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Transport in chemically and mechanically heterogeneous porous media V. Two-equation model for solute transport with adsorption

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In this paper we develop the two-equation model for solute transport and adsorption in a two-region model of a mechanically and chemically heterogeneous porous medium. The closure problem is derived and the coefficients in both the one- and two-equation models are determined on the basis of the Darcy-scale parameters. Numerical experiments are carried out for a stratified system at the aquifer scale, and the results are compared with the one-equation model presented in Part IV and the two-equation model developed in this paper. Good agreement between the two-equation model and the numerical experiments is obtained. In addition, the two-equation model is used, in conjunction with a moment analysis, to derive a one-equation, non-equilibrium model that is valid in the asymptotic regime. Numerical results are used to identify the asymptotic regime for the one-equation, non-equilibrium model. © 1998 Elsevier Science Limited.

Key words: porous media, solute transport, adsorption, mathematical modelling.

NOMENCLATURE

$a_{\gamma\kappa}$	$= A_{\gamma\kappa}/\mathcal{V}_\sigma$, 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, $\mathcal{V}$, 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, $\mathcal{V}_\infty$, m^2
$\mathbf{b}_{\eta\eta}$	vector field that maps $\nabla\{\langle c_\eta\rangle^\eta\}^\eta$ onto $\tilde{c}_\eta$, m.
$\mathbf{b}_{\eta\omega}$	vector field that maps $\nabla\{\langle c_\omega\rangle^\omega\}^\omega$ onto $\tilde{c}_\eta$, m.
$\mathbf{b}_{\omega\omega}$	vector field that maps $\nabla\{\langle c_\omega\rangle^\omega\}^\omega$ onto $\tilde{c}_\omega$, m.
$\mathbf{b}_{\omega\eta}$	vector field that maps $\nabla\langle c_\eta\rangle^\eta\}^\eta$ onto $\tilde{c}_\omega$, m.
c_γ	point concentration in the γ-phase, mol m^{-3}.
$\langle c_\eta\rangle^\eta$	Darcy-scale intrinsic average concentration for the β–σ system in the η-region, mol m^{-3}.
$\langle c_\omega\rangle^\omega$	Darcy-scale intrinsic average concentration for the β–σ system in the ω-region, mol m^{-3}.
$\{\langle c_\eta\rangle^\eta\}$	η-region superficial average concentration, mol m^{-3}.
$\{\langle c_\eta\rangle^\eta\}^\eta$	$= \varphi_\eta^{-1}\{\langle c_\eta\rangle^\eta\}$, η-region intrinsic average concentration, mol 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, mol m^{-3}.
$\tilde{c}_\eta$	$= \langle c_\eta\rangle^\eta - \{\langle c_\eta\rangle^\eta\}^\eta$, spatial deviation concentration for the η-region, mol m^{-3}.
$\{\langle c_\omega\rangle^\omega\}$	ω-region superficial average concentration, mol m^{-3}.
$\{\langle c_\omega\rangle^\omega\}^\omega$	$= \varphi_\omega^{-1}\{\langle c_\omega\rangle^\omega\}$, ω-region intrinsic average concentration, mol m^{-3}.
$\tilde{c}_\omega$	$= \langle c_\omega\rangle^\omega - \{\langle c_\omega\rangle^\omega\}^\omega$, spatial deviation concentration for the ω-region, mol m^{-3}.
$\mathbf{D}_\eta^*$	dispersion tensor for the β–σ system in the η-region, m^2s^{-1}.
$\mathbf{D}_\omega^*$	dispersion tensor for the β–σ system in the ω-region, m^2s^{-1}.
$\mathbf{D}_{\eta\eta}^{**}$	dominant dispersion tensor for the η-region transport equation, m^2s^{-1}.

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$\mathbf{D}^{**}_{\eta\omega}$ coupling dispersion tensor for the η-region transport equation, $m^2 s^{-1}$.

$\mathbf{D}^{**}_{\omega\omega}$ dominant dispersion tensor for the ω-region transport equation, $m^2 s^{-1}$.

$\mathbf{D}^{**}_{\omega\eta}$ coupling dispersion tensor for the ω-region transport equation, $m^2 s^{-1}$.

$\mathbf{D}^{**}$ large-scale, one-equation model dispersion tensor, $m^2 s^{-1}$.

$\mathbf{g}$ gravitational acceleration vector, $m\ s^{-2}$.

g magnitude of the gravitational acceleration vector, $m\ s^{-2}$.

$\mathbf{I}$ 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.

$\mathcal{K}_\eta$ $=\left[(\epsilon_\sigma a_{\gamma\kappa})_\eta/\epsilon_\eta\right]\partial\mathcal{F}/\partial\langle c_\eta\rangle^\eta$, dimensionless equilibrium coefficient for the η-region.

$\mathcal{K}_\omega$ $=\left[(\epsilon_\sigma a_{\gamma\kappa})_\omega/\epsilon_\omega\right]\partial\mathcal{F}/\partial\langle c_\omega\rangle^\omega$, dimensionless equilibrium coefficient for the ω-region.

ℓ_i $i = 1,2,3$, lattice vectors, m.

ℓ_η length scale for the η-region, m.

ℓ_ω length scale for the ω-region, m.

$\mathcal{L}_c$ length scale for the region averaged concentrations, m.

$\mathcal{L}$ aquifer length scale, m.

$\mathcal{L}_H$ length scale of the aquifer heterogeneities, m.

$\mathbf{n}_{\eta\omega}$ $= -\mathbf{n}_{\omega\eta}$, unit normal vector directed from the η-region towards the ω-region.

r_σ radius of the averaging volume, $\mathcal{V}_\sigma$, for the σ-region, m.

r_o radius of the averaging volume, $\mathcal{V}$, for the β–σ system, m.

r_η scalar that maps $\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta$ onto $\tilde{c}_\eta$.

r_ω scalar that maps $\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta$ onto $\tilde{c}_\omega$.

R_o radius of the averaging volume, $\mathcal{V}_\infty$, for the η–ω system, m.

t time, s.

$\langle\mathbf{v}_\beta\rangle_\eta$ Darcy-scale, superficial average velocity in the η-region, $m\ s^{-1}$.

$\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta$ intrinsic regional average velocity in the η-region, $m\ s^{-1}$.

$\{\langle\mathbf{v}_\beta\rangle_\eta\}$ $=\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta$, superficial regional average velocity in the η-region, $m\ s^{-1}$.

$\tilde{\mathbf{v}}_{\beta\eta}$ $=\langle\mathbf{v}_\beta\rangle_\eta - \{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta$, η-region spatial deviation velocity, $m\ s^{-1}$.

$\langle\mathbf{v}_\beta\rangle_\omega$ Darcy-scale, superficial average velocity in the ω-region, $m\ s^{-1}$.

$\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega$ intrinsic regional average velocity in the ω-region, $m\ s^{-1}$.

$\{\langle\mathbf{v}_\beta\rangle_\omega\}$ $=\varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega$, superficial regional average velocity in the ω-region, $m\ s^{-1}$.

$\tilde{\mathbf{v}}_{\beta\omega}$ $=\langle\mathbf{v}_\beta\rangle_\omega - \{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega$, ω-region spatial deviation velocity, $m\ s^{-1}$.

$\{\langle\mathbf{v}_\beta\rangle\}$ $=\varphi_\eta\{\langle\mathbf{v}_\beta\rangle_\eta\}^\eta + \varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega$, large-scale, superficial average velocity, $m\ s^{-1}$.

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 symbols

α^* mass exchange coefficient for the η–ω system, s^{-1}.

ϵ $=\epsilon_\beta + \epsilon_\sigma\epsilon_\gamma$, total porosity for the β–σ system.

ϵ_η $=\epsilon_{\beta\eta} + (\epsilon_\sigma\epsilon_\gamma)_\eta$, total porosity for the η-region.

ϵ_ω $=\epsilon_{\beta\omega} + (\epsilon_\sigma\epsilon_\gamma)_\omega$, total porosity for the ω-’“n.

$\{\epsilon\}$ $=\varphi_\eta\epsilon_\eta + \varphi_\omega\epsilon_\omega$, large-scale average porosity.

$\{\epsilon\}(1+\{\mathcal{K}\})$ $=\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta + \epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega$, large-scale average capacitance factor.

φ_η $= 1 - \varphi_\omega$, volume fraction of the η-region.

φ_ω $= 1 - \varphi_\eta$, volume fraction of the ω-region.

1 INTRODUCTION

Dispersion in heterogeneous media has received a great deal of attention from a variety of scientists who are concerned with mass transport in geological formations. It is commonly accepted that dispersion through natural systems such as aquifers and reservoirs involves many different length scales, from the pore scale to the field scale. If one considers the solute transport in such formations, these multiple scales may lead to anomalous and non-Fickian dispersion at the field scale.[1–4] Here we need to be precise and note that *anomalous dispersion* refers to the interpretation of field-scale data that does not fit the response of a field-scale homogeneous representation. Similarly, the existence of multiple scales has been related to the observation that dispersivity is field-scale dependent (see a review by Gelhar *et al*.[5]), and the theoretical implications of this idea have been discussed extensively.[6,7] Clearly, a field-scale description calls for a representation in terms of a heterogeneous domain, and we adopt this point of view in this paper.

1.1 Hierarchical systems

A schematic representation of the problem under consideration is illustrated in Fig. 1. While many intermediate scales could be incorporated into the analysis, this study is limited to four typical scales that can be described as follows:

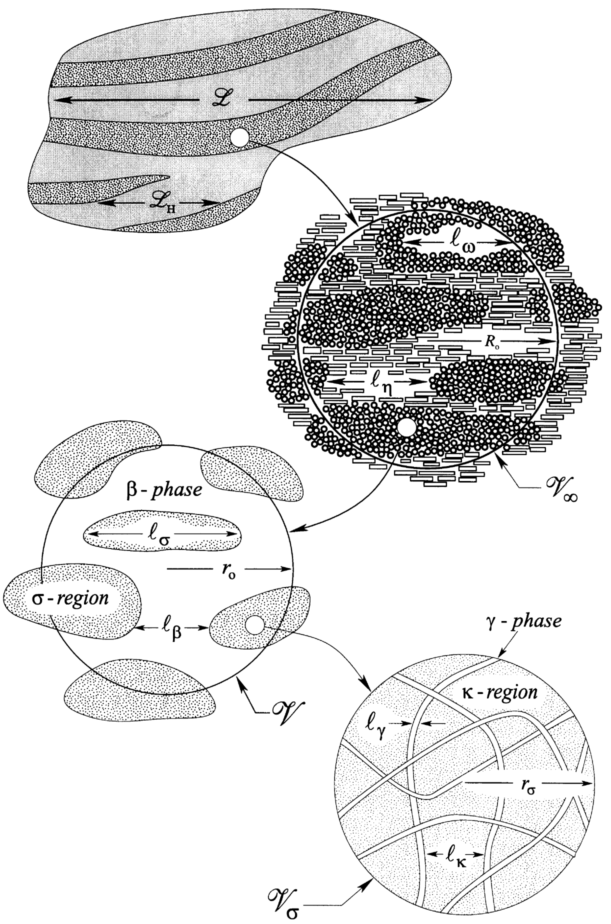

Fig. 1. Averaging volumes in a hierarchical porous medium.

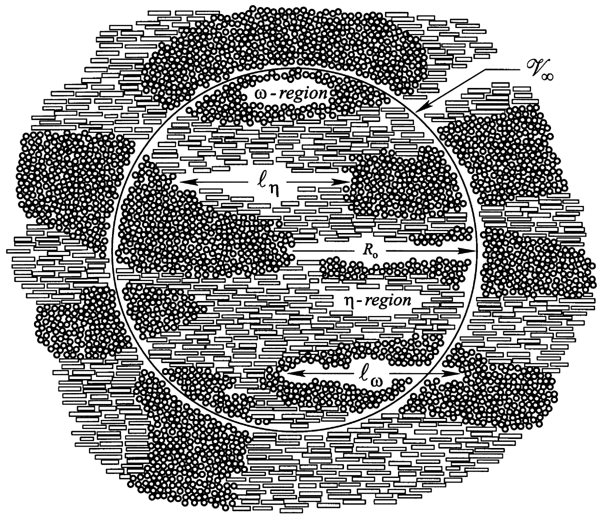

Fig. 2. Two-region model of a heterogeneous porous medium.

1. the macropore scale, in which averaging takes place over the volume $\mathcal{V}_\sigma$;
2. the Darcy scale, in which averaging takes place over the volume $\mathcal{V}$;
3. the local heterogeneity scale, in which averaging takes place over the volume $\mathcal{V}_\infty$;
4. the reservoir- or aquifer-scale heterogeneities, which have been identified by the length scale $\mathcal{L}_{\mathrm{H}}$ in Fig. 1; no averaging volume has been associated with this length scale since the governing equations will be solved numerically at this scale.

As we suggested in Part IV[8], many applications will require the addition of a micropore scale when the κ-region illustrated in Fig. 1 contains micropores, and many realistic systems may contain other intermediate length scales either within the β–σ system or within the heterogeneities associated with the averaging volume $\mathcal{V}_\infty$. When these length scales are disparate, the method of volume averaging can be used to carry information about the physical processes from a smaller length scale to a larger one, and eventually to the scale at which the final analysis is performed. When the length scales are not disparate, one is confronted with the problem of evolving heterogeneities.[4]

In this study we assume that the macropore scale, the Darcy scale and the local heterogeneity scale are conveniently separated. This assumption was also imposed on the analysis presented in Part IV[8], and there it led to a Darcy-scale representation of the dispersion process. The analysis required, among other constraints, that

$$\ell_\kappa, \ell_\gamma \ll r_\sigma \ll \ell_\beta, \ell_\sigma \ll r_{\mathrm{o}} \ll \ell_\eta, \ell_\omega \tag{1}$$

In the multiple-scale problem under consideration in this paper, Darcy-scale properties are point-dependent, and there is a need for a large-scale description. It is generally assumed[9,10] that local heterogeneity-scale permeability variations are 'stationary'. In other words, gradients of the large-scale averaged quantities, which are characteristic of the regional variations, may be assumed to have negligible impact on the change-of-scale problem for characteristic lengths equivalent to the large-scale averaging volume represented by the subscript ∞ in Fig. 1. Based on this assumption, and provided that the following length-scale constraints are satisfied:

$$\ell_\eta, \ell_\omega \ll R_{\mathrm{o}} \ll \mathcal{L}_{\mathrm{H}} \leq \mathcal{L} \tag{2}$$

there is some possibility that a large-scale description exists for the large-scale dispersion process. Here, we mention the *possible* existence of an averaged description to remind the reader that process-dependent scales are involved in the analysis, and this may lead to conditions that do not permit the development of closed-form volume-averaged transport equations.

Within this framework, we indicated in Part IV[8] how a local heterogeneity-scale equilibrium dispersion equation could be derived from the Darcy-scale problem provided that certain length and time scales constraints were fulfilled. In this paper, *we remove these latter constraints*, and we present an analysis leading to a large-scale, non-equilibrium model for solute dispersion in heterogeneous porous media. The removal of these constraints naturally leads to a better description of the process, and this is clearly demonstrated in our comparison between theory and numerical experiments. The penalty that one pays for this improved description is the increased number of effective coefficients that appear in the two-equation model. If laboratory experiments are required in order to determine these additional coefficients, one is confronted with an extremely difficult task; however, in our theoretical development all the coefficients can be determined on the basis of a single, representative unit cell. This means that all the coefficients in the large-scale averaged equations are self-consistent and based on a single model of the local heterogeneities.

The large-scale model that results from our analysis features large-scale properties which are point-dependent with a characteristic length scale, $\mathcal{L}_{\mathrm{H}}$, describing the regional heterogeneities. These regional heterogeneities are incorporated into any field-scale numerical description. They will certainly contribute to anomalous, non-Fickian field-scale behaviour, but this behaviour will be taken care of by the field-scale calculations and the large-scale averaged transport equations.

1.2 Large-scale averaging

Within this multiple-scale scheme, we focus our attention on the large-scale averaging volume illustrated in Fig. 2 and thus restrict the analysis to a two-region model of a heterogeneous porous medium. It is important to understand that the general theory is easily extended to systems containing *many distinct regions*, and an example of this is given by Ahmadi and Quintard[11]. Systems of the type illustrated in Fig. 2 are characterized by an intense advection in the more permeable region, while a more diffusive process takes place in the less permeable region. Observations of many similar systems, often referred to as systems with stagnant regions or mobile–immobile regions, have been reported in the literature (see reviews[12,13]). The expected large-scale behaviour is characterized by large-scale dispersion with retardation caused by the exchange of mass between the different zones. Models proposed for describing solute transport in such cases correspond to the introduction of a retardation factor in the dispersion equation, or a two-equation model for the mobile and immobile regions[14–21] (see also the reviews cited above[12,13]). Extensions of these models have been proposed for mobile water in both regions (Skopp *et al.*[22], for the case of small interaction between the two regions, and Gerke and van Genuchten[23]). In the paper by Gerke and van Genuchten, the solute inter-porosity exchange term is related intuitively to the water inter-porosity exchange term, i.e. in the case of local mechanical non-equilibrium, and to an estimate of the diffusive part that resembles previously proposed estimates in the case of mobile–immobile systems. It should be noted that the model of Gerke and van Genuchten[23] accounts for variably saturated porous media, a case that is beyond the scope of this paper.

