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.

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NOMENCLATURE

$\alpha_{\gamma\kappa}$ = $A_{\gamma\kappa}/V_{\gamma\kappa}$, interfacial area per unit volume, m$^{-1}$.

$A_{\gamma\kappa}$ = area of the $\gamma$-$\kappa$ interface contained in the averaging volume, $V_{\gamma\kappa}$, m$^2$.

$A_{\beta\sigma}$ = $A_{\beta\sigma}$, area of the $\beta$-$\sigma$ interface contained in the averaging volume, $V_{\beta\sigma}$, m$^2$.

$A_{\omega\eta}$ = area of the boundary between the $\eta$ and $\omega$-regions contained with the large-scale averaging volume, $V_{\omega\eta}$, m$^2$.

$b_{\eta\gamma}$, $b_{\\omega\kappa}$, $b_{\omega\eta}$, $b_{\eta\kappa}$ vector fields that maps $\nabla (c_{\eta\gamma}^0)^0$ onto $\hat{c}_{\eta\gamma}$, m.

$c_{\gamma}\eta$ point concentration in the $\gamma$-phase, mol m$^{-3}$.

$c_{\omega\eta}$ Darcy-scale intrinsic average concentration for the $\beta$-$\sigma$ system in the $\eta$-region, mol m$^{-3}$.

$c_{\omega\eta}$ Darcy-scale intrinsic average concentration for the $\beta$-$\sigma$ system in the $\omega$-region, mol m$^{-3}$.

$\{c_{\gamma}\eta\}$ $\eta$-region superficial average concentration, mol m$^{-3}$.

$\{c_{\omega\eta}\}^w$ $\omega$-region superficial average concentration, mol m$^{-3}$.

$\{c_{\gamma\eta}\}$ $\eta$-region intrinsic average concentration, mol m$^{-3}$.

$\{c_{\omega\eta}\}^w$ $\omega$-region intrinsic average concentration, mol m$^{-3}$.

$\epsilon_{\omega\sigma}$ spatial deviation concentration for the $\omega$-region, mol m$^{-3}$.

$\epsilon_{\omega\sigma}$ spatial deviation concentration for the $\omega$-region, mol m$^{-3}$.

$D_{\gamma\kappa}$ dispersion tensor for the $\gamma$-$\kappa$ system in the $\eta$-region, m$^2$s$^{-1}$.

$D_{\omega\eta}$ dispersion tensor for the $\omega$-region, m$^2$s$^{-1}$.

$D_{\gamma\kappa}$ dominant dispersion tensor for the $\eta$-region transport equation, m$^2$s$^{-1}$.
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.5,6 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.6,7), and the theoretical implications of this idea have been discussed extensively.5,6 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:
1. the macropore scale, in which averaging takes place over the volume $V_j$;
2. the Darcy scale, in which averaging takes place over the volume $V$;
3. the local heterogeneity scale, in which averaging takes place over the volume $V'_l$;
4. the reservoir- or aquifer-scale heterogeneities, which have been identified by the length scale $L_H$ 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 of this study, many applications will require the addition of a micropore scale when the $\kappa$-region illustrated in Fig. 1 contains micropores, and many realistic systems may contain other intermediate length scales either within the $\beta-\sigma$ system or within the heterogeneities associated with the averaging volume $V'_l$. 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.

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 of this study, and there it led to a Darcy-scale representation of the dispersion process. The analysis required, among other constraints, that

$$\ell_\alpha, \ell_\gamma \ll r_\epsilon, \ell_\beta, \ell_\sigma \ll r_\zeta, \ell_\omega$$

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 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 $\gamma$ in Fig. 1. Based on this assumption, and provided that the following length-scale constraints are satisfied:

$$\ell_\alpha, \ell_\gamma \ll \ell_\beta, \ell_\sigma \ll r_\epsilon, \ell_\omega$$

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 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, $L_p$, 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.

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). 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 (see also the reviews cited above). 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). 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 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.

The Darcy-scale process of solute transport with adsorption in the $\eta-\omega$ system shown in Fig. 2 is given by

\[
e_u(1+\kappa_u) \frac{\partial \langle c_u \rangle}{\partial t} + \nabla \cdot \left( \langle \mathbf{v_u} \rangle \langle c_u \rangle \right)
= \nabla \cdot \left( \mathbf{D_u} \frac{\partial \langle c_u \rangle}{\partial \eta} \right)
\]

\[= \nabla \cdot \left( \langle \mathbf{v_u} \rangle \langle c_u \rangle \right) - \nabla \cdot \left( \mathbf{D} \frac{\partial \langle c_u \rangle}{\partial \eta} \right)\]

(3)

B.C. 1: $\langle c_u \rangle \big|_{\eta=0} = \langle c_u \rangle \big|_{\eta=\infty}$, at $\eta_{\infty}$

