Volume Averaging of Transport Equations

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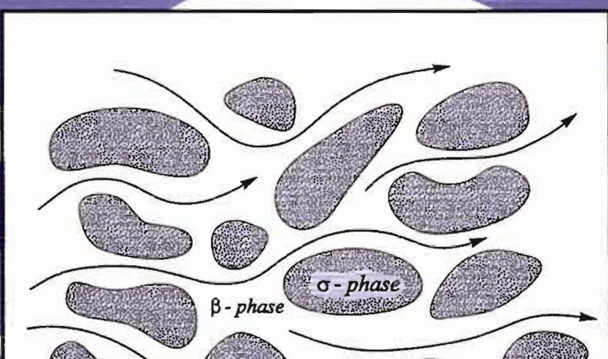

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Volume averaging of transport equations

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Abstract

This chapter illustrates how the method of volume averaging can be used to derive the Forchheimer equation and the convective-dispersion equation with nonlinear adsorption. These two equations have numerous applications in the analysis of transport in porous media, and they have been chosen for this study in order to illustrate the role of the averaging procedure *and* the closure problem in the development of volume averaged transport equations. In our analysis of the Navier-Stokes equations we find that the no-slip condition *does not play an important role* in the averaging procedure, but that it *dominates* the structure of the closure problem. On the other hand, our study of the convective-diffusion equation illustrates that the adsorption boundary condition makes an *important contribution* to the volume averaged transport equation, but contributes *very little* to the closure problem. We conclude that one must pay careful attention to the averaging procedure, the closure problem, and the boundary conditions in the development of multiphase transport equations.

Nomenclature

ROMAN LETTERS

a_v interfacial area per unit volume, m^{-1}.

$\mathscr{A}_{\beta\sigma}$ area of the β-σ interface contained in 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.

$A_{\beta\sigma}$ area of the β-σ interface contained within the averaging volume, m^2.

b vector field that maps $\mu_\beta \langle \mathbf{v}_\beta \rangle^\beta$ onto $\tilde{p}_\beta$ when inertial effects are negligible, or the vector field that maps $\nabla \langle c_A \rangle^\beta$ onto $\tilde{c}_A$, m^{-1}.

B tensor that maps $\tilde{\mathbf{v}}_\beta$ onto $\langle \mathbf{v}_\beta \rangle^\beta$ when inertial effects are negligible.

c_A	molar concentration of species A, moles/m^3.
$\langle c_A \rangle^\beta$	intrinsic average concentration of species A in the β-phase, moles/m^3.
$\tilde{c}_A$	$c_A - \langle c_A \rangle^\beta$, spatial deviation concentration of species A in the β-phase, moles/m^3.
$\mathscr{D}_\beta$	mixture diffusion coefficient for species A in the β-phase, m^2/s.
$\mathbf{D}^*$	dispersion tensor, m^2/s.
$\mathbf{g}$	gravitational acceleration, m/s^2.
$\mathbf{I}$	unit tensor.
ℓ_β	characteristic length for the β-phase, m.
ℓ_i	$i = 1, 2, 3$, lattice vectors, m.
L	generic characteristic length for macroscopic quantities, m.
L_ε	characteristic length associated with $\Delta\varepsilon_\beta$, m.
L_p	characteristic length associated with $\Delta\langle p_\beta \rangle^\beta$, m.
L_{p1}	characteristic length associated with $\Delta\left(\nabla\langle p_\beta \rangle^\beta\right)$, m.
L_{v}	characteristic length associated with $\Delta\langle \mathbf{v}_\beta \rangle^\beta$, m.
$L_{\mathrm{v}1}$	characteristic length associated with , m.
$L_{\mathrm{v}2}$	characteristic length associated with $\Delta\left(\nabla\nabla\langle \mathbf{v}_\beta \rangle^\beta\right)$, m.
$\mathbf{m}$	vector field that maps $\mu_\beta \langle \mathbf{v}_\beta \rangle^\beta$ onto $\tilde{p}_\beta$, m^{-1}.
$\mathbf{M}$	tensor that maps $\tilde{\mathbf{v}}_\beta$ onto $\langle \mathbf{v}_\beta \rangle^\beta$.
$\mathbf{n}_{\beta\sigma}$	unit normal vector directed from the β-phase toward the σ-phase.
p_β	total pressure in the β-phase, Pa.
$\langle p_\beta \rangle^\beta$	intrinsic average pressure in the β-phase, Pa.
$\langle p_\beta \rangle$	superficial average pressure in the β-phase, Pa.
$\tilde{p}_\beta$	$p_\beta - \langle p_\beta \rangle^\beta$, spatial deviation pressure, Pa.
$\mathbf{r}$	position vector, m.
r_o	radius of the averaging volume, m.
t	time, s.
t^*	characteristic process time, s.
$\mathbf{v}_\beta$	velocity in the β-phase, m/s.
$\langle \mathbf{v}_\beta \rangle^\beta$	intrinsic average velocity in the β-phase, m/s.

$\langle \mathbf{v}_\beta \rangle$ superficial average velocity in the β-phase, m/s.

$\tilde{\mathbf{v}}_\beta$ $\mathbf{v}_\beta - \langle \mathbf{v}_\beta \rangle^\beta$, spatial deviation velocity, m/s.

$\mathscr{V}$ local averaging volume, m^3.

V_β volume of the β-phase contained within the averaging volume, m^3.

$\mathbf{x}$ position vector locating the centroid of the averaging volume, m.

$\mathbf{y}_\beta$ position vector locating points in the β-phase relative to the centroid of the averaging volume, m.

GREEK LETTERS

ε_β $V_\beta / \mathscr{V}$, volume fraction of the β-phase.

ρ_β density of the β-phase, kg/m^3.

μ_β viscosity of the β-phase, Pa s.

ν_β kinematic viscosity of the β-phase, m^2/s.

1 Introduction

The two physical processes under consideration in this chapter are single-phase, incompressible flow in a rigid porous medium (Fig. 1), and mass transport of a chemical species with adsorption at the fluid-solid interface. We identify the fluid as the β-phase and the rigid solid as the σ-phase, and we list the governing differential equations describing these two processes as

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{1}$$

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

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}_\beta) = \mathscr{D}_\beta \nabla^2 c_A \tag{3}$$

Our analysis will be restricted to constant physical properties, ρ_β, μ_β, and $\mathscr{D}_\beta$, and we have arranged the transport equations in a form that illustrates their similarity. They *differ* by the fact that eqn 2 is a *vector* equation that

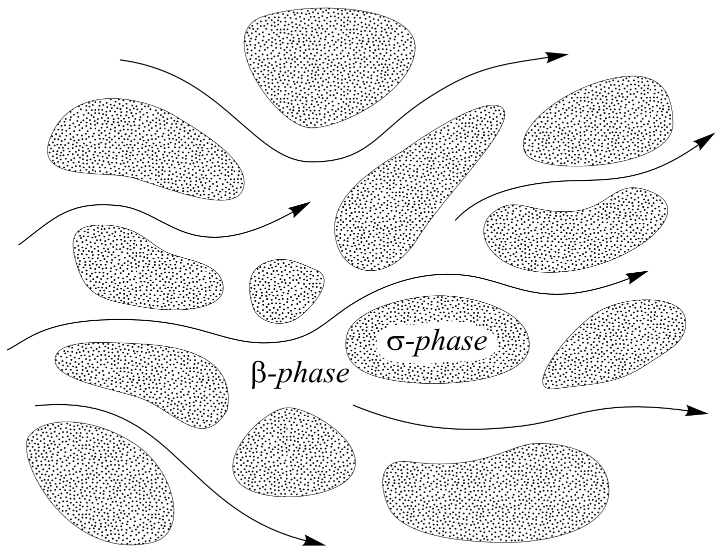

Figure 1
Flow in a Rigid Porous Medium

contains a *momentum source*, $-\nabla p_\beta + \rho_\beta \mathbf{g}$, while eqn 3 is a *scalar* equation; however, the key difference between the momentum transport process and the mass transport process is represented in terms of the interfacial boundary conditions that are given by

$$\text{B.C.1} \qquad \mathbf{v}_\beta = 0, \qquad at\ \mathscr{A}_{\beta\sigma} \tag{4}$$

$$\text{B.C.2} \qquad -\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_A = K_{eq} \frac{\partial c_A}{\partial t}, \qquad at\ \mathscr{A}_{\beta\sigma} \tag{5}$$

Here we have used $\mathscr{A}_{\beta\sigma}$ to represent the area of the β-σ interface contained within the macroscopic region (Fig. 2). Equation 4 represents the no-slip condition imposed at the fluid-solid interface, while eqn 5 describes the nonlinear adsorption process in which K_{eq} is a function of the bulk concentration, c_A. In addition to the interfacial boundary conditions, we need to state the boundary conditions at the entrances and exits of the macroscopic region (Fig. 2). We use $\mathscr{A}_{\beta e}$ to represent the β-phase entrances and exits associated with that region, and we express the boundary conditions as

B.C.3 $$\mathbf{v}_\beta = \mathbf{f}(\mathbf{r},t), \quad at\ \mathscr{A}_{\beta e} \tag{6}$$

B.C.4 $$c_A = f(\mathbf{r},t), \quad at\ \mathscr{A}_{\beta e} \tag{7}$$

In general, the boundary conditions for the velocity and concentration at $\mathscr{A}_{\beta e}$ are known only in terms of average quantities; however, it is important

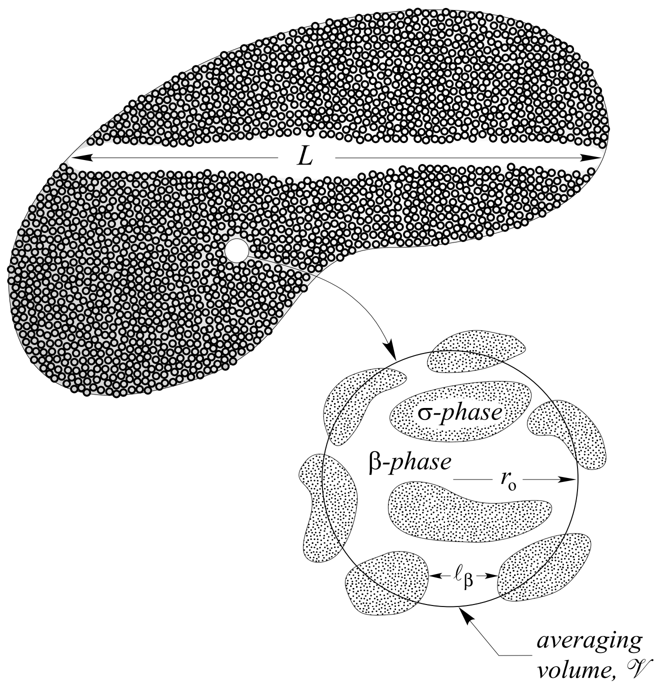

Figure 2
Macroscopic Region and Local Averaging Volume

to list the boundary conditions given by eqns 6 and 7 as a reminder of what we *do not know* about the processes under consideration. The conditions that apply at the boundary between a porous medium and a homogeneous fluid have been studied using numerical experiments by Prat (1989, 1990, 1992) and by Sahraoui and Kaviany (1992, 1993, 1994), and a general theoretical approach has been developed by Ochoa-Tapia and Whitaker (1995, 1996).

2 Volume averaging

In the method of volume averaging, one associates an averaging volume $\mathscr{V}$ with every point in space (both in the fluid phase *and* in the solid phase), and this allows one to define an average value at every point in space. The *superficial average* is defined by

$$\langle \psi_\beta \rangle = \frac{1}{\mathscr{V}} \int_{V_\beta} \psi_\beta \, dV \tag{8}$$

in which V_β represents the volume of the β-phase contained within the averaging volume. Here we have used ψ_β to represent any function defined in the β-phase, and we think of the average $\langle \psi_\beta \rangle$ as being associated with the centroid of the averaging volume (Fig. 3). The centroid is located by the

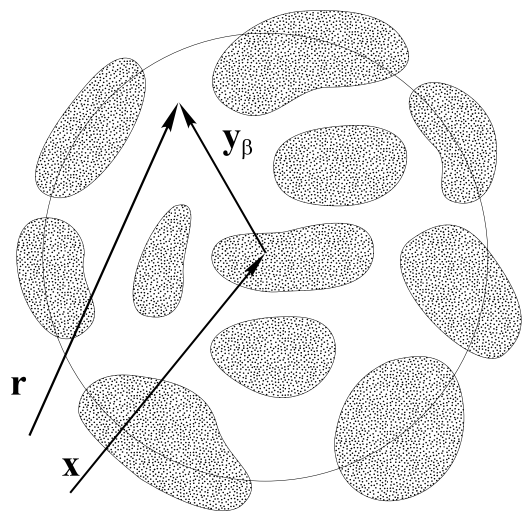

Figure 3
Position Vectors Associated with the Averaging Volume

position vector $\mathbf{x}$, and points in the β-phase *relative to the centroid* are located by $\mathbf{y}_\beta$. To be more precise about the definition given by eqn 8, we could write

$$\langle\psi_\beta\rangle\big|_{\mathbf{x}} = \frac{1}{\mathscr{V}} \int_{V_\beta(\mathbf{x})} \psi_\beta(\mathbf{x}+\mathbf{y}_\beta)\,dV_y \tag{9}$$

in order to clearly indicate that $\langle\psi_\beta\rangle$ is associated with the centroid and that integration is carried out with respect to the components of the relative position vector, $\mathbf{y}_\beta$. In general, we will use the simpler nomenclature indicated by eqn 8 with the idea that the specific details indicated in eqn 9 are understood.