In this paper, we propose a general formulation of these two-equation models using the method of large-scale averaging. We obtain an *explicit relationship* between the local scale structure and the large-scale equations, suitable for predictions of large-scale properties, which incorporates both coupled dispersive and diffusive contributions. Finally, this methodology is illustrated in the case of dispersion in a stratified system for which we compare the theory both with numerical experiments and with the non-equilibrium, one-equation model of Marle *et al.*[24]

The Darcy-scale process of solute transport with adsorption in the η–ω system shown in Fig. 2 is given by

$$\epsilon_\eta\left(1+\mathcal{K}_\eta\right)\frac{\partial\langle c_\eta\rangle^\eta}{\partial t}+\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta\right)=\nabla\cdot\left(\mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right) \tag{3}$$

$$\text{B.C.1}\quad \langle c_\eta\rangle^\eta=\langle c_\omega\rangle^\omega,\ \text{ at } A_{\eta\omega} \tag{4}$$

$$\text{B.C.2}\quad -\mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right)=-\mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega\langle c_\omega\rangle^\omega-\mathbf{D}^*_\omega\cdot\nabla\langle c_\omega\rangle^\omega\right),\ \text{ at } A_{\eta\omega} \tag{5}$$

$$\epsilon_\omega\left(1+\mathcal{K}_\omega\right)\frac{\partial\langle c_\omega\rangle^\omega}{\partial t}+\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega\langle c_\omega\rangle^\omega\right)=\nabla\cdot\left(\mathbf{D}^*_\omega\cdot\nabla\langle c_\omega\rangle^\omega\right) \tag{6}$$

Here $\mathcal{K}_\eta$ and $\mathcal{K}_\omega$ represent the Darcy-scale equilibrium adsorption coefficients, which may be non-linear functions of the concentrations, $\langle c_\eta\rangle^\eta$ and $\langle c_\omega\rangle^\omega$. In addition to the solute transport equations, we shall need to make use of the two Darcy-scale continuity equations that take the form

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\eta=0 \tag{7a}$$

$$\nabla\cdot\langle \mathbf{v}_\beta\rangle_\omega=0 \tag{7b}$$

along with the boundary condition for the normal component of the velocity, which is given by[25,26]

$$\text{B.C.3}\quad \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta=\mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\omega,\ \text{ at } A_{\eta\omega} \tag{8}$$

In Part IV[8] the region-average transport equations were developed, and the *superficial* average forms are given by

η-region:

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

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

$$-\underbrace{\nabla\cdot\left(\varphi_\eta\left\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\right\}^\eta\right)}_{large\text{-}scale\ dispersion}-\underbrace{\frac{1}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right)dA}_{inter\text{-}region\ flux}\tag{9a}$$

ω-region:

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

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

$$-\underbrace{\nabla\cdot\left(\varphi_\omega\left\{\tilde{\mathbf{v}}_{\beta\omega}\tilde{c}_\omega\right\}^\omega\right)}_{large\text{-}scale\ dispersion}-\underbrace{\frac{1}{\mathscr{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\left(\langle\mathbf{v}_\beta\rangle_\omega\langle c_\omega\rangle^\omega-\mathbf{D}^*_\omega\cdot\nabla\langle c_\omega\rangle^\omega\right)dA}_{inter\text{-}region\ flux}\tag{9b}$$

In our study of the one-equation model presented in Part IV, we made use of the single, large-scale continuity equation; however, in the analysis of mass transport processes using the two-equation model, we shall need the regional forms of the two continuity equations. These can be expressed as:

η-region:

$$\nabla\cdot\{\langle\mathbf{v}_\beta\rangle_\eta\}+\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\langle\mathbf{v}_\beta\rangle_\eta\,\mathrm{d}A=0\tag{10a}$$

ω-region:

$$\nabla\cdot\{\langle\mathbf{v}_\beta\rangle_\omega\}+\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\langle\mathbf{v}_\beta\rangle_\omega\,\mathrm{d}A=0\tag{10b}$$

Because the regional velocities are not solenoidal, as are the Darcy-scale velocities contained in eqns (7), one must take special care with the various forms of the regional continuity equations.

In eqns (9), we see various large-scale terms such as $\partial\{\langle c_\eta\rangle^\eta\}^\eta/\partial t$ in eqn (9a) and $\varphi_\omega\{\langle\mathbf{v}_\beta\rangle_\omega\}^\omega\{\langle c_\omega\rangle^\omega\}^\omega$ in eqn (9b), and we see other terms such as $\mathbf{n}_{\eta\omega}\tilde{c}_\eta$ and $\mathbf{v}_{\beta\omega}\tilde{c}_\omega$

that involve the *spatial deviation quantities*. In addition, the inter-region flux is specified entirely in terms of the *Darcy-scale variables* such as $\langle v_\beta \rangle_\eta$ and $\langle c_\omega \rangle^\omega$. In the following section we shall develop the closure problem which will allow us to determine the diffusive terms such as $\{\tilde{\mathbf{D}}^*_\eta \cdot \nabla \tilde{c}_\eta\}$ and the dispersive terms such as $\{\tilde{\mathbf{v}}_{\beta\omega} \tilde{c}_\omega\}^\omega$. More importantly, we shall develop a representation for the inter-region flux that is determined entirely by the closure problem. This means that the representation for the inter-region flux is limited by all the simplifications that are made in development of the closure problem.

2 CLOSURE PROBLEM

In the development of a one-equation model, one adds eqns (9a) and (9b) to obtain a single transport equation in which the inter-region flux terms cancel. In that case, the closure problem is used only to determine the effective coefficients associated with diffusion and dispersion. For the two-equation model under consideration here, the closure problem completely determines the *functional form* of the inter-region flux and the effective coefficients which appear in the representation of that flux. Closure problems can be developed in a relatively general manner; however, the development of a *local closure problem* requires the use of a spatially periodic model. This means that some very specific simplifications will be imposed on our representation for the inter-region flux and for the large-scale dispersion; however, these simplifications are not imposed on the other terms in eqns (9a) and (9b).

2.1 Inter-region flux

In the development of a two-equation model, we need to represent the inter-region flux terms in a useful form, and this means decomposing that flux into large-scale quantities and spatial deviation quantities. Directing our attention to the η-region transport equation, we make use of the decomposition

$$\langle c_\eta \rangle^\eta = \{\langle c_\eta \rangle^\eta\}^\eta + \tilde{c}_\eta \tag{11}$$

in order to express the inter-region flux as

$$\begin{aligned}\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \langle c_\eta\rangle^\eta - \mathbf{D}^*_\eta\cdot\nabla\langle c_\eta\rangle^\eta\right) \mathrm{d}A \\ = \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \{\langle c_\eta\rangle^\eta\} - \mathbf{D}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right) \mathrm{d}A \\ + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \tilde{c}_\eta - \mathbf{D}^*_\eta\cdot\nabla\tilde{c}_\eta\right) \mathrm{d}A\end{aligned} \tag{12}$$

The second term on the right-hand side of this result is in a convenient form for use with eqn (9a) since the unit cell closure calculations will provide us with values for both $\langle \mathbf{v}_\beta\rangle_\eta$ and $\mathbf{D}^*_\eta$; however, we need to consider carefully how we treat the first term. In the derivation of eqn (9a) we made use of the following decomposition for the dispersion tensor:

$$\mathbf{D}^*_\eta = \{\mathbf{D}^*_\eta\}^\eta + \tilde{\mathbf{D}}^*_\eta \tag{13}$$

When this decomposition is used with eqn (12), we can express the first term on the right-hand side as

$$\begin{aligned}\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot(\langle \mathbf{v}_\beta\rangle_\eta \{\langle c_\eta\rangle^\eta\}^\eta - \mathbf{D}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta)\, \mathrm{d}A = \\ \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\Big(\langle \mathbf{v}_\beta\rangle_\eta \{\langle c_\eta\rangle^\eta\}^\eta - \{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \\ + \tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\Big)\, \mathrm{d}A\end{aligned} \tag{14}$$

The large-scale averaged quantities can be removed from the first two terms on the right-hand side of eqn (14); however, we shall leave the gradient of the large-scale average concentration inside the third term to obtain

$$\begin{aligned}\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot(\langle \mathbf{v}_\beta\rangle_\eta \{\langle c_\eta\rangle^\eta\}^\eta - \mathbf{D}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta)\, \mathrm{d}A \\ = \left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}A\right]\{\langle c_\eta\rangle^\eta\}^\eta \\ - \left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\, \mathrm{d}A\right]\cdot\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \\ - \left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\, \mathrm{d}A\right]\end{aligned} \tag{15}$$

One can show that the first term on the right-hand side of this result is zero for a spatially periodic system. This occurs because the periodicity condition for the velocity,

$$\text{Periodicity :}\quad \langle \mathbf{v}_\beta\rangle_\eta(\mathbf{r}+\ell_i) = \langle \mathbf{v}_\beta\rangle_\eta(\mathbf{r}),\ i = 1,2,3 \tag{16}$$

allows us to write

$$\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}A = \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}A + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\mathrm{e}}} \mathbf{n}_{\eta\mathrm{e}}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}A \tag{17}$$

in which $A_{\eta\mathrm{e}}$ represents the area of entrances and exits for the η-region contained in a unit cell of a spatially periodic porous medium. Use of the divergence theorem and eqn (7) allows us to express eqn (17) as

$$\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}A = \frac{1}{\mathcal{V}_\infty}\int_{V_\eta} \nabla\cdot\langle \mathbf{v}_\beta\rangle_\eta\, \mathrm{d}V = 0 \tag{18}$$

and use of this result with eqn (15) leads to the form

$$\begin{aligned}\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \{\langle c_\eta\rangle^\eta\}^\eta - \mathbf{D}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right) \mathrm{d}A \\ = -\left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\, \mathrm{d}A\right]\cdot\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \\ - \left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\, \mathrm{d}A\right]\end{aligned} \tag{19}$$

Considering the first term on the right-hand side of this result, we make use of the averaging theorem to obtain

$$-\left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\,\mathrm{d}A\right]\cdot\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\langle c_\eta\rangle^\eta\}^\eta$$

$$=\nabla\varphi_\eta\cdot\{\mathbf{D}^*_\eta\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \tag{20}$$

For a spatially periodic system, $\nabla\varphi_\eta$ is zero and eqn (20) allows us to express eqn (19) as

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

$$=-\left[\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\,\mathrm{d}A\right] \tag{21}$$

We are now ready to return to eqn (12) and express that inter-region flux according to

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

$$=\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta-\mathbf{D}^*_\eta\cdot\nabla\tilde{c}_\eta-\tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right)\,\mathrm{d}A \tag{22}$$

Substitution of this result into eqn (9a) leads to a form of the large-scale average transport equation that is ready to receive results from the closure problem.

η-region:

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

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

$$-\underbrace{\nabla\cdot\left(\varphi_\eta\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\}^\eta\right)}_{\textit{large-scale dispersion}}-\underbrace{\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta-\mathbf{D}^*_\eta\cdot\nabla\tilde{c}_\eta-\tilde{\mathbf{D}}^*_\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right)dA}_{\textit{inter-region flux}} \tag{23a}$$

Here we should note that every term in this result is either a large-scale average quantity or a spatial deviation quantity *except for* the Darcy-scale velocity, $\langle\mathbf{v}_\beta\rangle_\eta$. This Darcy-scale quantity has not been decomposed like all the other terms, because it will be available to us directly by solution of the Darcy-scale mass and momentum equations for a unit cell in a spatially periodic model of a heterogeneous porous medium. The analogous result for the ω-region can be obtained from eqn (9b) and is given by

ω-region:

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

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

$$-\underbrace{\nabla\cdot\left(\varphi_\omega\{\tilde{\mathbf{v}}_{\beta\omega}\tilde{c}_\omega\}^\omega\right)}_{\textit{large-scale dispersion}}-\underbrace{\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}}\mathbf{n}_{\omega\eta}\cdot\left(\langle\mathbf{v}_\beta\rangle_\omega\tilde{c}_\omega-\mathbf{D}^*_\omega\cdot\nabla\tilde{c}_\omega-\tilde{\mathbf{D}}^*_\omega\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega\right)dA}_{\textit{inter-region flux}} \tag{23b}$$

In order to evaluate the terms in eqns (23a) and (23b) that contain the spatial deviation concentrations, we need to develop the closure problem for $\tilde{c}_\eta$ and $\tilde{c}_\omega$. The governing differential equation for $\tilde{c}_\eta$ can be obtained by subtracting the *intrinsic form* of eqn (23a) from the Darcy-scale equation for $\langle c_\eta\rangle^\eta$ that is given by eqn (3). We develop the intrinsic form of eqn (23a) by dividing that result by φ_η, and this leads to a rather complicated result. However, prior studies[27,28] clearly indicate that it is an acceptable approximation to ignore variations of the volume fraction, φ_η, *in the development of the closure problem*, and this means that the intrinsic form of eqn (23a) can be expressed as

$$\begin{aligned}\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t}+\nabla\cdot\left[\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right]\\ =\nabla\cdot\left[\{\mathbf{D}_\eta^*\}^\eta\cdot\left(\nabla\{\langle c_\eta\rangle^\eta\}^\eta+\frac{\varphi_\eta^{-1}}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{c}_\eta\,\mathrm{d}A\right)\right.\\ \left.+\left\{\tilde{\mathbf{D}}_\eta^*\cdot\nabla\tilde{c}_\eta\right\}^\eta\right]-\nabla\cdot(\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\}^\eta)\\ -\frac{\varphi_\eta^{-1}}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\Big(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta-\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta\\ -\tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\Big)\,\mathrm{d}A\end{aligned}\tag{24}$$

Subtraction of this result from eqn (3) leads to

$$\begin{aligned}\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\tilde{c}_\eta}{\partial t}+\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right)\\ =\nabla\cdot(\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta-\{\mathbf{D}_\eta^*\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta)\\ -\nabla\cdot\left[\frac{\varphi_\eta^{-1}\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{c}_\eta\,\mathrm{d}A+\left\{\tilde{\mathbf{D}}_\eta^*\cdot\nabla\tilde{c}_\eta\right\}^\eta\right]\\ +\nabla\cdot\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\}^\eta+\frac{\varphi_\eta^{-1}}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\Big(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta\\ -\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta-\tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\Big)\,\mathrm{d}A\end{aligned}\tag{25}$$

Directing our attention to the convective transport term in eqn (25), we make use of the velocity decomposition given by

$$\langle\mathbf{v}_\beta\rangle_\eta=\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta+\tilde{\mathbf{v}}_{\beta\eta}\tag{26}$$

to obtain

$$\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta=\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta+\tilde{\mathbf{v}}_{\beta\eta}\{\langle c_\eta\rangle^\eta\}^\eta\tag{27}$$

Within the framework of the closure problem, we can use eqns (10) and (18) to obtain

$$\nabla\cdot\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}=0\tag{28}$$

and since we are ignoring variations of φ_η, the continuity equation for the intrinsic regional average velocity takes the form

$$\nabla\cdot\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta=0\tag{29}$$

This result, along with the continuity equation given by eqn (7a) and the decomposition given by eqn (26), can be used to express the convective transport terms in eqn (25) as

$$\begin{aligned}\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\langle c_\eta\rangle^\eta-\left\{\langle\mathbf{v}_\beta\rangle_\eta\right\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right)=\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta\right)\\ +\tilde{\mathbf{v}}_{\beta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\end{aligned}\tag{30}$$

Use of the decomposition for the dispersion tensor given by eqn (13) leads to the following representation for the two dispersive fluxes:

$$\mathbf{D}_\eta^*\cdot\nabla\langle c_\eta\rangle^\eta-\{\mathbf{D}_\eta^*\}^\eta\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta=\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta+\tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\tag{31}$$

When eqns (30) and (31) are used in eqn (25), our transport equation for the spatial deviation concentration takes the form

$$\begin{aligned}\varepsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\tilde{c}_\eta}{\partial t}+\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta\right)+\underbrace{\tilde{\mathbf{v}}_{\beta\eta}\cdot\nabla\left\{\langle c_\eta\rangle^\eta\right\}^\eta}_{\textit{convective source}}-\nabla\cdot\left\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\right\}^\eta+\\ =\nabla\cdot\left(\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta\right)+\underbrace{\nabla\cdot\left(\tilde{\mathbf{D}}_\eta^*\cdot\nabla\left\{\langle c_\eta\rangle^\eta\right\}^\eta\right)}_{\textit{diffusive source}}-\nabla\cdot\left[\frac{\varphi_\eta^{-1}\left\{\mathbf{D}_\eta^*\right\}^\eta}{\mathcal{V}_\infty}\cdot\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\tilde{c}_\eta\,dA+\left\{\tilde{\mathbf{D}}_\eta^*\cdot\nabla\tilde{c}_\eta\right\}^\eta\right]\\ +\frac{\varphi_\eta^{-1}}{\mathcal{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta-\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta-\tilde{\mathbf{D}}_\eta^*\cdot\nabla\left\{\langle c_\eta\rangle^\eta\right\}^\eta\right)dA\end{aligned}\tag{32}$$

As a final simplification of this closure problem, we make use of the averaging theorem to write

$$\{\nabla\tilde{c}_\eta\} = \nabla\{\tilde{c}_\eta\} + \frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\tilde{c}_\eta \, dA \tag{33}$$

and setting the average of the deviation equal to zero allows us to express this result as

$$\frac{\varphi_\eta^{-1}}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\tilde{c}_\eta \, dA = \{\nabla\tilde{c}_\eta\}^\eta \tag{34}$$

