we construct order of magnitude estimates of the derivatives, we are attempting to *estimate* $\mathcal{OM}[(df/dx)]$ and $\mathcal{OM}\left[(d^2 f/dx^2)\right]$. In this problem we consider four simple functions represented by

$$f(x) = A \tag{4}$$

$$f(x) = 2A(x/L) \tag{5}$$

$$f(x) = 6A\left[(x/L) - (x/L)^2\right] \tag{6}$$

$$f(x) = A\left[1 + \sin 2\pi(x/L)\right] \tag{7}$$

Each of these functions has a *magnitude* equal to A, and our *order of magnitude estimates* of the function, and its first and second derivatives are given by Eqs. 1.

In this problem you are asked to *calculate* the magnitudes for the first and second derivatives according to Eqs. 3 and compare them with the *order of*

magnitude estimates given by Eqs. 1. After you have completed the entries to Table 1-14, use your knowledge of the functions given by Eqs. 4 through 7 to construct improved *order of magnitude estimates.*

TABLE 1-14. Comparison of magnitudes and estimates of the magnitude

	df/dx	df/dx	d^2f/dx^2	d^2f/dx^2
function	magnitude	estimate	magnitude	estimate
1		A/L		A/L^2
2		A/L		A/L^2
3		A/L		A/L^2
4		A/L		A/L^2

1-15. A steady, two-dimensional heat conduction problem is given by

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \tag{1}$$

B.C.1 $$T = T_o, \quad y = 0 \tag{2}$$

B.C.2 $$T = T_1, \quad y = b \tag{3}$$

B.C.3 $$T = T_o - (T_1 - T_o)\sin(3\pi y/2b), \quad x = 0 \tag{4}$$

B.C.4 $$T = T_o + (T_1 - T_o)(y/b)^2, \quad x = L \tag{5}$$

and the domain of interest is illustrated in Figure 1-15. If the length of the region

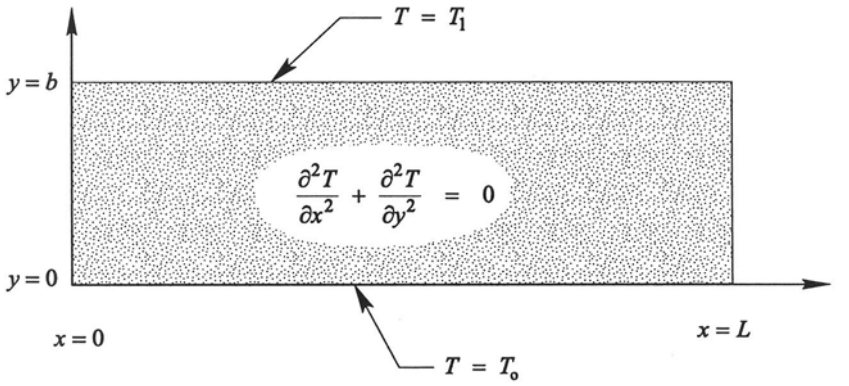


Figure 1-15. Two-dimensional, steady heat conduction

in the x-direction is *long enough*, one can guess that the average heat flux in the y-direction is given by

$$q_y\Big|_{avg} = k(T_o - T_1)/b \tag{6}$$

In this problem you are asked to use order of magnitude analysis in order to determine what is meant by *long enough*. It is convenient in problems of this type to decompose the solution for the temperature into the part that you think can adequately explain the phenomena and whatever is left. One convenient manner of doing this is to integrate the governing differential equation twice to obtain

$$T = -\int_{\xi=0}^{\xi=y}\int_{\eta=0}^{\eta=\xi}\frac{\partial^2 T}{\partial x^2}d\eta\, d\xi + C_1 y + C_2 \tag{7}$$

The boundary conditions given by Eqs. 1 and 2 can then be applied to obtain a solution that consists of a linear part and terms involving the integral of the second derivative with respect to x. Constructing estimates of the integrals will lead to the constraint that must be satisfied in order for Eq. 6 to be a valid representation for the heat flux.

1-16. Repeat Problem 1-15 for the boundary value problem given by

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \tag{1}$$

B.C.1 $$T = T_o, \quad y = 0 \tag{2}$$

B.C.2 $$T = T_1, \quad y = b \tag{3}$$

B.C.3 $$\frac{\partial T}{\partial x} = 0, \quad x = 0 \tag{4}$$

B.C.4 $$-k\frac{\partial T}{\partial x} = h(T - T_\infty), \quad x = L \tag{5}$$

in order to find a constraint involving the Biot number.

1-17. Consider the tensor $\langle \mathbf{y}_\gamma \mathbf{y}_\gamma \rangle$ and accept the intuitive relation

$$\frac{1}{\mathscr{V}}\int_{V_\gamma} \mathbf{y}_\gamma \mathbf{y}_\gamma dV = \frac{1}{\mathscr{V}}\int_{\mathscr{V}} \varepsilon_\gamma \mathbf{y}\mathbf{y} dV \tag{1}$$

Show that this leads to the convenient expression given by

$$\frac{1}{\mathscr{V}}\int_{\mathscr{V}} \mathbf{y}\mathbf{y}\,dV = \mathbf{I}\left(\frac{r_o^2}{5}\right) \tag{2}$$

and explain why

$$\frac{1}{\mathscr{V}}\int_{\mathscr{V}} \mathbf{y}\mathbf{y}\mathbf{y}\,dV = 0 \tag{3}$$

Use a Taylor series expansion for ε_γ about the centroid $\mathbf{x}$ in order to eventually arrive at the estimate

$$\frac{1}{\mathscr{V}}\int_{V_\gamma} \mathbf{y}_\gamma \mathbf{y}_\gamma\,dV = \mathbf{O}\left(\varepsilon_\gamma r_o^2\right) + \mathbf{O}\left(r_o^4 \nabla^2 \varepsilon_\gamma\right) \tag{4}$$

One must always keep in mind that this result is based on the intuitive idea expressed by Eq. 1.

1-18. Given an unconsolidated porous medium composed of particles, each of which has a volume V_p and an area A_p, show that the surface area per unit volume for the porous medium is given by

$$a_v = \frac{A_p}{V_p}(1 - \varepsilon_\gamma) \tag{1}$$

If the hydraulic diameter defined by

$$D_h = \frac{4 \times (\textit{void volume})}{\textit{wetted surface}} \tag{2}$$

is chosen to be the characteristic length, ℓ_γ, show that

$$\ell_\gamma = \frac{2d_p}{3}\frac{\varepsilon_\gamma}{1 - \varepsilon_\gamma} \tag{3}$$

in which $d_p = 6V_p/A_p$. In terms of the effective particle diameter d_p, the surface area per unit volume can be expressed as

$$a_v = \frac{6}{d_p}(1 - \varepsilon_\gamma) \tag{4}$$

As a model of a consolidated porous medium, consider a bundle of parallel capillary tubes of diameter D embedded in a solid. Given the porosity ε_γ, derive expressions for a_v and ℓ_γ.

1-19. Prove that Eq. 1.4-53 is consistent with Eqs. 1.4-51 and 1.4-52 by demonstrating that these latter two equations are invariant to a transformation of the form $\mathbf{r} = \bar{\mathbf{r}} + \ell_i$.

1-20. The following boundary value problem

$$\frac{d^2 c_A}{dx^2} = A \tag{1}$$

B.C.1 $$c_A = B, \qquad x = 0 \tag{2}$$

B.C.2 $$c_A = 0, \qquad x = L \tag{3}$$

can be solved by direct integration to obtain

$$c_A(x) = \frac{A}{2}\left(x^2 - Lx\right) + B\left(1 - \frac{x}{L}\right) \tag{4}$$

An alternate approach is to propose a solution of the form

$$c_A(x) = f(x)A + g(x)B \tag{5}$$

in which f and g are the *closure variables* that *map* the nonhomogeneous terms, A and B, onto the function, $c_A(x)$. Derive the two boundary value problems for f and g and show that the solution in terms of the closure variables produces the same result given by Eq. 4.

1-21. Prove that the solution to the boundary value problem given by Eqs. 1.4-60 is $\psi_\gamma = constant$. Do this by developing the boundary value problem for ψ_γ^2 and showing that it can be used to obtain

$$\int_{V_\gamma} \nabla\psi_\gamma \cdot \nabla\psi_\gamma \, dV = 0$$

Conclude from this that ψ_γ must be a constant.

1-22. Develop arguments leading to the following estimate

$$\mathscr{D}_\gamma s_\gamma = \mathbf{O}\left(\ell_\gamma k\right)$$

that was used in Sec. 1.4 to discard the convective-like term in the volume averaged diffusion equation.

1-23. In order to prove that the effective diffusivity tensor is symmetric, one must first use the boundary value problem given by Eqs. 1.4-58 to obtain

$$\nabla\cdot\left[\left(\nabla\mathbf{b}_\gamma\right)\mathbf{b}_\gamma\right] = \left(\nabla\mathbf{b}_\gamma\right)^{\mathrm{T}}\cdot\left(\nabla\mathbf{b}_\gamma\right) \tag{1}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa}\cdot\left(\nabla\mathbf{b}_\gamma\right)\mathbf{b}_\gamma = \mathbf{n}_{\gamma\kappa}\mathbf{b}_\gamma, \quad \text{at } A_{\gamma\kappa} \tag{2}$$

Periodicity: $$\mathbf{b}_\gamma(\mathbf{r}+\ell_i) = \mathbf{n}_{\gamma\kappa}\mathbf{b}_\gamma(\mathbf{r}), \quad i=1,2,3 \tag{3}$$

From this representation of the closure problem, one can show that Eq. 1.4-62 takes the form

$$\mathbf{D}_{eff} = \mathscr{D}_\gamma\left(\mathbf{I} - \frac{1}{V_\gamma}\int_{V_\gamma}\left(\nabla\mathbf{b}_\gamma\right)^{\mathrm{T}}\cdot\left(\nabla\mathbf{b}_\gamma\right)dV\right) \tag{4}$$

If λ and ν are arbitrary constant vectors, one can use this result to prove that

$$\lambda\cdot\mathbf{D}_{eff}\cdot\nu = \nu\cdot\mathbf{D}_{eff}\cdot\lambda \tag{5}$$

In this problem you are asked to provide the details of the proof that the effective diffusivity tensor is symmetric.

1-24. The catalytic, irreversible decomposition of species A to form products can sometimes be modeled as (see Problem 1-2)

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot\left(\mathscr{D}_\gamma\nabla c_{A\gamma}\right), \quad \text{in the } \gamma\text{-phase} \tag{1}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla c_{A\gamma} = \frac{k\,c_{A\gamma}}{1+K\,c_{A\gamma}}, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{2}$$

Form the volume average of Eq. 1 and indicate under what circumstances it takes the form

$$\varepsilon_\gamma\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma\mathbf{D}_{eff}\cdot\langle c_{A\gamma}\rangle^\gamma\right) - \frac{a_v k\langle c_{A\gamma}\rangle^\gamma}{1 + K\langle c_{A\gamma}\rangle^\gamma} \tag{3}$$

Develop the restrictions that must be imposed in order that the non-linear reaction rate can be expressed directly in terms of $\langle c_{A\gamma}\rangle^\gamma$.

1-25. The problem of diffusion and adsorption in a porous medium can be described by

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot\left(\mathscr{D}_\gamma\nabla c_{A\gamma}\right), \quad \text{in the } \gamma\text{-phase} \tag{1}$$

B.C.1 $$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla c_{A\gamma} = \frac{\partial c_{As}}{\partial t}, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{2}$$

in which c_{As} represents the surface concentration of species A. If the adsorption isotherm is linear and the condition of *local adsorption equilibrium* is valid, the surface concentration and be related to the bulk concentration according to (see Problem 1-3)

$$c_{As} = K_{eq} c_{A\gamma}, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{3}$$

In this problem, you are asked to derive the local volume averaged diffusion equation and develop a method of closure that can be used to determine the effective diffusivity tensor. Indicate under what circumstances the closure problem can be treated as quasi-steady, and under what circumstances the effective diffusivity tensor will be independent of the adsorption process.

When certain length and time-scale constraints are imposed, the local volume averaged diffusion equation takes the form;

$$\varepsilon_\gamma\left(1 + a_v K_{eq}/\varepsilon_\gamma\right)\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left[\varepsilon_\gamma\mathscr{D}_\gamma\left(\nabla\langle c_{A\gamma}\rangle^\gamma + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,dA\right)\right] \tag{4}$$

however, in order to use this result in the development of the closure problem, it is best to arrange it in a form containing *only* $\partial\langle c_A\rangle^\gamma/\partial t$ on the left hand side. Under these circumstances, the term representing adsorption becomes a *source term* in the closure problem.

1-26. The catalytic, irreversible decomposition of species A by a second order mechanism can be modeled as

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot\left(\mathscr{D}_\gamma\nabla c_{A\gamma}\right), \quad \text{in the } \gamma\text{-phase} \tag{1}$$

B.C.1
$$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla c_{A\gamma} = k c_{A\gamma}^2, \quad \text{at } \mathscr{A}_{\gamma\kappa} \tag{2}$$

Indicate under what circumstances the volume averaged diffusion equation can be expressed as

$$\varepsilon_\gamma\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma\mathbf{D}_{eff}\cdot\langle c_{A\gamma}\rangle^\gamma\right) - a_v k\left(\langle c_{A\gamma}\rangle^\gamma\right)^2 \tag{3}$$

Most of the analysis associated with this problem is available in the text; however, some effort must be directed toward the quantity $\langle c_{A\gamma}^2\rangle_{\gamma\kappa}$ that appears in the superficial average of Eq. 1.

Chapter 2

Transient Heat Conduction in Two-Phase Systems

In this chapter we consider the problem of heat conduction in two-phase systems without the complications associated with adsorption, chemical reaction, phase change, etc. Our objectives in this chapter are two-fold:

1. To study a process in which transport occurs in two phases.
2. To indicate how a *one-equation model* can be developed in order to describe transport in a *two-phase system.*

In the previous chapter we analyzed a process involving transport in one phase (the γ-phase) with the second phase (the κ-phase) providing only a boundary condition. Extending our studies to include transport in two phases is an important step since there are many important processes involving heat and mass transfer in both two and three-phase systems, and in many of these systems one can develop a reasonable model of the transport process using a *single transport equation.* Knowing how to derive this single transport equation and knowing when it is a valid representation of the process are the key objectives of this chapter.

2.1 Governing Equations and Boundary Conditions

The system under consideration is illustrated in Figure 2.1 and the governing equations and boundary conditions are given by

$$(\rho c_p)_\beta \frac{\partial T_\beta}{\partial t} = \nabla\cdot\left(k_\beta \nabla T_\beta\right), \quad \text{in the } \beta\text{-phase} \tag{2.1-1}$$

B.C.1
$$T_\beta = T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2.1-2}$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla T_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2.1-3}$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla\cdot\left(k_\sigma \nabla T_\sigma\right), \quad \text{in the } \sigma\text{-phase} \tag{2.1-4}$$

B.C.3
$$T_\beta = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{2.1-5}$$

B.C.4 $$T_\sigma = \mathscr{G}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\sigma e} \tag{2.1-6}$$

I.C.1 $$T_\beta = \mathscr{H}(\mathbf{r}), \quad \text{at } t = 0 \tag{2.1-7}$$

I.C.2 $$T_\sigma = \mathscr{I}(\mathbf{r}), \quad \text{at } t = 0 \tag{2.1-8}$$

The boundary conditions given by Eqs. 2.1-2 and 2.1-3 indicate that the temperature and the normal component of the heat flux are continuous at the β-σ interface. If chemical reaction, adsorption, or phase change takes place at the β-σ interface, a jump in the heat

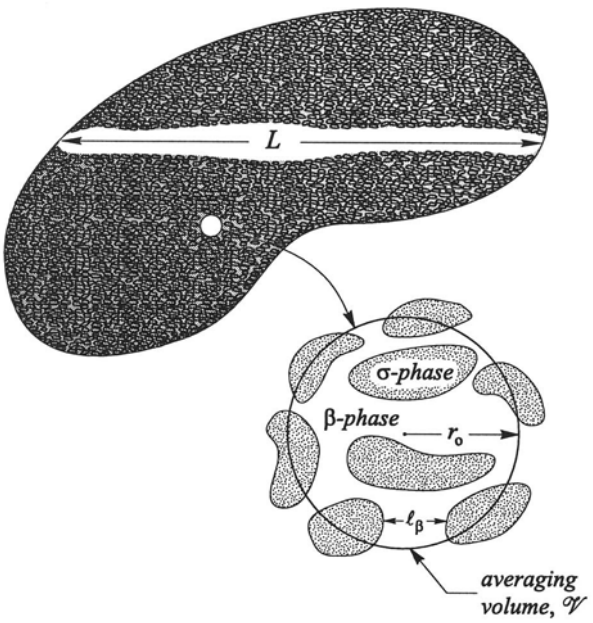


Figure 2.1. Macroscopic system

flux can occur and the heat transfer process becomes coupled to a mass transfer process. Under these circumstances, the problem becomes considerably more complex.

In our formulation of this transient heat conduction problem, we have used $\mathscr{A}_{\beta e}$ and $\mathscr{A}_{\sigma e}$ to represent the area of the entrances and exits for the β and σ-phases at the boundary of the macroscopic system. The boundary conditions at $\mathscr{A}_{\beta e}$ and $\mathscr{A}_{\sigma e}$ are generally known only in terms of the average temperature and not the point temperature, thus Eqs. 2.1-5 and 2.1-6 serve as reminders of what we *do not know* about T_β and T_σ. The same can be said of the initial conditions given by Eqs. 2.1-7 and 2.1-8; however, there are some processes for which one might be able to specify the point temperature at $t = 0$. The conditions for the average temperature that are applicable at the boundary between a porous medium and a homogeneous fluid have been developed by Ochoa-Tapia and Whitaker (1997, 1998a).

The details of the β-σ system are illustrated in Figure 2.2 where we have used ℓ_β and ℓ_σ to represent the characteristic lengths for the β and σ-phases respectively. In addition, we have used $\mathbf{n}_{\sigma\beta}$ to represent the unit normal vector directed *from* the σ-phase *toward* the β-phase, and we will consistently use the convention that $\mathbf{n}_{\sigma\beta} = -\mathbf{n}_{\beta\sigma}$ in which $\mathbf{n}_{\beta\sigma}$ represents the unit normal vector directed *from* the β-phase *toward* the σ-phase.

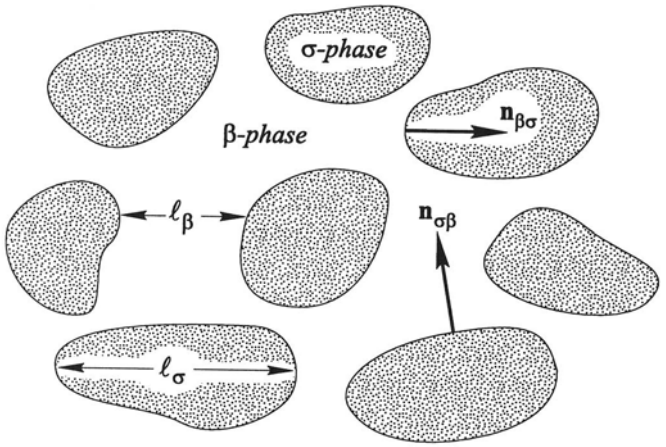


Figure 2.2. Rigid two-phase system

2.2 Spatial Smoothing

The process of volume averaging begins by forming the superficial average of Eq. 2.1-1

$$\frac{1}{\mathscr{V}}\int_{V_\beta}(\rho c_p)_\beta\frac{\partial T_\beta}{\partial t}dV = \frac{1}{\mathscr{V}}\int_{V_\beta}\nabla\cdot(k_\beta\nabla T_\beta)dV \tag{2.2-1}$$

and neglecting variations of $(\rho c_p)_\beta$ within the averaging volume to obtain

$$(\rho c_p)_\beta\frac{\partial\langle T_\beta\rangle}{\partial t} = \langle\nabla\cdot(k_\beta\nabla T_\beta)\rangle \tag{2.2-2}$$

Here we have considered the system to be rigid so that V_β is not a function of time. As in our study of diffusion in porous media, the desired dependent variable is an intrinsic average quantity and not the superficial average temperature that appears on the left hand side of Eq. 2.2-2. Thus we make use of the relation

$$\langle T_\beta\rangle = \varepsilon_\beta\langle T_\beta\rangle^\beta \tag{2.2-3}$$

and the fact that ε_β is independent of time to express Eq. 2.2-2 as

$$\varepsilon_\beta(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \langle \nabla \cdot (k_\beta \nabla T_\beta) \rangle \tag{2.2-4}$$

The left hand side of this result is in the final form, and we attack the right hand side with the spatial averaging theorem to obtain

$$\varepsilon_\beta(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \langle k_\beta \nabla T_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, dA \tag{2.2-5}$$

In our previous study of diffusion and reaction in porous media, the area integral of the interfacial flux was used to incorporate the heterogeneous reaction rate into the volume averaged transport equation. In this case, the area integral of the interfacial flux *connects* the β-phase transport equation to the σ-phase transport equation and our problem is more complex.

We will ignore the last term in Eq. 2.2-5 for the present and turn our attention to the second term involving the average of the β-phase heat flux vector. Once again we neglect variations of physical properties within the averaging volume (see Problem 1-11) and apply the averaging theorem to obtain

$$\langle k_\beta \nabla T_\beta \rangle = k_\beta \langle \nabla T_\beta \rangle = k_\beta \left[\nabla \langle T_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} T_\beta \, dA \right] \tag{2.2-6}$$

We can eliminate the superficial average temperature by the use of Eq. 2.2-3 and this leads to the following form of the volume averaged heat conduction equation for the β-phase:

$$\underbrace{\varepsilon_\beta(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot \left[k_\beta \left(\varepsilon_\beta \nabla \langle T_\beta \rangle^\beta + \langle T_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} T_\beta \, dA \right) \right]}_{\text{conduction}}$$

$$+ \underbrace{\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, dA}_{\substack{\text{interfacial} \\ \text{flux}}} \tag{2.2-7}$$

Two problems remain at this point; the area integral of $\mathbf{n}_{\beta\sigma} T_\beta$ and the interfacial flux term. We attack the first of these with the spatial decomposition of the temperature for the β-phase

$$T_\beta = \langle T_\beta \rangle^\beta + \tilde{T}_\beta \tag{2.2-8a}$$

and in our analysis of the σ-phase we will use the analogous decomposition given by

$$T_\sigma = \langle T_\sigma \rangle^\sigma + \tilde{T}_\sigma \tag{2.2-8b}$$

Use of Eq. 2.2-8a leads to the *non-local form* of Eq. 2.2-7 which can be expressed as

$$\varepsilon_\beta (\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left[k_\beta \left(\varepsilon_\beta \nabla \langle T_\beta \rangle^\beta + \langle T_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle T_\beta \rangle^\beta dA \right. \right. \\ \left. \left. + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right) \right] + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta dA \tag{2.2-9}$$

The term in brackets is identical in form to the volume averaged diffusive flux in Eq. 1.2-33, and this term can be greatly simplified if a *local representation* of this *non-local form* is acceptable. To obtain the local form we follow the development in Sec. 1.3 and make use of the simplification

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle T_\beta \rangle^\beta dA = - \langle T_\beta \rangle^\beta \nabla \varepsilon_\beta \tag{2.2-10}$$

This allows us to express Eq. 2.2-9 as

$$\varepsilon_\beta (\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left[k_\beta \left(\varepsilon_\beta \nabla \langle T_\beta \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right) \right] \\ + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta dA \tag{2.2-11}$$

Here one must be careful to remember that Eq. 2.2-10 is only valid when the following two length-scale constraints are satisfied

$$\ell_\beta << r_o, \qquad r_o^2 << L_\varepsilon L_{T1} \tag{2.2-12}$$

and we remind the reader that L_ε and L_{T1} are defined by the estimates

$$\nabla \varepsilon_\beta = \mathbf{O}\left(\frac{\Delta \varepsilon_\beta}{L_\varepsilon} \right), \qquad \nabla \nabla \langle T_\beta \rangle^\beta = \mathbf{O}\left(\frac{1}{L_{T1}} \nabla \langle T_\beta \rangle^\beta \right) \tag{2.2-13}$$

In arriving at Eq. 2.2-11, and the constraints indicated by Eq. 2.2-12, we have assumed that the β-σ system is *disordered* (Quintard and Whitaker, 1993a, 1994a-e) and this leads to the first length-scale constraint in Eq. 2.2-12. The definition of a disordered system and the development of the length-scale constraints given by Eq. 2.2-12 are given in Sec. 1.3. The σ-phase transport equation is analogous to Eq. 2.2-11 and we list the result as

$$\varepsilon_\sigma\left(\rho c_p\right)_\sigma \frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left[k_\sigma\left(\varepsilon_\sigma\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,dA\right)\right] + \frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla T_\sigma\,dA \tag{2.2-14}$$

Here we have made use of the nomenclature given by

$$\mathbf{n}_{\beta\sigma} = -\mathbf{n}_{\sigma\beta}\,, \qquad A_{\beta\sigma} = A_{\sigma\beta} \tag{2.2-15}$$

The first of these results from the fact that $\mathbf{n}_{\beta\sigma}$ represents the unit normal vector pointing *from* the β-phase *toward* the σ-phase whereas the unit normal vector $\mathbf{n}_{\sigma\beta}$ is pointing *from* the σ-phase *toward* the β-phase. The two interfacial areas represented by $A_{\beta\sigma}$ and $A_{\sigma\beta}$ are identical; however, we have used a nomenclature that is consistent with the unit normal vectors in an effort to avoid making a sign error in terms of $\mathbf{n}_{\beta\sigma}$ and $\mathbf{n}_{\sigma\beta}$. Equation 2.2-14 is naturally restricted by the analogous form of Eq. 2.2-12 which we list for completeness as

$$\ell_\sigma \ll r_0\,, \qquad r_0^2 \ll L_\varepsilon L_{T1} \tag{2.2-16}$$

If we were interested in developing separate equations for both the β-phase and the σ-phase, we would represent the interfacial flux in both Eqs. 2.2-11 and 2.2-14 in terms of average temperatures and spatial deviation temperatures and then go on to develop the closure problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$. This is often necessary if convective transport in the β-phase is important; however, for most problems of pure conduction one can use a *single average temperature* to describe the heat transfer process. In the next section we will derive the *one-equation model* for transient heat conduction, and we will develop the constraints associated with the *principle of local thermal equilibrium.*

The essential feature of the principle of local thermal equilibrium is that the equality

$$\langle T_\beta\rangle^\beta = \langle T_\sigma\rangle^\sigma \tag{2.2-17}$$

represents a *reasonable approximation.* If one accepts this idea, Eqs. 2.2-11 and 2.2-14 can be added to obtain

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left[(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA + \frac{k_\sigma}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right] \tag{2.2-18}$$

in which we have adopted the nomenclature represented by

$$\langle\rho\rangle C_p = \varepsilon_\beta(\rho c_p)_\beta + \varepsilon_\sigma(\rho c_p)_\sigma \tag{2.2-19}$$

In Eq. 2.2-18 the single temperature $\langle T\rangle$ is referred to as the *spatial average temperature* which is defined by

$$\langle T\rangle = \frac{1}{\mathscr{V}}\int_{\mathscr{V}} T\, dV = \varepsilon_\beta\langle T_\beta\rangle^\beta + \varepsilon_\sigma\langle T_\sigma\rangle^\sigma \tag{2.2-20}$$

and when the condition of local thermal equilibrium is valid we have

$$\langle T\rangle = \langle T_\beta\rangle^\beta = \langle T_\sigma\rangle^\sigma \tag{2.2-21}$$

To obtain a *closed form* of Eq. 2.2-18 we must develop representations for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ and this is done in Sec. 2.4. There we will find that the conduction terms on the right hand side of Eq. 2.2-18 can be expressed as

$$(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA + \frac{k_\sigma}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA = \mathbf{K}_{eff}\cdot\nabla\langle T\rangle \tag{2.2-22}$$

in which $\mathbf{K}_{eff}$ is the effective thermal conductivity tensor. This leads to the closed form of Eq. 2.2-18 given by

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left(\mathbf{K}_{eff}\cdot\nabla\langle T\rangle\right) \tag{2.2-23}$$

and the macroscopic boundary conditions for this equation are available in the work of Ochoa-Tapia and Whitaker (1998a)

2.2.1 THE FILTER

As in our study of diffusion and reaction in a porous catalyst, our volume averaged equation contains a filter that we identify explicitly as

$$\frac{k_\beta}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA + \frac{k_\sigma}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA = \left\{\begin{matrix} spatial \\ deviation \\ filter \end{matrix}\right\} \tag{2.2-24}$$

In our previous study of diffusion and reaction, we found that little more than the porosity passed through the filter for isotropic systems, while the situation was more

complex for anisotropic systems. For the case of heat conduction, we will find that the porosity is an important parameter, and under some circumstances the particle-particle contact will play a key role in the determination of the effective thermal conductivity.

Before going on to the derivation of Eq. 2.2-23 and the comparison of predicted values of $\mathbf{K}_{eff}$ with experimental results, we need to explore the idea of local thermal equilibrium; however, those readers who are willing to accept the condition of local thermal equilibrium can move directly to Sec. 2.4.

2.2.2 TWO-EQUATION MODEL

When local thermal equilibrium is *not valid*, one must develop the closed form of Eqs. 2.2-11 and 2.2-14, and Quintard and Whitaker (1993b) have shown that the two-equation model for transient heat transfer is given by

$$\varepsilon_\beta(\rho c_p)_\beta \frac{\partial\langle T_\beta\rangle^\beta}{\partial t} = \nabla\cdot\left(\mathbf{K}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{K}_{\beta\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma\right) - a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) \tag{2.2-25}$$

$$\varepsilon_\sigma(\rho c_p)_\sigma \frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left(\mathbf{K}_{\sigma\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{K}_{\sigma\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma\right) - a_v h\left(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta\right) \tag{2.2-26}$$

In their theoretical studies Quintard and Whitaker (1993b) were able to prove that the cross coefficients were equal

$$\mathbf{K}_{\beta\sigma} = \mathbf{K}_{\sigma\beta} \tag{2.2-27}$$

and solutions of the closure problems indicated that these coefficients were generally on the order of the smallest of either $\mathbf{K}_{\beta\beta}$ or $\mathbf{K}_{\sigma\sigma}$. Detailed numerical experiments were used to test the theory leading to Eqs. 2.2-25 through 2.2-27, and we will draw upon those results in our discussion of local thermal equilibrium in the next section.

2.3 Local Thermal Equilibrium

The phrase *local thermal equilibrium* is strictly associated with heat transfer in multiphase systems, and it should not be confused with the concept of *local thermodynamic equilibrium* (Truesdell, 1969). In studies of multiphase transport phenomena, one encounters *one-equation models* of heat and mass transfer that are constructed on the basis of local thermal and mass equilibrium. In this section we will examine the concept of local thermal equilibrium for transient heat conduction in a two-phase system and leave a variety of more complex heat and mass transfer problems for further study.

If one believes, on a purely intuitive basis, that $\langle T_\beta \rangle^\beta$ and $\langle T_\sigma \rangle^\sigma$ are essentially equal and can be represented by a single temperature, it is not unreasonable to put forth the assumption (Whitaker, 1988a)

ASSUMPTION: $$\langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma \tag{2.3-1}$$

and then explore the consequences. The theoretical consequences have already been indicated by Eqs. 2.2-18 through 2.2-23. While intuition often encourages the use of Eq. 2.3-1, a more prudent approach (Whitaker, 1977) is to represent the two intrinsic average temperatures in terms of the spatial average temperature and two Darcy-scale spatial deviation temperatures

$$\langle T_\beta \rangle^\beta = \langle T \rangle + \hat{T}_\beta, \quad \langle T_\sigma \rangle^\sigma = \langle T \rangle + \hat{T}_\sigma \tag{2.3-2}$$

and then identify the conditions for which $\hat{T}_\beta$ and $\hat{T}_\sigma$ are negligible. It is obvious that the condition indicated by Eq. 2.3-1 will be satisfied when the spatial deviations are zero, i.e.,

$$\hat{T}_\beta = 0, \quad \hat{T}_\sigma = 0, \quad \textit{local thermal equilibrium is valid} \tag{2.3-3}$$

This condition only occurs at *thermodynamic equilibrium*; however, it is possible that for some processes $\hat{T}_\beta$ and $\hat{T}_\sigma$ will be *small enough* so that these spatial deviation temperatures can be neglected. In order to determine what is meant by *small enough*, we substitute Eqs. 2.3-2 into Eqs. 2.2-11 and 2.2-14 and add the result to obtain

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} = \nabla \cdot \left[(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma) \nabla \langle T \rangle + \frac{k_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta \, dA + \frac{k_\sigma}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{T}_\sigma \, dA \right]$$

$$- \left[\varepsilon_\beta (\rho c_p)_\beta \frac{\partial \hat{T}_\beta}{\partial t} + \varepsilon_\sigma (\rho c_p)_\sigma \frac{\partial \hat{T}_\sigma}{\partial t} - \nabla \cdot \left(\varepsilon_\beta k_\beta \nabla \hat{T}_\beta \right) - \nabla \cdot \left(\varepsilon_\sigma k_\sigma \nabla \hat{T}_\sigma \right) \right] \tag{2.3-4}$$

If the last four terms are *negligible* (as opposed to being zero as indicated by Eq. 2.3-3), a valid one-equation model can be extracted from Eq. 2.3-4. By identifying the conditions for which the last four terms in Eq. 2.3-4 are negligible, the *intuition* represented by Eq. 2.3-1 will be replaced with a set of constraints that will indicate the *domain of validity* of the one-equation model.

We can simplify the last four terms in Eq. 2.3-4 by using the decompositions given by Eqs. 2.3-2 to conclude that (see Problem 2-1)

$$\varepsilon_\beta \hat{T}_\beta = -\varepsilon_\sigma \hat{T}_\sigma = \varepsilon_\beta \varepsilon_\sigma \left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right) \tag{2.3-5}$$

and if we are willing to ignore variations of the volume fractions in the last four terms we can express Eq. 2.3-4 as

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left[(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA + \frac{k_\sigma}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right]$$

$$- \left\{\varepsilon_\beta\varepsilon_\sigma\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) - \nabla\cdot\left[\varepsilon_\beta\varepsilon_\sigma\left(k_\beta - k_\sigma\right)\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right]\right\} \tag{2.3-6}$$

Here it becomes clear that we must be able to *estimate* the temperature difference $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ if we want to determine when the condition of local thermal equilibrium is valid.

The process of discarding the last four terms in Eq. 2.3-4 deserves some thought since there is more than one way in which the restrictions (Whitaker, 1988a) can be arranged. To begin with, it is prudent to discard various terms in an equation relative to the smallest non-zero term that is retained. Since the left hand side of Eq. 2.3-4 will be zero for a steady-state process, it seems wise to center our attention on the conduction term on the right hand side of Eq. 2.3-4. It is reasonable to use Eq. 2.2-22 as a representation of this term, and then base the condition of local thermal equilibrium on the following restrictions:

RESTRICTIONS:

I. $$\varepsilon_\beta\varepsilon_\sigma\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) << \nabla\cdot\left(\mathbf{K}_{eff}\cdot\nabla\langle T\rangle\right) \tag{2.3-7}$$

II. $$\nabla\cdot\left[\varepsilon_\beta\varepsilon_\sigma\left(k_\beta - k_\sigma\right)\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right] << \nabla\cdot\left(\mathbf{K}_{eff}\cdot\nabla\langle T\rangle\right) \tag{2.3-8}$$

To obtain useful forms of Eqs. 2.3-7 and 2.3-8, we need to estimate the time and space derivatives of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and $\langle T\rangle$. The estimates for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ are given by (see Sec. 1.3.2)

$$\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = \mathbf{O}\left[\frac{\Delta\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{t^*}\right] \tag{2.3-9}$$

$$\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = \mathbf{O}\left[\frac{\Delta\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{L_\Delta}\right] \tag{2.3-10a}$$

$$\nabla^2\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = O\left[\frac{\Delta\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{L_{\Delta 1} L_\Delta}\right] \tag{2.3-10b}$$

in which t^* is a characteristic process time, L_Δ is the characteristic length associated with the changes in $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$, and $L_{\Delta 1}$ is the characteristic length associated with the changes in $\nabla(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma)$. Since the temperature difference $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ represents a *deviation*, as indicated by Eqs. 2.3-2, we can approximate the *change in this difference* with the difference itself. This leads to the estimates

$$\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = O\left[\frac{\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{t^*}\right] \tag{2.3-11}$$

$$\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = O\left[\frac{\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{L_\Delta}\right] \tag{2.3-12a}$$

$$\nabla^2\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = O\left[\frac{\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{L_{\Delta 1} L_\Delta}\right] \tag{2.3-12b}$$

Turning our attention to the right hand side of Eqs. 2.3-7 and 2.3-8, we estimate the gradients of the spatial average temperature as

$$\nabla\langle T\rangle = O\left(\frac{\Delta\langle T\rangle}{L_T}\right) \tag{2.3-13}$$

$$\nabla\nabla\langle T\rangle = O\left(\frac{\Delta\langle T\rangle}{L_{T1} L_T}\right) \tag{2.3-14}$$

Here we think of L_{T1} as the characteristic length associated with *changes in the gradient* of the spatial averaged temperature, and if the gradient is constant the form of Eq. 2.3-14 indicates that L_{T1} is infinite. This situation occurs when the volume averaged heat conduction process is steady and one-dimensional.

When the estimates given by Eqs. 2.3-11 through 2.3-14 are used in Eqs. 2.3-7 and 2.3-8 we obtain the following two restrictions associated with the condition of local thermal equilibrium:

I. $$\frac{\varepsilon_\beta\varepsilon_\sigma\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right] L_{T1} L_T}{K_{eff}\, t^*}\left(\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{\Delta\langle T\rangle}\right) << 1 \tag{2.3-15}$$

II. $$\frac{\varepsilon_\beta \varepsilon_\sigma (k_\beta - k_\sigma)}{K_{eff}} \left(\frac{\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma}{\Delta \langle T \rangle} \right) << 1 \tag{2.3-16}$$

In extracting the second of these from Eq. 2.3-8, we have assumed that the length scales for $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$ are the same as those for $\langle T \rangle$, i.e. $L_{\Delta 1} L_\Delta \approx L_{T1} L_T$. For many systems of practical importance, the physical parameters and the length and time-scales will be such that

$$\frac{\varepsilon_\beta \varepsilon_\sigma \left[(\rho c_p)_\beta - (\rho c_p)_\sigma \right] L_{T1} L_T}{K_{eff}\, t^*} \leq \mathbf{O}(1) \tag{2.3-17}$$

$$\frac{\varepsilon_\beta \varepsilon_\sigma (k_\beta - k_\sigma)}{K_{eff}} = \mathbf{O}(1) \tag{2.3-18}$$

Under these circumstances, the condition of local thermal equilibrium will be dominated by the quantity $(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma) / \Delta \langle T \rangle$, and it is our ability to estimate this quantity that allows us to determine when local thermal equilibrium is valid and when it is not. The best estimate of $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$ is based on the governing differential equation for this quantity, along with the appropriate boundary and initial conditions. An analysis of the general heat transfer process is given by Whitaker (1991b), and in the following paragraphs we consider the special case of transient heat conduction.

2.3.1 ESTIMATE OF $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$

The governing differential equation for $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$ can only be developed in an approximate sense, and in order to keep the analysis as simple as possible we ignore variations in the volume fraction so that the β-phase transport equation given by Eq. 2.2-11 can be expressed as

$$(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left[k_\beta \left(\nabla \langle T_\beta \rangle^\beta + \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta \, dA \right) \right] + \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, dA \tag{2.3-19}$$

The analogous form for the σ-phase is obtained from Eq. 2.2-14 according to

$$(\rho c_p)_\sigma \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t} = \nabla \cdot \left[k_\sigma \left(\nabla \langle T_\sigma \rangle^\sigma + \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{T}_\sigma \, dA \right) \right] + \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla T_\sigma \, dA \tag{2.3-20}$$

It is not immediately obvious that subtracting Eq. 2.3-20 from Eq. 2.3-19 will lead us to a useful expression for the temperature difference $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$; however, we will explore this possibility to obtain

$$(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} - (\rho c_p)_\sigma \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t}$$

$$= \nabla \cdot \left[k_\beta \nabla \langle T_\beta \rangle^\beta - k_\sigma \nabla \langle T_\sigma \rangle^\sigma + \frac{k_\beta \varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA - \frac{k_\sigma \varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{T}_\sigma dA \right]$$

$$+ \frac{(\varepsilon_\beta \varepsilon_\sigma)^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta dA \tag{2.3-21}$$

Here the last term has been extracted from the interfacial flux terms in Eqs. 2.3-19 and 2.3-20 along with the flux boundary condition given by Eq. 2.1-3 (see Problem 2-2). We now make use of the representations given by Eqs. 2.3-2 so that the above result takes the form

$$(\rho c_p)_\beta \frac{\partial \hat{T}_\beta}{\partial t} - (\rho c_p)_\sigma \frac{\partial \hat{T}_\sigma}{\partial t} + \left[(\rho c_p)_\beta - (\rho c_p)_\sigma \right] \frac{\partial \langle T \rangle}{\partial t} = \nabla \cdot \left(k_\beta \nabla \hat{T}_\beta - k_\sigma \nabla \hat{T}_\sigma \right)$$

$$+ \nabla \cdot \left[(k_\beta - k_\sigma) \nabla \langle T \rangle + \frac{k_\beta \varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta \, dA - \frac{k_\sigma \varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{T}_\sigma \, dA \right]$$

$$+ \frac{(\varepsilon_\beta \varepsilon_\sigma)^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, dA \tag{2.3-22}$$

This still represents a relatively unattractive form; however, if we use the expressions given by Eq. 2.3-5 for $\hat{T}_\beta$ and $\hat{T}_\sigma$ we can arrange Eq. 2.3-22 in the form

$$\left[\varepsilon_\sigma(\rho c_p)_\beta + \varepsilon_\beta(\rho c_p)_\sigma\right]\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) - \nabla\cdot\left[(\varepsilon_\sigma k_\beta + \varepsilon_\beta k_\sigma)\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right]$$

$$= -\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial\langle T\rangle}{\partial t} + \nabla\cdot\left[(k_\beta - k_\sigma)\nabla\langle T\rangle + \frac{k_\beta\varepsilon_\beta^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,dA\right.$$

$$\left. - \frac{k_\sigma\varepsilon_\sigma^{-1}}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,dA\right] + \frac{(\varepsilon_\beta\varepsilon_\sigma)^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\,dA \tag{2.3-23}$$

Here we can see the beginnings of a transport equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ with the accumulation and conduction terms on the left hand side, and the so-called *source terms* involving the spatial and temporal derivatives of $\langle T\rangle$ on the right hand side. In order for this result to be useful, we require that it contain only terms involving $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and the derivatives of $\langle T\rangle$.