In addition to the superficial average, we will need to make use of the *intrinsic average* that is defined according to

$$\langle\psi_\beta\rangle^\beta = \frac{1}{V_\beta} \int_{V_\beta} \psi_\beta\,dV \tag{10}$$

The superficial and intrinsic averages are related by

$$\langle\psi_\beta\rangle = \varepsilon_\beta \langle\psi_\beta\rangle^\beta \tag{11}$$

in which ε_β is the volume fraction of the β-phase, or the porosity. While the nomenclature used here may appear to be cumbersome, it is extremely important to carefully distinguish between the superficial and intrinsic averages. Failure to do so leads to errors on the order of ε_β. For parameters that are linear in ε_β this means an error of a factor of three, while a factor of *ten* results if the dependence is quadratic.

2.1 Continuity equation

We begin the averaging process with the continuity equation and form the *superficial average* of eqn 1 to obtain

$$\frac{1}{\mathscr{V}} \int_{V_\beta} \nabla\cdot\mathbf{v}_\beta\,dV = \langle\nabla\cdot\mathbf{v}_\beta\rangle = 0 \tag{12}$$

In order to interchange integration and differentiation in eqn 12, we need to make use of the spatial averaging theorem (Howes and Whitaker, 1985; Whitaker, 1985) that can be expressed as

$$\langle \nabla \psi_\beta \rangle = \nabla \langle \psi_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \psi_\beta \, dA \tag{13}$$

Here $A_{\beta\sigma}$ represents the interfacial area contained within the averaging volume, and we have used $\mathbf{n}_{\beta\sigma}$ to represent the unit normal vector pointing *from* the β-phase *toward* the σ-phase. Use of the averaging theorem with eqn 12 yields

$$\langle \nabla \cdot \mathbf{v}_\beta \rangle = \nabla \cdot \langle \mathbf{v}_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathbf{v}_\beta \, dA = 0 \tag{14}$$

and the no-slip condition given by eqn 4 allows us to express the superficial average form of the continuity equation as

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle = 0 \tag{15}$$

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. We will also have occasion to use the continuity equation in terms of the *intrinsic average velocity* $\langle \mathbf{v}_\beta \rangle^\beta$, thus we make use of the relation between the superficial velocity and the intrinsic velocity

$$\langle \mathbf{v}_\beta \rangle = \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \tag{16}$$

to obtain an alternate form of the continuity equation given by

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta = -\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{17}$$

This form will be used in the development of the closure problem that that is discussed in Sec. 3.

2.2 Momentum equation

The superficial average of the Navier-Stokes equations can be expressed as

$$\langle\frac{\partial}{\partial t}(\rho_\beta \mathbf{v}_\beta)\rangle + \langle\nabla\cdot(\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta)\rangle = -\langle\nabla p_\beta\rangle + \langle\rho_\beta \mathbf{g}\rangle + \langle\mu_\beta \nabla\cdot\nabla \mathbf{v}_\beta\rangle \quad (18)$$

and since variations of the density and viscosity are considered to be negligible, we can write eqn 18 in the form

$$\rho_\beta\langle\frac{\partial \mathbf{v}_\beta}{\partial t}\rangle + \rho_\beta\langle\nabla\cdot(\mathbf{v}_\beta \mathbf{v}_\beta)\rangle = -\langle\nabla p_\beta\rangle + \varepsilon_\beta\rho_\beta \mathbf{g} + \mu_\beta\langle\nabla\cdot\nabla \mathbf{v}_\beta\rangle \quad (19)$$

Here we see the need to interchange integration and differentiation in every term except the one representing the gravitational force.

2.2.1 Inertial terms

We begin our analysis of eqn 19 by noting that the volume of the β-phase contained within the averaging volume is independent of time. This allows us to interchange time differentiation and spatial integration so that the first term in eqn 19 takes the form

$$\langle\frac{\partial \mathbf{v}_\beta}{\partial t}\rangle = \frac{1}{\mathscr{V}}\int_{V_\beta}\frac{\partial \mathbf{v}_\beta}{\partial t}dV = \frac{\partial}{\partial t}\left\{\frac{1}{\mathscr{V}}\int_{V_\beta}\mathbf{v}_\beta\, dV\right\} = \frac{\partial\langle\mathbf{v}_\beta\rangle}{\partial t} \quad (20)$$

Moving on to the convective inertial term in eqn 19, we make use of the averaging theorem given by eqn 13 to obtain

$$\langle\nabla\cdot(\mathbf{v}_\beta \mathbf{v}_\beta)\rangle = \nabla\cdot\langle\mathbf{v}_\beta \mathbf{v}_\beta\rangle + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta \mathbf{v}_\beta\, dA \quad (21)$$

and on the basis of the no-slip condition indicated by eqn 4 this result simplifies to

$$\langle\nabla\cdot(\mathbf{v}_\beta \mathbf{v}_\beta)\rangle = \nabla\cdot\langle\mathbf{v}_\beta \mathbf{v}_\beta\rangle \quad (22)$$

Use of eqns 20 and 22 in eqn 19 yields the following form of the superficial averaged Navier-Stokes equations.

$$\rho_\beta\frac{\partial\langle\mathbf{v}_\beta\rangle}{\partial t} + \rho_\beta\nabla\cdot\langle\mathbf{v}_\beta \mathbf{v}_\beta\rangle = -\langle\nabla p_\beta\rangle + \varepsilon_\beta\rho_\beta \mathbf{g} + \mu_\beta\langle\nabla\cdot\nabla \mathbf{v}_\beta\rangle \quad (23)$$

Here we are confronted with the average of a product, while it is the product of averages that we desire. In order to deal with this problem, we follow the type of analysis encountered in the time averaging of turbulent transport equations (Tennekes and Lumley, 1972) in which the velocity is decomposed into a time average and a temporal deviation. In the method of volume averaging, we decompose the velocity and pressure into *spatial averages* and a *spatial deviations*. Although the *superficial average velocity* is the preferred representation for the macroscopic velocity, it is best to use the *intrinsic average velocity* in the definition of the spatial deviation, thus we follow Gray (1975) and express the point velocity as

$$\mathbf{v}_\beta \quad = \quad \langle \mathbf{v}_\beta \rangle^\beta \quad + \quad \tilde{\mathbf{v}}_\beta \tag{24}$$

As in our discussion of the definition of the average given by eqns. 8 and 9, we could be more explicit concerning this decomposition and express it as

$$\mathbf{v}_\beta \Big|_{\mathbf{r}} \quad = \quad \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{r}} \quad + \quad \tilde{\mathbf{v}}_\beta \Big|_{\mathbf{r}} \tag{25}$$

in which $\mathbf{r}$ is the position vector illustrated in Fig. 3. When this representation is used in the convective inertial term in eqn 23, we obtain four contributions that are given explicitly by

$$\langle \mathbf{v}_\beta \mathbf{v}_\beta \rangle \quad = \quad \langle \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \rangle \; + \; \langle \langle \mathbf{v}_\beta \rangle^\beta \tilde{\mathbf{v}}_\beta \rangle \; + \; \langle \tilde{\mathbf{v}}_\beta \langle \mathbf{v}_\beta \rangle^\beta \rangle \; + \; \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \tag{26}$$

This represents a *non-local form* of the convective momentum flux since the average velocity $\langle \mathbf{v}_\beta \rangle^\beta$ is evaluated at points other than the centroid of the averaging volume. To be explicit about this matter, we refer to eqn 9 and express the first term on the right hand side of eqn 26 as

$$\langle \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \rangle \Big|_{\mathbf{x}} \quad = \quad \frac{1}{\mathscr{V}} \int\limits_{V_\beta(\mathbf{x})} \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} dV_y \tag{27}$$

This *non-local* form can be simplified to a *local* form if we can ignore variations of the intrinsic average velocity within the averaging volume (Carbonell and Whitaker, 1984). Under these circumstances, eqn 26 simplifies to

$$\langle \mathbf{v}_\beta \mathbf{v}_\beta \rangle \quad = \quad \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \langle 1 \rangle \; + \; \langle \mathbf{v}_\beta \rangle^\beta \langle \tilde{\mathbf{v}}_\beta \rangle \; + \; \langle \tilde{\mathbf{v}}_\beta \rangle \langle \mathbf{v}_\beta \rangle^\beta \; + \; \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \tag{28}$$

and it is consistent with this simplification to set the average of the spatial deviation equal to zero, i.e.,

$$\langle \tilde{\mathbf{v}}_\beta \rangle \quad = \quad 0 \tag{29}$$

Under these circumstances, eqn 28 simplifies to

$$\langle \mathbf{v}_\beta \mathbf{v}_\beta \rangle \quad = \quad \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \quad + \quad \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \tag{30}$$

in which we have made use of the fact that $\langle 1 \rangle = \varepsilon_\beta$. In order that eqn 29 be a valid approximation, Quintard and Whitaker (1994a) have shown that following length-scale constraints must be satisfied.

$$\ell_\beta \quad << \quad r_o \qquad\qquad r_o^2 \quad << \quad L_{v1} L_v \tag{31}$$

Here r_o is the radius of the averaging volume and ℓ_β is the characteristic length associated with the β-phase (Fig. 2). The large length-scales, L_{v1} and L_v, are defined by the estimates

$$\nabla \langle \mathbf{v}_\beta \rangle^\beta \; = \; \mathbf{O}\Big(\Delta \langle \mathbf{v}_\beta \rangle^\beta \big/ L_v \Big), \qquad \nabla\nabla \langle \mathbf{v}_\beta \rangle^\beta \; = \; \mathbf{O}\Big[\Delta \Big(\nabla \langle \mathbf{v}_\beta \rangle^\beta \Big) \Big/ L_{v1} \Big] \tag{32}$$

in which $\Delta \langle \mathbf{v}_\beta \rangle^\beta$ represents the change in the velocity that takes place over the distance L_v, and $\Delta\Big(\nabla \langle \mathbf{v}_\beta \rangle^\beta \Big)$ represents the change in the velocity gradient that takes place over the distance L_{v1}.

At this point we return to eqn 23 and make use of eqn 30 in order to express the volume averaged Navier-Stokes equations as

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle}{\partial t} \; + \; \varepsilon_\beta \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta \; + \; \rho_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \quad =$$

$$= \quad - \langle \nabla p_\beta \rangle \; + \; \varepsilon_\beta \rho_\beta \mathbf{g} \; + \; \mu_\beta \langle \nabla \cdot \nabla \mathbf{v}_\beta \rangle \tag{33}$$

Here we have made use of the fact that the divergence of $\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta$ is zero, and we can also make use of eqn 16 and the fact that ε_β is independent of time in order to express the local acceleration in terms of the intrinsic average velocity. This leads to

$$\varepsilon_\beta \rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \varepsilon_\beta \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$
$$= -\langle \nabla p_\beta \rangle + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \langle \nabla \cdot \nabla \mathbf{v}_\beta \rangle \tag{34}$$

At this point we can see the need for a *method of closure* that will allow us to predict the tensor $\langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle$; however, we will delay discussing the closure problem until we have completed the analysis of the right hand side of eqn 34 and until we have developed the volume averaged form of the convective-diffusion equation.

2.2.2 Pressure term

Use of the averaging theorem allows us to interchange integration and differentiation so that the gradient of the pressure takes the form

$$\langle \nabla p_\beta \rangle = \nabla \langle p_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} p_\beta \, dA \tag{35}$$

In order to represent this expression in terms of the *intrinsic* average pressure we use

$$\langle p_\beta \rangle = \varepsilon_\beta \langle p_\beta \rangle^\beta \tag{36}$$

so that eqn 35 takes the form

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \langle p_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} p_\beta \, dA \tag{37}$$

The decomposition for the pressure that is analogous to eqn 24 is given by

$$p_\beta = \langle p_\beta \rangle^\beta + \tilde{p}_\beta \tag{38}$$

and substitution of this result into the area integral in eqn 37 leads to the *non-local* form for the average of the pressure gradient

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \langle p_\beta \rangle^\beta \nabla \varepsilon_\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle p_\beta \rangle^\beta dA + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta dA \tag{39}$$

To develop the *local form*, we must remove the average pressure from the area integral in order to obtain

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle p_\beta \rangle^\beta dA = \left\{ \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA \right\} \langle p_\beta \rangle^\beta \tag{40}$$

This simplification is based on the following length-scale constraints (Quintard and Whitaker, 1994a)

$$\ell_\beta \ll r_\circ, \qquad \frac{r_\circ^2}{L_\varepsilon L_{p1}} \ll 1 \tag{41}$$

in which L_ε and L_{p1} are defined by the estimates

$$\nabla \varepsilon_\beta = \mathbf{O}\left(\frac{\Delta \varepsilon_\beta}{L_\varepsilon} \right), \qquad \nabla\nabla \langle p_\beta \rangle^\beta = \mathbf{O}\left[\frac{\Delta\left(\nabla \langle p_\beta \rangle^\beta \right)}{L_{p1}} \right] \tag{42}$$

From the averaging theorem we can extract a convenient representation for the area integral in eqn 40 that takes the form

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA = -\nabla \varepsilon_\beta \tag{43}$$

This provides us with

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \langle p_\beta \rangle^\beta dA = -(\nabla \varepsilon_\beta) \langle p_\beta \rangle^\beta \tag{44}$$

and substitution of this relation into eqn 39 yields

$$\langle \nabla p_\beta \rangle = \varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta dA \tag{45}$$

When this expression for the average of the gradient of the pressure is used in eqn 34, we obtain

$$\begin{aligned} \varepsilon_\beta \rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \varepsilon_\beta \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle &= \\ = -\varepsilon_\beta \nabla \langle p_\beta \rangle^\beta - \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta dA + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \langle \nabla \cdot \nabla \mathbf{v}_\beta \rangle & \end{aligned} \tag{46}$$

and we are ready to turn our attention to the viscous term.