Multiplication by $\{\mathbf{D}_\eta^*\}^\eta$ provides

$$\frac{\varphi_\eta^{-1}\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty}\cdot\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\tilde{c}_\eta \, dA = \{\{\mathbf{D}_\eta^*\}^\eta\cdot\nabla\tilde{c}_\eta\}^\eta \tag{35}$$

and this allows us to express eqn (32) in the slightly more compact form given by

$$\varepsilon_\eta(1+\mathscr{K}_\eta)\frac{\partial\tilde{c}_\eta}{\partial t} + \nabla\cdot(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta) + \underbrace{\tilde{\mathbf{v}}_{\beta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta}_{convective\ source} - \nabla\cdot\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\}^\eta =$$

$$= \nabla\cdot(\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta) + \underbrace{\nabla\cdot(\tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta)}_{diffusive\ source} - \nabla\cdot\{\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta\}^\eta$$

$$+ \frac{\varphi_\eta^{-1}}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta - \mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta - \tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right)dA \tag{36}$$

If we estimate the accumulation and diffusive terms according to

$$\epsilon_\eta(1+\mathcal{K}_\eta)\frac{\partial\tilde{c}_\eta}{\partial t} = \mathbf{O}\left[\frac{\epsilon_\eta(1+\mathcal{K}_\eta)\tilde{c}_\eta}{t^*}\right] \tag{37}$$

$$\nabla\cdot(\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta) = \mathbf{O}\left[\frac{\mathsf{D}_\eta^*\tilde{c}_\eta}{\ell_\eta^2}\right] \tag{38}$$

the closure equation for $\tilde{c}_\eta$ will be quasi-steady when the following constraint is satisfied:

$$\frac{\mathsf{D}_\eta^* t^*}{\ell_\eta^2\epsilon_\eta(1+\mathcal{K}_\eta)} \gg 1 \tag{39}$$

This *type of constraint* has already been imposed at both the small scale and the Darcy scale, and it is not unreasonable to impose it at the large scale, since $\mathbf{D}_\eta^*$ will increase with increasing values of ℓ_η. The convective transport term and the large-scale dispersive transport term in eqn (36) can be estimated according to

$$\nabla\cdot(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta) = \mathbf{O}\left[\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta/\ell_\eta\right] \tag{40}$$

$$\nabla\cdot\{\tilde{\mathbf{v}}_{\beta\eta}\tilde{c}_\eta\} = \mathbf{O}\left[\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta/\mathcal{L}_c\right] \tag{41}$$

and this allows us to neglect the large-scale dispersive transport whenever the length scales of the heterogeneities are constrained by

$$\ell_\eta, \ell_\omega \ll \mathcal{L}_c \tag{42}$$

Moving on to the diffusive terms, we keep eqn (38) in mind and estimate the non-local term as

$$\nabla\cdot\{\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta\} = \mathbf{O}\left[\frac{\mathsf{D}_\eta^*\tilde{c}_\eta}{\mathcal{L}_c\ell_\eta}\right] \tag{43}$$

and we see that this term can also be neglected whenever the constraint given by eqn (42) is satisfied.

On the basis of eqns (39) and (42) we shall simplify the transport equation for $\tilde{c}_\eta$ to the following form:

$$\nabla\cdot(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta) + \underbrace{\tilde{\mathbf{v}}_{\beta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta}_{convective\ source} = \nabla\cdot(\mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta) + \underbrace{\nabla\cdot(\tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta)}_{diffusive\ source} -$$

$$+ \frac{\varphi_\eta^{-1}}{\mathscr{V}_\infty}\int_{A_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\tilde{c}_\eta - \mathbf{D}_\eta^*\cdot\nabla\tilde{c}_\eta - \tilde{\mathbf{D}}_\eta^*\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right)dA \tag{44}$$

Here we note that our closure equation will be homogeneous in $\tilde{c}_\eta$ if the gradient of the regional average concentration is zero. For this reason we have identified the two terms involving this gradient as the *sources* of the $\tilde{c}_\eta$-field. An analogous form can be derived for the ω-region transport equation, and the two will be connected by the interfacial boundary conditions.

On the basis of eqns (4), (5) and (8), we see that the boundary conditions take the form

$$\text{B.C.1} \quad \langle c_\eta \rangle^\eta = \langle c_\omega \rangle^\omega, \ \text{at } A_{\eta\omega} \tag{45}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\eta^* \cdot \nabla \langle c_\eta \rangle^\eta = \mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\omega^* \cdot \nabla \langle c_\omega \rangle^\omega, \ \text{at } A_{\eta\omega} \tag{46}$$

and when we use the decompositions given by eqn (11), we shall obtain the boundary conditions in terms of the desired spatial deviation concentrations, $\tilde{c}_\eta$ and $\tilde{c}_\omega$. This leads us to the closure problem as follows.

2.2 Closure problem

$$\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \tilde{c}_\eta \right) + \underbrace{\tilde{\mathbf{v}}_{\beta\eta} \cdot \nabla \left\{ \langle c_\eta \rangle^\eta \right\}^\eta}_{convective\ source} = \nabla \cdot \left(\mathbf{D}_\eta^* \cdot \nabla \tilde{c}_\eta \right) + \underbrace{\nabla \cdot \left(\tilde{\mathbf{D}}_\eta^* \cdot \nabla \left\{ \langle c_\eta \rangle^\eta \right\}^\eta \right)}_{diffusive\ source} - $$
$$+ \frac{\varphi_\eta^{-1}}{\mathscr{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \tilde{c}_\eta - \mathbf{D}_\eta^* \cdot \nabla \tilde{c}_\eta - \tilde{\mathbf{D}}_\eta^* \cdot \nabla \left\{ \langle c_\eta \rangle^\eta \right\}^\eta \right) dA \tag{47a}$$

$$\text{B.C.1} \quad \tilde{c}_\eta = \tilde{c}_\omega + \underbrace{\left(\left\{ \langle c_\omega \rangle^\omega \right\}^\omega - \left\{ \langle c_\eta \rangle^\eta \right\}^\eta \right)}_{exchange\ source}, \quad at\ A_{\eta\omega} \tag{47b}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\eta^* \cdot \nabla \tilde{c}_\eta + \underbrace{\mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\eta^* \cdot \nabla \left\{ \langle c_\eta \rangle^\eta \right\}^\eta}_{diffusive\ source}$$
$$= \mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\omega^* \cdot \nabla \tilde{c}_\omega + \underbrace{\mathbf{n}_{\eta\omega} \cdot \mathbf{D}_\omega^* \cdot \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega}_{diffusive\ source}, \quad at\ A_{\eta\omega} \tag{47c}$$

$$\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \tilde{c}_\omega \right) + \underbrace{\tilde{\mathbf{v}}_{\beta\omega} \cdot \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega}_{convective\ source} = \nabla \cdot \left(\mathbf{D}_\omega^* \cdot \nabla \tilde{c}_\omega \right) + \underbrace{\nabla \cdot \left(\tilde{\mathbf{D}}_\omega^* \cdot \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega \right)}_{diffusive\ source}$$
$$+ \frac{\varphi_\omega^{-1}}{\mathscr{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \tilde{c}_\omega - \mathbf{D}_\omega^* \cdot \nabla \tilde{c}_\omega - \tilde{\mathbf{D}}_\omega^* \cdot \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega \right) dA \tag{47d}$$

$$\text{Periodicity}: \quad \tilde{c}_\eta(\mathbf{r} + \ell_i) = \tilde{c}_\eta(\mathbf{r}), \ \tilde{c}_\omega(\mathbf{r} + \ell_i) = \tilde{c}_\omega(\mathbf{r}), \quad i = 1, 2, 3 \tag{47e}$$

$$\text{Average}: \quad \{\tilde{c}_\eta\}^\eta = 0, \ \{\tilde{c}_\omega\}^\omega = 0 \tag{47f}$$

Here it should be clear that all the *sources*, or the non-homogeneous terms in this boundary value problem, can be expressed in terms of the two concentration gradients and the concentration difference, i.e.

$$\text{Sources}: \quad \nabla \left\{ \langle c_\eta \rangle^\eta \right\}^\eta, \ \nabla \left\{ \langle c_\omega \rangle^\omega \right\}^\omega, \ \left(\left\{ \langle c_\omega \rangle^\omega \right\}^\omega - \left\{ \langle c_\eta \rangle^\eta \right\}^\eta \right)$$

At this point we have replaced the original problem by a set of large-scale averaged equations and a local-scale closure problem involving the large-scale variables and the spatial deviations. Our objective now is to obtain an approximate solution of this problem. Following ideas developed in the treatment of heat transfer in porous media[27,29–32], or in dealing with the flow of a slightly compressible fluid in a heterogeneous porous medium[33,34], this suggests representations for the spatial deviation concentrations of the form

$$\tilde{c}_\eta = \mathbf{b}_{\eta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta + \mathbf{b}_{\eta\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega + r_\eta(\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta) \tag{48a}$$

$$\tilde{c}_\omega = \mathbf{b}_{\omega\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta + \mathbf{b}_{\omega\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega + r_\omega(\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta) \tag{48b}$$

in which we refer to $\mathbf{b}_{\eta\eta}$, $\mathbf{b}_{\omega\eta}$, r_ω, etc., as the *closure variables*. In terms of these closure variables, there are three closure problems that result from eqns (47), and the first of these is given by

Problem I

$$\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\mathbf{b}_{\eta\eta}\right) + \tilde{\mathbf{v}}_{\beta\eta} = \nabla\cdot(\mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\eta}) + \nabla\cdot\tilde{\mathbf{D}}^*_\eta - \varphi_\eta^{-1}\mathbf{c}_{\eta\eta} \tag{49a}$$

$$\text{B.C.1} \quad \mathbf{b}_{\eta\eta} = \mathbf{b}_{\omega\eta} \text{ at } A_{\eta\omega} \tag{49b}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\eta} + \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\eta = \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\eta} \text{ at } A_{\eta\omega} \tag{49c}$$

$$\nabla\cdot(\langle\mathbf{v}_\beta\rangle_\omega\mathbf{b}_{\omega\eta}) = \nabla\cdot(\mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\eta}) - \varphi_\omega^{-1}\mathbf{c}_{\omega\eta} \tag{49d}$$

$$\text{Periodicity}: \quad \mathbf{b}_{\eta\eta}(\mathbf{r}+\ell_i) = \mathbf{b}_{\eta\eta}(\mathbf{r}), \quad \mathbf{b}_{\omega\eta}(\mathbf{r}+\ell_i) = \mathbf{b}_{\omega\eta}(\mathbf{r}), \; i = 1,2,3 \tag{49e}$$

$$\text{Average}: \quad \{\mathbf{b}_{\eta\eta}\}^\eta = 0, \; \{\mathbf{b}_{\omega\eta}\}^\omega = 0 \tag{49f}$$

Here we have used the vectors $\mathbf{c}_{\eta\eta}$ and $\mathbf{c}_{\omega\eta}$ to represent the inter-region flux terms according to

$$\mathbf{c}_{\eta\eta} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\mathbf{b}_{\eta\eta} - \mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\eta} - \tilde{\mathbf{D}}^*_\eta\right) \mathrm{d}A \tag{50a}$$

$$\mathbf{c}_{\omega\eta} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta}\cdot(\langle\mathbf{v}_\beta\rangle_\omega\mathbf{b}_{\omega\eta} - \mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\eta}) \mathrm{d}A \tag{50b}$$

and these are related by

$$\mathbf{c}_{\eta\eta} = -\mathbf{c}_{\omega\eta} \tag{50c}$$

The second closure problem is related to the source, $\nabla\{\langle c_\omega\rangle^\omega\}^\omega$, and it is given by

Problem II

$$\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\mathbf{b}_{\eta\omega}\right) = \nabla\cdot(\mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\omega}) - \varphi_\eta^{-1}\mathbf{c}_{\eta\omega} \tag{51a}$$

$$\text{B.C.1} \quad \mathbf{b}_{\eta\omega} = \mathbf{b}_{\omega\omega}, \text{ at } A_{\eta\omega} \tag{51b}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\omega} = \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\omega} + \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\omega \text{ at } A_{\eta\omega} \tag{51c}$$

$$\nabla\cdot(\langle\mathbf{v}_\beta\rangle_\omega\mathbf{b}_{\omega\omega}) + \tilde{\mathbf{v}}_{\beta\omega} = \nabla\cdot(\mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\omega}) + \nabla\cdot\tilde{\mathbf{D}}^*_\omega - \varphi_\omega^{-1}\mathbf{c}_{\omega\omega} \tag{51d}$$

$$\text{Periodicity}: \quad \mathbf{b}_{\eta\omega}(\mathbf{r}+\ell_i) = \mathbf{b}_{\eta\omega}(\mathbf{r}), \; \mathbf{b}_{\omega\omega}(\mathbf{r}+\ell_i) = \mathbf{b}_{\omega\omega}(\mathbf{r}), \quad i = 1,2,3 \tag{51e}$$

$$\text{Average}: \quad \{\mathbf{b}_{\eta\omega}\}^\eta = 0, \; \{\mathbf{b}_{\omega\omega}\}^\omega = 0 \tag{51f}$$

In this case the two constant vectors are defined by

$$\mathbf{c}_{\eta\omega} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta\mathbf{b}_{\eta\omega} - \mathbf{D}^*_\eta\cdot\nabla\mathbf{b}_{\eta\omega}\right) \mathrm{d}A \tag{52a}$$

$$\mathbf{c}_{\omega\omega} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta}\cdot\left(\langle\mathbf{v}_\beta\rangle_\omega\mathbf{b}_{\omega\omega} - \mathbf{D}^*_\omega\cdot\nabla\mathbf{b}_{\omega\omega} - \tilde{\mathbf{D}}^*_\omega\right) \mathrm{d}A \tag{52b}$$

and they are related by

$$\mathbf{c}_{\eta\omega} = -\mathbf{c}_{\omega\omega} \tag{52c}$$

The third closure problem originates with the exchange source, $\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta$, and it takes the form

Problem III

$$\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta r_\eta\right) = \nabla\cdot(\mathbf{D}^*_\eta\cdot\nabla r_\eta) - \varphi_\eta^{-1}\alpha^* \tag{53a}$$

$$\text{B.C.1} \quad r_\eta = r_\omega + 1, \text{ at } A_{\eta\omega} \tag{53b}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\eta\cdot\nabla r_\eta = \mathbf{n}_{\eta\omega}\cdot\mathbf{D}^*_\omega\cdot\nabla r_\omega \text{ at } A_{\eta\omega} \tag{53c}$$

$$\nabla\cdot(\langle\mathbf{v}_\beta\rangle_\omega r_\omega) = \nabla\cdot(\mathbf{D}^*_\omega\cdot\nabla r_\omega) + \varphi_\omega^{-1}\alpha^* \tag{53d}$$

$$\text{Periodicity}: \quad r_\eta(\mathbf{r}+\ell_i) = r_\eta(\mathbf{r}), \; r_\omega(\mathbf{r}+\ell_i) = r_\omega(\mathbf{r}), \quad i = 1,2,3 \tag{53e}$$

$$\text{Average}: \quad \{r_\eta\}^\eta = 0, \; \{r_\omega\}^\omega = 0 \tag{53f}$$

Here the mass transfer coefficient, α*, is defined by

$$\alpha^* = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle\mathbf{v}_\beta\rangle_\eta r_\eta - \mathbf{D}^*_\eta\cdot\nabla r_\eta\right) \mathrm{d}A = +\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta}\cdot(\langle\mathbf{v}_\beta\rangle_\omega r_\omega - \mathbf{D}^*_\omega\cdot\nabla r_\omega) \mathrm{d}A \tag{54}$$

Rather than work directly with the closure variables, r_η and r_ω, it is convenient to define new variables according to

$$s_\eta = r_\eta, \;\; s_\omega = r_\omega + 1 \tag{55}$$

in order to represent the closure problem for the exchange coefficient in terms of a continuous closure variable. Under these circumstances we express the third closure problem as follows.

Problem III′

$$\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta s_\eta\right) = \nabla\cdot\left(\mathbf{D}_\eta^*\cdot\nabla s_\eta\right) - \varphi_\eta^{-1}\alpha^* \tag{56a}$$

$$\text{B.C.1} \quad s_\eta = s_\omega, \;\text{ at } A_{\eta\omega} \tag{56b}$$

$$\text{B.C.2} \quad \mathbf{n}_{\eta\omega}\cdot\mathbf{D}_\eta^*\cdot\nabla s_\eta = \mathbf{n}_{\eta\omega}\cdot\mathbf{D}_\omega^*\cdot\nabla s_\omega \;\text{ at } A_{\eta\omega} \tag{56c}$$

$$\nabla\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega s_\omega\right) = \nabla\cdot\left(\mathbf{D}_\omega^*\cdot\nabla s_\omega\right) + \varphi_\omega^{-1}\alpha^* \tag{56d}$$

$$\text{Periodicity:} \quad s_\eta(\mathbf{r}+\ell_i) = s_\eta(\mathbf{r}), \;\; s_\omega(\mathbf{r}+\ell_i) = s_\omega(\mathbf{r}), \quad i = 1,2,3 \tag{56e}$$

$$\text{Average:} \quad \{s_\eta\}^\eta = 0, \;\; \{s_\omega\}^\omega = 1 \tag{56f}$$

In this case the mass transfer coefficient takes the form

$$\alpha^* = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta s_\eta - \mathbf{D}_\eta^*\cdot\nabla s_\eta\right)\, \mathrm{d}A \tag{57}$$

These closure problems are similar to those that have been solved previously by Quintard and Whitaker[30,35,36], Fabrie *et al.*[37] and Quintard *et al.*[32], and they can be used to determine the coefficients that appear in both the two-equation model and the one-equation model that was developed in Part IV. The major difference between this development and previously studied two-equation models is associated with the spatial variations of the dispersion tensors due to their dependence on velocity fluctuations. As a consequence, new diffusive source terms appear in the closure problem in the form of the divergence of the deviation of the dispersion tensors. The derivation of the closure problem for the one-equation, equilibrium model is presented in Appendix A.

