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Transport in chemically and mechanically heterogeneous porous media IV: large-scale mass equilibrium for solute transport with adsorption

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In this article we consider the transport of an adsorbing solute in a two-region model of a chemically and mechanically heterogeneous porous medium when the condition of *large-scale mechanical equilibrium* is valid. Under these circumstances, a *one-equation* model can be used to predict the large-scale averaged velocity, but a *two-equation* model may be required to predict the regional velocities that are needed to accurately describe the solute transport process. If the condition of large-scale mass equilibrium is valid, the solute transport process can be represented in terms of a one-equation model and the analysis is greatly simplified. The constraints associated with the condition of large-scale mass equilibrium are developed, and when these constraints are satisfied the mass transport process can be described in terms of the large-scale average velocity, an average adsorption isotherm, and a single large-scale dispersion tensor. When the condition of large-scale mass equilibrium is not valid, two equations are required to describe the mass transfer process, and these two equations contain two adsorption isotherms, two dispersion tensors, and an exchange coefficient. The extension of the analysis to multi-region models is straight forward but tedious.

Key words: large-scale mechanical equilibrium, one-equation model, two-equation model
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Nomenclature

Roman letters
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$a_{\gamma\kappa}$	interfacial area per unit volume, m^{-1}
$A_{\gamma\kappa}$	area of the γ–κ interface contained in the averaging volume, $\mathcal{V}_\sigma$, m^2
$A_{\beta\sigma}$	$= A_{\sigma\beta}$, area of the β–σ interface contained in the averaging volume, $\mathcal{V}_\sigma$, m^2
$A_{\eta\omega}$	$= A_{\omega\eta}$, area of the boundary between the η and ω-regions contained with the large-scale averaging volume, $\mathcal{V}_\sigma$, m^2
$\mathbf{b}_{\sigma\eta}$	vector field that maps $\nabla\langle c_\eta\rangle^\eta$ onto $\tilde{c}_{\sigma\eta}$ in the η-region, m
$\mathbf{b}_{\beta\eta}$	vector field that maps $\nabla\langle c_\eta\rangle^\eta$ onto $\tilde{c}_{\beta\eta}$ in the η-region, m
$\mathbf{b}_{\sigma\omega}$	vector field that maps $\nabla\langle c_\omega\rangle^\omega$ onto $\tilde{c}_{\sigma\omega}$ in the ω-region, m
$\mathbf{b}_{\beta\omega}$	vector field that maps $\nabla\langle c_\omega\rangle^\omega$ onto $\tilde{c}_{\beta\omega}$ in the ω-region, m
$\mathbf{b}_\eta$	vector field that maps $\nabla\{\langle c\rangle\}$ onto $\tilde{c}_\eta$
$\mathbf{b}_\omega$	vector field that maps$\nabla\{\langle c\rangle\}$ onto $\tilde{c}_\omega$
c_γ	point concentration in the γ-phase, moles/m^3
$c_{\gamma s}$	adsorbed surface concentration at the γ–κ interface, moles/m^2
$\langle c_\gamma\rangle^\gamma$	intrinsic average concentration in the γ-phase, moles/m^3
c_σ	$= \langle c_\gamma\rangle^\gamma$, point concentration in the σ-region, moles/m^3
$\langle c_\sigma\rangle^\sigma$	intrinsic average concentration in the σ-region, moles/m^3
$\tilde{c}_\sigma$	$= c_\sigma - \langle c_\sigma\rangle^\sigma$, spatial deviation concentration in the σ-region, moles/m^3

c_β	point concentration in the β-phase, moles/m^3
$\langle c_\beta \rangle^\beta$	intrinsic average concentration in the β-phase, moles/m^3
$\tilde{c}_\beta$	$= c_\beta - \langle c_\beta \rangle^\beta$, spatial deviation concentration in the β-phase, moles/m^3
$\langle c_\eta \rangle^\eta$	$= \epsilon_{\beta\eta} \langle c_\beta \rangle^\beta_\eta + \epsilon_{\sigma\eta} \langle c_\sigma \rangle^\sigma_\eta$, Darcy-scale spatial average concentration for the β–σ system in the η-region, moles/m^3
$\langle c_\omega \rangle^\omega$	$= \epsilon_{\beta\omega} \langle c_\beta \rangle^\beta_\omega + \epsilon_{\sigma\omega} \langle c_\omega \rangle^\sigma_\omega$, Darcy-scale spatial average concentration for the β–σ system in the ω-region, moles/m^3
$\{\langle c_\eta \rangle^\eta\}$	η-region superficial average concentration, moles/m^3
$\{\langle c_\eta \rangle^\eta\}^\eta$	$= \varphi_\eta \{\langle c_\eta \rangle^\eta\}$, η-region intrinsic average concentration, moles/m^3
$\{\langle c \rangle\}$	$= \varphi_\eta \{\langle c_\eta \rangle^\eta\}^\eta + \varphi_\omega \{\langle c_\omega \rangle^\omega\}^\omega$, large-scale intrinsic average concentration, moles/m^3
$\tilde{c}_\eta$	$= \langle c_\eta \rangle^\eta - \{\langle c_\eta \rangle^\eta\}^\eta$, spatial deviation concentration for the η-region, moles/m^3.
$\hat{c}_\eta$	$= \{\langle c_\eta \rangle^\eta\}^\eta - \{\langle c \rangle\}$, large-scale spatial deviation for the η-region, moles/m^3
$\{\langle c_\omega \rangle^\omega\}$	ω-region superficial average concentration, moles/m^3
$\{\langle c_\omega \rangle^\omega\}^\omega$	$= \varphi_\omega \{\langle c_\omega \rangle^\omega\}$, ω-region intrinsic average concentration, moles/m^3
$\tilde{c}_\omega$	$= \langle c_\omega \rangle^\omega - \{\langle c_\omega \rangle^\omega\}^\omega$, spatial deviation concentration for the ω-region, moles/m^3
$\hat{c}_\omega$	$= \{\langle c_\omega \rangle^\omega\}^\omega - \{\langle c \rangle\}$, large-scale spatial deviation for the ω-region, moles/m^3
$\mathcal{D}_\gamma$	molecular diffusivity in the γ-phase, m^2/s
$\mathcal{D}_\beta$	molecular diffusivity in the β-phase, m^2/s
$\mathbf{D}^\gamma_{eff}$	effective diffusivity for the γ-phase, m^2/s
$\mathbf{D}_{eff}$	$= \epsilon_\gamma \mathbf{D}^\gamma_{eff}$, an alternate effective diffusivity for the γ-phase, m^2/s
$\mathbf{D}_{\sigma\eta}$	$= (\epsilon_\gamma \mathbf{D}^\gamma_{eff})_\eta$, diffusion tensor for the σ-region in the η-region, m^2/s
$\mathbf{D}_{\sigma\omega}$	$= (\epsilon_\gamma \mathbf{D}^\gamma_{eff})_\omega$, diffusion tensor for the σ-region in the ω-region, m^2/s
$\mathbf{D}^*_\eta$	dispersion tensor for the β–σ system in the η-region, m^2/s
$\mathbf{D}^*_\omega$	dispersion tensor for the β–σ system in the ω-region, m^2/s
$\mathbf{D}^{**}_{\eta\eta}$	dominant dispersion tensor for the η-region transport equation, m^2/s
$\mathbf{D}^{**}_{\omega\omega}$	dominant dispersion tensor for the ω-region transport equation, m^2/s
$\mathbf{D}^{**}$	large-scale, one-equation model dispersion tensor, m^2/s
$\mathbf{g}$	gravitational acceleration, m/s^2
$\mathbf{I}$	unit tensor
K_{eq}	$= \partial\mathcal{F}/\partial c_\gamma = \partial\mathcal{F}/\partial\langle c_\gamma \rangle^\gamma$, adsorption equilibrium coefficient, m
K	$= a_{\gamma\kappa} K_{eq}/\epsilon_\gamma$, dimensionless adsorption equilibrium coefficient for the σ-region
$\mathcal{K}_\eta$	$= [(\epsilon_\sigma a_{\gamma\kappa})_\eta/\epsilon_\eta]\partial\mathcal{F}/\partial\langle c_\eta \rangle^\eta$, dimensionless equilibrium coefficient for the η-region

K_ω	$= [(\epsilon_\sigma a_{\gamma\kappa})_\omega/\epsilon_\omega]\partial\mathcal{F}/\partial\langle c_\omega \rangle^\omega$, dimensionless equilibrium coefficient for the ω-region
ℓ_i	$i = 1, 2, 3$, lattice vectors, m
$\mathcal{L}_c$	characteristic length for region averaged concentrations, m
$\mathcal{L}$	aquifer or reservoir length scale, m
$\mathcal{L}_H$	length scale for the η–ω system, $\mathcal{L}_H \leq \mathcal{L}$, m
$\mathbf{n}_{\gamma\kappa}$	unit normal vector directed from the γ-phase toward the κ-phase
$\mathbf{n}_{\beta\sigma}$	$= -\mathbf{n}_{\sigma\beta}$, unit normal vector directed from the β-phase toward the σ-region
$\mathbf{n}_{\eta\omega}$	$= -\mathbf{n}_{\omega\eta}$, unit normal vector directed from the η-region toward the ω-region
$\mathbf{r}$	position vector, m
r_σ	radius of the small-scale averaging volume, $\mathcal{V}_\sigma$, m
r_0	radius of the Darcy-scale averaging volume, $\mathcal{V}$, m
R_0	radius of the large-scale averaging volume, $\mathcal{V}_\infty$, 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
$\langle \mathbf{v}_\beta \rangle$	$= \epsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta$ 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
$\{\langle \mathbf{v}_\beta \rangle_\eta\}^\eta$	intrinsic average velocity in the η-region, m/s
$\{\langle \mathbf{v}_\beta \rangle_\eta\}$	$= \varphi_\eta \{\langle \mathbf{v}_\beta \rangle_\eta\}^\eta$, superficial average velocity in the η-region, m/s
$\tilde{\mathbf{v}}_{\beta\eta}$	$= \langle \mathbf{v}_\beta \rangle_\eta - \{\langle \mathbf{v}_\beta \rangle_\eta\}^\eta$, η-region spatial deviation velocity, m/s
$\{\langle \mathbf{v}_\beta \rangle_\omega\}^\omega$	intrinsic average velocity in the ω-region, m/s
$\{\langle \mathbf{v}_\beta \rangle_\omega\}$	$= \varphi_\omega \{\langle \mathbf{v}_\beta \rangle_\omega\}^\omega$, superficial average velocity in the ω-region, m/s
$\tilde{\mathbf{v}}_{\beta\omega}$	$= \langle \mathbf{v}_\beta \rangle_\omega - \{\langle \mathbf{v}_\beta \rangle_\omega\}^\omega$, ω-region spatial deviation velocity, m/s
$\{\langle \mathbf{v}_\beta \rangle\}$	$= \varphi_\eta \{\langle \mathbf{v}_\beta \rangle_\eta\}^\eta + \varphi_\omega \{\langle \mathbf{v}_\beta \rangle_\omega\}^\omega$, large-scale, superficial average velocity, m/s
V_γ	volume of the γ-phase contained in the averaging volume, $\mathcal{V}_\sigma$, m^3
$\mathcal{V}_\sigma$	averaging volume for the γ–κ system, m^3
V_β	volume of the β-phase contained in the averaging volume, $\mathcal{V}$, m^3
$\mathcal{V}$	averaging volume for the β–σ system, m^3
V_η	volume of the η-region contained in the averaging volume, $\mathcal{V}_\infty$, m^3
V_ω	volume of the ω-region contained in the averaging volume, $\mathcal{V}_\infty$, m^3
$\mathcal{V}_\infty$	large-scale averaging volume for the η–ω system, m^3

Greek letters

α^*	mass exchange coefficient for the η–ω system, s^{-1}
ϵ_β	$= 1 - \epsilon_\sigma$, volume fraction of the β-phase
ϵ_γ	porosity of the σ-region
ϵ_σ	$= 1 - \epsilon_\beta$, volume fraction of the σ-region
ϵ_η	$= \epsilon_{\beta\eta} + (\epsilon_\sigma\epsilon_\gamma)_\eta$, total porosity for the β–σ system in the η-region
ϵ_ω	$= \epsilon_{\beta\omega} + (\epsilon_\sigma\epsilon_\gamma)_\omega$, total porosity for the β–σ system in the ω-region
$\{\epsilon\}$	$= \varphi_\eta\epsilon_\eta + \varphi_\omega\epsilon_\omega$, large-scale average porosity
$\{\epsilon\}(1+\{K\})$	$= \epsilon_\eta(1 + \mathcal{K}_\eta)\varphi_\eta + \epsilon_\omega(1 + \mathcal{K}_\omega)\varphi_\omega$, large-scale average capacitance factor
μ_β	shear coefficient of viscosity for the β-phase, Ns/m^2
ρ_β	mass density of the β-phase, kg/m^3
φ_η	$= 1 - \varphi_\omega$, volume fraction of the η-region
φ_ω	$= 1 - \varphi_\eta$, volume fraction of the ω-region

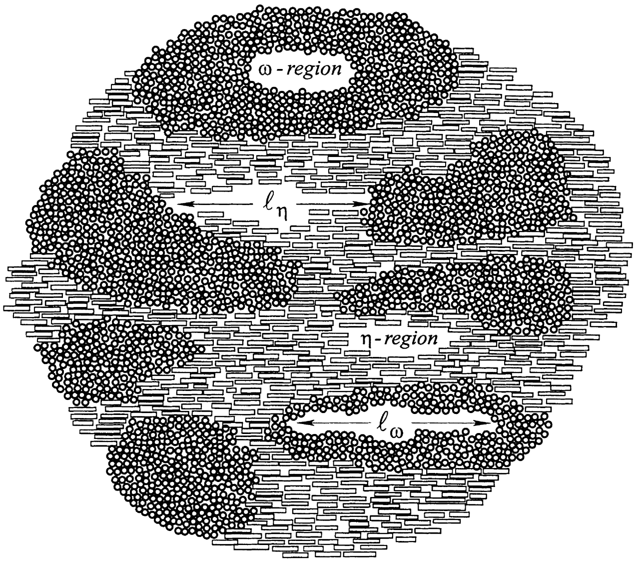

Fig. 1. Two-region model of a heterogeneous porous medium.

1 INTRODUCTION

A two-region model of a heterogeneous porous medium is shown in Fig. 1, and we would like to be able to accurately predict the solute transport process in such a system when the condition of large-scale *mechanical* equilibrium is valid. From a practical point of view, large-scale mechanical equilibrium occurs frequently and it permits the use of a one-equation model to predict the large-scale average velocity field. If a one-equation model suffices for the description of the mass transfer process, the large-scale form of Darcy's law can be used directly to determine the velocity field. If a two-equation model is required to accurately describe the mass transport process, we will need to make use of the regional form of Darcy's law that was presented in Part III.[1]

The general process of diffusion, nonlinear adsorption, and convective transport is assumed to take place in the hierarchical system[2] illustrated in Fig. 2. Diffusion and adsorption occur in the micropores and macropores contained within the σ-region, while diffusion, convection, and dispersion occur in the β-phase. We think of this latter process as occurring at the Darcy scale within the ω and η-regions. The ω and η-regions belong to other stratified regions, as illustrated in Fig. 2, and we would like to spatially smooth the transport processes that take place in those stratified regions. The length scale, $\mathcal{L}$, indicated in Fig. 2, should be thought of as the scale of an aquifer or the scale of a petroleum reservoir. The heterogeneities in that region have a length scale $\mathcal{L}_H$ which is bounded by $\mathcal{L}_H \leq \mathcal{L}$, and we have in mind that the transport equations that have been smoothed within the volume $\mathcal{V}_\infty$ will be solved numerically at the aquifer level. This means that spatial smoothing takes place at the *small scale* associated with the averaging volume $\mathcal{V}_\sigma$, at the *Darcy scale* associated with the averaging volume $\mathcal{V}$, and at the *large scale* associated with the averaging volume $\mathcal{V}_\infty$. The point at which one stops the averaging process and begins the direct numerical solution of the spatially smoothed equations depends on the quality of the information required and on the computational resources that are available. Averaging at the small scale would appear to be universally accepted; however a decision must be made concerning the use of either a one-equation model or a two-equation model.[3–5] Averaging at the Darcy scale would also appear to be universally accepted, and at this level one is again confronted with the choice between one- and two-equation models.

The original studies of two-equation models at the Darcy scale dealt with the problem of passive dispersion in single-phase systems. In order to explain a 'tailing effect' in pulse-injection dispersion experiments, early workers[6–10] separated the flow field into mobile and immobile regions and postulated separate equations for each region. These models provided improved agreement between theory and experiment at the expense of an additional adjustable parameter. This approach has been extended to mass transfer in heterogeneous systems by Passioura,[11] van Genuchten and Wierenga,[12] Rao *et al.*,[13] Gvirtzman *et al.*,[14] Corréa *et al.*,[15] and a comprehensive review has been prepared by Brusseau and Rao.[16]. Recently this model has been used to study the effect of solute size on transport in heterogeneous porous media[17].