2.2.3 Viscous term

Application of the averaging theorem to the last term in eqn 46 yields

$$\mu_\beta \langle \nabla \cdot \nabla \mathbf{v}_\beta \rangle = \mu_\beta \nabla \cdot \langle \nabla \mathbf{v}_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mu_\beta \nabla \mathbf{v}_\beta dA \tag{47}$$

and a second application of eqn 13 allows us to express the viscous term as

$$\begin{aligned} \mu_\beta \langle \nabla \cdot \nabla \mathbf{v}_\beta \rangle = \mu_\beta \left[\nabla \cdot \left(\nabla \langle \mathbf{v}_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{v}_\beta \, dA \right) \right] + \\ + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mu_\beta \nabla \mathbf{v}_\beta \, dA \end{aligned} \tag{48}$$

Use of this result in eqn 46 leads to the following form of the volume averaged Navier-Stokes equations

$$\varepsilon_\beta \rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \varepsilon_\beta \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$

$$= -\varepsilon_\beta \nabla \langle p_\beta \rangle^\beta - \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{p}_\beta dA + \varepsilon_\beta \rho_\beta \mathbf{g} + \tag{49}$$

$$+ \mu_\beta \left[\nabla \cdot \left(\nabla \langle \mathbf{v}_\beta \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{v}_\beta \, dA \right) \right] + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mu_\beta \nabla \mathbf{v}_\beta \, dA$$

Up to this point we have made no use of the boundary condition given by eqn 4; however, imposing the no-slip condition leads to an obvious simplification of the viscous term. In addition, we can repeat the procedure used earlier with the pressure gradient to obtain

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{v}_\beta \, dA = - \nabla \varepsilon_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \tilde{\mathbf{v}}_\beta dA \tag{50}$$

Here we have used the velocity decomposition given by the eqn 24, 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

$$\ell_\beta \ll r_\circ , \qquad \frac{r_\circ^2}{L_\varepsilon L_{v2}} \ll 1 \tag{51}$$

The characteristic length L_ε is defined by the first of eqns 42 while the new characteristic length L_{v2} is defined by the estimate

$$\nabla \nabla \nabla \langle \mathbf{v}_\beta \rangle^\beta = \mathbf{O} \left[\frac{\Delta \left(\nabla \nabla \langle \mathbf{v}_\beta \rangle^\beta \right)}{L_{v2}} \right] \tag{52}$$

Substitution of eqn 50 into eqn 49 and imposition of the no-slip condition allows us to express the volume averaged momentum equation as

$$\varepsilon_\beta \rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \varepsilon_\beta \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$

$$= -\varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle - \mu_\beta \nabla \varepsilon_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta +$$

$$+ \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \left[-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right] dA \tag{53}$$

If one replaces $\nabla \tilde{\mathbf{v}}_\beta$ with $\nabla \mathbf{v}_\beta$ on the basis that $\nabla \tilde{\mathbf{v}}_\beta >> \nabla \langle \mathbf{v}_\beta \rangle^\beta$, this result is identical to that given by Du Plessis (1994).

Equation 53 represents a *superficial average* form of the Navier-Stokes equations, i.e., each term represents a force *per unit volume of the porous medium*. Traditionally, the *intrinsic average* momentum equation is preferred since it provides a form containing $\nabla \langle p_\beta \rangle^\beta$ and this is a key quantity of interest. The *intrinsic average* form is obtained by dividing eqn 53 by ε_β to obtain

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$

$$= -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \left(\nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \varepsilon_\beta^{-1} \langle \mathbf{v}_\beta \rangle^\beta \nabla^2 \varepsilon_\beta \right) +$$

$$+ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \left[-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right] dA \tag{54}$$

Each term in this equation represents a force *per unit volume of the fluid phase*.

When the terms involving $\nabla\varepsilon_\beta$ and $\nabla^2\varepsilon_\beta$ *are important*, there is no simple representation for the area integral in eqn 54, and that means that there is no simple solution to the closure problem to be discussed in the next section. Regions in which the porosity varies rapidly are generally associated with the boundary between a porous medium and either a homogeneous fluid or a homogeneous solid. Those regions can be conveniently treated in terms of a *momentum jump condition*, the development of which is described by Ochoa-Tapia and Whitaker (1995).

If the porosity is assumed to be a constant, the terms involving gradients of ε_β can be discarded; however, we can be less restrictive and simply impose the length-scale constraint

$$L_\varepsilon \quad >> \quad L_v \tag{55}$$

so that eqn 54 simplifies to

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \underbrace{\rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle}_{volume\ filter} =$$

$$= -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \underbrace{\frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA}_{surface\ filter} \tag{56}$$

Here we have identified the term involving the volume average of $\tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta$ as a *volume filter*, while the last term involving the area integral of $-\mathbf{I}\,\tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta$ is referred to as a *surface filter*. We use these words because the microscale information that will be available in the closure problem will be *filtered* by these integrals. That is to say that not all the information available at the microscale will appear in the volume averaged momentum equation, and knowing how these filters function is an important aspect of the method of volume averaging.

The third term on the right hand side of eqn 56 represents 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 these circumstances the constraint given by eqn 55 fails (Quintard and Whitaker, 1994a). Given the length-scale constraints that have been imposed during the development of eqn 56, it is easy to demonstrate (Whitaker, 1986) that the Brinkman term is negligible; however, we will retain this term for completeness and comment further on the matter in subsequent paragraphs.

In order to obtain a closed form for eqn 56, we need to develop the boundary value problem for the spatial deviation quantities, $\tilde{p}_\beta$ and $\tilde{\mathbf{v}}_\beta$. Before developing the closure problem for the momentum equation, we need to examine the volume averaged form of the convective-diffusion equation.

2.3 Convective-diffusion equation

Because of the similarity between eqns 2 and 3, we can follow the development between eqn 18 and eqn 49 to obtain

$$\varepsilon_\beta \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta + \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_A \rangle =$$

$$= \mathscr{D}_\beta \nabla \cdot \left[\left(\nabla \langle c_A \rangle + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} c_A \, dA \right) \right] + \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_A \, dA \tag{57}$$

Here we have made use of the decomposition for the concentration

$$c_A = \langle c_A \rangle^\beta + \tilde{c}_A \tag{58}$$

and the convective transport term in eqn 3 has been treated in the manner indicated by eqns 24 through 30. Equation 57 is obviously analogous to eqn 49; however, we are not able to continue the analysis used with the momentum equation. To begin with, we cannot eliminate the integral of $\mathbf{n}_{\beta\sigma}c_A$ on the basis of something comparable to the no-slip condition, and this forces us to follow the treatment of the pressure gradient given by eqns 35 through 45 in order to arrive at

$$\nabla\langle c_A\rangle + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} c_A \, dA = \varepsilon_\beta \nabla\langle c_A\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{c}_A \, dA \tag{59}$$

Substitution of this result into eqn 57 provides

$$\varepsilon_\beta \frac{\partial\langle c_A\rangle^\beta}{\partial t} + \varepsilon_\beta\langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle c_A\rangle^\beta + \nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{c}_A\rangle =$$

$$= \mathscr{D}_\beta\nabla\cdot\left[\left(\varepsilon_\beta\nabla\langle c_A\rangle^\beta + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{c}_A \, dA\right)\right] + \frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_A \, dA \tag{60}$$

and we are now ready to turn our attention to the interfacial flux terms in both eqns 49 and 60. The last term in eqn 49 represents the viscous stress that the fluid exerts on the solid, and it must be determined as part of the *closure problem*. This is indicated by the fact that the dominant part of $\mu_\beta\nabla\mathbf{v}_\beta$ is represented by $\mu_\beta\nabla\tilde{\mathbf{v}}_\beta$ on the basis that $\nabla\tilde{\mathbf{v}}_\beta >> \nabla\langle\mathbf{v}_\beta\rangle^\beta$. On the other hand, the dominant part of the interfacial flux term in eqn 60 is represented in terms of the average concentration and this means that it is determined as part of the *averaging procedure*. Returning to the boundary condition given by eqn 5, we form the area integral and divide by $\mathscr{V}$

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_A \, dA = -\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} K_{eq}\frac{\partial c_A}{\partial t} dA \tag{61}$$

so that the adsorption process can be incorporated directly into the volume averaged mass transport equation. For the case of nonlinear adsorption, the coefficient K_{eq} is a function of the concentration, c_A; however, one can follow the development of Whitaker (1987, 1988) in order to represent the functional dependence as

$$K_{eq} = K_{eq}\big(\langle c_A\rangle^\beta\big) \tag{62}$$

This is based on the idea that $\tilde{c}_A << \langle c_A\rangle^\beta$ which is dramatically different than the momentum transport process where the no-slip condition requires that $\tilde{\mathbf{v}}_\beta \approx \langle \mathbf{v}_\beta\rangle^\beta$. If the intrinsic average concentration undergoes negligible changes within the averaging volume, we can remove K_{eq} from the integral so that eqn 61 takes the form

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot \mathscr{D}_\beta \nabla c_A\, dA = -K_{eq}\left\{\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \frac{\partial c_A}{\partial t}\, dA\right\} \tag{63}$$

Since the porous medium is considered to be rigid, we can interchange differentiation and integration leading to

$$\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot \mathscr{D}_\beta \nabla c_A\, dA = -a_{\mathrm{v}} K_{eq}\frac{\partial \langle c_A\rangle_{\beta\sigma}}{\partial t} \tag{64}$$

Here we have used a_{v} to represent the area per unit volume, while $\langle c_A\rangle_{\beta\sigma}$ represents the area averaged concentration. We define both these quantities explicitly as

$$a_{\mathrm{v}} = A_{\beta\sigma}/\mathscr{V}, \qquad \langle c_A\rangle_{\beta\sigma} = \frac{1}{A_{\beta\sigma}}\int_{A_{\beta\sigma}} c_A\, dA \tag{65}$$

Use of the decomposition given by eqn 58 allows us to express the area averaged concentration as

$$\langle c_A\rangle_{\beta\sigma} = \frac{1}{A_{\beta\sigma}}\int_{A_{\beta\sigma}} \langle c_A\rangle^\beta\, dA + \frac{1}{A_{\beta\sigma}}\int_{A_{\beta\sigma}} \tilde{c}_A\, dA \tag{66}$$

and when the spatial deviation concentration is small compared to the intrinsic average concentration, $\tilde{c}_A << \langle c_A\rangle^\beta$, we can simplify this result to

$$\langle c_A \rangle_{\beta\sigma} = \frac{1}{A_{\beta\sigma}} \int_{A_{\beta\sigma}} \langle c_A \rangle^{\beta} \, dA \tag{67}$$

Once again we assume that the intrinsic average concentration undergoes negligible changes within the averaging volume, and this leads to the simplification given by

$$\langle c_A \rangle_{\beta\sigma} = \langle c_A \rangle^{\beta} \tag{68}$$

Use of this result in the adsorption boundary condition given by eqn 64 provides a form

$$\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_A \, dA = - a_{\mathrm{v}} K_{eq} \frac{\partial \langle c_A \rangle^{\beta}}{\partial t} \tag{69}$$

that allows us to write eqn 60 as

$$\varepsilon_\beta \frac{\partial \langle c_A \rangle^{\beta}}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^{\beta} \cdot \nabla \langle c_A \rangle^{\beta} + \underbrace{\nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_A \rangle}_{volume\ filter} =$$

$$= \mathscr{D}_\beta \nabla \cdot \left[\left(\varepsilon_\beta \nabla \langle c_A \rangle^{\beta} + \underbrace{\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_A \, dA}_{surface\ filter} \right) \right] - a_{\mathrm{v}} K_{eq} \frac{\partial \langle c_A \rangle^{\beta}}{\partial t} \tag{70}$$

This completes our development of the volume averaged form of the convective-diffusion equation, and we note that like eqn 56 it contains both a volume filter and a surface filter. It is important to realize that eqn 70 represents *a superficial average* mass transport equation whereas eqn 56 is an *intrinsic average* momentum transport equation. The intrinsic average form results from a preference for a momentum transport equation that is based on the gradient of the intrinsic average pressure, $\nabla \langle p_\beta \rangle^{\beta}$, and this means that each term in eqn 56 represents a force per unit volume *of the fluid*. The mass transport equation is used in the form given by eqn 70 when it is convenient to retain the superficial velocity $\langle \mathbf{v}_\beta \rangle = \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta$, and this often occurs in steady-state processes involving adsorption and reaction. Under these circumstances, each term in eqn 70 represents moles per unit time per unit volume *of the porous medium*. In other cases, the intrinsic average mass transport equation is preferred and we will present an example in Sec. 6.

The terms on the left hand side of eqn 70 are analogous to those on the left hand side of eqn 56, and they result directly from the averaging procedure. On the other hand, the terms on the right hand side of eqn 70 are rather different than those on the right side of eqn 56, and this difference is caused by the different forms of the boundary conditions given by eqns 4 and 5 along with the constraints on the spatial deviation velocity and concentration that take the form $\tilde{\mathbf{v}}_\beta \approx \langle \mathbf{v}_\beta \rangle^\beta$ and $\tilde{c}_A << \langle c_A \rangle^\beta$.