In order to develop the closed forms of eqn (23a), we substitute the representation for $\tilde{c}_\eta$ given by eqn (48a) and make use of the change of variable indicated by eqn (55) to obtain

$$\begin{aligned}
&\epsilon_\eta(1+\mathcal{K}_\eta)\varphi_\eta\frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} + \nabla\cdot\left[\varphi_\eta\left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta\{\langle c_\eta\rangle^\eta\}^\eta\right] \\
&\quad - \nabla\cdot\left[\mathbf{d}_\eta\left(\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega\right)\right] - \mathbf{u}_{\eta\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \\
&\quad - \mathbf{u}_{\eta\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega = \nabla\cdot\left(\mathbf{D}_{\eta\eta}^{**}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right) \\
&\quad + \nabla\cdot\left(\mathbf{D}_{\eta\omega}^{**}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega\right) - \alpha^*\left(\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega\right)
\end{aligned} \tag{58}$$

Here the various coefficients are defined by

$$\mathbf{d}_\eta = \varphi_\eta\left\{\tilde{\mathbf{v}}_{\beta\eta}s_\eta - \mathbf{D}_\eta^*\cdot\nabla s_\eta\right\}^\eta \tag{59a}$$

$$\mathbf{u}_{\eta\eta} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \mathbf{b}_{\eta\eta} - \mathbf{D}_\eta^*\cdot\nabla\mathbf{b}_{\eta\eta} - \tilde{\mathbf{D}}_\eta^*\right)\, \mathrm{d}A \tag{59b}$$

$$\mathbf{u}_{\eta\omega} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta \mathbf{b}_{\eta\omega} - \mathbf{D}_\eta^*\cdot\nabla\mathbf{b}_{\eta\omega}\right)\, \mathrm{d}A \tag{59c}$$

$$\mathbf{D}_{\eta\eta}^{**} = \varphi_\eta\left\{\mathbf{D}_\eta^*\cdot\left(\mathbf{I}+\nabla\mathbf{b}_{\eta\eta}\right) - \tilde{\mathbf{v}}_{\beta\eta}\mathbf{b}_{\eta\eta}\right\}^\eta \tag{59d}$$

$$\mathbf{D}_{\eta\omega}^{**} = \varphi_\eta\left\{\mathbf{D}_\eta^*\cdot\nabla\mathbf{b}_{\eta\omega} - \tilde{\mathbf{v}}_{\beta\eta}\mathbf{b}_{\eta\omega}\right\}^\eta \tag{59e}$$

$$\alpha^* = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega}\cdot\left(\langle \mathbf{v}_\beta\rangle_\eta s_\eta - \mathbf{D}_\eta^*\cdot\nabla s_\eta\right)\, \mathrm{d}A \tag{59f}$$

In order to obtain the closed form of the ω-region transport equation, we follow the above development from eqn (23b) to arrive at

$$\begin{aligned}
&\epsilon_\omega(1+\mathcal{K}_\omega)\varphi_\omega\frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t} + \nabla\cdot\left[\varphi_\omega\{\langle \mathbf{v}_\beta\rangle_\omega\}^\omega\{\langle c_\omega\rangle^\omega\}^\omega\right] \\
&\quad - \nabla\cdot\left[\mathbf{d}_\omega\left(\{\langle c_\eta\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta\right)\right] - \mathbf{u}_{\omega\eta}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta \\
&\quad - \mathbf{u}_{\omega\omega}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega = \nabla\cdot\left(\mathbf{D}_{\omega\eta}^{**}\cdot\nabla\{\langle c_\eta\rangle^\eta\}^\eta\right) \\
&\quad + \nabla\cdot\left(\mathbf{D}_{\omega\omega}^{**}\cdot\nabla\{\langle c_\omega\rangle^\omega\}^\omega\right) - \alpha^*\left(\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta\right)
\end{aligned} \tag{60}$$

The coefficients in this case are analogous to those given by eqns (59), and for completeness we list them as

$$\mathbf{d}_\omega = \varphi_\omega\left\{\tilde{\mathbf{v}}_{\beta\omega}s_\omega - \mathbf{D}_\omega^*\cdot\nabla s_\omega\right\}^\omega \tag{61a}$$

$$\mathbf{u}_{\omega\omega} - \frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta}\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega \mathbf{b}_{\omega\omega} - \mathbf{D}_\omega^*\cdot\nabla\mathbf{b}_{\omega\omega} - \tilde{\mathbf{D}}_\omega^*\right)\, \mathrm{d}A \tag{61b}$$

$$\mathbf{u}_{\omega\eta} = -\frac{1}{\mathcal{V}_\infty}\int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta}\cdot\left(\langle \mathbf{v}_\beta\rangle_\omega \mathbf{b}_{\omega\eta} - \mathbf{D}_\omega^*\cdot\nabla\mathbf{b}_{\omega\eta}\right)\, \mathrm{d}A \tag{61c}$$

$$\mathbf{D}^{**}_{\omega\omega} = \varphi_\omega \left\{ \mathbf{D}^*_\omega \cdot (\mathbf{I} + \nabla \mathbf{b}_{\omega\omega}) - \tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\omega} \right\}^\omega \tag{61d}$$

$$\mathbf{D}^{**}_{\omega\eta} = \varphi_\omega \left\{ \mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_{\omega\eta} - \tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\eta} \right\}^\omega \tag{61e}$$

$$\alpha^* = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega s_\omega - \mathbf{D}^*_\omega \cdot \nabla s_\omega \right) \mathrm{d}A \tag{61f}$$

In the next section we shall present results for the coefficients given by eqns (59) and (61).

The large-scale equations, eqns (58) and (60), represent a generalized version of two-equation models for describing dispersion and adsorption in such systems, and it is interesting to discuss the theoretical status of the linear mass exchange term in these equations. On the basis of the assumptions we have made, the concentration deviations given by eqns (48), coupled with the Darcy-scale problem given by eqns (47), represent a simplified closure scheme for the large-scale averaged equations associated with the η- and ω-regions. A general solution would involve a more complicated expression for the exchange between the two effective media, and the retention of the transient form of the closure problem[38]. In the next section we test the present theory versus numerical experiments obtained for the case of stratified systems.

3 NUMERICAL EXPERIMENTS FOR STRATIFIED SYSTEMS

In this section, we present a complete analysis of the stratified system illustrated in Fig. 3 in the absence of adsorption effects. This system has a behaviour typical of the two-region models that have been studied previously[24,39–41], while being simple enough to allow for precise analysis. We first obtain Darcy-scale solutions that will serve as numerical experiments for a comparison with theoretical predictions.

3.1 Local problem

The local boundary value problem under investigation is defined below.

$$\epsilon_\eta \frac{\partial \langle c_\eta \rangle^\eta}{\partial t} + \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta \right) = \nabla \cdot \left(\mathbf{D}^*_\eta \cdot \nabla \langle c_\eta \rangle^\eta \right) \tag{62a}$$

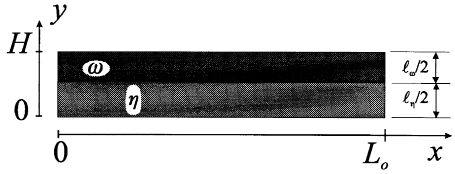

Fig. 3. Stratified model of a heterogeneous porous medium.

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle_\eta = 0 \tag{62b}$$

$$\langle \mathbf{v}_\beta \rangle_\eta = -\frac{\mathbf{K}_{\beta\eta}}{\mu_\beta} \cdot \left(\nabla \langle p_\beta \rangle^\beta_\eta - \varrho_\beta \mathbf{g} \right) \tag{62c}$$

$$\text{B.C.1} \quad \mathbf{n}_{\eta\omega} \cdot \langle \mathbf{v}_\beta \rangle_\eta = \mathbf{n}_{\eta\omega} \cdot \langle \mathbf{v}_\beta \rangle_\omega, \ \text{at } A_{\eta\omega} \tag{62d}$$

$$\text{B.C.2} \quad \langle p_\beta \rangle^\beta_\eta = \langle p_\beta \rangle^\beta_\omega, \ \text{at } A_{\eta\omega} \tag{62e}$$

$$\text{B.C.3} \quad \langle c_\eta \rangle^\eta = \langle c_\omega \rangle^\omega, \ \text{at } A_{\eta\omega} \tag{62f}$$

$$\begin{aligned} \text{B.C.4} \quad & -\mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \langle c_\eta \rangle^\eta - \mathbf{D}^*_\eta \cdot \nabla \langle c_\eta \rangle^\eta \right) \\ & = -\mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \langle c_\omega \rangle^\omega - \mathbf{D}^*_\omega \cdot \nabla \langle c_\omega \rangle^\omega \right), \ \text{at } A_{\eta\omega} \end{aligned} \tag{62g}$$

$$\epsilon_\omega \frac{\partial \langle c_\omega \rangle^\omega}{\partial t} + \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \langle c_\omega \rangle^\omega \right) = \nabla \cdot \left(\mathbf{D}^*_\omega \cdot \nabla \langle c_\omega \rangle^\omega \right) \tag{62h}$$

$$\nabla \cdot \langle \mathbf{v}_\beta \rangle_\omega = 0 \tag{62i}$$

$$\langle \mathbf{v}_\beta \rangle_\omega = -\frac{\mathbf{K}_{\beta\omega}}{\mu_\beta} \cdot \left(\nabla \langle p_\beta \rangle^\beta_\omega - \varrho_\beta \mathbf{g} \right) \tag{62j}$$

$$\text{B.C.5} \quad y = 0, H: \ \mathbf{n} \cdot \langle \mathbf{v}_\beta \rangle^\beta_\alpha = 0; \ \mathbf{n} \cdot \left(\mathbf{D}^*_\alpha \cdot \nabla \langle c_\alpha \rangle^\alpha \right) = 0; \quad \alpha = \eta, \omega \tag{62k}$$

$$\text{B.C.6} \quad x = 0: \ \langle p_\beta \rangle^\beta_\alpha = \varrho_\beta g \, \delta h; \ \langle c_\alpha \rangle^\alpha = 1; \ \alpha = \eta, \omega \tag{62l}$$

$$\text{B.C.7} \quad x = L_\mathrm{o}: \ \langle p_\beta \rangle^\beta_\alpha = 0; \ \mathbf{n} \cdot \left(\mathbf{D}^*_\alpha \cdot \nabla \langle c_\alpha \rangle^\alpha \right) = 0; \quad \alpha = \eta, \omega \tag{62m}$$

$$\text{I.C.} \quad t = 0: \ \langle c_\alpha \rangle^\alpha = 0, \ \alpha = \eta, \omega \tag{62n}$$

Here we note that all the concentrations are now dimensionless, so $\langle c_\alpha \rangle^\alpha$ represents a concentration made dimensionless by some reference concentration, c^o. The solution of this boundary value problem is trivial in terms of the velocity field, i.e. the velocities are constant in each region. Consequently, the dispersion tensors are constant in each region, and the closure problem can be simplified in the obvious manner. The two-dimensional concentration field was obtained by using the numerical model MT3D[42].

3.2 Closure problems and the large-scale problem

Analytical solutions of the equations of closure problems I and II above are readily obtained, and the associated large-scale problem is one-dimensional. The equations are given by

$$\left\{\langle \mathrm{v}_\beta\rangle_\eta\right\}^\eta = \mathbf{i}\cdot\left\{\langle \mathrm{v}_\beta\rangle_\eta\right\}^\eta = \text{constant} \tag{63a}$$

$$\begin{aligned}\epsilon_\eta\varphi_\eta \frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} + \varphi_\eta\left\{\langle \mathrm{v}_\beta\rangle_\eta\right\}^\eta \frac{\partial}{\partial x}\{\langle c_\eta\rangle^\eta\}^\eta \\ = (\mathsf{D}^{**}_{\eta\eta})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\eta\rangle^\eta\}^\eta + (\mathsf{D}^{**}_{\eta\omega})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\omega\rangle^\omega\}^\omega \\ -\alpha^*\left(\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega\right)\end{aligned} \tag{63b}$$

$$\begin{aligned}\epsilon_\omega\varphi_\omega \frac{\partial\{\langle c_\omega\rangle^\omega\}^\omega}{\partial t} + \varphi_\omega\{\langle \mathrm{v}_\beta\rangle_\omega\}^\omega \frac{\partial}{\partial x}\{\langle c_\omega\rangle^\omega\}^\omega \\ = (\mathsf{D}^{**}_{\omega\eta})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\eta\rangle^\eta\}^\eta + (\mathsf{D}^{**}_{\omega\omega})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\omega\rangle^\omega\}^\omega \\ -\alpha^*\left(\{\langle c_\omega\rangle^\omega\}^\omega - \{\langle c_\eta\rangle^\eta\}^\eta\right)\end{aligned} \tag{63c}$$

$$\{\langle \mathrm{v}_\beta\rangle_\omega\}^\omega = \mathbf{i}\cdot\{\langle \mathrm{v}_\beta\rangle_\omega\}^\omega = \text{constant} \tag{63d}$$

A complete discussion of associated large-scale boundary conditions is beyond the scope of this study, and we choose the following initial and boundary conditions:

$$\text{B.C.1} \quad x = 0,\ \{\langle c_\eta\rangle^\eta\}^\eta = \{\langle c_\omega\rangle^\omega\}^\omega = 1 \tag{64a}$$

$$\text{B.C.2} \quad x = L_o,\ \frac{\partial}{\partial x}\{\langle c_\eta\rangle^\eta\}^\eta = \frac{\partial}{\partial x}\{\langle c_\omega\rangle^\omega\}^\omega = 0 \tag{64b}$$

$$\text{I.C.} \quad t = 0,\ \{\langle c_\eta\rangle^\eta\}^\eta = \{\langle c_\omega\rangle^\omega\}^\omega = 0 \tag{64c}$$

In eqns (63), effective properties for the one-dimensional unit cell are given by

$$(\mathsf{D}^{**}_{\eta\eta})_{xx} = \varphi_\eta(\mathsf{D}^*_\eta)_{xx} \tag{65a}$$

$$(\mathsf{D}^{**}_{\eta\omega})_{xx} = (\mathsf{D}^{**}_{\omega\eta})_{xx} = 0 \tag{65b}$$

$$(\mathsf{D}^{**}_{\omega\omega})_{xx} = \varphi_\omega(\mathsf{D}^*_\omega)_{xx} \tag{65c}$$

$$\alpha^* = \frac{12}{(\ell_\eta + \ell_\omega)^2}\frac{(\mathsf{D}^*_\eta)_{yy}(\mathsf{D}^*_\omega)_{yy}}{\varphi_\omega(\mathsf{D}^*_\eta)_{yy} + \varphi_\eta(\mathsf{D}^*_\omega)_{yy}} \tag{65d}$$

It is important to note at this point that the periodic system representative of the problem expressed by eqns (62) is constituted of layers *twice as large* as those represented in Fig. 3, and we have used the appropriate unit cell associated with this periodic system in deriving eqn (65).

3.3 Numerical methods

Numerical solutions of the large-scale, one-dimensional problem are found by using the following procedure. First, the operator in the transport equation is split into three equations as shown here for the η-region equation:

$$\epsilon_\eta\varphi_\eta \frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} + \varphi_\eta\left\{\langle \mathrm{v}_\beta\rangle_\eta\right\}^\eta \frac{\partial}{\partial x}\{\langle c_\eta\rangle^\eta\}^\eta = 0 \tag{66a}$$

$$\begin{aligned}\epsilon_\eta\varphi_\eta \frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} = (\mathsf{D}^{**}_{\eta\eta})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\eta\rangle^\eta\}^\eta \\ + (\mathsf{D}^{**}_{\eta\omega})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\omega\rangle^\omega\}^\omega\end{aligned} \tag{66b}$$

$$\epsilon_\eta\varphi_\eta \frac{\partial\{\langle c_\eta\rangle^\eta\}^\eta}{\partial t} = -\alpha^*\left(\{\langle c_\eta\rangle^\eta\}^\eta - \{\langle c_\omega\rangle^\omega\}^\omega\right) \tag{66c}$$

Equations like eqn (66a) are solved by using an explicit second-order scheme[43,44], while diffusion equations like eqn (66b) are solved by using a second-order implicit scheme. Finally, eqn (66c) and the similar equation for the ω-region are solved analytically for one time-step. The resulting scheme is second-order with negligible numerical dispersion. Several cases were investigated ranging from negligible dispersion effects to important dispersion effects.

3.3.1 Case 1.

The system properties for this case are summarized in Table 1, and the concentrations fields obtained for $t = 8 \times 10^{+6}$ s are plotted in Fig. 4. This figure shows that advection in each stratum is the unique mechanism and that there is no mass exchange between the strata. This type of behaviour clearly calls for a large-scale, non-equilibrium description. From this computed field we obtain 'experimental' values for the large-scale averaged concentrations by averaging over cross-sections of the stratified medium. To obtain the theoretical results for this case, we first determine the effective properties for the two-equation model by solving the three closure problems, and these values are reported in Table 1. The one-dimensional, large-scale equations are then solved numerically to provide the theoretical concentrations that are plotted in Fig. 5. The results show very good agreement between theory and experiment, except for some limited numerical dispersion near the fronts. To illustrate the need for a large-scale, non-equilibrium approach, the average concentration corresponding to the one-equation model is plotted in Fig. 5. This curve obviously cannot be the solution of a classical

Table 1. Properties of the stratified system (case 1)

Unit Cell	$\ell_\eta = \ell_\omega$ (m)	φ_η	L_o/ℓ_η
	1	0.5	10

Physical Properties	$K_{\beta\eta}$ (10^{-12} m^2)	$K_{\beta\omega}$ (10^{-12} m^2)	ε_η	ε_ω
	1	0.1	0.38	0.30
	$(D^*_\eta)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\omega)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\eta)_{yy} / (D^*_\eta)_{xx}$	$(D^*_\omega)_{yy} / (D^*_\omega)_{xx}$
	0.	0.	1.	1.