In many of these prior studies, the length scales are not clearly identified. For example, the work of Coats and Smith[10] appears to be associated with the Darcy scale in an attempt to explain dispersion phenomena in packed beds, while the recent study of Corréa *et al.*[15] clearly deals with mass transfer in a dual porosity model of a porous medium. This means that the governing equations

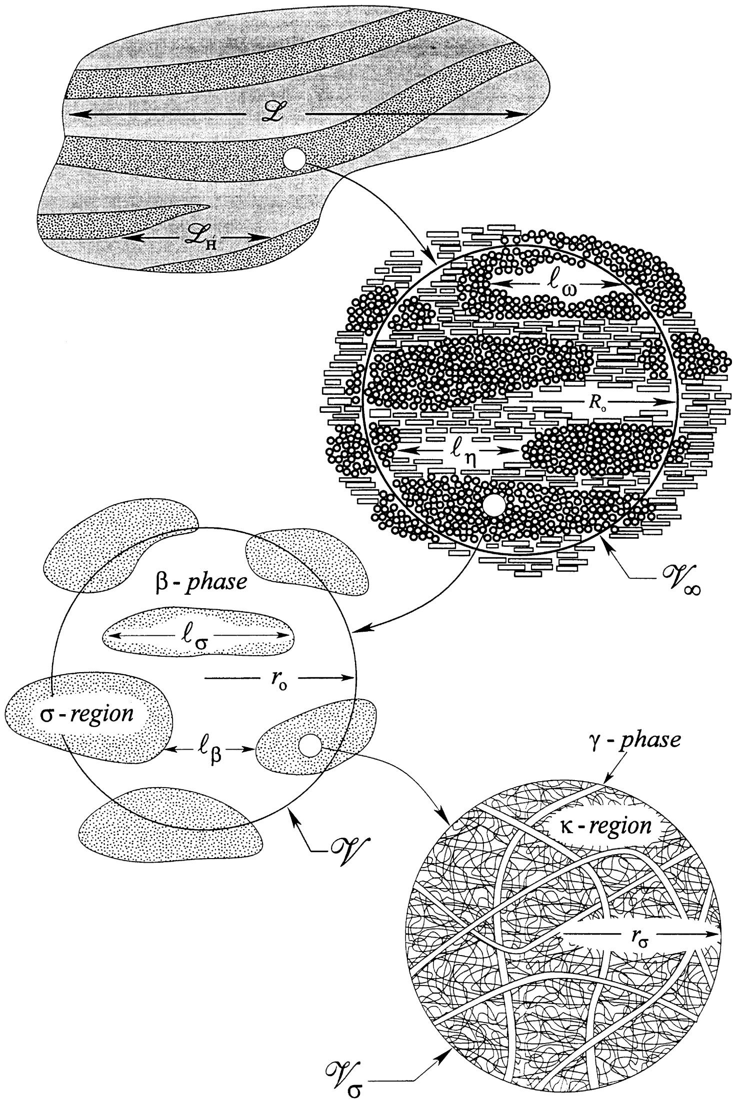

Fig. 2. Averaging volumes in a hierarchical porous medium.

are assumed to be valid at the large scale, i.e., they represent equations associated with the averaging volume, $\mathcal{V}_\infty$. In this work the length scales are clearly identified in Fig. 2; however, one must be careful to remember that real systems are more complex than the model that we have chosen to analyze.

1.1 Small-scale averaging

The σ-region illustrated in Fig. 3 consists of macropores that are identified as the γ-phase, and a microporous region identified as the κ-region. In many systems, ranging from packed bed catalytic reactors[3] to soil aggregates[5], the transport process in the microporous region plays a crucial role; however, in this study we will assume that the κ-region is *impermeable* so that transport in the σ-region takes place only in the γ-phase. It is assumed that the macropores in the σ-region illustrated in Fig. 3 are so small that convective transport is negligible, thus the problem of diffusion and *nonlinear adsorption* can be described by the following governing equation and interfacial boundary condition.

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

$$\text{B.C.1} \quad -\boldsymbol{n}_{\gamma\kappa} \cdot \mathcal{D}_\gamma \nabla c_\gamma = \frac{\partial c_{\gamma s}}{\partial t}, \quad \text{at the } \gamma\text{–}\kappa \text{ interface.} \tag{2}$$

Here we have used c_γ to represent the *bulk concentration* of the diffusing, adsorbing species, and $c_{\gamma s}$ to represent the adsorbed *surface concentration*. Since the κ-region is taken to be impermeable, we are not confronted with the problem of choosing between a one-equation model and a two-equation model. When transport takes place in the κ-region, one can follow the analysis of Whitaker[4] in order to derive the appropriate spatially smoothed transport equation and the associated closure problem.

Our treatment of the adsorption process is based on a functional relation of the general form given by

$$c_{\gamma s} = \mathcal{F}(c_\gamma) \tag{3}$$

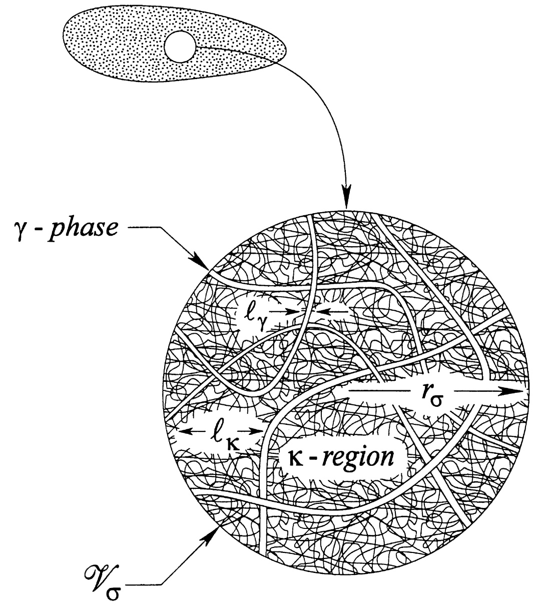

Fig. 3. Averaging volume for the γ-κ system.

and this allows us to express the boundary condition represented by eqn (2) as

$$\text{B.C.1} \quad -\boldsymbol{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma = K_{eq}\frac{\partial c_\gamma}{\partial t}, \quad \text{at the } \gamma\text{–}\kappa \text{ interface.} \tag{4}$$

eqn (3) and eqn (4) represent a condition that we identify as *local adsorption equilibrium*. Since mass is being transferred between the bulk and the surface, the system cannot be in a state of equilibrium; however, the departure from equilibrium may be *small enough* so that eqn (3) and eqn (4) represent a satisfactory approximation. What is meant by *small enough* is explained in Appendix A. In thinking about eqn (4), one must remember that the equilibrium coefficient need not be a constant, and that K_{eq} is given explicitly by

$$K_{eq} = \frac{\partial \mathcal{F}}{\partial c_\gamma}. \tag{5}$$

The *linear* adsorption problem has been studied by Plumb and Whitaker,[18,19] and we can follow their analysis to obtain the appropriate transport equation for diffusion with adsorption. That development begins with the definition of a *superficial* average concentration that takes the form

$$\langle c_\gamma \rangle = \frac{1}{\mathcal{V}_\sigma}\int_{V_\gamma} c_\gamma \mathrm{d}V \tag{6}$$

in which $\mathcal{V}_\sigma$ is the averaging volume shown in Fig. 3 and V_γ is the volume of the γ-phase contained within the averaging volume. One usually assumes that the *intrinsic* average concentration defined by

$$\langle c_\gamma \rangle^\gamma = \frac{1}{V_\gamma}\int_{V_\gamma} c_\gamma \mathrm{d}V \tag{7}$$

is the preferred concentration for describing the process of mass transport in porous media. These two concentrations are related by

$$\langle c_\gamma \rangle = \epsilon_\gamma \langle c_\gamma \rangle^\gamma \tag{8}$$

in which the volume fraction of the γ-phase is defined explicitly by

$$\epsilon_\gamma = V_\gamma / \mathcal{V}_\sigma. \tag{9}$$

Plumb and Whitaker[18,19] derived a small-scale, volume averaged transport equation for *linear adsorption* that is given by

$$\epsilon_\gamma(1 + a_{\gamma\kappa}K_{eq}/\epsilon_\gamma)\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot(\epsilon_\gamma \mathbf{D}^\gamma_{eff}\cdot\nabla\langle c_\gamma\rangle^\gamma). \tag{10}$$

Here we have used $a_{\gamma\kappa}$ to represent the interfacial area per unit volume of the porous medium and $\mathbf{D}^\gamma_{eff}$ to represent the effective diffusivity tensor for the γ-phase diffusion process. This definition of the effective diffusivity tensor is consistent with the work of Kim *et al.*;[20] however, it is not a universal definition and one often finds eqn (10) written in the form

$$\epsilon_\gamma(1 + a_{\gamma\kappa}K_{eq}/\epsilon_\gamma)\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot(\mathbf{D}_{eff}\cdot\nabla\langle c_\gamma\rangle^\gamma). \tag{11}$$

It is not clear that one form has any special advantage over the other; however, it is absolutely clear that one must be very careful when defining dependent variables and coefficients in multiphase transport equations since one can easily make errors on the order of ϵ_γ.

In order that the transport equation describing the *nonlinear adsorption process* have the same form as the transport equation for the linear process, we require that eqn (3) and eqn (5) can be expressed as

$$c_{\gamma s} = \mathcal{F}(\langle c_\gamma\rangle^\gamma), \quad K_{eq} = \frac{\partial\mathcal{F}}{\partial\langle c_\gamma\rangle^\gamma} \tag{12}$$

and the length-scale constraint associated with this simplification is developed in Appendix B. In addition, we require that variations of K_{eq} can be neglected within the averaging volume, and the length-scale constraint associated with this simplification is given in Appendix C.

The closure problem that is used to predict $\mathbf{D}^\gamma_{eff}$ in eqn (10) has been compared with experiments by Ryan *et al.*,[21] Kim *et al.*,[20], Quintard,[22] and Ochoa-Tapia *et al.*[23]. Good agreement between theory and experiment has been obtained for isotropic systems; however, anisotropic systems require further study and some interesting results are given by Quintard[22] and Ochoa-Tapia *et al.*[23] When the appropriate length and time-scale constraints are satisfied, eqn (10) is a valid representation of the process of diffusion and adsorption in the γ–κ system. Given eqn (10), we are ready to move on to the Darcy-scale averaging process associated with the β–σ system and the averaging volume $\mathcal{V}$ shown in Fig. 2.

1.2 Small-scale concentrations

At this point we wish to develop the spatially smoothed

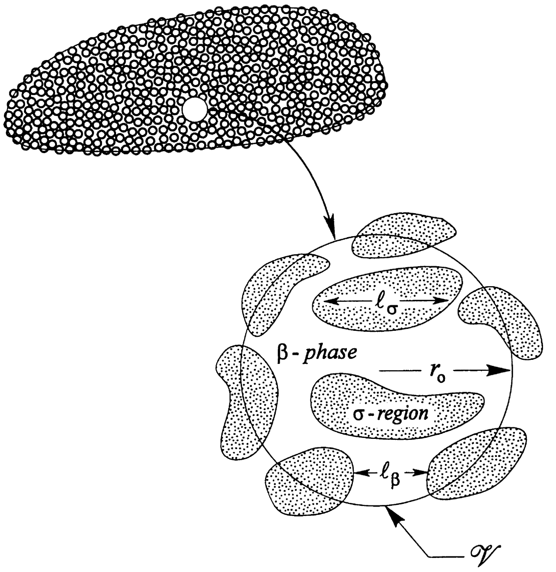

Fig. 4. Averaging volume for the β-σ system.

equations associated with the averaging volume $\mathcal{V}$ shown in Fig. 4. The system under consideration consists of the β-phase and the σ-region. In many cases we will be working with processes in which the σ-region contains *both* macropores *and* micropores, and we would like to make use of a nomenclature that can include both the case in which the κ-region is *impermeable* and the case in which it represents an *active microporous region*. To explore this problem, we note that the *spatial average concentration* in the σ-region represents the total moles per unit volume in that region. The spatial average concentration is given by

$$\langle c\rangle = \frac{1}{\mathcal{V}_\sigma}\int_{\mathcal{V}_\sigma} c \mathrm{d}V \qquad (13)$$

in which c represents the point concentration in both the γ-phase and the κ-region. This definition of the spatial average concentration is comparable to the definition of the spatial average temperature[24] used in the study of heat transfer in multiphase systems[25]. We can evaluate the separate parts of the integral in eqn (13) to arrive at

$$\langle c\rangle = \epsilon_\gamma\langle c_\gamma\rangle^\gamma + \epsilon_\kappa\langle c_\kappa\rangle^\kappa \qquad (14)$$

and this form is analogous to the representation of the spatial average *temperature* in a γ–κ system. We could be more precise and express the above result as

$$\langle c\rangle_\sigma = \epsilon_{\gamma\sigma}\langle c_\gamma\rangle^\gamma_\sigma + \epsilon_{\kappa\sigma}\langle c_\kappa\rangle^\kappa_\sigma. \qquad (15)$$

While this type of nomenclature appears to be overly complex, there is a logic associated with the choice and the placement of the indices since subscripts are always used to *identify location*, while superscripts are used only to *identify intrinsic averages*.

In order to determine when an average quantity is an *intrinsic average*, one considers the special case in which the point quantity is a constant. If the average quantity is equal to that constant, we say that it is an intrinsic average. For example, if the concentration in the γ-phase is the constant given by c_o, we see immediately that is an intrinsic average since eqn (7) gives

$$\langle c_\gamma\rangle^\gamma = \frac{1}{V_\gamma}\int_{V_\gamma} c_\gamma \mathrm{d}V = \frac{1}{V_\gamma}\int_{V_\gamma} c_o \mathrm{d}V = c_o. \qquad (16)$$

It is not always possible to identify intrinsic average concentrations in a unique manner when dealing with multiphase transport problems. For example, we can use eqn (15), along with the condition

$$c_\gamma = c_\kappa = c_o \qquad (17)$$

to show that

$$\langle c\rangle_\sigma = \epsilon_{\gamma\sigma}\langle c_\gamma\rangle^\gamma_\sigma + \epsilon_{\kappa\sigma}\langle c_\kappa\rangle^\kappa_\sigma = \epsilon_{\gamma\sigma}c_o + \epsilon_{\kappa\sigma}c_o = c_o. \qquad (18)$$

Thus we find that $\langle c\rangle_\sigma$ is an intrinsic average concentration *associated with* the σ-region. On the other hand, when the κ-region is impermeable, the definition given by eqn (15) immediately reduces to

$$\langle c\rangle_\sigma = \epsilon_{\gamma\sigma}\langle c_\gamma\rangle^\gamma_\sigma \qquad (19)$$

and in this case $\langle c\rangle_\sigma$ plays the role of a superficial average concentration *associated with* the γ-phase. The fact that a well-defined quantity, such as the spatial average concentration, is an intrinsic average *with respect to a region* and a superficial average with *respect to a phase* makes it rather difficult to identify a unique nomenclature that would carry one through the averaging process without the possibility of error. It would appear that one must either carry all of the nomenclature through every level of averaging or carefully redefine the variables at each level of averaging. In this work we follow the latter approach.

Returning again to Fig. 4, we note that the boundary value problem under consideration is given by

$$\epsilon_\gamma(1 + a_{\gamma\kappa}K_{eq}/\epsilon_\gamma)\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot(\epsilon_\gamma\mathbf{D}^\gamma_{eff}\cdot\nabla\langle c_\gamma\rangle^\gamma),$$

$$\text{in the } \sigma - \text{region} \qquad (20a)$$

$$\text{B.C.1 } \langle c_\gamma\rangle^\gamma = c_\beta, \text{ at the } \beta\text{–}\sigma \text{ interface} \qquad (20b)$$

$$\text{B.C.2 } -\mathbf{n}_{\sigma\beta}\cdot(\epsilon_\gamma\mathbf{D}^\gamma_{eff}\cdot\nabla\langle c_\gamma\rangle^\gamma) = -\mathbf{n}_{\sigma\beta}\cdot(\mathcal{D}_\beta\nabla c_\beta),$$

$$\text{at the } \beta\text{–}\sigma \text{ interface} \qquad (20c)$$

$$\frac{\partial c_\beta}{\partial t} + \nabla\cdot(\mathbf{v}_\beta c_\beta) = \nabla\cdot(\mathcal{D}_\beta\nabla c_\beta), \text{ in the } \beta - \text{phase}. \qquad (20d)$$

The boundary conditions used here are based on the type of analysis given by Ochoa-Tapia and Whitaker,[26–28] and they require the separation of length scales that normally occur between the σ-region and the β-phase.

If we average eqns 20 in their current form we will encounter an extremely cumbersome notation in terms of the σ-region transport equation. To avoid this problem, we define the following quantities

$$K = a_{\gamma\kappa}K_{eq}/\epsilon_\gamma, \; c_\sigma = \langle c_\gamma\rangle^\gamma, \; \epsilon_\gamma\mathbf{D}^\gamma_{eff} = \mathbf{D}_\sigma \qquad (21)$$

so that the problem under consideration takes the more compact form given by

$$\epsilon_\gamma(1+K)\frac{\partial c_\sigma}{\partial t}=\nabla\cdot(\mathbf{D}_\sigma\cdot\nabla c_\sigma),\ \text{in the } \sigma-\text{region} \quad (22a)$$

$$\text{B.C.1}\ c_\sigma=c_\beta,\ \text{at the } \beta\text{–}\sigma \text{ interface} \quad (22b)$$

$$\text{B.C.2}\ -\mathbf{n}_{\sigma\beta}\cdot(\mathbf{D}_\sigma\cdot\nabla c_\sigma)=-\mathbf{n}_{\sigma\beta}\cdot(\mathcal{D}_\beta\nabla c_\beta),$$

$$\text{at the}\quad \beta\text{–}\sigma \text{ interface} \quad (22c)$$

$$\frac{\partial c_\beta}{\partial t}+\nabla\cdot(\mathbf{v}_\beta c_\beta)=\nabla\cdot(\mathcal{D}_\beta\nabla c_\beta),\ \text{in the } \beta-\text{phase.} \quad (22d)$$

Here one must remember that c_σ represents an intrinsic average concentration with respect to the γ-phase, and that the volume fraction of the γ-phase has been incorporated into the definition of the effective diffusivity, $\mathbf{D}_\sigma$. This represents a situation that is subject to misinterpretation that can lead to errors on the order of ϵ_γ, thus the definitions given by eqn (21) must not be overlooked here or elsewhere in the analysis. One should think of eqns 22 as describing the transport process in both the ω and η-regions.