3 Closure

In order to obtain the closed form of eqn 56, we need to develop the governing differential equations and boundary conditions for $\tilde{\mathbf{v}}_\beta$ and $\tilde{p}_\beta$. This will eventually lead us to a local closure problem in terms of *closure variables* and a method of predicting the Darcy's law permeability tensor and the Forchheimer correction tensor that appear in the closed form. Once we have developed the closure problem for the momentum equation, we can follow a similar analysis in order to obtain the closure problems for the convective-dispersion equation.

3.1 Boundary condition

The no-slip boundary condition plays a key role in the closed form of eqn 56, thus we begin our analysis with eqn 4 and make use of the velocity decomposition represented by eqn 24 to obtain

$$\text{B.C.1} \qquad \tilde{\mathbf{v}}_\beta = -\underbrace{\langle \mathbf{v}_\beta \rangle^\beta}_{\substack{\textit{no-slip} \\ \textit{source}}}, \qquad at\ \mathscr{A}_{\beta\sigma} \tag{71}$$

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 remember that the no-slip condition did not have any obvious impact on the volume averaged form of the Navier-Stokes equations when it was imposed on eqn 49. However, the situation in the *closure problem* is quite different and we shall see in this section that eqn 71 *controls* the form of the closure problem.

3.2 Continuity equation

In order to develop the continuity equation for $\tilde{\mathbf{v}}_\beta$, we recall eqn 1

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{72}$$

along with the intrinsic average form given by eqn 17

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta = -\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{73}$$

Subtracting the latter from the former provides the continuity equation for the spatial deviation velocity

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = \underbrace{\varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta}_{source} \tag{74}$$

Since the three terms on the left hand side of this result are all on the order of order $\langle \mathbf{v}_\beta \rangle^\beta / \ell_\beta$ and the single 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 $\tilde{\mathbf{v}}_\beta - \text{field}$. This allows us to write the continuity equation as

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \tag{75}$$

and we are now ready to move on to the momentum equation for $\tilde{\mathbf{v}}_\beta$.

3.3 Momentum equation

Here we follow the same procedure indicated by eqns 72 through 75 and we recall the point and volume averaged momentum equations given by

$$\rho_\beta \frac{\partial \mathbf{v}_\beta}{\partial t} + \rho_\beta \mathbf{v}_\beta \cdot \nabla \mathbf{v}_\beta = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \tag{76}$$

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$

$$= -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \tag{77}$$

$$+ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA$$

Subtracting the second of these from the first provides the spatial deviation momentum equation that takes the form

$$\rho_\beta \frac{\partial \tilde{\mathbf{v}}_\beta}{\partial t} + \rho_\beta \mathbf{v}_\beta \cdot \nabla \tilde{\mathbf{v}}_\beta + \rho_\beta \tilde{\mathbf{v}}_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta -$$

$$- \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA + \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \tag{78}$$

Here we note that $\nabla \langle \mathbf{v}_\beta \rangle^\beta$ is a *parameter* in the equation for $\tilde{\mathbf{v}}_\beta$, but it is not a *source* for the $\tilde{\mathbf{v}}_\beta$-field in the way that $\langle \mathbf{v}_\beta \rangle^\beta$ is a *source* as indicated by eqn 71.

The closure equation given by eqn 78 can be simplified considerably on the basis of the following order of magnitude estimates:

$$\tilde{\mathbf{v}}_\beta = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta \right), \quad \nabla \tilde{\mathbf{v}}_\beta = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta \big/ \ell_\beta \right), \quad \nabla \langle \mathbf{v}_\beta \rangle^\beta = \mathbf{O}\left(\langle \mathbf{v}_\beta \rangle^\beta \big/ L_v \right) \tag{79}$$

The first of these results from the no-slip condition given by eqn 71, while the second and third are based on the characteristic lengths associated with $\tilde{\mathbf{v}}_\beta$ and $\langle \mathbf{v}_\beta \rangle^\beta$. If we are willing to accept the idea that the length scale associated with $\langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle$ is comparable to that for $\langle \mathbf{v}_\beta \rangle^\beta$, we can immediately simplify eqn 78 on the basis of

$$\rho_\beta \mathbf{v}_\beta \cdot \nabla \tilde{\mathbf{v}}_\beta \gg \rho_\beta \tilde{\mathbf{v}}_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \tag{80a}$$

$$\rho_\beta \mathbf{v}_\beta \cdot \nabla \tilde{\mathbf{v}}_\beta \quad >> \quad \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle \tag{80b}$$

This requires only the imposition of the length-scale constraint given by

$$\ell_\beta \quad << \quad L_{\mathrm{v}} \tag{81}$$

and this is entirely consistent with constraints that have already been imposed on the analysis. For many practical cases, one can make use of the quasi-steady simplification on the basis that

$$\rho_\beta \frac{\partial \tilde{\mathbf{v}}_\beta}{\partial t} \quad << \quad \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta \tag{82}$$

and this means that the following time-scale constraint will be imposed.

$$\frac{\nu_\beta t^*}{\ell_\beta^2} \quad >> \quad 1 \tag{83}$$

Here t^* represents the characteristic momentum process time, and ν_β is the kinematic viscosity.

At this point we have dealt with the *closure analogs* of eqns 1 and 2, along with the boundary condition given by eqn 4, and we need only construct a boundary condition associated with eqn 6 in order to complete the statement of the boundary value problem for the spatial deviation pressure and velocity. This boundary value problem provides the microscale information for the filters in eqn 56 and it can be expressed as

$$\rho_\beta \mathbf{v}_\beta \cdot \nabla \tilde{\mathbf{v}}_\beta \quad = \quad -\nabla \tilde{p}_\beta \; + \; \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta \; - \; \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA \tag{84}$$

$$\nabla \cdot \tilde{\mathbf{v}}_\beta \quad = \quad 0 \tag{85}$$

B.C.1 $$\tilde{\mathbf{v}}_\beta \quad = \quad -\underbrace{\langle \mathbf{v}_\beta \rangle^\beta}_{\substack{\textit{no-slip} \\ \textit{source}}} \, , \qquad \textit{at } \mathscr{A}_{\beta\sigma} \tag{86}$$

B.C.2
$$\tilde{\mathbf{v}}_\beta = \underbrace{\mathbf{g}(\mathbf{r},t)}_{source}, \qquad at\ \mathscr{A}_{\beta e} \tag{87}$$

in which the boundary condition given by eqn 87 is a reminder of what we *do not* know about the $\tilde{\mathbf{v}}_\beta$-field. 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 eqn 87 will influence the spatial deviation fields only in a region of thickness ℓ_β at the boundary of the macroscopic region (Fig. 2). This suggests that the boundary condition at $\mathscr{A}_{\beta e}$ can be ignored if we can find a suitable replacement.

3.4 Mass transport equation

In order to develop the boundary value problem for the spatial deviation concentration, $\tilde{c}_A$, we need to use the analogues of eqns 76 and 77. The first of these can be extracted directly from eqn 3 and is given by

$$\frac{\partial c_A}{\partial t} + \mathbf{v}_\beta \cdot \nabla c_A = \mathscr{D}_\beta \nabla^2 c_A \tag{88}$$

To obtain the analogue of eqn 77, we divide eqn 70 by ε_β to obtain an *intrinsic average* transport equation of the form

$$\frac{\partial \langle c_A \rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta + \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_A \rangle =$$

$$= \mathscr{D}_\beta \nabla^2 \langle c_A \rangle^\beta + \mathscr{D}_\beta \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \nabla \langle c_A \rangle^\beta + \tag{89}$$

$$+ \varepsilon_\beta^{-1} \mathscr{D}_\beta \nabla \cdot \left(\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_A \, dA \right) - \varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}$$

When eqn 89 is subtracted from eqn 88, the result can be arranged in the form

$$\frac{\partial \tilde{c}_A}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{c}_A + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{\text{convective}\\ \text{source}}} - \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_A \rangle =$$

$$= \mathscr{D}_\beta \nabla^2 \tilde{c}_A - \underbrace{\mathscr{D}_\beta \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{\text{diffusive}\\ \text{source}}} -$$

$$- \varepsilon_\beta^{-1} \mathscr{D}_\beta \nabla \cdot \left(\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_A \, dA \right) - \underbrace{\varepsilon_\beta^{-1} a_v K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{\text{adsorptive}\\ \text{source}}} \tag{90}$$

It is not difficult to develop arguments (Carbonell and Whitaker, 1983) indicating that the dispersive transport in this result is small compared to the convective transport

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_A \quad >> \quad \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{c}_A \rangle \tag{91}$$

and this result is analogous to that given by eqn 80b. The diffusive source can be neglected relative to the convective source

$$\mathscr{D}_\beta \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot \nabla \langle c_A \rangle^\beta \quad << \quad \tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta \tag{92}$$

when convection is important, and it can always be neglected relative to the diffusive *surface source* that results from the boundary condition given by eqn 5. In addition, there are straightforward arguments (Quintard and Whitaker, 1994b) in favor of neglecting the *non-local* diffusive transport relative to the *local* diffusive transport

$$\varepsilon_\beta^{-1} \mathscr{D}_\beta \nabla \cdot \left(\frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_A \, dA \right) \quad << \quad \mathscr{D}_\beta \nabla^2 \tilde{c}_A \tag{93}$$

On the basis of eqns 91 through 93, we can express the governing differential equation for the spatial deviation concentration as

$$\frac{\partial \tilde{c}_A}{\partial t} + \mathbf{v}_\beta \cdot \nabla \tilde{c}_A + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{\textit{convective} \\ \textit{source}}} = \mathscr{D}_\beta \nabla^2 \tilde{c}_A + $$
$$+ \underbrace{\varepsilon_\beta^{-1} a_\mathrm{v} K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{\textit{adsorptive} \\ \textit{source}}} \tag{94}$$

While the volume averaged mass transport problem under consideration will generally be transient, the governing equation at the closure level will almost always be quasi-steady. The constraint associated with this condition is analogous to that given by eqn 83 and it takes the form

$$\frac{\mathscr{D}_\beta t^*}{\ell_\beta^2} >> 1 \tag{95}$$

Here one must remember that t^* refers to the characteristic time associated with the mass transfer process and this may be different than the characteristic time associated with the momentum transfer process that appears in eqn 83. When the constraint indicated by eqn 95 is satisfied, eqn 94 can be simplified in the obvious manner leading to

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_A + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{\textit{convective} \\ \textit{source}}} = \mathscr{D}_\beta \nabla^2 \tilde{c}_A + \underbrace{\varepsilon_\beta^{-1} a_\mathrm{v} K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{\textit{adsorptive} \\ \textit{source}}} \tag{96}$$

Turning our attention to the flux boundary condition given by eqn 5, we make use of the decomposition given by eqn 58 to obtain

$$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_A \; - \; K_{eq} \frac{\partial \tilde{c}_A}{\partial t} \;=$$

B.C.1

$$= \; \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_A \rangle^\beta}_{\substack{diffusive \\ source}} \; + \; \underbrace{K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{adsorptive \\ source}}, \quad at \; \mathscr{A}_{\beta\sigma} \tag{97}$$

Since the governing differential equation has been restricted to the quasi-steady condition, it is reasonable to do the same for this boundary condition. This requires the restriction

$$\mathscr{D}_\beta \nabla \tilde{c}_A \quad >> \quad K_{eq} \frac{\partial \tilde{c}_A}{\partial t} \tag{98}$$

that leads to the constraint

$$\frac{\mathscr{D}_\beta t^*}{K_{eq} \ell_\beta} \quad >> \quad 1 \tag{99}$$

When this constraint is valid, the quasi-steady form of the mass transport problem takes the form

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_A \; + \; \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{convective \\ source}} \; = \; \mathscr{D}_\beta \nabla^2 \tilde{c}_A \; + \; \underbrace{\varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{adsorptive \\ source}} \tag{100}$$

B.C.1

$$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_A \; = \; \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_A \rangle^\beta}_{\substack{diffusive \\ source}} \; + \; \underbrace{K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{adsorptive \\ source}}, \; at \; \mathscr{A}_{\beta\sigma} \tag{101}$$

B.C.2

$$\tilde{c}_A \; = \; \underbrace{g(\mathbf{r}, t)}_{source}, \quad at \; \mathscr{A}_{\beta e} \tag{102}$$

Here we see that the structure of the closure problem for the convective-diffusion process with adsorption is significantly different from that given by eqns 84 through 87 for the momentum transport process. In eqn 100 the *convective source* represents a dominant effect, while no analogous term appears in the momentum transport problem. In the mass transport closure problem we need to consider the effect of *two different sources* and we will show how that is done in Sec. 5.