Flow Properties	δh (m)	$\langle \mathbf{v}_\beta \rangle_\eta$	$\langle \mathbf{v}_\beta \rangle_\omega$
	0.4	3 10^{-7}	0.3 10^{-7}

Effective Properties (Dispersion)	$(D^{**}_{\eta\eta})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\omega\omega})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\eta\omega})_{xx} = (D^{**}_{\omega\eta})_{xx}$ (10^{-9} m^2 s^{-1})
	0.	0.	0.
	α^* (10^{-9} s^{-1})		
	0.		

Note: All properties are taken equal to zero unless they are cited in the Table.
$\varrho_\beta\, g / \mu_\beta = 7.7\ 10^{+6}$ (m s)$^{-1}$

advection, dispersion equation. While these results may seem trivial, they emphasize that with a little additional complexity, i.e. the introduction of a two-equation model, it is possible to take into account mechanisms that would require an extremely complicated one-equation model.

3.3.2 Case 2

The system properties for this case are summarized in Table 2, and the concentration fields obtained for $t = 8 \times 10^{+6}$ s are plotted in Fig. 6. This figure shows that advection in each strata is the most important mechanism, while some cross-section diffusion is present, and this behaviour clearly calls for a large-scale, non-equilibrium model. The fields from the numerical experiments, the two-equation model and the one-equation model are plotted in Fig. 7, and there it is seen that the propagation of the front is considerably faster in the η-region. Dispersion is negligible; however, mass transfer between the strata is not zero and has a small influence on the concentration field in the region between the fronts. The results indicate relatively good agreement between the numerical experiments and theoretical calculations, especially for a case that has the reputation for not being 'Fickian' in terms of a one-equation model. Mass exchange between the strata is *underestimated* by the theoretical model, and several explanations can be proposed to explain this phenomenon. We list these as follows:

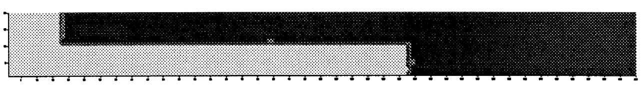

Fig. 4. Concentration at $t = 8 \times 10^{+6}$ s, case 1.

1. Possible numerical inaccuracies must not be forgotten; however, we think that numerical dispersion and

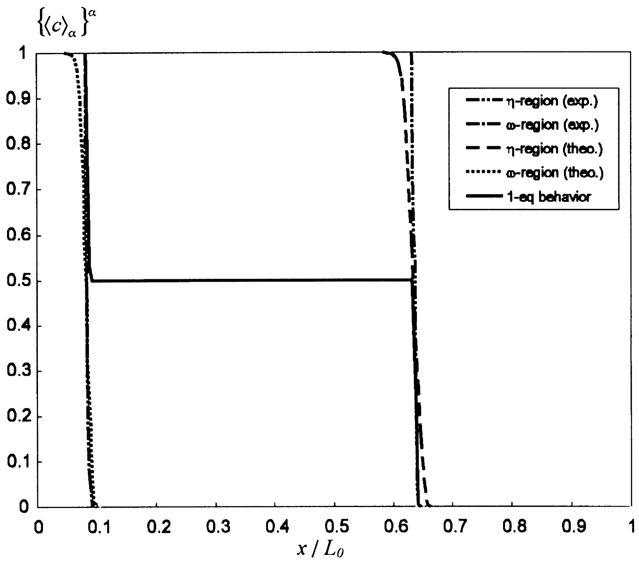

Fig. 5. Comparison between numerical experiments and 1D large-scale predictions ($t = 8 \times 10^{+6}$ s, case 1).

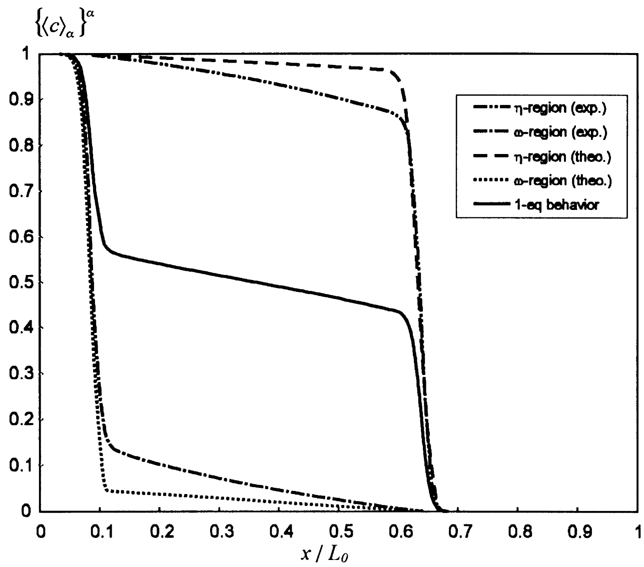

Fig. 7. Comparison between numerical experiments and 1D large-scale predictions ($t = 8 \times 10^{+6}$ s, case 2).

accuracy cannot explain all the observed differences. This remark is valid for all cases investigated in this paper, and we shall not repeat this argument in the next set of comments.

2. It has already been observed[45] that the theory under-estimates the exchanged flux at early times, while it naturally provides better estimates as time increases. This occurs because estimates of the concentration fields provided by the closure problems correspond to a *fully established* concentration wave in the medium. This is not the case in this particular simulation, since there is only a fringe of the strata that is affected by diffusion near the interface.

3.3.3 Case 3

This case corresponds to a system with higher dispersion effects, and the flow properties are given in Table 3. The concentration fields determined at the Darcy scale are plotted in Fig. 8, and all large-scale fields are shown in Fig. 9. The large-scale, one-equation behaviour is still characteristic of non-Fickian behaviour, while the two-equation model provides a first-order accurate description of the system behaviour with a limited error. Here we should reiterate that the closure problem given by eqns (51) through (53) is *not exact*, and this is generally the case. For especially simple systems, such as Stokes flow in a homogeneous, rigid porous medium, one can indeed develop exact closure problems[46–49]; however, the problem under consideration involves transient, convective transport in heterogeneous porous media and the demands on the closure problem are much greater.

3.3.4 Case 4

The concentration fields at the Darcy scale are shown in Fig. 10 and all large-scale fields in Fig. 11. This case corresponds to much higher dispersion effects. As a result, mass exchange between the strata is increased, and the entire process is closer to large-scale equilibrium. As expected, the difference between numerical experiments and theoretical predictions is small.

Finally, we have performed many numerical experiments under conditions leading to a large-scale equilibrium behaviour by increasing lateral dispersion. Under these circumstances both the two-equation model and the one-equation equilibrium model agree very well with the numerical experiments. This behaviour was of course expected.

4 ASYMPTOTIC BEHAVIOUR

In this section we are interested in the asymptotic behaviour of the stratified system under consideration. In the absence of any adsorption, it has been demonstrated by Marle *et al.*[24] that for sufficiently large times the average concentration obeys rather closely a dispersion equation given by

$$\{\epsilon\}\frac{\partial\{\langle c\rangle\}}{\partial t} + \{\langle \mathrm{v}_\beta\rangle\}\frac{\partial\{\langle c\rangle\}}{\partial x} = \left(\mathsf{D}^{**}_\infty\right)_{xx}\frac{\partial^2\{\langle c\rangle\}}{\partial x^2} \tag{67}$$

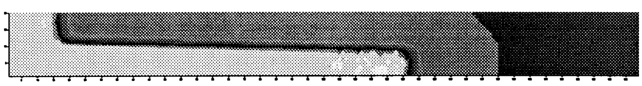

Fig. 6. Concentration at $t = 8 \times 10^{+6}$ s (case 2).

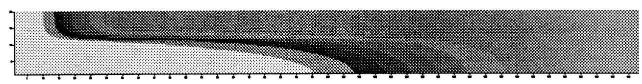

Fig. 8. Concentration at $t = 8 \times 10^{+6}$ s (case 3).

Table 2. Properties of the stratified system (case 2)

Unit Cell	$\ell_\eta = \ell_\omega$ (m)	φ_η	L_o/ℓ_η	
	1	0.5	10	
Physical Properties	$K_{\beta\eta}$ (10^{-12} m^2)	$K_{\beta\omega}$ (10^{-12} m^2)	ε_η	ε_ω
	1	0.1	0.38	0.30
	$(\mathsf{D}^*_\eta)_{xx}$ (10^{-9} m^2 s^{-1})	$(\mathsf{D}^*_\omega)_{xx}$ (10^{-9} m^2 s^{-1})	$(\mathsf{D}^*_\eta)_{yy} / (\mathsf{D}^*_\eta)_{xx}$	$(\mathsf{D}^*_\omega)_{yy} / (\mathsf{D}^*_\omega)_{xx}$
	0.38	0.27	1.	1.
Flow Properties	δh (m)	$\langle \mathbf{v}_\beta \rangle_\eta$	$\langle \mathbf{v}_\beta \rangle_\omega$	
	0.4	3 10^{-7}	0.3 10^{-7}	
Effective Properties (Dispersion)	$(\mathsf{D}^{**}_{\eta\eta})_{xx}$ (10^{-9} m^2 s^{-1})	$(\mathsf{D}^{**}_{\omega\omega})_{xx}$ (10^{-9} m^2 s^{-1})	$(\mathsf{D}^{**}_{\eta\omega})_{xx} = (\mathsf{D}^{**}_{\omega\eta})_{xx}$ (10^{-9} m^2 s^{-1})	
	0.19	0.135	0.0	
	α^* (10^{-9} s^{-1})			
	0.947			

Note: All properties are taken equal to zero unless they are cited in the Table.
$\varrho_\beta\, g / \mu_\beta = 7.7\ 10^{+6}$ (m s)$^{-1}$

The dispersion coefficient in this equation is given by

$$\begin{aligned}(\mathsf{D}^{**}_\infty)_{xx} &= \varphi_\eta (\mathsf{D}^*_\eta)_{xx} \\ &+ \varphi_\omega (\mathsf{D}^*_\omega)_{xx} + \frac{(\ell_\eta + \ell_\omega)^2}{12} \frac{(\epsilon_\eta \varphi_\eta \epsilon_\omega \varphi_\omega)^2}{(\epsilon_\eta \varphi_\eta + \epsilon_\omega \varphi_\omega)} \\ &\times \left[\frac{\varphi_\eta}{(\mathsf{D}^*_\eta)_{xx}} + \frac{\varphi_\omega}{(\mathsf{D}^*_\omega)_{xx}} \right] \left(\langle \mathrm{v}_\beta \rangle^\beta_\eta - \langle \mathrm{v}_\beta \rangle^\beta_\omega \right)^2 \end{aligned} \tag{68}$$

The derivation of this result makes use of the method of moments in a manner similar to the work of Aris[50], and these results have been extended to more general, random stratified systems[1,51]. The estimate of the large-scale asymptotic dispersion coefficient given by eqn (68) was found to agree very well with experimental data[24]. The one-equation model that was derived in Part IV has exactly the same form as eqn (67), when there is no adsorption, and this is given by

$$\{\epsilon\} \frac{\partial \{\langle c \rangle\}}{\partial t} + \{\langle \mathrm{v}_\beta \rangle\} \frac{\partial \{\langle c \rangle\}}{\partial x} = (\mathsf{D}^{**})_{xx} \frac{\partial^2 \{\langle c \rangle\}}{\partial x^2} \tag{69}$$

This equation is restricted by the approximation

$$\{\langle c_\eta \rangle^\eta\}^\eta = \{\langle c_\omega \rangle^\omega\}^\omega = \{\langle c \rangle\}, \quad \text{large-scale mass equilibrium} \tag{70}$$

and the predicted dispersion coefficient takes the form

$$(\mathsf{D}^{**})_{xx} = \varphi_\eta (\mathsf{D}^*_\eta)_{xx} + \varphi_\omega (\mathsf{D}^*_\omega)_{xx} \tag{71}$$

This relation is *significantly different* from the dispersion coefficient represented by eqn (68), which is determined by requiring that the moments of eqn (67) match the moments of the particular process under consideration. While Marle *et al.*[24] obtained rather good agreement between theory and

Table 3. Properties of the stratified system (case 3)

Unit Cell	$\ell_\eta = \ell_\omega$ (m)	φ_η	L_0/ℓ_η	
	1	0.5	10	
Physical Properties	$K_{\beta\eta}$ (10^{-12} m^2)	$K_{\beta\omega}$ (10^{-12} m^2)	ε_η	ε_ω
	1	0.1	0.38	0.30
	$(D^*_\eta)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\omega)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\eta)_{yy}/(D^*_\eta)_{xx}$	$(D^*_\omega)_{yy}/(D^*_\omega)_{xx}$
	30	3	0.1	0.1
Flow Properties	δh (m)	$\langle \mathbf{v}_\beta \rangle_\eta$	$\langle \mathbf{v}_\beta \rangle_\omega$	
	0.4	$3\ 10^{-7}$	$0.3\ 10^{-7}$	
Effective Properties (Dispersion)	$(D^{**}_{\eta\eta})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\omega\omega})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\eta\omega})_{xx} = (D^{**}_{\omega\eta})_{xx}$ (10^{-9} m^2 s^{-1})	
	15.	1.5	0.0	
	α^* (10^{-9} s^{-1})			
	1.64			

Note: All properties are taken equal to zero unless they are cited in the Table.
$\rho_\beta\, g / \mu_\beta = 7.7\ 10^{+6}$ (m s)$^{-1}$

experiment for the case of *passive dispersion* in a stratified system, it would be a mistake to modify eqn (67) with a retardation factor such as $(1+\{\mathcal{K}\})$ and expect it to represent accurately an adsorption process.

In order to compare our work with eqns (67) and (68), we studied a stratified system, having essentially an infinite length, that was subjected to a step change in the input concentration. Thus we again used eqns (63) through (65) with the length L_0 great enough for the downstream boundary condition to have no effect on the concentration profiles. The physical parameters were taken to be the same as those used in Case 4, so they are given in Table 4 with the exception of L_0/ℓ_η, which was of the order of 100. The concentration profiles at a distance of 20 m from the entrance are shown in Fig. 12, from which are seen a variety of different results. The one-equation equilibrium model that is characterized by eqns (69)–(71) clearly exhibits a lack of dispersion compared with the one-equation non-equilibrium model of Marle *et al.*[24]. The results from the two-equation model indicate that the concentration profile for the ω-region lies below that for the η-region, and this is required since the velocity in the ω-region is a factor of ten *less than* the velocity in the η-region. At the leading edge of the front, the results from the two-equation model bracket the value predicted by eqns (67) and (68), while at the trailing edge of the front, the non-equilibrium one-equation model of Marle *et al.*[24] clearly over-predicts the concentration. The average concentration predicted by the two-equation model is given by

$$\{\langle c\rangle\} = \varphi_\eta\{\langle c_\eta\rangle^\eta\}^\eta + \varphi_\omega\{\langle c_\omega\rangle^\omega\}^\omega \qquad (72)$$

in which $\{\langle c_\eta\rangle^\eta\}^\eta$ and $\{\langle c_\omega\rangle^\omega\}^\omega$ *are not constrained* by eqn (70). We consider this average concentration to be the

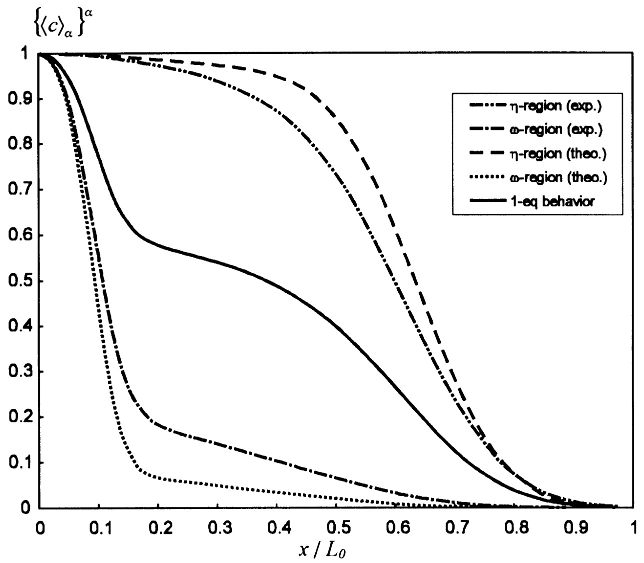

Fig. 9. Comparison between numerical experiments and 1D large-scale predictions ($t = 8 \times 10^{+6}$ s, case 3).