We can make use of the work of Quintard and Whitaker (1993b) in order to express the interfacial flux as

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\,dA = -a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) \tag{2.3-24}$$

and we can introduce the *mixed-mode parameters* defined by

$$(\rho c_p)_{\beta\sigma} = \varepsilon_\sigma(\rho c_p)_\beta + \varepsilon_\beta(\rho c_p)_\sigma\,, \qquad k_{\beta\sigma} = \varepsilon_\sigma k_\beta + \varepsilon_\beta k_\sigma \tag{2.3-25}$$

so that our transport equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ takes the form

$$(\rho c_p)_{\beta\sigma}\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) - \nabla\cdot\left[k_{\beta\sigma}\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right] + (\varepsilon_\beta\varepsilon_\sigma)^{-1}a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)$$

$$= -\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial\langle T\rangle}{\partial t} + \nabla\cdot\left[(k_\beta - k_\sigma)\nabla\langle T\rangle + \frac{k_\beta\varepsilon_\beta^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,dA\right.$$

$$\left. - \frac{k_\sigma\varepsilon_\sigma^{-1}}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,dA\right] \tag{2.3-26}$$

When local thermal equilibrium is valid, we will show in Sec. 2.4 that

$$\tilde{T}_\beta = \tilde{T}_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2.3-27}$$

and we will also show that the spatial deviation temperatures can be represented by

$$\tilde{T}_\beta = \mathbf{b}_\beta \cdot \nabla\langle T\rangle, \quad \tilde{T}_\sigma = \mathbf{b}_\sigma \cdot \nabla\langle T\rangle \tag{2.3-28}$$

As an approximation, we can use these two results in Eq. 2.3-26 to obtain the following transport equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$:

$$\underbrace{(\rho c_p)_{\beta\sigma}\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}_{\text{accumulation}} - \underbrace{\nabla\cdot\left[k_{\beta\sigma}\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right]}_{\text{conduction}}$$

$$+ \underbrace{(\varepsilon_\beta\varepsilon_\sigma)^{-1}a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}_{\text{exchange}} \tag{2.3-29}$$

$$= -\underbrace{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial\langle T\rangle}{\partial t}}_{\text{accumulation source}} + \underbrace{\nabla\cdot\left[\left(k_\beta - k_\sigma\right)\left(\mathbf{I} + \mathbf{C}_{\beta\sigma}\right)\cdot\nabla\langle T\rangle\right]}_{\text{conduction source}}$$

Here the second order tensor, $\mathbf{C}_{\beta\sigma}$, is defined by

$$\mathbf{C}_{\beta\sigma} = \frac{(\varepsilon_\beta\varepsilon_\sigma)^{-1}k_{\beta\sigma}}{\left(k_\beta - k_\sigma\right)\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{b}_\beta\, dA \tag{2.3-30}$$

and we refer to $\mathbf{C}_{\beta\sigma}$ as the *phase geometry tensor* since it provides important information concerning the physical properties of the two phases and the manner in which the two phases are arranged. One should note that the right hand side of Eq. 2.3-29 is zero when the physical properties of the two phases are equal, and this suggests the intuitively appealing result that

$$\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma = 0, \quad \text{when} \quad k_\beta = k_\sigma \quad \text{and} \quad (\rho c_p)_\beta = (\rho c_p)_\sigma \tag{2.3-31}$$

One must keep in mind that this conclusion is based entirely on the governing differential equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and *does not* take into account the influence of either the boundary conditions or the initial condition.

In order to use Eq. 2.3-29 to estimate $\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)/\Delta\langle T\rangle$ we need estimates of the derivatives of $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and $\langle T\rangle$. We begin with the left hand side of Eq. 2.3-29

and estimate the space and time derivatives in the manner indicated by Eqs. 2.3-11 and 2.3-12. This leads to

$$\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = \mathbf{O}\left[\frac{\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{t^*}\right] \tag{2.3-32}$$

$$\nabla^2\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) = \mathbf{O}\left[\frac{\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)}{L_{T1}L_T}\right] \tag{2.3-33}$$

in which we have again assumed that $L_{\Delta 1}L_\Delta \approx L_{T1}L_T$. Use of these results allows us to estimate the left hand side of Eq. 2.3-29 as

$$(\rho c_p)_{\beta\sigma}\frac{\partial}{\partial t}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) - \nabla\cdot\left[k_{\beta\sigma}\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)\right] + (\varepsilon_\beta\varepsilon_\sigma)^{-1}a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right)$$

$$= \left\{\underbrace{\mathbf{O}\left[\frac{(\rho c_p)_{\beta\sigma}}{t^*}\right]}_{\text{accumulation}} + \underbrace{\mathbf{O}\left[\frac{k_{\beta\sigma}}{L_{T1}L_T}\right]}_{\text{conduction}} + \underbrace{\frac{a_v h}{\varepsilon_\beta\varepsilon_\sigma}}_{\text{exchange}}\right\}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) \tag{2.3-34}$$

Here one must keep in mind that the signs ($\pm$) of the three estimates are generally unknown. If the terms representing *accumulation*, *conduction*, and *exchange* are the same order of magnitude, our overall estimate will not be very reliable since we do not know whether the terms will add to produce a result that is *large* or will subtract to produce a result that is *small*. When we examine the right hand side of Eq. 2.3-29, we find a different situation since we can use Eq. 2.2-23 to express those two terms as

$$-\underbrace{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial\langle T\rangle}{\partial t}}_{\text{accumulation source}} + \underbrace{\nabla\cdot\left[\left(k_\beta - k_\sigma\right)\left(\mathbf{I}+\mathbf{C}_{\beta\sigma}\right)\cdot\nabla\langle T\rangle\right]}_{\text{conduction source}} \tag{2.3-35}$$

$$= -\frac{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\nabla\cdot\left(\mathbf{K}_{eff}\cdot\nabla\langle T\rangle\right)}{\langle\rho\rangle C_p} + \nabla\cdot\left[\left(k_\beta - k_\sigma\right)\left(\mathbf{I}+\mathbf{C}_{\beta\sigma}\right)\cdot\nabla\langle T\rangle\right]$$

It is reasonable to ignore variations in $\mathbf{K}_{eff}$ and $(k_\beta - k_\sigma)(\mathbf{I}+\mathbf{C}_{\beta\sigma})$ so that this result takes the form

$$
\begin{aligned}
&- \underbrace{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial \langle T\rangle}{\partial t}}_{\text{accumulation source}} + \underbrace{\nabla\cdot\left[\left(k_\beta - k_\sigma\right)\left(\mathbf{I} + \mathbf{C}_{\beta\sigma}\right)\cdot\nabla\langle T\rangle\right]}_{\text{conduction source}} \\
&= \left\{\left(k_\beta - k_\sigma\right)\left(\mathbf{I} + \mathbf{C}_{\beta\sigma}\right) - \frac{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\mathbf{K}_{eff}}{\langle\rho\rangle C_p}\right\} : \nabla\nabla\langle T\rangle
\end{aligned}
\tag{2.3-36}
$$

At this point we express the second derivative of the temperature as

$$
\nabla\nabla\langle T\rangle = \mathbf{O}\left(\frac{\Delta\langle T\rangle}{L_{T1}L_T}\right) \tag{2.3-37}
$$

in order to obtain an estimate of the form

$$
\begin{aligned}
&- \underbrace{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\frac{\partial \langle T\rangle}{\partial t}}_{\text{accumulation source}} + \underbrace{\nabla\cdot\left[\left(k_\beta - k_\sigma\right)\left(\mathbf{I} + \mathbf{C}_{\beta\sigma}\right)\cdot\nabla\langle T\rangle\right]}_{\text{conduction source}} \\
&= \mathbf{O}\left\{\left(k_\beta - k_\sigma\right)\left(1 + \mathrm{C}_{\beta\sigma}\right) - \frac{\left[(\rho c_p)_\beta - (\rho c_p)_\sigma\right]\mathrm{K}_{eff}}{\langle\rho\rangle C_p}\right\}\left(\frac{\Delta\langle T\rangle}{L_{T1}L_T}\right)
\end{aligned}
\tag{2.3-38}
$$

in which $\mathrm{C}_{\beta\sigma}$ and K_{eff} are suitable norms of $\mathbf{C}_{\beta\sigma}$ and $\mathbf{K}_{eff}$. Substitution of this result, along with Eq. 2.3-34, into the governing differential equation for $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ leads to the following estimate:

$$
\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{\Delta\langle T\rangle} = \mathbf{O}\left(\frac{\ell_{\beta\sigma}}{L}\right)^2 \left\{\frac{\left[\frac{\left(k_\beta - k_\sigma\right)\left(1 + \mathrm{C}_{\beta\sigma}\right)}{k_{\beta\sigma}}\right] - \left[\frac{\left((\rho c_p)_\beta - (\rho c_p)_\sigma\right)}{\langle\rho\rangle C_p}\frac{\mathrm{K}_{eff}}{k_{\beta\sigma}}\right]}{\underbrace{1}_{\text{exchange}} + \underbrace{\mathbf{O}\left(\frac{\ell_{\beta\sigma}}{L}\right)^2}_{\text{conduction}} + \underbrace{\mathbf{O}\left(\frac{\ell_{\beta\sigma}^2}{\alpha_{\beta\sigma}t^*}\right)}_{\text{accumulation}}}\right\}
\tag{2.3-39}
$$

Here we have defined the mixed-mode thermal diffusivity as

$$
\alpha_{\beta\sigma} = \frac{k_{\beta\sigma}}{(\rho c_p)_{\beta\sigma}} \tag{2.3-40}
$$

and the mixed-mode, small length scale is given by

$$\ell_{\beta\sigma}^2 = \frac{\varepsilon_\beta \varepsilon_\sigma k_{\beta\sigma}}{a_v h} \tag{2.3-41}$$

For simplicity we have replaced $L_{T1}\, L_T$ with L^2, and one must remember that these two length scales will depend on time for transient processes. It is of some importance to note that L_{T1} will be *infinite* for all steady, one-dimensional conduction processes, and for these conditions Eq. 2.3-39 indicates $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$ will be zero. This means that local thermal equilibrium is always valid for steady, *one-dimensional* heat conduction. For many systems we expect that the following estimates will be satisfactory:

$$\frac{\left((\rho c_p)_\beta - (\rho c_p)_\sigma\right)}{\langle \rho \rangle C_p} \frac{\mathsf{K}_{eff}}{k_{\beta\sigma}} = \mathbf{O}(1), \qquad \left[\frac{\left(k_\beta - k_\sigma\right)\left(1 + \mathsf{C}_{\beta\sigma}\right)}{k_{\beta\sigma}}\right] = \mathbf{O}(1) \tag{2.3-42}$$

Under these circumstances the ratio of length scales, $(\ell_{\beta\sigma}/L)^2$, will control the estimate given by Eq. 2.3-39, and will thus determine when the condition of local thermal equilibrium is valid.

Earlier we pointed out that information about a field, such as $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$, was best obtained by an examination of the governing differential equation, the boundary conditions, and the initial condition. However, the estimate of $\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma$ given by Eq. 2.3-39 is based *only* on the governing differential equation and thus must be used with some care. For all its limitations, Eq. 2.3-39 does provide us with an estimate of $\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma\right)/\Delta\langle T \rangle$ in terms of the system parameters and this means that it can be used with Eqs. 2.3-15 and 2.3-16 to produce *constraints* that identify the *domain of validity* of the one-equation model. From the estimate given by Eq. 2.3-39 and the two restrictions given by Eqs. 2.3-15 and 2.3-16, we can see that local thermal equilibrium will always be achieved when any one of the following three conditions occurs:

1. Either ε_β or ε_σ tends to zero.
2. The difference in the β-phase and σ-phase physical properties tends to zero.
3. The square of the ratio of length scales, $(\ell_{\beta\sigma}/L)^2$, tends to zero.

2.3.2 COMPARISON WITH EXPERIMENT

Every theory should be compared with experiment, and the estimate given by Eq. 2.3-39 is no exception. A comparison with laboratory experiments would be extremely difficult; however, a comparison with numerical experiments is possible and this has been done by Quintard and Whitaker (1993b, 1995a) who studied the spatially periodic array of cylinders shown in Figure 2.3. The experiment consisted of solving a boundary

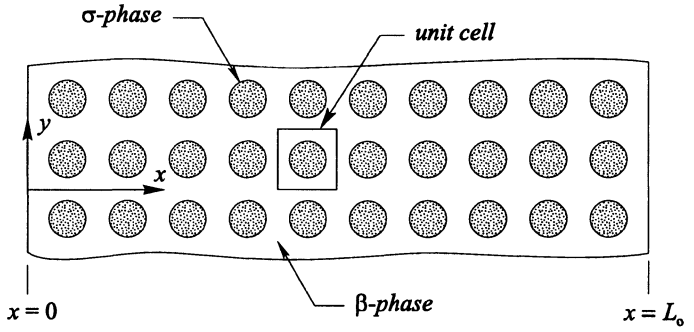


Figure 2.3. System used for numerical experiment

value problem to produce values of T_β and T_σ which were integrated over the β and σ-phases contained in the unit cell illustrated in Figure 2.3. This provided the "experimental" values of $\langle T_\beta \rangle^\beta$ and $\langle T_\sigma \rangle^\sigma$ as a function of x and t while "theoretical" values of $\langle T \rangle$ were obtain from Eq. 2.2-23 and the theory described in Sec. 2.4. The boundary conditions for the macroscopic system were as follows:

B.C.1 $$T_\beta = T_0, \quad \text{at } x = L_0, \quad t \geq 0 \tag{2.3-43}$$

B.C.2 $$T_\beta = T_1, \quad \text{at } x = 0, \quad t > 0 \tag{2.3-44}$$

I.C. $$T_\beta = T_0, \quad T_\sigma = T_0, \quad t = 0 \tag{2.3-45}$$

The parameters for one of the numerical experiments performed by Quintard and Whitaker (1993b, 1995a) are given in Table 2.1, and those parameters are representative of a porous medium composed of glass beads and air with a volume fraction of the

TABLE 2.1. Properties of a Two-Phase System. Numerical Experiment

k_β (W/m-K)	k_σ (W/m-K)	$(\rho c_p)_\beta$ (Jm^3-K)	$(\rho c_p)_\sigma$ (Jm^3-K)	K_{eff}/k_β (W/m-K)
0.026	0.5	1202	1.7×10^6	2.1

continuous phase given by $\varepsilon_\beta = 0.62$. The thermal conductivities in the two phases differ by about a factor of 20, while the heat capacities differ by about a factor of one thousand. The effective thermal conductivity is dominated by the conductivity of the β-phase and is about twice the value of k_β. The numerical results for $\langle T_\beta \rangle^\beta$ and $\langle T_\sigma \rangle^\sigma$ are presented in terms of dimensionless temperatures defined by

$$\langle \Theta_\beta \rangle^\beta = \frac{\langle T_\beta \rangle^\beta - T_o}{T_1 - T_o}, \qquad \langle \Theta_\sigma \rangle^\sigma = \frac{\langle T_\sigma \rangle^\sigma - T_o}{T_1 - T_o} \tag{2.3-46}$$

A comparison of these two intrinsic average temperatures can be used to determine whether the condition of local thermal equilibrium is satisfied for the system described by the parameters given in Table 2.1. This comparison is shown in Figure 2.4 where we

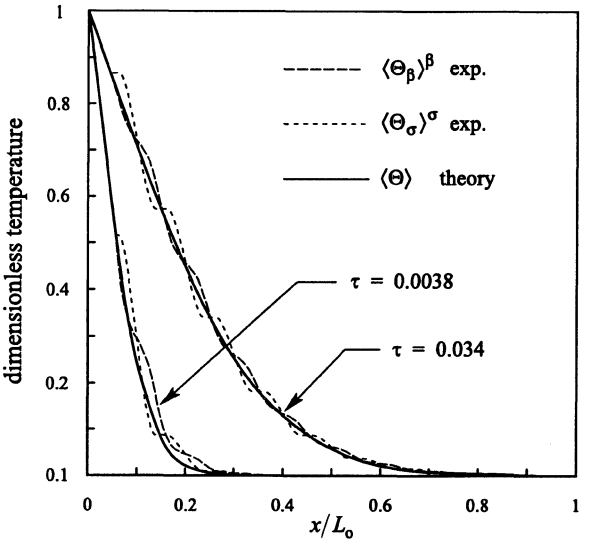


Figure 2.4. Comparison between theory and numerical experiments for the parameters in Table 2.1.

have also presented results for the dimensionless spatial average temperature defined by

$$\langle \Theta \rangle = \frac{\langle T \rangle - T_o}{T_1 - T_o} \tag{2.3-47}$$

This temperature was calculated using the one-equation model given by Eq. 2.2-23 and it represents a *theoretical result.* The values shown in Figure 2.4 are for two dimensionless times, $\tau = 0.0038$ and $\tau = 0.034$, where τ is defined by

$$\tau = \frac{K_{eff}\, t}{\langle \rho \rangle C_p L_o^2} \tag{2.3-48}$$

We expect steady state, and therefore local thermal equilibrium, to occur for values of τ on the order of 0.3, thus the temperature profiles shown in Figure 2.4 are far from steady state. One should keep in mind that the system is originally in local thermal equilibrium according to the initial condition given by Eq. 2.3-45. At short times there is a departure from local thermal equilibrium; however, the agreement between the experimental values

of $\langle\Theta_\beta\rangle^\beta$ and $\langle\Theta_\sigma\rangle^\sigma$ clearly indicates that local thermal equilibrium is achieved for dimensionless times greater than or equal to 0.0038.

Not only do the results shown in Figure 2.4 indicate that local thermal equilibrium is achieved for $\tau \geq 0.0038$, but they also indicate excellent agreement between the experimental results and the theoretical values. One need only think about using $\langle\Theta_\beta\rangle^\beta$ and $\langle\Theta_\sigma\rangle^\sigma$ to compute an experimental value of the spatial average temperature

$$\langle\Theta\rangle_{exp} = \varepsilon_\beta\langle\Theta_\beta\rangle^\beta + \varepsilon_\sigma\langle\Theta_\sigma\rangle^\sigma \tag{2.3-49}$$

in order to see the excellent agreement between the theory and the numerical experiments.

To explore the validity of the estimate given by Eq. 2.3-39, we express it in terms of the dimensionless temperatures according to

$$\langle\Theta_\beta\rangle^\beta - \langle\Theta_\sigma\rangle^\sigma = O\left(\frac{\ell_{\beta\sigma}}{L}\right)^2 \left\{ \frac{\left[\frac{(k_\beta - k_\sigma)(1+C_{\beta\sigma})}{k_{\beta\sigma}}\right] - \left[\frac{((\rho c_p)_\beta - (\rho c_p)_\sigma)}{\langle\rho\rangle C_p}\frac{K_{eff}}{k_{\beta\sigma}}\right]}{\underbrace{1}_{\text{exchange}} + \underbrace{O\left(\frac{\ell_{\beta\sigma}}{L}\right)^2}_{\text{conduction}} + \underbrace{O\left(\frac{\ell_{\beta\sigma}^2}{\alpha_{\beta\sigma}t^*}\right)}_{\text{accumulation}}} \right\} \tag{2.3-50}$$

Quintard and Whitaker (1995a) have evaluated the right hand side of this result for the conditions illustrated in Table 2.1, and for the two dimensionless times indicated in Figure 2.4, they obtained the following estimates:

$$\langle\Theta_\beta\rangle^\beta - \langle\Theta_\sigma\rangle^\sigma = O(0.1), \quad \tau = 0.0038 \tag{2.3-51a}$$

$$\langle\Theta_\beta\rangle^\beta - \langle\Theta_\sigma\rangle^\sigma = O(0.015), \quad \tau = 0.0345 \tag{2.3-51b}$$

This first of these would seem to be quite reasonable while the second would appear to underestimate the difference between $\langle\Theta_\beta\rangle^\beta$ and $\langle\Theta_\sigma\rangle^\sigma$. Given the number of estimates that are required to evaluate the right hand side of Eq. 2.3-50, we conclude that Eqs. 2.3-51 are in reasonably good agreement with the numerical experiments.

One of the interesting characteristics illustrated by $\langle\Theta_\beta\rangle^\beta$ and $\langle\Theta_\sigma\rangle^\sigma$ is the small-scale fluctuation associated with the characteristic length of the unit cell, ℓ_β. These fluctuations were first observed by Prat (1989, 1990, 1992) in a set of numerical experiments dealing with the boundary condition between a porous medium and a homogeneous fluid, and the matter has been investigated in detail by Quintard and

Whitaker (1994a-e). In their study, it was proved that the *proper average* to be used with spatially periodic porous media is a weighted average known as the *cellular average*. By proper average, we mean an average that is devoid of fluctuations at the small length-scale. The cellular average can be obtained by averaging the results shown in Figure 2.4 over a unit cell, and a little thought will indicate that this second average of $\langle\Theta_\beta\rangle^\beta$ and $\langle\Theta_\sigma\rangle^\sigma$ would produce a result that would be indistinguishable from the theoretical values represented by $\langle\Theta\rangle$. In addition to proving that the cellular average was the proper average to use with spatially periodic porous media, Quintard and Whitaker (1994a-e) demonstrated that the traditional spatial average is the proper average for disordered systems.

Perhaps the most unusual aspect of the results presented in Figure 2.4 is the fact that excellent agreement between theory and experiment has been obtained even when the traditional length-scale constraints *have not been* satisfied. For the system illustrated in Figure 2.3 and the results shown in Figure 2.4, we see that the characteristic lengths, ℓ_β, r_o, and L are all essentially the same order of magnitude and not at all disparate as suggested by the traditional constraints given by (Whitaker, 1969)

$$\ell_\beta \ll r_o \ll L \tag{2.3-52}$$

In addition to the experimental results illustrated in Figure 2.4, Quintard and Whitaker (1993b, 1995a) carried out calculations for several other systems, and compared their results with both the one-equation model given by Eq. 2.2-23 and the two-equation model represented by Eqs. 2.2-25 and 2-26. The main conclusion that can be drawn from the numerical experiments is that the ratio of temperature changes can usually be approximated by

$$\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{\Delta\langle T\rangle} = \mathbf{O}\left(\ell_{\beta\sigma}/L\right)^2\left[\mathbf{O}(1-10)\right] \tag{2.3-53}$$

and this result is entirely consistent with the use of Eqs. 2.3-42 in the estimate given by Eq. 2.3-39. When using Eq. 2.3-53, one must remember that L^2 has been used to represent $L_{T1}\,L_T$ and that L^2 will depend on time for transient processes. A reasonable estimate of this macroscopic length scale for transient processes is given by

$$L^2(t) = \mathbf{O}\left(K_{eff}\,t/\langle\rho\rangle C_p\right) \tag{2.3-54}$$

and this suggests that one can always find significant differences between $\langle T_\beta\rangle^\beta$ and $\langle T_\sigma\rangle^\sigma$ if the time is small enough. On the other hand, at short times the difference between $\langle T_\beta\rangle^\beta$ and $\langle T_\sigma\rangle^\sigma$ may be controlled by the initial condition and this was not taken into account in the development of Eq. 2.3-39.

We close this section by noting that Eq. 2.3-53 can be used with reasonable confidence to identify conditions for which local thermal equilibrium is valid, and that Quintard and Whitaker (1995a) have given convenient analytical expressions for $a_v h$

that can used to determine $\ell_{\beta\sigma}$ as defined by Eqs. 2.3-41. For regular arrays of cylinders one can use Chang's unit cell to obtain

$$\frac{a_v h \ell_\beta^2}{k_\beta} = \frac{8\pi\varepsilon_\beta^2}{\left[\varepsilon_\sigma(R+1)-3\right]\varepsilon_\beta - 4\ln\left(\sqrt{\varepsilon_\sigma}\right)}, \quad \textit{cylinders} \tag{2.3-55}$$

where R is given by

$$R = \varepsilon_\beta k_\beta / \varepsilon_\sigma k_\sigma \tag{2.3-56}$$

For regular arrays of spheres one finds

$$\frac{a_v h \ell_\beta^2}{k_\beta} = \frac{40\alpha\left(\alpha^2+\alpha+1\right)\kappa}{(1+5\kappa)+\alpha(2+\kappa)+\left(\alpha^4+2\alpha^3+3\alpha^2\right)(1-\kappa)}, \quad \textit{spheres} \tag{2.3-57}$$

in which the parameters α and κ are defined by

$$\alpha = \left(1-\varepsilon_\beta\right)^{\frac{1}{3}}, \qquad \kappa = k_\sigma / k_\beta \tag{2.3-58}$$

In both Eq. 2.3-55 and Eq. 2.3-57, we have used ℓ_β to represent the characteristic length for the β-phase and the manner in which ℓ_β is related to the parameters describing Chang's unit cell is described by Quintard and Whitaker (1995a).

2.4 Closure

In order to obtain a closed form of Eq. 2.2-18 we need to develop the boundary value problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$, and much of our analysis in this section follows that presented in Chapter 1. We recall the original boundary value problem from Sec. 2.1

$$(\rho c_p)_\beta \frac{\partial T_\beta}{\partial t} = \nabla\cdot(k_\beta \nabla T_\beta), \quad \text{in the } \beta\text{-phase} \tag{2.4-1}$$

B.C.1 $$T_\beta = T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2.4-2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla T_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2.4-3}$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla\cdot(k_\sigma \nabla T_\sigma), \quad \text{in the } \sigma\text{-phase} \tag{2.4-4}$$

B.C.3 $$T_\beta = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{2.4-5}$$

B.C.4 $$T_\sigma = \mathscr{G}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\sigma e} \tag{2.4-6}$$

and note that the spatially smoothed form of Eq. 2.4-1 was given in Sec. 2.2 as

$$\varepsilon_\beta(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left[k_\beta \left(\varepsilon_\beta \nabla \langle T_\beta \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right) \right] + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \, dA \tag{2.4-7}$$

Here one must be careful to remember that this result is only valid when the following two length-scale constraints are satisfied

$$\ell_\beta \ll r_0 , \quad r_0^2 \ll L_\varepsilon L_{TI} \tag{2.4-8}$$

The spatial deviation temperature in Eq. 2.4-7 is defined by

$$\tilde{T}_\beta = T_\beta - \langle T_\beta \rangle^\beta \tag{2.4-9}$$

and in order to develop the governing differential equation for $\tilde{T}_\beta$ we need to subtract the *intrinsic form* of Eq. 2.4-7 from Eq. 2.4-1. This is obtained by dividing Eq. 2.4-7 by ε_β and the result can be expressed as

$$(\rho c_p)_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left(k_\beta \nabla \langle T_\beta \rangle^\beta \right) + \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot k_\beta \nabla \langle T_\beta \rangle^\beta \tag{2.4-10}$$

$$+ \varepsilon_\beta^{-1} \nabla \cdot \left[\frac{k_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right] + \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta dA$$

If we subtract Eq. 2.4-10 from Eq. 2.4-1 and make use of the definition of $\tilde{T}_\beta$ given by Eq. 2.4-9, we obtain the following governing differential equation for the spatial deviation temperature.

$$\underbrace{(\rho c_p)_\beta \frac{\partial \tilde{T}_\beta}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot \left(k_\beta \nabla \tilde{T}_\beta \right)}_{\text{conduction}} - \underbrace{\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot k_\beta \nabla \langle T_\beta \rangle^\beta}_{\text{conductive source}} - \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \left[\frac{k_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right]}_{\text{non-local conduction}}$$

$$- \underbrace{\frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta dA}_{\text{interfacial flux}} \tag{2.4-11}$$

This result is analogous to the governing equation for the spatial deviation concentration given by Eq. 1.4-8; however, in this case we must deal directly with the interfacial flux and we begin that process by using Eq. 2.2-8 in order to express the interfacial flux as

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla T_\beta dA = -(\nabla \varepsilon_\beta)\cdot k_\beta \nabla \langle T_\beta\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \tilde{T}_\beta dA \qquad (2.4\text{-}12)$$

When this result is used in Eq. 2.4-11 we obtain the following governing differential equation for the spatial deviation temperature in the β-phase:

$$(\rho c_p)_\beta \frac{\partial \tilde{T}_\beta}{\partial t} = \nabla\cdot(k_\beta \nabla \tilde{T}_\beta) - \varepsilon_\beta^{-1}\nabla\cdot\left[\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta dA\right] - \frac{\varepsilon_\beta^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \tilde{T}_\beta dA \qquad (2.4\text{-}13)$$

The third term in this result represents a non-local contribution since it involves values of $\tilde{T}_\beta$ associated with points other than the centroid of the averaging volume. Our arguments for neglecting the non-local term are identical to those presented in Sec. 1.4, and we make use of that development in order to express Eq. 2.4-13 as

$$\underbrace{(\rho c_p)_\beta \frac{\partial \tilde{T}_\beta}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot(k_\beta \nabla \tilde{T}_\beta)}_{\text{conduction}} - \underbrace{\frac{\varepsilon_\beta^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \tilde{T}_\beta dA}_{\text{interfacial flux}} \qquad (2.4\text{-}14)$$

Even when volume averaged heat conduction process is unsteady, the closure problem will generally be quasi-steady. This occurs because the following constraints

$$\frac{\alpha_\beta t^*}{\ell_\beta^2} >> 1, \quad \frac{\alpha_\sigma t^*}{\ell_\sigma^2} >> 1, \quad \text{closure process is quasi-steady} \qquad (2.4\text{-}15)$$

are usually satisfied. Under these circumstances we can express the closure problem associated with Eqs. 2.4-1 through 2.4-6 as

$$\nabla\cdot(k_\beta \nabla \tilde{T}_\beta) = \frac{\varepsilon_\beta^{-1}}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \tilde{T}_\beta dA \qquad (2.4\text{-}16a)$$

B.C.1
$$\tilde{T}_\beta = \tilde{T}_\sigma + \langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta, \quad \text{at } \mathscr{A}_{\beta\sigma} \qquad (2.4\text{-}16b)$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \tilde{T}_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla \tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \langle T_\beta\rangle^\beta - \mathbf{n}_{\beta\sigma}\cdot k_\alpha \nabla \langle T_\sigma\rangle^\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma} \qquad (2.4\text{-}16c)$$

$$\nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) \;=\; \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma dA \tag{2.4-16d}$$

B.C.3
$$\tilde{T}_\beta \;=\; f(\mathbf{r},t)\,,\quad \text{at } \mathscr{A}_{\beta e} \tag{2.4-16e}$$

B.C.4
$$\tilde{T}_\sigma \;=\; g(\mathbf{r},t)\,,\quad \text{at } \mathscr{A}_{\sigma e} \tag{2.4-16f}$$

Equations 2.4-16 represent the starting point for the *two-equation model* closure problem (Quintard and Whitaker, 1993b, Sec. III) that leads to the two-equation model represented by Eqs. 2.2-25 and 2.2-26. If we ignore the contributions of the non-homogeneous terms associated with B.C.3 and B.C.4, we see that there are three source terms, $\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta$, $\nabla\langle T_\beta\rangle^\beta$, and $\nabla\langle T_\sigma\rangle^\sigma$ that are the *generators* of the $\tilde{T}_\beta$ and $\tilde{T}_\sigma$-fields. If we were willing to impose local thermal equilibrium, i.e.,

$$\langle T_\beta\rangle^\beta \;=\; \langle T_\sigma\rangle^\sigma \;=\; \langle T\rangle \tag{2.4-17}$$

these three sources would be replaced by the single source, $\nabla\langle T\rangle$. However, we should remember that Eq. 2.4-17 is the *mathematical consequence* of the *restrictions* given by Eqs. 2.3-7 and 2.3-8. Just because something is *small enough* to be neglected in the macroscopic equation does not necessarily mean that it is *small enough* to be neglected in the closure problem.

2.4.1 LOCAL THERMAL EQUILIBRIUM

To explore local thermal equilibrium, *as it applies to the closure problem*, we need to examine the interfacial boundary conditions which we write as

B.C.1
$$\tilde{T}_\beta \;=\; \tilde{T}_\sigma \;-\; \left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right),\quad \text{at } \mathscr{A}_{\beta\sigma} \tag{2.4-18}$$

B.C.2
$$\begin{aligned}-\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta \;=\; &-\mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{T}_\sigma \;+\; \mathbf{n}_{\beta\sigma}\cdot(k_\beta - k_\sigma)\nabla\langle T\rangle \\ &+\; \mathbf{n}_{\beta\sigma}\cdot k_{\beta\sigma}\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right),\quad \text{at } \mathscr{A}_{\beta\sigma}\end{aligned} \tag{2.4-19}$$

Here $k_{\beta\sigma}$ represents the mix-mode thermal conductivity defined by

$$k_{\beta\sigma} \;=\; \varepsilon_\sigma k_\beta \;+\; \varepsilon_\beta k_\sigma \tag{2.4-20}$$

In order for local thermal equilibrium to be valid *at the closure level*, we require that the following two restrictions be satisfied

$$\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma \;<<\; \tilde{T}_\beta, \tilde{T}_\sigma \tag{2.4-21}$$

$$\mathbf{n}_{\beta\sigma}\cdot k_{\beta\sigma}\nabla\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right) \;<<\; \mathbf{n}_{\beta\sigma}\cdot(k_\beta - k_\sigma)\nabla\langle T\rangle \tag{2.4-22}$$

The second of these is easy to put into a useful form, and we need only apply the estimates given in Sec. 2.3 to express Eq. 2.4-22 as

$$\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{\Delta\langle T\rangle} \ll \frac{k_\beta - k_\sigma}{k_{\beta\sigma}} \tag{2.4-23}$$

This result can be used with Eq. 2.3-53 to obtain

$$\left(\frac{\ell_{\beta\sigma}}{L}\right)^2 \ll \frac{k_\beta - k_\sigma}{k_{\beta\sigma}} \tag{2.4-24}$$

and for many problems of practical interest this constraint is easily satisfied.

In order to deal with the restriction given by Eq. 2.4-21 we need estimates of the spatial deviation temperatures. When the constraint indicated by Eq. 2.4-24 is satisfied, we can simplify the flux boundary condition given by Eq. 2.4-19 to the following form

B.C.2 $$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta + \mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma = \underbrace{\mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle}_{\text{source}} \tag{2.4-25}$$

Here we have placed both spatial deviation fluxes on the left hand side and retained the source term on the right hand side. One should think of the source as being distributed between the two phases.

In order to develop a constraint associated with the restriction given by Eq. 2.4-21, we need estimates of $\tilde{T}_\beta$ and $\tilde{T}_\sigma$. When local thermal equilibrium is valid in the closure problem, Eq. 2.4-18 will provide

$$\tilde{T}_\beta = \mathbf{O}(\tilde{T}_\sigma) \tag{2.4-26}$$

and we want to distribute the source on the right hand side of Eq. 2.4-25 in a manner that is consistent with Eq. 2.4-26. To accomplish this, we distribute the fluxes according to

$$\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta = \varphi\left[\mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle\right] \tag{2.4-27}$$

$$\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma = (1-\varphi)\left[\mathbf{n}_{\beta\sigma}\cdot(k_\sigma - k_\beta)\nabla\langle T\rangle\right] \tag{2.4-28}$$

in which the parameter φ is restricted by $0 \le \varphi \le 1$. From these two results we obtain the following estimates for the spatial deviation temperatures

$$\tilde{T}_\beta = \mathbf{O}\left[\varphi\ell_\beta\left(\frac{k_\sigma - k_\beta}{k_\beta}\right)\nabla\langle T\rangle\right] \tag{2.4-29}$$

$$\tilde{T}_\sigma = \mathbf{O}\left[(1-\varphi)\ell_\sigma\left(\frac{k_\sigma - k_\beta}{k_\sigma}\right)\nabla\langle T\rangle\right] \tag{2.4-30}$$

If we now impose the condition indicated by Eq. 2.4-26, we find that φ is given by

$$\varphi = \mathbf{O}\left[\ell_\sigma / k_\sigma \Big/ \left(\frac{\ell_\sigma}{k_\sigma} + \frac{\ell_\beta}{k_\beta}\right)\right] \tag{2.4-31}$$

and our estimates of $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ can be expressed as

$$\tilde{T}_\beta = \mathbf{O}\left(\tilde{T}_\sigma\right) = \mathbf{O}\left[\left(\frac{k_\sigma}{\ell_\sigma} + \frac{k_\beta}{\ell_\beta}\right)^{-1} (k_\beta - k_\sigma)\nabla\langle T\rangle\right] \tag{2.4-32}$$

It is convenient to represent this estimate in the form

$$\tilde{T}_\beta \, , \tilde{T}_\sigma = \mathbf{O}\left[\frac{\ell_\beta \ell_\sigma (k_\beta - k_\sigma)}{\ell_\sigma k_\beta + \ell_\beta k_\sigma} \nabla\langle T\rangle\right] \tag{2.4-33}$$

in order to indicate the intuitively appealing result that both $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ are zero under the following circumstances

1. Either ε_β or ε_σ is zero.
2. The thermal conductivities are equal, $k_\beta = k_\sigma$.
3. The spatial average temperature is constant, $\nabla\langle T\rangle = 0$.

One might also like to have an estimate requiring that $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ be zero when $(\rho c_p)_\beta = (\rho c_p)_\sigma$; however, that condition is circumvented by the quasi-steady nature of the closure problem given by Eqs. 2.4-16.

Use of Eq. 2.4-33 in the restriction given by Eq. 2.4-21 leads to the inequality

$$\frac{\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma}{\Delta\langle T\rangle} << \frac{\ell_\beta \ell_\sigma (k_\beta - k_\sigma)}{L_T(\ell_\sigma k_\beta + \ell_\beta k_\sigma)} \tag{2.4-34}$$

and with the aid of Eq. 2.4-24 we can express this result as

$$\left(\frac{\ell_{\beta\sigma}}{L}\right)^2 << \frac{\ell_\beta \ell_\sigma (k_\beta - k_\sigma)}{L_T(\ell_\sigma k_\beta + \ell_\beta k_\sigma)} \tag{2.4-35}$$

In order to clarify the meaning of this constraint, we recall Eqs. 2.3-37 through 2.3-39 which indicate that L^2 is given by

$$L^2 = L_{T1} L_T \tag{2.4-36}$$

and we use this result in Eq. 2.4-35 to obtain

$$\frac{\ell_{\beta\sigma}}{L_{T1}} \ll \frac{\ell_\beta \ell_\sigma (k_\beta - k_\sigma)}{\ell_{\beta\sigma}(\ell_\sigma k_\beta + \ell_\beta k_\sigma)} \tag{2.4-37}$$

For many practical applications, the right hand side of this inequality will be on the order of one, thus the constraint will be satisfied whenever $\ell_{\beta\sigma}$ is small compared to L_{T1}. We should remember that this latter macroscopic length-scale is defined by the order of magnitude estimate

$$\nabla\nabla\langle T\rangle = \mathbf{O}\left[\nabla\langle T\rangle / L_{T1}\right] \tag{2.4-38}$$

thus L_{T1} is infinite for steady, one-dimensional heat conduction processes.

We are now in a position to make use of the simplifications provided by Eqs. 2.4-21 and 2.4-22 so that the closure problem given by Eqs. 2.4-16 can be expressed as

$$\nabla\cdot(k_\beta \nabla\tilde{T}_\beta) = \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla\tilde{T}_\beta dA \tag{2.4-39a}$$

B.C.1
$$\tilde{T}_\beta = \tilde{T}_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{2.4-39b}$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla\tilde{T}_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\beta - k_\sigma)\nabla\langle T\rangle, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{2.4-39c}$$

$$\nabla\cdot(k_\sigma \nabla\tilde{T}_\sigma) = \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma \nabla\tilde{T}_\sigma dA \tag{2.4-39d}$$

B.C.3
$$\tilde{T}_\beta = f(\mathbf{r}, t), \quad \text{at } \mathscr{A}_{\beta e} \tag{2.4-39e}$$

B.C.4
$$\tilde{T}_\sigma = g(\mathbf{r}, t), \quad \text{at } \mathscr{A}_{\sigma e} \tag{2.4-39f}$$

Obviously we have no intention of solving for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ in the macroscopic region illustrated in Figure 2.1, but instead we want to determine these two spatial deviation temperatures in some representative region such as we have illustrated in Figure 2.4.

2.4.2 LOCAL CLOSURE PROBLEM

In order to discard B.C.3 and B.C.4 and develop a local closure problem, we need to adopt the model of a spatially periodic system and replace Eqs. 2.4-39 with

$$k_\beta \nabla^2\tilde{T}_\beta = \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla\tilde{T}_\beta dA \tag{2.4-40a}$$

B.C.1
$$\tilde{T}_\beta = \tilde{T}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-40b}$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla\tilde{T}_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot(k_\beta - k_\sigma)\nabla\langle T\rangle\big|_x, \quad \text{at } A_{\beta\sigma} \tag{2.4-40c}$$

$$k_\sigma \nabla^2 \tilde{T}_\sigma = \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla \tilde{T}_\sigma dA \tag{2.4-40d}$$

Periodicity: $$\tilde{T}_\beta(\mathbf{r}+\ell_i) = \tilde{T}_\beta(\mathbf{r}), \quad \tilde{T}_\sigma(\mathbf{r}+\ell_i) = \tilde{T}_\sigma(\mathbf{r}), \quad i = 1, 2, 3 \tag{2.4-40e}$$

Here it is important to understand that the representative region shown in Figure 2.4 can be arbitrarily complex (Ahmadi and Quintard, 1996) and thus contain all the important

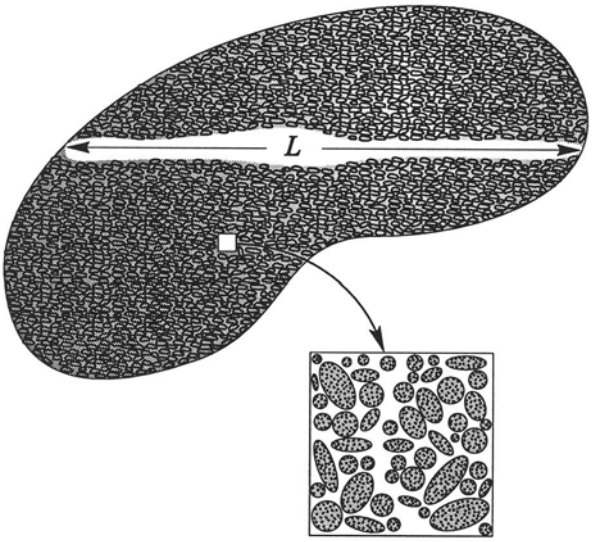


Figure 2.4. Representative region of the β-σ system

geometrical characteristics of the β-σ system. Under these circumstances the weak boundary conditions given by Eq. 2.4-40e do not play an important role in the determination of the effective thermal conductivity tensor. In our formulation of the local closure problem, we have ignored variations of k_β and k_σ within the unit cell and we have evaluated the gradient of the spatial average temperature at the centroid. This latter simplification is discussed in Sec. 1.4 and is based on the length-scale constraint

$$r_o \ll L_{T1} \tag{2.4-41}$$

Within the framework of a *local closure problem*, the area integrals representing the interfacial flux are related by (see Problem 2-3)

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta dA = -\frac{1}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla \tilde{T}_\sigma dA \tag{2.4-42}$$

and this means that the boundary value problem given by Eqs. 2.4-40 contains a single undetermined integral. If this integral were specified, Eqs. 2.4-40 could be used to determine $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ only to within a single arbitrary constant. Both the integral associated with the interfacial flux, and the arbitrary constant associated with $\tilde{T}_\beta$ and $\tilde{T}_\sigma$, can be determined by imposing the following conditions on the average values of the spatial deviation temperatures:

Average: $$\langle \tilde{T}_\beta \rangle^\beta = 0, \quad \langle \tilde{T}_\sigma \rangle^\sigma = 0 \tag{2.4-43}$$

In subsequent paragraphs we will indicate how these conditions can be used to solve the closure problem, and why they are *unnecessary for the case of symmetric unit cells.*

2.4.3 CLOSURE VARIABLES

Given that the single non-homogeneous term in the local closure problem is proportional to $\nabla\langle T\rangle|_x$ we express $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ as

$$\tilde{T}_\beta = \mathbf{b}_\beta \cdot \nabla\langle T\rangle + \psi_\beta \tag{2.4-44a}$$

$$\tilde{T}_\sigma = \mathbf{b}_\sigma \cdot \nabla\langle T\rangle + \psi_\sigma \tag{2.4-44b}$$

in which $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ are referred to as the closure variables (see Problem 2-4) and it is understood that $\nabla\langle T\rangle$ is evaluated at the centroid. We specify these two vector fields according to the following boundary value problem

$$k_\beta \nabla^2 \mathbf{b}_\beta = \frac{\varepsilon_\beta^{-1}}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_\beta dA \tag{2.4-45a}$$

B.C.1 $$\mathbf{b}_\beta = \mathbf{b}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-45b}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_\beta = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{b}_\sigma + \mathbf{n}_{\beta\sigma}(k_\beta - k_\sigma), \quad \text{at } A_{\beta\sigma} \tag{2.4-45c}$$

$$k_\sigma \nabla^2 \mathbf{b}_\sigma = \frac{\varepsilon_\sigma^{-1}}{\mathscr{V}} \int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla \mathbf{b}_\sigma dA \tag{2.4-45d}$$

Periodicity: $$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{b}_\sigma(\mathbf{r}+\ell_i) = \mathbf{b}_\sigma(\mathbf{r}), \quad i = 1, 2, 3 \tag{2.4-45e}$$

and leave it as an exercise for the reader (see Problem 2-5) to demonstrate that $\psi_\beta = \psi_\sigma = constant$. This constant will have no influence on the closed form of the macroscopic equation since it will not pass through the filters represented by the area integrals in Eq. 2.2-18. One can prove that $\mathbf{b}_\beta = \mathbf{b}_\sigma = constant$ when $k_\beta = k_\sigma$ (see

Problem 2-6), thus the source, $\mathbf{n}_{\beta\sigma}(k_\beta - k_\sigma)$, in Eq. 2.4-45c is entirely responsible for generating contributions to $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ that will pass through the filter.