1.3 Darcy-scale averaging

The volume average form of eqn (22) is given by

$$\underbrace{\varepsilon_\sigma\varepsilon_\gamma(1+K)\frac{\partial\langle c_\sigma\rangle^\sigma}{\partial t}}_{\textit{accumulation}} = \underbrace{\nabla\cdot\left[\mathbf{D}_\sigma\cdot\left(\varepsilon_\sigma\nabla\langle c_\sigma\rangle^\sigma+\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{c}_\sigma\,dA\right)\right]}_{\textit{diffusion in the } \sigma\textit{-region}}$$

$$+\underbrace{\frac{1}{\mathscr{V}}\int_{A_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot\mathbf{D}_\sigma\cdot\nabla c_\sigma\,dA}_{\textit{exchange with the } \beta\textit{-phase}} \quad (23)$$

in which the spatial deviation concentration, $\tilde{c}_\sigma$, is defined by the decomposition[29]

$$c_\sigma=\langle c_\sigma\rangle^\sigma+\tilde{c}_\sigma. \quad (24)$$

In deriving eqn (23) we have ignored variations of the equilibrium coefficient within the averaging volume, and the length-scale constraint that must be satisfied in this case is given in Appendix C. In addition, we have assumed that the coefficient K can be represented as a function of $\langle c_\sigma\rangle^\sigma$ and this simplification is discussed in Appendix B.

The intrinsic average concentration in the σ-region is defined by

$$\langle c_\sigma\rangle^\sigma=\frac{1}{V_\sigma}\int_{V_\sigma}\langle c_\gamma\rangle^\gamma\mathrm{d}V \quad (25)$$

and the *volume fraction* of the σ-region is given explicitly as

$$\epsilon_\sigma=V_\sigma/V. \quad (26)$$

It is important to keep these definitions in mind since one can easily make an error on the order of ϵ_σ or ϵ_σ^{-1} if one does not carefully distinguish between *intrinsic* averages and *superficial* averages.

The volume averaged form of the β-phase transport equation has the same form as eqn (23) except for the presence of the convective transport and the dispersive transport.

$$\underbrace{\varepsilon_\beta\frac{\partial\langle c_\beta\rangle^\beta}{\partial t}}_{\textit{accumulation}}+\underbrace{\nabla\cdot\left(\varepsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta\langle c_\beta\rangle^\beta\right)}_{\textit{convection}} = \underbrace{\nabla\cdot\left[\mathscr{D}_\beta\left(\nabla\langle c_\beta\rangle^\beta+\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{c}_\beta\,dA\right)\right]}_{\textit{diffusion in the } \beta\textit{-phase}} \quad (27)$$

$$-\underbrace{\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{c}_\beta\rangle}_{\textit{dispersion}}+\underbrace{\frac{1}{\mathscr{V}}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\mathscr{D}_\beta\nabla c_\beta\,dA}_{\textit{exchange with the } \sigma\textit{-phase}}$$

Once again we have decomposed the concentration according to

$$c_\beta=\langle c_\beta\rangle^\beta+\tilde{c}_\beta \quad (28)$$

and in eqn (23) and eqn (27) we see the need for a closure problem in order to develop useful representations for the spatial deviation concentrations, $\tilde{c}_\sigma$ and $\tilde{c}_\beta$. In deriving eqn (27) from eqn (22), we have treated the flow as incompressible, and we have made use of the continuity equation in the following forms

$$\nabla\cdot\mathbf{v} = 0 \tag{29a}$$

$$\nabla\cdot(\epsilon_\beta\langle\mathbf{v}_\beta\rangle^\beta) = 0. \tag{29b}$$

The second of these requires that the σ-region be treated as impermeable in terms of convective transport, and this is consistent with the diffusion-adsorption equation given by eqn (22). For completeness, we note that the intrinsic average concentration associated with the β-phase is given by

$$\langle c_\beta\rangle^\beta = \frac{1}{V_\beta}\int_{V_\beta} c_\beta \mathrm{d}V \tag{30}$$

while the *volume fraction* of the β-phase is defined in a manner analogous to eqn (26) and this requires that $\epsilon_\beta = 1\text{-}\epsilon_\sigma$.

At this point in the analysis of the β–σ system, we encounter a recurring problem that arises whenever one attacks a problem of multiphase or multi-region transport phenomena. The problem is this: are the two concentrations, $\langle c_\sigma\rangle^\sigma$ and $\langle c_\beta\rangle^\beta$, *close enough* so that they can be treated as equal, or are these two concentrations *sufficiently different* so that separate transport equations must be retained in order to develop an acceptable model? For many problems of practical importance, the length scales, ℓ_β and ℓ_σ, shown in Fig. 4 are very small compared to the characteristic process length scale. Under these circumstances, the concentration in the σ-region is essentially equal to the concentration in the β-phase and the principle of local mass equilibrium is valid. Plumb and Whitaker[18,19] have explored this problem, and we will accept their analysis of local mass equilibrium and the length and time-scale constraints that are associated with that condition.

1.4 Darcy-scale concentrations

In a manner similar to the definition of the small-scale spatial average concentration given by eqn (13), one can define a Darcy-scale *spatial average concentration* according to

$$\langle c\rangle = \frac{1}{\mathcal{V}}\int_{\mathcal{V}} c\mathrm{d}V. \tag{31}$$

This, in turn, can be expressed in terms of the intrinsic averages in the β-phase and the σ-region according to

$$\langle c\rangle = \epsilon_\beta\langle c_\beta\rangle^\beta + \epsilon_\sigma\langle c_\sigma\rangle^\sigma. \tag{32}$$

One can see that $\langle c\rangle$ is an *intrinsic average concentration* with respect to the β–σ system; however, if the σ-region is impermeable, $\langle c\rangle$ becomes a *superficial average concentration* with respect to the β-phase. There are many practical problems in which the σ-region is impermeable, and there are many problems in which the σ-region contains both macropores and micropores, thus it is difficult to generate a unique nomenclature for the Darcy-scale concentration. At this point we will follow our previous change of nomenclature associated with the small-scale averaging process and define two new concentrations for the η and ω-regions according to

$$\langle c_\eta\rangle^\eta = \epsilon_{\beta\eta}\langle c_\beta\rangle^\beta_\eta + \epsilon_{\sigma\eta}\langle c_\sigma\rangle^\sigma_\eta \text{ in the } \eta - \text{region} \tag{33a}$$

$$\langle c_\omega\rangle^\omega = \epsilon_{\beta\omega}\langle c_\beta\rangle^\beta_\omega + \epsilon_{\sigma\omega}\langle c_\sigma\rangle^\sigma_\omega \text{ in the } \omega - \text{region.} \tag{33b}$$

Our choice of nomenclature here is dictated by the fact that the σ-region is necessarily active in a process that involves adsorption, thus the spatial average concentration defined by eqn (31) plays the role of an intrinsic average concentration.

1.5 Local mass equilibrium

The mathematical consequence of local mass equilibrium in the η-region is that

$$\langle c_\sigma\rangle^\sigma_\eta = \langle c_\beta\rangle^\beta_\eta = \langle c_\eta\rangle^\eta \tag{34}$$

and when this condition is valid we can add eqn (23) and eqn (27) to obtain the Darcy-scale, one-equation model for solute transport with absorption that is given by

η-region

$$\begin{aligned}
&\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t} + \nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)\\
&\quad = \nabla\cdot\left[\mathcal{D}_\beta\left(\epsilon_{\beta\eta}\nabla\langle c_\eta\rangle^\eta + \frac{1}{\mathcal{V}}\int_{A_{\beta\alpha}}\mathbf{n}_{\beta\sigma}\tilde{c}_{\beta\eta}\mathrm{d}A\right)\right.\\
&\qquad\left. + \mathbf{D}_{\sigma\eta}\cdot\left(\epsilon_{\sigma\eta}\nabla\langle c_\eta\rangle^\eta + \frac{1}{\mathcal{V}}\int_{A_{\alpha\beta}}\mathbf{n}_{\sigma\beta}\tilde{c}_{\sigma\eta}\mathrm{d}A\right)\right]\\
&\qquad + \nabla\cdot\langle\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_{\beta\eta}\rangle.
\end{aligned} \tag{35}$$

Here we note that the superficial average velocity is given by

$$\langle\mathbf{v}_\beta\rangle_\eta = \epsilon_{\beta\eta}\langle\mathbf{v}_\beta\rangle^\beta_\eta \tag{36}$$

and that the equilibrium coefficient, $\mathcal{K}_\eta$, and the *total porosity*, ϵ_η, are defined explicitly by

$$\mathcal{K}_\eta = \frac{(\epsilon_\sigma a_{\gamma\kappa})_\eta}{\epsilon_\eta}\frac{\partial\mathcal{F}}{\partial\langle c_\eta\rangle^\eta},\ \epsilon_\eta = \epsilon_{\beta\eta} + (\epsilon_\sigma\epsilon_\gamma)_\eta. \tag{37}$$

One should note that the effective diffusivity for the σ-region has been explicitly associated with the η-region, while the β-phase diffusivity has not. This has been done with the idea that $\mathcal{D}_\beta$ will not undergo significant changes from the η-region to the ω-region, while $\mathbf{D}_\sigma$ may undergo very significant changes and thus needs to be explicitly identified in terms of the region. The ω-region equation is analogous to eqn (35) and we will list the closed form in subsequent paragraphs.

In this development of the η-region Darcy-scale transport equation we *have not* followed the nomenclature used by Plumb and Whitaker[18,19] who *did not* express their results in terms of the total porosity, ϵ_η, but instead used the various volume fractions contained in the definition of the total porosity. The nomenclature that is used in this development has been chosen specifically to be consistent with subsequent experimental studies. We will refer to the quantity $\epsilon_\eta(1+\mathcal{K}_\eta)$ in eqn (35) as the *capacitance factor* since it plays the same role in large-scale mass equilibrium

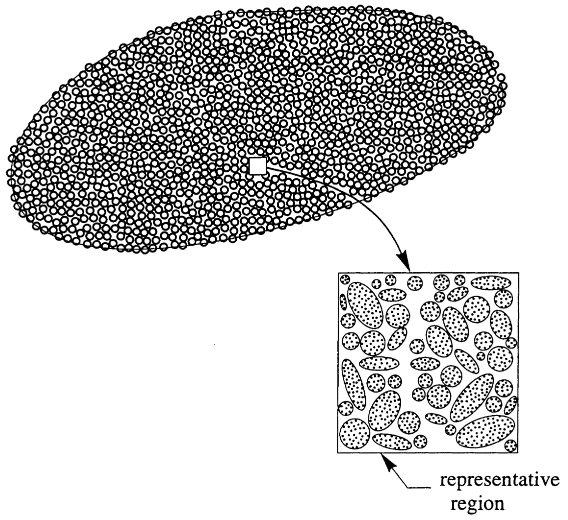

Fig. 5. Representative region for the β-σ system.

as the *heat capacity* does in local thermal equilibrium. In the heat transfer process, significant differences in the heat capacity create departures from local thermal equilibrium during transient processes. In the same way, significant differences in the *capacitance factor* will cause departures from large-scale mass equilibrium during transient processes. This is perhaps more clearly seen in terms of the *retardation factor*,$(1 + \mathcal{K}_\eta)$, that modifies the speed of a pulse of a chemical solute. Different retardation factors in the η and ω-regions will lead to a separation of pulses in the two regions and this will create departures from large-scale mass equilibrium.

The closure problem for the spatial deviation concentrations, $\tilde{c}_\sigma$ and $\tilde{c}_\beta$, is based on the representations

$$\tilde{c}_{\sigma\eta} = \mathbf{b}_{\sigma\eta}\cdot\nabla\langle c_\eta\rangle^\eta \tag{38a}$$

$$\tilde{c}_{\beta\eta} = \mathbf{b}_{\beta\eta}\cdot\nabla\langle c_\eta\rangle^\eta \tag{38b}$$

in which $\mathbf{b}_{\sigma\eta}$ and $\mathbf{b}_{\beta\eta}$ are referred to as the *closure variables*. The nomenclature used in eqns 38 follows that of Quintard and Whitaker[24] rather than that of Plumb and Whitaker[18,19] who developed the closure problem for this particular process of dispersion and adsorption. In some representative region of the β–σ system, such as we have illustrated in Fig. 5, the closure problem for $\mathbf{b}_{\sigma\eta}$ and $\mathbf{b}_{\beta\eta}$ takes the form

η-region

$$0 = \mathbf{D}_{\sigma\eta} : \nabla\nabla\mathbf{b}_{\sigma\eta} - \epsilon_{\sigma\eta}^{-1}\mathbf{c}_{\sigma\eta}, \text{ in the } \sigma - \text{region} \tag{39a}$$

$$\text{B.C.1 } \mathbf{b}_{\sigma\eta} = \mathbf{b}_{\beta\eta}, \text{ at } A_{\beta\sigma} \tag{39b}$$

$$\begin{aligned}\text{B.C.2 } -\mathbf{n}_{\sigma\beta}\cdot(\mathbf{D}_{\sigma\eta}\cdot\nabla\mathbf{b}_{\sigma\eta}) &= -\mathbf{n}_{\sigma\beta}\cdot(\mathcal{D}_\beta\nabla\mathbf{b}_{\beta\eta}) \\ &\quad - \mathbf{n}_{\sigma\beta}\cdot(\mathcal{D}_\beta\mathbf{I} - \mathbf{D}_{\sigma\eta}), \text{ at } A_{\beta\sigma}\end{aligned} \tag{39c}$$

$$\tilde{\mathbf{v}}_{\beta\eta} + \mathbf{v}_{\beta\eta}\cdot\nabla\mathbf{b}_{\beta\eta} = \mathcal{D}_\beta\nabla^2\mathbf{b}_{\beta\eta} - \epsilon_{\beta\eta}^{-1}\mathbf{c}_{\beta\eta}, \text{ in the } \beta - \text{phase} \tag{39d}$$

Periodicity:

$$\mathbf{b}_{\sigma\eta}(\mathbf{r} + \ell_i) = \mathbf{b}_{\sigma\eta}(\mathbf{r}), \; \mathbf{b}_{\beta\eta}(\mathbf{r} + \ell_i) = \mathbf{b}_{\beta\eta}(\mathbf{r}), \; i = 1, 2, 3 \tag{39e}$$

Average:

$$\langle\mathbf{b}_{\sigma\eta}\rangle^\sigma = 0, \; \langle\mathbf{b}_{\beta\eta}\rangle^\beta = 0. \tag{39f}$$

Here the two constant vectors are given by

$$\mathbf{c}_{\sigma\eta} = \frac{1}{\mathcal{V}}\int_{A_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\cdot\mathbf{D}_{\sigma\eta}\cdot\nabla\mathbf{b}_{\sigma\eta}\,\mathrm{d}A, \; \mathbf{c}_{\beta\eta} = \frac{1}{\mathcal{V}}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\mathcal{D}_\beta\nabla\mathbf{b}_{\beta\eta}\,\mathrm{d}A \tag{40}$$

and on the basis of the second boundary condition they are related according to

$$\mathbf{c}_{\sigma\eta} = -\mathbf{c}_{\beta\eta}. \tag{41}$$

When convective transport in the β-phase is negligible, the closure problem reduces to that for heat conduction in a two-phase system[30,31] or diffusion in a two-phase system.[32] In those cases, arguments have been developed in favor of $\mathbf{c}_{\sigma\eta} = \mathbf{c}_{\beta\eta} = 0$, and Quintard and Whitaker[24] have proved this result for symmetric unit cells. In the general case, eqn (39) are needed to determine these two constant vectors. A little thought will indicate that eqn (39) can be used to determine $\mathbf{b}_{\sigma\eta}$ and $\mathbf{b}_{\beta\eta}$ *to within a single arbitrary constant* provided that the constant vectors, $\mathbf{c}_{\sigma\eta}$ and $\mathbf{c}_{\beta\eta}$, are known. The point to be understood here is that eqn (39) represent a standard boundary value problem for transport in two phases with the exception that there is no Dirichlet condition that establishes the level of the functions $\mathbf{b}_{\sigma\eta}$ and $\mathbf{b}_{\beta\eta}$. This means that if $\mathbf{b}_{\sigma\eta}$ and $\mathbf{b}_{\beta\eta}$ are solutions to eqn (39), then $\mathbf{b}_{\sigma\eta} + \mathbf{c}_o$ and $\mathbf{b}_{\beta\eta} + \mathbf{c}_o$, in which $\mathbf{c}_o$ is an arbitrary constant vector, are also solutions. This arbitrary constant vector can be removed by the imposition of the first of eqn (39f), while the constant vectors $\mathbf{c}_{\sigma\eta}$ and $\mathbf{c}_{\beta\eta}$ that are related by eqn (41) are determined by the second of eqn (39f). The procedure for dealing with $\mathbf{c}_{\sigma\eta}$ and $\mathbf{c}_{\beta\eta}$ is discussed by Quintard and Whitaker[24,33] and by Quintard *et al.*[34]

1.6 Closed form

When the representations given by eqns 38 are used in eqn (35), we obtain the closed form of our Darcy-scale dispersion-adsorption equation that takes the form

$$\epsilon_\eta(1 + \mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t} + \nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right) = \nabla\cdot(\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta) \tag{42}$$

in which the dispersion tensor is defined by

$$\mathbf{D}_\eta^* = \epsilon_{\beta\eta}\mathcal{D}_\beta\mathbf{I} + \epsilon_{\sigma\eta}\mathbf{D}_{\sigma\eta} + \frac{(\mathcal{D}_\beta\mathbf{I} - \mathbf{D}_{\sigma\eta})}{\mathcal{V}} \cdot \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathbf{b}_{\beta\eta}\,\mathrm{d}A - \epsilon_{\beta\eta}\langle\tilde{\mathbf{v}}_{\beta\eta_{\sigma\eta}}\mathbf{b}_{\sigma\eta}\rangle^\beta. \tag{43}$$

One must be extremely careful to note the definition of this dispersion coefficient since it differs by a factor of $\epsilon_{\beta\eta}$ from that used by Plumb and Whitaker[18,19] and other investigators.