4 Local closure problem for momentum transport

It should be obvious that we do not want to solve either eqns 84 through 87 or eqns 100 through 102 in the entire macroscopic region (Fig. 2), but instead we wish to solve the closure problems in some *representative region* (Fig. 4). To do so, we must be willing to discard the boundary conditions

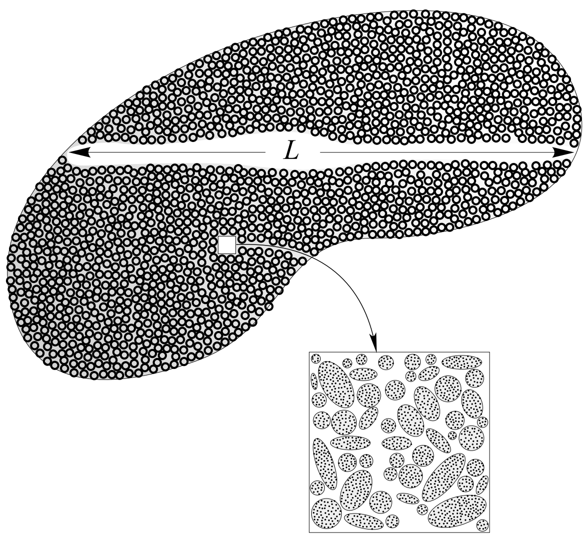

Figure 4-3
Representative Region

given by eqns 87 and 102 and replace them with some *local conditions* associated with a representative region. This naturally leads us to treat the representative region (Fig. 4) as a unit cell in a spatially periodic model of a porous medium so that our momentum closure problem takes the form

$$\rho_\beta \mathbf{v}_\beta \cdot \nabla \tilde{\mathbf{v}}_\beta = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA \quad (103)$$

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \quad (104)$$

B.C.1 $$\tilde{\mathbf{v}}_\beta = -\underbrace{\langle \mathbf{v}_\beta \rangle^\beta}_{\substack{\textit{no-slip}\\ \textit{source}}}, \qquad at\ \mathscr{A}_{\beta\sigma} \tag{105}$$

Periodicity: $$\tilde{p}_\beta(\mathbf{r}+\ell_i) = \tilde{p}_\beta(\mathbf{r}), \quad \tilde{\mathbf{v}}_\beta(\mathbf{r}+\ell_i) = \tilde{\mathbf{v}}_\beta(\mathbf{r}), \quad i=1,2,3 \tag{106}$$

Average: $$\langle \tilde{\mathbf{v}}_\beta \rangle^\beta = 0 \tag{107}$$

Here we require that the average of the spatial deviation velocity be zero, and this condition is necessary in order to evaluate the integral in eqn 103. The constraints associated with eqn 105 were given earlier by eqn 31. It is important to note that the periodicity condition given by eqn 106 is *consistent with* a spatially periodic model *only* if the source in eqn 105 is a constant. To explore the idea that $\langle \mathbf{v}_\beta \rangle^\beta$ can be treated as a constant, we consider a Taylor series expansion for $\langle \mathbf{v}_\beta \rangle^\beta$ about the centroid of the representative region (Fig. 4). This is given by

$$\langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}+\mathbf{y}_\beta} = \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \mathbf{y}_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \Big|_{\mathbf{x}} + \ldots\ldots. \tag{108}$$

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.

$$r_\circ \ll L_\mathrm{v} \tag{109}$$

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 $r_\circ$.

4.1 Closure variables for momentum transfer

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 (Whitaker, 1969)

$$\tilde{\mathbf{v}}_\beta = \mathsf{M} \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{u} \tag{110}$$

$$\tilde{p}_\beta = \mu_\beta \mathbf{m} \cdot \langle \mathbf{v}_\beta \rangle^\beta + \xi \tag{111}$$

in which **u** is a vector and ξ is a scalar. We are free to specify $\mathbf{M}$ and $\mathbf{m}$ in any way we wish, and we specify these two functions by means of the following closure problem

$$\left(\rho_\beta \mathbf{v}_\beta / \mu_\beta\right) \cdot \nabla \mathbf{M} = -\nabla \mathbf{m} + \nabla^2 \mathbf{M} - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{m} + \nabla \mathbf{M}\right) dA \tag{112a}$$

$$\nabla \cdot \mathbf{M} = 0 \tag{112b}$$

B.C.1 $$\mathbf{M} = -\mathbf{I}, \quad at\ A_{\beta\sigma} \tag{112c}$$

Periodicity: $$\mathbf{m}(\mathbf{r} + \ell_i) = \mathbf{m}(\mathbf{r}), \quad \mathbf{M}(\mathbf{r} + \ell_i) = \mathbf{M}(\mathbf{r}), \quad i = 1, 2, 3 \tag{112d}$$

Average: $$\langle \mathbf{M} \rangle^\beta = 0 \tag{112e}$$

When $\mathbf{M}$ and $\mathbf{m}$ are specified in this manner, one can use eqns 110 and 111 in the closure problem for $\tilde{\mathbf{v}}_\beta$ and $\tilde{p}_\beta$ to develop the boundary value problem for **u** and ξ. From that problem one can prove that the vector **u** is *zero* and that the scalar ξ is a *constant*, and the proof is given elsewhere (Whitaker, 1996). Since the constant ξ will not pass through the filter represented by the area integral in eqn 103, we can express the spatial deviation velocity and pressure as

$$\tilde{\mathbf{v}}_\beta = \mathbf{M} \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{113}$$

$$\tilde{p}_\beta = \mu_\beta \mathbf{m} \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{114}$$

These two representations can now be used to develop the closed form of the volume averaged momentum equation.

4.2 Closed form of the momentum equation

To obtain the closed form of the volume averaged momentum equation, we first recall eqn 56

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\mathbf{v}}_\beta \tilde{\mathbf{v}}_\beta \rangle =$$

$$= -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta \right) dA \tag{115}$$

and make use of eqns 113 and 114 to obtain

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} + \rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \nabla \cdot \langle \mathbf{v}_\beta \rangle^\beta + \rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle^\beta \cdot \langle \mathbf{M}^{\mathrm{T}} \mathbf{M} \rangle \cdot \langle \mathbf{v}_\beta \rangle^\beta \right)$$

$$= -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \tag{116}$$

$$+ \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{m} + \nabla \mathbf{M} \right) dA \right\} \cdot \langle \mathbf{v}_\beta \rangle^\beta$$

At this point we want to demonstrate that the macroscopic inertial terms in eqn 116 are negligible, and to do so we need estimates of the inertial terms on the left hand side of eqn 116 and of the dominant viscous term on the right hand side. From the closure problem given by eqns 112 we note that

$$\mathbf{M} = \mathbf{O}(1) \tag{117}$$

and that the characteristic length for $\mathbf{M}$ is the small length scale, ℓ_β. Directing our attention specifically to eqn 112a, we obtain

$$\left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{m} + \nabla \mathbf{M} \right) dA \right\} = \mathbf{O}\left(\ell_\beta^{-2} \right) + \mathbf{O}\left(\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta / \mu_\beta \ell_\beta \right) \tag{118}$$

and this can be used to estimate the last term in eqn 116 as

$$\mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{m} + \nabla \mathbf{M} \right) dA \right\} \cdot \langle \mathbf{v}_\beta \rangle^\beta \quad = \tag{119}$$

$$= \quad \mathbf{O}\left(\mu_\beta \langle \mathbf{v}_\beta \rangle^\beta \big/ \ell_\beta^2 \right) \; + \; \mathbf{O}\left(\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \big/ \ell_\beta \right)$$

and we need to compare this with estimates of the inertial terms in eqn 116.

We begin with the first term on the left hand side of eqn 116 and estimate the local acceleration as

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} \quad = \quad \mathbf{O}\left(\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \big/ t^* \right) \tag{120}$$

Moving on to the second term, we represent the volume averaged velocity in terms of the magnitude and the unit tangent vector

$$\langle \mathbf{v}_\beta \rangle^\beta \quad = \quad \langle \mathrm{v}_\beta \rangle^\beta \boldsymbol{\lambda} \tag{121}$$

in order to obtain

$$\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \quad = \quad \rho_\beta \langle \mathrm{v}_\beta \rangle^\beta \boldsymbol{\lambda} \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \quad = \quad \rho_\beta \langle \mathrm{v}_\beta \rangle^\beta \frac{d \langle \mathbf{v}_\beta \rangle^\beta}{d s} \tag{122}$$

Here we have made use of the fact that $\boldsymbol{\lambda} \cdot \nabla$ is the directional derivative, and we have used s to represent the arclength measured along a volume averaged streamline. We can use the definition of the *inertial length* (Whitaker, 1982) to express our estimate of the convective inertial term as

$$\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta \quad = \quad \mathbf{O}\left[\rho_\beta \left(\langle \mathrm{v}_\beta \rangle^\beta \right)^2 \big/ L_\rho \right] \tag{123}$$

Our estimate of the third term on the left hand side of eqn 116 is given by

$$\rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle^\beta \cdot \langle \mathbf{M}^{\mathrm{T}} \mathbf{M} \rangle \cdot \langle \mathbf{v}_\beta \rangle^\beta \right) \quad = \quad \mathbf{O}\left(\rho_\beta \varepsilon_\beta^{-1} \langle \mathbf{v}_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \big/ L_{\mathrm{v}} \right) \tag{124}$$

in which L_{v} is defined by the first of eqns 32. A little thought will indicate that $L_{\mathrm{v}} \leq L_{\rho}$ thus we seek only the constraints associated with the following two restrictions

$$\rho_\beta \frac{\partial \langle \mathbf{v}_\beta \rangle^\beta}{\partial t} \quad << \quad \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{Im} + \nabla \mathbf{M} \right) dA \right\} \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{125}$$

$$\rho_\beta \varepsilon_\beta^{-1} \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle^\beta \cdot \langle \mathbf{M}^{\mathrm{T}} \mathbf{M} \rangle \cdot \langle \mathbf{v}_\beta \rangle^\beta \right) \quad << \quad \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{Im} + \nabla \mathbf{M} \right) dA \right\} \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{126}$$

Directing our attention to the first of these, we use the estimates given by eqns 119 and 120 and require only that the local acceleration be small compared to the viscous effect to conclude that the macroscopic flow is quasi-steady when

$$\frac{\nu_\beta t^*}{\ell_\beta^2} \quad >> \quad 1 \tag{127}$$

This result is identical to that given by eqn 83 which was imposed in the development of the momentum closure problem. Moving on to the second restriction given by eqn 126, we employ the estimates given by eqns 119 and 124 to obtain

$$\frac{\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \ell_\beta}{\mu_\beta} \left(\ell_\beta / L_{\mathrm{v}} \right) \quad << \quad 1, \qquad \ell_\beta \quad << \quad L_{\mathrm{v}} \tag{128}$$

There are a wide variety of processes for which the constraints given by both eqn 127 and eqn 128 will be satisfied and the closed form of the momentum equation will simplify to

$$0 \;=\; -\nabla\langle p_\beta\rangle^\beta \;+\; \rho_\beta \mathbf{g} \;+\; \mu_\beta \nabla^2 \langle \mathbf{v}_\beta\rangle^\beta \;+\; \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{m} + \nabla \mathsf{M}\right) dA \right\} \cdot \langle \mathbf{v}_\beta\rangle^\beta \tag{129}$$

Here we have what appears to be Darcy's law with the Brinkman correction; however, the Forchheimer correction term is contained in the area integral as pointed out by Ruth and Ma (1992) and by Ma and Ruth (1993). In the next section we will examine that integral carefully.

4.3 Structure of the closure problem

Rather than attack the closure problem directly, as suggested by eqns 112 and 129, it is reasonable to decompose the problem into two parts. The first part will produce a Darcy's law permeability that depends only on the geometry of the porous medium under consideration, and the second part will lead to an inertial correction, i.e., the Forchheimer equation (Forchheimer, 1901). To accomplish this decomposition, we represent $\mathbf{m}$ and M as

$$\mathbf{m} \;=\; \mathbf{b} + \mathbf{c}\,, \qquad \mathsf{M} \;=\; \mathsf{B} + \mathsf{C} \tag{130}$$

and replace the representations given by eqns 113 and 114 with

$$\tilde{p}_\beta \;=\; \mu_\beta \mathbf{b}\cdot\langle \mathbf{v}_\beta\rangle^\beta + \mu_\beta \mathbf{c}\cdot\langle \mathbf{v}_\beta\rangle^\beta\,, \quad \tilde{\mathbf{v}}_\beta \;=\; \mathsf{B}\cdot\langle \mathbf{v}_\beta\rangle^\beta + \mathsf{C}\cdot\langle \mathbf{v}_\beta\rangle^\beta \tag{131}$$

At this point we *define* the vector $\mathbf{b}$ and the tensor B by the following closure problem

PROBLEM I

$$0 \;=\; -\nabla \mathbf{b} + \nabla^2 \mathsf{B} - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{b} + \nabla \mathsf{B}\right) dA \tag{132a}$$

$$\nabla \cdot \mathsf{B} \;=\; 0 \tag{132b}$$

B.C.1 $$\mathsf{B} \;=\; -\mathbf{I}\,, \quad at\ A_{\beta\sigma} \tag{132c}$$

Periodicity: $\mathbf{b}(\mathbf{r}+\ell_i) = \mathbf{b}(\mathbf{r})\,, \quad \mathsf{B}(\mathbf{r}+\ell_i) = \mathsf{B}(\mathbf{r})\,, \quad i=1,2,3$ (132d)

Average: $$\langle \mathsf{B} \rangle^\beta = 0 \tag{132e}$$

Given this definition of $\mathbf{b}$ and B, we can substitute eqns 130 and 131 into the closure problem given by eqns 99 through 103 in order to obtain the following closure problem for $\mathbf{c}$ and C.