It is important to understand that the integrals in Eqs. 2.4-45a and 2.4-45d are related by

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{b}_\beta \, dA \;=\; -\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma \nabla \mathbf{b}_\sigma \, dA \;=\; \mathbf{c} \tag{2.4-46}$$

thus there is a single *undetermined constant vector* in the boundary value problem given by Eqs. 2.4-45. If this constant were known, one could use Eqs. 2.4-45 to determine $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ only to within another *arbitrary constant vector.* If the averages of $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ are set equal to zero, this leads to the following condition on the averages of the mapping vectors.

Averages: $$\langle \mathbf{b}_\beta \rangle^\beta = 0, \qquad \langle \mathbf{b}_\sigma \rangle^\sigma = 0 \tag{2.4-47}$$

These two conditions can be used to specify *both* the arbitrary constant associated with $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ and the undetermined constant represented by Eq. 2.4-46, and in the following paragraphs we indicate how this can be done.

2.4.4 ARBITRARY UNIT CELLS

In order to develop a general solution for the closure problem given by Eqs. 2.4-45, we make use of Eqs. 2.4-46 and 2.4-47 to express the closure problem as

$$k_\beta \nabla^2 \mathbf{b}_\beta = \varepsilon_\beta^{-1}\mathbf{c} \tag{2.4-48a}$$

B.C.1 $$\mathbf{b}_\beta = \mathbf{b}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-48b}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{b}_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla \mathbf{b}_\sigma + \mathbf{n}_{\beta\sigma}(k_\beta - k_\sigma), \quad \text{at } A_{\beta\sigma} \tag{2.4-48c}$$

$$k_\sigma \nabla^2 \mathbf{b}_\sigma = -\varepsilon_\sigma^{-1}\mathbf{c} \tag{2.4-48d}$$

Periodicity: $$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{b}_\sigma(\mathbf{r}+\ell_i) = \mathbf{b}_\sigma(\mathbf{r}), \quad i = 1,2,3 \tag{2.4-48e}$$

Averages: $$\langle \mathbf{b}_\beta \rangle^\beta = 0, \qquad \langle \mathbf{b}_\sigma \rangle^\sigma = 0 \tag{2.4-48f}$$

We now decompose the closure variables according to

$$\mathbf{b}_\beta = \mathbf{b}_\beta^\circ + \mathbf{B}_\beta \cdot \mathbf{c} \tag{2.4-49a}$$

$$\mathbf{b}_\sigma = \mathbf{b}_\sigma^\circ + \mathbf{B}_\sigma \cdot \mathbf{c} \tag{2.4-49b}$$

where the new closure variables are defined by two boundary value problems. The first of these is given by:

Problem I

$$k_\beta \nabla^2 \mathbf{b}_\beta^\circ = 0 \tag{2.4-50a}$$

B.C.1 $$\mathbf{b}_\beta^\circ = \mathbf{b}_\sigma^\circ, \quad \text{at } A_{\beta\sigma} \tag{2.4-50b}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_\beta^\circ = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{b}_\sigma^\circ + \mathbf{n}_{\beta\sigma}(k_\beta - k_\sigma), \quad \text{at } A_{\beta\sigma} \tag{2.4-50c}$$

$$k_\sigma \nabla^2 \mathbf{b}_\sigma^\circ = 0 \tag{2.4-50d}$$

Periodicity: $$\mathbf{b}_\beta^\circ(\mathbf{r}+\ell_i) = \mathbf{b}_\beta^\circ(\mathbf{r}), \quad \mathbf{b}_\sigma^\circ(\mathbf{r}+\ell_i) = \mathbf{b}_\sigma^\circ(\mathbf{r}), \quad i = 1, 2, 3 \tag{2.4-50e}$$

Average: $$\langle \mathbf{b}_\beta^\circ \rangle^\beta = 0 \tag{2.4-50f}$$

Here we see that Eqs. 2.4-50a through 2.4-50e determine $\mathbf{b}_\beta^\circ$ and $\mathbf{b}_\sigma^\circ$ to within a single arbitrary constant vector, and it is Eq. 2.4-50f that specifies this constant. The boundary value problem that determines $\mathbf{B}_\beta$ and $\mathbf{B}_\sigma$ is given by

Problem II

$$k_\beta \nabla^2 \mathbf{B}_\beta = \varepsilon_\beta^{-1} \mathbf{I} \tag{2.4-51a}$$

B.C.1 $$\mathbf{B}_\beta = \mathbf{B}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-51b}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{B}_\beta = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{B}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-51c}$$

$$k_\sigma \nabla^2 \mathbf{B}_\sigma = -\varepsilon_\sigma^{-1} \mathbf{I} \tag{2.4-51d}$$

Periodicity: $$\mathbf{B}_\beta(\mathbf{r}+\ell_i) = \mathbf{B}_\beta(\mathbf{r}), \quad \mathbf{B}_\sigma(\mathbf{r}+\ell_i) = \mathbf{B}_\sigma(\mathbf{r}), \quad i = 1, 2, 3 \tag{2.4-51e}$$

Average: $$\langle \mathbf{B}_\beta \rangle^\beta = 0 \tag{2.4-51f}$$

Here we see that Eqs. 2.4-51a through 2.4-51e determine $\mathbf{B}_\beta$ and $\mathbf{B}_\sigma$ to within a single arbitrary constant tensor, and it is Eq. 2.4-51f that specifies this tensor. On the basis of Eqs. 2.4-50f and 2.4-51f, we see that the constraint on the average given by the first of Eqs. 2.4-48f is automatically satisfied. The second of Eqs. 2.4-48f can be used to determine the constant vector in Eqs. 2.4-48a and 2.4-48d according to

$$\mathbf{c} = -\left(\langle \mathbf{B}_\sigma \rangle^\sigma\right)^{-1} \cdot \langle \mathbf{b}_\sigma^\circ \rangle^\sigma \tag{2.4-52}$$

Since the non-homogeneous terms in the boundary value problem for $\mathbf{B}_\beta$ and $\mathbf{B}_\sigma$ are both constants proportional to the unit tensor, one can prove that these two tensors can be determined by the solution of a scalar-valued boundary value problem (see Problem 2-7). For symmetric unit cells, we can prove that the constant vector $\mathbf{c}$ is zero and the solution of the closure problem is simplified.

2.4.5 SYMMETRIC UNIT CELLS

In order to prove that the undetermined constant represented by Eq. 2.4-46 is zero for symmetric unit cells, one begins by using the periodicity condition and divergence theorem for $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ to obtain

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{b}_\beta dA = \frac{1}{\mathscr{V}}\int_{V_\beta} k_\beta \nabla^2 \mathbf{b}_\beta dV \tag{2.4-53}$$

$$\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma \nabla \mathbf{b}_\sigma dA = \frac{1}{\mathscr{V}}\int_{V_\sigma} k_\sigma \nabla^2 \mathbf{b}_\sigma dV \tag{2.4-54}$$

Next, one follows the type of analysis given in Sec. 1.5 to prove (see Problem 2-8) that the components of $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ are *skew-symmetric* for a *symmetric* unit cell. Since ∇^2 is a *symmetric operator*, and the components of $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ are *skew-symmetric functions*, the volume integrals of $\nabla^2\mathbf{b}_\beta$ and $\nabla^2\mathbf{b}_\sigma$ must be zero for any unit cell that is completely symmetric. This means that Eqs. 2.4-53 and 2.4-54 can be expressed as

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{b}_\beta dA = \frac{1}{\mathscr{V}}\int_{V_\beta} k_\beta \nabla^2 \mathbf{b}_\beta dV = 0 \tag{2.4-55}$$

$$\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma \nabla \mathbf{b}_\sigma dA = \frac{1}{\mathscr{V}}\int_{V_\sigma} k_\sigma \nabla^2 \mathbf{b}_\sigma dV = 0 \tag{2.4-56}$$

and under these circumstances the closure problem represented by Eqs. 2.4-45 simplifies to the form originally presented by Nozad *et al.* (1985a). This is given by

$$\nabla^2 \mathbf{b}_\beta = 0 \tag{2.4-57a}$$

B.C.1
$$\mathbf{b}_\beta = \mathbf{b}_\sigma, \quad \text{at } A_{\beta\sigma} \tag{2.4-57b}$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot\nabla\mathbf{b}_\beta = -\mathbf{n}_{\beta\sigma}\cdot\kappa\nabla\mathbf{b}_\sigma + \mathbf{n}_{\beta\sigma}(1-\kappa), \quad \text{at } A_{\beta\sigma} \tag{2.4-57c}$$

$$\nabla^2 \mathbf{b}_\sigma = 0 \tag{2.4-57d}$$

Periodicity:
$$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{b}_\sigma(\mathbf{r}+\ell_i) = \mathbf{b}_\sigma(\mathbf{r}), \quad i = 1,2,3 \tag{2.4-57e}$$

in which the parameter κ is defined by

$$\kappa = k_\sigma / k_\beta \tag{2.4-58}$$

When $\kappa = 0$ our closure problem for heat conduction naturally reduces to the closure problem for diffusion given by Eqs. 1.4-58. For non-symmetric unit cells, we have no

proof that the integrals in Eqs. 2.4-45a and 2.4-45d are zero, nor do we have a proof that this undetermined constant is negligible; however, comparison with experiment suggests that the effects of non-symmetric unit cells are not particularly important.

2.4.6 CLOSED FORM

In order to obtain the closed form of the macroscopic equation, we recall Eq. 2.2-18

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left[(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma)\nabla\langle T\rangle + \frac{k_\beta}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta\, dA + \frac{k_\sigma}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\, dA\right] \tag{2.4-59}$$

along with the representations for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ that took the form

$$\tilde{T}_\beta = \mathbf{b}_\beta\cdot\nabla\langle T\rangle + \psi_\beta \tag{2.4-60}$$

$$\tilde{T}_\sigma = \mathbf{b}_\sigma\cdot\nabla\langle T\rangle + \psi_\sigma \tag{2.4-61}$$

When used with a spatially periodic model, the area integrals in Eq. 2.4-59 have the characteristic that

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}dA = 0, \qquad \frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}dA = 0 \tag{2.4-62}$$

and this means that if ψ_β and ψ_σ are constants (see Problem 2-5), they cannot pass through these filters. Under these circumstances we can substitute Eqs. 2.4-60 and 2.4-61 into Eq. 2.4-59 to obtain the following closed form

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left(\mathbf{K}_{eff}\cdot\nabla\langle T\rangle\right) \tag{2.4-63}$$

Here the effective thermal conductivity tensor is defined by

$$\mathbf{K}_{eff} = \left(\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma\right)\mathbf{I} + \frac{(k_\beta - k_\sigma)}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathbf{b}_\beta dA \tag{2.4-64}$$

and in the next section we compare theoretical calculations of $\mathbf{K}_{eff}$ for isotropic systems with several sets of experimental data. One can prove that the thermal conductivity tensor determined by Eqs. 2.4-64 and 2.4-48 is symmetric, i.e.,

$$\mathbf{K}_{eff} = \mathbf{K}_{eff}^{\mathrm{T}} \tag{2.4-65}$$

and the proof will be left as an exercise for the reader (see Problem 2-9).

2.5 Comparison Between Theory and Experiment

In this section we wish to compare experimental values of the effective thermal conductivity with theoretical values determined by the solution of Eqs. 2.4-57 and the representation of $\mathbf{K}_{eff}$ given by Eq. 2.4-64. All the experimental studies were based on the assumption that $\mathbf{K}_{eff}$ was a constant, thus Eq. 2.4-63 was employed in the form

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} = \mathbf{K}_{eff} : \nabla\nabla \langle T \rangle \tag{2.5-1}$$

For comparison with experimental results, it is convenient to work with a dimensionless form of this result given by

$$\frac{\mathbf{K}_{eff}}{k_\beta} = \left(\varepsilon_\beta + \varepsilon_\sigma \kappa\right)\mathbf{I} + \frac{(1-\kappa)}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_\beta dA \tag{2.5-2}$$

in which $\kappa = k_\sigma / k_\beta$ as indicated earlier by Eq. 2.4-58.

Nozad *et al.* (1985a) have solved the closure problem given by Eqs. 2.4-57 for the simple, two-dimensional unit cell shown in Figure 2.5. This produces an isotropic

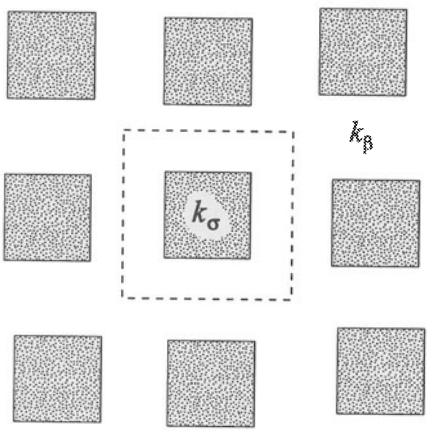


Figure 2.5. Unit cell in a two-dimensional, spatially periodic porous medium

effective thermal conductivity tensor, thus only a single component of the vector fields $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ is required in order to determine K_{eff}. The computed values of K_{eff}/k_β are shown in Figure 2.6 along with results determined by Perrins *et al.* (1979) who used an extension of the method of Rayleigh (1892). Similar results have been obtained by Sahraoui and Kaviany (1993) using direct numerical simulation for heat conduction in a unit cell, and one can prove (see Problem 2-10) that the results obtained in this manner are identical to those given by the solution of Eqs. 2.4-57. Figure 2.6 illustrates results

for a wide range of values of $\kappa = k_\sigma / k_\beta$ and three different geometries: a square array of squares, a square array of cylinders, and a hexagonal array of cylinders. One can see a slight influence of geometry, but for all practical purposes the dimensionless effective thermal conductivity depends only on ε_β and κ. Once again we should think of the area integral in Eq. 2.5-2 as a filter, and then ask the question: What characteristics of the boundary value problem given by Eqs. 2.4-57 pass through the filter? For the case of non-touching particles, only the volume fraction and the ratio of thermal conductivities pass through the filter.

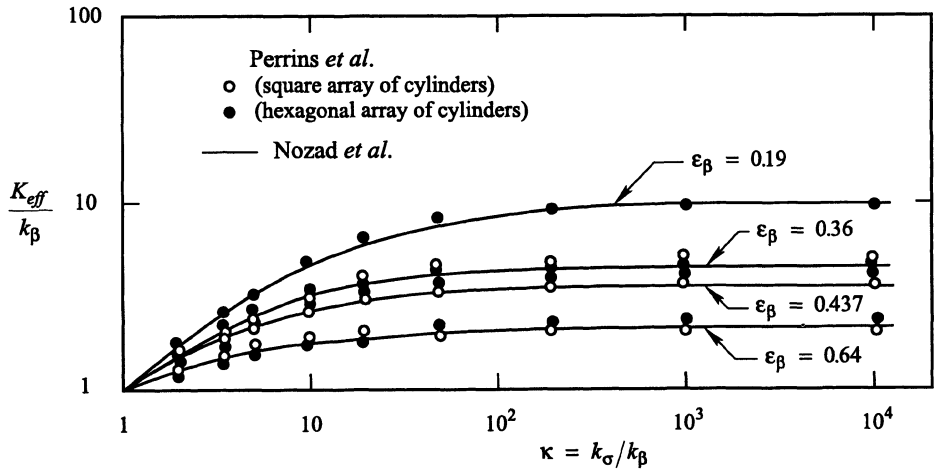


Figure 2.6. Effective thermal conductivity for two-dimensional arrays of non-touching particles

One can use the closure problem given by Eqs. 2.4-57 and an asymptotic analysis for small values of κ^{-1} to demonstrate that K_{eff}/k_β is independent of κ for large values of κ, and the intuitive explanation is quite straightforward. When k_σ for the non-touching particles is much, much larger than k_β for the continuous phase, the temperature in each particle becomes uniform. Further increases in k_σ have no influence on the temperature distribution in the σ-phase and the effective thermal conductivity is controlled entirely by k_β and the geometry of the two-phase system. For the geometries represented in Figure 2.6, the geometrical effects are almost entirely accounted for by ε_β.

2.5.1 MAXWELL'S CLOSURE PROBLEM

For a two-phase system made up on non-touching particles, Chang's (1982, 1983) unit cell shown in Figure 2.7 represents an attractive model. As we mentioned in Sec. 1.6,

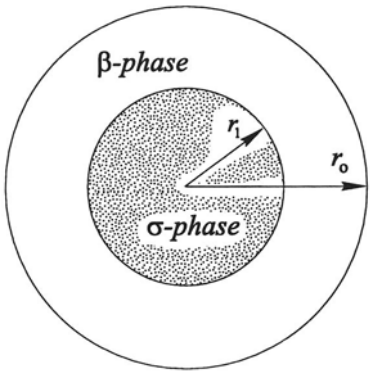


Figure 2.7. Chang's unit cell for the β-σ system

Chang's unit cell leads to Maxwell's model with the special form of the closure problem given by

B.C.1
$$\mathbf{b}_\beta = 0, \quad r = r_1 \tag{2.5-3a}$$

$$\nabla^2 \mathbf{b}_\beta = 0, \quad r_o < r \le r_1 \tag{2.5-3b}$$

B.C.2
$$\mathbf{b}_\beta = \mathbf{b}_\sigma, \quad r = r_o \tag{2.5-3c}$$

B.C.3
$$-\mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{b}_\beta = -\mathbf{n}_{\beta\sigma} \cdot \kappa \nabla \mathbf{b}_\sigma + \mathbf{n}_{\beta\sigma}(1-\kappa), \quad r = r_o \tag{2.5-3d}$$

$$\nabla^2 \mathbf{b}_\sigma = 0, \quad 0 \le r \le r_o \tag{2.5-3e}$$

For two-dimensional arrays of non-touching cylinders (Rayleigh, 1892) this closure problem leads to (Ochoa-Tapia *et al.*, 1994)

$$\frac{K_{eff}}{k_\beta} = \frac{2\kappa - \varepsilon_\beta(\kappa-1)}{2 + \varepsilon_\beta(\kappa-1)}, \quad \textit{cylinders} \tag{2.5-4}$$

and the results for the effective conductivity are essentially identical to the calculations of Nozad *et al.* (1985a). For a three-dimensional array of spheres, Eqs. 2.5-3 provide the following result (Maxwell, 1881)

$$\frac{K_{eff}}{k_\beta} = \frac{3\kappa - 2\varepsilon_\beta(\kappa-1)}{3 + \varepsilon_\beta(\kappa-1)}, \quad \textit{spheres} \tag{2.5-5}$$

and this solution produces values of the effective thermal conductivity that are slightly higher than the two-dimensional version given by Eq. 2.5-4.

For non-consolidated porous media, there is obviously particle-particle contact and when κ is much larger than one this contact plays an important role in the determination of the effective thermal conductivity. In order to account for this effect, Nozad *et al.* (1985a) made use of the two-dimensional model illustrated in Figure 2.8.

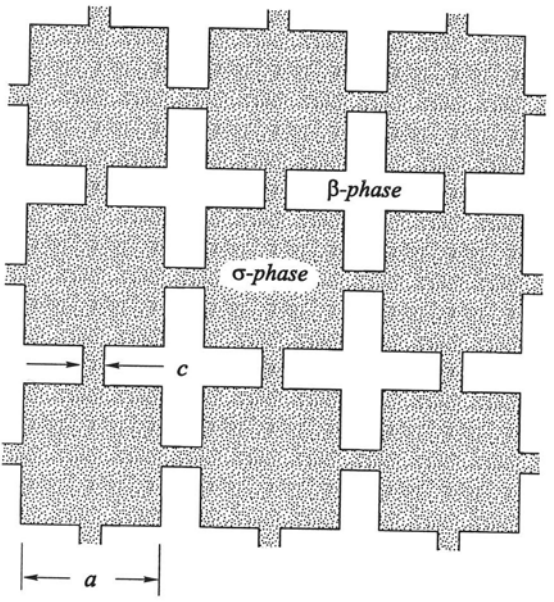


Figure 2.8. Two-dimensional square array with particle-particle contact

The fractional contact area is given by c/a, and this represents a parameter that can only be determined by a detailed study of the appropriate solid mechanics problem. The effective thermal conductivities calculated by Nozad (1983) using this geometrical model and the closure problem given by Eqs. 2.4-57 are shown in Figure 2.9 for a value of $c/a = 0.02$. The agreement with a wide range of experimental results is quite good, especially when one takes into account the variations in the void fraction which ranges from $\varepsilon_\beta = 0.31$ to $\varepsilon_\beta = 0.52$. Nozad's calculations for non-touching particles are also illustrated in Figure 2.9 along with Maxwell's theory given by Eq. 2.5-5. The latter is in excellent agreement with the experimental data for values of κ less than one hundred. When $\kappa = k_\sigma / k_\beta$ tends to zero, the closure problem given by Eqs. 2.5-3 reduces to the closure problem for the effective diffusivity and one recovers Eq. 1.6-13 which is compared with experimental results in Figure 1.10. While the predicted effective diffusivities are too high by about 20%, the results shown in Figures 1.10 and 2.9 indicate that Chang's unit cell can be used with the method of volume averaging to produce reliable effective transport coefficients for a wide range of values of the parameter κ, and this has led Ochoa-Tapia *et al.* (1994) to explore this approach for a variety of transport processes in two-phase media.

In an experimental study, Nozad *et al.* (1985b) measured the effective thermal conductivity for a narrow range of porosities, and the comparison of those results with the theory is shown in Figure 2.10. The agreement between theory and experiment is extremely good; however, there are important characteristics of the theoretical

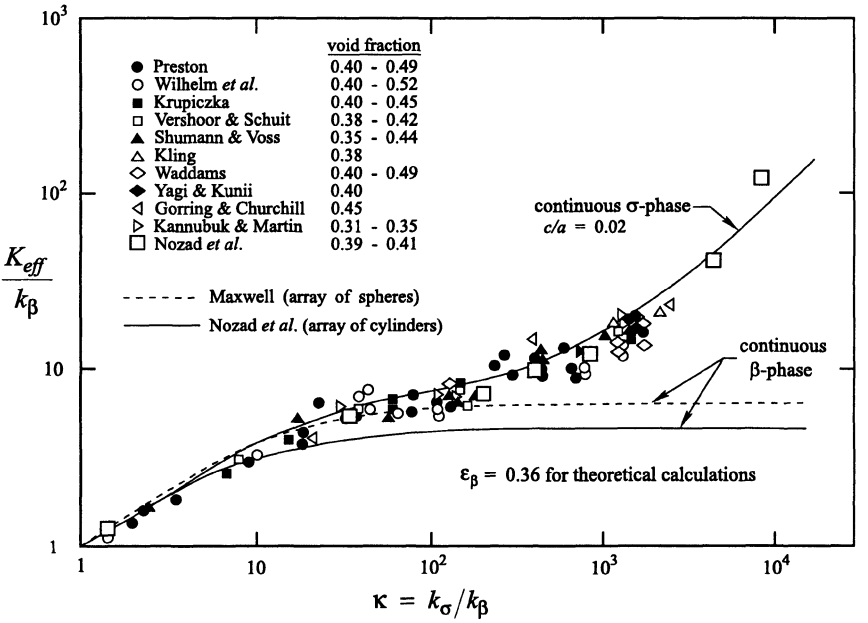


Figure 2.9. Theoretical and experimental values of the effective thermal conductivity

calculations that differ from the experiments. The two-dimensional model illustrated in Figure 2.8 is different from the three-dimensional character of the experimental systems, and the spatially periodic boundary conditions used in the closure problem given by Eqs. 2.4-57 are not consistent with the random nature of the non-consolidated systems represented in Figures 2.9 and 2.10. From the results presented in Figure 1.10 for the effective diffusivity, and from Eqs. 2.5-4 and 2.5-5, we know that there are differences between two and three-dimensional models; however, these differences are not great. The fact that the periodic boundary conditions do not play a particularly important role is confirmed (for diffusive processes) by the good agreement between results obtained using Chang's unit cell and those obtained using a spatially periodic model. To be clear about this point, we note that the solution of Eqs. 2.5-3 (*non-periodic boundary conditions*) for a two-dimensional array of cylinders leads to Rayleigh's (1892) theory given by Eq. 2.5-4, while the solution of Eqs. 2.4-57 (*periodic boundary conditions*) for a two-dimensional array of cylinders (Ochoa, 1989) leads to results that are essentially identical to Eq. 2.5-4. In a general study of periodic and non-periodic systems, Quintard and Whitaker (1993a) demonstrated that the difference between these two types of systems is not particularly important for diffusive processes, and we conclude that the existence of the adjustable parameter, c/a, does not invalidate the successful comparison of theory and experiment illustrated in Figure 2.10. However, it is certain that the *fitted value* of c/a is sensitive to the details of the numerical scheme used to solve the closure problem given by Eqs. 2.4-57. To emphasize this particular point, we note that Nozad *et al.* (1985a) obtained good agreement between theory and experiment

for $c/a = 0.02$, while Sahraoui and Kaviany (1993) concluded that the value of c/a should be 0.002.

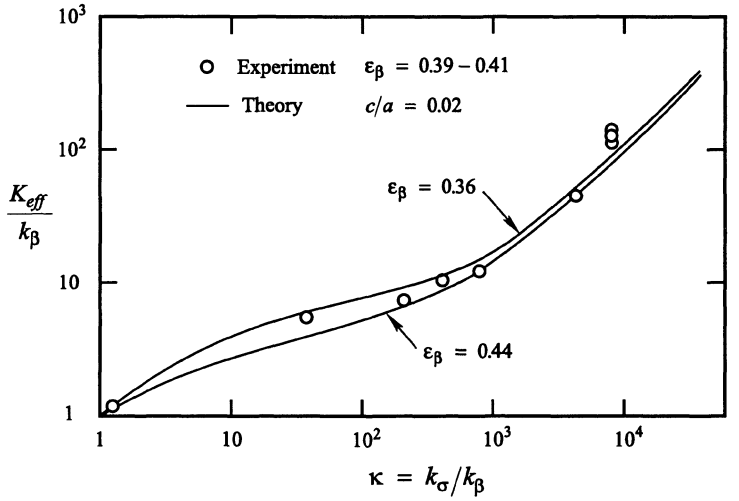


Figure 2.10. Effective thermal conductivities for a narrow range of porosity

An interesting example of the influence of particle-particle contact is the case of point-contact, i.e., $c/a \rightarrow 0$, that was studied by Batchelor and O'Brien (1977). They considered a regular array of spheres and developed a solution for large values of $\kappa = k_\sigma/k_\beta$ in terms of an inner expansion. The result took the form

$$\frac{K_{eff}}{k_\beta} = 4\ln(\kappa) - 11 \qquad (2.5\text{-}6)$$

in which the number eleven represents an adjustable parameter that can only be determined precisely by matching the inner expansion with an outer expansion. The value of the adjustable parameter was chosen on the basis of experimental data with values of κ ranging from 30 to 3000. The analysis of Batchelor and O'Brien is compared with that of Nozad *et al.* in Figure 2.11 where the *good contact* results represent an expansion in terms of κ^{-1}. This leads to a linear dependence of K_{eff}/k_β on κ instead of the logarithmic dependence for the *point contact* condition.

The theory of Batchelor and O'Brien (1977) has been compared with experiment by Shonnard and Whitaker (1989) and the results, along with those of Swift (1966), are shown in Figure 2.12. The experiment performed by Shonnard and Whitaker consisted of bringing two spheres into point contact in a unit cell, thus the experiment was designed explicitly to test the theory of Batchelor and O'Brien. Errors resulted from the fact that it was difficult to maintain a uniform temperature gradient and it was difficult to

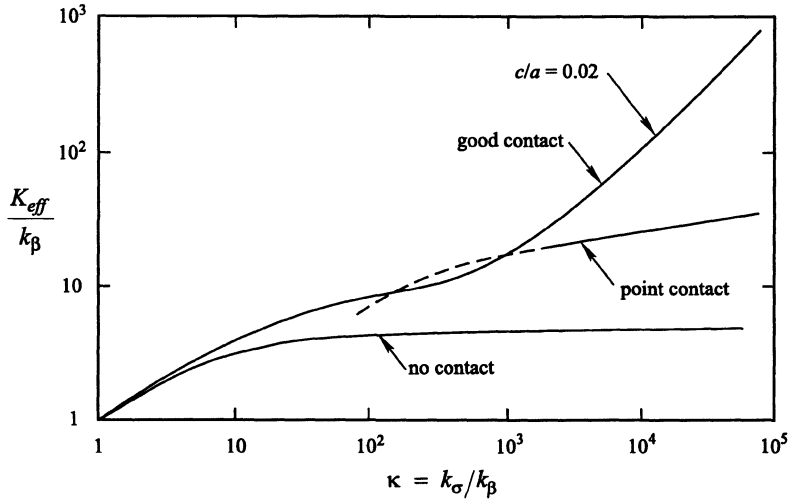


Figure 2.11. Effective thermal conductivity for good contact, point contact, and no contact

completely eliminate natural convection since the diameter of the spheres was on the order of 5 cm. Nevertheless, the experimental results of Shonnard and Whitaker tend to confirm the theory of Batchelor and O'Brien. The results of Swift were obtained with packed metal powders for which the particle diameter was on the order of hundreds of micrometers, thus *no specific effort was made to create a point-contact porous medium.*

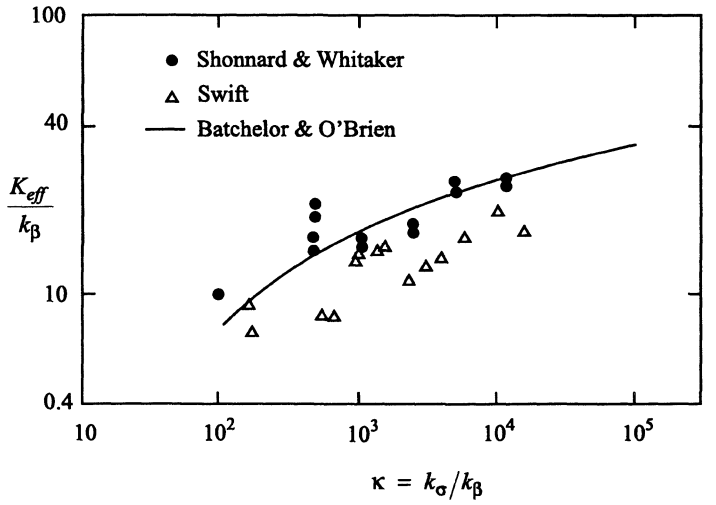


Figure 2.12. Comparison of theory and experiment for point-contact heat conduction

We would expect Swift's results to exhibit the type of behavior illustrated in Figure 2.9 rather than the *point contact* behavior shown in Figure 2.12, but it is clear that they do not.

2.6 Conclusions

In this chapter we have examined the process of transient heat conduction in two-phase systems. We have developed constraints associated with the principle of local thermal equilibrium, and these constraints are in reasonable agreement with numerical experiments. When the condition of local thermal equilibrium is valid, the heat transfer process can be represented in terms of a one-equation model. The closure problem associated with the one-equation model was developed and values of the effective thermal conductivity were compared with experimental values for non-consolidated porous media. Good agreement between theory and experiment was obtain provided that the particle-particle contact was taken into account in terms of an adjustable parameter.

2.7. Problems*

2-1. Show how the Darcy-scale temperature deviations defined by Eqs. 2.3-2 can be used to obtain the form indicated by Eqs. 2.3-5.

2-2. Indicate how the last term in Eq. 2.3-21 is obtained from Eq. 2.3-19, Eq. 2.3-20, and the interfacial flux boundary condition given by Eq. 2.1-3.

2-3. Show how the flux boundary condition given by Eqs. 2.4-40c can be used to develop the integral condition represented by Eq. 2.4-42.

2-4. Given the following steady, one-dimensional heat conduction problem

B.C.1
$$T_\beta = 0, \quad x = 0 \tag{1}$$

$$\frac{d^2 T_\beta}{dx^2} = \Phi_\beta, \quad \text{in the } \beta\text{-phase} \tag{2}$$

B.C.2
$$T_\beta = T_\sigma, \quad x = \ell_\beta \tag{3}$$

B.C.3
$$-k_\beta \frac{dT_\beta}{dx} = -k_\sigma \frac{dT_\sigma}{dx} + \Omega_{\beta\sigma}, \quad x = \ell_\beta \tag{4}$$

$$\frac{d^2 T_\sigma}{dx^2} = 0, \quad \text{in the } \sigma\text{-phase} \tag{5}$$

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* Solutions to all problems are available from the author.

B.C.4 $$T_\sigma = 0, \qquad x = \ell_\beta + \ell_\sigma \tag{6}$$

develop a solution in terms of the *closure variables* the appear in the representations

$$T_\beta = f_\beta(x)\Phi_\beta + g_\beta(x)\Omega_{\beta\sigma}, \qquad T_\sigma = f_\sigma(x)\Phi_\beta + g_\sigma(x)\Omega_{\beta\sigma} \tag{7}$$

Take Φ_β and $\Omega_{\beta\sigma}$ to be constants and show that the solution in terms of the closure variables gives the same result as the *direct solution* that is given by

$$T_\beta = \tfrac{1}{2}\Phi_\beta x^2 - \left[\tfrac{1}{2}\Phi_\beta \ell_\beta\left(\frac{2+\varphi}{1+\varphi}\right) + \frac{\Omega_{\beta\sigma}}{k_\beta(1+\varphi)}\right]x \tag{8}$$

$$T_\sigma = \left[\frac{\Phi_\beta \ell_\beta^2}{2\ell_\sigma}\left(\frac{1}{1+\varphi}\right) + \frac{\Omega_{\beta\sigma}}{k_\sigma}\left(\frac{\varphi}{1+\varphi}\right)\right]x - \left(\frac{\ell_\beta + \ell_\sigma}{1+\varphi}\right)\left[\frac{\Phi_\beta \ell_\beta^2}{2\ell_\sigma} + \frac{\varphi\Omega_{\beta\sigma}}{k_\sigma}\right] \tag{9}$$

in which the dimensionless parameter φ is defined by

$$\varphi = \ell_\beta k_\sigma / \ell_\sigma k_\beta \tag{10}$$

2-5. Develop the boundary value problem for ψ_β and ψ_σ which are defined by Eqs. 2.4-44, and identify the circumstances for which you can demonstrate that these two variables are equal to a constant. Follow the approach suggested in Problem 1-21.

2-6. Prove that $\mathbf{b}_\beta = \mathbf{b}_\sigma = constant$ when the thermal conductivity of the β-phase is equal to that of the σ-phase. Restrict you analysis to symmetric unit cells and note that the proof is similar to that used in Problem 2-5.

2-7. Given the boundary value problem

$$k_\beta \nabla^2 \mathbf{B}_\beta = \varepsilon_\beta^{-1}\mathbf{I} \tag{1}$$

B.C.1 $$\mathbf{B}_\beta = \mathbf{B}_\sigma, \qquad at\ A_{\beta\sigma} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{B}_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla \mathbf{B}_\sigma, \qquad at\ A_{\beta\sigma} \tag{3}$$

$$k_\sigma \nabla^2 \mathbf{B}_\sigma = -\varepsilon_\sigma^{-1}\mathbf{I} \tag{4}$$

Periodicity: $$\mathbf{B}_\beta(\mathbf{r}+\ell_i) = \mathbf{B}_\beta(\mathbf{r}), \quad \mathbf{B}_\sigma(\mathbf{r}+\ell_i) = \mathbf{B}_\sigma(\mathbf{r}), \quad i = 1,2,3 \tag{5}$$

Averages: $$\langle \mathbf{B}_\beta \rangle^\beta = 0 \tag{6}$$

prove that $\mathbf{B}_\beta$ and $\mathbf{B}_\sigma$ can be expressed as

$$\mathbf{B}_\beta = B_\beta \mathbf{I} \tag{7a}$$

$$\mathbf{B}_\sigma = B_\sigma \mathbf{I} \tag{7b}$$

and derive the boundary value problem for B_β and B_σ.

2-8. Consider the closure problem given by Eqs. 2.4-48, and show that it reduces to the closure problem given by Eqs. 2.4-57 for the case of *completely symmetric unit cells*. Consider only the x-components of the vectors $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ given by

$$b_\beta = \mathbf{i}\cdot\mathbf{b}_\beta, \qquad b_\sigma = \mathbf{i}\cdot\mathbf{b}_\sigma \tag{1}$$

and a unit cell that is symmetric in x. Develop the closure problem for b_β and b_σ and consider a coordinate transformation of the type

$$x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z} \tag{2}$$

in which $\bar{x} = -x$, $\bar{y} = y$, $\bar{z} = z$. The constants in Eqs. 2.4-48a and 2.4-48d are invariant to the coordinate transformation indicated by Eq. 2. Show that

$$b_\beta(x,y,z) = -b_\beta(-x,y,z), \qquad b_\sigma(x,y,z) = -b_\sigma(-x,y,z) \tag{3}$$

and that, by analogy, $\mathbf{b}_\beta$ and $\mathbf{b}_\sigma$ are completely skew-symmetric for a unit cell that is completely symmetric. Indicate why this leads to the result

$$\mathbf{c} = \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla \mathbf{b}_\beta dA = \frac{1}{\mathscr{V}}\int_{V_\beta} k_\beta \nabla^2 \mathbf{b}_\beta dV = 0 \tag{4}$$

$$\mathbf{c} = -\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma \nabla \mathbf{b}_\sigma dA = -\frac{1}{\mathscr{V}}\int_{V_\sigma} k_\sigma \nabla^2 \mathbf{b}_\sigma dV = 0 \tag{5}$$

thus proving that Eqs. 2.4-48 simplify to Eqs. 2.4-57 for completely symmetric unit cells.

2-9. Use Eqs. 2.4-48 in order to prove that the thermal conductivity tensor is symmetric, i.e., $\mathbf{K}_{eff} = \mathbf{K}_{eff}^{T}$. Notice that the dyadic product of $\mathbf{b}_\beta$ with the boundary condition given by Eq. 2.4-48c will lead to a boundary condition containing the term $(k_\beta - k_\sigma)\mathbf{n}_{\beta\sigma}\mathbf{b}_\beta$, and it is this term which appears in the expression for the thermal conductivity tensor given by Eq. 2.4-64.

2-10. Sahraoui and Kaviany (1993) determined the effective thermal conductivity for the system illustrated in Figure 2.5 by first solving the following boundary value problem associated with the unit cell illustrated in Figure 2-10.

$$0 = \frac{\partial^2 T_\beta}{\partial x^2} + \frac{\partial^2 T_\beta}{\partial y^2}, \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$T_\beta = T_o, \quad \text{at } x = 0 \tag{2}$$

B.C.2 $$T_\beta = T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

B.C.3 $$-\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{4}$$

B.C.4 $$T_\beta = T_l, \quad \text{at } x = L \tag{5}$$

B.C.5&6 $$\frac{\partial T_\beta}{\partial y} = 0 \quad y = 0, L \tag{6}$$

$$0 = \frac{\partial^2 T_\sigma}{\partial x^2} + \frac{\partial^2 T_\sigma}{\partial y^2}, \quad \text{in the } \sigma\text{-phase} \tag{7}$$

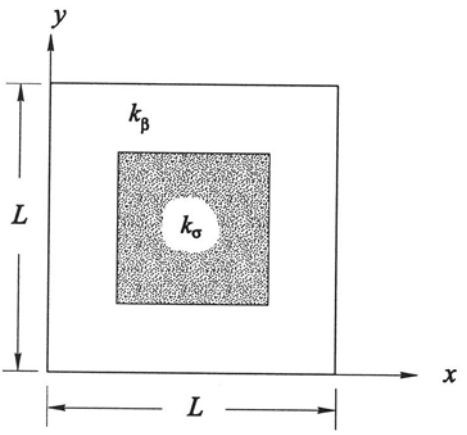

Figure 2-10. Unit cell used for the determination of the effective thermal conductivity

Given the temperature field in the β-phase, the average heat flux was computed according to

$$\langle q_x \rangle\big|_{x=0} = -\frac{1}{L} \int_{y=0}^{y=L} k_\beta \frac{\partial T_\beta}{\partial x} dy \tag{8}$$

and this was used to determine an effective thermal conductivity on the basis of

$$\langle q_x \rangle\big|_{x=0} = K_{eff} \frac{T_o - T_l}{L} \tag{9}$$

The boundary conditions given by Eqs. 2 and 5 are intuitive; however, they can be *proved* to be the correct representations for a spatially periodic system on the basis of the closure problem given by Eqs. 2.4-57. To do so, one begins with

$$T_\beta = \langle T \rangle + \tilde{T}_\beta = \langle T \rangle + \mathbf{b}_\beta \cdot \nabla \langle T \rangle \tag{10}$$

and then considers the special case in which

$$\nabla \langle T \rangle = \mathbf{i} \frac{\partial \langle T \rangle}{\partial x} \tag{11}$$

The fact that $\mathbf{i} \cdot \mathbf{b}_\beta$ is skew-symmetric for a symmetric unit cell can then be used to develop the boundary conditions given by Eqs. 2 and 5.

2-11. Consider a β-σ system in which the σ-phase is a rigid solid and the β-phase is a stagnant fluid. If a uniform, homogeneous thermal source exists in the σ-phase, the heat conduction process can be described by

$$(\rho c_p)_\beta \frac{\partial T_\beta}{\partial t} = \nabla \cdot (k_\beta \nabla T_\beta), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$T_\beta = T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla T_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla \cdot (k_\sigma \nabla T_\sigma) + \Phi_\sigma, \quad \text{in the } \sigma\text{-phase} \tag{4}$$

Consider Φ_σ to be a constant and develop the one-equation model for heat conduction. Carefully identify the constraints that must be satisfied and develop the closure problem that can be used to predict the effective thermal conductivity tensor.

2-12. Develop the constraints associated with the principle of local thermal equilibrium for the heat conduction process described in Problem 2-11.

2-13. When chemical reactions take place in porous catalysts, the heat conduction process can be described by

$$(\rho c_p)_\gamma \frac{\partial T_\gamma}{\partial t} = \nabla \cdot (k_\gamma \nabla T_\gamma), \quad \text{in the } \gamma - \text{phase} \tag{1}$$

B.C.1 $$T_\gamma = T_\kappa, \quad \text{at the } \gamma - \kappa \text{ interface} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\gamma\kappa} \cdot k_\gamma \nabla T_\gamma = -\mathbf{n}_{\gamma\kappa} \cdot k_\kappa \nabla T_\kappa + \Omega_{\gamma\kappa}, \quad \text{at the } \gamma - \kappa \text{ interface} \tag{3}$$

$$(\rho c_p)_\kappa \frac{\partial T_\kappa}{\partial t} = \nabla\cdot(k_\kappa \nabla T_\kappa), \quad \text{in the } \kappa-\text{phase} \tag{4}$$

Here $\Omega_{\gamma\kappa}$ represents the source or sink of thermal energy at the γ-κ interface owing to heterogeneous chemical reactions. Under realistic conditions $\Omega_{\gamma\kappa}$ depends on the temperature and the concentration of the reactants; however, in this problem $\Omega_{\gamma\kappa}$ should be treated as a constant in order to develop a one-equation model for the transient heat conduction process. In addition, the porous medium should be treated as homogeneous. Assume that local thermal equilibrium is valid and develop the closure problem that is required to predict the effective thermal conductivity tensor.

2-14. Develop the constraints associated with the principle of local thermal equilibrium for the heat conduction process described in Problem 2-13. The interfacial flux terms must be treated carefully, and in the absence of a complete study of the two-equation model one is forced to estimate how the thermal source is distributed between the two fluxes. Use the estimate given by Whitaker (1986c)

$$-\frac{1}{\mathscr{V}}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}\cdot k_\gamma \nabla T_\gamma \, dA = a_v h\left(\langle T_\gamma\rangle^\gamma - \langle T_\kappa\rangle^\kappa\right) + \frac{a_v \Omega_{\gamma\kappa}}{1+\mathbf{O}\left(\ell_\gamma k_\kappa/\ell_\kappa k_\gamma\right)}$$

in order to complete the analysis.