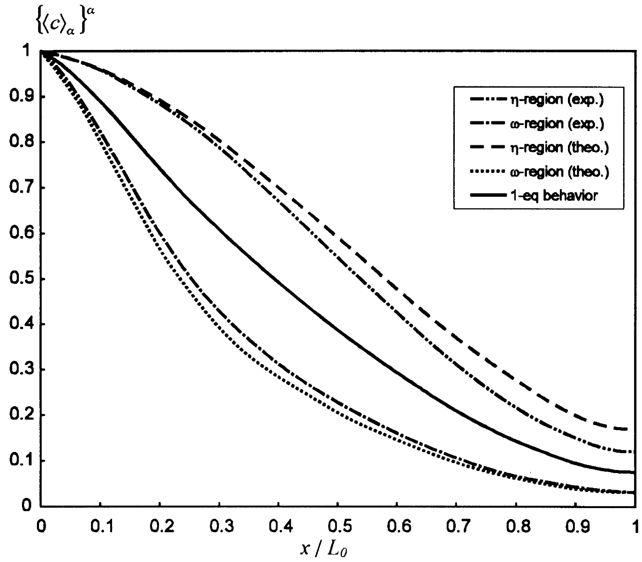

Fig. 11. Comparison between numerical experiments and 1D large-scale predictions ($t = 8 \times 10^{+6}$ s, case 4).

best predictor of the large-scale average concentration, and this generally lies below the values predicted by eqns (67) and (68). This means that the time and length-scale constraints that are imposed on eqns (67) and (68) are not satisfied at a distance of 20 m for the conditions listed in Table 4. The comparison is seen more clearly in Fig. 13, where we present the time derivative of the concentration profiles. These represent values of $\partial\{\langle c\rangle\}/\partial t$, determined at a distance of 20 m, as a function of time. These curves can also be thought of as concentration profiles for a pulse input condition, and they clearly indicate that eqns (67) and (68) do not predict a symmetric pulse at a distance of 20 m. When the distance is increased to 66.5 m, the agreement between all the models improves significantly, and the results for the concentration profiles are shown in Fig. 14. The one-equation equilibrium model provides the *worst representation*, while the two-equation model is in good agreement with the work of Marle *et al.*[24]. The time derivatives of the concentration profiles are shown in Fig. 15, and there we see rather good agreement between the average concentration determined on the basis of the two-equation model and eqn (72) and the one-equation non-equilibrium model given by eqns (67) and (68). On the other hand, the one-equation equilibrium model developed in Part IV illustrates rather poor agreement with the other two results.

The direct study of the asymptotic behaviour of the two-equation model is presented in Appendix B, where we show analytically that the asymptotic longitudinal dispersion coefficient is given by

$$(\mathsf{D}^{**}_\infty)_{xx} = (\mathsf{D}^{**}_{\eta\eta})_{xx} + (\mathsf{D}^{**}_{\eta\omega})_{xx} + (\mathsf{D}^{**}_{\omega\eta})_{xx} + (\mathsf{D}^{**}_{\omega\omega})_{xx} + \frac{\left(\epsilon_\omega\varphi_\omega\left\{\langle \mathrm{v}_\beta\rangle_\eta\right\} - \epsilon_\eta\varphi_\eta\left\{\langle \mathrm{v}_\beta\rangle_\omega\right\}\right)^2}{\alpha^*\left(\epsilon_\eta\varphi_\eta + \epsilon_\omega\varphi_\omega\right)} \tag{73}$$

Introducing the expression for α^* given by eqn (73), we obtain an expression for the asymptotic longitudinal dispersion coefficient equal to the one proposed by Marle *et al.*[24]. This result suggests the following comments:

1. The two-equation model has an asymptotic behaviour that reflects exactly the behaviour deduced from a direct analysis of the Darcy-scale problem. Since the two-equation model can be applied to more general systems than stratified media, our result represents an important extension of the theory.
2. The value of the asymptotic longitudinal dispersion coefficient depends on α^*. Therefore, the comparison is a test of the validity of the large-scale closure problem. We have presented in Parts I and II a comparison with several estimates of the exchange coefficient published in the literature for purely diffusive problems. They may differ by as much as a factor of 3. The comparison with the result by Marle *et al.*[24] shows that the proposed theory gives an exact result.

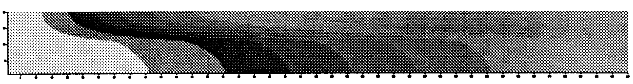

Fig. 10. Concentration at $t = 8 \times 10^{+6}$ s (case 4).

5 CONCLUSIONS

In this paper we have introduced a first-order version of a two-equation model describing a class of local non-equilibrium dispersion problems in heterogeneous porous media. A comparison with numerical experiments for

Table 4. Properties of the stratified system (case 4)

Unit Cell	$\ell_\eta = \ell_\omega$ (m)	φ_η	L_o/ℓ_η
	1	0.5	10

Physical Properties	$K_{\beta\eta}$ (10^{-12} m^2)	$K_{\beta\omega}$ (10^{-12} m^2)	ε_η	ε_ω
	1	0.1	0.38	0.30
	$(D^*_\eta)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\omega)_{xx}$ (10^{-9} m^2 s^{-1})	$(D^*_\eta)_{yy} / (D^*_\eta)_{xx}$	$(D^*_\omega)_{yy} / (D^*_\omega)_{xx}$
	300	30	0.1	0.1

Flow Properties	δh (m)	$\langle \mathbf{v}_\beta \rangle_\eta$	$\langle \mathbf{v}_\beta \rangle_\omega$
	0.4	3 10^{-7}	0.3 10^{-7}

Effective Properties (Dispersion)	$(D^{**}_{\eta\eta})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\omega\omega})_{xx}$ (10^{-9} m^2 s^{-1})	$(D^{**}_{\eta\omega})_{xx} = (D^{**}_{\omega\eta})_{xx}$ (10^{-9} m^2 s^{-1})
	150.	15	0.0
	α^* (10^{-9} s^{-1})		
	16.4		

Note: All properties are taken equal to zero unless they are cited in the Table.
$\varrho_\beta\, g / \mu_\beta = 7.7\ 10^{+6}$ (m s)$^{-1}$

stratified systems has demonstrated the ability of the two-equation model to describe most of the large-scale non-equilibrium behaviour of such bimodal heterogeneous systems. The agreement was found to be reasonable for a wide range of large-scale Peclet numbers from negligible diffusion/dispersion effects to dominant diffusion/dispersion effects. In addition to the comparison with numerical experiments, we have also compared our two-equation model with the one-equation non-equilibrium model developed by Marle *et al.*[24] for the special case of *passive dispersion* in a stratified system. The asymptotic results are identical, and this represents a successful comparison with the laboratory experiments that were used by Marle *et al.*[24] as a test of their theory. At present there would appear to be no laboratory experiments for the case of dispersion and adsorption in stratified systems; however, the numerical experiments can be considered as a reliable verification of the essential features of the two-equation model.

An improved model could be achieved with the use of higher-order, transient closure problems. On the other hand, the improvement of the predictions of the two-equation model over those available from the one-equation model is significant, and may be sufficient for many practical purposes. This is a matter of choice for a particular application.

Although interest in two-equation models has long been recognized in the literature, our contribution lies in the introduction of the closure problems that give some reliable link between the lower-scale and the upper-scale structures. The development of numerical methods to solve the closure problems in more general cases could be used in connection with any deterministic or statistical representation of the

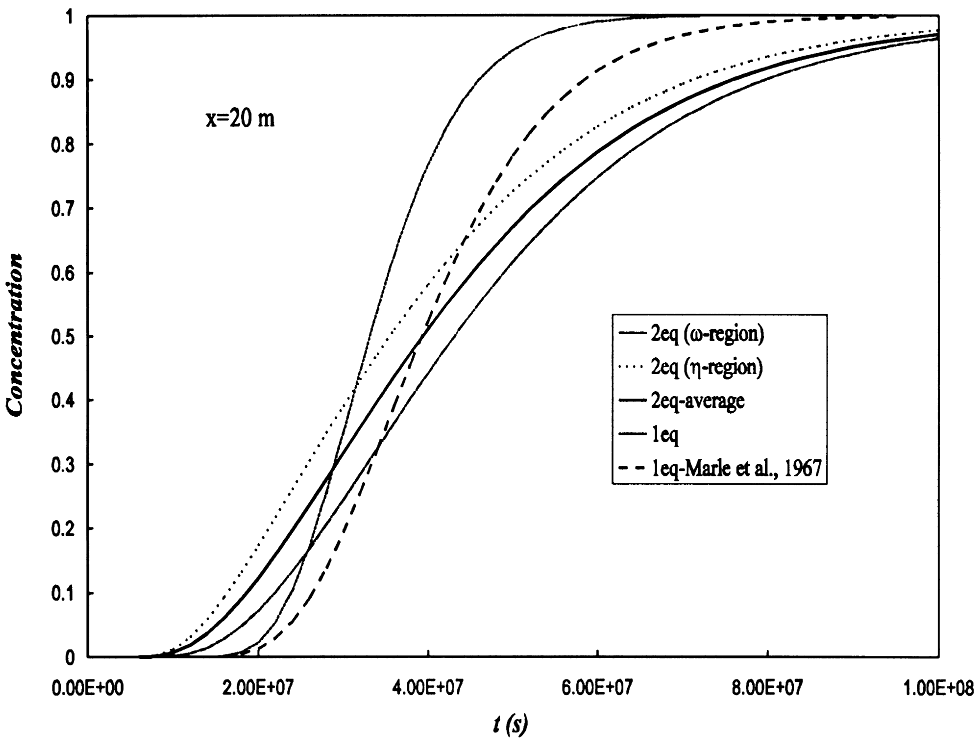

Fig. 12. Asymptotic behaviour of the different large-scale models: concentration fields (case 4; $x = 20$ m).

heterogeneities, thus providing valuable tools for engineering purposes.

Finally, it must be pointed out that the development presented in this paper is limited to solute transport with negligible density variations and viscosity variations. Gravity-induced gradients may have a significant influence on the flow pattern[41], and it is well known that viscous fingering may develop when viscosity gradients are important, thus affecting dramatically the concentration field. It is not clear at this point whether these effects can be introduced into the analysis in a simple manner.

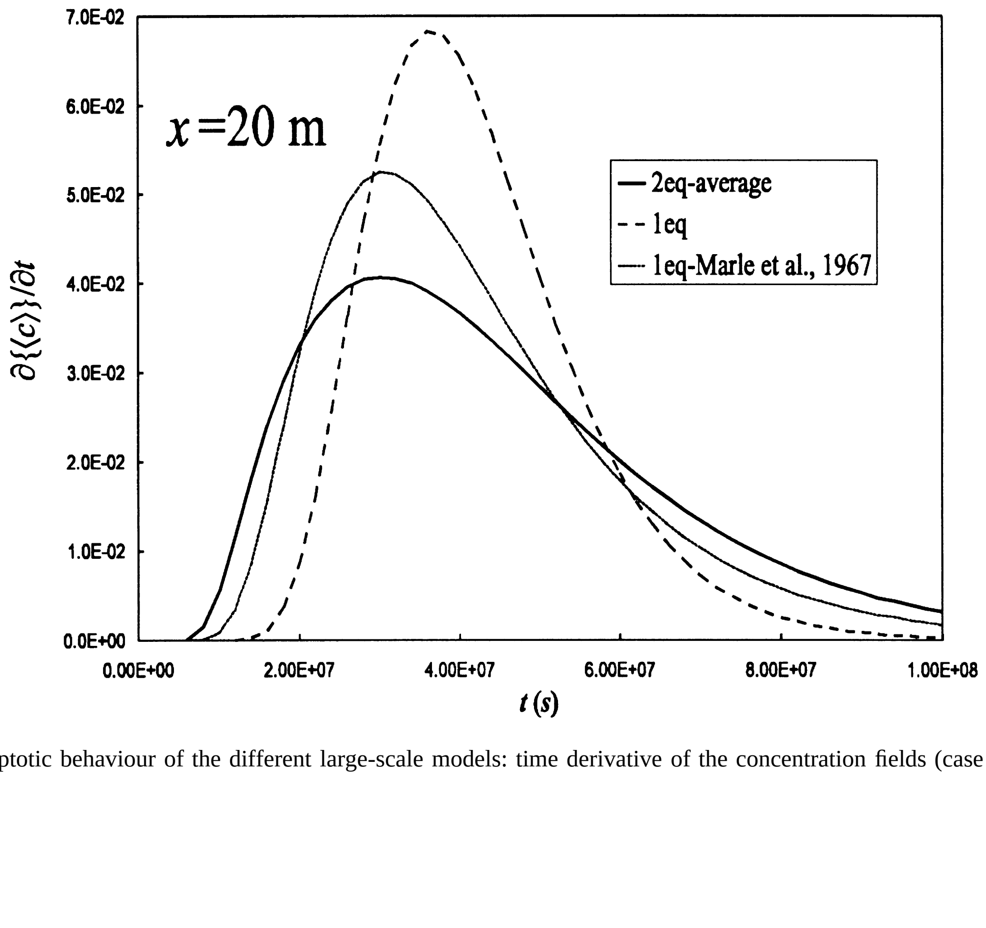

Fig. 13. Asymptotic behaviour of the different large-scale models: time derivative of the concentration fields (case 4; $x = 20$ m).

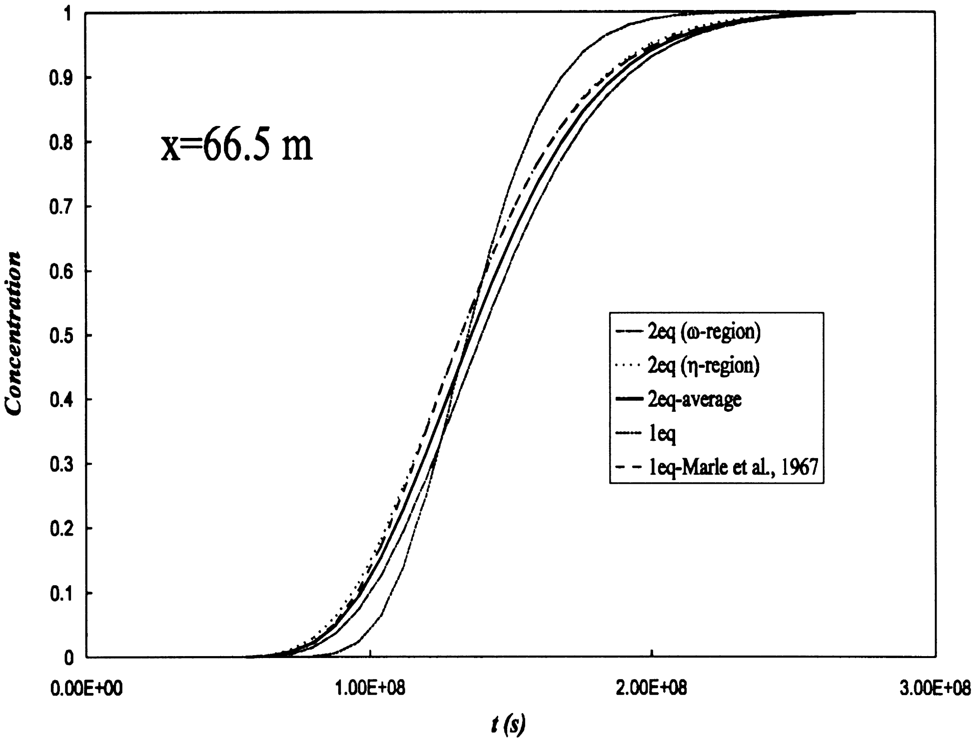

Fig. 14. Asymptotic behaviour of the different large-scale models: concentration fields (case 4; $x = 66.5$ m).