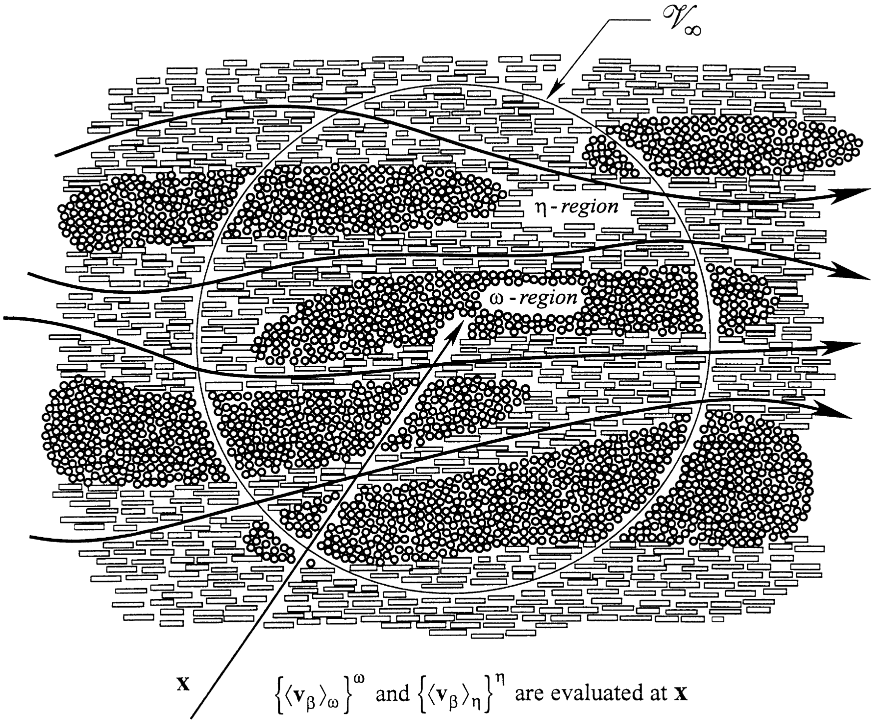

Fig. 6. Determination of region averaged velocities.

Although the *exact* closure problem given by eqns 39 has not been solved, and thus predicted values of $\mathbf{D}^*_\eta$ have not been compared with experiment, results for *similar problems* have been obtained by Eidsath *et al.*[35] for passive dispersion, by Nozad *et al.*[30] and Quintard and Whitaker[24] for transient conduction in two-phase systems, by Ochoa *et al.*[32] for diffusion in two-phase systems, and by Quintard and Whitaker[33] for active dispersion. For the case in which $\mathbf{D}_\sigma$ is isotropic, the closure problem given by eqn (28) is identical to the heat transfer problem that has been explored in detail by Quintard *et al.*[34] for the two-equation model at the Darcy-scale, and results for the one-equation model will be presented in Part V.[36]

2 LARGE-SCALE AVERAGING

We are now ready to turn our attention to the main subject of this paper which is the problem of solute transport with adsorption in a mechanically and chemically heterogeneous porous medium. We have illustrated an averaging volume for such a system in Fig. 6, and we describe the transport process in terms of the boundary value problem given by

$$\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}+\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)=\nabla\cdot\left(\mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right) \tag{44a}$$

$$\text{B.C.1}\ \langle c_\eta\rangle^\eta=\langle c_\omega\rangle^\omega,\ \text{ at } A_{\eta\omega} \tag{44b}$$

$$\text{B.C.2}\ -\mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right)=$$

$$=-\mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega\langle c_\omega\rangle^\omega-\mathbf{D}^*_\omega\cdot\nabla\langle c_\omega\rangle^\omega\right),\ \text{ at } A_{\eta\omega} \tag{44c}$$

$$\epsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\langle c_\omega\rangle^\omega}{\partial t}+\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega\langle c_\omega\rangle^\omega\right)=\nabla\cdot\left(\mathbf{D}^*_\omega\cdot\nabla\langle c_\omega\rangle^\omega\right). \tag{44d}$$

In addition to the solute transport equations and the concentration and flux conditions imposed at the boundary between the η-region and the ω-region, we will also list the continuity equations for the two regions according to

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\eta=0 \tag{45a}$$

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega=0. \tag{45b}$$

Both of these results are obtained from eqn (29) by replacing $\epsilon_\beta\langle \mathbf{v}_\beta\rangle^\beta$ with the superficial velocity, $\langle \mathbf{v}_\beta\rangle$. At the boundary between the η- and ω-regions, we take the normal components of $\langle \mathbf{v}_\beta\rangle_\eta$ and $\langle \mathbf{v}_\beta\rangle_\omega$ to be continuous as indicated by the condition

$$\text{B.C.3}\ \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta=\mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\omega,\ \text{ at } A_{\eta\omega}. \tag{46}$$

This requires that any *surface velocity* associated with the boundary be negligible.[26,27]

The averaging volume for large-scale averaging is shown in Fig. 6, and we need to define three averages associated with the averaging volume identified by $\mathcal{V}_\infty$. The first of these is the *regional superficial average* defined by

$$\{\langle c_\eta\rangle^\eta\}^\eta=\frac{1}{\mathcal{V}_\infty}\int_{V_\eta}\langle c_\eta\rangle^\eta \mathrm{d}V. \tag{47a}$$

The second is the *regional intrinsic average* that we express as

$$\{\langle c_\eta\rangle^\eta\}^\eta = \frac{1}{V_\eta}\int_{V_\eta}\langle c_\eta\rangle^\eta \mathrm{d}V \tag{47b}$$

in which V_η represents the volume of the η-region contained in the averaging volume. In addition to these regional averages, we will also need the *large-scale spatial average* defined by

$$\{\langle c\rangle\} = \frac{1}{\mathcal{V}_\infty}\int_{\mathcal{V}_\infty}\langle c\rangle \mathrm{d}V = \frac{1}{\mathcal{V}_\infty}\int_{V_\eta}\langle c_\eta\rangle^\eta \mathrm{d}V + \frac{1}{\mathcal{V}_\infty}\int_{V_\omega}\langle c_\omega\rangle^\omega \mathrm{d}V = \varphi_\eta\{\langle c_\eta\rangle^\eta\}^\eta + \varphi_\omega\{\langle c_\omega\rangle^\omega\}^\omega \tag{47c}$$

in which volume fractions of the η- and ω-regions are expressed as

$$\varphi_\eta = V_\eta/\mathcal{V}_\infty, \quad \varphi_\omega = V_\omega/\mathcal{V}_\infty. \tag{48}$$

The definition given by eqn (47c) has precisely the characteristics of the earlier definitions given by eqn (13) and eqn (31), and one needs to keep this definition in mind during subsequent developments.

2.1 Large-scale average equations

We now express the large-scale superficial average of the η-region transport equation as

$$\left\{\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}\right\} + \left\{\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)\right\} = \left\{\nabla\cdot\left(\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right)\right\}. \tag{49}$$

In the process of small-scale averaging,[18,19] we ignored variations of K_{eq} over the averaging volume, $\mathcal{V}_\sigma$. At the next level of averaging we ignored variations of $\epsilon_\gamma(1+K)$ over the Darcy-scale averaging volume, $\mathcal{V}$, and at this point in the analysis we are going to ignore variations of $\epsilon_\eta(1+\mathcal{K}_\eta)$ over the large-scale averaging volume, $\mathcal{V}_\infty$. The length-scale constraints associated with these simplifications are presented in Appendix C. In addition to the imposition of the length-scale constraints associated with the spatial variation of the adsorption isotherm, we have also scaled up the adsorption isotherm so that eqn (37) is interpreted as

$$\mathcal{K}_\eta = \frac{(\epsilon_\sigma a_{\gamma\kappa})_\eta}{\epsilon_\eta}\left[\frac{\partial\mathcal{F}}{\partial\{\langle c_\eta\rangle^\eta\}^\eta}\right], \quad \epsilon_\eta = \epsilon_{\beta\eta} + (\epsilon_\sigma\epsilon_\gamma)_\eta. \tag{50}$$

The length-scale constraint associated with this simplification is given in Appendix B and there we have indicated the consequences of the failure of the length-scale constraints associated with the scale up of the adsorption isotherm.

Given the assumption of negligible variations of $\epsilon_\eta\,(1+\mathcal{K}_\eta)$ over the volume $\mathcal{V}_\infty$, we can express the accumulation term in eqn (49) as

$$\left\{\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}\right\} = \epsilon_\eta(1+\mathcal{K}_\eta)\left\{\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}\right\} = \epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}}{\partial t}. \tag{51}$$

The superficial average is related to the intrinsic average by

$$\{\langle c_\eta\rangle^\eta\} = \varphi_\eta\{\langle c_\eta\rangle^\eta\}^\eta \tag{52}$$

and this allows us to express the accumulation term as

$$\left\{\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}\right\} = \epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}. \tag{53}$$

To analyze the convective and dispersive transport terms in eqn (41), we need the large-scale version of the spatial averaging theorem that takes the form

$$\{\nabla\langle\psi_\eta\rangle^\eta\} = \nabla\{\langle\psi_\eta\rangle^\eta\} + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\langle\psi_\eta\rangle^\eta \mathrm{d}V. \tag{54}$$

Use of this theorem allows us to express the convective transport term as

$$\left\{\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)\right\} = \nabla\cdot\left\{\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)\right\} + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta \mathrm{d}A \tag{55}$$

while the dispersive transport term is given by

$$\left\{\nabla\cdot\left(\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right)\right\} = \nabla\cdot\left\{\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right\} + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right)\mathrm{d}A. \tag{56}$$

Use of eqn (53), eqn (55) and eqn (56) in eqn (49) leads to

$$\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} + \nabla\cdot\left\{\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)\right\} = \nabla\cdot\left\{\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right\} - \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta - \mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right)\mathrm{d}A. \tag{57}$$

Even though we have accepted the simplification that the η and ω-regions are homogeneous, we cannot ignore variations in $\mathbf{D}_\eta^*$ since this term will depend on the velocity field, $\langle\mathbf{v}_\beta\rangle_\eta$. Under some circumstances, $\langle\mathbf{v}_\beta\rangle_\eta$ may be a constant; however, this would be the exception rather than the rule, thus we must take into account possible variations in $\mathbf{D}_\eta^*$ as was done in the original study of passive dispersion by Plumb and Whitaker,[37,38] but which was not done in the subsequent study of solute transport with adsorption.[18,19] The variations in $\mathbf{D}_\eta^*$ can be represented in terms of the following decomposition

$$\mathbf{D}_\eta^* = \{\mathbf{D}_\eta^*\}^\eta + \tilde{\mathbf{D}}_\eta^* \tag{58}$$

and we can use this result along with the averaging theorem to express the first term on the right hand side of eqn (57) as

$$\nabla\cdot\left\{\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right\} = \nabla\cdot\left[\left\{\mathbf{D}_\eta^*\right\}^\eta\cdot\left\{\nabla\langle c_\eta\rangle^\eta\right\} + \left\{\tilde{\mathbf{D}}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta\right\}\right]$$

$$= \nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\nabla \{ \langle c_\eta \rangle^\eta \} + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \langle c_\eta \rangle^\eta \mathrm{d}A \right) + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} \right]. \tag{59}$$

This leads to a large-scale transport equation for the η-region given by

$$\epsilon_\eta (1 + \mathcal{K}_\eta) \varphi_\eta \frac{\partial \{ \langle c_\eta \rangle^\eta \}^\eta}{\partial t} + \nabla \cdot \{ (\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta) \}$$
$$= \nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\nabla \{ \langle c_\eta \rangle^\eta \} + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \langle c_\eta \rangle^\eta \mathrm{d}A \right) + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} \right] - \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot (\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta - \mathbf{D}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta) \mathrm{d}A. \tag{60}$$

Here we note that the accumulation term is expressed in terms of the large-scale intrinsic average concentration, $\{\langle c_\eta \rangle^\eta\}^\eta$, and this is exactly the quantity that we would like to be able to determine.

The convective transport term in eqn (60) is given in terms of the average of a product rather that the product of averages, and the diffusive term is represented both in terms of the large-scale *superficial* average, $\{\langle c_\eta \rangle^\eta\}$, and the Darcy-scale average, $\langle c_\eta \rangle^\eta$. The large-scale superficial average can be eliminated by the use of eqns 44 in order to obtain a representation in terms of the large-scale *intrinsic* average, $\{\langle c_\eta \rangle\}^\eta$, and we can eliminate $\langle c_\eta \rangle^\eta$ by means of a decomposition of the Darcy-scale quantities. For the η-region these are given by

$$\langle c_\eta \rangle^\eta = \{ \langle c_\eta \rangle^\eta \}^\eta + \tilde{c}_\eta \tag{61}$$

$$\langle \mathbf{v}_\beta \rangle^\eta = \{ \langle \mathbf{v}_\beta \rangle_\eta \}^\eta + \tilde{\mathbf{v}}_{\beta\eta}. \tag{62}$$

Decompositions of this type must be introduced at every level of averaging, although they were not shown explicitly for the small-scale averaging process that lead to the diffusion-adsorption equation given by eqn (10). The decompositions for the Darcy-scale averaging process are given by eqn (24) and eqn (28), and we have used the same type of nomenclature for the deviation quantities, $\tilde{c}_\eta$ and $\tilde{\mathbf{v}}_{\beta\eta}$, contained in eqn (61) and eqn (62). This means that one must be very careful not to confuse $\tilde{c}_\eta$ as defined by eqn (61) with $\tilde{c}_\beta$ as defined by eqn (28). The logic behind the nomenclature employed to identify deviations is that a *tilde* is used for any deviation that is the difference between two quantities having *different characteristic lengths*. If we use eqn (61) and eqn (62) in the diffusive term in eqn (60), we can follow the development in Carbonell and Whitaker[39] or in Quintard and Whitaker[24] to obtain

$$\nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\nabla \{ \langle c_\eta \rangle^\eta \} + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \langle c_\eta \rangle^\eta \mathrm{d}A \right) + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} \right] = \nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\varphi_\eta \nabla \{ \langle c_\eta \rangle^\eta \}^\eta + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta \mathrm{d}A \right) + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} \right]. \tag{63}$$

If the decompositions defined by eqn (61) and eqn (62) are used with the convective transport term in eqn (60), we can follow Plumb and Whitaker[18,19] to obtain

$$\{ \langle \mathbf{v}_\beta \rangle_\eta \langle c \rangle_\eta \} = \varphi_\eta \{ \langle \mathbf{v}_\beta \rangle_\eta \}^\eta \{ \langle c \rangle_\eta \}^\eta + \varphi_\eta \{ \tilde{\mathbf{v}}_{\beta\eta} \tilde{c}_\eta \}^\eta. \tag{64}$$

Use of eqn (63) and eqn (64) in eqn (60) leads us closer to a transport equation that contains only $\{\langle c \rangle_\eta\}^\eta$ and $\tilde{c}_\eta$. This is given by

$$\epsilon_\eta (1 + \mathcal{K}_\eta) \varphi_\eta \frac{\partial \{ \langle c_\eta \rangle^\eta \}^\eta}{\partial t} + \nabla \cdot [\varphi_\eta \{ \langle \mathbf{v}_\beta \rangle_\eta \}^\eta \{ \langle c_\eta \rangle^\eta \}^\eta]$$
$$= \nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\varphi_\eta \nabla \{ \langle c_\eta \rangle^\eta \}^\eta + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta \mathrm{d}A \right) + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} \right] - \nabla \cdot (\varphi_\eta \{ \tilde{\mathbf{v}}_{\beta\eta} \tilde{c}_\eta \}^\eta) - \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot (\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta - \mathbf{D}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta) \mathrm{d}A. \tag{65}$$

We now turn our attention to the term involving $\tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta$ and use the decomposition given by eqn (53) to obtain

$$\left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right\} = \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \{ \langle c_\eta \rangle^\eta \}^\eta \right\} + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \tilde{c}_\eta \right\}. \tag{66}$$

If we continue to ignore variations of average quantities within the averaging volume, the first term on the right hand side of this result is zero on the basis of

$$\left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \{ \langle c_\eta \rangle^\eta \}^\eta \right\} = \left\{ \tilde{\mathbf{D}}_\eta^* \right\} \cdot \nabla \{ \langle c_\eta \rangle^\eta \}^\eta. \tag{67}$$

Under these circumstances eqn (65) can be represented entirely in terms of $\{\langle c_\eta \rangle^\eta\}^\eta$ and $\tilde{c}_\eta$ except for the last term that represents the inter-region flux. This form is given explicitly as