2-15. In an experimental study of transient heat conduction in a two-phase system, Glatzmaier and Ramirez (1988) described the process in terms of the following point equations

$$(\rho c_p)_\beta \frac{\partial T_\beta}{\partial t} = \nabla\cdot(k_\beta \nabla T_\beta), \quad \text{in the } \beta-\text{phase} \tag{1}$$

B.C.1
$$T_\beta = T_\sigma, \quad \text{at the } \beta-\sigma \text{ interface} \tag{2}$$

B.C.2
$$-\mathbf{n}_{\beta\sigma}\cdot k_\beta \nabla T_\beta = -\mathbf{n}_{\beta\sigma}\cdot k_\sigma \nabla T_\sigma, \quad \text{at the } \beta-\sigma \text{ interface} \tag{3}$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla\cdot(k_\sigma \nabla T_\sigma), \text{in the } \sigma-\text{phase} \tag{4}$$

The volume averaged forms of both Eqs. 1 and 4 are identical in form and are given by Eqs. 2.2-11 and 2.2-14. Glatzmaier and Ramirez assumed that the conductive fluxes in these equations could be expressed as

$$k_\beta\left(\varepsilon_\beta\nabla\langle T_\beta\rangle^\beta+\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\,dA\right) = \mathbf{K}_\beta\cdot\nabla\langle T_\beta\rangle^\beta \tag{5a}$$

$$k_\sigma\left(\varepsilon_\sigma\nabla\langle T_\sigma\rangle^\sigma+\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{T}_\sigma\,dA\right) = \mathbf{K}_\sigma\cdot\nabla\langle T_\sigma\rangle^\sigma \tag{5b}$$

and they assumed that the interfacial flux took the form

$$-\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\,dA = a_v h\left(\langle T_\beta\rangle^\beta-\langle T_\sigma\rangle^\sigma\right) \tag{6}$$

A more thorough approach would make use of the decompositions given by Eqs. 2.2-8 to arrive at

$$-\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla T_\beta\,dA = -\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\langle T_\beta\rangle^\beta\,dA-\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta\,dA \tag{7a}$$

$$-\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla T_\sigma\,dA = -\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\langle T_\sigma\rangle^\sigma\,dA-\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA \tag{7b}$$

The closure problem can then be used to predict the correct functional forms for the conductive flux and the interfacial flux in the volume averaged transport equations. In the analysis of the closure problem, assume that variations of $\nabla\langle T_\beta\rangle^\beta$, $\nabla\langle T_\sigma\rangle^\sigma$, and $\langle T_\beta\rangle^\beta-\langle T_\sigma\rangle^\sigma$ can be neglected so that the functional dependence of $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ can be easily deduced and used to prove that the correct form of the two-equation model is given by Eqs. 2.2-25 and 2.2-26.

2-16. The problem of diffusion in two-phase systems can be described by (Ochoa *et al.*, 1986)

$$\frac{\partial c_\beta}{\partial t} = \nabla\cdot\left(\mathscr{D}_\beta\nabla c_\beta\right), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$c_\beta = K_{eq}\,c_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_\beta = -\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\sigma\nabla c_\sigma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

$$\frac{\partial c_\sigma}{\partial t} = \nabla\cdot\left(\mathscr{D}_\sigma\nabla c_\sigma\right), \quad \text{in the } \sigma\text{-phase} \tag{4}$$

Here c_β and c_σ represent the concentrations of the diffusing species in the β and σ-phases respectively, and K_{eq} represents the equilibrium coefficient for a linear equilibrium relation. In this problem you are asked to:

1. Identify an average concentration that can be used to construct a one-equation model of the diffusion process. Be sure to define this concentration so that all spatial deviation concentrations are zero when the system is at equilibrium. State the *assumptions* associated with the principle of local mass equilibrium, then state the *restrictions*, but do not attempt to develop the *constraints*.

2. Develop the closure problem for the one-equation model, and show how it can be transformed to the same closure problem used to determine the effective thermal conductivity tensor.

2-17. The problem of diffusion in a packed bed of porous particles can be described by (Whitaker, 1988c)

$$\frac{\partial c_\beta}{\partial t} = \nabla\cdot(\mathscr{D}_\beta \nabla c_\beta), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$c_\beta = \langle c_A\rangle^\gamma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_\beta = -\mathbf{n}_{\beta\sigma}\cdot\varepsilon_\gamma\mathbf{D}_{eff}\cdot\langle c_A\rangle^\gamma, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

$$\varepsilon_\gamma\frac{\partial\langle c_A\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma\mathbf{D}_{eff}\cdot\nabla\langle c_A\rangle^\gamma\right), \quad \text{in the porous particle} \tag{4}$$

The system under consideration is illustrated in Figure 2-17 where the porous particles are identified as the σ-region. The void space in the packed bed is identified as the β-phase, and the point concentration of species A in this phase is be represented by c_β. The boundary conditions given by Eqs. 2 and 3 can be inferred from the studies of Ochoa-Tapia and Whitaker (1998a). In this problem you are asked to develop the one-equation model for diffusion in the system shown in Figure 2-17, along with the closure problem that will allow you to predict the overall effective diffusivity tensor.

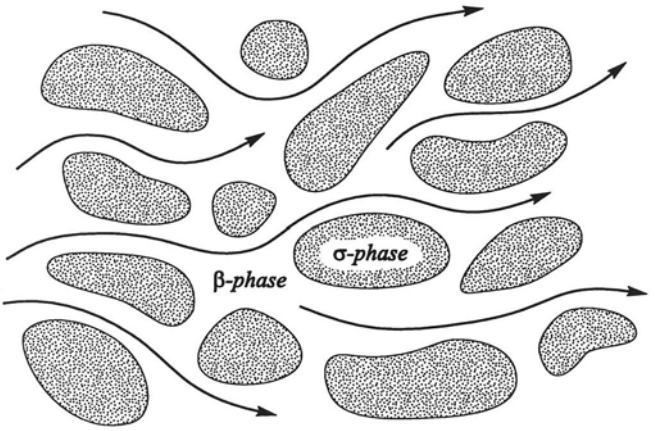

Figure 2-17. Packed bed of porous particles

2-18. If the system described in Problem 2-16 contains a membrane between the β and σ-phases, and if a linear, homogeneous reaction takes place in the σ-phase, the boundary value problem takes the form (Wood and Whitaker, 1998)

$$\frac{\partial c_\beta}{\partial t} = \nabla\cdot(\mathscr{D}_\beta\nabla c_\beta)\,, \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_\beta = k\left(c_\beta - K_{eq}c_\sigma\right), \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_\beta = -\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\sigma\nabla c_\sigma\,, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3}$$

$$\frac{\partial c_\sigma}{\partial t} = \nabla\cdot(\mathscr{D}_\sigma\nabla c_\sigma) - \mu c_\sigma\,, \quad \text{in the } \sigma\text{-phase} \tag{4}$$

If the membrane permeability k is *sufficiently large* and the reaction rate coefficient μ is *sufficiently small*, the principle of *local mass equilibrium* will be valid and a one-equation, equilibrium model can be developed. `Assume that the condition of local mass equilibrium is valid and develop the one-equation, equilibrium model.

2-19. For the process described in Problem 2-18, small values of k and large values of μ typically lead to the necessity for a *two-equation model*; however, if the reaction rate coefficient is *large enough* so that

$$K_{eq}c_\sigma \ll c_\beta\,, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{1}$$

a *pseudo* one-equation model results. In this case the boundary conditions given by Eqs. 2 and 3 of Problem 2-18 can be replaced with

$$\text{B.C.} \qquad -\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_{\beta}\nabla c_{\beta} = k\,c_{\beta}\,, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

and a volume averaged transport equation for the β-phase can be derived that is equivalent to the result presented for the γ-phase in Chapter 1. We refer to this as the pseudo one-equation model since the system is described in terms of two concentrations. The concentration in the β-phase is determined by a transport equation for $\langle c_{\beta}\rangle^{\beta}$ while the concentration in the σ-phase is specified by

$$\langle c_{\sigma}\rangle^{\sigma} = 0\,, \quad \text{pseudo one-equation model} \tag{3}$$

In this problem you are asked to find the constraint that leads to Eq. 1 and then make use of the developments in Chapter 1 to determine the form of the effective diffusivity tensor and the effective reaction rate coefficient for the pseudo one-equation model.

2-20. Develop the constraints associated with the principle of local mass equilibrium as it applies to Problem 2-18.

Chapter 3

Dispersion in Porous Media

In this chapter we will study the simplest possible convective transport process; that of passive convection and diffusion in a rigid, impermeable porous medium. The word passive is used to mean that there is no adsorption or reaction at the fluid-solid interface, nor is there any mass transfer from the fluid phase to the solid phase since the latter is impermeable. Very few real processes are passive in the sense used here; however, it is best to begin our studies of convective transport with as few complications as possible.

3.1 Governing Equations and Boundary Conditions

We consider a fluid-solid system such as the one illustrated in Figure 3.1. The fluid phase is identified as the β-phase while the rigid and impermeable solid is represented by the σ-phase. The governing equation, the initial condition, and the boundary conditions are given by

$$\frac{\partial c_{A\beta}}{\partial t} + \nabla\cdot(c_{A\beta}\mathbf{v}_\beta) = \nabla\cdot\left(\mathscr{D}_\beta\nabla c_{A\beta}\right), \quad \text{in the } \beta\text{-phase} \tag{3.1-1}$$

B.C.1
$$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_{A\beta} = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{3.1-2}$$

B.C.2
$$c_{A\beta} = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{3.1-3}$$

I.C.
$$c_{A\beta} = \mathscr{G}(\mathbf{r}), \quad \text{at } t = 0 \tag{3.1-4}$$

Here we have used $\mathscr{A}_{\beta\sigma}$ to represent the area of the β-σ interface contained within the macroscopic region shown in Figure 3.2, while $\mathscr{A}_{\beta e}$ identifies the area of entrances and exits associated with the macroscopic region. It is important to keep in mind that Eq. 3.1-1 is limited to dilute solutions for which $c_{A\beta} << c_\beta$, and that $\mathscr{D}_\beta$ is a mixture diffusivity defined by Eq. 1.1-15.

The problem described by Eqs. 3.1-1 through 3.1-4 differs from that of pure diffusion in porous media only because of the presence of the convective transport term, thus our analysis will be very similar to that given in Chapter 1. In our treatment of the convective-diffusion equation given by Eq. 3.1-1, we will consider only incompressible flow so that the continuity equation takes the form

$$\nabla\cdot\mathbf{v}_\beta = 0 \tag{3.1-5}$$

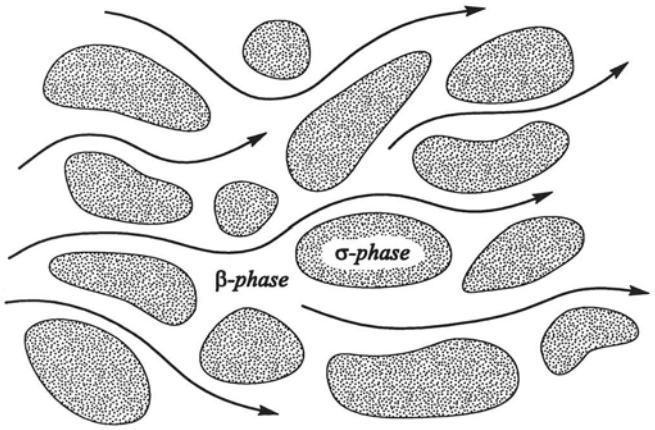

Figure 3.1. Convective transport in a fluid-solid system

Often the fluid mechanical problem associated with dispersion in porous media can be described by Stokes' equations which lead to Darcy's law for the volume averaged velocity. The derivation of Darcy's law is presented in Chapter 4 and the development of the more general Forchheimer equation is given elsewhere (Whitaker, 1996).

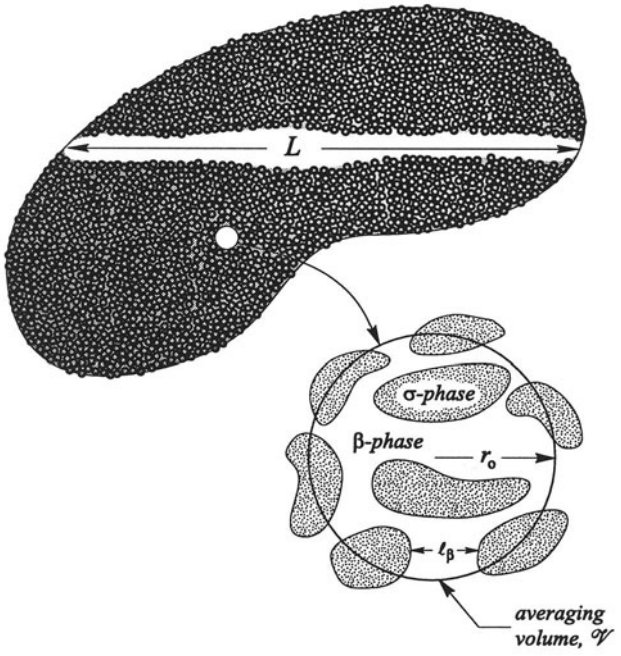

Figure 3.2. Macroscopic region

3.2 Spatial Smoothing

We begin the process of spatial smoothing by forming the superficial average of Eq. 3.1-1 to obtain

$$\frac{1}{\mathscr{V}}\int_{V_\beta}\frac{\partial c_{A\beta}}{\partial t}dV + \frac{1}{\mathscr{V}}\int_{V_\beta}\nabla\cdot(\mathbf{v}_\beta c_{A\beta})dV = \frac{1}{\mathscr{V}}\int_{V_\beta}\nabla\cdot\left(\mathscr{D}_\beta\nabla c_{A\beta}\right)dV \tag{3.2-1}$$

In terms of the nomenclature used in the previous two chapters, we express this result as

$$\left\langle\frac{\partial c_{A\beta}}{\partial t}\right\rangle + \langle\nabla\cdot(\mathbf{v}_\beta c_{A\beta})\rangle = \langle\nabla\cdot(\mathscr{D}_\beta\nabla c_{A\beta})\rangle \tag{3.2-2}$$

and we note that the σ-phase is rigid so that the accumulation term can be expressed as

$$\left\langle\frac{\partial c_{A\beta}}{\partial t}\right\rangle = \frac{\partial\langle c_{A\beta}\rangle}{\partial t} \tag{3.2-3}$$

As in our previous studies of diffusion and heat conduction, we seek an equation for the intrinsic average concentration, thus we make use of

$$\langle c_{A\beta}\rangle = \varepsilon_\beta\langle c_{A\beta}\rangle^\beta \tag{3.2-4}$$

so that Eq. 3.2-2 takes the form

$$\varepsilon_\beta\frac{\partial\langle c_{A\beta}\rangle^\beta}{\partial t} + \langle\nabla\cdot(\mathbf{v}_\beta c_{A\beta})\rangle = \langle\nabla\cdot(\mathscr{D}_\beta\nabla c_{A\beta})\rangle \tag{3.2-5}$$

Once again we have used the fact that the σ-phase is rigid so that ε_β is independent of time. Turning our attention to the convective transport term, we employ the averaging theorem to obtain

$$\langle\nabla\cdot(\mathbf{v}_\beta c_{A\beta})\rangle = \nabla\cdot\langle\mathbf{v}_\beta c_{A\beta}\rangle + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta c_{A\beta}\,dA \tag{3.2-6}$$

Since the σ-phase is treated as a rigid, impermeable solid, we impose the condition

$$\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{3.2-7}$$

so that Eq. 3.2-6 simplifies to

$$\langle\nabla\cdot(\mathbf{v}_\beta c_{A\beta})\rangle = \nabla\cdot\langle\mathbf{v}_\beta c_{A\beta}\rangle \tag{3.2-8}$$

Use of this result in Eq. 3.2-5 provides us with

$$\varepsilon_\beta\frac{\partial\langle c_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot\langle\mathbf{v}_\beta c_{A\beta}\rangle = \langle\nabla\cdot(\mathscr{D}_\beta\nabla c_{A\beta})\rangle \tag{3.2-9}$$

and we need only follow the type of development given in Sec. 1.2 to arrive at the form

$$\varepsilon_\beta \frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t} + \nabla \cdot \langle \mathbf{v}_\beta c_{A\beta} \rangle = \nabla \cdot \left[\mathscr{D}_\beta \left(\varepsilon_\beta \nabla \langle c_{A\beta} \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA \right) \right] + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_{A\beta} \, dA \tag{3.2-10}$$

Here we should remember that this result requires that we impose the following length scale constraints:

$$\ell_\beta \ll r_0 , \qquad r_0^2 \ll L_\varepsilon L_{C1} \tag{3.2-11}$$

In our study of diffusion and reaction in Chapter 1, the interfacial flux term was used to *join* the governing equation and the boundary condition that described the heterogeneous chemical reaction. In our study of heat conduction in Chapter 2, the interfacial flux term *joined* the β-phase transport equation to the σ-phase transport equation. In many problems of great practical importance, diffusion, adsorption, and reaction will be taking place within the σ-phase illustrated in Figure 3.1, and for those processes the interfacial flux term in Eq. 3.2-10 will *join* the β-phase transport process to the process taking place in the σ-phase. In this study we treat only the case of passive dispersion, thus we impose the boundary condition given by Eq. 3.1-2 and express Eq. 3.2-10 as

$$\varepsilon_\beta \frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t} + \nabla \cdot \langle \mathbf{v}_\beta c_{A\beta} \rangle = \nabla \cdot \left[\mathscr{D}_\beta \left(\varepsilon_\beta \nabla \langle c_{A\beta} \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA \right) \right] \tag{3.2-12}$$

Our analysis of the right hand side of this result will follow that given in Chapter 1, and the only new problem with which we are confronted is the convective transport term, $\langle \mathbf{v}_\beta c_{A\beta} \rangle$.

3.2.1 CONVECTIVE TRANSPORT

We begin our analysis with the spatial decompositions

$$c_{A\beta} = \langle c_{A\beta} \rangle^\beta + \tilde{c}_{A\beta} , \qquad \mathbf{v}_\beta = \langle \mathbf{v}_\beta \rangle^\beta + \tilde{\mathbf{v}}_\beta \tag{3.2-13}$$

so that the volume averaged convective transport is described as

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \left\langle \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta + \tilde{\mathbf{v}}_\beta \langle c_{A\beta} \rangle^\beta + \langle \mathbf{v}_\beta \rangle^\beta \tilde{c}_{A\beta} + \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \right\rangle \tag{3.2-14}$$

At this point we put forth the *hypothesis* that variations of volume averaged quantities can be ignored within the averaging volume, and this allows us to express Eq. 3.2-14 as

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta + \langle \tilde{\mathbf{v}}_\beta \rangle \langle c_{A\beta} \rangle^\beta + \langle \mathbf{v}_\beta \rangle^\beta \langle \tilde{c}_{A\beta} \rangle + \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle \tag{3.2-15}$$

The removal of averaged quantities from volume integrals is certainly consistent with much of the analysis in Chapters 1 and 2, and if we make use of this simplification with Eqs. 3.2-13 we obtain

$$\langle \tilde{\mathbf{v}}_\beta \rangle = 0, \qquad \langle \tilde{c}_{A\beta} \rangle = 0 \tag{3.2-16}$$

Under these circumstances our volume averaged convective transport simplifies to

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta + \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle \tag{3.2-17}$$

Substitution of this result into Eq. 3.2-12 provides the following form of our volume averaged convective-diffusion equation

$$\underbrace{\varepsilon_\beta \frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot \left(\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta \right)}_{\text{convective transport}} =$$

$$= \underbrace{\nabla \cdot \left[\mathscr{D}_\beta \left(\varepsilon_\beta \nabla \langle c_{A\beta} \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA \right) \right]}_{\text{diffusive transport}} - \underbrace{\nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\text{dispersive transport}} \tag{3.2-18}$$

At this point we need only develop the closure problem for $\tilde{c}_{A\beta}$ in order to obtain a closed form; however, before moving on to the closure problem in Sec. 3.3 we need to think about the filter that appears in Eq. 3.2-18 and we need to consider the approximation associated with Eqs. 3.2-16 and 3.2-17.

3.2.2 THE FILTER

The filter that appears in Eq. 3.2-18 can be expressed as

$$\left\{ \begin{matrix} \textit{spatial} \\ \textit{deviation} \\ \textit{filter} \end{matrix} \right\} = \frac{\mathscr{D}_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA - \frac{1}{\mathscr{V}} \int_{V_\beta} \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \, dV \tag{3.2-19}$$

and here we see what could be referred to as a *diffusive filter*, involving the interaction between $\mathbf{n}_{\beta\sigma}$ and $\tilde{c}_{A\beta}$, and a *convective filter*, involving the interaction between $\tilde{\mathbf{v}}_\beta$ and $\tilde{c}_{A\beta}$. In Chapter 1 we saw that very little geometrical information passed through the *diffusive filter* for isotropic systems, while in Chapter 2 we saw that the details of the

particle-particle contact passed through the *conductive filter* when k_σ / k_β was large compared to one. In our discussion of experimental results in Sec. 3.4, we will see that much more geometrical information will pass through the convective filter in Eq. 3.2-19 and this will make the prediction of dispersion coefficients much more difficult than the prediction of effective diffusivities.

3.2.3 SIMPLIFICATION OF THE CONVECTIVE TRANSPORT

Before continuing our analysis of Eq. 3.2-18, we need to explore the restrictions that are associated with the simplified representation of the convective transport given by Eq. 3.2-17. We begin with Eq. 3.2-14

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \left\langle \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta + \tilde{\mathbf{v}}_\beta \langle c_{A\beta} \rangle^\beta + \langle \mathbf{v}_\beta \rangle^\beta \tilde{c}_{A\beta} + \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \right\rangle \tag{3.2-20}$$

and note that the *average of the average* can be expressed precisely according to

$$\left\langle \langle c_{A\beta} \rangle^\beta \right\rangle \Big|_{\mathbf{x}} = \frac{1}{\mathscr{V}} \int_{V_\beta(\mathbf{x})} \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} dV \tag{3.2-21}$$

Here $\mathbf{y}_\beta$ represents the position vector relative to the centroid as illustrated in Figure 3.3. Taylor series expansions about the centroid of the averaging volume can be used to express the average concentration and velocity as

$$\langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} = \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}} + \mathbf{y}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}} + \tfrac{1}{2} \mathbf{y}_\beta \mathbf{y}_\beta : \nabla\nabla \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}} + \ldots \tag{3.2-22a}$$

$$\langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} = \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \mathbf{y}_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \tfrac{1}{2} \mathbf{y}_\beta \mathbf{y}_\beta : \nabla\nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \ldots \tag{3.2-22b}$$

These results can be used to express the superficial averages of the spatial deviations according to

$$\langle \tilde{c}_{A\beta} \rangle \Big|_{\mathbf{x}} = - \langle \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}} - \tfrac{1}{2} \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle : \nabla\nabla \langle c_{A\beta} \rangle^\beta \Big|_{\mathbf{x}} - \ldots \tag{3.2-23a}$$

$$\langle \tilde{\mathbf{v}}_\beta \rangle \Big|_{\mathbf{x}} = - \langle \mathbf{y}_\beta \rangle \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} - \tfrac{1}{2} \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle : \nabla\nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} - \ldots \tag{3.2-23b}$$

Substitution of Eqs. 3.2-22 and 3.2-23 into Eq. 3.2-20 leads to the following expression for the local volume averaged convective transport (see Problem 3-1):

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \underbrace{\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta}_{\substack{\text{traditional} \\ \text{convective} \\ \text{flux}}} + \underbrace{\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\substack{\text{traditional} \\ \text{dispersive} \\ \text{flux}}}$$

$$+ \underbrace{\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta + \langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{additional macroscopic dispersion}} + \underbrace{\tfrac{1}{2} \langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \mathbf{y}_\beta \rangle : \nabla\nabla \langle c_{A\beta} \rangle^\beta}_{\text{skewness}}$$

$$+ \underbrace{\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \tilde{c}_{A\beta} \rangle + \tfrac{1}{2} \langle \mathbf{y}_\beta \mathbf{y}_\beta \tilde{c}_{A\beta} \rangle : \nabla\nabla \langle \mathbf{v}_\beta \rangle^\beta}_{\text{additional microscopic dispersion}} + \ldots.$$

(3.2-24)

Here we have used the phrase *additional macroscopic dispersion* to describe the terms that are directly proportional to $\nabla \langle c_{A\beta} \rangle^\beta$. The *skewness* term is identified as such because it will cause a pulse to become asymmetric, and the terms involving $\tilde{c}_{A\beta}$ are referred to as *additional microscopic dispersion* since they will generate terms proportional to $\nabla \langle c_{A\beta} \rangle^\beta$ indirectly through the closure problem.

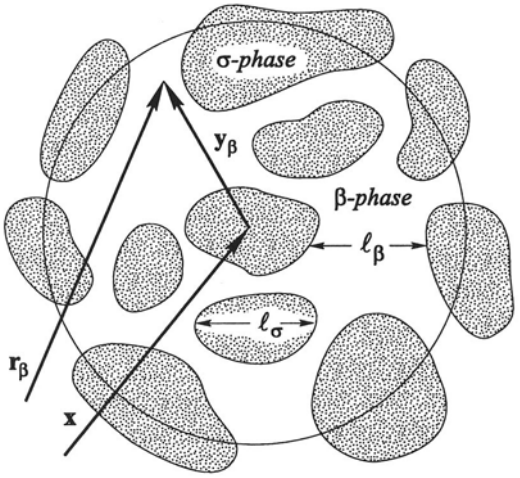

Figure 3.3. Position vectors associated with the averaging volume

While the skewness term in Eq. 3.2-24 needs to be kept in mind, it will not be part of our comparison between theory and experiment, thus for our purposes the convective transport given by Eq. 3.2-24 can be simplified to

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \underbrace{\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta}_{\substack{\text{traditional} \\ \text{convective} \\ \text{flux}}} + \underbrace{\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\substack{\text{traditional} \\ \text{dispersive} \\ \text{flux}}}$$

$$+ \underbrace{\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta + \langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{additional macroscopic dispersion}} \tag{3.2-25}$$

$$+ \underbrace{\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \tilde{c}_{A\beta} \rangle + \tfrac{1}{2} \langle \mathbf{y}_\beta \mathbf{y}_\beta \tilde{c}_{A\beta} \rangle : \nabla\nabla \langle \mathbf{v}_\beta \rangle^\beta}_{\text{additional microscopic dispersion}} + \ldots.$$

There is certainly some intuitive appeal for neglecting the last two terms relative to the traditional dispersive flux on the basis of length-scale arguments. This would lead to

$$\langle \mathbf{v}_\beta c_{A\beta} \rangle = \underbrace{\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta}_{\substack{\text{traditional} \\ \text{convective} \\ \text{flux}}} + \underbrace{\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\substack{\text{traditional} \\ \text{dispersive} \\ \text{flux}}}$$

$$+ \underbrace{\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta + \langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{additional macroscopic dispersion}} \tag{3.2-26}$$

however, it is more difficult to justify the neglect of the *additional macroscopic dispersion* relative to the traditional contribution given by $\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle$. The first contribution to the additional macroscopic dispersion might be important if there are *significant local heterogeneities* (Volkov *et al,* 1986) that produce large values of $\nabla \langle \mathbf{v}_\beta \rangle^\beta$. Estimates of this term can be obtained from measured porosity variations, while a reasonable estimate of the magnitude of $\langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle$ is given in Problem 1-17. The second contribution involves $\langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle$, and it is difficult to estimate this type of term. For uniform flow in a spatially periodic porous medium, one can demonstrate that $\langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle$ is zero, but in a real porous medium this term might make a contribution to the dispersive flux. If we wish to neglect these two terms in order to obtain the traditional form given by Eq. 3.2-17, we must impose the following two restrictions (see Problem 3-2)

$$\left(\nabla \langle \mathbf{v}_\beta \rangle^\beta\right)^T \cdot \langle \mathbf{y}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta \ll \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle^\beta \tag{3.2-27a}$$

$$\langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle \cdot \nabla \langle c_{A\beta} \rangle^\beta \ll \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle^\beta \tag{3.2-27b}$$

In order to develop useful constraints on the basis of these inequalities, we need an estimate of $\tilde{c}_{A\beta}$ and this will be available to us when we develop the closure problem in the next section.

3.2.4 CONTINUITY EQUATION

The development of the closure problem requires the *intrinsic average* form of the volume averaged transport equation given by Eq. 3.2-18, and we need to make use of the volume averaged continuity equation in order to develop this form. We recall Eq. 3.1-5

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{3.2-28}$$

and form the superficial average to obtain

$$\langle \nabla \cdot \mathbf{v}_\beta \rangle = 0 \tag{3.2-29}$$

Use of the averaging theorem immediately leads us to

$$\langle \nabla \cdot \mathbf{v}_\beta \rangle = \nabla \cdot \langle \mathbf{v}_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{v}_\beta \, dA \tag{3.2-30}$$

and since the β-σ interface is impermeable we see that the volume averaged continuity equation takes the form

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle = 0 \tag{3.2-31}$$

If we express the superficial average velocity in terms of the intrinsic average velocity, Eq. 3.2-31 becomes

$$\nabla \cdot \left(\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \right) = 0 \tag{3.2-32}$$

There is a preference for working with the superficial average velocity since it is solenoidal as indicated by Eq. 3.2-31; however, the form given by Eq. 3.2-32 can be applied directly to Eq. 3.2-18. For compressible flow, the continuity equation takes on a more complex form (see Problem 3-3)

3.3 Closure for Passive Dispersion

To develop the governing differential equation for $\tilde{c}_{A\beta}$, we recall the original boundary value problem and make use of the continuity equation given by Eq. 3.2-28 to obtain

$$\frac{\partial c_{A\beta}}{\partial t} + \mathbf{v}_\beta \cdot \nabla c_{A\beta} = \nabla \cdot \left(\mathscr{D}_\beta \nabla c_{A\beta} \right), \quad \text{in the } \beta\text{-phase} \tag{3.3-1}$$

B.C.1
$$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_{A\beta} = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{3.3-2}$$

B.C.2
$$c_{A\beta} = \mathscr{F}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{3.3-3}$$

I.C.
$$c_{A\beta} = \mathscr{G}(\mathbf{r}), \quad \text{at } t = 0 \tag{3.3-4}$$

This represents the starting point for our development of the volume averaged transport equation given by Eq. 3.2-18. Use of the volume averaged continuity equation represented by Eq. 3.2-32 allows us to express Eq. 3.2-18 as

$$\underbrace{\varepsilon_\beta \frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial t}}_{\text{accumulation}} + \underbrace{\varepsilon_\beta \langle \mathbf{v}_\beta\rangle^\beta \cdot \nabla \langle c_{A\beta}\rangle^\beta}_{\text{convective transport}} \tag{3.3-5}$$

$$= \underbrace{\nabla \cdot \left[\mathscr{D}_\beta \left(\varepsilon_\beta \nabla \langle c_{A\beta}\rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta}\, dA \right) \right]}_{\text{diffusive transport}} - \underbrace{\nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta}\rangle}_{\text{dispersive transport}}$$

and the *intrinsic form* of this result is obtained by dividing by ε_β. This can be expressed as

$$\frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta\rangle^\beta \cdot \nabla \langle c_{A\beta}\rangle^\beta = \nabla \cdot \left(\mathscr{D}_\beta \nabla \langle c_{A\beta}\rangle^\beta \right) \tag{3.3-6}$$

$$+ \varepsilon_\beta^{-1} \nabla \cdot \left[\frac{\mathscr{D}_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta}\, dA \right] + \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \left(\mathscr{D}_\beta \nabla \langle c_{A\beta}\rangle^\beta \right) - \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta}\rangle$$

From the decompositions presented in Sec. 3.2

$$c_{A\beta} = \langle c_{A\beta}\rangle^\beta + \tilde{c}_{A\beta}, \qquad \mathbf{v}_\beta = \langle \mathbf{v}_\beta\rangle^\beta + \tilde{\mathbf{v}}_\beta \tag{3.3-7}$$

we see that subtracting Eq. 3.3-5 from Eq. 3.3-1 yields the governing equation for $\tilde{c}_{A\beta}$ given by

$$\frac{\partial \tilde{c}_{A\beta}}{\partial t} + \mathbf{v}_\beta \cdot \nabla c_{A\beta} - \langle \mathbf{v}_\beta\rangle^\beta \cdot \nabla \langle c_{A\beta}\rangle^\beta = \underbrace{\nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta} \right)}_{\text{diffusion}} \tag{3.3-8}$$

$$- \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \left[\frac{\mathscr{D}_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta}\, dA \right]}_{\text{non-local diffusion}} - \underbrace{\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \mathscr{D}_\beta \nabla \langle c_{A\beta}\rangle^\beta}_{\text{diffusive source}} + \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta}\rangle}_{\text{non-local convection}}$$

Here two terms have been identified as *non-local* since they involve values of the dependent variable evaluated at points throughout the averaging volume rather than at the centroid. The second and third terms in Eq. 3.3-8 can be rearranged according to

$$\mathbf{v}_\beta \cdot \nabla c_{A\beta} - \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta = \mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta \tag{3.3-9}$$

and when this is used in Eq. 3.3-8 we obtain

$$\underbrace{\frac{\partial \tilde{c}_{A\beta}}{\partial t}}_{\text{accumulation}} + \underbrace{\mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta}}_{\text{convection}} + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{convective source}} = \underbrace{\nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta} \right)}_{\text{diffusion}}$$

$$- \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \left[\frac{\mathscr{D}_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA \right]}_{\text{non-local diffusion}} - \underbrace{\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \mathscr{D}_\beta \nabla \langle c_{A\beta} \rangle^\beta}_{\text{diffusive source}} + \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\text{non-local convection}} \tag{3.3-10}$$

The non-local diffusion term can be discarded on the basis of

$$\varepsilon_\beta^{-1} \nabla \cdot \left[\frac{\mathscr{D}_\beta}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} \, dA \right] << \nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta} \right) \tag{3.3-11}$$

and the arguments associated with this simplification are given in Sec. 1.4. We can also follow the development in Sec. 1.4 to discard the diffusive source in Eq. 3.3-10 on the basis of the length-scale constraint given by (see Problem 3-4)

$$\ell_\beta << L_\varepsilon \tag{3.3-12}$$

This constraint is automatically satisfied in homogeneous porous media for which L_ε is infinite, and if we impose Eqs. 3.3-11 and 3.3-12 on our transport equation for $\tilde{c}_{A\beta}$ we obtain

$$\underbrace{\frac{\partial \tilde{c}_{A\beta}}{\partial t}}_{\text{accumulation}} + \underbrace{\mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta}}_{\text{convection}} + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{convective source}} = \underbrace{\nabla \cdot (\mathscr{D}_\beta \nabla \tilde{c}_{A\beta})}_{\text{diffusion}} + \underbrace{\varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle}_{\text{non-local convection}} \tag{3.3-13}$$

The order of magnitude of the *non-local* convective transport term can be expressed as

$$\varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta \tilde{c}_{A\beta} / L \right) \tag{3.3-14}$$

Here we have made use of the no-slip condition which requires that $\tilde{\mathbf{v}}_\beta$ be the same order of magnitude as $\langle \mathbf{v}_\beta \rangle^\beta$, and we have used L as the characteristic length associated with the term $\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle$. The order of magnitude of the *local* convective transport is given by

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta \tilde{c}_{A\beta} / \ell_\beta\right) \tag{3.3-15}$$

and this indicates that the non-local convective transport can be neglected when ever

$$\ell_\beta << L \tag{3.3-16}$$

Under these circumstances our transport equation for the spatial deviation concentration takes the form

$$\frac{\partial \tilde{c}_{A\beta}}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{convective source}} = \nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta}\right) \tag{3.3-17}$$

and we can complete the closure problem for $\tilde{c}_{A\beta}$ by writing the initial and boundary conditions analogous to Eqs. 3.3-2 through 3.3-4 as

B.C.1 $$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_{A\beta} = \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_{A\beta} \rangle^\beta}_{\text{diffusive source}}, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{3.3-18}$$

B.C.2 $$\tilde{c}_{A\beta} = f(\mathbf{r}, t), \quad \text{at } \mathscr{A}_{\beta e} \tag{3.3-19}$$

I.C. $$\tilde{c}_{A\beta} = g(\mathbf{r}), \quad \text{at } t = 0 \tag{3.3-20}$$

While many dispersion processes will be inherently unsteady, the closure problem for $\tilde{c}_{A\beta}$ will be quasi-steady whenever the following constraint is satisfied

$$\frac{\mathscr{D}_\beta t^*}{\delta_\beta^2} >> 1 \tag{3.3-21}$$

This constraint is based on an estimate of the diffusive transport term given by

$$\nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta}\right) = \mathbf{O}\left(\mathscr{D}_\beta \tilde{c}_{A\beta} / \delta_\beta^2\right) \tag{3.3-22}$$

along with the inequality

$$\frac{\partial \tilde{c}_{A\beta}}{\partial t} << \nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta}\right) \tag{3.3-23}$$

When the transport process is purely diffusive, one can follow the developments in Chapter 1 to conclude that

$$\delta_\beta \approx \ell_\beta, \quad \text{diffusive process} \tag{3.3-24}$$

On the other hand, when convective transport is important, the situation is more complex and we will say more about the length scale, δ_β, in subsequent paragraphs.

The quasi-steady closure problem takes the form

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{convective source}} = \nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta} \right) \tag{3.3-25}$$

B.C.1

$$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_{A\beta} = \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_{A\beta} \rangle^\beta}_{\text{diffusive source}}, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{3.3-26}$$

B.C.2

$$\tilde{c}_{A\beta} = f(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{3.3-27}$$

and it becomes clear that $\tilde{c}_{A\beta}$ will depend on $\mathbf{r}$, t, and $\nabla \langle c_{A\beta} \rangle^\beta$, in addition to any parameters that appear in the boundary condition imposed at $\mathscr{A}_{\beta e}$.

3.3.1 LOCAL CLOSURE PROBLEM

It should be obvious that we have no intention of solving for $\tilde{c}_{A\beta}$ in the macroscopic region illustrated in Figure 3.2, but instead we wish only to determine $\tilde{c}_{A\beta}$ in some *representative region* so that the area and volume integrals in Eq. 3.2-18 can be expressed in a closed form. A representative region is illustrated in Figure 3.4 and in order to solve the closure problem in that region we must be willing to discard the boundary condition given by Eq. 3.3-27. Given that $\tilde{c}_{A\beta}$ is dominated by the small length scale, the boundary condition imposed at $\mathscr{A}_{\beta e}$ can influence the $\tilde{c}_{A\beta}$-field only in a very thin region near the entrances and exits of the macroscopic system. This means that the governing differential equation, Eq. 3.3-25, and the interfacial boundary condition, Eq. 3.3-26, dominate the $\tilde{c}_{A\beta}$-field. However, if we discard the boundary condition given by Eq. 3.3-27, we must treat the representative region shown in Figure 3.4 as a unit cell in a spatially periodic model of a porous medium. This leads us the closure problem given by

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta}_{\text{convective source}} = \nabla \cdot \left(\mathscr{D}_\beta \nabla \tilde{c}_{A\beta} \right) \tag{3.3-28}$$

B.C.1

$$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_{A\beta} = \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_{A\beta} \rangle^\beta}_{\text{diffusive source}}, \quad \text{at } A_{\beta\sigma} \tag{3.3-29}$$

Periodicity:

$$\tilde{c}_{A\beta}(\mathbf{r} + \ell_i) = \tilde{c}_{A\beta}(\mathbf{r}), \quad i = 1, 2, 3 \tag{3.3-30}$$

When the Dirichlet condition given by Eq. 3.3-27 is replaced by the periodic condition given by Eq. 3.3-30, we lose the ability to completely specify the $\tilde{c}_{A\beta}$-field. This results from the fact that Eqs. 3.3-28 through 3.3-30 only specify $\tilde{c}_{A\beta}$ to within an arbitrary constant. We could eliminate this arbitrary constant by requiring that the average of $\tilde{c}_{A\beta}$ be zero; however, this is not necessary since a constant will not pass through the filter indicated by Eq. 3.2-19.

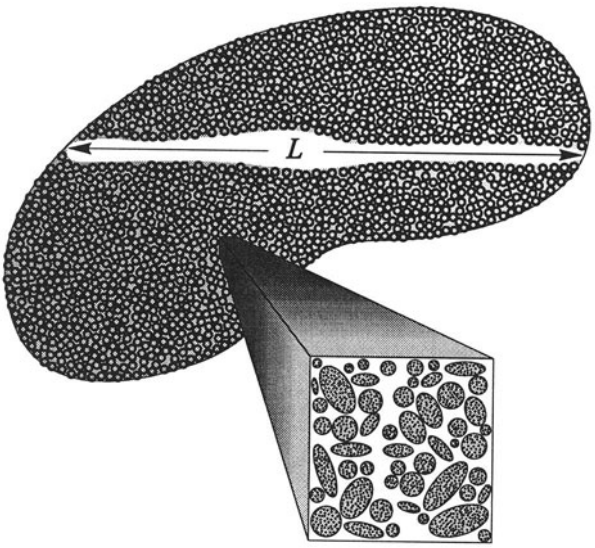

Figure 3.4. Representative region

The use of a spatially periodic condition for $\tilde{c}_{A\beta}$ is based on the assumption that the gradient of the intrinsic average concentration can be treated as a constant within the unit cell. In order to identify the length-scale constraint associated with this simplification, we follow the development presented earlier in Sec. 1.4 and expand $\nabla\langle c_{A\beta}\rangle^{\beta}$ about the centroid of the unit cell.

$$\nabla\langle c_{A\beta}\rangle^{\beta}\Big|_{x+y_\beta} = \nabla\langle c_{A\beta}\rangle^{\beta}\Big|_{x} + \mathbf{y}_\beta\cdot\nabla\nabla\langle c_{A\beta}\rangle^{\beta}\Big|_{x} + \ldots\ldots \tag{3.3-31}$$

Given the estimate of the second derivative

$$\nabla\nabla\langle c_{A\beta}\rangle^{\beta} = \mathbf{O}\left(\frac{\nabla\langle c_{A\beta}\rangle^{\beta}}{L_{c1}}\right) \tag{3.3-32}$$

we see that variations in $\nabla\langle c_{A\beta}\rangle^{\beta}$ can be ignored within a unit cell when the following length-scale constraint is valid.

$$r_o \ll L_{c1} \tag{3.3-33}$$

Here we have assumed that the characteristic length for the unit cell must be equal to or less than r_o, thus the magnitude of $\mathbf{y}_\beta$ is restricted by $|\mathbf{y}_\beta| \leq r_o$. Equation 3.3-33 was presented in Chapter 1 as Eq. 1.4-50 and the analogous result for the heat conduction process described in Chapter 2 was given by Eq. 2.4-41.

3.3.2 CLOSURE VARIABLE

Given that the two non-homogeneous terms in the closure problem for $\tilde{c}_{A\beta}$ are proportional to $\nabla\langle c_{A\beta}\rangle^{\beta}\big|_{\mathbf{x}}$, we are motivated to express $\tilde{c}_{A\beta}$ as

$$\tilde{c}_{A\beta} = \mathbf{b}_{\beta}\cdot\nabla\langle c_{A\beta}\rangle^{\beta} + \psi_{\beta} \tag{3.3-34}$$

in which it is understood that $\nabla\langle c_{A\beta}\rangle^{\beta}$ is evaluated at the centroid. Once again, we refer to $\mathbf{b}_{\beta}$ as the *closure variable* which is specified by the following boundary value problem:

$$\tilde{\mathbf{v}}_{\beta} + \mathbf{v}_{\beta}\cdot\nabla\mathbf{b}_{\beta} = \mathscr{D}_{\beta}\nabla^2\mathbf{b}_{\beta} \tag{3.3-35a}$$

B.C.1 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_{\beta}\nabla\mathbf{b}_{\beta} = \mathbf{n}_{\beta\sigma}\mathscr{D}_{\beta}, \quad \text{at } A_{\beta\sigma} \tag{3.3-35b}$$

Periodicity: $$\mathbf{b}_{\beta}(\mathbf{r}+\ell_i) = \mathbf{b}_{\beta}(\mathbf{r}), \quad i=1,2,3 \tag{3.3-35c}$$

It is left as an exercise for the reader (see Problem 3-5) to prove that ψ_{β} is a constant that will not pass through the filters represented by the area and volume integrals in Eq. 3.2-19.