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APPENDIX A: CLOSURE FOR THE ONE-EQUATION MODEL

In Part IV we expressed the one-equation equilibrium model as

$$\{\epsilon\}(1+\{\mathcal{K}\})\frac{\partial\{\langle c\rangle\}}{\partial t}+\nabla\cdot\left(\{\langle \mathbf{v}_\beta\rangle\}\{\langle c\rangle\}\right)=\nabla\cdot\left(\mathbf{D}^{**}\cdot\nabla\{\langle c\rangle\}\right) \tag{A1}$$

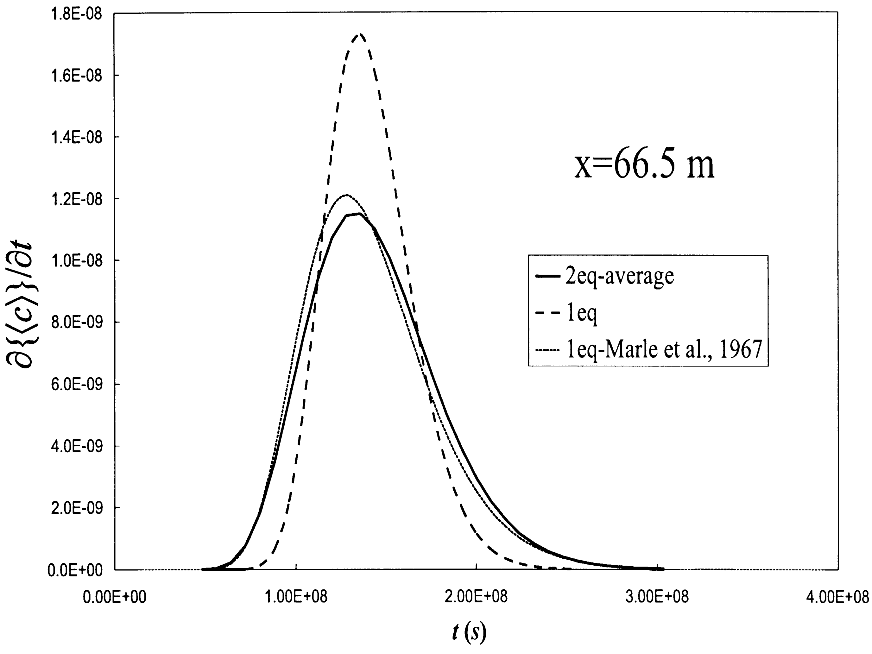

Fig. 15. Asymptotic behaviour of the different large-scale models: time derivative of the concentration fields (case 4; $x = 66.5$ m).

in which the large-scale dispersion tensor is defined by

$$\mathbf{D}^{**} = \varphi_\eta \{\mathbf{D}_\eta^*\}^\eta + \varphi_\omega \{\mathbf{D}_\omega^*\}^\omega + \frac{\{\mathbf{D}_\eta^*\}^\eta - \{\mathbf{D}_\omega^*\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_\eta \, \mathrm{d}A + \left\{\tilde{\mathbf{D}}_\eta^* \cdot \nabla \mathbf{b}_\eta\right\} + \left\{\tilde{\mathbf{D}}_\omega^* \cdot \nabla \mathbf{b}_\omega\right\} - \left(\varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_\eta\}^\eta + \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_\omega\}^\omega\right) \quad \text{(A2)}$$

In order to derive these two results from the two-equation model presented in this paper, we first add eqns (58) and (60) and impose the approximations

$$\{\langle c\rangle_\eta\}^\eta = \{\langle c\rangle_\omega\}^\omega = \{\langle c\rangle\} \quad \text{(A3)}$$

to obtain

$$\left[\epsilon_\eta (1+\mathcal{K}_\eta)\varphi_\eta + \epsilon_\omega (1+\mathcal{K}_\omega)\varphi_\omega\right] \frac{\partial\{\langle c\rangle\}}{\partial t} + \nabla\cdot\left[\left(\varphi_\eta \left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta + \varphi_\omega \left\{\langle \mathbf{v}_\beta\rangle_\omega\right\}^\omega\right)\{\langle c\rangle\}\right] - \left(\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} + \mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega}\right)\cdot\nabla\{\langle c\rangle\} = \nabla\cdot\left[\left(\mathbf{D}_{\eta\eta}^{**} + \mathbf{D}_{\eta\omega}^{**} + \mathbf{D}_{\omega\eta}^{**} + \mathbf{D}_{\omega\omega}^{**}\right)\cdot\nabla\{\langle c\rangle\}\right] \quad \text{(A4)}$$

Use of the definitions

$$\{\epsilon\}(1+\{\mathcal{K}\}) = \epsilon_\eta (1+\mathcal{K}_\eta)\varphi_\eta + \epsilon_\omega (1+\mathcal{K}_\omega)\varphi_\omega \quad \text{(A5)}$$

$$\{\langle \mathbf{v}_\beta\rangle\} = \varphi_\eta \left\{\langle \mathbf{v}_\beta\rangle_\eta\right\}^\eta + \varphi_\omega \left\{\langle \mathbf{v}_\beta\rangle_\omega\right\}^\omega \quad \text{(A6)}$$

allows us to simplify this result to obtain the traditional accumulation and convective transport term according to

$$\{\epsilon\}(1+\{\mathcal{K}\}) \frac{\partial\{\langle c\rangle\}}{\partial t} + \nabla\cdot\left(\{\langle \mathbf{v}_\beta\rangle\}\{\langle c\rangle\}\right) - \left(\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} + \mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega}\right)\cdot\nabla\{\langle c\rangle\} = \nabla\cdot\left[\left(\mathbf{D}_{\eta\eta}^{**} + \mathbf{D}_{\eta\omega}^{**} + \mathbf{D}_{\omega\eta}^{**} + \mathbf{D}_{\omega\omega}^{**}\right)\cdot\nabla\{\langle c\rangle\}\right] \quad \text{(A7)}$$

In order to determine the form of the overall dispersion tensor, we recall the definitions of the four dispersion tensors in the above equation, given by

$$\mathbf{D}_{\eta\eta}^{**} = \varphi_\eta \left\{\mathbf{D}_\eta^* \cdot (\mathbf{I} + \nabla \mathbf{b}_{\eta\eta}) - \tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\right\}^\eta \quad \text{(A8a)}$$

$$\mathbf{D}_{\eta\omega}^{**} = \varphi_\eta \left\{\mathbf{D}_\eta^* \cdot \nabla \mathbf{b}_{\eta\omega} - \tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\omega}\right\}^\eta \quad \text{(A8b)}$$

$$\mathbf{D}_{\omega\eta}^{**} = \varphi_\omega \left\{\mathbf{D}_\omega^* \cdot \nabla \mathbf{b}_{\omega\eta} - \tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\eta}\right\}^\omega \quad \text{(A8c)}$$

$$\mathbf{D}_{\omega\omega}^{**} = \varphi_\omega \left\{\mathbf{D}_\omega^* \cdot (\mathbf{I} + \nabla \mathbf{b}_{\omega\omega}) - \tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\omega}\right\}^\omega \quad \text{(A8d)}$$

These representations need to be arranged in a form that will allow us to extract the relation given by eqn (A2), and we begin this rearrangement with eqn (A8a) to obtain

$$\begin{aligned}\mathbf{D}_{\eta\eta}^{**} &= \varphi_\eta \left\{\mathbf{D}_\eta^* \cdot (\mathbf{I} + \nabla \mathbf{b}_{\eta\eta}) - \tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\right\}^\eta \\ &= \varphi_\eta \left[\{\mathbf{D}_\eta^*\}^\eta + \{\mathbf{D}_\eta^* \cdot \nabla \mathbf{b}_{\eta\eta}\}^\eta - \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\}^\eta\right] \\ &= \varphi_\eta \left[\{\mathbf{D}_\eta^*\}^\eta + \left\{\{\mathbf{D}_\eta^*\}^\eta \cdot \nabla \mathbf{b}_{\eta\eta} + \tilde{\mathbf{D}}_\eta^* \cdot \nabla \mathbf{b}_{\eta\eta}\right\}^\eta - \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\}^\eta\right]\end{aligned} \quad \text{(A9)}$$

We can remove the regional average from the averaging process to obtain

$$\left\{\{\mathbf{D}_\eta^*\}^\eta \cdot \nabla \mathbf{b}_{\eta\eta}\right\}^\eta = \{\mathbf{D}_\eta^*\}^\eta \cdot \{\nabla \mathbf{b}_{\eta\eta}\}^\eta \quad \text{(A10)}$$

and then use the averaging theorem in order to express this term as

$$\{\nabla \mathbf{b}_{\eta\eta}\}^\eta = \nabla \{\mathbf{b}_{\eta\eta}\}^\eta + \frac{1}{V_\eta} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\eta} \, \mathrm{d}A \quad \text{(A11)}$$

Here we have ignored variations of φ_η, since we are working with the equations of closure problems I and II above. From eqn (49) we have

$$\{\mathbf{b}_{\eta\eta}\}^\eta = 0 \quad \text{(A12)}$$

and so eqn (A10) takes the form

$$\left\{\{\mathbf{D}_\eta^*\}^\eta \cdot \nabla \mathbf{b}_{\eta\eta}\right\}^\eta = \{\mathbf{D}_\eta^*\}^\eta \cdot \frac{1}{V_\eta} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\eta} \, \mathrm{d}A \quad \text{(A13)}$$

Use of this result in eqn (A9) allows us to express $\mathbf{D}_{\eta\eta}^{**}$ in the form

$$\mathbf{D}_{\eta\eta}^{**} = \varphi_\eta \left[\{\mathbf{D}_\eta^*\}^\eta + \{\mathbf{D}_\eta^*\}^\eta \cdot \frac{1}{V_\eta} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\eta} \, \mathrm{d}A + \left\{\tilde{\mathbf{D}}_\eta^* \cdot \nabla \mathbf{b}_{\eta\eta}\right\}^\eta - \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\}^\eta\right] \quad \text{(A14)}$$

which is more conveniently written as

$$\mathbf{D}_{\eta\eta}^{**} = \varphi_\eta \{\mathbf{D}_\eta^*\}^\eta + \frac{\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\eta} \, \mathrm{d}A + \varphi_\eta \left\{\tilde{\mathbf{D}}_\eta^* \cdot \nabla \mathbf{b}_{\eta\eta}\right\}^\eta - \varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\eta}\}^\eta \quad \text{(A15a)}$$

If we repeat this procedure with eqns (A8b), (A8c) and (A8d), we obtain

$$\mathbf{D}_{\eta\omega}^{**} = \frac{\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\omega} \, \mathrm{d}A + \varphi_\eta \left\{\tilde{\mathbf{D}}_\eta^* \cdot \nabla \mathbf{b}_{\eta\omega}\right\}^\eta - \varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_{\eta\omega}\}^\eta \quad \text{(A15b)}$$

$$\mathbf{D}_{\omega\eta}^{**} = \frac{\{\mathbf{D}_\omega^*\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \mathbf{b}_{\omega\eta} \, \mathrm{d}A + \varphi_\omega \left\{\tilde{\mathbf{D}}_\omega^* \cdot \nabla \mathbf{b}_{\omega\eta}\right\}^\omega - \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\eta}\}^\omega \quad \text{(A15c)}$$

$$\mathbf{D}_{\eta\eta}^{**} = \varphi_\omega \{\mathbf{D}_\omega^*\}^\omega + \frac{\{\mathbf{D}_\omega^*\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \mathbf{b}_{\omega\omega} \, \mathrm{d}A + \varphi_\omega \left\{\tilde{\mathbf{D}}_\omega^* \cdot \nabla \mathbf{b}_{\omega\omega}\right\}^\omega - \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_{\omega\omega}\}^\omega \quad \text{(A15d)}$$

If we sum these four equations, we begin to obtain something that resembles the definition given by eqn (A2):

$$\begin{aligned}\mathbf{D}_{\eta\eta}^{**} + \mathbf{D}_{\eta\omega}^{**} + \mathbf{D}_{\omega\eta}^{**} + \mathbf{D}_{\omega\omega}^{**} &= \varphi_\eta \{\mathbf{D}_\eta^*\}^\eta + \varphi_\omega \{\mathbf{D}_\omega^*\}^\omega \\ &+ \frac{\{\mathbf{D}_\eta^*\}^\eta}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} (\mathbf{b}_{\eta\eta} + \mathbf{b}_{\eta\omega}) \, \mathrm{d}A \\ &+ \frac{\{\mathbf{D}_\omega^*\}^\omega}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} (\mathbf{b}_{\omega\eta} + \mathbf{b}_{\omega\omega}) \, \mathrm{d}A \\ &+ \varphi_\eta \left\{\tilde{\mathbf{D}}_\eta^* \cdot \nabla (\mathbf{b}_{\eta\eta} + \mathbf{b}_{\eta\omega})\right\}^\eta + \varphi_\omega \left\{\tilde{\mathbf{D}}_\omega^* \cdot \nabla (\mathbf{b}_{\omega\eta} + \mathbf{b}_{\omega\omega})\right\} \\ &- \varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} (\mathbf{b}_{\eta\eta} + \mathbf{b}_{\eta\omega})\}^\eta - \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} (\mathbf{b}_{\omega\eta} + \mathbf{b}_{\omega\omega})\}^\omega\end{aligned} \quad \text{(A16)}$$

and the resemblance becomes clearer when we make use of the combined closure variables defined by

$$\mathbf{b}_\eta = \mathbf{b}_{\eta\eta} + \mathbf{b}_{\eta\omega}, \ \ \mathbf{b}_\omega = \mathbf{b}_{\omega\eta} + \mathbf{b}_{\omega\omega} \tag{A17}$$

Use of these relations in eqn (A16) leads to

$$\begin{aligned}\mathbf{D}^{**}_{\eta\eta} + \mathbf{D}^{**}_{\eta\omega} + \mathbf{D}^{**}_{\omega\eta} + \mathbf{D}^{**}_{\omega\omega} &= \varphi_\eta \{\mathbf{D}^*_\eta\}^\eta + \varphi_\omega \{\mathbf{D}^*_\omega\}^\omega \\ &+ \frac{\{\mathbf{D}^*_\eta\}^\eta}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_\eta \, dA \\ &+ \frac{\{\mathbf{D}^*_\omega\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \mathbf{b}_\omega \, dA \\ &+ \varphi_\eta \left\{ \tilde{\mathbf{D}}^*_\eta \cdot \nabla \mathbf{b}_\eta \right\}^\eta + \varphi_\omega \left\{ \tilde{\mathbf{D}}^*_\omega \cdot \nabla \mathbf{b}_\omega \right\} \\ &- \varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_\eta\}^\eta - \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_\omega\}^\omega \end{aligned} \tag{A18}$$

At this point one need only recognize that $\mathbf{n}_{\omega\eta} = -\mathbf{n}_{\eta\omega}$ and make use of the two boundary conditions given by eqns (49) and (51) to conclude that

$$\begin{aligned}\mathbf{D}^{**}_{\eta\eta} + \mathbf{D}^{**}_{\eta\omega} + \mathbf{D}^{**}_{\omega\eta} + \mathbf{D}^{**}_{\omega\omega} = \mathbf{D}^{**} &= \varphi_\eta \{\mathbf{D}^*_\eta\}^\eta + \varphi_\omega \{\mathbf{D}^*_\omega\}^\omega \\ &+ \frac{\{\mathbf{D}^*_\eta\}^\eta - \{\mathbf{D}^*_\omega\}^\omega}{\mathcal{V}_\infty} \cdot \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \mathbf{b}_\eta \, dA + \left\{ \tilde{\mathbf{D}}^*_\eta \cdot \nabla \mathbf{b}_\eta \right\} \\ &+ \left\{ \tilde{\mathbf{D}}^*_\omega \cdot \nabla \mathbf{b}_\omega \right\} - \left(\varphi_\eta \{\tilde{\mathbf{v}}_{\beta\eta} \mathbf{b}_\eta\}^\eta + \varphi_\omega \{\tilde{\mathbf{v}}_{\beta\omega} \mathbf{b}_\omega\}^\omega \right) \end{aligned} \tag{A19}$$

Use of this result with eqn (A7) provides the more compact form of the one-equation model given by

$$\begin{aligned}\{\epsilon\}\left(1 + \{\mathcal{K}\}\right) \frac{\partial \{\langle c \rangle\}}{\partial t} &+ \nabla \cdot \left(\{\langle \mathbf{v}_\beta \rangle\} \{\langle c \rangle\} \right) \\ &- \left(\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} + \mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega} \right) \cdot \nabla \{\langle c \rangle\} = \nabla \cdot \left(\mathbf{D}^{**} \cdot \nabla \{\langle c \rangle\} \right) \end{aligned} \tag{A20}$$

In order to calculate values of the dispersion tensor, $\mathbf{D}^{**}$, we need the closure problem that produces the closure variables $\mathbf{b}_\eta$ and $\mathbf{b}_\omega$. On the basis of the definitions given by eqn (A17) and the following definitions for the constants in the two-equation model closure problems:

$$\mathbf{c}_\eta = \mathbf{c}_{\eta\eta} + \mathbf{c}_{\eta\omega}, \ \ \mathbf{c}_\omega = \mathbf{c}_{\omega\eta} + \mathbf{c}_{\omega\omega} \tag{A21}$$

we can add eqns (49) and (51) to obtain

$$\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \mathbf{b}_\eta \right) + \tilde{\mathbf{v}}_{\beta\eta} = \nabla \cdot \left(\mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_\eta \right) + \nabla \cdot \tilde{\mathbf{D}}^*_\eta - \varphi_\eta^{-1} \mathbf{c}_\eta \tag{A22a}$$

$$\text{B.C.1} \quad \mathbf{b}_\eta = \mathbf{b}_\omega \ \text{at} \ A_{\eta\omega} \tag{A22b}$$

$$\begin{aligned}\text{B.C.2} \quad \mathbf{n}_{\eta\omega} \cdot \mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_\eta &= \mathbf{n}_{\eta\omega} \cdot \mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_\omega \\ &+ \mathbf{n}_{\eta\omega} \cdot \left(\mathbf{D}^*_\omega - \mathbf{D}^*_\eta \right) \ \text{at} \ A_{\eta\omega} \end{aligned} \tag{A22c}$$

$$\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \mathbf{b}_\omega \right) + \tilde{\mathbf{v}}_{\beta\omega} = \nabla \cdot \left(\mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_\omega \right) + \nabla \cdot \tilde{\mathbf{D}}^*_\omega - \varphi_\omega^{-1} \mathbf{c}_\omega \tag{A22d}$$

$$\text{Periodicity:} \quad \mathbf{b}_\eta(\mathbf{r} + \ell_i) = \mathbf{b}_\eta(\mathbf{r}), \ \ \mathbf{b}_\omega(\mathbf{r} + \ell_i) = \mathbf{b}_\omega(\mathbf{r}), \quad i = 1, 2, 3 \tag{A22e}$$

$$\text{Average:} \quad \{\mathbf{b}_\eta\}^\eta = 0, \ \ \{\mathbf{b}_\omega\}^\omega = 0 \tag{A22f}$$

At this point we are ready to move on to the non-traditional convective transport terms in eqn (A20), and from eqns (59) and (61) we have

$$\mathbf{u}_{\eta\eta} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \mathbf{b}_{\eta\eta} - \mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_{\eta\eta} - \tilde{\mathbf{D}}^*_\eta \right) dA \tag{A23a}$$

$$\mathbf{u}_{\eta\omega} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \mathbf{b}_{\eta\omega} - \mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_{\eta\omega} \right) dA \tag{A23b}$$

$$\mathbf{u}_{\omega\eta} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \mathbf{b}_{\omega\eta} - \mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_{\omega\eta} \right) dA \tag{A23c}$$

$$\mathbf{u}_{\omega\omega} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \mathbf{b}_{\omega\omega} - \mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_{\omega\omega} - \tilde{\mathbf{D}}^*_\omega \right) dA \tag{A23d}$$

Use of the definitions of the closure variables given by eqn (A17) allows us to add pairs of these equations to obtain

$$\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\langle \mathbf{v}_\beta \rangle_\eta \mathbf{b}_\eta - \mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_\eta - \tilde{\mathbf{D}}^*_\eta \right) dA \tag{A24a}$$

$$\mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega} = -\frac{1}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\langle \mathbf{v}_\beta \rangle_\omega \mathbf{b}_\omega - \mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_\omega - \tilde{\mathbf{D}}^*_\omega \right) dA \tag{A24b}$$

On the basis of the boundary condition given by eqn (8):

$$\text{B.C.3} \quad \mathbf{n}_{\eta\omega} \cdot \langle \mathbf{v}_\beta \rangle_\eta = \mathbf{n}_{\eta\omega} \cdot \langle \mathbf{v}_\beta \rangle_\omega, \ \ \text{at} \ A_{\eta\omega} \tag{A25}$$

we can add eqns (A24a) and (A24b) to obtain

$$\begin{aligned}\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} + \mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega} &= \frac{1}{\mathcal{V}_\infty} \int_{A_{\eta\omega}} \mathbf{n}_{\eta\omega} \cdot \left(\mathbf{D}^*_\eta \cdot \nabla \mathbf{b}_\eta + \tilde{\mathbf{D}}^*_\eta \right) dA \\ &+ \frac{1}{\mathcal{V}_\infty} \int_{A_{\omega\eta}} \mathbf{n}_{\omega\eta} \cdot \left(\mathbf{D}^*_\omega \cdot \nabla \mathbf{b}_\omega + \tilde{\mathbf{D}}^*_\omega \right) dA \end{aligned} \tag{A26}$$

Integrating eqn (A22c) over the area $A_{\eta\omega}$ indicates that the two integrals in this result sum to zero:

$$\mathbf{u}_{\eta\eta} + \mathbf{u}_{\eta\omega} + \mathbf{u}_{\omega\eta} + \mathbf{u}_{\omega\omega} = 0 \tag{A27}$$

so eqn (A20) simplifies to

$$\{\epsilon\}\left(1 + \{\mathcal{K}\}\right) \frac{\partial \{\langle c \rangle\}}{\partial t} + \nabla \cdot \left(\{\langle \mathbf{v}_\beta \rangle\} \{\langle c \rangle\} \right) = \nabla \cdot \left(\mathbf{D}^{**} \cdot \nabla \{\langle c \rangle\} \right) \tag{A28}$$

We refer to this form as the one-equation equilibrium model, since it is based on the condition of large-scale equilibrium.