---

$$\underbrace{\varepsilon_\eta (1 + \mathcal{K}_\eta) \varphi_\eta \frac{\partial \{ \langle c_\eta \rangle^\eta \}^\eta}{\partial t}}_{\textit{accumulation and adsorption}} + \underbrace{\nabla \cdot \left[\varphi_\eta \{ \langle \mathbf{v}_\beta \rangle_\eta \}^\eta \{ \langle c_\eta \rangle^\eta \}^\eta \right]}_{\textit{large-scale convection}}$$
$$= \underbrace{\nabla \cdot \left[\{ \mathbf{D}_\eta^* \}^\eta \cdot \left(\varphi_\eta \nabla \{ \langle c_\eta \rangle^\eta \}^\eta + \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta \, dA \right) + \{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \tilde{c}_\eta \} \right]}_{\textit{large-scale diffusion}}$$

$$
- \underbrace{\nabla \cdot \left(\varphi_\eta \left\{ \tilde{\mathbf{v}}_{\beta\eta} \tilde{c}_\eta \right\}^\eta \right)}_{\textit{large-scale dispersion}} - \underbrace{\frac{1}{\mathscr{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta - \mathbf{D}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta \right) dA}_{\textit{inter-region flux}} \tag{68}
$$

The ω-region transport equation has exactly the same form as this result, and for completeness we list it as

$$
\underbrace{\varepsilon_\omega (1 + \mathscr{K}_\omega) \varphi_\omega \frac{\partial \left\{ \langle c_\omega \rangle^\omega \right\}^\omega}{\partial t}}_{\textit{accumulation and adsorption}} + \underbrace{\nabla \cdot \left[\varphi_\omega \left\{ \langle \mathbf{v}_\beta \rangle_\omega \right\}^\omega \left\{ \langle c_\omega \rangle^\omega \right\}^\omega \right]}_{\textit{large-scale convection}}
$$

$$
= \underbrace{\nabla \cdot \left[\left\{ \mathbf{D}_\omega^* \right\}^\omega \cdot \left(\varphi_\omega \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega + \frac{1}{\mathscr{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \tilde{c}_\omega \, dA \right) + \left\{ \tilde{\mathbf{D}}_\omega^* \cdot \nabla \tilde{c}_\omega \right\} \right]}_{\textit{large-scale diffusion}}
$$

$$
- \underbrace{\nabla \cdot \left(\varphi_\omega \left\{ \tilde{\mathbf{v}}_{\beta\omega} \tilde{c}_\omega \right\}^\omega \right)}_{\textit{large-scale dispersion}} - \underbrace{\frac{1}{\mathscr{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \langle c_\omega \rangle^\omega - \mathbf{D}_\omega^* \cdot \nabla \langle c_\omega \rangle^\omega \right) dA}_{\textit{inter-region flux}} \tag{69}
$$

To develop a two-equation model for solute transport with adsorption, we need to analyze the inter-region flux terms in order to obtain transport equations that are represented entirely in terms of intrinsic large-scale average concentrations and spatial deviation concentrations. However, if the two concentrations, $\{\langle c_\eta \rangle^\eta\}^\eta$ and $\{\langle c_\omega \rangle^\omega\}^\omega$ are *essentially equal*, eqn (68) and eqn (69) can be added together to obtain a one-equation model, and we refer to this condition as *large-scale mass equilibrium*. The simplification inherent in a one-equation model is significant, and such a model should always be used if it is a valid representation of the transport process. The mathematical consequence of large-scale mass equilibrium is given by

$$
\{\langle c_\eta \rangle^\eta\}^\eta = \{\langle c_\omega \rangle^\omega\}^\omega = \{\langle c \rangle\},
$$

$$
\text{large} - \text{scale mass equilibrium} \tag{70}
$$

and when this approximation is valid we can add eqn (68) and eqn (69) to obtain

$$
\{\epsilon\}(1 + \{\mathcal{K}\}) \frac{\partial \{\langle c \rangle\}}{\partial t} + \nabla \cdot \left(\{\langle \mathbf{v}_\beta \rangle\} \{\langle c \rangle\} \right)
$$

$$
= \nabla \cdot \left[\left(\varphi_\eta \{\mathbf{D}_\eta^*\}^\eta + \varphi_\omega \{\mathbf{D}_\omega^*\}^\omega \right) \cdot \nabla \{\langle c \rangle\} \right]
$$

$$
+ \nabla \cdot \left[\frac{\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \tilde{c}_\eta \mathrm{d}A + \left\{ \tilde{\mathbf{D}}_\eta^* \cdot \nabla \tilde{c}_\eta \right\} \right.
$$

$$
\left. + \frac{\{\mathbf{D}_\omega^*\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \tilde{c}_\omega \mathrm{d}A + \left\{ \tilde{\mathbf{D}}_\omega^* \cdot \nabla \tilde{c}_\omega \right\} \right]
$$

$$
- \nabla \cdot \left[\varphi_\eta \left\{ \tilde{\mathbf{v}}_{\beta\eta} \tilde{c}_\eta \right\}^\eta + \varphi_\omega \left\{ \tilde{\mathbf{v}}_{\beta\omega} \tilde{c}_\omega \right\}^\omega \right]. \tag{71}
$$

Here we have simplified the representation of the one-equation model by using the following definitions

$$
\{\epsilon\} = \varphi_\eta \epsilon_\eta + \varphi_\omega \epsilon_\omega \tag{72a}
$$

$$
\{\langle \mathbf{v}_\beta \rangle\} = \varphi_\eta \left\{ \langle \mathbf{v}_\beta \rangle_\eta \right\}^\eta + \varphi_\omega \left\{ \langle \mathbf{v}_\beta \rangle_\omega \right\}^\omega \tag{72b}
$$

$$
\{\epsilon\}(1 + \{\mathcal{K}\}) = \epsilon_\eta (1 + \mathcal{K}_\eta) \varphi_\eta + \epsilon_\omega (1 + \mathcal{K}_\omega) \varphi_\omega. \tag{72c}
$$

When the condition of large-scale mass equilibrium is valid, we will demonstrate in Part V that the spatial deviation concentrations can be expressed as

$$
\tilde{c}_\eta = \mathbf{b}_\eta \cdot \nabla \{\langle c \rangle\}, \ \tilde{c}_\omega = \mathbf{b}_\omega \cdot \nabla \{\langle c \rangle\} \tag{73}
$$

and that $\tilde{c}_\eta$ and $\tilde{c}_\omega$ satisfy the boundary condition given by

$$
\text{B.C.1} \ \tilde{c}_\eta = \tilde{c}_\omega, \ \text{at} \ A_{\eta\omega}. \tag{74}
$$

This allows us to express eqn (71) in the relatively simple form

$$
\{\epsilon\}(1 + \{\mathcal{K}\}) \frac{\partial \{\langle c \rangle\}}{\partial t} + \nabla \cdot \left(\{\langle \mathbf{v}_\beta \rangle\} \{\langle c \rangle\} \right)
$$

$$
= \nabla \cdot \left(\mathbf{D}^{**} \cdot \nabla \{\langle c \rangle\} \right) \tag{75}
$$

in which the one-equation model, large-scale dispersion tensor is defined by

$$\begin{aligned}\mathbf{D}^{**} &= \varphi_\eta\{\mathbf{D}^*_\eta\}^\eta + \varphi_\omega\{\mathbf{D}^*_\omega\}^\omega \\ &\quad + \frac{\{\mathbf{D}^*_\eta\}^\eta - \{\mathbf{D}^*_\omega\}^\omega}{\mathcal{V}_\infty}\cdot\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\mathbf{b}_\eta\,\mathrm{d}A + \left\{\tilde{\mathbf{D}}^*_\eta\cdot\nabla\mathbf{b}\eta\right\} \\ &\quad + \left\{\tilde{\mathbf{D}}^*_\omega\cdot\nabla\mathbf{b}\omega\right\} - \left(\varphi_\eta\{\tilde{\mathbf{v}}_{\beta\eta}\mathbf{b}_\eta\}^\eta + \varphi_\omega\{\tilde{\mathbf{v}}_{\beta\omega}\mathbf{b}_\omega\}^\omega\right).\end{aligned} \tag{76}$$

The large-scale averaged velocity that appears in eqn (75) is given by the large-scale form of Darcy's law that was presented in Part III.[1] For completeness we list that result as

$$\{\langle\mathbf{v}\rangle\} = -\frac{1}{\mu_\beta}\mathbf{K}^*_\beta\cdot\left(\nabla\left\{\langle P_\beta\rangle^\beta\right\} - \rho_\beta\mathbf{g}\right) \tag{77}$$

and note that it is based on the idea that the σ-region is impermeable to convective transport.

3 LARGE-SCALE MASS EQUILIBRIUM

The restrictions associated with eqn (70) are, at this point, purely intuitive. If the physical and chemical properties of the η- and ω-regions do not differ *too much*, eqn (70) should be an acceptable approximation; however, we need to know what is meant by *too much* before we can proceed with confidence. If one believes that $\{\langle c_\eta\rangle^\eta\}^\eta = \{\langle c_\omega\rangle^\omega\}^\omega$ is a *reasonable approximation*, it is prudent to propose decompositions of the form

$$\{\langle c_\eta\rangle^\eta\}^\eta = \{\langle c\rangle\} + \hat{c}_\eta,\ \ \{\langle c_\omega\rangle^\omega\}^\omega = \{\langle c\rangle\} + \hat{c}_\omega \tag{78}$$

and then identify the conditions for which $\hat{c}_\eta$ and $\hat{c}_\omega$ make a negligible contribution to the transport process. In eqn (78) we have followed the nomenclature of Part III[1] and used a *circumflex* to identify a spatial deviation concentration that is associated with two quantities *having the same length scale*. These results should be contrasted with that given by eqn (61) where we have used a tilde to identify a spatial deviation concentration associated with two concentrations *having different length scales*. If we substitute eqn (78) into eqn (68) and eqn (69) and add the results, we obtain

$$\begin{aligned}&\{\epsilon\}(1+\{\mathcal{K}\})\frac{\partial\{\langle c\rangle\}}{\partial t} + \nabla\cdot(\{\langle\mathbf{v}_\beta\rangle\}\{\langle c\rangle\}) \\ &\quad = \nabla\cdot\left[\left(\varphi_\eta\{\mathbf{D}^*_\eta\}^\eta + \varphi_\omega\{\mathbf{D}^*_\omega\}^\omega\right)\cdot\nabla\{\langle c\rangle\}\right] \\ &\qquad + \nabla\cdot\left[\frac{\{\mathbf{D}^*_\eta\}^\eta}{\mathcal{V}_\infty}\cdot\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{c}_\eta\,\mathrm{d}A + \left\{\tilde{\mathbf{D}}^*_\eta\cdot\nabla\tilde{c}_\eta\right\}\right. \\ &\qquad \left. + \frac{\{\mathbf{D}^*_\omega\}^\omega}{\mathcal{V}_\infty}\cdot\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\tilde{c}_\omega\,\mathrm{d}A + \left\{\tilde{\mathbf{D}}^*_\omega\cdot\nabla\tilde{c}_\omega\right\}\right] \\ &\qquad - \nabla\cdot\left[\varphi_\eta\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\}^\eta + \varphi_\omega\{\tilde{\mathbf{v}}_{\beta\omega}\tilde{c}_\omega\}^\omega\right] \\ &\qquad - \epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\hat{c}_\eta}{\partial t} - \epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega\frac{\partial\hat{c}_\omega}{\partial t} \\ &\qquad - \nabla\cdot\left[\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta\hat{c}_\eta + \varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\hat{c}_\omega\right] \\ &\qquad + \nabla\cdot\left[\varphi_\eta\{\mathbf{D}{*}_\eta\}^\eta\cdot\nabla\hat{c}_\eta + \varphi_\omega\{\mathbf{D}{*}_\omega\}^\omega\cdot\nabla\hat{c}_\omega\right].\end{aligned} \tag{79}$$

When the last four terms in this result are negligible, one only needs to develop the closure problem for $\tilde{c}_\eta$ and $\tilde{c}_\omega$ in order to arrive at the one-equation model given by eqn (75). As an *approximation*, we can use that closure problem to simplify eqn (79) to

$$\begin{aligned}&\{\epsilon\}(1+\{\mathcal{K}\})\frac{\partial\{\langle c\rangle\}}{\partial t} + \nabla\cdot(\{\langle\mathbf{v}_\beta\rangle\}\{\langle c\rangle\}) \\ &\quad = \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right) \\ &\quad - \epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\hat{c}_\eta}{\partial t} - \epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega\frac{\partial\hat{c}_\omega}{\partial t} \\ &\qquad - \nabla\cdot\left[\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta\hat{c}_\eta + \varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\hat{c}_\omega\right] \\ &\qquad + \nabla\cdot\left[\varphi_\eta\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\hat{c}_\eta + \varphi_\omega\{\mathbf{D}^*_\omega\}^\omega\cdot\nabla\hat{c}_\omega\right].\end{aligned} \tag{80}$$

A reasonable set of restrictions associated with the principle of large-scale mass equilibrium can be expressed as

$$\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\hat{c}_\eta}{\partial t} - \epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega\frac{\partial\hat{c}_\omega}{\partial t} \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right) \tag{81a}$$

$$\nabla\cdot\left[\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta\hat{c}_\eta + \varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\hat{c}_\omega\right] \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right) \tag{81b}$$

$$\nabla\cdot\left[\varphi_\eta\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\hat{c}_\eta + \varphi_\omega\{\mathbf{D}^*_\omega\}^\omega\cdot\nabla\hat{c}_\omega\right] \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right) \tag{81c}$$

however, these are of little value unless we can say something specific about $\hat{c}_\eta$ and $\hat{c}_\omega$. A little thought will indicate that eqn (78) can be used with eqn (47) in order to express the large-scale deviations as

$$\hat{c}_\eta = \varphi_\omega\left[\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega\right] \tag{82a}$$

$$\hat{c}_\omega = \varphi_\eta\left[\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta\right]. \tag{82b}$$

Use of these results in eqns 81 provides a much more useful set of restrictions given by

$$\begin{aligned}&\varphi_\eta\varphi_\omega\left[\epsilon_\eta(1+\mathcal{K}_\eta) - \epsilon_\omega(1+\mathcal{K}_\omega)\right]\frac{\partial}{\partial t}\left[\{\langle c_\eta\rangle^\eta\}^\eta\right. \\ &\qquad \left. - \{\langle c_\omega\rangle^\omega\}^\omega\right] \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right)\end{aligned} \tag{83a}$$

$$\begin{aligned}&\nabla\cdot\left[\varphi_\eta\varphi_\omega\left(\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta - \{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\right)\left(\{\langle c_\eta\rangle^\eta\}^\eta\right.\right. \\ &\qquad \left.\left. - \{\langle c_\omega\rangle^\omega\}^\omega)\right] \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right)\end{aligned} \tag{83b}$$

$$\begin{aligned}&\nabla\cdot\left[\varphi_\eta\varphi_\omega\left(\{\mathbf{D}^*_\eta\}^\eta - \{\mathbf{D}^*_\omega\}^\omega\right)\cdot\nabla\left(\{\langle c_\eta\rangle^\eta\}^\eta\right.\right. \\ &\qquad \left.\left. - \{\langle c_\omega\rangle^\omega\}^\omega\right)\right] \ll \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right).\end{aligned} \tag{83c}$$

These restrictions have an appealing form in that they will be *automatically satisfied* when the chemical and mechanical properties of the two regions are the same. For the general case, these restrictions will only be useful if we can obtain an estimate of the difference between the two regional concentrations, and in order to develop an estimate of this difference, we need to develop the governing differential equation for $\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega$. A governing equation for this quantity can be obtained by subtracting eqn (69) from eqn (68), but before carrying out that operation we wish to express those two regional transport equations in a simplified and approximate form that is quite consistent with the exact representation that will be given in Part V.[36] We express eqn (68) as

$$\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}+\nabla\cdot\left[\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right]$$
$$=\nabla\cdot\left[\varphi_\eta\mathbf{D}^{**}_{\eta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right]-\alpha^*\left(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\right) \tag{84}$$

while eqn (69) takes the analogous form given by

$$\epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t}+\nabla\cdot\left[\varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\{\langle c_\omega\rangle^\omega\}^\omega\right]$$
$$=\nabla\cdot\left[\varphi_\omega\mathbf{D}^{**}_{\omega\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega\right]-\alpha^*\left(\{\langle c_\omega\rangle^\omega\}^\omega-\{\langle c_\eta\rangle^\eta\}^\eta\right). \tag{85}$$

In a more detailed analysis of the two-equation model, we will find additional convective transport terms and coupled diffusive fluxes; however, eqn (84) and eqn (85) are reasonable representations of the physics and they can be used to develop reasonable estimates of the concentration difference, $\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega$. In order to derive a governing equation for this concentration difference, we first divide eqn (76) and eqn (77) by φ_η and φ_ω, respectively to obtain

$$\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}+\nabla\cdot\left(\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right)$$
$$=\nabla\cdot\left(\mathbf{D}^{**}_{\eta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right)-\varphi_\eta^{-1}\alpha^*\left(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\right) \tag{86}$$

$$\epsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t}+\nabla\cdot\left(\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\{\langle c_\omega\rangle^\omega\}^\omega\right)$$
$$=\nabla\cdot\left(\mathbf{D}^{**}_{\omega\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega\right)-\varphi_\omega^{-1}\alpha^*\left(\{\langle c_\omega\rangle^\omega\}^\omega-\{\langle c_\eta\rangle^\eta\}^\eta\right). \tag{87}$$

In order to illustrate the algebraic path that one follows after subtracting eqn (87) from eqn (86), we will begin with the first term in each equation and after completing that analysis we will simply list the final result for the entire process. Use of eqn (78) allows us to write

$$\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}-\epsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t}$$
$$=\left[\epsilon_\eta(1+\mathcal{K}_\eta)-\epsilon_\omega(1+\mathcal{K}_\omega)\right]\frac{\partial\{\langle c\rangle\}}{\partial t}$$
$$+\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\hat{c}_\eta}{\partial t}-\epsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\hat{c}_\omega}{\partial t}. \tag{88}$$

We now make use of eqns 82 to eliminate the spatial deviation concentrations in terms of the difference between the two regional average concentrations. This leads to

$$\varepsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}-\varepsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t}$$
$$=\left[\varepsilon_\eta(1+\mathcal{K}_\eta)\varphi_\omega+\varepsilon_\omega(1+\mathcal{K}_\omega)\varphi_\eta\right]\frac{\partial}{\partial t}\left(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\right)$$
$$+\underbrace{\left[\varepsilon_\eta(1+\mathcal{K}_\eta)-\varepsilon_\omega(1+\mathcal{K}_\omega)\right]\frac{\partial\{\langle c\rangle\}}{\partial t}}_{\textit{source}} \tag{89}$$

The first term on the right hand side of this result represents the accumulation term in a transport equation for the concentration difference, while the second term represents a *source* in that transport equation. If the *capacitance factors* associated with adsorption and accumulation in the two regions are identical, the source term will be zero.