3.3.3 CLOSED FORM

In order to develop the closed form of our convective-dispersion equation that was presented in Sec. 3.2, we recall Eq. 3.2-18 in the form

$$\underbrace{\varepsilon_{\beta}\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla\cdot\left(\varepsilon_{\beta}\langle\mathbf{v}_{\beta}\rangle^{\beta}\langle c_{A\beta}\rangle^{\beta}\right)}_{\text{convective transport}} = \underbrace{\nabla\cdot\left[\varepsilon_{\beta}\mathscr{D}_{\beta}\left(\nabla\langle c_{A\beta}\rangle^{\beta} + \frac{1}{V_{\beta}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{c}_{A\beta}\,dA\right)\right]}_{\text{diffusive transport}} - \underbrace{\nabla\cdot\langle\tilde{\mathbf{v}}_{\beta}\tilde{c}_{A\beta}\rangle}_{\text{dispersive transport}} \tag{3.3-36}$$

and substitute Eq. 3.3-34 in order to obtain

$$\varepsilon_\beta \frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot\left(\varepsilon_\beta \langle \mathbf{v}_\beta\rangle^\beta \langle c_{A\beta}\rangle^\beta\right) \tag{3.3-37}$$

$$= \nabla\cdot\left[\varepsilon_\beta \mathscr{D}_\beta\left(\mathbf{I} + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathbf{b}_\beta\, dA\right)\cdot\nabla\langle c_{A\beta}\rangle^\beta\right] - \nabla\cdot\left(\langle \tilde{\mathbf{v}}_\beta \mathbf{b}_\beta\rangle\cdot\nabla\langle c_{A\beta}\rangle^\beta\right)$$

Here we have used the fact that the constant ψ_β will not pass through the filters represented by the area and volume integrals in Eq. 3.3-36, and we have removed $\nabla\langle c_{A\beta}\rangle^\beta$ from both the area and volume integrals in that equation. We can now define and effective diffusivity tensor according to

$$\mathbf{D}_{eff} = \mathscr{D}_\beta\left(\mathbf{I} + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathbf{b}_\beta\, dA\right) \tag{3.3-38}$$

which is analogous to the effective diffusivity defined in Chapter 1 by Eq. 1.4-62. We can also define a *hydrodynamic* dispersion tensor by

$$\mathbf{D}_\beta = -\langle \tilde{\mathbf{v}}_\beta \mathbf{b}_\beta\rangle^\beta \tag{3.3-39}$$

in which the intrinsic volume average is used so that the hydrodynamic dispersion tensor, like the effective diffusivity tensor, will be an intrinsic quantity and not a superficial quantity. We now define the total dispersion tensor according to

$$\mathbf{D}_\beta^* = \mathbf{D}_{eff} + \mathbf{D}_\beta \tag{3.3-40}$$

so that the closed form of the convection-dispersion equation represented by Eq. 3.3-37 can be expressed as

$$\varepsilon_\beta \frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot\left(\varepsilon_\beta \langle \mathbf{v}_\beta\rangle^\beta \langle c_{A\beta}\rangle^\beta\right) = \nabla\cdot\left(\varepsilon_\beta \mathbf{D}_\beta^*\cdot\nabla\langle c_{A\beta}\rangle^\beta\right) \tag{3.3-41}$$

In Chapters 1 and 2, we were able to use the closure problems to prove that the effective diffusivity tensor and the effective thermal conductivity tensor were symmetric; however, for dispersion one cannot follow the same procedure to prove that $\mathbf{D}_\beta^*$ is symmetric (see Problem 3-6). One often sees Eq. 3.3-41 in a form that is appropriate for processes in which the porous medium is homogeneous. For that case, we can write Eq. 3.3-41 as

$$\frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle c_{A\beta}\rangle^\beta = \mathbf{D}_\beta^* : \nabla\nabla\langle c_{A\beta}\rangle^\beta \tag{3.3-42}$$

and this is the form given by Carbonell and Whitaker (1983). When Eq. 3.3-42 is a valid approximation of Eq. 3.3-41, only the symmetric part of the dispersion tensor plays a role in the transport equation; however, the skew-symmetric part may enter into a particular problem because of a flux boundary condition (see Problem 3-7).

At this point we need only solve Eqs. 3.3-35 for the closure variable $\mathbf{b}_\beta$ so that the total dispersion tensor can be calculated and theory can be compared with experiment; however, before doing that we need to return to the problem of the small length-scale, δ_β, in order to establish what is meant by the quasi-steady constraint on the closure problem.

3.3.4 SMALL LENGTH SCALE

In order to simplify the governing differential equation for $\tilde{c}_{A\beta}$ given by Eq. 3.3-17 from a transient form to the quasi-steady form given by Eq. 3.3-25, we imposed the following time-scale constraint:

$$\text{CONSTRAINT:} \qquad \frac{\mathscr{D}_\beta t^*}{\delta_\beta^2} >> 1 \tag{3.3-43}$$

For diffusive processes, we can use $\delta_\beta \approx \ell_\beta$ in order to give this constraint a reasonably precise meaning; however, when convective transport effects are important, diffusion of the $\tilde{c}_{A\beta}$-field occurs *both* within the concentration boundary layer *and* outside of the boundary layer. In addition, there is both a volume source and a surface source of the $\tilde{c}_{A\beta}$-field as indicated by Eqs. 3.3-28 and 3.3-29, and we need to have some idea how these sources influence the dispersion coefficient defined by Eq. 3.3-40.

In order to examine the small length scale associated with the dispersion process, we direct our attention to the closure problem for the $\mathbf{b}_\beta$-field In that boundary value problem, we note that there is a *convective volume source* represented by $\tilde{\mathbf{v}}_\beta$ in Eq. 3.3-35a and a *diffusive surface source* represented by $\mathbf{n}_{\beta\sigma}\mathscr{D}_\beta$ in Eq. 3.3-35b. The volume average of the former is zero while the surface area average of the latter is zero, thus these sources are distributed in a complex manner throughout the unit cell illustrated in Figure 3.4. Since $\tilde{\mathbf{v}}_\beta$ changes sign over the distance ℓ_β, this might *suggest* that the characteristic length for $\tilde{c}_{A\beta}$ is ℓ_β when convective effects are important. While the convective source is distributed in a complex manner, it does take an especially simple form at the β-σ interface where $\tilde{\mathbf{v}}_\beta = -\langle \mathbf{v}_\beta \rangle^\beta$. This means that Eq. 3.3-35a leads to

$$-\langle \mathbf{v}_\beta \rangle^\beta = \mathscr{D}_\beta \nabla^2 \mathbf{b}_\beta \,, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3.3-44}$$

while the flux boundary condition given by Eq. 3.3-35b can be expressed as

B.C.1 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla\mathbf{b}_\beta = \mathbf{n}_{\beta\sigma}\mathscr{D}_\beta, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{3.3-45}$$

From this latter result we conclude that

$$\mathscr{D}_\beta\nabla\mathbf{b}_\beta = \mathbf{O}\left(\mathscr{D}_\beta\mathbf{I}\right), \quad \text{near the } \beta\text{-}\sigma \text{ interface} \tag{3.3-46}$$

and when this result is used in Eq. 3.3-44 it suggests that

$$\frac{\langle v_\beta\rangle^\beta\delta_\beta}{\mathscr{D}_\beta} = \mathbf{O}(1), \quad \text{near the } \beta\text{-}\sigma \text{ interface} \tag{3.3-47}$$

We now define a Péclet number according to

$$Pe = \frac{\langle v_\beta\rangle^\beta\ell_\beta}{\mathscr{D}_\beta} \tag{3.3-48}$$

so that Eq. 3.3-47 can be used to express δ_β as

$$\delta_\beta \approx \ell_\beta/Pe \tag{3.3-49}$$

This indicates that the length scale associated with the *diffusive surface source* is quite different than the length scale associated with the *convective volume source*, and we express this idea as

$$\left\{\begin{matrix}\textit{diffusive surface source}\\ \textit{length scale}\end{matrix}\right\} \approx \ell_\beta/Pe \tag{3.3-50}$$

$$\left\{\begin{matrix}\textit{convective volume source}\\ \textit{length scale}\end{matrix}\right\} \approx \ell_\beta \tag{3.3-51}$$

In order to determine which of these length scales dominates the dispersion process, and therefore which of these length scales should be used in the constraint given by Eq. 3.3-43, we need to assess the importance of the *diffusive surface source* and the *convective volume source*. The *average value* of the volume source is zero,

$$\left\{\begin{matrix}\textit{average}\\ \textit{volume}\\ \textit{source}\end{matrix}\right\} = \frac{1}{V_\beta}\int_{V_\beta}\tilde{\mathbf{v}}_\beta dV = 0 \tag{3.3-52}$$

while the order of magnitude of the volume source per unit volume is given by

$$\left\{\begin{matrix}\textit{order of magnitude}\\ \textit{of the volume source}\end{matrix}\right\} = \frac{1}{\mathscr{V}}\int_{V_\beta}\left|\tilde{\mathbf{v}}_\beta\right| dV = \mathbf{O}\left(\varepsilon_\beta\langle v_\beta\rangle^\beta\right) \tag{3.3-53}$$

Similarly, the average value of the surface source is zero

$$\left\{\begin{matrix}average\\surface\\source\end{matrix}\right\} = \frac{1}{A_{\beta\sigma}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla\mathbf{b}_\beta\, dA = \frac{1}{A_{\beta\sigma}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathscr{D}_\beta\, dA = 0 \quad (3.3\text{-}54)$$

while the order of magnitude of this source per unit volume can be expressed as

$$\left\{\begin{matrix}order\ of\ magnitude\\of\ the\ surface\ source\end{matrix}\right\} = \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \left|\mathbf{n}_{\beta\sigma}\mathscr{D}_\beta\right| dA = \mathbf{O}\left(a_v\mathscr{D}_\beta\right) \quad (3.3\text{-}55)$$

On the basis of Eqs. 3.3-53 and 3.3-55 we see that

$$\frac{volume\ source}{surface\ source} = \mathbf{O}\left[\frac{\varepsilon_\beta\langle v_\beta\rangle^\beta}{a_v\mathscr{D}_\beta}\right] \quad (3.3\text{-}56)$$

Since $a_v \sim \ell_\beta^{-1}$ we see that the estimates associated with this result lead to

$$\frac{volume\ source}{surface\ source} = \mathbf{O}(Pe) \quad (3.3\text{-}57)$$

This indicates that it is the volume source that dominates at large Péclet numbers, and under these circumstances it would seem that the diffusive transfer that takes place *outside the boundary layer* is the dominant term in Eq. 3.3-17. Under these circumstances the dominant small length scale would be given by

$$\delta_\beta \approx \ell_\beta\,, \quad \text{dominant small length scale} \quad (3.3\text{-}58)$$

and the constraint given by Eq. 3.3-43 should be expressed as

$$\text{CONSTRAINT:} \qquad \frac{\mathscr{D}_\beta t^*}{\ell_\beta^2} >> 1 \quad (3.3\text{-}59)$$

Eidsath *et al.* (1983) have pointed out that this result is not always satisfied for typical laboratory experiments, and unsteady closure problems may be necessary for the interpretation of some laboratory experiments.

3.4 Comparison Between Theory and Experiment

In order to compare theory and experiment, we must first solve the Navier-Stokes equations for some representative region. This will provide the velocity field, $\mathbf{v}_\beta$, and from this we can calculate $\langle\mathbf{v}_\beta\rangle^\beta$ and then $\tilde{\mathbf{v}}_\beta$. The original calculations of this type were carried out by Eidsath (1981) for periodic arrays of cylinders such as the in-line cylinders shown in Figure 3.5. The mixture of cylindrical and rectangular surfaces for a unit cell associated with an array of cylinders motivated Eidsath to use a finite element method to solve the governing differential equations; however, finite difference

(Launder and Massey, 1978) and finite volume (Quintard and Whitaker, 1995b) methods can also be used to obtain the solutions. The fluid mechanical calculations of Eidsath (1981) were compared with the experimental results of Bergelin *et al.* (1950) and the comparison for several different arrays of cylinders is given in Eidsath *et al.* (1983). The solution for the $\mathbf{b}_\beta$-field given by Eqs. 3.3-35 can be carried out using essentially the same numerical code that provides the velocity field, and once the components of the vector $\mathbf{b}_\beta$ are known the effective diffusivity tensor and the hydrodynamic dispersion tensor can be calculated using Eqs. 3.3-38 and 3.3-39. These, in turn, can be used to calculate the total dispersion tensor defined by Eq. 3.3-40, and the longitudinal and lateral components of $\mathbf{D}_\beta^*$ can then be compared with experimental results that are interpreted on the basis of Eq. 3.3-42.

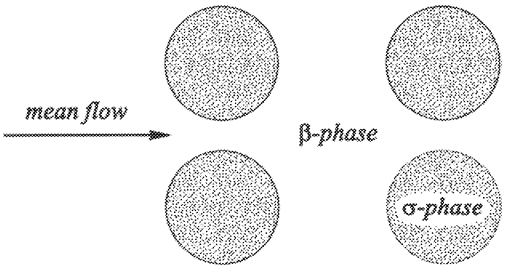

Figure 3.5. In-line cylinders

From dimensional analysis, one knows that the dimensionless quantity $\mathbf{D}_\beta^* / \mathscr{D}_\beta$ will depend on the Reynolds number, the Péclet number, and the dimensionless parameters that are needed to describe the geometry of the spatially periodic model. In order to compare theory with experiment, or one theoretical calculation with another, one must take care to insure that all quantities are defined in a consistent manner. For example, one could interpret dispersion experiments with the local volume averaged transport equation

$$\varepsilon_\beta \frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t} + \nabla \cdot \left(\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_{A\beta} \rangle^\beta \right) = \nabla \cdot \left(\mathbf{D}_\beta' \cdot \nabla \langle c_{A\beta} \rangle^\beta \right) \tag{3.4-1}$$

and this would lead to a dispersion coefficient that is smaller by a factor of ε_β than the one defined by Eqs. 3.3-38 through 3.3-40. By the same token, there are a variety of ways in which the Reynolds number and Péclet number can be defined, and if one is not absolutely clear about these definitions confusion can result.

3.4.1 COMPARISON WITH EXPERIMENT

In experimental systems, it would appear that the most appropriate characteristic velocity is the intrinsic velocity, $\langle \mathbf{v}_\beta \rangle^\beta$, and it seems best to define the Reynolds number and the

Péclet number using the magnitude of this velocity which we designate by $\langle v_\beta \rangle^\beta$. In non-consolidated porous media, particles are often characterized by the *effective particle diameter*

$$d_p = 6V_p/A_p \tag{3.4-2}$$

in which V_p is the volume of the particle and A_p is the surface area of the particle. One could use d_p as the characteristic length in the definitions of the Reynolds number and Péclet number; however, in studies of heat transfer in packed beds and tube bundles (Whitaker, 1972, 1983b) it was found that the *hydraulic diameter* provided a more attractive characteristic length. The hydraulic diameter, D_h, for a porous medium can be defined by

$$D_h = 4 \frac{\left\{ \begin{array}{l} \textit{volume of the porous} \\ \textit{medium available for flow} \end{array} \right\}}{\left\{ \begin{array}{l} \textit{area of the fluid - solid interface associated} \\ \textit{with the volume available for flow} \end{array} \right\}} \tag{3.4-3}$$

and this can also be expressed as

$$D_h = 4\varepsilon_\beta / a_v \tag{3.4-4}$$

This indicates that the hydraulic diameter is composed of two of the important parameters used to characterize the geometry of a porous medium. For a non-consolidated porous medium, Eq. 3.4-4 can also be expressed as

$$D_h = 4\left(V_p/A_p\right)\frac{\varepsilon_\beta}{1-\varepsilon_\beta} \tag{3.4-5}$$

and this led Eidsath *et al.* (1983) to choose the small-scale characteristic length as

$$\ell^* = d_p\left(\frac{\varepsilon_\beta}{1-\varepsilon_\beta}\right) \tag{3.4-6}$$

This choice for the small length-scale provides a *particle Reynolds number* defined by

$$Re_p = \frac{\rho_\beta \langle v_\beta \rangle^\beta d_p}{\mu_\beta}\left(\frac{\varepsilon_\beta}{1-\varepsilon_\beta}\right) \tag{3.4-7}$$

while the *particle Péclet number* takes the form

$$Pe_p = \frac{\langle v_\beta \rangle^\beta d_p}{\mathscr{D}_\beta}\left(\frac{\varepsilon_\beta}{1-\varepsilon_\beta}\right) \tag{3.4-8}$$

Eidsath (1981) carried out dispersion calculations for Péclet numbers ranging from 1.0 to 10^4 and for Reynolds numbers of 0.006 and 56.1. The higher Reynolds number

produced longitudinal dispersions coefficients that were only 10% greater than those obtained under Stokes flow conditions, thus the results presented here are all for Reynolds numbers on the order of 0.006.

The experimental results of Gunn and Pryce (1969) for the longitudinal dispersion coefficient, D^*_{xx}, represent an attractive set of data since they were obtained for both ordered and disordered systems. While the former are often disdained as not being "real" porous media, they provide an excellent test of theoretical results and they lead to important insight into the influence of order and disorder on the process of dispersion. The results of Gunn and Pryce (1969) are shown in Figure 3.6 along with the calculations of Eidsath *et al.* (1983) for a system of in-line cylinders having a porosity of 0.37. The theoretical results are in excellent agreement with the experimental data for

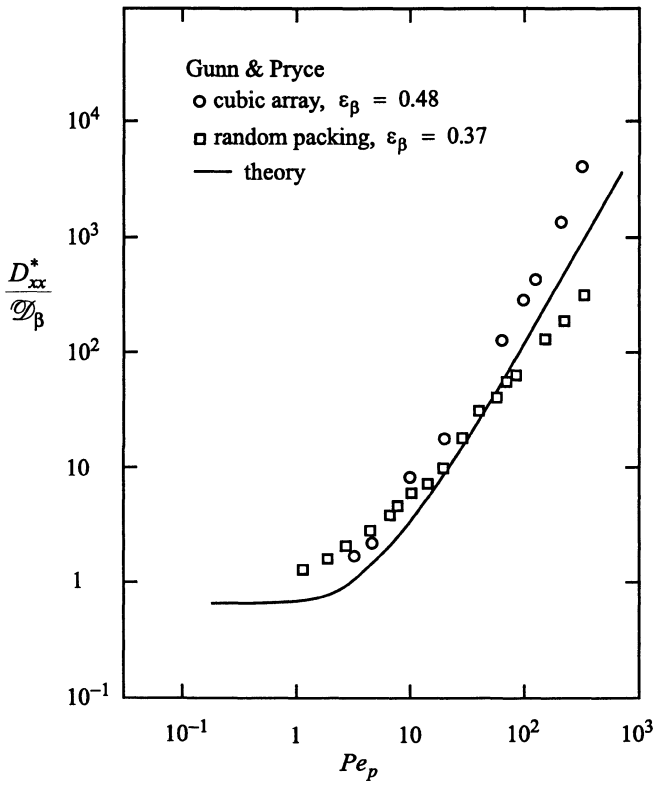

Figure 3.6. Theory and experiment for ordered and random packing of spheres

Péclet numbers less than 100; however, the trend of the two sets of data is rather different with the cubic array illustrating a much stronger dependence on the Péclet number than the random packing. The Péclet-number dependence of the theoretical values for in-line cylinders is quite close to that illustrated by the cubic array, and it is

not improbable that theoretical calculations for a cubic array would be in excellent agreement with the experimental results. As of this writing, those calculations have not been carried out; however, the computational power available when Eidsath's work was done is trivial compared to current standards and the complete three-dimensional calculations will soon appear. Although the experimental data are not extensive, they give a clear indication that longitudinal dispersion coefficients *increase with increasing order.*

The use of simple unit cells, such as the one illustrated in Figure 3.5, provides reasonable agreement with measured *longitudinal dispersion coefficients* for moderate Péclet numbers. This indicates that the complexities associated with real systems are largely *filtered* by the area and volume integrals in Eq. 3.2-19. The situation for *lateral dispersion coefficients* is quite different, and in Figure 3.7 we see very poor agreement

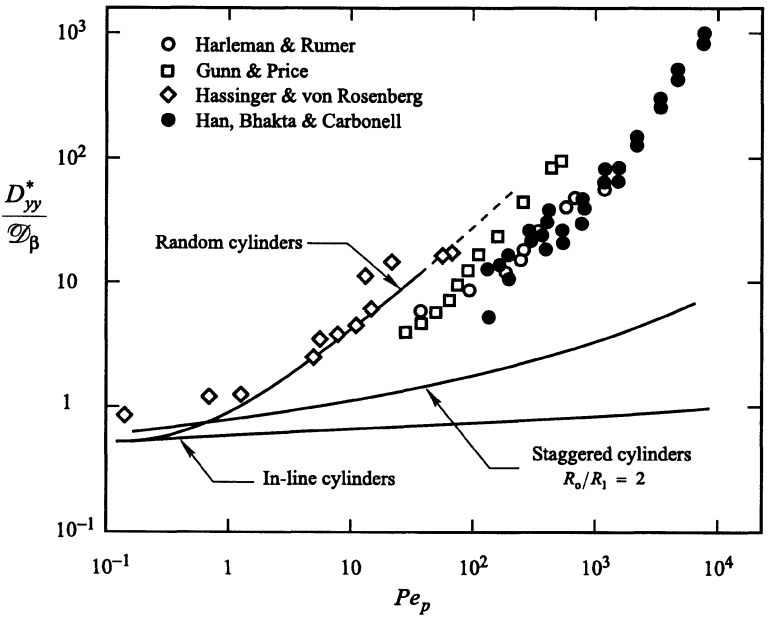

Figure 3.7. Theoretical and experimental values for the lateral dispersion coefficient in randomly packed beds

between theory and experiment for simple unit cells. The results for in-line cylinders represent the calculations of Eidsath *et al.* (1983) for the system shown in Figure 3.5 while the results for staggered cylinders with $r_o / r_1 = 2$ were determined using the configuration shown in Figure 3.8. In both cases, the predicted values of D^*_{yy} are *much less* than the measured values. The calculated values of D^*_{yy} for the in-line cylinders shown in Figure 3.7 illustrate a weaker dependence on the Péclet number than the staggered cylinders shown in Figure 3.8, and the reason must certainly be the diminished lateral motion that occurs in the system of in-line cylinders.

The most interesting theoretical results shown in Figure 3.7 are for unit cells composed of random cylinders. Noble *et al.* (1998) obtained those results using unit cells consisting of dozens of randomly distributed cylinders, and while the results are limited because of the complexity of the numerical calculations, the agreement with the experimental data is extremely attractive. From the calculations of Noble (1997) and of Eidsath (1981), it is clear that lateral dispersion coefficients *increase with increasing disorder.* This is just the opposite type of behavior that we see in Figure 3.6 for longitudinal dispersion coefficients.

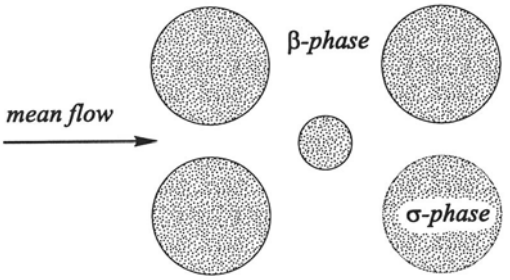

Figure 3.8. Array of staggered cylinders of unequal diameter

The good agreement between theory and experiment illustrated in Figure 3.6 is somewhat misleading because of the limited nature of the data. If we examine the more extensive data shown in Figure 3.9, we see a significant difference between the theory based on the system illustrated in Figure 3.5 and the measured values of the longitudinal dispersion coefficient for a wide range of Péclet numbers. We have included in that figure the Taylor-Aris theory (Taylor, 1953; Aris, 1956) for a bundle of capillary tubes which can be represented by (see Problem 3-8)

$$\frac{D^*_{xx}}{\mathscr{D}_\beta} \sim 0.002\, Pe_p^2\,, \quad \textit{bundle of capillary tubes} \tag{3.4-9}$$

The results for flow orthogonal to the array of in-line cylinders illustrated in Figure 3.5 are quite different and can be expressed as

$$\frac{D^*_{xx}}{\mathscr{D}_\beta} \sim 0.07\, Pe_p^{1.7}\,, \quad \textit{in-line cylinders} \tag{3.4-10}$$

Both of these results *deviate significantly* from the major portion of the experimental data that can be approximated by

$$\frac{D^*_{xx}}{\mathscr{D}_\beta} \sim 0.7\, Pe_p^{1.2}\,, \quad \textit{randomly packed beds} \tag{3.4-11}$$

This clearly indicates that simple, two-dimensional unit cells cannot be used to explain longitudinal dispersion phenomena for large Péclet numbers; however, the randomly

distributed cylinders used by Noble *et al.* (1997) are in remarkably good agreement with the functional dependence indicated by Eq. 3.4-11.

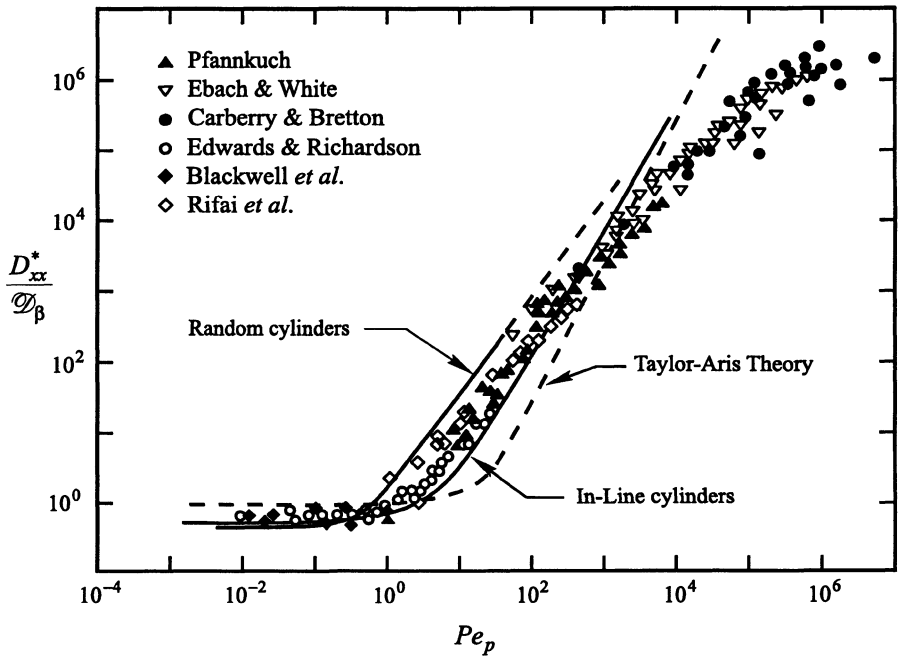

Figure 3.9. Theory and experiment for randomly packed beds

The experimental data for very high Péclet numbers *should not be considered* in the comparison between theory and experiment since those data were obtained under conditions which do not satisfy the quasi-steady constraint given by Eq. 3.3-59. Han *et al.* (1985) studied axial dispersion in packed beds in which the axial dispersion coefficient was measured at five different locations in the bed. This allowed them to determine that the constraint associated with the quasi-steady condition is given by

$$\frac{\mathscr{D}_\beta t^*}{d_p^2} \geq 0.3, \quad \textit{experimental result for packed beds} \tag{3.4-12}$$

Here t^* represents the distance traveled by a pulse divided by the intrinsic average velocity, and d_p represents the effective particle diameter (see Problem 1-18). Most of the experimental data obtained by Ebach and White (1958) and by Carberry and Breton (1958) do not satisfy the constraint given by Eq. 3.4-12, and it is not appropriate to compare their results with the theory given by Eqs. 3.3-35. The experimental work of Han *et al.* (1985) clearly indicates that axial dispersion coefficients increase with increasing time until an asymptotic value is reached, and their experimental studies are

confirmed by the numerical experiments of Paine *et al.* (1983) for dispersion in capillary tubes. The behavior of the high-Péclet number data shown in Figure 3.9 is caused by two competing phenomena. In the domain where the closure problem is unsteady, the axial dispersion coefficient *increases with increasing velocity* but *decreases with decreasing time.* Since the time associated with a measurement made at a fixed point in a packed bed decreases with increasing velocity, we have two competing effects that cancel and tend to produce dispersion coefficients that are nearly independent of the Péclet number.

3.4.2 COMPARISON WITH OTHER CALCULATIONS

Since the original work of Eidsath (1981), the solution of the closure problem given by Eqs. 3.3-35 has been carried out by other workers. The results are compared in Figure 3.10 where we have shown the original calculations presented by Eidsath *et al.* (1983), along with the more recent calculations of Edwards *et al.* (1991, 1993), Sahraoui and Kaviany (1994), and Quintard and Whitaker (1994f). The comparison in this case is not

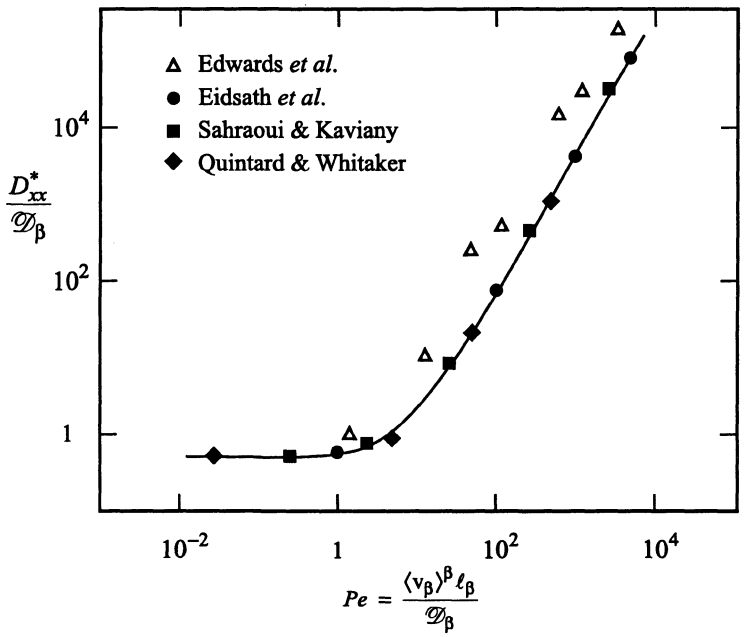

Figure 3.10. Theoretical calculations for square arrays of circular cylinders

based on the particle Péclet number, but instead we have used the *cell Péclet number* which is defined by

$$Pe = \frac{\langle v_\beta \rangle^\beta \ell_\beta}{\mathscr{D}_\beta} \tag{3.4-13}$$

with the length scale, ℓ_β, identified explicitly in Figure 3.11. The cell Péclet number has

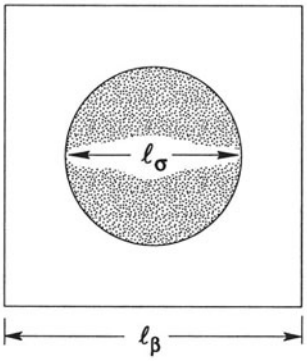

Figure 3.11. Lengths associated with a unit cell

been used for this comparison in order to avoid any confusion concerning the definition of this dimensionless group. For Péclet numbers ranging from 1 to 10,000 we see excellent agreement between Eidsath *et al.* (1983), Sahraoui and Kaviany (1994), and Quintard and Whitaker (1994f), while the calculations of Edwards *et al.* (1991, 1993) are larger by about a factor of ε_β^{-1}. The computational techniques represented in Figure 3.10 are finite element (Eidsath *et al.*, 1983 and Edwards *et al.*, 1991, 1993), finite difference (Sahraoui and Kaviany, 1994), and finite volume (Quintard and Whitaker, 1994f). More recently, Noble *et al.* (1998) have used the lattice Boltzmann method to solve the closure problem, and their results for a periodic array of squares are compared with those of Eidsath (1981) in Table 3.1. The agreement is excellent, and it seems clear

Table 3.1. Theoretical calculations for square arrays of square cylinders

	Eidsath	Noble *et al.*
	$D^*_{xx}/\mathscr{D}_\beta$	$D^*_{xx}/\mathscr{D}_\beta$
$Pe = 1$	0.641	0.643
$Pe = 10$	3.91	3.96
$Pe = 100$	263	267
$Pe = 1000$	14,290	14,810

that one can solve Eqs. 3.3-35 with confidence using a variety of numerical methods. For the single exception, the reader is referred to Edwards *et al.* (1991) who provide some definitive comments concerning the disparity between their results and the work of others.

3.5 Conclusions

In this chapter we have examined the process of passive dispersion, and we have compared theoretical results with experimental values for both ordered and disordered packed beds of spheres. The comparison indicates that longitudinal dispersion coefficients *increase* with increasing order while lateral dispersion coefficients *decrease* with increasing order. Our comparison between theory and experiment indicates that simple unit cells cannot be used to predict dispersion coefficients with confidence, while unit cells composed of dozens of randomly distributed cylinders provide remarkably good agreement with experimental data. The experimental data for longitudinal dispersion coefficients clearly indicate that the quasi-steady constraint associated with the closure problem can be easily violated in typical experimental systems and this tends to occur for high values of the Péclet number.

3.6 Problems*

3-1. Verify Eq. 3.2-24 on the basis of the expansions given by Eqs. 3.2-22 and 3.2-23.

3-2. In place of the *assumptions* indicated by Eqs. 3.2-16, one can draw upon the *restrictions* given by Eqs. 3.2-27 to support the form of the convective transport represented by Eq. 3.2-17. In this problem you are asked to explore the *constraints* associated with Eqs. 3.2-17, and these are difficult to develop because of the complexity of terms such as $\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle^\beta$ or as $\langle \tilde{\mathbf{v}}_\beta \mathbf{y}_\beta \rangle$. Some help is available for the first of these terms since one can use Eqs. 3.3-36 through 3.3-39 to show that

$$\langle \tilde{\mathbf{v}}_\beta \tilde{c}_{A\beta} \rangle^\beta = -\mathbf{D}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta \tag{1}$$

Note that this representation assumes that the restrictions given by Eqs. 3.2-27 are valid; however, Eq. 1 should provide a reasonable estimate even when the additional terms in Eq. 3.2-25 are not negligible. The experimental results for longitudinal and lateral dispersion suggest that

$$\mathbf{D}_\beta^* / \mathscr{D}_\beta = \mathbf{O}(Pe) \tag{2}$$

and one can make use of this result to extract some length-scale constraints from Eqs. 3.2-27. The constraint associated with Eq. 3.2-27a should be reliable; however, the development of a satisfactory constraint for Eq. 3.2-27b is quite difficult.

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* Solutions to all problems are available from the author.

3-3. For compressible flow in a rigid porous medium, the continuity equation can be expressed as

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot \left(\rho_\beta \mathbf{v}_\beta \right) = 0 \tag{1}$$

and the volume averaged form is given by

$$\varepsilon_\beta \frac{\partial \langle \rho_\beta \rangle^\beta}{\partial t} + \nabla \cdot \left(\varepsilon_\beta \langle \rho_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \right) + \nabla \cdot \left(\langle \tilde{\rho}_\beta \tilde{\mathbf{v}}_\beta \rangle \right) = 0 \tag{2}$$

Hsu and Cheng (1988) have suggested that the dispersive transport can be expressed as

$$\langle \tilde{\rho}_\beta \tilde{\mathbf{v}}_\beta \rangle = -\mathbf{D}_h \cdot \nabla \langle \rho_\beta \rangle^\beta \tag{3}$$

and in this problem you are asked to identify the simplifications that lead to this result.

3-4. Develop the constraint given by Eq. 3.3-12.

3-5. Prove that the function ψ_β in Eq. 3.3-34 is a constant when the mapping vector $\mathbf{b}_\beta$ is determined by Eqs. 3.3-35. Do this by developing the boundary value problem for ψ_β^2 and showing that it can be used to obtain $\nabla \psi_\beta = 0$.

3-6. Use the closure problem given by Eqs. 3.3-35 to explore the possibility that the total dispersivity tensor $\mathbf{D}_\beta^*$ is symmetric. Begin by forming the dyadic product of Eqs. 3.3-35 with the closure variable $\mathbf{b}_\beta$, and then search for a result that would lead to $\lambda \cdot \mathbf{D}_\beta^* \cdot \nu = \nu \cdot \mathbf{D}_\beta^* \cdot \lambda$ in which λ and ν are arbitrary unit vectors.

3-7. When Eq. 3.3-42 represents a valid description of the dispersion process, one can prove that only the symmetric part of $\mathbf{D}_\beta^*$ influences the transport equation. This can be accomplished by decomposing the dispersion tensor into its irreducible parts and making use of the orthogonality characteristics associated with the irreducible parts of second order tensors. Carry out this proof to show that only the symmetric part of $\mathbf{D}_\beta^*$ need be retained in Eq. 3.3-42. When a particular problem involves a flux boundary condition containing the term, $\mathbf{n} \cdot \mathbf{D}_\beta^* \cdot \nabla \langle c_{A\beta} \rangle^\beta$, the skew-symmetric part of $\mathbf{D}_\beta^*$ cannot be automatically discarded.

3-8. The process of passive mass transport of a pulse of solute (species A) in a capillary tube can be described by

$$\frac{\partial c_{A\beta}}{\partial t} + v_z \frac{\partial c_{A\beta}}{\partial z} = \mathscr{D}_\beta \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_{A\beta}}{\partial r} \right) + \frac{\partial^2 c_{A\beta}}{\partial z^2} \right] \tag{1}$$

I.C. $$c_{A\beta} = \mathscr{F}(z), \quad t = 0 \tag{2}$$

B.C.1 $$\frac{\partial c_{A\beta}}{\partial r} = 0, \quad r = r_o \tag{3}$$

B.C.2&3 $$c_{A\beta} = 0, \quad z = \pm \infty \tag{4}$$

One can think of a bundle of capillary tubes as a model of a porous medium in which the fluid is the β-phase and the solid is the σ-phase. The intrinsic average concentration is the area average concentration defined by

$$\langle c_{A\beta} \rangle^\beta = \frac{1}{\pi r_o^2} \int_{r=0}^{r=r_o} 2\pi r c_{A\beta} \, dr \tag{5}$$

and you are asked to develop the governing differential equation for this concentration. In that equation the dispersion coefficient should have the form

$$D_{zz} = \mathscr{D}_\beta \left[1 + \frac{1}{48} \left(\langle v_z \rangle^\beta r_o / \mathscr{D}_\beta \right)^2 \right] \tag{6}$$

The velocity in the tube is given by

$$v_z = 2\langle v_z \rangle^\beta \left[1 - (r/r_o)^2 \right] \tag{7}$$

in which $\langle v_z \rangle^\beta$ is the area averaged velocity. You should restrict your analysis by

$$\frac{\mathscr{D}_\beta t^*}{r_o^2} >> 1, \quad \frac{L^2}{r_o^2} >> 1, \quad \frac{\mathscr{D}_\beta L}{\langle v_z \rangle^\beta r_o^2} >> 1 \tag{8}$$

in which L should be thought of as the time-dependent *pulse width*. The result you seek is known as Taylor-Aris dispersion theory and it provides the following governing differential equation for $\langle c_{A\beta} \rangle^\beta$:

$$\frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t} + \langle v_z \rangle^\beta \frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial z} = \mathscr{D}_\beta \left[1 + \tfrac{1}{48} Pe^2 \right] \frac{\partial^2 \langle c_{A\beta} \rangle^\beta}{\partial z^2} \tag{9}$$

In order to estimate the pulse width, L, consider a coordinate transformation to a frame of reference moving with the fluid. This is given by

$$\bar{z} = z - \langle v_\beta \rangle^\beta t \tag{10}$$

and it allows one to express the time derivative in the fixed frame as

$$\left.\frac{d\langle c_{A\beta}\rangle^\beta}{dt}\right|_z = \left.\frac{d\langle c_{A\beta}\rangle^\beta}{dt}\right|_{\bar{z}} - \langle v_\beta \rangle^\beta \frac{\partial \langle c_{A\beta}\rangle^\beta}{\partial z} \tag{11}$$

Substitution of this result into Eq. 9 leads to

$$\left.\frac{d\langle c_{A\beta}\rangle^\beta}{dt}\right|_{\bar{z}} = \mathscr{D}_\beta\left[1 + \frac{1}{48}Pe^2\right]\frac{\partial^2 \langle c_{A\beta}\rangle^\beta}{\partial \bar{z}^2} \tag{12}$$

in which we have made use of the relation given by

$$\frac{\partial^2 \langle c_{A\beta}\rangle^\beta}{\partial z^2} = \frac{\partial^2 \langle c_{A\beta}\rangle^\beta}{\partial \bar{z}^2} \tag{13}$$

One can make use of Eq. 12 to estimate the pulse width as a function of time and then develop a single constraint of the form

$$\sqrt{\frac{\mathscr{D}_\beta t^*}{r_o^2}} >> \sqrt{48} \tag{14}$$

This represents the most severe of the three constraints given by Eq. 8.

3-9. In order to gain some insight into the process of chromatographic separations, it is helpful to analyze the following problem of convection, diffusion, and adsorption in a capillary tube

$$\frac{\partial c_{A\beta}}{\partial t} + v_z \frac{\partial c_{A\beta}}{\partial z} = \mathscr{D}_\beta\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_{A\beta}}{\partial r}\right) + \frac{\partial^2 c_{A\beta}}{\partial z^2}\right] \tag{1}$$

I.C. $$c_{A\beta} = \mathscr{F}(z), \quad t = 0 \tag{2}$$

B.C.1 $$-\mathscr{D}_\beta \frac{\partial c_{A\beta}}{\partial r} = K_{eq}\frac{\partial c_{A\beta}}{\partial t}, \quad r = r_o \tag{3}$$

B.C.2&3 $$c_{A\beta} = 0, \quad z = \pm\infty \tag{4}$$

In Chapter 1 (see Problem 1-4) the process of diffusion and reaction in a capillary tube was considered, and the governing differential equation for the area averaged concentration was obtained subject to an *approximation* of the form

$$c_{A\beta} = \langle c_{A\beta}\rangle^\beta, \quad \text{at } r = r_o \tag{5}$$

If one accepts this approximation, one can form the area average of Eq. 1 to easily obtain what is known as the *chromatographic equation.* It is consistent with the *approximation* represented by Eq. 5 to impose the condition

$$\tilde{c}_{A\beta} = 0 \tag{6}$$

and this means that the dispersive transport is negligible. Show that the area average of Eq. 1 can be arranged in the form

$$\frac{\partial \langle c_{A\beta} \rangle^{\beta}}{\partial t} + u_p \frac{\partial \langle c_{A\beta} \rangle^{\beta}}{\partial z} = D_{zz} \frac{\partial^2 \langle c_{A\beta} \rangle^{\beta}}{\partial z^2} \tag{7}$$

where the *pulse velocity* is given by

$$u_p = \frac{\langle v_z \rangle^{\beta}}{\left(1+2K_{eq}/r_o\right)} \tag{8}$$

The quantity $(1+2K_{eq}/r_o)$ is often referred to as the retardation factor.

3-10. The problem of diffusion, convection, and adsorption in a capillary tube can be analyzed without imposing the restrictions given by Eqs. 5 and 6 in Problem 3-9. To do so one must first form the area average of the point equation and then develop the closure problem for $\tilde{c}_{A\beta}$. In your analysis of the closure problem you should identify the constraints that are necessary so that

$$\tilde{c}_{A\beta} << \langle c_{A\beta} \rangle^{\beta} \tag{1}$$

The quasi-steady closure problem will contain two source terms, thus suggesting a representation of the form

$$\tilde{c}_{A\beta} = b_{\beta} \frac{\partial \langle c_{A\beta} \rangle^{\gamma}}{\partial z} + s_{\beta} \frac{\partial \langle c_{A\beta} \rangle^{\beta}}{\partial t} \tag{2}$$

Set up and solve the boundary value problems for the closure variables, b_{β} and s_{β}, and use the results to determine the coefficients that appear in the area averaged transport equation. Two unusual terms

$$\frac{\partial^2 \langle c_{A\beta} \rangle^{\beta}}{\partial t^2} \quad \text{and} \quad \frac{\partial^2 \langle c_{A\beta} \rangle^{\beta}}{\partial t \partial z} \tag{3}$$

will appear in the transport equation for $\langle c_{A\beta} \rangle^{\beta}$. On the basis of the constraints that have already been imposed in order to achieve the condition indicated by Eq. 1, you will be able to neglect the term involving the second derivative with respect to time. Demonstrate that this is the case.