APPENDIX B: MOMENT ANALYSIS OF THE TWO-EQUATION MODEL

A complete analysis of the three-dimensional moments associated with the two-equation model can be found in Zanotti and Carbonell[29]. In this Appendix, we present a similar analysis with the emphasis on the asymptotic behaviour of the system as a whole, i.e. the average concentration for the two regions, in order to compare our work with that of Marle *et al.*[24].

We consider a one-dimensional, large-scale flow described by the two-equation model given by

$$\epsilon_\eta\varphi_\eta\frac{\partial}{\partial t}\{\langle c_\eta\rangle^\eta\}^\eta+\{\langle \mathrm{v}_\beta\rangle_\eta\}\frac{\partial}{\partial x}\{\langle c_\eta\rangle^\eta\}^\eta = (\mathsf{D}^{**}_{\eta\eta})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\eta\rangle^\eta\}^\eta+(\mathsf{D}^{**}_{\eta\omega})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\omega\rangle^\omega\}^\omega - \alpha^*(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega) \quad \text{(B1a)}$$

$$\epsilon_\omega\varphi_\omega\frac{\partial}{\partial t}\{\langle c_\omega\rangle^\omega\}^\omega+\{\langle \mathrm{v}_\beta\rangle_\omega\}\frac{\partial}{\partial x}\{\langle c_\omega\rangle^\omega\}^\omega = (\mathsf{D}^{**}_{\omega\omega})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\omega\rangle^\omega\}^\omega+(\mathsf{D}^{**}_{\omega\eta})_{xx}\frac{\partial^2}{\partial x^2}\{\langle c_\eta\rangle^\eta\}^\eta - \alpha^*(\{\langle c_\omega\rangle^\omega\}^\omega-\{\langle c_\eta\rangle^\eta\}^\eta) \quad \text{(B1b)}$$

We consider the special case of an infinite medium with the following boundary condition:

$$\lim_{x\to\pm\infty}\{\langle c_\eta\rangle^\eta\}^\eta=0 \text{ and } \lim_{x\to\pm\infty}\{\langle c_\omega\rangle^\omega\}^\omega=0 \quad \text{(B2)}$$

along with a similar condition for all derivatives of the concentrations. We adopt the following change of variable:

$$X=x-V_r t/\{\epsilon\} \quad \text{(B3)}$$

so that eqns (B1) takes the form

$$\epsilon_\eta\varphi_\eta\frac{\partial}{\partial t}\{\langle c_\eta\rangle^\eta\}^\eta+\left(\{\langle \mathrm{v}_\beta\rangle_\eta\}-\frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\frac{\partial}{\partial X}\{\langle c_\eta\rangle^\eta\}^\eta = (\mathsf{D}^{**}_{\eta\eta})_{xx}\frac{\partial^2}{\partial X^2}\{\langle c_\eta\rangle^\eta\}^\eta+(\mathsf{D}^{**}_{\eta\omega})_{xx}\frac{\partial^2}{\partial X^2}\{\langle c_\omega\rangle^\omega\}^\omega - \alpha^*(\{\langle c_\eta\rangle^\eta\}^\eta-\{\langle c_\omega\rangle^\omega\}^\omega) \quad \text{(B4a)}$$

$$\epsilon_\omega\varphi_\omega\frac{\partial}{\partial t}\{\langle c_\omega\rangle^\omega\}^\omega+\left(\{\langle \mathrm{v}_\beta\rangle_\omega\}-\frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\frac{\partial}{\partial X}\{\langle c_\omega\rangle^\omega\}^\omega = (\mathsf{D}^{**}_{\omega\omega})_{xx}\frac{\partial^2}{\partial X^2}\{\langle c_\omega\rangle^\omega\}^\omega+(\mathsf{D}^{**}_{\omega\eta})_{xx}\frac{\partial^2}{\partial X^2}\{\langle c_\eta\rangle^\eta\}^\eta - \alpha^*(\{\langle c_\omega\rangle^\omega\}^\omega-\{\langle c_\eta\rangle^\eta\}^\eta) \quad \text{(B4b)}$$

We define the spatial moments associated with the concentration fields as

$$\mu_{\alpha,n}=\int_{-\infty}^{+\infty}X^n\{\langle c_\alpha\rangle^\alpha\}^\alpha\,\mathrm{d}X,\ \ \alpha=\eta,\omega \quad \text{(B5)}$$

Multiplying eqns (B4) by X^n and integrating by parts, we obtain the following set of governing equations for the moments:

$$\epsilon_\eta\varphi_\eta\frac{\partial\mu_{\eta,n}}{\partial t}=n\left(\{\langle \mathrm{v}_\beta\rangle_\eta\}-\frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_{\eta,n-1} + n(n-1)(\mathsf{D}^{**}_{\eta\eta})_{xx}\mu_{\eta,n-2} + n(n-1)(\mathsf{D}^{**}_{\eta\omega})_{xx}\mu_{\omega,n-2}-\alpha^*(\mu_{\eta,n}-\mu_{\omega,n}) \quad \text{(B6a)}$$

$$\epsilon_\omega\varphi_\omega\frac{\partial\mu_{\omega,n}}{\partial t}=n\left(\{\langle \mathrm{v}_\beta\rangle_\omega\}-\frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_{\omega,n-1} + n(n-1)(\mathsf{D}^{**}_{\omega\omega})_{xx}\mu_{\omega,n-2} + n(n-1)(\mathsf{D}^{**}_{\omega\eta})_{xx}\mu_{\eta,n-2} -\alpha^*(\mu_{\omega,n}-\mu_{\eta,n}) \quad \text{(B6b)}$$

These equations can be solved sequentially, starting with moments of order zero. All calculations presented below have been performed within SCIENTIFIC WORKPLACE™ using the MAPLE™ library.

Moments of order

The set of differential equations to be solved is

$$\epsilon_\eta\varphi_\eta\frac{\partial\mu_{\eta,0}}{\partial t}=-\alpha^*(\mu_{\eta,0}-\mu_{\omega,0}) \quad \text{(B7a)}$$

$$\epsilon_\omega\varphi_\omega\frac{\partial\mu_{\omega,0}}{\partial t}=-\alpha^*(\mu_{\omega,0}-\mu_{\eta,0}) \quad \text{(B7b)}$$

and the general solution is given by

$$\{\epsilon\}\mu_{\eta,0}=\epsilon_\eta\varphi_\eta g_{\eta,0}+\epsilon_\omega\varphi_\omega g_{\omega,0} + \exp\left(-\alpha^* t\frac{\{\epsilon\}}{\epsilon_\eta\varphi_\eta\epsilon_\omega\varphi_\omega}\right) \times(\epsilon_\omega\varphi_\omega g_{\eta,0}-\epsilon_\omega\varphi_\omega g_{\omega,0}) \quad \text{(B8a)}$$

$$\{\epsilon\}\mu_{\omega,0}=\epsilon_\eta\varphi_\eta g_{\eta,0}+\epsilon_\omega\varphi_\omega g_{\omega,0} + \exp\left(-\alpha^* t\frac{\{\epsilon\}}{\epsilon_\eta\varphi_\eta\epsilon_\omega\varphi_\omega}\right) \times(\epsilon_\eta\varphi_\eta g_{\omega,0}-\epsilon_\eta\varphi_\eta g_{\eta,0}) \quad \text{(B8b)}$$

where $g_{\eta,0}$ and $g_{\omega,0}$ are the initial values. Adding eqns (B8), we obtain the following result:

$$\{\epsilon\}\mu_{\mathrm{o}}=\epsilon_\eta\varphi_\eta\mu_{\eta,0}+\epsilon_\omega\varphi_\omega\mu_{\omega,0} =\epsilon_\eta\varphi_\eta g_{\eta,0}+\epsilon_\omega\varphi_\omega g_{\omega,0}=\text{constant} \quad \text{(B9)}$$

In addition, we get

$$\lim_{t\to\infty} \mu_{\eta,0} = \lim_{t\to\infty} \mu_{\omega,0} = \frac{\epsilon_\eta\varphi_\eta\mu_{\eta,0} + \epsilon_\omega\varphi_\omega\mu_{\omega,0}}{\{\epsilon\}} = \mu_o \tag{B10}$$

Moments of order 1

From eqns (B6) we get

$$\epsilon_\eta\varphi_\eta \frac{\partial\mu_{\eta,1}}{\partial t} = \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_{\eta,0} - \alpha^*\left(\mu_{\eta,1} - \mu_{\omega,1}\right) \tag{B11a}$$

$$\epsilon_\omega\varphi_\omega \frac{\partial\mu_{\omega,1}}{\partial t} = \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} - \frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_{\omega,0} - \alpha^*\left(\mu_{\omega,1} - \mu_{\eta,1}\right) \tag{B11b}$$

Adding these two equations, we obtain

$$\begin{aligned}\{\epsilon\}\frac{\partial\mu_1}{\partial t} &= \epsilon_\eta\varphi_\eta\frac{\partial\mu_{\eta,1}}{\partial t} + \epsilon_\omega\varphi_\omega\frac{\partial\mu_{\omega,1}}{\partial t} \\ &= \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_{\eta,0} \\ &\quad + \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} - \frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_{\omega,0}\end{aligned} \tag{B12}$$

The asymptotic behaviour is such that

$$\lim_{t\to\infty}\left(\{\epsilon\}\frac{\partial\mu_1}{\partial t}\right) = \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_o + \left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} - \frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_o \tag{B13}$$

The reference velocity that makes the right-hand side of this equation equal to zero is

$$V_r = \left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} + \left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} \tag{B14}$$

and we shall use this value for V_r in the following paragraphs.

Using symbolic calculus, we were able to obtain the following limits:

$$\lim_{t\to\infty} \mu_{\eta,1} = \frac{\epsilon_\eta\varphi_\eta f_\eta + \epsilon_\omega\varphi_\omega f_\omega}{\{\epsilon\}} + \epsilon_\omega\varphi_\omega\mu_o\frac{\left(\epsilon_\omega\varphi_\omega\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \epsilon_\eta\varphi_\eta\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\}\right)}{\alpha^*\{\epsilon\}^2} \tag{B15a}$$

$$\lim_{t\to\infty} \mu_{\omega,1} = \frac{\epsilon_\eta\varphi_\eta f_\eta + \epsilon_\omega\varphi_\omega f_\omega}{\{\epsilon\}} - \epsilon_\eta\varphi_\eta\mu_o\frac{\left(\epsilon_\omega\varphi_\omega\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \epsilon_\eta\varphi_\eta\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\}\right)}{\alpha^*\{\epsilon\}^2} \tag{B15b}$$

where

$$f_\alpha = \mu_{\alpha,1}(t=0), \ \ \alpha = \eta, \omega \tag{B15c}$$

Moments of order 2

The governing equations for the moments of order 2 are

$$\begin{aligned}\epsilon_\eta\varphi_\eta\frac{\partial\mu_{\eta,2}}{\partial t} &= 2\left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_{\eta,1} \\ &\quad + 2\left(\mathsf{D}^{**}_{\eta\eta}\right)_{xx}\mu_{\eta,0} + 2\left(\mathsf{D}^{**}_{\eta\omega}\right)_{xx}\mu_{\omega,0} \\ &\quad - \alpha^*\left(\mu_{\eta,2} - \mu_{\omega,2}\right)\end{aligned} \tag{B16a}$$

$$\begin{aligned}\epsilon_\omega\varphi_\omega\frac{\partial\mu_{\omega,2}}{\partial t} &= 2\left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} - \frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_{\omega,1} \\ &\quad + 2\left(\mathsf{D}^{**}_{\omega\omega}\right)_{xx}\mu_{\omega,0} + 2\left(\mathsf{D}^{**}_{\omega\eta}\right)_{xx}\mu_{\eta,0} \\ &\quad - \alpha^*\left(\mu_{\omega,2} - \mu_{\eta,2}\right)\end{aligned} \tag{B16b}$$

When these two equations are added, we obtain

$$\begin{aligned}\{\epsilon\}\frac{\partial\mu_2}{\partial t} &= \epsilon_\eta\varphi_\eta\frac{\partial\mu_{\eta,2}}{\partial t} + \epsilon_\omega\varphi_\omega\frac{\partial\mu_{\omega,2}}{\partial t} \\ &= 2\left[\left(\mathsf{D}^{**}_{\eta\eta}\right)_{xx} + \left(\mathsf{D}^{**}_{\omega\eta}\right)_{xx}\right]\mu_{\eta,0} \\ &\quad + 2\left[\left(\mathsf{D}^{**}_{\omega\omega}\right)_{xx} + \left(\mathsf{D}^{**}_{\eta\omega}\right)_{xx}\right]\mu_{\omega,0} \\ &\quad + 2\left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \frac{\epsilon_\eta\varphi_\eta V_r}{\{\epsilon\}}\right)\mu_{\eta,1} \\ &\quad + 2\left(\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\} - \frac{\epsilon_\omega\varphi_\omega V_r}{\{\epsilon\}}\right)\mu_{\omega,1}\end{aligned} \tag{B17}$$

The asymptotic limit is obtained by taking the limit of this equation and using eqns (B15) and (B10) to obtain

$$\begin{aligned}\{\epsilon\}\frac{\partial\mu_2}{\partial t} &= 2\left[\left(\mathsf{D}^{**}_{\eta\eta}\right)_{xx} + \left(\mathsf{D}^{**}_{\omega\eta}\right)_{xx} + \left(\mathsf{D}^{**}_{\eta\omega}\right)_{xx} + \left(\mathsf{D}^{**}_{\omega\omega}\right)_{xx}\right]\mu_o \\ &\quad + 2\frac{\left(\epsilon_\omega\varphi_\omega\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \epsilon_\eta\varphi_\eta\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\}\right)^2}{\alpha^*\{\epsilon\}^2}\mu_o\end{aligned} \tag{B18}$$

We are now in a position to conclude that the asymptotic behaviour of the two-equation model can be represented by a dispersion equation of the form

$$\{\epsilon\}\frac{\partial\{\langle c\rangle\}}{\partial t} + \left\{\left\langle \mathrm{v}_\beta\right\rangle\right\}\frac{\partial\{\langle c\rangle\}}{\partial x} = \left(\mathsf{D}^{**}_\infty\right)_{xx}\frac{\partial^2\{\langle c\rangle\}}{\partial x^2} \tag{B19}$$

where the asymptotic dispersion coefficient is given by

$$\begin{aligned}\left(\mathsf{D}^{**}_\infty\right)_{xx} &= \left[\left(\mathsf{D}^{**}_{\eta\eta}\right)_{xx} + \left(\mathsf{D}^{**}_{\omega\eta}\right)_{xx} + \left(\mathsf{D}^{**}_{\eta\omega}\right)_{xx} + \left(\mathsf{D}^{**}_{\omega\omega}\right)_{xx}\right] \\ &\quad + \frac{\left(\epsilon_\omega\varphi_\omega\left\{\left\langle \mathrm{v}_\beta\right\rangle_\eta\right\} - \epsilon_\eta\varphi_\eta\left\{\left\langle \mathrm{v}_\beta\right\rangle_\omega\right\}\right)^2}{\alpha^*\{\epsilon\}^2}\end{aligned} \tag{B20}$$

One should note that this development *does not* make the assumption that the initial conditions are similar for both regions.

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