It is convenient to define a mixed mode capacitance factor according to,

$$\left[\epsilon(1+\mathcal{K})\right]_{\eta\omega}=\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\omega+\epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\eta \tag{90}$$

and we remark that the constraints for any type of local or large-scale equilibrium always involve mixed mode parameters of this type. Use of this result in eqns 81 provides

$$\varepsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}-\varepsilon_\omega(1+\mathcal{K}_\omega)\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t}$$
$$=\left[\varepsilon(1+\mathcal{K})\right]_{\eta\omega}\frac{\partial}{\partial t}\left(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\right)$$

$$+\underbrace{\Big[\varepsilon_\eta\big(1+\mathscr{K}_\eta\big)-\varepsilon_\omega\big(1+\mathscr{K}_\omega\big)\Big]\frac{\partial\{\langle c\rangle\}}{\partial t}}_{source} \tag{91}$$

If we repeat the procedure leading to eqn (91) for all the terms in eqn (86) and eqn (87), we obtain the following transport equation for the difference between the two regional concentrations.

$$\begin{aligned}
&\big[\varepsilon(1+\mathscr{K})\big]_{\eta\omega}\frac{\partial}{\partial t}\Big(\big\{\langle c_\eta\rangle^\eta\big\}^\eta-\big\{\langle c_\omega\rangle^\omega\big\}^\omega\Big)+\nabla\cdot\Big[\big\{\langle \mathbf{v}_\beta\rangle_{\eta\omega}\big\}^{\eta\omega}\Big(\big\{\langle c_\eta\rangle^\eta\big\}^\eta-\big\{\langle c_\omega\rangle^\omega\big\}^\omega\Big)\Big]\\
&-\nabla\cdot\Big[\{\mathbf{D}\}^{**}_{\eta\omega}\cdot\nabla\Big(\big\{\langle c_\eta\rangle^\eta\big\}^\eta-\big\{\langle c_\omega\rangle^\omega\big\}^\omega\Big)\Big]+\frac{\alpha^*}{\varphi_\eta\varphi_\omega}\Big(\big\{\langle c_\eta\rangle^\eta\big\}^\eta-\big\{\langle c_\omega\rangle^\omega\big\}^\omega\Big)\\
&=-\underbrace{\Big[\varepsilon_\eta\big(1+\mathscr{K}_\eta\big)-\varepsilon_\omega\big(1+\mathscr{K}_\omega\big)\Big]\frac{\partial\{\langle c\rangle\}}{\partial t}}_{source}-\underbrace{\nabla\cdot\Big[\Big(\big\{\langle \mathbf{v}_\beta\rangle_\eta\big\}^\eta-\big\{\langle \mathbf{v}_\beta\rangle_\omega\big\}^\omega\Big)\{\langle c\rangle\}\Big]}_{source}\\
&+\underbrace{\nabla\cdot\Big[\big(\mathbf{D}^{**}_{\eta\eta}-\mathbf{D}^{**}_{\omega\omega}\big)\cdot\nabla\{\langle c\rangle\}\Big]}_{source}
\end{aligned} \tag{92}$$

Here we have defined the mixed mode velocity and dispersion tensor according to

$$\{\langle\mathbf{v}\rangle_{\eta\omega}\}^{\eta\omega}=\varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta+\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega \tag{93}$$

$$\{\mathbf{D}\}^{**}_{\eta\omega}=\varphi_\omega\mathbf{D}^{**}_{\eta\eta}+\varphi_\eta\mathbf{D}^{**}_{\omega\omega}. \tag{94}$$

The result given by eqn (92) is rather complex; however, we can extract an order of magnitude estimate for the concentration difference if we are willing to make use of estimates of the type

$$\begin{aligned}
\frac{\partial}{\partial t}\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)&=\mathbf{O}\left[\frac{\Delta\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)}{t^*}\right]\\
&=\mathbf{O}\left[\frac{\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)}{t^*}\right].
\end{aligned} \tag{95a}$$

Here we have assumed that the *change* of the concentration difference is on the order of the difference itself since this quantity is directly related to the spatial deviation concentration, $\hat{c}_\eta$, and we think of the average of the deviation as being small compared to the deviation itself. The spatial derivatives can be expressed in a manner analogous to eqn (95) and we list the results as

$$\nabla\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)=\mathbf{O}\left[\frac{\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)}{\mathcal{L}_c}\right] \tag{95b}$$

$$\nabla\cdot\big[\nabla\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)\big]=\mathbf{O}\left[\frac{\big(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega\big)}{\mathcal{L}_c^2}\right]. \tag{95c}$$

Here one should think of $\mathcal{L}_c$ as the characteristic length associated with the region averaged concentrations. It is necessarily constrained by the classic length scale constraints associated with the method of volume averaging, ℓ_ω, $\ell_\eta \ll R_o \ll \mathcal{L}_c$, and the upper bound for $\mathcal{L}_c$ will be the aquifer or reservoir length scale illustrated in Fig. 1 as $\mathcal{L}$. For the large-scale intrinsic average concentration we use the analogous estimates given by

$$\frac{\partial\{\langle c\rangle\}}{\partial t}=\mathbf{O}\left[\frac{\Delta\{\langle c\rangle\}}{t^*}\right] \tag{96a}$$

$$\nabla\{\langle c\rangle\}=\mathbf{O}\left[\frac{\Delta\{\langle c\rangle\}}{\mathcal{L}_c}\right] \tag{96b}$$

$$\nabla\cdot[\nabla\{\langle c\rangle\}]=\mathbf{O}\left[\frac{\Delta\{\langle c\rangle\}}{\mathcal{L}_c^2}\right] \tag{96c}$$

and when these estimates, along with those given by eqns 95, are substituted into eqn (92) we can extract an estimate of the difference between the regional concentrations. The algebraic effort is rather lengthy and details for this type of analysis are given by Whitaker[40] and by Quintard and Whitaker.[41] Here we list only the result that takes the form

$$\frac{\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega}{\Delta\{\langle c\rangle\}}=\frac{\mathbf{O}[\mathrm{A}+\mathrm{B}+\mathrm{C}]}{\mathbf{O}[1+\mathrm{D}+\mathrm{E}+\mathrm{F}]}. \tag{97}$$

in which the six terms on the right hand side are given by

$$\mathrm{A}=\mathbf{O}\left[\frac{\epsilon_\eta(1+\mathcal{K}_\eta)-\epsilon_\omega(1+\mathcal{K}_\omega)}{\big[\epsilon(1+\mathcal{K})\big]_{\eta\omega}}\right] \tag{98a}$$

$$\mathrm{B}=\mathbf{O}\left[\frac{\big(\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta-\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\big)t^*}{\big[\epsilon(1+\mathcal{K})\big]_{\eta\omega}\mathcal{L}_c}\right] \tag{98b}$$

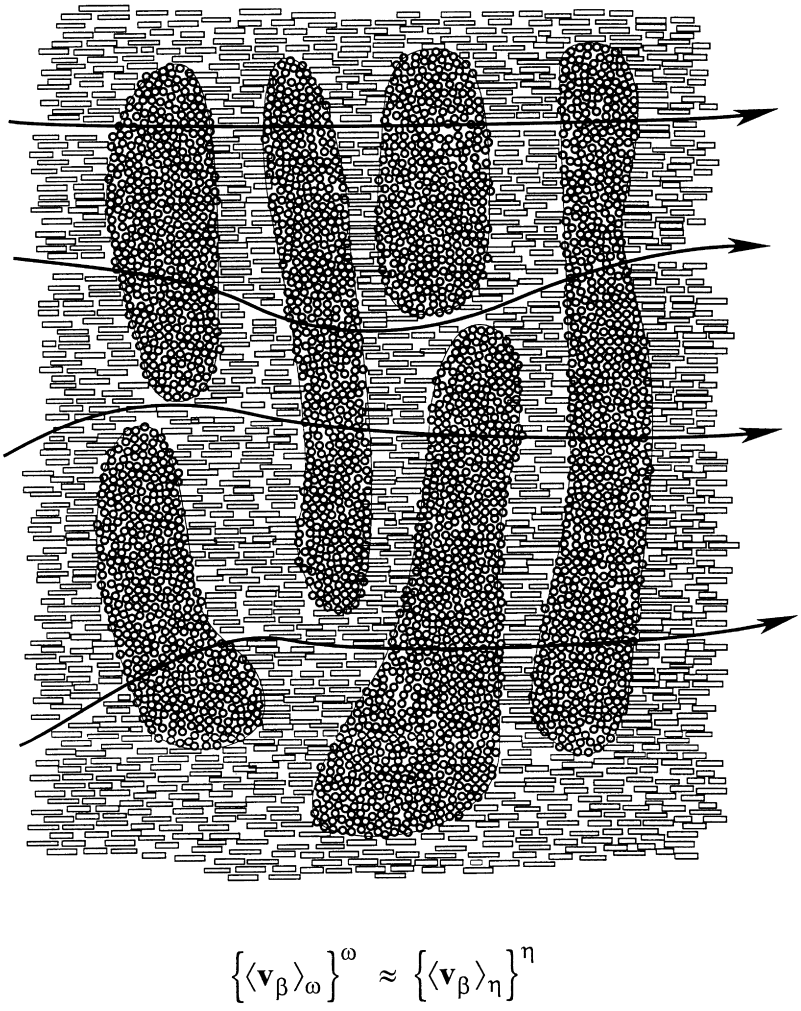

Fig. 7. Flow normal to a stratified system.

$$C = \mathbf{O}\left[\frac{\left(\mathbf{D}^{**}_{\eta\eta} - \mathbf{D}^{**}_{\omega\omega}\right)\mathrm{t}^*}{\left[\epsilon(1+\mathcal{K})\right]_{\eta\omega}\mathcal{L}^2_{\mathrm{c}}}\right] \tag{98c}$$

$$D = \mathbf{O}\left[\frac{\left\{\langle \mathbf{v}_\beta \rangle_{\eta\omega}\right\}^{\eta\omega} t^*}{\left[\epsilon(1+\mathcal{K})\right]_{\eta\omega}\mathcal{L}_c}\right] \tag{98d}$$

$$E = \mathbf{O}\left[\frac{\{\mathbf{D}\}^{**}_{\eta\omega} t^*}{\left[\epsilon(1+\mathcal{K})\right]_{\eta\omega}\mathcal{L}^2_c}\right] \tag{98e}$$

$$F = \mathbf{O}\left[\frac{\alpha^* t^*}{\varphi_\eta\varphi_\omega\left[\epsilon(1+\mathcal{K})\right]_{\eta\omega}}\right]. \tag{98f}$$

These quantities can be used with eqn (97) in order to estimate the difference between the two regional concentrations; however, difficulties can arise because the sign of the terms given by eqns 98 are not necessarily obvious. Because of this, it is possible that terms may either add or cancel to produce dramatically different results. When a single term dominates the denominator on the right hand side of eqn (97), and a single term dominates the numerator, one can obtain a reliable estimate of the concentration difference in terms of $\Delta\{\langle c \rangle\}$. When this is not the case, one must be able to determine the sign of the estimates given by eqns 98 and for some simple processes this is feasible.[41]

The result obtained from eqn (97) can be used with the restrictions given by eqns 83 which can be arranged in the form

$$\frac{\varphi_\eta\varphi_\omega\left[\epsilon_\eta(1+\mathcal{K}_\eta) - \epsilon_\omega(1+\mathcal{K}_\omega)\right]\mathcal{L}^2_c}{\mathbf{D}^{**}t^*} \times \frac{\left[\left\{\langle c_\eta\rangle^\eta\right\}^\eta - \left\{\langle c_\omega\rangle^\omega\right\}^\omega\right]}{\Delta\left\{\langle c\rangle\right\}} \ll 1 \tag{99a}$$

$$\frac{\varphi_\eta\varphi_\omega\left(\left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta - \left\{\langle \mathbf{v}_\beta\rangle_\omega\right\}^\omega\right)\mathcal{L}_c}{\mathbf{D}^{**}} \times \frac{\left[\left\{\langle c_\eta\rangle^\eta\right\}^\eta - \left\{\langle c_\omega\rangle^\omega\right\}^\omega\right]}{\Delta\left\{\langle c\rangle\right\}} \ll 1 \tag{99b}$$

$$\frac{\varphi_\eta\varphi_\omega\left(\left\{\mathbf{D}^*_\eta\right\}^\eta - \left\{\mathbf{D}^*_\omega\right\}^\omega\right)\mathcal{L}_c}{\mathbf{D}^{**}} \frac{\left[\left\{\langle c_\eta\rangle^\eta\right\}^\eta - \left\{\langle c_\omega\rangle^\omega\right\}^\omega\right]}{\Delta\left\{\langle c\rangle\right\}} \ll 1. \tag{99c}$$

It is important to note that all three restrictions will be *automatically satisfied* when the volume fraction of either region tends to zero, i.e., $\varphi_\eta \to 0$ or $\varphi_\omega \to 0$. In addition, the *individual restrictions* will be automatically satisfied under the following circumstances:

I. The capacitance factors are equal: $\epsilon_\eta(1+\mathcal{K}_\eta) = \epsilon_\omega(1+\mathcal{K}_\omega)$.
II. The regional velocities are equal: $\{\langle \mathbf{v}_\beta\rangle_\eta\}^\eta = \{\langle \mathbf{v}_\beta\rangle_\omega\}^\omega$
III. The regional dispersion tensors are equal: $\{\mathbf{D}^*_\eta\}^\eta = \{\mathbf{D}^*_\omega\}^\omega$

Since regions that have different mechanical properties are likely to have different chemical properties, porous media that are mechanically heterogeneous are likely to be chemically heterogeneous. This suggests that the constraint constructed on the basis of eqn (99) and eqn (97) may be the most important of the three restrictions since $\epsilon_\eta(1+\mathcal{K}_\eta)$ and $\epsilon_\omega(1+\mathcal{K}_\omega)$ are always likely to be different. On the other hand, if we are dealing with a steady transport process, the constraint given by eqn (99) is automatically satisfied. Given the enormous range of permeabilities that exist in most aquifers or reservoirs, one might also expect to find widely varying regional velocities and this could lead to the failure of the constraint indicated by eqn (99) and eqn (97). This would certainly seem to be the case for the system illustrated in Fig. 6 when $\mathbf{K}_{\beta\eta} \gg \mathbf{K}_{\beta\omega}$ since this would lead to $\{\langle \mathbf{v}_\beta\rangle_\eta\}^\eta \gg \{\langle \mathbf{v}_\beta\rangle_\omega\}^\omega$ and the failure of the constraint given by eqn (99) and eqn (97). On the other hand, if the flow were orthogonal to a stratified system, such as we have indicated in Fig. 7, the two regional velocities would be essentially equal and the constraint associated by the velocity would be satisfied.