In order to extract a convective-dispersion equation having the classical form, one must eliminate the mixed derivative term. This can be achieved, at the expense of a severe constraint, by considering that $\langle c_{A\beta}\rangle^{\beta}$ is quasi-steady in a frame of reference moving at the *pulse velocity*. This moving frame is defined by

$$\bar{z} = z - u_p t \tag{4}$$

in which u_p is the pulse velocity. The spatial moments of $\langle c_{A\beta}\rangle^{\beta}$ are given by

$$m_n = \int_{-\infty}^{+\infty} \langle c_{A\beta}\rangle^{\beta} z^n dz, \qquad n = 0, 1, 2, ... \tag{5}$$

and the pulse velocity is defined explicitly as the time rate of change of the first reduced moment, i.e.,

$$u_p = \frac{d}{dt}(m_1/m_0) \tag{6}$$

This will provide the result given by Eq. 8 of Problem 3-9.

If the mixed derivative term in the area averaged transport equation is treated as quasi-steady in the moving frame indicated by Eq. 4, one can show that

$$\frac{\partial^2 \langle c_{A\beta}\rangle^{\beta}}{\partial t \partial z} \cong -u_p \frac{\partial^2 \langle c_{A\beta}\rangle^{\beta}}{\partial z^2} \tag{7}$$

Use of this result allows the area averaged transport equation to be expressed as

$$\frac{\partial \langle c_{A\beta}\rangle^{\beta}}{\partial t} + \frac{\langle v_z\rangle^{\beta}}{1+k} \frac{\partial \langle c_{A\beta}\rangle^{\beta}}{\partial z} = D_{zz} \frac{\partial^2 \langle c_{A\beta}\rangle^{\beta}}{\partial z^2} \tag{8}$$

in which the dispersion coefficient is given by

$$D_{zz} = \mathscr{D}_{\beta}\left\{\frac{1}{1+k} + \frac{1}{48}\left(\frac{\langle v_z\rangle^{\beta} r_o}{\mathscr{D}_{\beta}}\right)^2 \left[\frac{1+5k}{(1+k)^2}\right]\right\} \tag{9}$$

and the dimensionless equilibrium coefficient is defined by

$$k = 2K_{eq}/r_o \tag{10}$$

Develop the constraint associated with the approximation given by Eq. 7 and solve the closure problem in order to show that the dispersion coefficient is given by Eq. 9.

3-11. Re-examine the boundary value problem given in Problem 3-10 from the perspective of Golay (1958) who eliminated the source term, $\partial\langle c_{A\beta}\rangle^{\beta}/\partial t$, in the closure problem by means of the approximation

$$\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial t} \cong -u_p \frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial z} \tag{1}$$

This led to a closure problem containing the single source term, $\partial\langle c_{A\beta}\rangle^{\beta}/\partial z$, and an area averaged transport equation containing the mixed derivative, $\partial^2\langle c_{A\beta}\rangle^{\beta}/\partial t\,\partial z$. This was represented in the manner indicated by Eq. 7 in Problem 3-10 in order to obtain a convective-dispersion equation of the form

$$\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial t} + \frac{\langle v_z\rangle^{\beta}}{1+k}\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial z} = D_{zz}\frac{\partial^2\langle c_{A\beta}\rangle^{\beta}}{\partial z^2} \tag{2}$$

In this case the dispersion coefficient is given by

$$D_{zz} = \mathscr{D}_{\beta}\left\{\frac{1}{1+k} + \frac{1}{48}\left(\frac{\langle v_z\rangle^{\beta} r_o}{\mathscr{D}_{\beta}}\right)^2\left[\frac{1+6k+11k^2}{(1+k)^3}\right]\right\} \tag{3}$$

and you are asked to develop this result beginning with the boundary value problem given in Problem 3-10.

3-12. If a pulse of species A is injected into a capillary tube in which an instantaneous, heterogeneous chemical reaction takes place, the transport process is described by the following boundary value problem

$$\frac{\partial c_{A\beta}}{\partial t} + v_z\frac{\partial c_{A\beta}}{\partial z} = \mathscr{D}_{\beta}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_{A\beta}}{\partial r}\right) + \frac{\partial^2 c_{A\beta}}{\partial z^2}\right] \tag{1}$$

I.C. $$c_{A\beta} = \mathscr{F}(r,z), \qquad t=0 \tag{2}$$

B.C.1 $$c_{A\beta} = 0, \qquad r=r_o \tag{3}$$

First derive the area averaged transport equation, and then develop the quasi-steady closure problem for the case in which the spatial deviation concentration is constrained by $\tilde{c}_{A\beta} << \langle c_{A\beta}\rangle^{\beta}$. This condition exists when the mass transfer process between the fluid and the wall is essentially complete; nevertheless, the analysis leads to some interesting results. Show that the closed form of the area averaged transport equation can be expressed as

$$\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial t} + \frac{5}{3}\langle v_z\rangle^{\beta}\frac{\partial\langle c_{A\beta}\rangle^{\beta}}{\partial z} = D_{zz}\frac{\partial^2\langle c_{A\beta}\rangle^{\beta}}{\partial z^2} - \frac{2k_{loc}}{r_o}\langle c_{A\beta}\rangle^{\beta} \tag{4}$$

Here the local mass transfer coefficient is given by

$$k_{loc} = \frac{4\mathscr{D}_\beta}{r_o} \tag{5}$$

and the dispersion coefficient takes the form

$$D_{zz} = \mathscr{D}_\beta \left[1 + \left(\frac{\langle v_z \rangle^\beta r_o}{12\mathscr{D}_\beta} \right)^2 \right] \tag{6}$$

These results are slightly different from those determined by Paine *et al.* (1983) by direct numerical solution of the boundary value problem. Their studies led to

$$k_{loc} \approx \frac{3\mathscr{D}_\beta}{r_o} \tag{7}$$

$$D_{zz} \approx \mathscr{D}_\beta \left[1 + \left(\frac{\langle v_z \rangle^\beta r_o}{14\mathscr{D}_\beta} \right)^2 \right] \tag{8}$$

In addition, Paine *et al.* (1983) found that the convective transport was augmented by a factor of 1.57 while Eq. 4 indicates a factor of 1.67. The differences are probably due to the fact that the numerical method was not very accurate when the concentration was small enough so that $\tilde{c}_{A\beta} << \langle c_{A\beta} \rangle^\beta$.

3-13. Consider the problem of dispersion and adsorption (Whitaker, 1997) in porous media as described by the following governing differential equation and boundary condition

$$\frac{\partial c_{A\beta}}{\partial t} + \nabla \cdot (\mathbf{v}_\beta c_{A\beta}) = \nabla \cdot \left(\mathscr{D}_\beta \nabla c_{A\beta} \right), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C. $$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_{A\beta} = K_{eq} \frac{\partial c_{A\beta}}{\partial t}, \quad \text{at the } \beta\text{-}\sigma \text{ interface} \tag{2}$$

Consider only homogeneous porous media so that the porosity can be treated as a constant, and assume that the flow is incompressible so that the continuity equation takes the form

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{3}$$

The σ-phase is rigid, thus the no-slip condition can be imposed at the β-σ interface.

In this problem you are asked to develop the volume averaged form of the convective-diffusion equation along with the closure problem that will allow you

to predict the coefficients which appear in that equation. Show that the following constraints

$$\frac{\mathscr{D}_\beta t^*}{\ell_\beta^2} >> 1, \qquad \frac{\mathscr{D}_\beta t^*}{\ell_\beta K_{eq}} >> 1 \tag{4}$$

must be satisfied in order that the closure problem can be treated as quasi-steady.

3-14. If the σ-phase illustrated in Figure 3.1 is taken to be the porous catalyst that was studied in Chapter 1, we have the classic problem of mass transport and reaction in a catalytic packed bed reactor. This situation is illustrated in Figure 3-14 where the porous catalyst has been identified as the σ-region. The governing equations and boundary conditions for this process can be expressed as

$$\frac{\partial c_{A\beta}}{\partial t} + \nabla\cdot(\mathbf{v}_\beta c_A) = \nabla\cdot(\mathscr{D}_\beta \nabla c_{A\beta}), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1 $$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_{A\beta} = -\varepsilon_\gamma \mathbf{D}_{eff}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma, \quad \text{at the } \beta\text{-}\sigma \text{ boundary} \tag{2}$$

B.C.2 $$c_{A\beta} = \langle c_{A\gamma}\rangle^\gamma, \quad \text{at the } \beta\text{-}\sigma \text{ boundary} \tag{3}$$

$$\varepsilon_\gamma \frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma \mathbf{D}_{eff}\cdot\nabla\langle c_{A\gamma}\rangle^\gamma\right) - a_v k\langle c_{A\gamma}\rangle^\gamma, \quad \text{in the } \sigma\text{-region} \tag{4}$$

Here we have used $c_{A\beta}$ to represent the point concentration in the β-phase, and $\langle c_{A\gamma}\rangle^\gamma$ to represent the intrinsic volume averaged concentration in the γ-phase that is contained in the σ-region. The boundary conditions are based on the studies of Ochoa-Tapia and Whitaker (1995a-b, 1997, 1998a-b) who have developed jump conditions for the boundary between a porous medium and a homogeneous fluid. If the principle of local mass equilibrium is valid, the mass transport process in a packed bed catalytic reactor can be described by a one-equation model. In terms of the averaging volume shown in Figure 3-14, the average concentration in the one-equation model is defined by

$$\{c_A\} = \frac{1}{\mathscr{V}}\int_{V_\beta} c_{A\beta}\, dV + \frac{1}{\mathscr{V}}\int_{V_\sigma}\langle c_{A\gamma}\rangle^\gamma\, dV \tag{5}$$

and you are asked to derive the governing differential equation for $\{c_A\}$.

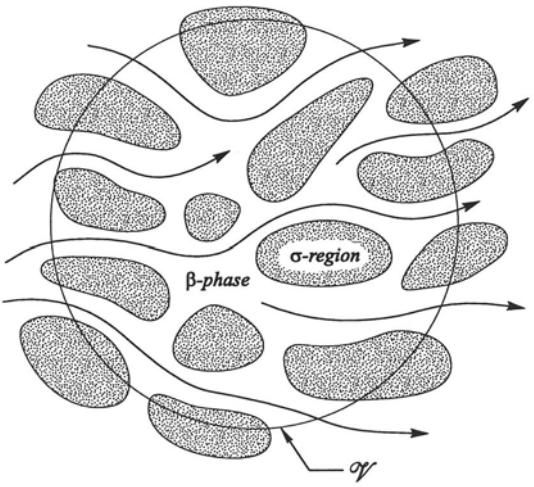

Figure 3-14. Mass transport and reaction in a packed bed catalytic reactor

3-15. In order that a one-equation model can be used to represent the mass transport process in the packed bed catalytic reactor described in Problem 3-14, the principle of local mass equilibrium must be valid. In this problem, you are asked to develop the constraints associated with this condition.

3-16. When the constraints associated with local mass equilibrium *are not* valid, the one-equation model for a packed bed catalytic reactor must be replaced with a two-equation model. In this problem you are asked to develop the two-equation model associated with Eqs. 1 through 4 of Problem 3-14. In order to simplify the nomenclature, the original problem should be expressed as

$$\frac{\partial c_{A\beta}}{\partial t} + \nabla\cdot(\mathbf{v}_\beta c_{A\beta}) = \nabla\cdot(\mathscr{D}_\beta \nabla c_{A\beta}), \quad \text{in the } \beta\text{-phase} \tag{1}$$

B.C.1
$$-\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_{A\beta} = -\mathbf{D}_\sigma\cdot\nabla c_{A\sigma}, \quad \text{at the } \beta\text{-}\sigma \text{ boundary} \tag{2}$$

B.C.2
$$c_{A\beta} = c_{A\sigma}, \quad \text{at the } \beta\text{-}\sigma \text{ boundary} \tag{3}$$

$$\varepsilon_\gamma \frac{\partial c_{A\sigma}}{\partial t} = \nabla\cdot(\mathbf{D}_\sigma\cdot\nabla c_{A\sigma}) - a_v k c_{A\sigma}, \quad \text{in the } \sigma\text{-region} \tag{4}$$

Chapter 4

Single-Phase Flow in Homogeneous Porous Media: Darcy's Law

The process of single-phase flow in rigid porous media is of importance to a variety of engineers and scientists who are concerned with problems ranging from the financial aspects of oil movement in petroleum reservoirs to the social problems of groundwater flows in polluted aquifers. In this chapter we will explore the simplest aspect of this problem i.e., incompressible flow in homogeneous porous media, while in Chapter 5 we will explore the problem of flow in heterogeneous media. Our treatment of homogeneous porous media is based on prior studies by Whitaker (1986d), Barrère *et al.* (1992), and Quintard and Whitaker (1994c).

4.1 Volume Averaging

The physical process under consideration is that of single-phase flow in a rigid porous medium, such as we have illustrated in terms of the β-σ system shown in Figure 4.1.

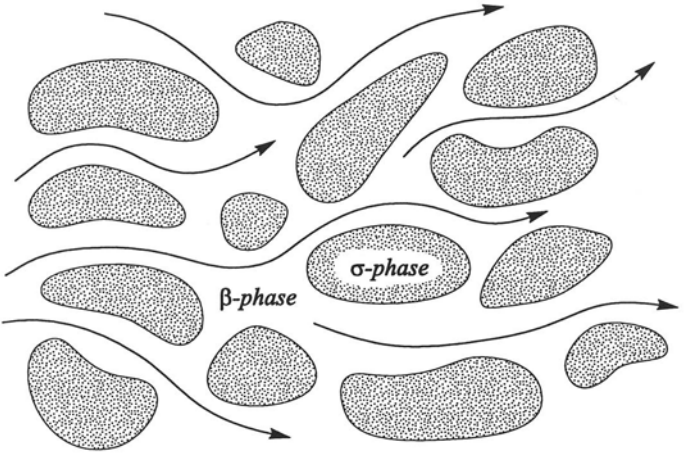

Figure 4.1. Flow in a rigid porous medium

The boundary value problem describing flow in the macroscopic region shown in Figure 4.2 is given by

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta, \quad \text{in the } \beta\text{-phase} \tag{4.1-1}$$

$$\nabla \cdot \mathbf{v}_\beta = 0, \quad \text{in the } \beta\text{-phase} \tag{4.1-2}$$

B.C.1
$$\mathbf{v}_\beta = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{4.1-3}$$

B.C.2
$$\mathbf{v}_\beta = \mathbf{f}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{4.1-4}$$

Here $\mathscr{A}_{\beta\sigma}$ represents the area of the β-σ interface contained within the macroscopic region illustrated in Figure 4.2, while $\mathscr{A}_{\beta e}$ represents the β-phase entrances and exits associated with that region.

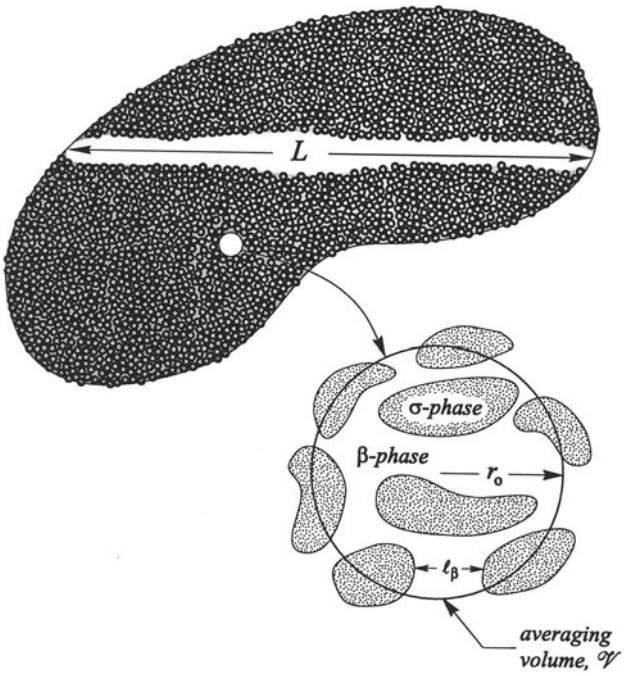

Figure 4.2. Macroscopic region and local averaging volume

4.1.1 CONTINUITY EQUATION

We begin the averaging process with the continuity equation and form the superficial average of Eq. 4.1-2 to obtain

$$\frac{1}{\mathscr{V}}\int_{V_\beta} \nabla\cdot\mathbf{v}_\beta\, dV \;=\; \langle\nabla\cdot\mathbf{v}_\beta\rangle \;=\; 0 \tag{4.1-5}$$

Use of the averaging theorem yields

$$\langle\nabla\cdot\mathbf{v}_\beta\rangle \;=\; \nabla\cdot\langle\mathbf{v}_\beta\rangle + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta\, dA \;=\; 0 \tag{4.1-6}$$

and the boundary condition given by Eq. 4.1-3 allows us to express the superficial average form of the continuity equation as

$$\nabla\cdot\langle\mathbf{v}_\beta\rangle \;=\; 0 \tag{4.1-7}$$

The fact that the *superficial average* velocity, $\langle\mathbf{v}_\beta\rangle$, is solenoidal encourages its use as the preferred representation of the macroscopic or volume averaged velocity field. This situation is quite different from that encountered in Chapters 1, 2, and 3, where we suggested that *intrinsic average* concentrations and temperatures were the preferred dependent variables. We will also need the continuity equation expressed in terms of the intrinsic average velocity, $\langle\mathbf{v}_\beta\rangle^\beta$, thus we use the relation between the superficial velocity and the intrinsic velocity

$$\langle\mathbf{v}_\beta\rangle \;=\; \varepsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta \tag{4.1-8}$$

to obtain an alternate form of the continuity equation given by

$$\nabla\cdot\langle\mathbf{v}_\beta\rangle^\beta \;=\; -\varepsilon_\beta^{-1}\nabla\varepsilon_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta \tag{4.1-9}$$

We have already used this form of the continuity equation in our study of the closure problem for passive dispersion, and we will use it again in our study of the closure problem for single-phase flow in rigid porous media.

4.1.2 MOMENTUM EQUATION

The superficial average of Stokes' equations can be expressed as

$$0 \;=\; -\langle\nabla p_\beta\rangle + \langle\rho_\beta\mathbf{g}\rangle + \langle\mu_\beta\nabla\cdot\nabla\mathbf{v}_\beta\rangle \tag{4.1-10}$$

Variations of the density and viscosity within the averaging volume can be ignored, allowing us to write Eq. 4.1-10 in the form

$$0 \;=\; -\langle\nabla p_\beta\rangle + \varepsilon_\beta\rho_\beta\mathbf{g} + \mu_\beta\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle \tag{4.1-11}$$

We begin by directing our attention to the first term, and make use of the averaging theorem to represent the average of the gradient of the pressure as

$$\langle \nabla p_\beta \rangle = \nabla \langle p_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} p_\beta \, dA \tag{4.1-12}$$

While the *superficial average velocity* is generally preferred in the analysis of flow in porous media, the *intrinsic average pressure* is used exclusively because it more closely corresponds to the measured value or the value that one could impose as a boundary condition. To obtain the intrinsic average pressure, we use

$$\langle p_\beta \rangle = \varepsilon_\beta \langle p_\beta \rangle^\beta \tag{4.1-13}$$

in order to express Eq. 4.1-12 as

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \langle p_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} p_\beta \, dA \tag{4.1-14}$$

As in our studies of heat and mass transfer, we will need to decompose the point values of the pressure and velocity according to

$$p_\beta = \langle p_\beta \rangle^\beta + \tilde{p}_\beta \,, \qquad \mathbf{v}_\beta = \langle \mathbf{v}_\beta \rangle^\beta + \tilde{\mathbf{v}}_\beta \tag{4.1-15}$$

and the use of the first of these in Eq. 4.1-14 leads to the *non-local form* for the average of the pressure gradient

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \langle p_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle p_\beta \rangle^\beta dA + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta \, dA \tag{4.1-16}$$

To develop the *local form*, we remove the average pressure from the area integral according to the development given in Sec. 1.3, and this leads to

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle p_\beta \rangle^\beta dA = \left\{ \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA \right\} \langle p_\beta \rangle^\beta = - (\nabla \varepsilon_\beta) \langle p_\beta \rangle^\beta \tag{4.1-17}$$

Substitution of this result into Eq. 4.1-16 provides the following expression for the average of a gradient that we have used in previous chapters:

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta \, dA \tag{4.1-18}$$

One should remember that the length-scale constraints associated with this result are given by

$$\ell_\beta \ll r_o , \quad r_o^2 \ll L_\varepsilon L_{p1} \tag{4.1-19}$$

in which L_ε and L_{p1} are defined by the estimates (see Sec. 1.3.2)

$$\nabla\varepsilon_\beta = \mathbf{O}\left(\Delta\varepsilon_\beta / L_\varepsilon\right) , \quad \nabla\nabla\langle p_\beta\rangle^\beta = \mathbf{O}\left[\nabla\langle p_\beta\rangle^\beta / L_{p1}\right] \tag{4.1-20}$$

Substitution of Eq. 4.1-18 into Eq. 4.1-11 provides

$$0 = -\varepsilon_\beta\nabla\langle p_\beta\rangle^\beta - \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{p}_\beta\, dA + \varepsilon_\beta\rho_\beta\mathbf{g} + \mu_\beta\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle \tag{4.1-21}$$

and we are ready to turn our attention to the viscous term. Application of the averaging theorem yields

$$\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle = \nabla\cdot\langle\nabla\mathbf{v}_\beta\rangle + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\nabla\mathbf{v}_\beta\, dA \tag{4.1-22}$$

and we now repeat the procedure used with the pressure gradient to obtain

$$\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle = \nabla\cdot\langle\nabla\mathbf{v}_\beta\rangle - \nabla\varepsilon_\beta\cdot\nabla\langle\mathbf{v}_\beta\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\nabla\tilde{\mathbf{v}}_\beta\, dA \tag{4.1-23}$$

Here we have used the velocity decomposition given by the second of Eqs. 4.1-15, and we have removed $\nabla\langle\mathbf{v}_\beta\rangle^\beta$ from the area integral on the basis of the length-scale constraints given by

$$\ell_\beta \ll r_o , \quad r_o^2 \ll L_\varepsilon L_{v2} \tag{4.1-24}$$

The characteristic length L_ε is defined by the first of Eqs. 4.1-20 while the new characteristic length L_{v2} is defined by the estimate

$$\nabla\nabla\nabla\langle\mathbf{v}_\beta\rangle^\beta = \mathbf{O}\left[\nabla\nabla\langle\mathbf{v}_\beta\rangle^\beta / L_{v2}\right] \tag{4.1-25}$$

A second application of the averaging theorem to Eq. 4.1-23 provides

$$\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle = \nabla^2\langle\mathbf{v}_\beta\rangle + \nabla\cdot\left[\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathbf{v}_\beta\, dA\right] - \nabla\varepsilon_\beta\cdot\nabla\langle\mathbf{v}_\beta\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\nabla\tilde{\mathbf{v}}_\beta\, dA \tag{4.1-26}$$

and on the basis of the no-slip condition given by Eq. 4.1-3 this can be simplified to

$$\langle\nabla\cdot\nabla\mathbf{v}_\beta\rangle = \nabla^2\langle\mathbf{v}_\beta\rangle - \nabla\varepsilon_\beta\cdot\nabla\langle\mathbf{v}_\beta\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\nabla\tilde{\mathbf{v}}_\beta\, dA \tag{4.1-27}$$

We are now ready use this result along with Eq. 4.1-18 in Eq. 4.1-11 to obtain

$$0 = -\varepsilon_\beta \nabla\langle p_\beta\rangle^\beta + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \nabla^2\langle \mathbf{v}_\beta\rangle - \mu_\beta \nabla\varepsilon_\beta \cdot \nabla\langle \mathbf{v}_\beta\rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla\tilde{\mathbf{v}}_\beta\right) dA \tag{4.1-28}$$

The superficial velocity can be eliminated by using Eq. 4.1-8, and the result can be arranged in the form

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta\left(\nabla^2\langle \mathbf{v}_\beta\rangle^\beta + \varepsilon_\beta^{-1}\nabla\varepsilon_\beta \cdot \nabla\langle \mathbf{v}_\beta\rangle^\beta + \varepsilon_\beta^{-1}\langle \mathbf{v}_\beta\rangle^\beta \nabla^2\varepsilon_\beta\right) + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla\tilde{\mathbf{v}}_\beta\right) dA \tag{4.1-29}$$

If the porosity is assumed to be constant, the terms involving gradients of ε_β can be discarded; however, it would be more appropriate to impose the restrictions

$$\varepsilon_\beta^{-1}\nabla\varepsilon_\beta \cdot \nabla\langle \mathbf{v}_\beta\rangle^\beta << \nabla^2\langle \mathbf{v}_\beta\rangle^\beta, \qquad \varepsilon_\beta^{-1}\langle \mathbf{v}_\beta\rangle^\beta \nabla^2\varepsilon_\beta << \nabla^2\langle \mathbf{v}_\beta\rangle^\beta \tag{4.1-30}$$

and leave it as an exercise for the reader to develop the appropriate constraints (see Problem 4-1). Given these restrictions, we can express Eq. 4.1-29 as

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2\langle \mathbf{v}_\beta\rangle^\beta + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla\tilde{\mathbf{v}}_\beta\right) dA \tag{4.1-31}$$

The third term in this result is generally referred to as the *Brinkman correction* (Brinkman, 1947) and it is easy to show that it is negligible compared to the last term for homogeneous porous media. Often the Brinkman correction is retained to allow for the use of boundary conditions involving continuity of the volume averaged velocity; however, such boundary conditions are usually imposed in regions where $L_\varepsilon \approx L_v$ and under those circumstances the restrictions given by Eqs. 4.1-30 usually fail. In addition, the length-scale constraints given by Eqs. 4.1-19 and 4.1-24 generally fail in those regions and the entire analysis leading to Eq. 4.1-31 needs to be reconsidered. This has been done by Ochoa-Tapia and Whitaker (1995a-b) who used the non-local form of the volume averaged Stokes' equations to develop a jump condition that is applicable at the boundary between a porous medium and a homogeneous fluid.

In order to demonstrate that the Brinkman correction is negligible under the circumstances that have been imposed during the derivation of Eq. 4.1-31, we need to develop estimates of the last two terms in that equation. Since the spatial deviation

velocity undergoes significant variations over the small length-scale ℓ_β, we have the estimate

$$\nabla\tilde{\mathbf{v}}_\beta = \mathbf{O}\left(\tilde{\mathbf{v}}_\beta/\ell_\beta\right) \tag{4.1-32}$$

and on the basis of the no-slip condition we know that the magnitude of $\tilde{\mathbf{v}}_\beta$ is given by

$$\tilde{\mathbf{v}}_\beta = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta\right) \tag{4.1-33}$$

This means that the area integral in Eq. 4.1-31 can be estimated as

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA = \mathbf{O}\left(\frac{\mu_\beta\langle \mathbf{v}_\beta\rangle^\beta}{\ell_\beta^2}\right) \tag{4.1-34}$$

in which we have made use of the fact that $A_{\beta\sigma}/\mathscr{V}$ is on the order of ℓ_β^{-1} and we have assumed that $\tilde{p}_\beta$ is not greater than $\mu_\beta\nabla\tilde{\mathbf{v}}_\beta$. Our estimate of the Brinkman correction is given by (see Problem 4-2)

$$\mu_\beta\nabla^2\langle \mathbf{v}_\beta\rangle^\beta = \mathbf{O}\left(\frac{\mu_\beta\langle \mathbf{v}_\beta\rangle^\beta}{L_{v1}L_v}\right) \tag{4.1-35}$$

This estimate leads us to conclude that

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA >> \mu_\beta\nabla^2\langle \mathbf{v}_\beta\rangle \tag{4.1-36}$$

except in regions where extremely large gradients in the volume averaged velocity occur. In these regions Eq. 4.1-31 cannot be considered to be a valid form of the volume averaged Stokes' equations. This means that the Brinkman correction is unimportant for flow in homogeneous porous media and could be discarded on the basis of the length-scale constraints that have been imposed in the development of Eq. 4.1-31. However, at this point we will retain the generality of Eq. 4.1-31 and remind the reader that it is constrained by Eqs. 4.1-19, 4.1-24, and 4.1-30.

4.2 Closure

In order to develop the closed form of Eq. 4.1-31, we need to develop the governing differential equations and boundary conditions for $\tilde{\mathbf{v}}_\beta$ and $\tilde{p}_\beta$. This will lead us to a local closure problem in terms of *closure variables* and a method of predicting the permeability tensor that appears in Darcy's law.

4.2.1 BOUNDARY CONDITION

The no-slip boundary condition plays a key role in the closed form of Eq. 4.1-31, thus we begin our analysis with Eq. 4.1-3 and make use of the velocity decomposition represented by the second of Eqs. 4.1-15 to obtain

B.C.1
$$\tilde{\mathbf{v}}_\beta = \underbrace{-\langle \mathbf{v}_\beta \rangle^\beta}_{\text{source}}, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{4.2-1}$$

Here we have identified the intrinsic average velocity, evaluated at the β-σ interface, as a *source*, and we will soon see that it is the dominant source in this closure problem. It is of some interest to note that the no-slip condition did not have any dramatic impact on the volume averaged form of the Stokes' equations when it was imposed on Eq. 4.1-26. However, the situation in the closure problem is quite different, and we shall see in the following paragraphs that Eq. 4.2-1 *controls* the form of the closure problem.

4.2.2 CONTINUITY EQUATION

In order to develop the continuity equation for $\tilde{\mathbf{v}}_\beta$, we recall Eq. 4.1-2

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{4.2-2}$$

along with the intrinsic average form given by Eq. 4.1-9

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta = -\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{4.2-3}$$

Subtracting the latter from the former provides the continuity equation for the spatial deviation velocity

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = \underbrace{\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta}_{\text{source}} \tag{4.2-4}$$

Since the terms on the left hand side of this result are on the order of order $\langle \mathbf{v}_\beta \rangle^\beta / \ell_\beta$ and the term on the right hand is on the order of $\langle \mathbf{v}_\beta \rangle^\beta / L_\varepsilon$, we can see that the source will have a negligible influence on the $\tilde{\mathbf{v}}_\beta$ – field. This allows us to write the continuity equation as

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \tag{4.2-5}$$

and we are now ready to move on to the momentum equation for $\tilde{\mathbf{v}}_\beta$.

4.2.3 MOMENTUM EQUATION

Here we follow the same procedure indicated by Eqs. 4.2-2 through 4.2-5 and recall the point and volume averaged momentum equations given by

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \tag{4.2-6}$$

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2\langle \mathbf{v}_\beta\rangle^\beta + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA \tag{4.2-7}$$

Subtracting the second of these from the first provides the spatial deviation momentum equation that takes the form

$$0 = -\nabla\tilde{p}_\beta + \mu_\beta\nabla^2\tilde{\mathbf{v}}_\beta - \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA \tag{4.2-8}$$

At this point we have dealt with Eqs. 4.1-1 through 4.1-3, and we need only construct a boundary condition associated with Eq. 4.1-4 in order to complete the statement of the boundary value problem for the spatial deviation pressure and velocity.

4.2.4 CLOSURE PROBLEM

We summarize the closure problem, in terms of $\tilde{p}_\beta$ and $\tilde{\mathbf{v}}_\beta$, in a form analogous to Eqs. 4.1-1 through 4.1-4, but with an additional constraint on the average of $\tilde{\mathbf{v}}_\beta$.

$$0 = -\nabla\tilde{p}_\beta + \mu_\beta\nabla^2\tilde{\mathbf{v}}_\beta - \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA \tag{4.2-9}$$

$$\nabla\cdot\tilde{\mathbf{v}}_\beta = 0 \tag{4.2-10}$$

B.C.1
$$\tilde{\mathbf{v}}_\beta = -\underbrace{\langle \mathbf{v}_\beta\rangle^\beta}_{\text{source}}, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{4.2-11}$$

B.C.2
$$\tilde{\mathbf{v}}_\beta = \underbrace{\mathbf{g}(\mathbf{r},t)}_{\text{source}}, \quad \text{at } \mathscr{A}_{\beta e} \tag{4.2-12}$$

Average:
$$\langle\tilde{\mathbf{v}}_\beta\rangle^\beta = 0 \tag{4.2-13}$$

In Sec. 1.3 we discussed the matter of setting the average of a spatial deviation equal to zero; however, we did not use that condition in the studies presented in Chapters 1, 2, and 3. For this particular problem Eq. 4.2-13 is *essential*; however, we *need not impose* this type of condition on $\tilde{p}_\beta$, and we shall see why in subsequent paragraphs.

In order to develop the length-scale constraints associated with Eq. 4.2-13, we return to Eq. 3.2-23b in order to express the average of the deviation as

$$\langle\tilde{\mathbf{v}}_\beta\rangle^\beta = -\langle \mathbf{y}_\beta\rangle^\beta\cdot\nabla\langle\mathbf{v}_\beta\rangle^\beta - \tfrac{1}{2}\langle\mathbf{y}_\beta\mathbf{y}_\beta\rangle^\beta : \nabla\nabla\langle\mathbf{v}_\beta\rangle^\beta - \ldots. \tag{4.2-14}$$

Since the magnitude of $\tilde{\mathbf{v}}_\beta$ is on the order of $\langle\mathbf{v}_\beta\rangle^\beta$, we know that Eq. 4.2-13 is the mathematical consequence of the inequality given by

$$\langle \tilde{\mathbf{v}}_\beta \rangle^\beta \ll \langle \mathbf{v}_\beta \rangle^\beta \tag{4.2-15}$$

This requires that the following two length-scale constraints be satisfied

$$\langle \mathbf{y}_\beta \rangle^\beta \ll L_v \qquad r_o^2 \ll L_{v1} L_v \tag{4.2-16}$$

From the work of Quintard and Whitaker (1994a-e) on disordered porous media, we know that

$$\langle \mathbf{y}_\beta \rangle^\beta \ll \ell_\beta , \qquad \textit{when} \quad r_o >> \ell_\beta \tag{4.2-17}$$

and this means that the first of the inequalities given by Eqs. 4.2-16 is easily satisfied. The second of those inequalities presents a problem only in regions where the average velocity undergoes extremely rapid changes (Ochoa-Tapia and Whitaker, 1995a-b).

The boundary condition given by Eq. 4.2-12 is a reminder of what we *do not know* about the $\tilde{\mathbf{v}}_\beta$ - field rather than what we *do know*. However, we do know that $\mathbf{g}(\mathbf{r},t)$ is on the order of $\langle \mathbf{v}_\beta \rangle^\beta$, and we do know that the boundary condition given by Eq. 4.2-11 will influence the spatial deviation fields only in a region of thickness ℓ_β at the boundary of the macroscopic region. This suggests that the boundary condition at $\mathscr{A}_{\beta e}$ can be ignored if we can find a suitable replacement.

4.2.5 LOCAL CLOSURE PROBLEM

Obviously we do not want to solve Eqs. 4.2-9 through 4.2-12 in the macroscopic region illustrated in Figure 4.2; instead, we wish to solve the closure problem in some representative region such as the one illustrated in Figure 4.3. To do so, we must be willing to discard the boundary condition given by Eq. 4.2-12 and replace it with some *local condition* associated with the representative region shown in Figure 4.3. This naturally leads us to treat the representative region as a unit cell in a spatially periodic model of a porous medium so that our closure problem takes the form

$$0 = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA \tag{4.2-18}$$

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \tag{4.2-19}$$

B.C.1 $$\tilde{\mathbf{v}}_\beta = -\underbrace{\langle \mathbf{v}_\beta \rangle^\beta}_{\text{source}}, \quad \text{at } A_{\beta\sigma} \tag{4.2-20}$$

Periodicity: $$\tilde{p}_\beta(\mathbf{r}+\ell_i) = \tilde{p}_\beta(\mathbf{r}), \quad \tilde{\mathbf{v}}_\beta(\mathbf{r}+\ell_i) = \tilde{\mathbf{v}}_\beta(\mathbf{r}), \quad i = 1,2,3 \tag{4.2-21}$$

Average: $$\langle \tilde{\mathbf{v}}_\beta \rangle^\beta = 0 \tag{4.2-22}$$

The periodicity condition is consistent with a spatially periodic model *only* if the source in Eq. 4.2-11 can be considered as a constant or is itself spatially periodic. A Taylor

series expansion for $\langle \mathbf{v}_\beta \rangle^\beta$ about the centroid of the representative region shown in Figure 4.3 takes the form

$$\langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} = \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \mathbf{y}_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \ldots . \tag{4.2-23}$$

and from this we can see that $\langle \mathbf{v}_\beta \rangle^\beta$ can be treated as a constant in the local closure problem provided that the following length-scale constraint is satisfied.

$$r_\circ \ll L_v \tag{4.2-24}$$

Here we have assumed that the characteristic length of the representative unit cell will always be on the order of $r_\circ$ or smaller than $r_\circ$.

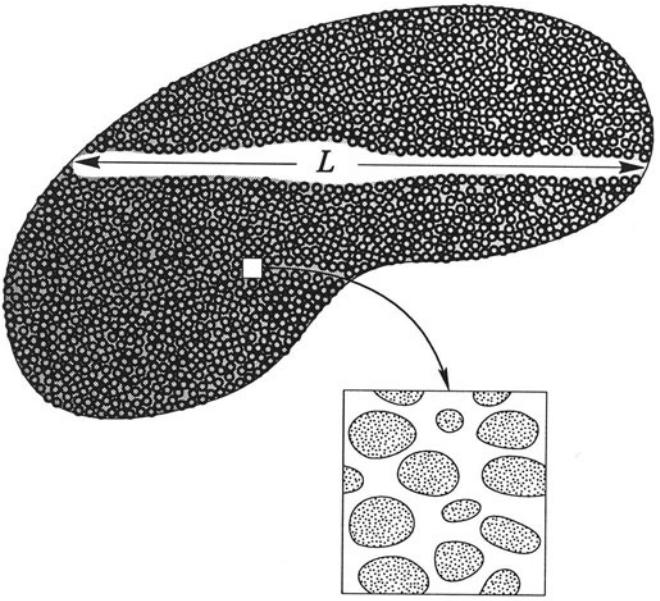

Figure 4.3. Representative region of the β-σ system

Given the single, constant source in the boundary value problem for $\tilde{p}_\beta$ and $\tilde{\mathbf{v}}_\beta$, we propose a solution for the spatial deviation velocity and pressure of the form

$$\tilde{\mathbf{v}}_\beta = \mathbf{B}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \psi_\beta \tag{4.2-25}$$

$$\tilde{p}_\beta = \mu_\beta \mathbf{b}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mu_\beta \xi_\beta \tag{4.2-26}$$

If we think of ψ_β and ξ_β as arbitrary functions, we are free to specify $\mathbf{B}_\beta$ and $\mathbf{b}_\beta$ in any way we wish, thus we can specify these two function by means of the following closure problem

$$0 = -\nabla\mathbf{b}_\beta + \nabla^2\mathbf{B}_\beta - \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\mathbf{b}_\beta + \nabla\mathbf{B}_\beta\right)dA \tag{4.2-27a}$$

$$\nabla\cdot\mathbf{B}_\beta = 0 \tag{4.2-27b}$$

B.C.1 $$\mathbf{B}_\beta = -\mathbf{I}, \quad \text{at } A_{\beta\sigma} \tag{4.2-27c}$$

Periodicity: $$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{B}_\beta(\mathbf{r}+\ell_i) = \mathbf{B}_\beta(\mathbf{r}), \quad i = 1,2,3 \tag{4.2-27d}$$

Average: $$\langle\mathbf{B}_\beta\rangle^\beta = 0 \tag{4.2-27e}$$

It will be left as an exercise for the reader to show that when Eqs. 4.2-25 and 4.2-27 are used in the closure problem given by Eqs. 4.2-18 through 4.2-22, one can prove that the vector ψ_β is *zero* and that the scalar ξ_β is a *constant* (see Problem 4-3). Since the constant ξ_β will not pass through the filter represented by the area integral in Eq. 4.1-31, we can express the spatial deviation velocity and pressure as

$$\tilde{\mathbf{v}}_\beta = \mathbf{B}_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta \tag{4.2-28}$$

$$\tilde{p}_\beta = \mu_\beta\mathbf{b}_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta \tag{4.2-29}$$

These two representations can now be used to develop the closed form of the volume averaged momentum equation.

4.2.6 CLOSED FORM

To obtain the closed form of the volume averaged momentum equation, we first recall Eq. 4.1-31

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta\mathbf{g} + \mu_\beta\nabla^2\langle\mathbf{v}_\beta\rangle^\beta + \frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\tilde{p}_\beta + \mu_\beta\nabla\tilde{\mathbf{v}}_\beta\right)dA \tag{4.2-30}$$

and make use of Eqs. 4.2-28 and 4.2-29 to obtain

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta\mathbf{g} + \mu_\beta\nabla^2\langle\mathbf{v}_\beta\rangle^\beta + \mu_\beta\left\{\frac{1}{V_\beta}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\mathbf{b}_\beta + \nabla\mathbf{B}_\beta\right)dA\right\}\cdot\langle\mathbf{v}_\beta\rangle^\beta \tag{4.2-31}$$

We identify the term in braces as

$$\frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}b_\beta + \nabla\mathbf{B}_\beta\right)dA \;=\; -\varepsilon_\beta\mathbf{K}_\beta^{-1} \tag{4.2-32}$$

where $\mathbf{K}_\beta$ is the *permeability tensor.* Use of this result in Eq. 4.2-31 leads to

$$0 \;=\; -\nabla\langle p_\beta\rangle^\beta + \rho_\beta\mathbf{g} + \mu_\beta\nabla^2\langle\mathbf{v}_\beta\rangle^\beta - \mu_\beta\mathbf{K}_\beta^{-1}\cdot\varepsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta \tag{4.2-33}$$

in which each term represents a force *per unit volume of the fluid,* i.e., Eq. 4.2-33 is an *intrinsic average equation.* This is the preferred form of the momentum equation; however, the *preferred velocity* is the superficial velocity that appears in the continuity equation given by Eq. 4.1-7, and this is the reason why the definition given by Eq. 4.2-32 contains the porosity as a multiplier.

The superficial velocity is related to the intrinsic velocity by $\langle\mathbf{v}_\beta\rangle = \varepsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta$ and this allows us to express Eq. 4.2-33 as

$$\langle\mathbf{v}_\beta\rangle \;=\; -\frac{\mathbf{K}_\beta}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle^\beta - \rho_\beta\mathbf{g}\right) + \mathbf{K}_\beta\cdot\nabla^2\langle\mathbf{v}_\beta\rangle^\beta \tag{4.2-34}$$

This is known as Darcy's law with the *Brinkman correction* and in the literature there is confusion regarding the velocity that appears in the Brinkman correction. Sometimes one finds the intrinsic velocity as indicated in Eq. 4.2-34, while more often one finds the superficial velocity accompanied by a correction known as the *Brinkman viscosity.* This empiricism results from the failure to carefully distinguish between the intrinsic velocity and the superficial velocity. At this point, we note that the length-scale constraints used in the derivation of Eq. 4.2-34 require that

$$\mathbf{K}_\beta\cdot\nabla^2\langle\mathbf{v}_\beta\rangle^\beta \;<<\; \langle\mathbf{v}_\beta\rangle \tag{4.2-35}$$

and under these circumstances it is appropriate to express Eq. 4.2-34 as

$$\langle\mathbf{v}_\beta\rangle \;=\; -\frac{\mathbf{K}_\beta}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle^\beta - \rho_\beta\mathbf{g}\right) \tag{4.2-36}$$

The one-dimensional version of this result was first discovered experimentally by Darcy (1856), and early theoretical explanations were given by Irmai (1958), Matheron (1965), Whitaker (1966), Slattery (1967), and Marle (1967). Equation 4.2-36 forms the basis for the analysis of a wide range of physical phenomena which often require extensions to include the effect of inertia, compressibility, and coupling with heat and mass transfer (Bear, 1972; Greenkorn, 1983; Bear and Bachmat, 1991). The experimental measurement of the permeability is discussed in detail by Dullien (1992), and the theoretical determination is described in the following paragraphs.