PROBLEM II

$$\underbrace{\left(\rho_\beta \mathbf{v}_\beta / \mu_\beta\right)\cdot\nabla\mathsf{B}}_{source} + \left(\rho_\beta \mathbf{v}_\beta / \mu_\beta\right)\cdot\nabla\mathsf{C} = $$

$$= -\nabla\mathbf{c} + \nabla^2\mathsf{C} - \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(-\mathbf{I}\mathbf{c}+\nabla\mathsf{C}\right)dA \tag{133a}$$

$$\nabla\cdot\mathsf{C} = 0 \tag{133b}$$

B.C.1 $$\mathsf{C} = 0\,, \quad at\ A_{\beta\sigma} \tag{133c}$$

Periodicity: $\mathbf{c}(\mathbf{r}+\ell_i) = \mathbf{c}(\mathbf{r})\,, \quad \mathsf{C}(\mathbf{r}+\ell_i) = \mathsf{C}(\mathbf{r})\,, \quad i=1,2,3$ (133d)

Average: $$\langle \mathsf{C} \rangle^\beta = 0 \tag{133e}$$

In order to determine $\mathbf{c}$ and C from this boundary value problem, one needs to first solve eqns 132 for the B-field and then calculate the velocity field on the basis of the Navier-Stokes equations. Methods for solving the Navier-Stokes equations in spatially periodic systems are described in the literature (Snyder and Stewart, 1966; Zick and Homsy, 1982; Eidsath et al., 1983; Quintard and Whitaker, 1995).

In order to clarify the structure of the closed form of the volume averaged Navier-Stokes equations, we make use of eqns 130 in eqn 129 to obtain

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta\rangle^\beta +$$

$$+ \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{b} + \nabla \mathbf{B}\right) dA \right\} \cdot \langle \mathbf{v}_\beta\rangle^\beta + \tag{134}$$

$$+ \mu_\beta \left\{ \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(-\mathbf{I}\mathbf{c} + \nabla \mathbf{C}\right) dA \right\} \cdot \langle \mathbf{v}_\beta\rangle^\beta$$

At this point it is convenient to define the Darcy's law permeability tensor by

$$\frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left[-\mathbf{I}\mathbf{b} + \nabla \mathbf{B}\right] dA = -\varepsilon_\beta \mathbf{K}^{-1} \tag{135}$$

and the *Forchheimer correction tensor* by

$$\frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left[-\mathbf{I}\mathbf{c} + \nabla \mathbf{C}\right] dA = -\varepsilon_\beta \mathbf{K}^{-1} \cdot \mathbf{F} \tag{136}$$

It is important to notice that the definitions of $\mathbf{K}$ and $\mathbf{F}$ have been deliberately chosen to produce a momentum equation containing the *superficial average* velocity rather than the intrinsic average velocity that appears in eqn 134. Use of these two definitions in eqn 134 leads to a result

$$0 = -\nabla\langle p_\beta\rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta\rangle^\beta - \mu_\beta \mathbf{K}^{-1} \cdot \langle \mathbf{v}_\beta\rangle - \mu_\beta \mathbf{K}^{-1} \cdot \mathbf{F} \cdot \langle \mathbf{v}_\beta\rangle \tag{137}$$

that can be arranged in the form

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}}{\mu_\beta}\left(\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g} - \underbrace{\mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta}_{\substack{\textit{Brinkman} \\ \textit{correction}}} \right) - \underbrace{\mathbf{F}\cdot\langle \mathbf{v}_\beta \rangle}_{\substack{\textit{Forchheimer} \\ \textit{correction}}} \tag{138}$$

On the basis of the length-scale constraints that have already been imposed, we can ignore variations of the porosity and express this result entirely in terms of the superficial velocity. This leads to

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}}{\mu_\beta}\left(\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g} - \underbrace{\left(\mu_\beta / \varepsilon_\beta\right) \nabla^2 \langle \mathbf{v}_\beta \rangle}_{\substack{\textit{Brinkman} \\ \textit{correction}}} \right) - \underbrace{\mathbf{F}\cdot\langle \mathbf{v}_\beta \rangle}_{\substack{\textit{Forchheimer} \\ \textit{correction}}} \tag{139}$$

In the literature there is some confusion regarding the viscosity that appears with the Brinkman correction, and it is indeed possible to express eqn 139 as

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}}{\mu_\beta}\left(\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g} - \underbrace{\mu_\beta^* \nabla^2 \langle \mathbf{v}_\beta \rangle}_{\substack{\textit{Brinkman} \\ \textit{correction}}} \right) - \underbrace{\mathbf{F}\cdot\langle \mathbf{v}_\beta \rangle}_{\substack{\textit{Fochheimer} \\ \textit{correction}}} \tag{140}$$

One can then refer to μ_β^* as the *Brinkman viscosity*; however, such an approach does not contribute a great deal to our understanding of flow through porous media. The introduction of a quantity referred to as the Brinkman viscosity would appear to result from the failure to carefully identify the difference between the superficial average velocity and the intrinsic average velocity.

From the closure problem given by eqns 132, we know that the vector **b** and the tensor $\mathbf{B}$ are purely geometric quantities, and that the Darcy's law permeability tensor can be estimated as

$$\mathbf{K} = \mathbf{O}(\ell_\beta^2) \tag{141}$$

If we return to the second closure problem given by eqns 133, we can see that the only nonhomogeneous term in that boundary value problem is the *source* represented by $(\rho_\beta \mathbf{v}_\beta / \mu_\beta)\cdot\nabla\mathbf{B}$. The tensor $\mathbf{B}$ is a dimensionless quantity of order one, and has a characteristic length of ℓ_β, and when this information is used in eqn 133a we have the estimate

$$\mathbf{C} \;=\; \mathbf{O}\Big(\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \ell_\beta \big/ \mu_\beta\Big) \tag{142}$$

Given that $\mathbf{K} = \mathbf{O}(\ell_\beta^2)$ we can use eqn 136 to conclude that the Forchheimer correction tensor is on the order of the Reynolds number, i.e.,

$$\mathbf{F} \;=\; \mathbf{O}\Big(\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta \ell_\beta \big/ \mu_\beta\Big) \tag{143}$$

If $\mathbf{F}$ is a linear function of the Reynolds number, we will obtain the expected quadratic form of the Forchheimer equation.

We can learn something about the functional dependence of $\mathbf{F}$ by considering the case for which the inertial terms are small enough so that $\mathbf{C} << \mathbf{B}$. This allows us to simplify eqn 133a according to

$$\underbrace{\big(\rho_\beta \mathbf{v}_\beta / \mu_\beta\big) \cdot \nabla \mathbf{B}}_{source} \;>>\; \big(\rho_\beta \mathbf{v}_\beta / \mu_\beta\big) \cdot \nabla \mathbf{C} \tag{144}$$

When $\mathbf{C} << \mathbf{B}$ we can use the second of eqns 131 to express the velocity as

$$\mathbf{v}_\beta \;=\; (\mathbf{I} + \mathbf{B}) \cdot \langle \mathbf{v}_\beta \rangle^\beta \tag{145}$$

and this result, along with eqn 144 allows us to express eqns 133 as

$$\frac{\rho_\beta \langle \mathbf{v}_\beta \rangle^\beta}{\mu_\beta} \cdot (\mathbf{I} + \mathbf{B})^{\mathrm{T}} \cdot \nabla \mathbf{B} \;=\; -\nabla \mathbf{c} \;+\; \nabla^2 \mathbf{C} \;-\; \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \big(-\mathbf{I}\mathbf{c} + \nabla \mathbf{C}\big)\, dA \tag{146a}$$

$$\nabla \cdot \mathbf{C} \;=\; 0 \tag{146b}$$

B.C. 1 $$\mathbf{C} \;=\; 0\,, \qquad at\ A_{\beta\sigma} \tag{146c}$$

Periodicity: $$\mathbf{c}(\mathbf{r} + \ell_i) \;=\; \mathbf{c}(\mathbf{r})\,, \qquad \mathbf{C}(\mathbf{r} + \ell_i) \;=\; \mathbf{C}(\mathbf{r})\,, \qquad i = 1, 2, 3 \tag{146d}$$

Average: $$\langle \mathbf{C} \rangle^\beta \;=\; 0 \tag{146e}$$

Here it becomes apparent that $\mathbf{C}$ will be a linear function of $\langle \mathbf{v}_\beta \rangle^\beta$, and on the basis of eqn 136 we see that $\mathbf{F}$ will also be a linear function of $\langle \mathbf{v}_\beta \rangle^\beta$. One must keep in mind that these conclusions are based on the constraint that inertial effects are small enough so that $\mathbf{C} \ll \mathbf{B}$, and when this condition is *not valid* the functional dependence of $\mathbf{F}$ must be determined by the solution of the general form of PROBLEM II that is given by eqns 133. A more thorough analysis of PROBLEM II is given elsewhere (Whitaker, 1996), and the result suggests that $\mathbf{F}$ may be a linear function of $\langle \mathbf{v}_\beta \rangle^\beta$ for a wide range of Reynolds numbers.

The problem stated by eqns 1, 2 and 4 has also been studied by means of the method of spatial homogenization (Bensoussan et al., 1978; Sanchez-Palencia, 1980; Ene and Poliševski, 1987). Using that technique, and both Mei and Auriault (1991) and Wodie and Levy (1991) found that the first inertial correction to Darcy's law was a *cubic function* of the velocity rather than the *quadratic dependence* illustrated by eqns 146 and the form of the Forchheimer correction tensor given in eqns 136 and 137. Hassanizadeh and Gray (1987) have also examined this problem and conclude that the Forchheimer equation should contain both quadratic and cubic terms.

4.4 Solution of the momentum closure problem

At this point we are ready to return to the closure problem given by eqns 132, and make use of the definition given by eqn 135 so that the closure problem can eventually be expressed in a relatively simple form. Use of eqn 135 leads to

$$-\nabla \mathbf{b} \quad + \quad \nabla^2 \mathbf{B} \quad = \quad -\varepsilon_\beta \mathbf{K}^{-1} \tag{147a}$$

$$\nabla \cdot \mathbf{B} \quad = \quad 0 \tag{147b}$$

B.C. 1
$$\mathbf{B} \quad = \quad -\mathbf{I}, \qquad at\ A_{\beta\sigma} \tag{147c}$$

Periodicity:
$$\mathbf{b}(\mathbf{r}+\ell_i) \ = \ \mathbf{b}(\mathbf{r}), \quad \mathbf{B}(\mathbf{r}+\ell_i) \ = \ \mathbf{B}(\mathbf{r}), \qquad i = 1, 2, 3 \tag{147d}$$

Average:
$$\langle \mathbf{B} \rangle^\beta \quad = \quad 0 \tag{147e}$$

In order to develop a convenient computational method for the determination of $\mathbf{K}$, we first define a new vector $\mathbf{d}$ and a new tensor $\mathbf{D}$ according to

$$\mathbf{d} = -\varepsilon_\beta^{-1}\mathbf{b}\cdot\mathbf{K}\,, \qquad \mathbf{D} = -\varepsilon_\beta^{-1}(\mathbf{B}+\mathbf{I})\cdot\mathbf{K} \tag{148}$$

In terms of the vector $\mathbf{d}$ and the tensor $\mathbf{D}$, the closure problem given by eqns 147 takes the form

$$-\nabla\mathbf{d} + \nabla^2\mathbf{D} = \mathbf{I} \tag{149a}$$

$$\nabla\cdot\mathbf{D} = 0 \tag{149b}$$

B.C. 1 $$\mathbf{D} = 0\,, \qquad at\ A_{\beta\sigma} \tag{149c}$$

Periodicity: $$\mathbf{d}(\mathbf{r}+\ell_i) = \mathbf{d}(\mathbf{r})\,, \quad \mathbf{D}(\mathbf{r}+\ell_i) = \mathbf{D}(\mathbf{r})\,, \quad i=1, 2, 3 \tag{149d}$$

Average: $$\langle\mathbf{D}\rangle^\beta = -\varepsilon_\beta^{-1}\mathbf{K} \tag{149e}$$

Here we see that the constraint on the average of $\tilde{\mathbf{v}}_\beta$, given earlier by eqn 107, is required in order to determine the permeability tensor as indicated by eqn 149e.

The solution of eqns 149a through 149d is straightforward and is identical to methods used to solve the Stokes' equations. To see the similarity, we form the scalar product of eqns 149a through 149d with an arbitrary unit vector, λ, and use the following definitions

$$\mathbf{d}\cdot\lambda = \tilde{p}\,, \qquad \mathbf{D}\cdot\lambda = \mathbf{v}\,, \qquad \mathbf{I}\cdot\lambda = \nabla\langle p\rangle^\beta \tag{150}$$

so that our closure problem takes the form

$$-\nabla\tilde{p} + \nabla^2\mathbf{v} = \nabla\langle p\rangle^\beta \tag{151a}$$

$$\nabla\cdot\mathbf{v} = 0 \tag{151b}$$

B.C. 1 $$\mathbf{v} = 0\,, \qquad at\ A_{\beta\sigma} \tag{151c}$$

Periodicity: $$\tilde{p}(\mathbf{r}+\ell_i) = \tilde{p}(\mathbf{r}), \quad \mathbf{v}(\mathbf{r}+\ell_i) = \mathbf{v}(\mathbf{r}), \quad i = 1, 2, 3 \tag{151d}$$

In actual fact, this is the *form* of the 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 eqns 151 can be accomplished with routine and well-established methods. After having solved eqns 151, one can make use of eqn 149e and the second of eqns 150 to obtain

$$\lambda \cdot \mathsf{K} \cdot \lambda = -\varepsilon_\beta \lambda \cdot \langle \mathbf{v} \rangle^\beta \tag{152}$$

and from this one can calculate all the components of the permeability tensor. In thinking about eqns 150 through 152, one must remember that the "pressure" has units of *length*, and the "velocity" has units of *length squared*.