4 MECHANICAL AND CHEMICAL HETEROGENEITIES

For many flow processes in heterogeneous porous media, the condition of *large-scale mechanical equilibrium* is valid and the constraints associated with this condition were developed in Part III.[1] Since the two-region model for compressible, single-phase flow is identical in form to the process of transient heat conduction in a two-phase system, we can use a detailed study of local thermal equilibrium[41] as a verification of the theory developed in Part III. When the condition of large-scale mechanical equilibrium is valid, the fluid mechanical problem can be described in terms of a single continuity equation and the large-scale form of Darcy's law which can be expressed as

$$\nabla\cdot\{\langle \mathbf{v}_\beta\rangle\} = 0 \tag{100}$$

$$\{\langle \mathbf{v}_\beta\rangle\} = -\frac{1}{\mu_\beta}\mathbf{K}^*_\beta\cdot\left(\nabla\left\{\langle p_\beta\rangle^\beta\right\} - \rho_\beta \mathbf{g}\right). \tag{101}$$

If the condition of large-scale mass equilibrium is valid, the process of solute transport with adsorption is described by

$$\{\epsilon\}(1+\{\mathcal{K}\})\frac{\partial\{\langle c\rangle\}}{\partial t} + \nabla\cdot\left(\{\langle \mathbf{v}_\beta\rangle\}\{\langle c\rangle\}\right) = \nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right). \tag{102}$$

The constraints associated with eqn (100) and eqn (101) are relatively easy to satisfy; however, those associated with eqn (102) may be much more difficult to satisfy and this will lead to the need for multi-region models. The key constraint associated with large-scale mass equilibrium *would appear to be* given by eqn (99). In thinking about that constraint, one must remember that the capacitance factor is influenced by the adsorption equilibrium relation and the various volume fractions that appear in eqn (37). Thus it is possible that the adsorption equilibrium relation given by eqn (3) *could be identical* for both the η-region and the ω-region, while the capacitance factors for these two regions *could be different*. While the importance of the difference in the capacitance factors is most evident in eqn (99), this difference also appears in eqn (98) and thus influences the estimate indicated by eqn (97). Our studies of large-scale mechanical equilibrium[42,43] and local thermal equilibrium[41] clearly indicate that this condition is always satisfied for steady, uniform flow. Under certain circumstances, this means that the regional velocities can differ greatly, $\{\langle \mathbf{v}_\beta\rangle_\eta\}^\eta \gg \{\langle \mathbf{v}_\beta\rangle_\omega\}^\omega$, while eqn (100) and 101 still provide valid representations of the large-scale averaged velocity and pressure. On the other hand, when the regional velocities differ greatly, the restriction given by eqn (99) may fail and the condition of large-scale mass equilibrium will not be valid. The regional velocities are available to us in terms of the regional form of Darcy's law; however, more convenient representations were given in Part III[1] and we list them as

$$\left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta = \varphi_\eta^{-1}\mathbf{M}^*_{\beta\eta}\cdot\left\{\langle \mathbf{v}_\beta\rangle\right\},\ \text{in the } \eta - \text{region} \tag{103}$$

$$\left\{\langle \mathbf{v}_\beta\rangle_\omega\right\}^\omega = \varphi_\omega^{-1}\mathbf{M}^*_{\beta\omega}\cdot\left\{\langle \mathbf{v}_\beta\rangle\right\},\ \text{in the } \omega - \text{region.} \tag{104}$$

In this representation, the mapping tensors $\mathbf{M}^*_{\beta\eta}$ and $\mathbf{M}^*_{\beta\omega}$ are given by the solution of a closure problem that is equivalent to the closure problem that one needs to solve in order to predict the large-scale permeability tensor, $\mathbf{K}^*_\eta$.

It is important to remember that large-scale mechanical equilibrium and large-scale mass equilibrium are both controlled by local heterogeneities, but beyond that they may not be closely coupled. In Part V[36] we will develop the closure problem for the two-equation model and present results that illustrate this fact.

5 CONCLUSIONS

In this work we have developed the regional forms of the solute transport equation, along with the one-equation model for solute transport with adsorption. The regional forms have been used to develop the constraints associated with the condition of large-scale mass equilibrium, and we have derived a governing differential equation for the difference between the regional concentrations. This provides an estimate of the concentration difference, which in turn allows us to make some definite statements about the validity of a one-equation, solute transport model. These statements take the form of constraints that are given by eqns (99) in conjunction with the normalized concentration difference that is estimated according to eqn (97).

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APPENDIX A LOCAL ADSORPTION EQUILIBRIUM

In the absence of surface transport[44] and heterogeneous reaction[45], the jump condition[46] at the $\gamma-\kappa$ interface for a dilute solution of the diffusing species can be expressed as

Jump condition

$$\underbrace{\frac{\partial c_{\gamma s}}{\partial t}}_{\substack{\text{surface}\\ \text{accumulation}}} = \underbrace{-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla c_\gamma}_{\substack{\text{interfacial}\\ \text{flux}}}, \quad \textit{at the } \gamma\text{-}\kappa \textit{ interface} \tag{A1}$$

By itself, the jump condition is not sufficient to solve the mass transport problem under consideration, and in order to connect the surface concentration, $c_{\gamma s}$, to the bulk concentration, c_γ, we make use of a relatively general interfacial flux constitutive equation given by

Interfacial flux constitutive equation

$$-\mathbf{n}_{\gamma\kappa}\cdot\mathscr{D}_\gamma\nabla c_\gamma = \underbrace{\mathscr{R}(c_\gamma, c_{\gamma s})}_{\substack{\text{rate of}\\ \text{adsorption}}} - \underbrace{k_{-1}c_{\gamma s}}_{\substack{\text{rate of}\\ \text{desorption}}} \tag{A2}$$

Both eqns (A1) and (A2) are dynamic relations in which the surface concentration need not be in equilibrium with the bulk concentration. To be explicit about this point, we express the equilibrium relation in the form

$$c^{eq}_{\gamma s} = \mathcal{F}(c_\gamma). \tag{A3}$$

In order to determine under what circumstances we can replace $c_{\gamma s}$ with the equilibrium surface concentration given by eqn (A3), we first decompose the surface concentration according to

$$c_{\gamma s} = c^{eq}_{\gamma s} + c^*_{\gamma s}. \tag{A4}$$

Under equilibrium conditions $c^*_{\gamma s}$ is zero, and for some dynamic conditions $c^*_{\gamma s}$ is small enough so that $c_{\gamma s}$ in eqn (A1) can be replaced with $c^{eq}_{\gamma s}$. Our objective in this appendix is to determine what is meant by small enough.

Substitution of eqn (A4) in the jump condition given by eqn (A1) leads to

$$\frac{\partial c^{eq}_{\gamma s}}{\partial t} = -\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma - \frac{\partial c^*_{\gamma s}}{\partial t}. \tag{A5}$$

Use of eqn (A3) along with the definition of K_{eq} given by eqn (5) in the text allows us to write eqn (A5) as

$$K_{eq}\frac{\partial c_\gamma}{\partial t} = -\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma - \frac{\partial c^*_{\gamma s}}{\partial t}. \tag{A6}$$

In order for this result to simplify to the jump condition given by eqn (4) in the text, the following restriction must be valid

$$\frac{\partial c^*_{\gamma s}}{\partial t} \ll \mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma. \tag{A7}$$

In order to be useful, this restriction must be replaced with a constraint,[47,48] and this can be accomplished with the aid of the interfacial flux constitutive equation. Returning to eqn (A2), we expand the rate of adsorption in a Taylor series about the equilibrium surface concentration to provide the following representation:

$$\begin{aligned}\mathcal{R}(c_\gamma, c_{\gamma s}) &= \mathcal{R}(c_\gamma, c^{eq}_{\gamma s}) + (c_{\gamma s} - c^{eq}_{\gamma s})\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}\\ &\quad + \tfrac{1}{2}(c_{\gamma s} - c^{eq}_{\gamma s})^2\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}} + \cdots.\end{aligned} \tag{A8}$$

Use of this result, along with the decomposition given by eqn (A4), allows us to write eqn (A2) as

$$\begin{aligned}-\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma &= \mathcal{R}(c_\gamma, c^{eq}_{\gamma s}) + (c^*_{\gamma s})\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}\\ &\quad + \tfrac{1}{2}(c^*_{\gamma s})^2\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}} + \cdots - k_{-1}c^{eq}_{\gamma s} - k_{-1}c^*_{\gamma s}.\end{aligned} \tag{A9}$$

A little thought based on eqn (A2) will indicate that

$$\mathcal{R}(c_\gamma, c^{eq}_{\gamma s}) - k_{-1}c^{eq}_{\gamma s} = 0 \tag{A10}$$

and when this condition is employed with eqn (A9) we obtain

$$-\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma=(c^*_{\gamma s})\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\tfrac{1}{2}(c^*_{\gamma s})^2\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\cdots-k_{-1}c^*_{\gamma s}. \tag{A11}$$

Use of this representation for the interfacial flux in the restriction given by eqn (A7) leads to

$$\frac{\partial c^*_{\gamma s}}{\partial t}\ll(c^*_{\gamma s})\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\tfrac{1}{2}(c^*_{\gamma s})^2\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\cdots-k_{-1}c^*_{\gamma s}. \tag{A12}$$

We now estimate the time rate of change of $c^*_{\gamma s}$ according to

$$\frac{\partial c^*_{\gamma s}}{\partial t}=\mathbf{O}\left(\frac{\Delta c^*_{\gamma s}}{t^*}\right) \tag{A13}$$

and use this result with eqn (A14) to obtain the following constraint:

$$\left\{\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\tfrac{1}{2}(c^*_{\gamma s})\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\cdots-k_{-1}\right\}t^*\gg\frac{\Delta c^*_{\gamma s}}{c^*_{\gamma s}} \tag{A14}$$

since $\Delta c^*_{\gamma s}$ will always be less than $c^*_{\gamma s}$ we can replace this result with the more conservative constraint given by

Constraint

$$\left\{\left[\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\tfrac{1}{2}(c^*_{\gamma s})\left[\frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}\right]_{c_{\gamma s}=c^{eq}_{\gamma s}}+\cdots-k_{-1}\right\}t^*\gg 1. \tag{A15}$$

When this constraint is satisfied, the surface concentration can be represented by

$$c_{\gamma s}=\mathcal{F}(c_\gamma) \tag{A16}$$

even though the system is not at equilibrium in the strict sense of the word. This means that eqn (4) and eqn (5) in the text accurately describe the adsorption process at the γ–κ interface.

Appendix A.1 Example

We can illustrate the constraint given by eqn (A15) in terms of the Langmuir isotherm for which the rate of adsorption takes the form

$$\mathcal{R}=k_1(1-\theta)c_\gamma. \tag{A17}$$

Here θ represents the fraction of adsorption sites that are occupied by the adsorbed species. This fraction can be represented as

$$\theta=c_{\gamma s}/c^\infty_{\gamma s} \tag{A18}$$

in which $c^\infty_{\gamma s}$ represents the surface concentration when all adsorption sites are occupied. Eqn (A19) and eqn (A20) can be used to express the equilibrium surface concentration in the classic form

$$c^{eq}_{\gamma s}=\frac{Kc_\gamma}{1+K_Ac_\gamma} \tag{A19}$$

in which K and K_A are given by

$$K=k_1/k_{-1},\ \ K_A=k_1/(k_{-1}c^\infty_{\gamma s}). \tag{A20}$$

From eqns (A19) and (A20) we obtain

$$\frac{\partial\mathcal{R}}{\partial c_{\gamma s}}=\frac{k_1c_\gamma}{c^\infty_{\gamma s}},\ \ \frac{\partial^2\mathcal{R}}{\partial c^2_{\gamma s}}=0 \tag{A21}$$

and this allows us to express the constraint given by eqn (A15) as

$$\{k_{-1}+k_1c_\gamma/c^\infty_{\gamma s}\}t^*\gg 1. \tag{A22}$$

APPENDIX B SCALE-UP OF THE ADSORPTION ISOTHERM

In the process of spatial smoothing at several scales, we have scaled up the equilibrium relation. In this appendix, we present the length-scale constraints associated with this process.

Appendix B.1 Small scale

When the condition of *local adsorption equilibrium* is valid, the relation between the surface concentration and the bulk concentration can be expressed as

$$c_{\gamma s}=\mathcal{F}(c_\gamma). \tag{B1}$$

This allows us to represent the surface accumulation as

$$\frac{\partial c_{\gamma s}}{\partial t}=\left(\frac{\partial\mathcal{F}}{\partial c_\gamma}\right)\frac{\partial c_\gamma}{\partial t}. \tag{B2}$$

The equilibrium function in eqn (B1) can be expanded in a Taylor series about the average concentration to obtain

$$\mathcal{F}(c_\gamma)=\mathcal{F}\left(\langle c_\gamma\rangle^\gamma\right)+\left(c_\gamma-\langle c_\gamma\rangle^\gamma\right)\left(\frac{\partial\mathcal{F}}{\partial c_\gamma}\right)\Bigg|_{c_\gamma=\langle c_\gamma\rangle^\gamma}+\tfrac{1}{2}\left(c_\gamma-\langle c_\gamma\rangle^\gamma\right)^2\left(\frac{\partial^2\mathcal{F}}{\partial c^2_\gamma}\right)\Bigg|_{c_\gamma=\langle c_\gamma\rangle^\gamma}+\cdots \tag{B3}$$

On the basis of the spatial decomposition given by

$$c_\gamma=\langle c_\gamma\rangle^\gamma+\tilde{c}_\gamma \tag{B4}$$

our representation takes the form

$$\mathcal{F}(c_\gamma)=\mathcal{F}\left(\langle c_\gamma\rangle^\gamma\right)+\left(\tilde{c}_\gamma\right)\left(\frac{\partial\mathcal{F}}{\partial c_\gamma}\right)\Bigg|_{c_\gamma=\langle c_\gamma\rangle^\gamma}+\tfrac{1}{2}\left(\tilde{c}_\gamma\right)^2\left(\frac{\partial^2\mathcal{F}}{\partial c^2_\gamma}\right)\Bigg|_{c_\gamma=\langle c_\gamma\rangle^\gamma}+\cdots \tag{B5}$$

From the closure problem[18,19], we know that the spatial deviation concentration can be estimated by

$$\tilde{c}_\gamma = \mathbf{O}\left(\ell_\gamma \nabla \langle c_\gamma \rangle^\gamma\right) \tag{B6}$$

where ℓ_γ is the small length scale illustrated in Fig. 3. Use of eqn (B6) in eqn (B5), and neglecting the higher order terms, leads to

$$\mathcal{F}(c_\gamma) = \mathcal{F}\left(\langle c_\gamma \rangle^\gamma\right) + \mathbf{O}\left(\ell_\gamma \nabla \langle c_\gamma \rangle^\gamma\right) \left(\frac{\partial \mathcal{F}}{\partial c_\gamma}\right)\Bigg|_{c_\gamma = \langle c_\gamma \rangle^\gamma}. \tag{B7}$$

We now impose the *restriction*[47,48]

$$\left(\ell_\gamma \nabla \langle c_\gamma \rangle^\gamma\right) \left(\frac{\partial \mathcal{F}}{\partial c_\gamma}\right)\Bigg|_{c_\gamma = \langle c_\gamma \rangle^\gamma} \ll \mathcal{F}\left(\langle c_\gamma \rangle^\gamma\right) \tag{B8}$$

so that eqn (B7) can be used to express eqn (B1) in the form

$$c_{\gamma s} = \mathcal{F}\left(\langle c_\gamma \rangle^\gamma\right) \tag{B9}$$

which is the first of eqn (12) in the text. In order to obtain a *constraint* on the basis of eqn (B8), we estimate the concentration gradient as

$$\nabla \langle c_\gamma \rangle^\gamma = \mathbf{O}\left(\frac{\Delta \langle c_\gamma \rangle^\gamma}{\Delta L}\right) = \mathbf{O}\left(\frac{\langle c_\gamma \rangle^\gamma}{L_c}\right). \tag{B10}$$

Here $\Delta \langle c_\gamma \rangle^\gamma$ represents the change in the concentration that occurs over the distance ΔL, and L_c represents a characteristic distance associated with the concentration $\langle c_\gamma \rangle^\gamma$. The estimate given by eqn (B10) represents a definition of L_c that is based on the idea that one can indeed estimate the gradient of $\langle c_\gamma \rangle^\gamma$. From Fig. 2, we see that the distance ΔL is constrained by

$$\Delta L \leq \ell_\sigma. \tag{B11}$$

Use eqn (B10) in eqn (B8) leads to

$$\ell_\gamma \frac{\langle c_\gamma \rangle^\gamma}{L_c} \left(\frac{\partial \mathcal{F}}{\partial c_\gamma}\right)\Bigg|_{c_\gamma = \langle c_\gamma \rangle^\gamma} \ll \mathcal{F}\left(\langle c_\gamma \rangle^\gamma\right) \tag{B12}$$

and when this constraint is satisfied we know that eqn (B9) is a valid approximation.

Appendix B.2 Example

In order to extract a specific result from eqn (B12), we consider the Langmuir isotherm represented by

$$c_{\gamma s} = \mathcal{F}(c_\gamma) = \frac{K c_\gamma}{1 + K_A c_\gamma}. \tag{B13}$$

With a bit of algebra one finds that this allows us to express eqn (B12) as

$$\frac{\ell \gamma}{L_c} \ll 1 + K_A \langle c_\gamma \rangle^\gamma. \tag{B14}$$

Since $K_A \langle c_\gamma \rangle^\gamma \geq 0$, this constraint can be replaced with

$$\frac{\ell \gamma}{L_c} \ll 1. \tag{B15}$$

When this constraint is satisfied, eqn (B9) is a valid approximation for eqn (B1). Under these circumstances, eqn (12) in the main body of the paper are acceptable approximations for the scaled up equilibrium relation. We can summarize the scale-up approximation for the adsorption isotherm as

$$K_{eq} = \frac{\partial \mathcal{F}}{\partial c_\gamma} \text{ scales up to } K_{eq} = \frac{\partial \mathcal{F}}{\partial \langle c_\gamma \rangle^\gamma} \tag{B16}$$

and a similar procedure is followed at the next level of averaging.

Appendix B.3 Darcy scale

At this level, the scale-up of the adsorption isotherm takes place between eqn (22) and eqn (23) where we assume that

$$c_{\gamma s} = \mathcal{F}\left(\langle c_\gamma \rangle^\gamma\right) \tag{B17}$$

can be replaced with

$$c_{\gamma s} = \mathcal{F}\left(\langle c_\sigma \rangle^\sigma\right). \tag{B18}$$

In this case eqn (B17) replaces eqn (B1) and eqn (B18) replaces eqn (B9). In terms of the scale up suggested by eqn (B16), we now write

$$K_{eq} = \frac{\partial \mathcal{F}}{\partial \langle c_\gamma \rangle^\gamma} \text{ scales up to } K_{eq} = \frac{\partial \mathcal{F}}{\partial \langle c_\sigma \rangle^\sigma} \tag{B19}$$

and the constraint analogous to eqn (B15) is given by

$$\frac{\ell \sigma}{L_c} \ll 1 \tag{B20}$$

in which ℓ_σ is the characteristic length for the σ-region that is illustrated in Fig. 2. The characteristic length, L_c, in eqn (B18) is defined in terms of the estimate given by

$$\nabla \langle c_\sigma \rangle^\sigma = \mathbf{O}\left(\frac{\Delta \langle c_\sigma \rangle^\sigma}{\Delta L}\right) = \mathbf{O}\left(\frac{\langle c_\sigma \rangle^\sigma}{L_c}\right). \tag{B21}$$

In this case we need to understand that the distance ΔL is constrained by

$$\Delta L \leq \ell_\eta,\ \ell_\omega \tag{B22}$$

where ℓ_η and ℓ_ω are the characteristic lengths for the η- and ω-regions that are illustrated in Fig. 2. When the constraint indicated by eqn (B20) is satisfied, we consider eqn (23) in the main body of the text to be a valid representation of the Darcy-scale adsorption and diffusion process in the σ-region.