4.2.7 SOLUTION OF THE CLOSURE PROBLEM

At this point we are ready to return to the closure problem given by Eqs. 4.2-27, and make use of the definition given by Eq. 4.2-32 so that the closure problem can eventually be expressed in a relatively simple form. Use of Eq. 4.2-32 leads to

$$0 = -\nabla \mathbf{b}_\beta + \nabla^2 \mathbf{B}_\beta + \varepsilon_\beta \mathbf{K}_\beta^{-1} \tag{4.2-37a}$$

$$\nabla \cdot \mathbf{B}_\beta = 0 \tag{4.2-37b}$$

B.C.1 $$\mathbf{B}_\beta = -\mathbf{I}, \quad \text{at } A_{\beta\sigma} \tag{4.2-37c}$$

Periodicity: $$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{B}_\beta(\mathbf{r}+\ell_i) = \mathbf{B}_\beta(\mathbf{r}), \quad i=1,2,3 \tag{4.2-37d}$$

Average: $$\langle \mathbf{B}_\beta \rangle^\beta = 0 \tag{4.2-37e}$$

In order to develop a convenient computational method for the determination of $\mathbf{K}_\beta$, we first define a new tensor $\mathbf{B}_\beta^\circ$ according to

$$\mathbf{B}_\beta^\circ = \mathbf{B}_\beta + \mathbf{I} \tag{4.2-38}$$

and this allows us to express the closure problem as

$$0 = -\nabla \mathbf{b}_\beta + \nabla^2 \mathbf{B}_\beta^\circ + \varepsilon_\beta \mathbf{K}_\beta^{-1} \tag{4.2-39a}$$

$$\nabla \cdot \mathbf{B}_\beta^\circ = 0 \tag{4.2-39b}$$

B.C.1 $$\mathbf{B}_\beta^\circ = 0, \quad \text{at } A_{\beta\sigma} \tag{4.2-39c}$$

Periodicity: $$\mathbf{b}_\beta(\mathbf{r}+\ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{B}_\beta^\circ(\mathbf{r}+\ell_i) = \mathbf{B}_\beta^\circ(\mathbf{r}), \quad i=1,2,3 \tag{4.2-39d}$$

Average: $$\langle \mathbf{B}_\beta^\circ \rangle^\beta = \mathbf{I} \tag{4.2-39e}$$

Our next step is to define a new vector field and a new tensor field according to

$$\mathbf{d}_\beta = \varepsilon_\beta^{-1} \mathbf{b}_\beta \cdot \mathbf{K}_\beta, \quad \mathbf{D}_\beta = \varepsilon_\beta^{-1} \mathbf{B}_\beta^\circ \cdot \mathbf{K}_\beta \tag{4.2-40}$$

In terms of the vector $\mathbf{d}_\beta$ and the tensor $\mathbf{D}_\beta$, we see that Eqs. 4.2-39 take the form

$$0 = -\nabla \mathbf{d}_\beta + \nabla^2 \mathbf{D}_\beta + \mathbf{I} \tag{4.2-41a}$$

$$\nabla \cdot \mathbf{D}_\beta = 0 \tag{4.2-41b}$$

B.C.1 $$\mathbf{D}_\beta = 0, \quad \text{at } A_{\beta\sigma} \tag{4.2-41c}$$

Periodicity: $$\mathbf{d}_\beta(\mathbf{r}+\ell_i) = \mathbf{d}_\beta(\mathbf{r}), \quad \mathbf{D}_\beta(\mathbf{r}+\ell_i) = \mathbf{D}_\beta(\mathbf{r}), \quad i=1,2,3 \tag{4.2-41d}$$

Average: $$\langle \mathbf{D}_\beta \rangle^\beta = \varepsilon_\beta^{-1} \mathbf{K}_\beta \tag{4.2-41e}$$

Here one can see that the constraint on the average of $\tilde{\mathbf{v}}_\beta$, given by Eq. 4.2-13, is *required* in order to determine the permeability tensor as indicated by Eq. 4.2-41e (see Problem 4-4). This situation is very different from our studies in Chapters 1 through 3 where the constraints on the average of the spatial deviation temperature and concentration were generally ignored. The difference results from the difference in the boundary conditions, and this clearly indicates that both governing differential equations and boundary conditions play crucial roles in the structure of volume averaged transport equations. The closure problem given by Eqs. 4.2-41 can be used to prove that the permeability tensor is symmetric and the proof is left as an exercise for the reader (see Problem 4-5).

The solution of Eqs. 4.2-41a through 4.2-41d is straightforward and is identical to methods used to solve Stokes' equations. To see the similarity, we form the scalar product of Eqs. 4.2-41a through 4.2-41d with an arbitrary unit vector, λ, and use the following definitions

$$\mathbf{d}_\beta \cdot \lambda = \tilde{p}, \quad \mathbf{D}_\beta \cdot \lambda = \mathbf{v}, \quad \mathbf{I} \cdot \lambda = -\nabla \langle p \rangle^\beta \tag{4.2-42}$$

so that our closure problem "looks like"

$$0 = -\nabla \tilde{p} + \nabla^2 \mathbf{v} - \nabla \langle p \rangle^\beta \tag{4.2-43a}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{4.2-43b}$$

B.C.1 $$\mathbf{v} = 0, \quad \text{at } A_{\beta\sigma} \tag{4.2-43c}$$

Periodicity: $$\tilde{p}(\mathbf{r}+\ell_i) = \tilde{p}(\mathbf{r}), \quad \mathbf{v}(\mathbf{r}+\ell_i) = \mathbf{v}(\mathbf{r}), \quad i = 1, 2, 3 \tag{4.2-43d}$$

In actual fact, this is the *form* of Stokes' equations that were first solved for periodic systems by Snyder and Stewart (1966), thus we see that the solution of the closure problem given by Eqs. 4.2-41 can be accomplished with routine and well-established methods. After having solved Eqs. 4.2-43, one can make use of Eq. 4.2-41e and the second of Eqs. 4.2-42 to obtain

$$\nu \cdot \mathbf{K}_\beta \cdot \lambda = \varepsilon_\beta \nu \cdot \langle \mathbf{v} \rangle^\beta \tag{4.2-44}$$

and from this one can calculate all the components of the permeability tensor. In thinking about Eqs. 4.2-43, one must remember that the "pressure" has units of *length*, and the "velocity" has units of *length squared.*

4.3 Comparison Between Theory and Experiment

The closure problem represented by Eqs. 4.2-41 has been solved by Eidsath (1981), Zick and Homsy (1982), and others (Synder and Stewart, 1966; Sorenson and Stewart, 1974; Sangani and Acrivos, 1982) for arrays of spheres and cylinders. The results for the permeability can be made dimensionless in terms of the characteristic length $d_p \varepsilon_\beta / (1-\varepsilon_\beta)$ that was used in the study of dispersion in Chapter 3. The comparison

between theory and experiment is conveniently done in terms of the Blake-Kozeny equation (Bird *et al.*, 1960) which makes use of $d_p\varepsilon_\beta/(1-\varepsilon_\beta)$ as a characteristic length. When the Kozeny coefficient is set equal to 5.0 this correlation takes the form

$$\frac{K(1-\varepsilon_\beta)^2}{d_p^2\,\varepsilon_\beta^3} = \frac{1}{180} \tag{4.3-1}$$

It is of some interest to note that this result is identical to the modified Ergun equation (with the Reynolds number equal to zero) proposed by Macdonald *et al.* (1979), who estimated that Eq. 4.3-1 predicts experimental results for unconsolidated porous media with an accuracy of $\pm 50\%$.

In Figure 4.4 we have shown the theoretical calculations of Zick and Homsy (1982) for three different arrays of spheres, along with the experimental studies of

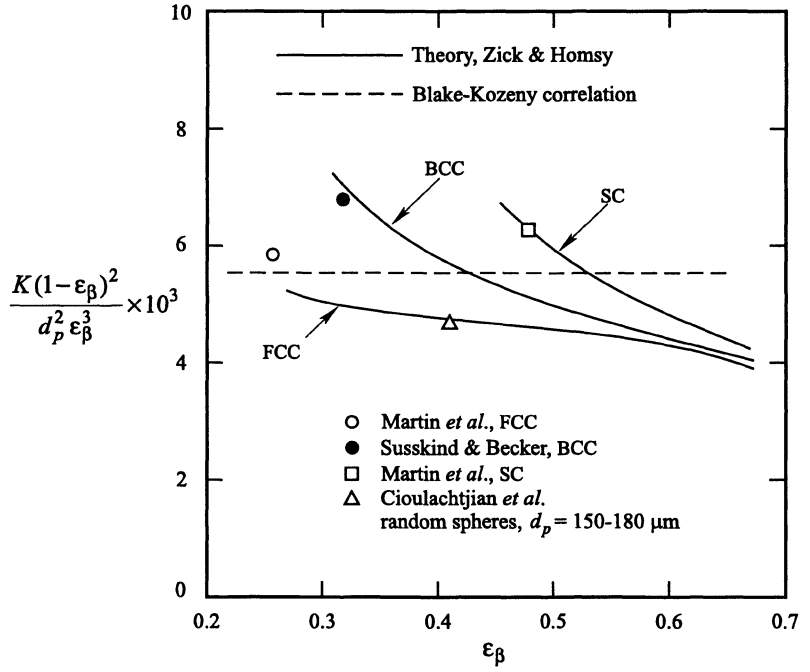

Figure 4.4. Comparison between theory and experiment

Martin *et al.* (1951) for a face-centered cubic array and a simple cubic array, and the results of Susskind and Becker (1967) for a body-centered cubic array. The theoretical results are in excellent agreement with the experimental results for regular arrays of spheres and are consistent with the Blake-Kozeny correlation. The latter does not illustrate the same porosity dependence as the theoretical results; however, the correlation is based on simple scaling arguments and experimental data having a limited

range of porosity. The experimental result of Cioulachtjian *et al.* (1992) for randomly packed spheres is in perfect agreement with the theory for the face-centered cubic array; however, one could hardly have predicted this a priori. Obviously we need to develop methods of characterizing systems that are more sophisticated than simply using the porosity, ε_β, and the characteristic length, $d_p\varepsilon_\beta/(1-\varepsilon_\beta)$.

Eidsath (1981) solved the closure problem for two-dimensional arrays of cylinders, and the comparison with the experimental work of Bergelin *et al.* (1950) is shown in Table 4.1. There we see that the permeability for two-dimensional systems is significantly *lower* than that for three-dimensional systems, and we again see good agreement between theory and experiment.

Table 4.1
Theory and Experiment for Flow Through Arrays of Cylinders
$K(1-\varepsilon_\beta)^2/d_p^2\varepsilon_\beta^3 \times 10^3$

Model	Experiment Bergelin *et al.* (1950)	Theory Eidsath (1981)
Triangular array $\varepsilon_\beta = 0.418$	3.28	3.68
Inclined square array $\varepsilon_\beta = 0.497$	2.31	2.37
Staggered square array $\varepsilon_\beta = 0.497$	2.31	2.27

4.4 Conclusions

In this chapter we have presented a derivation of Darcy's law for homogeneous porous media. Much of the analysis follows directly from our studies in the previous chapters; however, in this case we have seen that the presence of a Dirichlet condition, i.e., the no-slip condition, alters the analysis in some important ways. While the no-slip condition contributes nothing to the form of the volume averaged Stokes' equations that were presented in Sec. 4.2, it *controls* the form of the closure problem that was developed in Sec. 4.3. In addition to providing the only source for the closure problem, it also required that we impose the constraint that the average of the spatial deviation velocity be zero. The comparison between theory and experiment is rather limited, but the results are excellent for the permeabilities determined for regular arrays of spheres. Both the theoretical and experimental results clearly indicate that we need to identify the key structural parameters in order to use the theory to predict permeabilities with confidence.

4.5 Problems*

4-1. Develop the constraints associated with the restrictions that are given by Eq. 4.1-30.

4-2. The arguments leading to Eqs. 4.1-34 through 4.1-36 contain the tacit assumption that the particle diameter is comparable to the pore diameter. While this is acceptable for the typical non-consolidated porous medium, it is not correct for a high porosity porous medium. Consider a porous medium characterized by two length scales, ℓ_σ for the solid phase and ℓ_β for the fluid phase, and explore the possibility that the Brinkman correction may *not* be negligible. In particular, you will want to examine the case for which $1-\varepsilon_\beta << 1$.

4-3. Given the representations for the spatial deviation velocity and pressure

$$\tilde{\mathbf{v}}_\beta = \mathbf{B}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \psi_\beta$$

$$\tilde{p}_\beta = \mu_\beta \mathbf{b}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mu_\beta \xi_\beta$$

and the closure problem represented by Eqs. 4.2-27, prove that the vector ψ_β is zero and that the scalar ξ_β is a constant.

4-4. Use the closure problem given by Eqs. 4.2-41 to predict the Darcy's law permeability for a bundle of parallel capillary tubes having a tube radius of r_o and a porosity of ε_β.

4-5. Prove that the permeability tensor, $\mathbf{K}_\beta$, is symmetric. Do this by using the closure problem given by Eqs. 4.2-41 to develop *two* new closure problems; one for the scalar and vector fields, $s_o = \mathbf{d}_\beta \cdot \lambda$ and $\mathbf{w}_o = \mathbf{D}_\beta \cdot \lambda$, and another for the scalar and vector fields, $s_1 = \mathbf{d}_\beta \cdot \nu$ and $\mathbf{w}_1 = \mathbf{D}_\beta \cdot \nu$ in which λ and ν are arbitrary constant vectors. Form the scalar product of $\mathbf{w}_1$ with the first closure problem, and then construct the intrinsic average of the governing differential equation to obtain

$$0 = -\langle (\nabla \mathbf{w}_o)^T : (\nabla \mathbf{w}_1) \rangle^\beta + \varepsilon_\beta^{-1} \lambda \cdot \mathbf{K}_\beta \cdot \nu$$

A similar result is obtained by forming the scalar product of $\mathbf{w}_o$ with the second closure problem. One can then make use of the relation

$$(\nabla \mathbf{w}_o)^T : (\nabla \mathbf{w}_1) = (\nabla \mathbf{w}_1)^T : (\nabla \mathbf{w}_o)$$

---

* Solutions to all problems are available from the author.

to prove that

$$\lambda \cdot \mathbf{K}_\beta \cdot \nu \;=\; \nu \cdot \mathbf{K}_\beta \cdot \lambda$$

and therefore that $\mathbf{K}_\beta$ is symmetric.

4-6. In the derivation of Darcy's law it was assumed that the rigid solid phase was fixed in space. If the rigid solid phase is moving with a *constant velocity* $\mathbf{u}_\sigma$, relative to some inertial frame, what is the form of Darcy's law relative to that inertial frame?

4-7. In a *compressible* aquifer, the σ-phase particles illustrated in Figure 4-7 undergo a rearrangement when the hydrostatic pressure is increased. This means that the *porous medium is compressible* even though the fluid and solid

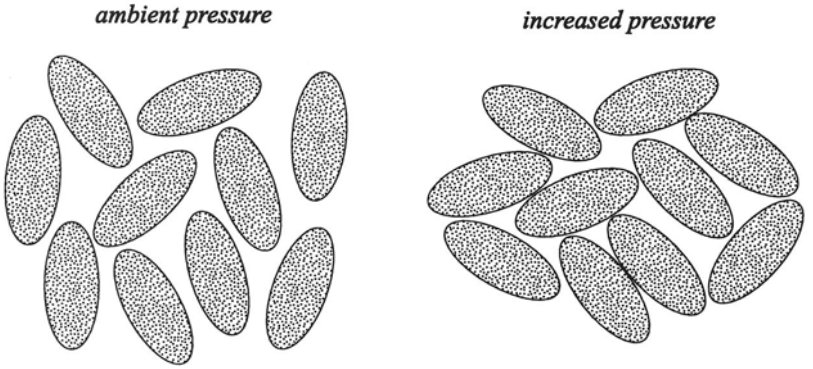

Figure 4-7. Compressible porous medium

phases can be treated as incompressible. In this problem you are asked to develop the volume averaged form of the continuity equation for the porous medium illustrated in Figure 4-7. Even though the fluid density can be treated as a constant, it is convenient to begin with the general form given by

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot (\rho_\beta \mathbf{v}_\beta) \;=\; 0 \tag{1}$$

In order to interchange integration and differentiation in the first term, one must use the general transport theorem

$$\frac{d}{dt} \int_{\mathscr{V}_a(t)} \psi_\beta \, dV \;=\; \int_{\mathscr{V}_a(t)} \frac{\partial \psi_\beta}{\partial t} dV \;+\; \int_{\mathscr{A}_a(t)} \psi_\beta \, \mathbf{w} \cdot \mathbf{n} \, dA \tag{2}$$

in which $\mathscr{V}_a(t)$ represents an arbitrary, time-dependent volume and $\mathscr{A}_a(t)$ represents the bounding surface of this volume. The speed of displacement of the bounding surface is given by $\mathbf{w}\cdot\mathbf{n}$ where $\mathbf{n}$ is the outwardly directed unit normal vector. Since $\mathscr{V}_a(t)$ is arbitrary, it can be set equal to $V_\beta(t)$ in order to obtain the special form that is needed in the analysis of Eq. 1. For the compressible aquifer under consideration, the boundary condition at the β-σ interface can be expressed as

$$\text{B.C.} \qquad \mathbf{v}_\beta = \mathbf{v}_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}(t) \tag{3}$$

provided that the σ-phase particles are impermeable.

4-8. In order to extend the analysis in the text to include inertial effects, one must replace the Stokes equations with the Navier-Stokes equations. Under these circumstances, the problem under investigation takes the form

$$\frac{\partial}{\partial t}(\rho_\beta \mathbf{v}_\beta) + \nabla\cdot(\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta$$

$$\nabla\cdot\mathbf{v}_\beta = 0$$

$$\text{B.C.} \qquad \mathbf{v}_\beta = 0, \quad \text{at } \mathscr{A}_{\beta\sigma}$$

In this problem you are asked to demonstrate that the volume average form of the Navier-Stokes equation can be expressed as (Whitaker, 1996)

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle^\beta - \rho_\beta \mathbf{g}\right) - \mathbf{F}_\beta\cdot\langle \mathbf{v}_\beta\rangle$$

Here $\mathbf{K}_\beta$ is the Darcy's law permeability tensor determined by the closure problem given in the text, while $\mathbf{F}_\beta$ is the Forchheimer correction tensor (Forchheimer, 1901). In order to develop a closure problem that can be used to determine $\mathbf{F}_\beta$, one should assume that the point velocity, $\mathbf{v}_\beta$, will be available from the solution of the Navier-Stokes equations in a representative unit cell.

Chapter 5

Single-Phase Flow in Heterogeneous Porous Media

In the previous chapter we analyzed the process of single-phase flow in homogeneous porous media, and the result was a proof of Darcy's law and a method of predicting the permeability tensor. In this chapter we consider porous media that are clearly heterogeneous, i.e., porous media in which there are abrupt and significant changes in the permeability. Such systems can be referred to as *mechanically heterogeneous* in order to distinguish them from porous media in which there are abrupt and significant changes in the chemical characteristics. These systems are referred to as *chemically heterogeneous*. Most geological systems tend to be both mechanically and chemically heterogeneous, but in this chapter we will be concerned only with the influence of mechanical heterogeneities.

5.1 Introduction

In Figure 5.1 we have illustrated a two-region model of a heterogeneous porous medium, and in that system we are confronted with two length scales. One length scale is associated with the pores or the particles, and these have been designated by ℓ_β and ℓ_σ in the previous chapter. A second length scale is associated with the thickness of the distinct layers that make up the stratified porous medium. If the two length scales, ℓ_ω and ℓ_η, are comparable, we are confronted with the 2-scale version of Cushman's (1984) N-scale problem. If ℓ_ω and ℓ_η are disparate and large compared to ℓ_β and ℓ_σ, we have a 3-scale problem. Within the ω and η-regions, a small averaging volume is used in the derivation of Darcy's law, and the permeability tensors associated with those regions are indicated by $\mathbf{K}_{\beta\omega}$ and $\mathbf{K}_{\beta\eta}$. The large averaging volume illustrated in Figure 5.1 is used to develop the *large-scale form* of Darcy's law and the single permeability tensor associated with that form is indicated by $\mathbf{K}^*_\beta$. Stratified systems of the type illustrated in Figure 5.1 are representative of petroleum reservoirs; however, in this study we will be concerned with more general systems such as the one illustrated in Figure 5.2. There we have identified the large-scale averaging volume as $\mathscr{V}_\infty$ and the length scales for the ω and η-regions are again identified by ℓ_ω and ℓ_η.

We begin this analysis with the following governing equations and boundary conditions:

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta, \quad \text{in the } \beta\text{-phase} \tag{5.1-1}$$

$$\nabla \cdot \mathbf{v}_\beta = 0, \quad \text{in the } \beta\text{-phase} \tag{5.1-2}$$

B.C.1
$$\mathbf{v}_\beta = 0, \quad \text{at } \mathscr{A}_{\beta\sigma} \tag{5.1-3}$$

B.C.2
$$\mathbf{v}_\beta = \mathbf{f}(\mathbf{r},t), \quad \text{at } \mathscr{A}_{\beta e} \tag{5.1-4}$$

Here we think of $\mathscr{A}_{\beta\sigma}$ as the interfacial area contained within some *homogeneous porous medium*, such as the ω-region illustrated in Figure 5.2, while $\mathscr{A}_{\beta e}$ represents the

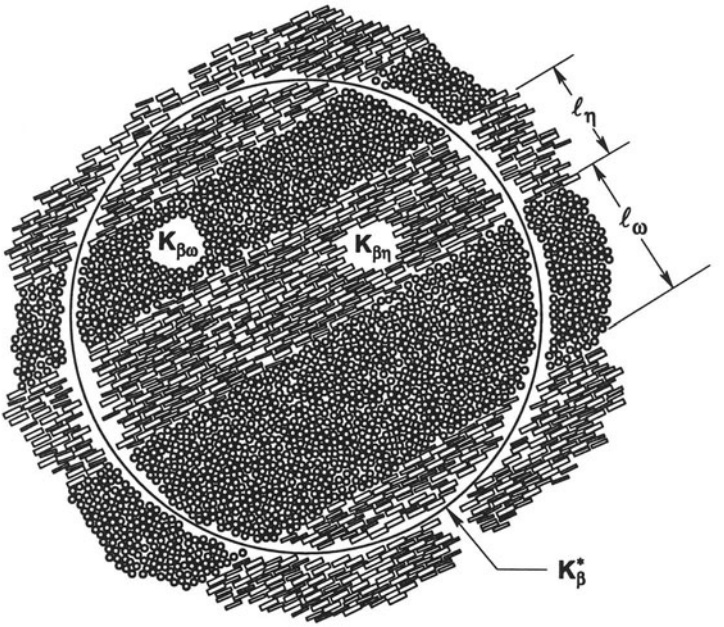

Figure 5.1. Two-region model of a heterogeneous porous medium

area of entrances and exits for that region. In an attempt to be precise about what we mean by a *homogeneous porous medium*, we draw upon the definition given by Quintard and Whitaker (1987)

> A porous medium is homogeneous *with respect to* a given averaging volume and a given process when the effective transport coefficients in the volume averaged transport equations are independent of position. If a porous medium is not homogeneous, it is heterogeneous.

The first level of averaging associated with Eqs. 5.1-1 through 5.1-4 was discussed in Chapter 4 and the results are given by

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle^\beta - \rho_\beta \mathbf{g}\right) \tag{5.1-5}$$

$$\nabla\cdot\langle \mathbf{v}_\beta \rangle = 0 \tag{5.1-6}$$

In addition to the Darcy-scale governing differential equations for momentum and mass, we will need conditions that are applicable at the boundary between the ω and η-regions

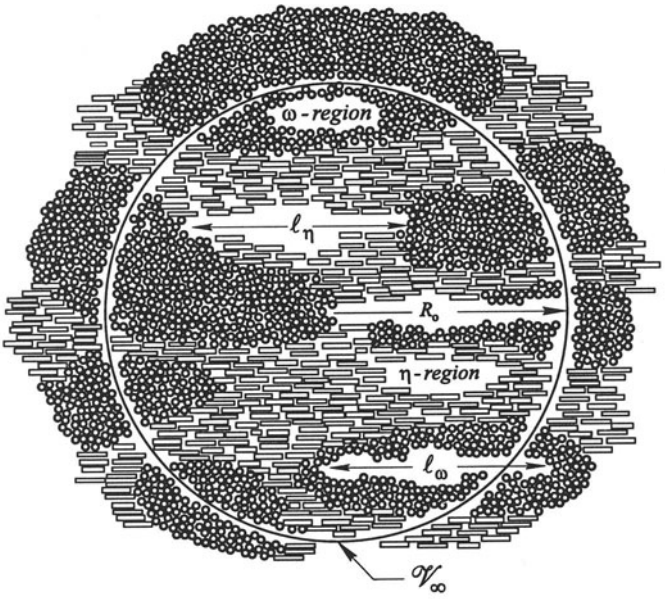

Figure 5.2. Large-scale averaging volume

illustrated in Figure 5.2. This matter has been explored by Quintard and Whitaker (1987) who concluded that it is reasonable to require continuity of the pressure, $\langle p_\beta\rangle^\beta$, and continuity of the normal component of the velocity, $\langle \mathbf{v}_\beta \rangle$, at the ω-η boundary. We will make use of these conditions in the next section; however, the precise nature of the jump condition at this boundary still needs to be developed following the type of analysis given by Ochoa-Tapia and Whitaker (1995a-b).

5.2 Large-Scale Averaging

The momentum and continuity equations that describe single-phase flow in the heterogeneous porous medium illustrated in Figure 5.2 are given by

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega = 0, \quad \text{in the } \omega\text{-region} \tag{5.2-1}$$

$$\langle \mathbf{v}_\beta\rangle_\omega = -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle_\omega^\beta - \rho_\beta\mathbf{g}\right), \quad \text{in the } \omega\text{-region} \tag{5.2-2}$$

B.C.1 $$\mathbf{n}_{\omega\eta}\cdot\langle \mathbf{v}_\beta\rangle_\omega = \mathbf{n}_{\omega\eta}\cdot\langle \mathbf{v}_\beta\rangle_\eta, \quad \text{at the } \omega\text{-}\eta \text{ boundary} \tag{5.2-3}$$

B.C.2 $$\langle p_\beta\rangle_\omega^\beta = \langle p_\beta\rangle_\eta^\beta, \quad \text{at the } \omega\text{-}\eta \text{ boundary} \tag{5.2-4}$$

$$\langle \mathbf{v}_\beta\rangle_\eta = -\frac{\mathbf{K}_{\beta\eta}}{\mu_\beta}\cdot\left(\nabla\langle p_\beta\rangle_\eta^\beta - \rho_\beta\mathbf{g}\right), \quad \text{in the } \eta\text{-region} \tag{5.2-5}$$

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\eta = 0, \quad \text{in the } \eta\text{-region} \tag{5.2-6}$$

Here we have used $\mathbf{n}_{\omega\eta}$ to represent the unit normal vector pointing from the ω-region toward the η-region, and this convention leads to

$$\mathbf{n}_{\omega\eta} = -\mathbf{n}_{\eta\omega} \tag{5.2-7}$$

In this formulation of the flow problem, we have ignored the boundary conditions for the velocity at the entrances and exits of the large-scale system since we have assumed that they will not play a role in either the form of the volume averaged equations or the closure equations.

The problem presented by Eqs. 5.2-1 through 5.2-6 was analyzed directly by Quintard and Whitaker (1987); however, there is a definite advantage in arranging the equations in the form of a *diffusion* or *conduction* problem. This allows us to take advantage of all that we have learned in Chapters 1 and 2 since the *multi-region* transport process suggested by Figure 5.2 is mathematically analogous to the *multi-phase* processes studied earlier. In order to arrange Eqs. 5.2-1 through 5.2-6 in the form of a conduction problem, we define a new pressure, P_β, according to

$$P_\beta = p_\beta + \rho_\beta\varphi \tag{5.2-8}$$

Here φ is the gravitational potential function defined by

$$\varphi = -\mathbf{g}\cdot\mathbf{r} + C \tag{5.2-9}$$

in which C is an arbitrary constant. The intrinsic average of Eq. 5.2-8 is given by

$$\langle P_\beta\rangle^\beta = \langle p_\beta\rangle^\beta + \rho_\beta\langle\varphi\rangle^\beta \tag{5.2-10}$$

and if we express the position vector locating points in the β-phase as $\mathbf{r}_\beta = \mathbf{x} + \mathbf{y}_\beta$ the average of the potential function takes the form

$$\langle\varphi\rangle^\beta = -\mathbf{g}\cdot\left(\mathbf{x} + \langle \mathbf{y}_\beta\rangle^\beta\right) + C \tag{5.2-11}$$

Substituting this result into Eq. 5.2-10 and taking the derivative with respect to $\mathbf{x}$ leads to

$$\nabla\langle P_\beta\rangle^\beta = \nabla\langle p_\beta\rangle^\beta - \rho_\beta \mathbf{g}\cdot\left(\mathbf{I}+\nabla\langle \mathbf{y}_\beta\rangle^\beta\right) \tag{5.2-12}$$

For disordered porous media we have $\nabla\langle \mathbf{y}_\beta\rangle^\beta << \mathbf{I}$ and our expression for the gradient of $\langle P_\beta\rangle^\beta$ reduces to

$$\nabla\langle P_\beta\rangle^\beta = \nabla\langle p_\beta\rangle^\beta - \rho_\beta \mathbf{g} \tag{5.2-13}$$

Use of this result in Eqs. 5.2-1 through 5.2-6 allows us to describe the physical process of single-phase flow in the system illustrated in Figure 5.2 by the following equations and boundary conditions:

$$\nabla\cdot\left(\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\right) = 0, \quad \text{in the } \omega\text{-region} \tag{5.2-14}$$

B.C.1
$$\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta = \mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\eta}\cdot\nabla\langle P_\beta\rangle_\eta^\beta, \quad \text{at } A_{\omega\eta} \tag{5.2-15}$$

B.C.2
$$\langle P_\beta\rangle_\omega^\beta = \langle P_\beta\rangle_\eta^\beta, \quad \text{at } A_{\omega\eta} \tag{5.2-16}$$

$$\nabla\cdot\left(\mathbf{K}_{\beta\eta}\cdot\nabla\langle P_\beta\rangle_\eta^\beta\right) = 0, \quad \text{in the } \eta\text{-region} \tag{5.2-17}$$

At this point we must be very careful to note that we have neglected variations in the viscosity within the macroscopic region under consideration. This is not the same as ignoring variations of μ_β *within the averaging volume*, but rather it is equivalent to imposing a restriction of the type

$$\mu_\beta^{-1}\nabla\mu_\beta\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta << \nabla\cdot\left(\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\right) \tag{5.2-18}$$

There may be important processes involving single-phase flow in heterogeneous porous media for which Eq. 5.2-18 is not an acceptable restriction.

When Eqs. 5.2-14 through 5.2-17 are valid, the process of single-phase flow in heterogeneous porous media is mathematically analogous to steady heat conduction in a two-phase system. The transformation from Eqs. 5.2-1 through 5.2-6 to Eqs. 5.2-14 through 5.2-17 is an important one since a great deal of work has been done on the problem of heat conduction in two-phase systems (Nozad *et al.*, 1985; Kaviany, 1991; Nield and Bejan, 1992; Quintard and Whitaker, 1993b and 1995a), and we can use that work to help us understand the problem of single-phase flow in heterogeneous porous media.

In the method of large-scale averaging we will make use of both superficial averages and intrinsic averages, and we will begin our analysis of Eqs. 5.2-14 through 5.2-17 with the definitions of these two averages. Given some Darcy-scale quantity in the ω-region, $\langle\psi_\beta\rangle_\omega^\beta$, we refer to the large-scale averaging volume illustrated in Figure 5.2 and define the *superficial regional average* as

$$\left\{\langle\psi_\beta\rangle_\omega^\beta\right\} = \frac{1}{\mathscr{V}_\infty}\int_{V_\omega}\langle\psi_\beta\rangle_\omega^\beta\, dV \tag{5.2-19}$$

while the *intrinsic regional average* is given by

$$\left\{\langle\psi_\beta\rangle_\omega^\beta\right\}^\omega = \frac{1}{V_\omega}\int_{V_\omega}\langle\psi_\beta\rangle_\omega^\beta\, dV \tag{5.2-20}$$

These two averages are related according to

$$\left\{\langle\psi_\beta\rangle_\omega^\beta\right\} = \varphi_\omega\left\{\langle\psi_\beta\rangle_\omega^\beta\right\}^\omega \tag{5.2-21}$$

in which the volume fraction of the ω-region is given explicitly by

$$\varphi_\omega = V_\omega/\mathscr{V}_\infty \tag{5.2-22}$$

The averaging theorem (Howes and Whitaker, 1985) for a two-region model can be expressed as

$$\left\{\nabla\langle\psi_\beta\rangle_\omega^\beta\right\} = \nabla\left\{\langle\psi_\beta\rangle_\omega^\beta\right\} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\langle\psi_\beta\rangle_\omega^\beta\, dA \tag{5.2-23}$$

along with an analogous form for the η-region. While the nomenclature illustrated in Eqs. 5.2-19 through 5.2-23 appears to be overly complex, there is some logic in that the *subscripts always identify phases or regions* while the presence of a superscript always indicates an intrinsic average. Even though the process under investigation is mathematically analogous to the process of heat conduction in a two-phase system, the physics of single-phase flow in heterogeneous porous media is considerably more complex and it is best to retain the complex nomenclature as a reminder of the physics.

On the basis of the definition given by Eq. 5.2-19, we express the superficial average of Eq. 5.2-14 as

$$\left\{\nabla\cdot\left(\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\right)\right\} = 0 \tag{5.2-24}$$

and use the averaging theorem to obtain

$$\nabla\cdot\left\{\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\right\} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\, dA = 0 \tag{5.2-25}$$

If we are willing to ignore variations of $\mathbf{K}_{\beta\omega}$ within the averaging volume, a second application of the averaging theorem allows us to write Eq. 5.2-25 as

$$\nabla\cdot\left[\mathbf{K}_{\beta\omega}\cdot\left(\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\langle P_\beta\rangle_\omega^\beta\,dA\right)\right]+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\,dA=0 \tag{5.2-26}$$

Here we are confronted with several problems, the first of which is the presence of the *superficial* regional average pressure. As in our study of single-phase flow in homogeneous porous media, we prefer to work with an *intrinsic average* pressure defined according to

$$\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega=\frac{1}{V_\omega}\int_{V_\omega}\langle P_\beta\rangle_\omega^\beta\,dV \tag{5.2-27}$$

The superficial average is related to the intrinsic average by

$$\left\{\langle P_\beta\rangle_\omega^\beta\right\}=\varphi_\omega\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega \tag{5.2-28}$$

and substitution of this result into Eq. 5.2-26 provides

$$\nabla\cdot\left[\mathbf{K}_{\beta\omega}\cdot\left(\varphi_\omega\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega+\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega\nabla\varphi_\omega+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\langle P_\beta\rangle_\omega^\beta\,dA\right)\right]+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\,dA=0 \tag{5.2-29}$$

In order to eliminate the *local* volume averaged pressure, $\langle P_\beta\rangle_\omega^\beta$, from this result, we use the regional spatial deviation pressure defined by the decomposition

$$\langle P_\beta\rangle_\omega^\beta=\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega+\tilde{P}_{\beta\omega} \tag{5.2-30}$$

Here we have made use of a tilde to indicate a spatial deviation that is defined by two quantities having *different characteristic lengths*, thus $\tilde{P}_{\beta\omega}$ is *analogous* to $\tilde{c}_{A\gamma}$ as defined in Chapter 1 and to $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ as defined in Chapter 2. In addition, $\tilde{P}_{\beta\omega}$ is *similar* to the spatial deviation pressure, $\tilde{p}_\beta$, that was defined in Chapter 4; however, one must remember that the length scales associated with $\tilde{p}_\beta$ are ℓ_β and L whereas the length scales associated with $\tilde{P}_{\beta\omega}$ are ℓ_ω and $\mathscr{L}$. Later in this development we will use a circumflex to indicate a spatial deviation defined by two quantities having *the same characteristic length*, and this will be consistent with the definition of $\hat{T}_\beta$ and $\hat{T}_\sigma$ that was given in Chapter 2.

Use of the decomposition indicated by Eq. 5.2-30 in the large-scale averaged equation represented by Eq. 5.2-29 leads to the *non-local form* of the regional averaged pressure equation given by

$$\nabla\cdot\left[\mathbf{K}_{\beta\omega}\cdot\left(\varphi_\omega\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega+\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega\nabla\varphi_\omega+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega dV+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}\,dA\right)\right]$$

$$+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\,dA \quad = \quad 0 \tag{5.2-31}$$

A non-local theory of two-phase flow in heterogeneous porous media has been explored by Quintard and Whitaker (1990a-b); however, we can avoid this complication whenever the following length-scale constraints are satisfied:

$$\ell_\omega \;<<\; R_\circ\,, \qquad R_\circ^2 \;<<\; \mathscr{L}_\varphi\mathscr{L}_{P1} \tag{5.2-32}$$

Here ℓ_ω represents the characteristic length for the ω-region, $R_\circ$ is the radius of the large-scale averaging volume, and $\mathscr{L}_\varphi$ and $\mathscr{L}_{P1}$ are characteristic length scales defined by the following order of magnitude estimates

$$\nabla\varphi_\omega \;=\; \mathbf{O}\left(\Delta\varphi_\omega/\mathscr{L}_\varphi\right), \qquad \nabla\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega \;=\; \mathbf{O}\left[\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega\Big/\mathscr{L}_{P1}\right] \tag{5.2-33}$$

When the constraints indicated by Eqs. 5.2-32 are valid, we can remove $\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega$ from the area integral and make use of a special form of the averaging theorem to obtain

$$\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega dA \;=\; \left[\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\,dA\right]\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega \;=\; -\nabla\varphi_\omega\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega \tag{5.2-34}$$

Use of this result in Eq. 5.2-31 provides the regional average form of Eq. 5.2-14

$$\nabla\cdot\left[\mathbf{K}_{\beta\omega}\cdot\left(\varphi_\omega\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}\,dA\right)\right]+\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\,dA \;=\; 0 \tag{5.2-35}$$

and by analogy the regional averaged form of Eq. 5.2-17 is given by

$$\nabla\cdot\left[\mathbf{K}_{\beta\eta}\cdot\left(\varphi_\eta\nabla\left\{\langle P_\beta\rangle_\eta^\beta\right\}^\eta+\frac{1}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{P}_{\beta\eta}\,dA\right)\right]+\frac{1}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\mathbf{K}_{\beta\eta}\cdot\nabla\langle P_\beta\rangle_\eta^\beta\,dA\;=\;0 \tag{5.2-36}$$

At this point we are confronted with the same question we encountered in our study of transient heat conduction, i.e., do we need a two-equation model for the two pressures in the ω and η-regions, or will a one-equation model suffice.

5.2.1 LARGE-SCALE MECHANICAL EQUILIBRIUM

When the condition of *large-scale mechanical equilibrium* is valid, we can obtain a single equation for the large-scale average pressure defined by

$$\left\{\langle P_\beta\rangle^\beta\right\}\;=\;\frac{1}{\mathscr{V}_\infty}\int_{\mathscr{V}_\infty}\langle P_\beta\rangle^\beta\,dV\;=\;\varphi_\omega\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega+\varphi_\eta\left\{\langle P_\beta\rangle_\eta^\beta\right\}^\eta \tag{5.2-37}$$

Here one should keep in mind that $\left\{\langle P_\beta\rangle^\beta\right\}$ is an *intrinsic* average pressure. In order to identify the circumstances for which a one-equation model for $\left\{\langle P_\beta\rangle^\beta\right\}$ is valid, we use the decompositions

$$\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega\;=\;\left\{\langle P_\beta\rangle^\beta\right\}+\hat{P}_{\beta\omega} \tag{5.2-38a}$$

$$\left\{\langle P_\beta\rangle_\eta^\beta\right\}^\eta\;=\;\left\{\langle P_\beta\rangle^\beta\right\}+\hat{P}_{\beta\eta} \tag{5.2-38b}$$

and then search for conditions that allow us to neglect the *large-scale deviations*, $\hat{P}_{\beta\omega}$ and $\hat{P}_{\beta\eta}$. Here we note that we have used a circumflex to denote a spatial deviation associated with two quantities having the same length scale. This is consistent with the temperature deviations, $\hat{T}_\beta$ and $\hat{T}_\sigma$, that we defined in Chapter 2; however, we must remember that the length scale associated with $\hat{P}_{\beta\omega}$ and $\hat{P}_{\beta\eta}$ is the large length-scale denoted by $\mathscr{L}_P$. Adding in Eqs. 5.2-35 and 5.2-36, and making use of Eqs. 5.2-38, leads to the single equation given by

$$\nabla\cdot\left[\left(\varphi_\omega\mathbf{K}_{\beta\omega}+\varphi_\eta\mathbf{K}_{\beta\eta}\right)\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\}+\frac{\mathbf{K}_{\beta\omega}}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}\,dA+\frac{\mathbf{K}_{\beta\eta}}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{P}_{\beta\eta}dA\right]$$

$$+\;\nabla\cdot\left(\varphi_\omega\mathbf{K}_{\beta\omega}\cdot\nabla\hat{P}_{\beta\omega}+\varphi_\eta\mathbf{K}_{\beta\eta}\cdot\nabla\hat{P}_{\beta\eta}\right)\;=\;0 \tag{5.2-39}$$

Here we have made use of the flux boundary condition given by Eq. 5.2-15 in order to eliminate the final terms in Eqs. 5.2-35 and 5.2-36. Equation 5.2-39 is essentially the steady-state analog of Eq. 2.3-4, and a one-equation model results when the following constraint is satisfied:

$$\varphi_{\beta\omega}\mathbf{K}_{\omega}\cdot\nabla\hat{P}_{\beta\omega} + \varphi_{\beta\eta}\mathbf{K}_{\eta}\cdot\nabla\hat{P}_{\beta\eta} \;<<\; \mathbf{K}^{*}_{\beta}\cdot\nabla\left\{\langle P_{\beta}\rangle^{\beta}\right\} \tag{5.2-40}$$

Here we have made use of the closure problem discussed in Sec. 5.3 that leads to

$$\left(\varphi_{\omega}\mathbf{K}_{\beta\omega}+\varphi_{\eta}\mathbf{K}_{\beta\eta}\right)\cdot\nabla\left\{\langle P_{\beta}\rangle^{\beta}\right\} + \frac{\mathbf{K}_{\beta\omega}}{\mathscr{V}_{\infty}}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}\,dA + \frac{\mathbf{K}_{\beta\eta}}{\mathscr{V}_{\infty}}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{P}_{\beta\eta}dA$$
$$= \mathbf{K}^{*}_{\beta}\cdot\nabla\left\{\langle P_{\beta}\rangle^{\beta}\right\} \tag{5.2-41}$$

in which $\mathbf{K}^{*}_{\beta}$ is the *large-scale* permeability tensor. When the restriction given by Eq. 5.2-40 is satisfied, we say that the principle of large-scale mechanical equilibrium is valid and $\left\{\langle P_{\beta}\rangle^{\beta}\right\}$ becomes an acceptable approximation for both $\left\{\langle P_{\beta}\rangle^{\beta}_{\omega}\right\}^{\omega}$ and $\left\{\langle P_{\beta}\rangle^{\beta}_{\eta}\right\}^{\eta}$. We can simplify Eq. 5.2-40 by recognizing that the large-scale deviations can be expressed as

$$\hat{P}_{\beta\omega} = \varphi_{\eta}\left[\left\{\langle P_{\beta}\rangle^{\beta}_{\omega}\right\}^{\omega} - \left\{\langle P_{\beta}\rangle^{\beta}_{\eta}\right\}^{\eta}\right] \tag{5.2-42a}$$

$$\hat{P}_{\beta\eta} = \varphi_{\omega}\left[\left\{\langle P_{\beta}\rangle^{\beta}_{\eta}\right\}^{\eta} - \left\{\langle P_{\beta}\rangle^{\beta}_{\omega}\right\}^{\omega}\right] \tag{5.2-42b}$$

in order to obtain a restriction of the form

$$\varphi_{\omega}\varphi_{\eta}\left(\mathbf{K}_{\beta\omega} - \mathbf{K}_{\beta\eta}\right)\cdot\nabla\left[\left\{\langle P_{\beta}\rangle^{\beta}_{\omega}\right\}^{\omega} - \left\{\langle P_{\beta}\rangle^{\beta}_{\eta}\right\}^{\eta}\right] \;<<\; \mathbf{K}^{*}_{\beta}\cdot\nabla\left\{\langle P_{\beta}\rangle^{\beta}\right\} \tag{5.2-43}$$

At this point we need an estimate of the difference between the two regional averaged pressures, and we obtain this estimate in the manner outlined in Sec. 2.3. This leads to a constraint of the form

$$\varphi_{\omega}\varphi_{\eta}\left(\mathbf{K}_{\beta\omega} - \mathbf{K}_{\beta\eta}\right)\Lambda \;<<\; \mathbf{K}^{*}_{\beta} \tag{5.2-44}$$

in which the parameter Λ is estimated by

$$\Lambda = \frac{O\left(\frac{K_{\beta\omega} - K_{\beta\eta}}{K_{\omega\eta}}\right)}{1 + O\left[\frac{\mathscr{L}_{P1}\left(A_{\omega\eta}/\mathscr{V}_{\infty}\right)}{\varphi_{\omega}\varphi_{\eta}\left(\frac{K_{\omega\eta}}{\mathscr{L}_{P1}}\right)\left(\frac{\ell_{\omega}}{K_{\beta\omega}} + \frac{\ell_{\eta}}{K_{\beta\eta}}\right)}\right]} \tag{5.2-45}$$

Here we have used $K_{\beta\omega}$ and $K_{\beta\eta}$ as suitable norms of the tensors $\mathbf{K}_{\beta\omega}$ and $\mathbf{K}_{\beta\eta}$ in order to simplify the algebraic manipulation required to obtain this result, and we have used $K_{\omega\eta}$ to represent the *mixed-mode* quantity defined by

$$K_{\omega\eta} = \varphi_{\eta}K_{\beta\omega} + \varphi_{\omega}K_{\beta\eta} \tag{5.2-46}$$

At this point it is important to note that $\mathscr{L}_{P1}$ is based on the estimate given by Eq. 5.2-33, thus $\mathscr{L}_{P1}$ is infinite and $\Lambda \to 0$ for a one-dimensional flow in the large-scale sense. This means that the one-equation model is always valid for one-dimensional flows and this result is consistent with the numerical experiments of Quintard and Whitaker (1993b, 1995a). For two-dimensional flows $\mathscr{L}_{P1}$ will be finite and the one-equation model may fail when the difference between $K_{\beta\omega}$ and $K_{\beta\eta}$ is on the order of the larger of the two, and when $\mathscr{L}_{P1}$ is on the order of either ℓ_{ω} or ℓ_{η}.