In order to determine the Forchheimer correction tensor, we could solve the closure problem given by eqns 133; however, it is more convenient to solve the original closure problem given by eqns 112 and then extract the tensor F from the final result. We can express eqns 112 as

$$\left(\rho_\beta \mathbf{v}_\beta / \mu_\beta\right) \cdot \nabla \mathsf{M} = -\nabla \mathbf{m} + \nabla^2 \mathsf{M} + \varepsilon_\beta \mathsf{H}^{-1} \tag{153a}$$

$$\nabla \cdot \mathsf{M} = 0 \tag{153b}$$

B.C. 1 $$\mathsf{M} = -\mathsf{I}, \quad \text{at } A_{\beta\sigma} \tag{153c}$$

Periodicity: $$\mathbf{m}(\mathbf{r}+\ell_i) = \mathbf{m}(\mathbf{r}), \quad \mathsf{M}(\mathbf{r}+\ell_i) = \mathsf{M}(\mathbf{r}), \quad i = 1, 2, 3 \tag{153d}$$

Average: $$\langle \mathsf{M} \rangle^\beta = 0 \tag{153e}$$

in which H is a constant tensor defined by

$$\mathsf{H}^{-1} = \mathsf{K}^{-1}\left(\mathsf{I} + \mathsf{F}\right) \tag{154}$$

The constraint given by eqn 153e is used to determine the tensor H, and an iterative numerical method can be used to carry out this type of calculation (Quintard and Whitaker, 1993). However, it is more convenient to define the new dependent variables

$$\mathbf{m}_o \;=\; \mathbf{m}\,\varepsilon_\beta^{-1}\cdot\mathbf{H}\,, \qquad \mathbf{M}_o \;=\; \left(\mathbf{M}+\mathbf{I}\right)\cdot\varepsilon_\beta^{-1}\cdot\mathbf{H} \tag{155}$$

so that the closure problem given by eqns 152 takes the form

$$\left(\rho_\beta \mathbf{v}_\beta/\mu_\beta\right)\cdot\nabla\mathbf{M}_o \;=\; -\nabla\mathbf{m}_o \;+\; \nabla^2\mathbf{M}_o \;+\; \mathbf{I} \tag{156a}$$

$$\nabla\cdot\mathbf{M}_o \;=\; 0 \tag{156b}$$

B.C.1 $$\mathbf{M}_o \;=\; 0\,, \quad \text{at } A_{\beta\sigma} \tag{156c}$$

Periodicity: $$\mathbf{m}_o(\mathbf{r}+\ell_i) \;=\; \mathbf{m}_o(\mathbf{r})\,, \quad \mathbf{M}_o(\mathbf{r}+\ell_i) \;=\; \mathbf{M}_o(\mathbf{r})\,, \quad i=1,2,3 \tag{156d}$$

Average: $$\langle\mathbf{M}_o\rangle^\beta \;=\; \varepsilon_\beta^{-1}\mathbf{H} \tag{156e}$$

Here we can see that this boundary value problem has essentially the same form as one would encounter in a study of the Navier-Stokes equations for steady, incompressible flow in a spatially periodic system, and it is shown elsewhere (Whitaker, 1996) that eqns 156 are *exactly equivalent* to the Navier-Stokes equations. The problem can be transformed to a vector problem in the same manner that eqns 149 were transformed to eqns 151, and the application of standard numerical techniques will allow one to determine the tensor $\mathbf{H}$ by means of eqn 156e. Knowing the tensor $\mathbf{H}$ on the basis of eqns 156, and the tensor $\mathbf{K}$ on the basis of eqns 149, we can determine the Forchheimer correction tensor according to

$$\mathbf{F} \;=\; \mathbf{K}\cdot\mathbf{H}^{-1} \;-\; \mathbf{I} \tag{157}$$

The advantage of solving two closure problems in order to determine $\mathbf{K}$ and $\mathbf{F}$ is that there is a great deal of information available concerning the Darcy's law permeability tensor, and the solution of the first closure problem allows one to make use of that information. Elsewhere (Whitaker, 1996) it is shown that the closure problem given by eqns 156 can be used to prove that the Darcy's law permeability tensor is symmetric

$$\mathbf{K} \;=\; \mathbf{K}^{\mathrm{T}} \tag{158}$$

while the Forchheimer correction tensor $\mathbf{F}$ determined by eqn 157 is not.

5 Local closure problem for mass transport

Our development of the local closure problem associated with eqns 100 through 102 follows that for the momentum closure problem and leads to

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_A + \underbrace{\tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_A \rangle^\beta}_{\substack{convective\\source}} = \mathscr{D}_\beta \nabla^2 \tilde{c}_A + \underbrace{\varepsilon_\beta^{-1} a_v K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{adsorptive\\source}} \tag{159}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \tilde{c}_A = \underbrace{\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla \langle c_A \rangle^\beta}_{\substack{diffusive\\source}} + \underbrace{K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t}}_{\substack{adsorptive\\source}}, \quad at \ A_{\beta\sigma} \tag{160}$$

$$\text{Periodicity:} \qquad \tilde{c}_A(\mathbf{r} + \ell_i) = \tilde{c}_A(\mathbf{r}), \qquad i = 1, 2, 3 \tag{161}$$

This boundary value problem only determines $\tilde{c}_A$ to within an arbitrary constant and we could eliminate this constant by requiring that the average of the spatial deviation concentration be zero. This would be consistent with our treatment of $\tilde{\mathbf{v}}_\beta$, as indicated by eqn 106; however, the arbitrary constant associated with $\tilde{c}_A$ is of no importance since this constant will not pass through either the volume filter or the surface filter that are contained in eqn 70. In our treatment of eqns 159 through 161 we will assume that the sources undergo negligible variation within a unit cell, and this allows us to represent the spatial deviation concentration in terms of *closure variables*.

5.1 Closure variables for mass transfer

The presence of the two sources in the mass transport closure problem suggests a representation of the form

$$\tilde{c}_A = \mathbf{b} \cdot \nabla \langle c_A \rangle^\beta + s K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \psi \tag{162}$$

in which $\mathbf{b}$ and s are closure variables and ψ is an undetermined scalar. We are free to specify the vector $\mathbf{b}$ and the scalar s in any manner we wish and a prudent way to define these two closure variables is in terms of two local closure problems. The first of these defines the vector field that maps $\nabla\langle c_A\rangle^\beta$ onto $\tilde{c}_A$

PROBLEM I

$$\tilde{\mathbf{v}}_\beta + \mathbf{v}_\beta \cdot \nabla \mathbf{b} = \mathscr{D}_\beta \nabla^2 \mathbf{b} \tag{163a}$$

B.C.1 $$-\mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{b} = \mathbf{n}_{\beta\sigma}, \quad at \ A_{\beta\sigma} \tag{163b}$$

Periodicity: $$\mathbf{b}(\mathbf{r} + \ell_i) = \mathbf{b}(\mathbf{r}), \quad i = 1, 2, 3 \tag{163c}$$

while the second defines the scalar that maps $K_{eq}\,\partial\langle c_A\rangle^\beta/\partial t$ onto $\tilde{c}_A$.

PROBLEM II

$$\mathbf{v}_\beta \cdot \nabla s = \mathscr{D}_\beta \nabla^2 s + \varepsilon_\beta^{-1} a_v \tag{164a}$$

B.C.1 $$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla s = 1, \quad at \ A_{\beta\sigma} \tag{164b}$$

Periodicity: $$s(\mathbf{r} + \ell_i) = s(\mathbf{r}), \quad i = 1, 2, 3 \tag{164c}$$

When the closure variables are specified in this manner, one can follow previous studies (Ryan *et al*., 1981; Carbonell and Whitaker, 1983; Whitaker, 1986) to prove that ψ is a constant that will not pass through the two filters in eqn 70. Under these circumstances, the representation given by eqn 162 can be replaced with

$$\tilde{c}_A = \mathbf{b} \cdot \nabla\langle c_A\rangle^\beta + s\,K_{eq} \frac{\partial\langle c_A\rangle^\beta}{\partial t} \tag{165}$$

and this result can be used to develop the closed form of eqn 70.

5.2 Closed form of the mass transport equation

Substitution of eqn 165 into eqn 70 leads to a closed form of the volume averaged mass transport equation

$$\varepsilon_\beta \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta + \varepsilon_\beta \mathbf{d} \cdot \nabla \left(K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t} \right) =$$

$$= \varepsilon_\beta \mathbf{D}^* : \nabla\nabla \langle c_A \rangle^\beta - a_v K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t} \tag{166}$$

in which we have used the following definitions of the dimensionless vector **d** and the dispersion tensor $\mathbf{D}^*$.

$$\varepsilon_\beta \mathbf{d} = \langle s \tilde{\mathbf{v}}_\beta \rangle - \frac{1}{\mathscr{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathscr{D}_\beta s \, dA \tag{167}$$

$$\varepsilon_\beta \mathbf{D}^* = \varepsilon_\beta \mathscr{D}_\beta \left(\mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b} \, dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b} \rangle \tag{168}$$

For simplicity we have ignored any variations of **u** and $\mathbf{D}^*$; however, this limitation can easily be removed. Normally one arranges eqn 166 in the form

$$\varepsilon_\beta \left(1 + \varepsilon_\beta^{-1} a_v K_{eq} \right) \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta +$$

$$+ \varepsilon_\beta \mathbf{d} \cdot \nabla \left(K_{eq} \frac{\partial \langle c_A \rangle^\beta}{\partial t} \right) = \varepsilon_\beta \mathbf{D}^* : \nabla\nabla \langle c_A \rangle^\beta \tag{169}$$

and in many applications the mixed derivative term is discarded.

If the adsorption isotherm is *nonlinear*, K_{eq} is a function of $\langle c_A \rangle^\beta$ as indicated by eqn 62; however, for linear adsorption K_{eq} is a constant and eqn 169 simplifies to

$$\varepsilon_\beta \left(1 + \varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq}\right) \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta + \varepsilon_\beta \mathbf{d} K_{eq} \cdot \nabla \left(\frac{\partial \langle c_A \rangle^\beta}{\partial t} \right) = \varepsilon_\beta \mathbf{D}^* : \nabla\nabla \langle c_A \rangle^\beta \tag{170}$$

For chromatographic processes, this result can be simplified following the original analysis of Golay (1952). For pulsed systems, we identify the pulse velocity by $\mathbf{u}_p$ and express the time derivative of the concentration as

$$\frac{\partial \langle c_A \rangle^\beta}{\partial t} = \left. \frac{d \langle c_A \rangle^\beta}{dt} \right|_{\mathbf{u}_p} - \mathbf{u}_p \cdot \nabla \langle c_A \rangle^\beta \tag{171}$$

Here the subscript $\mathbf{u}_p$ is used to indicate the time derivative as determined by an observer moving at the velocity $\mathbf{u}_p$. When the following restriction is valid

$$\frac{\partial \langle c_A \rangle^\beta}{\partial t} \gg \left. \frac{d \langle c_A \rangle^\beta}{dt} \right|_{\mathbf{u}_p} \tag{172}$$

the mixed derivative term in eqn 170 can be expressed as

$$\varepsilon_\beta \mathbf{d} K_{eq} \cdot \nabla \left(\frac{\partial \langle c_A \rangle^\beta}{\partial t} \right) = -\varepsilon_\beta K_{eq} \mathbf{d} \mathbf{u}_p : \nabla\nabla \langle c_A \rangle^\beta \tag{173}$$

Use of this result in eqn 170 leads to a chromatographic equation in the form

$$\frac{\partial \langle c_A \rangle^\beta}{\partial t} + \frac{\langle \mathbf{v}_\beta \rangle^\beta}{\left(1 + \varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq}\right)} \cdot \nabla \langle c_A \rangle^\beta = \left(\frac{\mathbf{D}^* + K_{eq} \mathbf{d} \mathbf{u}_p}{1 + \varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq}} \right) : \nabla\nabla \langle c_A \rangle^\beta \tag{174}$$

This clearly indicates that the pulse velocity is given by

$$\mathbf{u}_p = \frac{\langle \mathbf{v}_\beta \rangle^\beta}{\left(1 + \varepsilon_\beta^{-1} a_{\mathrm{v}} K_{eq}\right)} \tag{175}$$

and that the dispersion tensor in this intrinsic averaged mass transport equation is a complex function of the equilibrium coefficient K_{eq}. It is convenient to express eqn 174 as

$$\frac{\partial \langle c_A \rangle^\beta}{\partial t} + \frac{\langle \mathbf{v}_\beta \rangle^\beta}{\left(1 + \varepsilon_\beta^{-1} a_v K_{eq}\right)} \cdot \nabla \langle c_A \rangle^\beta = \mathbf{D}^{**} : \nabla\nabla \langle c_A \rangle^\beta \tag{176}$$

in which the dispersion tensor takes the form

$$\mathbf{D}^{**} = \frac{\mathbf{D}^{*}\left(1 + \varepsilon_\beta^{-1} a_v K_{eq}\right) + K_{eq}\,\mathbf{d}\langle \mathbf{v}_\beta \rangle^\beta}{\left(1 + \varepsilon_\beta^{-1} a_v K_{eq}\right)^2} \tag{177}$$

In order to determine $\mathbf{D}^{**}$ one must solve the two closure problems given by eqns 163 and 164, and the solution procedure is described by various authors (Eidsath *et al*., 1983; Sahraoui and Kaviany 1994; Quintard and Whitaker, 1994b, 1995).