Appendix B.4 Large scale

The next scale up of the adsorption isotherm takes place between eqn (44) and (57), and this scale up for the η-region can be expressed as

$$K_{eq} = \frac{\partial \mathcal{F}}{\partial \langle c_\eta \rangle^\eta} \text{ scales up to } K_{eq} = \frac{\partial \mathcal{F}}{\partial \{\langle c_\eta \rangle^\eta\}^\eta} \tag{B23}$$

In the main body of the text, this scale up is also illustrated by eqn (37) and eqn (50) which we repeat here as

$$\mathcal{K}_\eta = \frac{(\epsilon_\sigma a_{\gamma\kappa})_\eta}{\epsilon_\eta}\frac{\partial \mathcal{F}}{\partial\langle c_\eta\rangle^\eta} \textit{ scales up to}$$

$$\mathcal{K}_\eta = \frac{(\epsilon_\sigma a_{\gamma\kappa})_\eta}{\epsilon_\eta}\frac{\partial \mathcal{F}}{\partial\{\langle c_\eta\rangle^\eta\}^\eta}. \tag{B24}$$

Without going through the details, we note that the length-scale constraint associated with this simplification is given by

$$\frac{\ell_\eta}{\mathcal{L}_H} \ll 1. \tag{B25}$$

Naturally, a comparable constraint exists for the ω-region.

It seems probable that there are many systems for which this series of simplifications will not be valid and the adsorption isotherm can not be scaled up as indicated by eqn (B23). If the scale up represented by eqn (B16) were not valid, one would be forced to return to eqn (B5) and express that representation as

First correction

$$\mathcal{F}(c_\gamma) = \mathcal{F}\left(\langle c_\gamma\rangle^\gamma\right) + \left(\tilde{c}_\gamma\right)\left(\frac{\partial\mathcal{F}}{\partial c_\gamma}\right)\bigg|_{c_\gamma = \langle c_\gamma\rangle^\gamma}. \tag{B26}$$

From Plumb and Whitaker[18,19] we know that the dominant part of the spatial deviation concentration can be expressed as

$$\tilde{c}_\gamma = \mathbf{b}_\gamma\cdot\nabla\langle c_\gamma\rangle^\gamma \tag{B27}$$

thus the *corrected* form of the adsorption isotherm is given by

$$\mathcal{F}(c_\gamma) = \mathcal{F}\left(\langle c_\gamma\rangle^\gamma\right) + \mathcal{G}\left(\langle c_\gamma\rangle^\gamma, \mathbf{b}_\gamma\cdot\nabla\langle c_\gamma\rangle^\gamma\right). \tag{B28}$$

The volume averaged form of eqn (1) in the main body of the paper is given by

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot(\mathcal{D}_\gamma\nabla c_\gamma) - \frac{1}{\mathcal{V}}\int_{A_{\gamma\kappa}}\frac{\partial c_{\gamma s}}{\partial t}\mathrm{d}A \tag{B29}$$

and use of eqn (B1) and eqn (B29) leads to the form

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot\langle\mathcal{D}_\gamma\nabla c_\gamma\rangle - a_{\gamma\kappa}\frac{\partial}{\partial t}\left[\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}} c_{\gamma s}\mathrm{d}A\right]. \tag{B30}$$

When the *corrected* adsorption isotherm is used with this general form, we obtain

$$\begin{aligned}\epsilon_\gamma(1 + a_{\gamma\kappa}K_{eq}/\epsilon_\gamma)\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} &= \nabla\cdot(\mathcal{D}_\gamma\nabla c_\gamma)\\ &- a_{\gamma\kappa}\frac{\partial}{\partial t}\left[\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\mathcal{G}\left(\langle c_\gamma\rangle^\gamma, \mathbf{b}_\gamma\cdot\nabla\langle c_\gamma\rangle^\gamma\right)\mathrm{d}A\right].\end{aligned} \tag{B31}$$

Here we see that a nonlinear adsorption process will give rise to mixed space–time derivatives and it will require information from the closure problem to accurately determine the form of the accumulation term in the volume averaged transport equation. It would appear that this represents a new aspect of the problem of mass transport with adsorption that has yet to be explored.

APPENDIX C LENGTH-SCALE CONSTRAINTS ASSOCIATED WITH VARIATIONS OF THE ADSORPTION ISOTHERM

In the process of spatial smoothing at several scales, we have ignored variations of the equilibrium relation within the averaging volume. In this appendix, we present the length-scale constraints associated with this process.

Appendix C.1 Small scale

The starting point for the analysis of diffusion and adsorption in the σ-region is given by

$$\frac{\partial c_\gamma}{\partial t} = \nabla\cdot(\mathcal{D}_\gamma\nabla c_\gamma), \text{ in the } \gamma - \text{phase} \tag{C1}$$

$$\text{B.C.1} - \mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma = \frac{\partial c_{\gamma s}}{\partial t}, \text{ at the } \gamma\text{–}\kappa \text{ interface} \tag{C2}$$

and the volume averaged form can be expressed as

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot\langle\mathcal{D}_\gamma\nabla c_\gamma\rangle - \frac{1}{\mathcal{V}}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_\gamma\mathrm{d}A. \tag{C3}$$

Application of the adsorption boundary condition provides

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot\langle\mathcal{D}_\gamma\nabla c_\gamma\rangle - \frac{1}{\mathcal{V}}\int_{A_{\gamma\kappa}}\frac{\partial c_{\gamma s}}{\partial t}\mathrm{d}A \tag{C4}$$

and we can use eqn (A16) and (B9) to express the surface accumulation term according to

$$c_{\gamma s} = \mathcal{F}\left(\langle c_\gamma\rangle^\gamma\right), \quad \frac{\partial c_{\gamma s}}{\partial t} = K_{eq}\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t}. \tag{C5}$$

Here the equilibrium coefficient is defined explicitly by

$$K_{eq} = \frac{\partial\mathcal{F}}{\partial\langle c_\gamma\rangle^\gamma} \tag{C6}$$

and use of eqn (C5) in eqn (C4) leads to

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot\langle\mathcal{D}_\gamma\nabla c_\gamma\rangle - a_{\mathrm{v}}\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}K_{eq}\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t}\mathrm{d}A. \tag{C7}$$

If we can remove the integrand from the area integral, eqn (C7) simplifies to

$$\epsilon_\gamma\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} = \nabla\cdot\langle\mathcal{D}_\gamma\nabla c_\gamma\rangle - a_{\mathrm{v}}K_{eq}\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} \tag{C8}$$

and from this we can obtain eqn (10) in the main body of the paper. In order to explore the process of removing an averaged quantity from an area integral, we make use of the nomenclature

$$\langle\Omega_\gamma\rangle^\gamma = K_{eq}\frac{\partial\langle c_\gamma\rangle^\gamma}{\partial t} \tag{C9}$$

and note that $\langle\Omega_\gamma\rangle^\gamma$ can be expanded in a Taylor series about the centroid of the averaging volume to obtain

$$\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}+\mathbf{y}_\gamma}=\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}+\mathbf{y}_\gamma\cdot\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}$$
$$+\tfrac{1}{2}\mathbf{y}_\gamma\mathbf{y}_\gamma:\nabla\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}+\cdots. \qquad \text{(C10)}$$

We can now express the area integral in eqn (C7) in terms of the expansion given by eqn (C10) in order to obtain

$$\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}+\mathbf{y}_\gamma}\mathrm{d}A=\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}$$
$$+\left\{\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\mathbf{y}_\gamma\mathrm{d}A\right\}\cdot\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}$$
$$+\tfrac{1}{2}\left\{\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\mathbf{y}_\gamma\mathbf{y}_\gamma\mathrm{d}A\right\}:\nabla\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}+\cdots \qquad \text{(C11)}$$

This can be expressed in more compact form according to

$$\frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}+\mathbf{y}_\gamma}\mathrm{d}A=\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}+\langle\mathbf{y}_\gamma\rangle_{\gamma\kappa}\cdot\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}$$
$$+\tfrac{1}{2}\langle\mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}:\nabla\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}+\cdots$$

and we see that averaged quantities can be removed from interfacial area integrals when the following restrictions are valid:

$$\langle\mathbf{y}_\gamma\rangle_{\gamma\kappa}\cdot\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}\ll\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}} \qquad \text{(C13)}$$

$$\langle\mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}:\nabla\nabla\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}\ll\langle\Omega_\gamma\rangle^\gamma\Big|_{\mathbf{x}}. \qquad \text{(C14)}$$

Restrictions of this type have been under consideration since the original work of Carbonell and Whitaker[39] and recent numerical experiments.[39] To begin with, we need to construct estimates of the gradients in eqn (C13) and eqn (C14). The first of these can be expressed as

$$\nabla\langle\Omega_\gamma\rangle^\gamma=\mathbf{O}\left(\frac{\Delta\langle\Omega_\gamma\rangle^\gamma}{\Delta L}\right) \qquad \text{(C15)}$$

in which $\Delta\langle\Omega_\gamma\rangle^\gamma$ is the change in $\langle\Omega_\gamma\rangle^\gamma$ that takes place over the distance ΔL. It is convenient to define a length L_Ω by expressing eqn (C15) as

$$\nabla\langle\Omega_\gamma\rangle^\gamma=\mathbf{O}\left(\frac{\Delta\langle\Omega_\gamma\rangle^\gamma}{\Delta L}\right)=\mathbf{O}\left(\frac{\langle\Omega_\gamma\rangle^\gamma}{L_\Omega}\right). \qquad \text{(C16)}$$

When this is used with eqn (C13) we obtain

$$\langle\mathbf{y}_\gamma\rangle_{\gamma\kappa}/L_\Omega\ll 1. \qquad \text{(C17)}$$

The work of Quintard and Whitaker[33] suggests that $\langle\mathbf{y}_\gamma\rangle_{\gamma\kappa}<\ell_\gamma$, thus the constraint associated with the restriction given by eqn (C13) takes the form

$$\ell_\gamma/L_\Omega\ll 1. \qquad \text{(C18)}$$

Here one must remember that L_Ω is a characteristic length defined by eqn (C16) and that this characteristic length is determined by the variations of $K_{eq}\partial\langle c_\gamma\rangle^\gamma/\partial t$. Since K_{eq} will depend on $\langle c_\gamma\rangle^\gamma$ for a nonlinear adsorption isotherm, the manner in which $K_{eq}\partial\langle c_\gamma\rangle^\gamma/\partial t$ varies may be difficult to determine *a priori*. Our estimate of the second derivative in eqn (C14) begins with

$$\nabla\nabla\langle\Omega_\gamma\rangle^\gamma=\mathbf{O}\left[\frac{\Delta\left(\nabla\langle\Omega_\gamma\rangle^\gamma\right)}{\Delta L}\right] \qquad \text{(C19)}$$

in which $\Delta\left(\nabla\langle\Omega_\gamma\rangle^\gamma\right)$ is the change in $\nabla\langle\Omega_\gamma\rangle^\gamma$ that takes place over the distance ΔL. Following the previous estimate, we define a length $L_{\Omega1}$ by expressing eqn (C19) as

$$\nabla\nabla\langle\Omega_\gamma\rangle^\gamma=\mathbf{O}\left[\frac{\Delta\left(\nabla\langle\Omega_\gamma\rangle^\gamma\right)}{\Delta L}\right]=\mathbf{O}\left[\frac{\nabla\langle\Omega_\gamma\rangle^\gamma}{L_{\Omega1}}\right]. \qquad \text{(C20)}$$

Using eqn (C16) in this result provides us with our final estimate of the second derivative

$$\nabla\nabla\langle\Omega_\gamma\rangle^\gamma=\mathbf{O}\left[\frac{\Delta\left(\nabla\langle\Omega_\gamma\rangle^\gamma\right)}{\Delta L}\right]=\mathbf{O}\left[\frac{\langle\Omega_\gamma\rangle^\gamma}{L_{\Omega1}L_\Omega}\right]. \qquad \text{(C21)}$$

Use of this result in the restriction given by eqn (C14) leads to

$$\frac{\langle\mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}}{L_{\Omega1}L_\Omega}\ll 1 \qquad \text{(C22)}$$

and a little thought will indicate that $\langle\mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}\approx r_\sigma^2$ where r_σ is the radius of the averaging volume shown in Fig. 3. This estimate of $\langle\mathbf{y}_\gamma\mathbf{y}_\gamma\rangle_{\gamma\kappa}$ allows us to express eqn (C22) as

$$\frac{r_\sigma^2}{L_{\Omega1}L_\Omega}\ll 1. \qquad \text{(C23)}$$

It seems quite plausible that the constraints given by eqns (C18) and (C23) will be satisfied for most real systems. That is to say that significant variations of $K_{eq}\partial\langle c_\gamma\rangle^\gamma/\partial t$ will take place over distances that are large compared to either ℓ_γ or r_σ. As we move up the length scales illustrated in Fig. 2, it may be more difficult to satisfy constraints of the type represented by eqns (C18) and (C23).

Appendix C.2 Darcy scale

In the Darcy scale averaging for the σ-region, the diffusion and adsorption equation given by

$$\epsilon_\gamma(1+K)\frac{\partial c_\sigma}{\partial t}=\nabla\cdot(\mathbf{D}_\sigma\cdot\nabla c_\sigma) \qquad \text{(C24)}$$

in which the coefficient K is defined by

$$K=a_{\gamma\kappa}K_{eq}/\epsilon_\gamma. \qquad \text{(C25)}$$

In the averaging process, $\epsilon_\gamma(1 + K)$ is removed from a volume integral according to the simplification indicated by

$$\frac{1}{\mathcal{V}}\int_{V_\sigma}\epsilon_\gamma(1+K)\frac{\partial c_\sigma}{\partial t}\mathrm{d}V = \epsilon_\gamma(1+K)\left\{\frac{1}{\mathcal{V}}\int_{V_\sigma}\frac{\partial c_\sigma}{\partial t}\mathrm{d}V\right\}. \tag{C26}$$

If we let $\Omega_\sigma = \epsilon_\gamma(1 + K)$, we can repeat the procedure outlined by eqns C7 through C23 to obtain the following two constraints

$$\ell_\sigma/L_\Omega \ll 1 \tag{C27}$$

$$\frac{r_0^2}{L_{\Omega 1}L\Omega} \ll 1. \tag{C28}$$

Here we must remember that the characteristic lengths, L_Ω and $L_{\Omega 1}$, are now defined by the estimates

$$\nabla[\epsilon_\gamma(1+K)] = \mathbf{O}\left[\frac{\epsilon_\gamma(1+K)}{L_\Omega}\right] \tag{C29}$$

$$\nabla\nabla[\epsilon_\gamma(1+K)] = \mathbf{O}\left[\frac{\epsilon_\gamma(1+K)}{L_{\Omega 1}L_\Omega}\right]. \tag{C30}$$

In order to determine the characteristic length associated with the Darcy scale, one must have some idea about the isotherm as represented by eqn (C25). Here one must remember that

$$K = a_{\gamma\kappa}K_{eq}/\epsilon_\gamma \tag{C31}$$

where K_{eq} is given by eqn (C6). If the isotherm is linear, K_{eq} is a constant and L_Ω and $L_{\Omega 1}$ will differ from infinity only because of variations in ϵ_γ and $a_{\gamma\kappa}$. If the isotherm, represented by eqn (C5), is nonlinear, one needs to examine the constraints given by eqns (C27) and (C28) with some care. If the constraints are not satisfied, we are faced with a situation in which a coefficient cannot be linearized over the averaging volume and this leads to a very complex problem that has been explored only briefly by Quintard and Whitaker.[49]

Appendix C.3 Large scale

In the process of large-scale averaging for the η-region, we have made use of the simplification indicated by

$$\left\{\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\langle c\rangle_\eta}{\partial t}\right\} = \epsilon_\eta(1+\mathcal{K}_\eta)\left\{\frac{\partial\langle c\rangle_\eta}{\partial t}\right\}. \tag{C32}$$

If we let $\Omega_\eta = \epsilon_\eta(1 + \mathcal{K}_\eta)$, we can repeat the procedure outlined by eqns C7 through C23 to obtain the following two constraints

$$\ell_\eta/L_\Omega \ll 1 \tag{C33}$$

$$\frac{R_0^2}{L_{\Omega 1}L_\Omega} \ll 1. \tag{C34}$$

Now the characteristic lengths, L_Ω and $L_{\Omega 1}$, are defined by the estimates

$$\nabla[\epsilon_\eta(1+\mathcal{K}_\eta)] = \mathbf{O}\left[\frac{\epsilon_\eta(1+\mathcal{K}_\eta)}{L_\Omega}\right] \tag{C35}$$

$$\nabla\nabla[(1+\mathcal{K}_\eta)] = \mathbf{O}\left[\frac{\epsilon_\eta(1+\mathcal{K}_\eta)}{L_{\Omega 1}L_\Omega}\right]. \tag{C36}$$

Once again we note that these constraints will, for all practical purposes, be satisfied if the isotherm is linear. For the nonlinear case, knowledge of the isotherm represented by eqn (C25) is essential.

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