If we accept the condition of large-scale mechanical equilibrium, the restriction given by Eq. 5.2-40 can be imposed on Eq. 5.2-39 so that our governing differential equation for $\left\{\langle P_{\beta}\rangle^{\beta}\right\}$ takes the form

$$\nabla\cdot\left[\left(\varphi_{\omega}\mathbf{K}_{\beta\omega} + \varphi_{\eta}\mathbf{K}_{\beta\eta}\right)\cdot\nabla\left\{\langle P_{\beta}\rangle^{\beta}\right\} + \frac{\mathbf{K}_{\beta\omega}}{\mathscr{V}_{\infty}}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}\,dA + \frac{\mathbf{K}_{\beta\eta}}{\mathscr{V}_{\infty}}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{P}_{\beta\eta}\,dA\right] = 0 \tag{5.2-47}$$

This simplification is justified by Eqs. 5.2-44 and 5.2-45 and one must keep in mind that these relations are based on order of magnitude estimates, thus they can only *suggest* under what circumstances the one-equation model is valid. The one-equation model for heat conduction that was presented in Chapter 2 is strongly supported by the numerical experiments of Quintard and Whitaker (1993b, 1995a); however, those studies were carried out using two-phase systems with *isotropic* thermal conductivities. If the Darcy-scale permeabilities, $\mathbf{K}_{\beta\omega}$ and $\mathbf{K}_{\beta\eta}$, are highly *anisotropic*, Eqs. 5.2-44 and 5.2-45 should be re-derived using the tensorial nature of these parameters (see Problem 5-1).

5.3 Closure

In order to obtain a closed form of Eq. 5.2-47 we need to develop representations for $\tilde{P}_{\beta\omega}$ and $\tilde{P}_{\beta\eta}$ in terms of the dependent variable $\left\{\langle P_\beta\rangle^\beta\right\}$. One can follow the study of heat conduction given in Chapter 2 to see how this is done, and here we simply note that the spatial deviation pressures can be represented as

$$\tilde{P}_{\beta\omega} = \mathbf{b}_\omega \cdot \nabla\left\{\langle P_\beta\rangle^\beta\right\}, \qquad \tilde{P}_{\beta\eta} = \mathbf{b}_\eta \cdot \nabla\left\{\langle P_\beta\rangle^\beta\right\} \tag{5.3-1}$$

in which the closure variables, $\mathbf{b}_\omega$ and $\mathbf{b}_\eta$, are determined by the following boundary value problem

$$\mathbf{K}_{\beta\omega} : \nabla\nabla\mathbf{b}_\omega = 0, \quad \text{in the } \omega\text{-region} \tag{5.3-2a}$$

B.C.1 $$\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\mathbf{b}_\omega = \mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\eta}\cdot\nabla\mathbf{b}_\eta + \mathbf{n}_{\omega\eta}\cdot\left(\mathbf{K}_{\beta\eta}-\mathbf{K}_{\beta\omega}\right), \quad \text{at } A_{\omega\eta} \tag{5.3-2b}$$

B.C.2 $$\mathbf{b}_\omega = \mathbf{b}_\eta, \quad \text{at } A_{\omega\eta} \tag{5.3-2c}$$

$$\mathbf{K}_{\beta\eta} : \nabla\nabla\mathbf{b}_\eta = 0, \quad \text{in the } \eta\text{-region} \tag{5.3-2d}$$

Periodicity: $$\mathbf{b}_\omega(\mathbf{r}+\ell_i) = \mathbf{b}_\omega(\mathbf{r}), \quad \mathbf{b}_\eta(\mathbf{r}+\ell_i) = \mathbf{b}_\eta(\mathbf{r}), \quad i=1,2,3 \tag{5.3-2e}$$

Substitution of Eqs. 5.3-1 into the large-scale averaged equation for $\left\{\langle P_\beta\rangle^\beta\right\}$ given by Eq. 5.2-46 leads to

$$\nabla\cdot\left(\mathbf{K}^*_\beta\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\}\right) = 0 \tag{5.3-3}$$

in which the large-scale permeability is given by

$$\mathbf{K}^*_\beta = \varphi_\omega\mathbf{K}_{\beta\omega} + \varphi_\eta\mathbf{K}_{\beta\eta} + \frac{\left(\mathbf{K}_{\beta\omega}-\mathbf{K}_{\beta\eta}\right)}{\mathscr{V}_\infty}\cdot\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\mathbf{b}_\omega\, dA \tag{5.3-4}$$

One can see that Eqs 5.3-2 determine $\mathbf{b}_\omega$ and $\mathbf{b}_\eta$ to within a single arbitrary constant; however, this constant does not pass through the filter represented by the area integral in Eq. 5.3-4.

5.4 Darcy's Law

In addition to Eq. 5.3-3, we need the large-scale form of the continuity equation and the large-scale form of Darcy's law. To develop these relations we return to the formulation of the large-scale problem given originally by

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega \;=\; 0\,, \quad \text{in the } \omega\text{ - region} \tag{5.4-1}$$

$$\langle \mathbf{v}_\beta\rangle_\omega \;=\; -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta}\cdot\left(\nabla\langle P_\beta\rangle_\omega^\beta\right), \quad \text{in the } \omega\text{ - region} \tag{5.4-2}$$

B.C.1 $$\mathbf{n}_{\omega\eta}\cdot\langle \mathbf{v}_\beta\rangle_\omega \;=\; \mathbf{n}_{\omega\eta}\cdot\langle \mathbf{v}_\beta\rangle_\eta\,, \quad \text{at the } \omega\text{-}\eta \text{ boundary} \tag{5.4-3}$$

B.C.2 $$\langle P_\beta\rangle_\omega^\beta \;=\; \langle P_\beta\rangle_\eta^\beta\,, \quad \text{at the } \omega\text{-}\eta \text{ boundary} \tag{5.4-4}$$

$$\langle \mathbf{v}_\beta\rangle_\eta \;=\; -\frac{\mathbf{K}_{\beta\eta}}{\mu_\beta}\cdot\left(\nabla\langle P_\beta\rangle_\eta^\beta\right), \quad \text{in the } \eta\text{ - region} \tag{5.4-5}$$

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\eta \;=\; 0\,, \quad \text{in the } \eta\text{ - region} \tag{5.4-6}$$

From this representation of the process, we want to extract the traditional forms of the continuity and momentum equations.

5.4.1 CONTINUITY EQUATION

The regional average of Eq. 5.4-1 is given by

$$\frac{1}{\mathscr{V}_\infty}\int_{V_\omega}\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega\, dV \;=\; \left\{\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega\right\} \;=\; 0 \tag{5.4-7}$$

and use of the averaging theorem allows us to write this result in the form

$$\nabla\cdot\left\{\langle \mathbf{v}_\beta\rangle_\omega\right\} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\langle \mathbf{v}_\beta\rangle_\omega\, dA \;=\; 0 \tag{5.4-8}$$

The analogous result for the η-region is given by

$$\nabla\cdot\left\{\langle \mathbf{v}_\beta\rangle_\eta\right\} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, dA \;=\; 0 \tag{5.4-9}$$

and we can add these two results to obtain the *large scale* continuity equation

$$\nabla\cdot\left\{\langle \mathbf{v}_\beta\rangle\right\} \;=\; 0 \tag{5.4-10}$$

Here we have defined the large-scale average velocity according to

$$\left\{\langle \mathbf{v}_\beta\rangle\right\} \;=\; \left\{\langle \mathbf{v}_\beta\rangle_\omega\right\} + \left\{\langle \mathbf{v}_\beta\rangle_\eta\right\} \;=\; \varphi_\omega\left\{\langle \mathbf{v}_\beta\rangle_\omega\right\}^\omega + \varphi_\eta\left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta \tag{5.4-11}$$

and we note that *no constraints* are necessary to obtain the continuity equation given by Eq. 5. 4-10.

5.4.2 MOMENTUM EQUATION

The *regional average* of Eq. 5.4-2 can be expressed as

$$\left\{\langle \mathbf{v}_\beta \rangle_\omega\right\} = -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta}\cdot\left\{\nabla\langle P_\beta\rangle_\omega^\beta\right\} \tag{5.4-12}$$

provided we are willing to neglect variations of $\mathbf{K}_{\beta\omega}$ within the averaging volume. At this point we can repeat the type of analysis given by Eqs. 5.2-24 through 5.2-35 to obtain

$$\left\{\langle \mathbf{v}_\beta \rangle_\omega\right\} = -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta}\cdot\left(\varphi_\omega\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega + \frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{P}_{\beta\omega}dA\right) \tag{5.4-13}$$

When the condition of large-scale mechanical equilibrium is valid, we can replace $\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega$ with $\left\{\langle P_\beta\rangle^\beta\right\}$ and the spatial deviation pressure can be represented by

$$\tilde{P}_{\beta\omega} = \mathbf{b}_\omega\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\}, \qquad \tilde{P}_{\beta\eta} = \mathbf{b}_\eta\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\} \tag{5.4-14}$$

This leads to the *regional form* of Darcy's law (Quintard and Whitaker, 1998a)

$$\left\{\langle \mathbf{v}_\beta \rangle_\omega\right\} = -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta}\cdot\left(\varphi_\omega\mathbf{I} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\mathbf{b}_\omega\,dA\right)\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\} \tag{5.4-15}$$

and we remind the reader that this representation is only valid when the condition of large-scale mechanical equilibrium is applicable. The analogous form for the η-region is given by

$$\left\{\langle \mathbf{v}_\beta \rangle_\eta\right\} = -\frac{\mathbf{K}_{\beta\eta}}{\mu_\beta}\cdot\left(\varphi_\eta\mathbf{I} + \frac{1}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\mathbf{b}_\eta dA\right)\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\} \tag{5.4-16}$$

and these two results can be added to obtain

$$\left\{\langle \mathbf{v}_\beta \rangle\right\} = -\frac{\mathbf{K}_\beta^*}{\mu_\beta}\cdot\nabla\left\{\langle P_\beta\rangle^\beta\right\} \tag{5.4-17}$$

Here the large-scale permeability tensor is defined explicitly by Eq. 5.3-4. On the basis of Eqs. 5.2-8 through 5.2-13 one can show that

$$\nabla\left\{\langle P_\beta\rangle^\beta\right\} = \nabla\left\{\langle p_\beta\rangle^\beta\right\} - \rho_\beta\mathbf{g} \tag{5.4-18}$$

and this allows us to summarize the large-scale forms of the continuity equation and Darcy's law as

$$\nabla \cdot \left\{ \langle \mathbf{v}_\beta \rangle \right\} = 0 \tag{5.4-19}$$

$$\left\{ \langle \mathbf{v}_\beta \rangle \right\} = -\frac{\mathbf{K}_\beta^*}{\mu_\beta} \cdot \left(\nabla \left\{ \langle p_\beta \rangle^\beta \right\} - \rho_\beta \mathbf{g} \right) \tag{5.4-20}$$

Since this result is identical to the form of Darcy's law obtained in Chapter 4, one might argue that it could have been obtained directly by averaging the Stokes' equations over the large-scale averaging volume, $\mathscr{V}_\infty$. This is indeed true; however, it would be extremely difficult to solve the closure problem presented in Chapter 4 for a representative region of a heterogeneous porous medium. On the other hand, the solution of the closure problem given in Sec. 5.3 is relatively straightforward and should accurately predict $\mathbf{K}_\beta^*$ if sufficient information concerning the structure of the system is available.

5.5 Comparison Between Theory and Experiment

There would appear to no readily available source of measured large-scale permeabilities with which to compare the theoretical values of $\mathbf{K}_\beta^*$. However, when the Darcy-scale permeabilities, $\mathbf{K}_{\beta\omega}$ and $\mathbf{K}_{\beta\eta}$, are isotropic, the closure problem is identical to that used to predict the effective thermal conductivity tensor, and the comparison between theory and experiment presented in Chapter 2 can be used to confirm the validity of the theory for $\mathbf{K}_\beta^*$. In addition, if $\mathbf{K}_{\beta\omega}$ is isotropic and $\mathbf{K}_{\beta\eta}$ is zero the closure problem given by Eqs. 5.3-2 is identical to that described in Chapter 1 for the process of diffusion. The good agreement between theory and experiment for the case of diffusion in porous media can thus be used to partly confirm the validity of the theory for $\mathbf{K}_\beta^*$. While these two special cases encourage one to accept the theory, it must be noted that the structure of a typical heterogeneous porous media is considerably more complex than the systems examined in Chapters 1 and 2 and the theory obviously needs to be tested for more realistic porous media. An important aspect of the theory is the determination of the *characteristics* of the ω and η-regions that *pass through the filter* and thus contribute to the large-scale permeability tensor, $\mathbf{K}_\beta^*$.

5.6 Conclusions

In this chapter we have briefly examined the 2-scale problem of single-phase flow in hierarchical porous media. The general techniques associated with the method of large-scale averaging have been presented in terms of a two-region model of a heterogeneous porous medium. The extension to multi-region models is straightforward, and the application to heterogeneous porous media with continuously varying properties is described by Quintard and Whitaker (1987) and Plumb and Whitaker (1988a-b). The more general problem of transport in chemically and mechanically heterogeneous porous media has been considered by Quintard and Whitaker (1996a-b, 1998a-c).

5.7 Problems

5-1. Develop the complete tensorial form of Eqs. 5.2-43 through 5.2-45 by avoiding approximations of the type

$$\mathbf{K}_{\omega\eta}^{-1}\cdot\left(\mathbf{K}_{\beta\omega}-\mathbf{K}_{\beta\eta}\right) = \mathbf{O}\left[\left(K_{\beta\omega}-K_{\beta\eta}\right)/K_{\omega\eta}\right] \tag{1}$$

Begin with Eqs. 5.2-35 and 5.2-36 and ignore variations of φ_ω in order to obtain simplified forms of those equations. Subtract the two equations to develop the governing equation for the difference between the regional pressures that appear in Eqs. 5.2-41. As an approximation, make use of the representations for $\tilde{P}_{\beta\omega}$ and $\tilde{P}_{\beta\eta}$ given by Eqs. 5.3-1 in order to define a region geometry tensor $\mathbf{C}_{\omega\eta}$ that is comparable to the phase geometry tensor introduced in Sec. 2.3. The transport equation for the difference between the regional pressures will contain an integral involving $\nabla\langle P_\beta\rangle_\omega^\beta$ that can be approximated by (Quintard and Whitaker, 1996a-b)

$$\frac{1}{\mathscr{V}_\omega}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\mathbf{K}_{\beta\omega}\cdot\nabla\langle P_\beta\rangle_\omega^\beta\,dA = \mathbf{O}\left[\alpha\left(\left\{\langle P_\beta\rangle_\omega^\beta\right\}^\omega - \left\{\langle P_\beta\rangle_\eta^\beta\right\}^\eta\right)\right] \tag{2}$$

Here α is an exchange coefficient originally introduced by Barenblatt *et al.* (1960) and values are given by Quintard and Whitaker (1996b).

5-2. Consider the stratified system illustrated in Figure 5-2 and demonstrate that the large-scale permeability defined by Eq. 5.3-4 takes the form (Quintard and Whitaker, 1987)

$$\mathbf{K}_\beta^* = \varphi_\omega\mathbf{K}_{\beta\omega}+\varphi_\eta\mathbf{K}_{\beta\eta}+\frac{\varphi_\omega\varphi_\eta\left(\mathbf{K}_{\beta\omega}-\mathbf{K}_{\beta\eta}\right)\cdot(\mathbf{ii})\cdot\left(\mathbf{K}_{\beta\eta}-\mathbf{K}_{\beta\omega}\right)}{\mathbf{i}\cdot\left(\varphi_\omega\mathbf{K}_{\beta\eta}+\varphi_\eta\mathbf{K}_{\beta\omega}\right)\cdot\mathbf{i}} \tag{1}$$

Make use of Eqs. 5.3-2 to determine $\mathbf{b}_\omega$ and $\mathbf{b}_\eta$ which only depend on x.

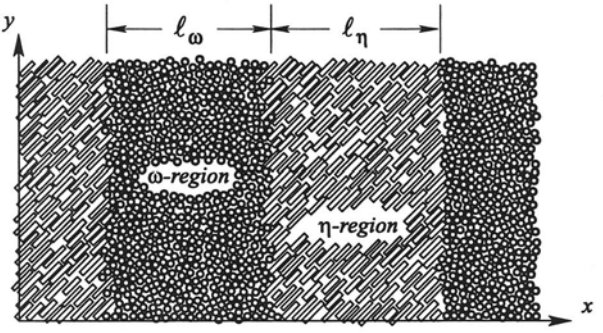

Figure 5-2. Stratified porous medium

Appendix

Tensor Algebra

This appendix represents a very brief review of vectors and tensors as they are used in this specific monograph. More detailed treatments are available in the studies of McConnell (1957), Simmonds (1982), and many others. Solutions to the problems given at the end of this appendix are available from the author.

A.1. INDEX NOTATION

Any vector (sometimes referred to as a *first order tensor*) can be expressed in rectangular Cartesian coordinates as

$$\mathbf{a} = \mathbf{i}a_x + \mathbf{j}a_y + \mathbf{k}a_z \tag{A1}$$

in which $\mathbf{i}, \mathbf{j}$, and $\mathbf{k}$ are the orthogonal unit base vectors and a_x, a_y, and a_z are the components of $\mathbf{a}$. The vector can also be written as

$$\mathbf{a} = \mathbf{e}_1 a_1 + \mathbf{e}_2 a_2 + \mathbf{e}_3 a_3 \tag{A2}$$

in which $\mathbf{e}_1, \mathbf{e}_2$, and $\mathbf{e}_3$ have been used to replace $\mathbf{i}, \mathbf{j}$, and $\mathbf{k}$, and a_1, a_2, and a_3 have been used to replace a_x, a_y, and a_z. The numerical indices used in Eq. A2 allow us to represent a vector as

$$\mathbf{a} = \sum_{i=1}^{i=3} \mathbf{e}_i a_i \tag{A3}$$

and if we impose the *summation convention* we can express this result in the compact form given by

$$\mathbf{a} = \mathbf{e}_i a_i \tag{A4}$$

Clearly the rule associated with the summation convention is that *repeated indices are summed from* 1 *to* 3.

The dot or scalar product between two vectors can be expressed as

$$\mathbf{a} \cdot \mathbf{b} = ab\cos\theta \tag{A5}$$

in which a and b represent the magnitudes of the two vectors, $\mathbf{a}$ and $\mathbf{b}$, and θ represents the angle between the two vectors. One can also express the scalar product as

$$\mathbf{a}\cdot\mathbf{b} = a_x b_x + a_y b_y + a_z b_z \tag{A6}$$

In terms of index notation this result takes the form

$$\mathbf{a}\cdot\mathbf{b} = a_1 b_1 + a_2 b_2 + a_3 b_3 \tag{A7}$$

or in terms of the summation convention, we obtain

$$\mathbf{a}\cdot\mathbf{b} = a_i b_i \tag{A8}$$

Vector equations can be expressed as

$$\mathbf{a} = \mathbf{b} \tag{A9}$$

and in terms of the components this result provides

$$\begin{aligned} a_x &= b_x \\ a_y &= b_y \\ a_z &= b_z \end{aligned} \tag{A10}$$

Index notation can be used to express these three equations in the form

$$\begin{aligned} a_1 &= b_1 \\ a_2 &= b_2 \\ a_3 &= b_3 \end{aligned} \tag{A11}$$

and a more compact representation is given by

$$a_i = b_i\,, \quad i = 1, 2, 3 \tag{A12}$$

In this equation, the index i appears only once in each term in the equation and it is referred to as a free index. The *free index convention* requires that any free index represents 1, 2, and 3 and use of this convention allows us to write Eq. A12 as

$$a_i = b_i \tag{A13}$$

A.2. DYADIC PRODUCT

The dyadic product between two vectors is represented by **ab** and is generally referred to as a tensor, but more precisely referred to as a *second order tensor.* Using index notation and the summation convention, we can express the dyadic product as

$$\mathbf{ab} = \mathbf{e}_i a_i \mathbf{e}_j b_j \tag{A14}$$

Here the *summation convention* is applied twice, i.e.,

$$\mathbf{e}_i a_i = \mathbf{e}_1 a_1 + \mathbf{e}_2 a_2 + \mathbf{e}_3 a_3 \quad \text{and} \quad \mathbf{e}_j b_j = \mathbf{e}_1 b_1 + \mathbf{e}_2 b_2 + \mathbf{e}_3 b_3 \tag{A15}$$

One must be careful never to repeat an index more that once since this will most certainly cause confusion. For example, in the term $\mathbf{e}_i a_i \mathbf{e}_i b_i$ one does not know how to apply the summation convention.

A.3. KRONECKER DELTA

The Kronecker delta appears often in problems involving tensor manipulation. The dot product between two unit base vectors is represented by

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij} \tag{A16}$$

in which δ_{ij} is referred to as the Kronecker delta. It represents the components of the unit tensor

$$\mathbf{I} = \mathbf{e}_i \mathbf{e}_j \delta_{ij} \tag{A17}$$

and it has the characteristic that

$$\delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases} \tag{A18}$$

Often one encounters the Kronecker delta in a single contraction with a second order tensor, i.e. $\delta_{ij} B_{jk}$. It will be left to the reader to show that this leads to replacing j with i according to

$$\delta_{ij} B_{jk} = B_{ik} \tag{A19}$$

For the double contraction we obtain

$$\delta_{ik} \delta_{ij} B_{jk} = B_{ii} \tag{A20}$$

in which B_{ii} is referred to as the *trace*.

A.4. DUMMY INDICES

Repeated indices are often referred to as "dummy indices" since they have the same characteristic as a dummy variable of integration. For example, in Eq. A4 one can re-label i to be n to obtain

$$\mathbf{a} = \mathbf{e}_i a_i = \mathbf{e}_n a_n \tag{A21}$$

The process of re-labeling can be used to complete a number of proofs that are given as problems in Sec. A.7.

A.5. TRANSPOSE OF A TENSOR

The transpose of a tensor $\mathbf{B}$ is defined to be the tensor $\mathbf{B}^{\mathrm{T}}$ such that

$$\mathbf{a} \cdot \mathbf{B} \cdot \mathbf{c} = \mathbf{c} \cdot \mathbf{B}^{\mathrm{T}} \cdot \mathbf{a} \tag{A22}$$

If the tensor $\mathbf{B}$ is defined by

$$\mathbf{B} = \mathbf{e}_i \mathbf{e}_j B_{ij} \tag{A23}$$

one can use Eq. A22 to show that the transpose takes the form

$$\mathbf{B}^{\mathrm{T}} = \mathbf{e}_i \mathbf{e}_j B_{ji} \tag{A24}$$

This means that the transpose can be created by interchanging the rows and the columns in the same way that one creates the transpose of a square matrix. In terms of matrix notation one would express the components of $\mathbf{B}$ as

$$B = \begin{bmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{bmatrix} \tag{A25}$$

while the components of the transpose $\mathbf{B}^{\mathrm{T}}$ are given by

$$B^{\mathrm{T}} = \begin{bmatrix} B_{11} & B_{21} & B_{31} \\ B_{12} & B_{22} & B_{32} \\ B_{13} & B_{23} & B_{33} \end{bmatrix} \tag{A26}$$

A.6. INVERSE OF A TENSOR

The tensor $\mathbf{B}$ is *invertible* when the following conditions are satisfied:

1. If $\mathbf{a}$ and $\mathbf{b}$ are vector fields such that $\mathbf{B}\cdot\mathbf{a} = \mathbf{B}\cdot\mathbf{b}$, then $\mathbf{a} = \mathbf{b}$.
2. For every vector field $\mathbf{c}$ there exits a vector field $\mathbf{d}$ such that $\mathbf{B}\cdot\mathbf{d} = \mathbf{c}$.

The inverse of $\mathbf{B}$ is identified by $\mathbf{B}^{-1}$ and it has the property that

$$\mathbf{B}^{-1}\cdot\mathbf{B} = \mathbf{B}\cdot\mathbf{B}^{-1} = \mathbf{I} \tag{A27}$$

A.7. PROBLEMS

1. Prove that $\mathbf{A}:\mathbf{D} = \mathbf{D}:\mathbf{A}$, i.e., the double dot (or double contraction) of two tensors is commutative. Carry out the proof for two cases:

a) $\mathbf{A} = \mathbf{ab}$ and $\mathbf{D} = \mathbf{cd}$
b) $\mathbf{A} = \mathbf{e}_i \mathbf{e}_j A_{ij}$ and $\mathbf{D} = \mathbf{e}_k \mathbf{e}_l D_{kl}$

In the first case make use of the fact that $\mathbf{a}\cdot\mathbf{d} = \mathbf{d}\cdot\mathbf{a}$, and in the second case carry out the summations and regroup the terms or re-label them in an appropriate manner in order to complete the proof. When using Gibbs' notation one should follow the "nesting convention" which dictates that the elements of the dyad that are closest together are multiplied first. This leads to

$$(\mathbf{ab})\cdot(\mathbf{cd}) = \mathbf{a}(\mathbf{b}\cdot\mathbf{c})\mathbf{d}$$

If this convention is not followed confusion can result.

2. Given the tensor $\mathbf{B} = \mathbf{e}_i\mathbf{e}_j B_{ij}$ and the definition of the transpose

$$\mathbf{a}\cdot\mathbf{B}\cdot\mathbf{c} \;=\; \mathbf{c}\cdot\mathbf{B}^{\mathrm{T}}\cdot\mathbf{a}$$

show that the transpose takes the forms

$$\mathbf{B}^{\mathrm{T}} \;=\; \mathbf{e}_i\mathbf{e}_j B_{ji}\,, \quad \text{or} \quad \mathbf{B}^{\mathrm{T}} \;=\; \mathbf{e}_j\mathbf{e}_i B_{ij}$$

3. Use the result from Problem 2 to prove that $\mathbf{a}\cdot\mathbf{B} = \mathbf{B}^{\mathrm{T}}\cdot\mathbf{a}$

4. If $D_{ij} = -D_{ji}$ prove that $\lambda_i D_{ij}\lambda_j = 0$. In Gibbs' notation we would express this problem as: If $\mathbf{D} = -\mathbf{D}^{\mathrm{T}}$ prove that $\lambda\cdot\mathbf{D}\cdot\lambda = 0$.

5. Given any second order tensor $\mathbf{A}$ and any vector $\mathbf{b}$, prove that

$$\nabla\cdot(\mathbf{A}\cdot\mathbf{b}) \;=\; (\nabla\cdot\mathbf{A})\cdot\mathbf{b} \;+\; \mathbf{A}^{\mathrm{T}}:\nabla\mathbf{b}$$

6. Any second order tensor $\mathbf{A}$ can be represented in terms of its *irreducible parts* according to

$$\mathbf{A} \;=\; \mathbf{A}^{\mathrm{I}} \;+\; \mathbf{A}^{\mathrm{II}} \;+\; \mathbf{A}^{\mathrm{III}}$$

In this representation $\mathbf{A}^{\mathrm{I}}$ is a symmetric and traceless tensor, $\mathbf{A}^{\mathrm{II}}$ is a skew-symmetric tensor, and $\mathbf{A}^{\mathrm{III}}$ is one third the unit tensor times the trace of $\mathbf{A}$. In terms of index notation we identify the irreducible parts as

$$A^{\mathrm{I}}_{ij} \;=\; \tfrac{1}{2}(A_{ij}+A_{ji}) - \tfrac{1}{3}\delta_{ij}A_{kk}\,, \quad A^{\mathrm{II}}_{ij} \;=\; \tfrac{1}{2}(A_{ij}-A_{ji})\,, \quad A^{\mathrm{III}}_{ij} \;=\; \tfrac{1}{3}\delta_{ij}(A_{kk})$$

Prove that these three irreducible parts are orthogonal, i.e.,

$$\mathbf{A}^{\mathrm{I}}:\mathbf{A}^{\mathrm{II}} \;=\; 0 \qquad \mathbf{A}^{\mathrm{II}}:\mathbf{A}^{\mathrm{III}} \;=\; 0 \qquad \mathbf{A}^{\mathrm{III}}:\mathbf{A}^{\mathrm{I}} \;=\; 0$$

7. Use the results of Problem 6 to prove that $(\mathbf{A}+\mathbf{A}^{\mathrm{T}}):(\mathbf{B}^{\mathrm{T}}) = \tfrac{1}{2}(\mathbf{A}+\mathbf{A}^{\mathrm{T}}):(\mathbf{B}+\mathbf{B}^{\mathrm{T}})$ for any two second order tensors $\mathbf{A}$ and $\mathbf{B}$.

8. Given the two tensors $\mathbf{A}$ and $\mathbf{B}$, prove that $(\mathbf{A}\cdot\mathbf{B})^{\mathrm{T}} \;=\; \mathbf{B}^{\mathrm{T}}\cdot\mathbf{A}^{\mathrm{T}}$

9. Given the tensor $\mathbf{B} = \mathbf{A}^{\mathrm{T}}\cdot\mathbf{A}$, prove that $\mathbf{B}$ is symmetric for any tensor $\mathbf{A}$

10. If $\mathbf{B}$ is a symmetric tensor, prove that the inverse $\mathbf{B}^{-1}$ is also symmetric. Hint: Use the definition of the inverse $\mathbf{B}\cdot\mathbf{B}^{-1} = \mathbf{I}$ and make use of Problem 8.

11. Demonstrate that $(\mathbf{A}+\mathbf{B})^{\mathrm{T}} = \mathbf{A}^{\mathrm{T}}+\mathbf{B}^{\mathrm{T}}$.

12. Given a tensor $\mathbf{A}$ that satisfies the relation $\mathbf{c}\cdot\mathbf{A}\cdot\mathbf{d}=\mathbf{d}\cdot\mathbf{A}\cdot\mathbf{c}$, prove that $\mathbf{A}$ is symmetric.

13. Prove that $\left(\mathbf{A}^{-1}\right)^{\mathrm{T}}=\left(\mathbf{A}^{\mathrm{T}}\right)^{-1}$. Hint: Use the result from Problem 8.

14. Given two tensors, $\mathbf{A}$ and $\mathbf{B}$, prove that $(\mathbf{A}\cdot\mathbf{B})^{-1}=\mathbf{B}^{-1}\cdot\mathbf{A}^{-1}$.

15. Prove that $\left(\mathbf{A}^{-1}\right)^{-1}=\mathbf{A}$.

16. Given the divergence theorem

$$\int_{\mathscr{V}}\nabla\cdot\mathbf{b}\,dV \;=\; \int_{\mathscr{A}}\mathbf{n}\cdot\mathbf{b}\,dA$$

derive the *scalar version* using the substitution $\mathbf{b}=s\mathbf{c}$ in which s is an arbitrary scalar and $\mathbf{c}$ is an arbitrary constant vector. Also derive the *tensor version* using the substitution $\mathbf{b}=\mathbf{A}\cdot\mathbf{c}$ in which $\mathbf{A}$ is any arbitrary tensor and $\mathbf{c}$ is an arbitrary constant vector.

Nomenclature*

a_v	interfacial area per unit volume, m^{-1}
$\mathscr{A}_{\beta\sigma}$	area of the β-σ interface contained with the macroscopic region, m^2
$\mathscr{A}_{\beta e}$	area of the entrances and exits of the β-phase at the boundary of the macroscopic region, m^2
$\mathscr{A}_{\sigma e}$	area of the entrances and exits of the σ-phase at the boundary of the macroscopic region, m^2
$\mathscr{A}_{\gamma\kappa}$	area of the γ-κ interface contained within the macroscopic region, m^2
$\mathscr{A}_{\gamma e}$	area of the entrances and exits of the γ-phase at the boundary of the macroscopic region, m^2
$A_{\beta\sigma}$	$A_{\sigma\beta}$, area of the β-σ interface contained within the averaging volume, m^2
$A_{\gamma\kappa}$	area of the γ-κ interface contained within the averaging volume, m^2
$A_{\gamma e}$	area of the entrances and exits of the γ-phase contained within the averaging volume, m^2
$\mathbf{b}_\alpha$	vector field that maps $\nabla\langle c_{A\alpha}\rangle^\alpha$ onto $\tilde{c}_{A\alpha}$ for the α-phase (α = γ, β), m
$\mathbf{B}_\beta$	tensor field that maps $\langle \mathbf{v}_\beta\rangle^\beta$ onto $\tilde{\mathbf{v}}_\beta$
$\mathbf{b}_\sigma$	vector field that maps $\nabla\langle T\rangle$ onto $\tilde{T}_\sigma$, m
$\mathbf{b}_\beta$	vector field that maps $\nabla\langle T\rangle$ onto $\tilde{T}_\beta$, m; the vector field that maps $\mu_\beta\langle \mathbf{v}_\beta\rangle^\beta$ onto $\tilde{p}_\beta$, m^{-1}
$\mathbf{b}_\omega$	vector field that maps $\nabla\left\{\langle P_\beta\rangle^\beta\right\}$ onto $\tilde{P}_{\beta\omega}$, m
$\mathbf{b}_\eta$	vector field that maps $\nabla\left\{\langle P_\beta\rangle^\beta\right\}$ onto $\tilde{P}_{\beta\eta}$, m
$c_{A\alpha}$	molar concentration of species A in the α-phase, moles/m^3
c_{As}	surface molar concentration of species A, moles/m^2
c_α	total molar concentration in the α-phase, moles/m^3
$\langle c_{A\alpha}\rangle$	superficial average concentration of species A in the α-phase, moles/m^3
$\langle c_{A\alpha}\rangle^\alpha$	intrinsic average concentration of species A in the α-phase, moles/m^3
$\langle c_{A\gamma}\rangle_{\gamma\kappa}$	area averaged concentration of species A over the γ-κ interface, moles/m^3
$\tilde{c}_{A\alpha}$	$c_{A\alpha} - \langle c_{A\alpha}\rangle^\alpha$, spatial deviation concentration of species A in the α-phase, moles/m^3
c_p	constant pressure heat capacity, kcal/kg K

* The letter α is used to represent the γ, κ, β, and σ phases in addition to the ω and η regions that appear in Chapter 5.

C_p $\left[\varepsilon_\beta(\rho c_p)_\beta + \varepsilon_\sigma(\rho c_p)_\sigma\right] / (\varepsilon_\beta \rho_\beta + \varepsilon_\sigma \rho_\sigma)$, mass fraction weighted, constant pressure heat capacity, kcal/kg K

$\mathscr{D}_{AB}$ binary molecular diffusion coefficient for species A and B, m^2/s

$\mathscr{D}_\alpha$ mixture diffusion coefficient for species A in the α-phase, m^2/s

$\mathbf{D}_{eff}$ effective diffusivity tensor, m^2/s

$\mathbf{D}_\beta$ hydrodynamic dispersion tensor, m^2/s

$\mathbf{D}_\beta^*$ $\mathbf{D}_{eff} + \mathbf{D}_\beta$, total dispersivity tensor, m^2/s

$\mathbf{g}$ gravitational acceleration, m/s^2

$\mathbf{I}$ unit tensor

k_β thermal conductivity of the β-phase, W/mK

k_σ thermal conductivity of the σ-phase, W/mK

$\mathbf{K}_{eff}$ effective thermal conductivity tensor for the β-σ system, W/mK

k_1 adsorption rate constant, m/s

k_{-1} desorption rate constant, s^{-1}

k_s intrinsic surface reaction rate coefficient, s^{-1}

k pseudo heterogeneous reaction rate coefficient, m/s

$\mathbf{K}_\beta$ Darcy's law permeability tensor, m^2

$\mathbf{K}_{\beta\omega}$ Darcy's law permeability tensor for the ω-region, m^2

$\mathbf{K}_{\beta\eta}$ Darcy's law permeability tensor for the η-region, m^2

$\mathbf{K}_\beta^*$ large-scale Darcy's law permeability tensor, m^2

ℓ_α characteristic length for the α-phase, m

ℓ_i $i = 1, 2, 3$, lattice vectors, m

L characteristic length for macroscopic quantities, m

L_ε characteristic length for $\nabla\varepsilon$, m

L_c characteristic length for $\nabla\langle c_{A\alpha}\rangle^\alpha$, m

L_{c1} characteristic length for $\nabla\nabla\langle c_{A\alpha}\rangle^\alpha$, m

L_T characteristic length for $\nabla\langle T_\beta\rangle^\beta$, $\nabla\langle T_\sigma\rangle^\sigma$ or $\nabla\langle T\rangle$, m

L_{T1} characteristic length for $\nabla\nabla\langle T_\beta\rangle^\beta$, $\nabla\nabla\langle T_\sigma\rangle^\sigma$ or $\nabla\nabla\langle T\rangle$, m

$\mathscr{L}_\varphi$ characteristic length for $\nabla\varphi_\omega$ or $\nabla\varphi_\eta$, m

$\mathscr{L}_{P1}$ characteristic length for $\nabla\nabla\left\{\langle P_\beta\rangle_\omega^\beta\right\}$ and $\nabla\nabla\left\{\langle P_\beta\rangle_\eta^\beta\right\}$, m

$\mathbf{N}_A$ $c_A\mathbf{v}_A$, molar flux of species A, moles/m^2s

$\mathbf{n}_{\beta\sigma}$ $-\mathbf{n}_{\sigma\beta}$, unit normal vector directed from the β-phase toward the σ-phase

$\mathbf{n}_{\gamma\kappa}$ unit normal vector directed from the γ-phase toward the κ-phase

$\mathbf{n}_{\gamma e}$ outwardly directed unit normal vector for the entrances and exits of the γ-phase contained within the averaging volume

$\mathbf{n}_{\omega\eta}$ $-\mathbf{n}_{\eta\omega}$, unit normal vector directed from the ω-region toward the η-region

p_β	total pressure in the β-phase, Pa
$\langle p_\beta \rangle^\beta$	intrinsic average pressure in the β-phase, Pa
$\langle p_\beta \rangle$	$\varepsilon_\beta \langle p_\beta \rangle^\beta$, superficial average pressure in the β-phase, Pa
$\left\{ \langle p_\beta \rangle_\alpha^\beta \right\}^\alpha$	intrinsic regional average pressure for the β-phase in the α-region, Pa
$\left\{ \langle p_\beta \rangle_\alpha^\beta \right\}$	$\varphi_\alpha \left\{ \langle p_\beta \rangle_\alpha^\beta \right\}^\alpha$, superficial regional average pressure of the β-phase in the α-region, Pa
$\left\{ \langle p_\beta \rangle^\beta \right\}$	$\varphi_\omega \left\{ \langle p_\beta \rangle_\omega^\beta \right\}^\omega + \varphi_\eta \left\{ \langle p_\beta \rangle_\eta^\beta \right\}^\eta$, large-scale average pressure for the β-phase, Pa
$\mathbf{r}$	position vector, m
$\mathbf{r}_\alpha$	position vector locating points in the α-phase, m
r_o	radius of the averaging volume or characteristic length of a unit cell, m
R_A	molar rate of production of species A owing to homogeneous chemical reaction, moles/m^{3}s
R_{As}	molar rate of production of species A owing to *heterogeneous* chemical reaction, moles/m^{2}s
s_γ	scalar field that maps $\langle c_{A\gamma} \rangle^\gamma$ onto $\tilde{c}_{A\gamma}$
t	time, s
t^*	characteristic process time, s; dimensionless time
T_α	temperature of the α-phase, K
$\tilde{T}_\alpha$	$T_\alpha - \langle T_\alpha \rangle^\alpha$, spatial deviation temperature of the α-phase, K
$\langle T \rangle$	$\varepsilon_\beta \langle T_\beta \rangle^\beta + \varepsilon_\sigma \langle T_\sigma \rangle^\sigma$, spatial average temperature of the β-σ system, K
$\hat{T}_\alpha$	$\langle T_\alpha \rangle^\alpha - \langle T \rangle$, large-scale spatial deviation temperature for the α-phase, K
$\mathbf{v}_A$	species A velocity, m/s
$\mathbf{v}_\beta$	mass average velocity in the β-phase, m/s
$\langle \mathbf{v}_\beta \rangle^\beta$	intrinsic volume average velocity in the β-phase, m/s
$\langle \mathbf{v}_\beta \rangle$	$\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta$, superficial volume average velocity in the β-phase, m/s
$\tilde{\mathbf{v}}_\beta$	$\mathbf{v}_\beta - \langle \mathbf{v}_\beta \rangle^\beta$, local spatial deviation velocity, m/s
$\left\{ \langle \mathbf{v}_\beta \rangle_\alpha \right\}$	superficial regional average velocity for the α-region, m/s
$\left\{ \langle \mathbf{v}_\beta \rangle_\alpha \right\}^\alpha$	intrinsic regional average velocity for the α-region, m/s
$\left\{ \langle \mathbf{v}_\beta \rangle \right\}$	$\varphi_\omega \left\{ \langle \mathbf{v}_\beta \rangle_\omega \right\}^\omega + \varphi_\eta \left\{ \langle \mathbf{v}_\beta \rangle_\eta \right\}^\eta$, large-scale average velocity, m/s
V_α	volume of the α-phase or α-region (α = β,σ,γ,κ,η,ω) contained within an averaging volume, m^3
$\mathscr{V}$	local averaging volume, m^3
$\mathscr{V}_\infty$	large-scale averaging volume, m^3

$x_{A\alpha}$	mole fraction of species A in the α-phase
$\mathbf{x}$	position vector locating the centroid of the averaging volume, m
$\mathbf{y}_\alpha$	position vector locating points in the α-phase relative to the centroid of the averaging volume, m

Greek letters

ε_α	volume fraction of the α-phase, $V_\alpha/\mathscr{V}$
κ	k_σ/k_β, ratio of thermal conductivities
ϕ	particle Thiele modulus, typically of the form $\sqrt{kL^2 a_v/D_{eff}}$
φ	pore Thiele modulus, typically of the form $\sqrt{k/a_v\mathscr{D}}$
φ_α	$V_\alpha/\mathscr{V}_\infty$, volume fraction of the α-region
λ	arbitrary unit vector
$\rho_{A\alpha}$	species A mass density in the α-phase, kg/m^3
ρ_α	total mass density in the α-phase, kg/m^3
$\langle\rho\rangle$	spatial average mass density, kg/m^3
ν	arbitrary unit vector
μ_β	coefficient of viscosity for the β-phase, Pa s
ψ_α	arbitrary function associated with the α-phase
$\omega_{A\alpha}$	mass fraction of species A in the α-phase

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