6 Comparison with experiment

When we think about comparing theory with experiment, we have in mind experiments that could be used to both test the averaging procedure and the prediction of the effective coefficients that appear in the volume averaged transport equations. In terms of the momentum equation

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}}{\mu_\beta}\left(\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g}\right) - \mathbf{F} \cdot \langle \mathbf{v}_\beta \rangle \tag{178}$$

this means that we would like to verify the several length-scale constraints that were imposed in the averaging procedure and we would like to compare measured and predicted values of the Darcy's law permeability tensor $\mathbf{K}$ and the Forchheimer correction tensor $\mathbf{F}$. From extensive experimental studies (see Macdonald *et al*., 1979 for a review), there is evidence that $\mathbf{F} \sim \langle \mathbf{v}_\beta \rangle^\beta$ which is consistent with the discussion given in Sec. 4.3 and elsewhere (Whitaker, 1996). However, there would appear to be no solutions of the closure problem for $\mathbf{F}$ that can be compared directly with experimental data. For the Darcy's law permeability tensor, there are solutions of the closure problem given by eqns 149 (Zick and Homsy, 1982) that compare quite well with experimental data for several regular arrays of spheres (Martin *et al*., 1951; Susskind and Becker, 1967). The comparison has been presented by Barrère *et al*. (1992) and by Quintard and Whitaker (1994a) who also included experimental results for random spheres having a relatively narrow particle size distribution. There would seem to be little doubt that the closure problem represented by eqns 149 can be used with confidence to predict the Darcy's law permeability tensor. However, at this time we do not know exactly what geometrical characteristics of a porous medium (other than the porosity) will pass through the *surface filter* contained in eqn 56.

Comparison of the mass transport equation

$$\varepsilon_\beta \left(1 + \varepsilon_\beta^{-1} a_v K_{eq}\right) \frac{\partial \langle c_A \rangle^\beta}{\partial t} + \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_A \rangle^\beta + \varepsilon_\beta \mathbf{d}\, K_{eq} \cdot \nabla \left(\frac{\partial \langle c_A \rangle^\beta}{\partial t} \right) = \varepsilon_\beta \mathbf{D}^* : \nabla\nabla \langle c_A \rangle^\beta \tag{179}$$

with experiment is limited to *qualitative* observations of chromatographic phenomena and *quantitative* comparisons between theory and experiment for the case in which $K_{eq} = 0$. Detailed comparisons between theory and experiment for longitudinal and lateral dispersion coefficients have been presented by Eidsath *et al*., 1983, and by Plumb and Whitaker, 1990, and a summary of computational results associated with the closure problem given by eqns 163 has been given by Quintard and Whitaker, 1994b. The comparison between theory and experiment is based on the use of simple unit cells and the comparison clearly indicates that simple unit cells are insufficient to capture the observed phenomena. Plumb and Whitaker (1988, 1990) have suggested that large-scale averaging may provide a means of incorporating the necessary complexity that is clearly exhibited by the experimental data, but conclusive results are unavailable at this time. From the comparisons between theory and experiment, it is clear that we must understand the role of the surface and volume filters in eqn 70 before we can use the theory to predict the dispersion tensor with confidence.

7 Conclusions

Beginning with momentum and mass transport equations of the form

$$\frac{\partial}{\partial t}(\rho_\beta \mathbf{v}_\beta) + \nabla \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta$$

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}_\beta) = \mathscr{D}_\beta \nabla^2 c_A$$

along with boundary conditions given by

B.C.1 $$\mathbf{v}_\beta = 0, \quad at\ \mathscr{A}_{\beta\sigma}$$

B.C.2 $$-\mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_\beta \nabla c_A = K_{eq} \frac{\partial c_A}{\partial t}, \quad at\ \mathscr{A}_{\beta\sigma}$$

we have derived the volume averaged momentum and mass transport equations represented by eqns 178 and 179. The striking difference between eqn 178 and eqn 179 results both from the presence of a momentum source, $-\nabla p_\beta + \rho_\beta \mathbf{g}$, in the Navier-Stokes equations and from the difference in the nature of the interfacial boundary conditions. The form of eqn 178 is dominated by the *closure problem* and the no-slip boundary condition, while the form of eqn 179 is dominated by the *averaging procedure* and the adsorption boundary condition. This clearly indicates that one must pay careful attention to the *averaging procedure*, the *closure problem*, and the *boundary conditions* when developing volume averaged transport equations for multiphase systems.

References

Barrère, J., Olivier, G., and Whitaker, S. 1992, On the closure problem for Darcy's law, Transport in Porous Media **7**, 209 - 222.

Bensoussan, A., Lions, J.L. and Papanicolaou, G., 1978, *Asymptotic Analysis for Periodic Structures*, North-Holland Publishing Company, Amsterdam, The Netherlands.

Brinkman, H.C. 1947, A calculation of the viscous force exerted by a flowing fluid on a dense swarm of particles, App. Sci. Res. **A1**, 27-34.

Carbonell, R.G. and Whitaker, S., 1983, Dispersion in pulsed systems II: Theoretical developments for passive dispersion in porous media, Chem. Engng. Sci. **38**, 1795-1802.

Carbonell, R.G. and Whitaker, S. 1984, Heat and mass transfer in porous media, pages 123 - 198 in *Fundamentals of Transport Phenomena in Porous Media*, edited by J. Bear and M.Y. Corapcioglu, Martinus Nijhoff Publishers, Dordrecht, The Netherlands.

Darcy, H. 1856, Les Fontaines Publiques de la Ville de Dijon, Dalmont, Paris.

Du Plessis, J.P. 1994, Analytical quantification of coefficients in the Ergun equation for fluid friction in a packed bed, Transport in Porous Media **16**, 189-207.

Eidsath, A.B. 1981, Flow and dispersion in spatially periodic porous media: A finite element study, MS Thesis, Department of Chemical Engineering, University of California at Davis.

Eidsath, A.B., Carbonell, R.G., Whitaker, S., and Herrmann, L.R., 1983, Dispersion in pulsed systems III: Comparison between theory and experiments for packed beds, Chem. Engng. Sci. **38,** 1803-1816.

Ene, H.I. and Poliševski, D., 1987, *Thermal Flow in Porous Media*, D. Reidel Publishing Company, Dordrecht, The Netherlands.

Forchheimer, P. 1901, Wasserbewegung durch Boden, Z. Ver. Deutsch. Ing. **45**, 1782-1788.

Golay, M.J.E. 1958, Chromatographic separations, in *Gas Chromatography*, edited by D.H. Desty, Butterworths, London.

Gray, W.G., 1975, A derivation of the equations for multiphase transport, Chem. Engng. Sci. **30**, 229-233.

Hassanizadeh, S.M. and Gray, W.G. 1987, High velocity flow in porous media, Transport in Porous Media, **2**, 521-531.

Howes, F.A. and Whitaker, S., 1985, The spatial averaging theorem revisited, Chem. Engng. Sci. **40,** 1387-1392.

Ma, H. and Ruth, D.W. 1993, The microscopic analysis of high Forchheimer number flow in porous media, Transport in Porous Media **13**, 139-160.

Macdonald, I.F., El-Sayed, M.S., Mow, K., and Dullien, F.A.L. 1979, Flow through porous media: The Ergun equation revisited, Ind. Eng. Chem. Fundam. **18**, 199-208.

Martin, J.J., McCabe, W.L., and Mourad, C.C. 1951, Pressure drop through stacked spheres--effect of orientation, Chem. Engng. Prog. **47**, 91-98.

Mei, C.C. and Auriault, J.-L. 1991, The effect of weak inertia on flow through a porous medium, J. Fluid Mech. **222**, 647-663.

Ochoa-Tapia, J.A. and Whitaker, S. 1995, Momentum transfer at the boundary between a porous medium and a homogeneous fluid I: Theoretical development, Int. J. Heat Mass Trans. **38**, 2635-2646.

Ochoa-Tapia, J.A. and Whitaker, S. 1995, Momentum transfer at the boundary between a porous medium and a homogeneous fluid II: Comparison with experiment, Int. J. Heat Mass Trans. **38**, 2647-2655.

Ochoa-Tapia, J.A. and Whitaker, S. 1997, Heat transfer at the boundary between a porous medium and a homogeneous fluid, Int. J. Heat Mass Trans. **40**, 2691-2707.

Plumb, O.A. and Whitaker, S., 1988, Dispersion in heterogeneous porous media I: Local volume averaging and large-scale averaging, Water Resour. Res. **24,** 913-926.

Plumb, O.A. and Whitaker, S., 1988, Dispersion in heterogeneous porous media II: Predictions for stratified and two-dimensional spatially periodic systems, Water Resour. Res. **24**, 927-938.

Plumb, O.A. and Whitaker, S., 1990, Diffusion, adsorption, and dispersion in porous media: Small-scale averaging and local volume averaging, Chapter V in *Dynamics of Fluids in Hierarchical Porous Media*, edited by J.H. Cushman, Academic Press, New York.

Plumb, O.A. and Whitaker, S., 1990, Diffusion, adsorption, and dispersion in heterogeneous porous media: The method of large-scale averaging, Chapter VI in *Dynamics of Fluids in Hierarchical Porous Media*, edited by J.H. Cushman, Academic Press, New York.

Prat, M. 1989, On the boundary conditions at the macroscopic level, Transport in Porous Media **4**, 259-280.

Prat, M. 1990, Modeling of heat transfer by conduction in a transition region between a porous medium and an external fluid, Transport in Porous Media **5**, 71-95.

Prat, M. 1992, Some refinements concerning he boundary conditions at the macroscopic level, Transport in Porous Media **7**, 147-161.

Quintard, M. and Whitaker, S. 1993, One and two-equation models for transient diffusion processes in two-phase systems, pages 369-465 in *Advances in Heat Transfer*, Vol. 23, Academic Press, New York.

Quintard, M. and Whitaker, S. 1994a, Transport in ordered and disordered porous media I: The cellular average and the use of weighting functions, Transport in Porous Media **14**, 163-177.

Quintard, M. and Whitaker, S. 1994a, Transport in ordered and disordered porous media II: Generalized volume averaging, Transport in Porous Media **14**, 179-206.

Quintard, M. and Whitaker, S. 1994a, Transport in ordered and disordered porous media III: Closure and comparison between theory and experiment, Transport in Porous Media, **15**, 31-49.

Quintard, M. and Whitaker, S. 1994a, Transport in ordered and disordered porous media IV: Computer generated porous media, Transport in Porous Media, **15**, 51-70.

Quintard, M. and Whitaker, S. 1994a, Transport in ordered and disordered porous media V: Geometrical results for two-dimensional systems, Transport in Porous Media, **15**, 183-196.

Quintard, M. and Whitaker, S. 1994b, Convection, dispersion, and interfacial transport of contaminants: Homogeneous porous media, Adv. Water Resour., **17**, 221-239.

Quintard, M. and Whitaker, S. 1995, Aerosol filtration: An analysis using the method of volume averaging, J. Aerosol Sci., **26**, 1227-1255.

Ruth, D.W. and Ma, H. 1993, Numerical analysis of viscous, incompressible flow in a diverging-converging RUC, Transport in Porous Media **13**, 161-177.

Ryan, D., Carbonell, R.G., and Whitaker, S., 1981 A theory of diffusion and reaction in porous media, AIChE Symposium Series, #202, Vol. 71, pages 46-62.

Sahraoui, M. and Kaviany, M. 1992, Slip and no-slip velocity boundary conditions at interface of porous, plain media, Int. J. Heat Mass Trans. **35**, 927-943.

Sahraoui, M. and Kaviany, M. 1993, Slip and no-slip temperature boundary conditions at interface of porous, plain media I: Conduction, Int. J. Heat Mass Trans. **36**, 1019-1033.

Sahroui, M. and Kaviany, M. 1994, Slip and no-slip temperature boundary conditions at the interface of porous, plain media: Convection, Int. J. Heat Mass Trans. **37**, 1029-1044.

Sanchez-Palencia, E., 1980, Non-homogeneous media and vibration theory, *Lecture Notes in Physics* **127**, Springer-Verlag, New York.

Snyder, L.J. and Stewart, W.E. 1966, Velocity and pressure profiles for Newtonian creeping flow in regular packed beds of spheres, AIChE Journal **12**, 167-173.

Sorensen, J.P. and Stewart, W.E. 1974, Computation of forced convection in slow flow through ducts and packed beds II: Velocity profile in a simple array of spheres, Chem. Engng. Sci. **29**, 817-819.

Susskind, H. and Becker, W. 1967, Pressure drop in geometrically ordered packed beds of spheres, AIChE Journal, **13**, 1155-1163.

Tennekes, H. and Lumley, J.L. 1972, *A First Course in Turbulence*, The MIT Press, Cambridge, Massachusetts.

Whitaker, S. 1969, Advances in the theory of fluid motion in porous media, I&EC **61**, 14-28.

Whitaker, S. 1982, Laws of continuum physics for single-phase, single-component systems, *Handbook of Multiphase Systems*, edited by G. Hetsroni, Hemisphere Publishing Corporation, New York, pages 1-5 to 1-35.

Whitaker, S. 1985, A simple geometrical derivation of the spatial averaging theorem. Chem. Engr. Ed. **19**, 18-21 and 50-52.

Whitaker, S. 1986, Flow in porous media I: A theoretical derivation of Darcy's law, Transport in Porous Media **1,** 3-25.

Whitaker, S. 1996, The Forchheimer equation: A theoretical development, Transport in Porous Media **25**, 27-61.

Wodie, J.- C. and Levy, T. 1991, Correction non linéaire de la loi de Darcy, C.R. Acad. Sci. Paris, t. **312**, Série II, 157-161.

Zick, A.A. and Homsy, G.M. 1982, Stokes' flow through periodic arrays of spheres, J. Fluid Mech. **115**, 13-26.