B.C. 2: $-n_{aw} \langle \mathbf{v_u} \rangle \langle c_u \rangle \big|_{\eta=0} - \mathbf{D} \frac{\partial \langle c_u \rangle}{\partial \eta} \big|_{\eta=0} = 0$

(4)

$\epsilon_u(1+\kappa_u) \frac{\partial \langle c_u \rangle}{\partial t} + \nabla \cdot \left( \langle \mathbf{v_u} \rangle \langle c_u \rangle \right) = \nabla \cdot \left( \mathbf{D_u} \frac{\partial \langle c_u \rangle}{\partial \eta} \right)$

(5)

Here $\kappa_u$ and $\kappa_w$ represent the Darcy-scale equilibrium adsorption coefficients, which may be non-linear functions of the concentrations, $\langle c_u \rangle^o$ and $\langle c_w \rangle^o$. In addition to the solute transport equations, we shall need to make use of the two Darcy-scale continuity equations that take the form

\[\nabla \cdot \langle \mathbf{j_u} \rangle = 0\]

(7a)

\[\nabla \cdot \langle \mathbf{j_w} \rangle = 0\]

(7b)

along with the boundary condition for the normal component of the velocity, which is given by

\[n_{aw} \langle \mathbf{j_u} \rangle \big|_{\eta=0} = n_{aw} \langle \mathbf{j_w} \rangle \big|_{\eta=0} \]

(8)

In Part IV the region-average transport equations were developed, and the superficial average forms are given by
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:

\[ h - \text{region:} \]
\[
\varepsilon_h \left(1 + \mathcal{X}_h \right) \frac{\partial \{ c_h \}^\eta}{\partial t} + \nabla \cdot \left[ \mu_h \left( \{ v_h \} \right) \{ c_h \}^\eta \right] = \\
\left[ \frac{\nabla \cdot \{ D_h^\eta \} \cdot \{ c_h \}^\eta \cdot \nabla \{ c_h \}^\eta}{\eta} \right] - \\
\left[ \frac{1}{\eta^2} \int_{A_{h\eta}} n_{h\eta} c_{\eta} dA \right] - \\
\left[ \frac{1}{\eta^2} \int_{A_{\eta\eta}} \left( \{ v_h \} \cdot \{ c_{\eta} \} \right) \cdot \left( \{ c_h \} \cdot \{ c_{\eta} \} \right) dA \right]
\]

\[ q - \text{region:} \]
\[
\varepsilon_q \left(1 + \mathcal{X}_q \right) \frac{\partial \{ c_q \}^\omega}{\partial t} + \nabla \cdot \left[ \mu_q \left( \{ v_q \} \right) \{ c_q \}^\omega \right] = \\
\left[ \frac{\nabla \cdot \{ D_q^\omega \} \cdot \{ c_q \}^\omega \cdot \nabla \{ c_q \}^\omega}{\omega} \right] - \\
\left[ \frac{1}{\omega^2} \int_{A_{q\omega}} n_{q\omega} c_{\omega} dA \right] - \\
\left[ \frac{1}{\omega^2} \int_{A_{\omega\omega}} \left( \{ v_q \} \cdot \{ c_{\omega} \} \right) \cdot \left( \{ c_q \} \cdot \{ c_{\omega} \} \right) dA \right]
\]

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 eqn (9), we see various large-scale terms such as \( \nabla \cdot \{ D_h^\eta \} \cdot \{ c_h \} \) in eqn (9a) and \( \nabla \cdot \{ D_q^\omega \} \cdot \{ c_q \} \) in eqn (9b), and we see other terms such as \( n_{h\eta} c_{\eta} \) and \( v_{h\eta} c_{\eta} \).

\[ \eta\text{-region:} \]
\[
\nabla \cdot \{ \langle v_h \rangle \} + \frac{1}{q^\eta} \int_{A_{h\eta}} n_{h\eta} \langle v_h \rangle dA = 0 \quad (10a)
\]

\[ \omega\text{-region:} \]
\[
\nabla \cdot \{ \langle v_q \rangle \} + \frac{1}{q^\omega} \int_{A_{q\omega}} n_{q\omega} \langle v_q \rangle dA = 0 \quad (10b)
\]
that involve the spatial deviation quantities. In addition, the inter-region flux is specified entirely in terms of the Darcy-scale variables such as \( \langle \psi \rangle_q \) and \( \langle c \rangle_q \). In the following section we shall develop the closure problem which will allow us to determine the diffusive terms such as \( \mathbf{D} \nabla \langle c \rangle_q \) and the dispersive terms such as \( \mathbf{V} \nabla \langle c \rangle_q \). More importantly, we shall develop a representation for the inter-region flux terms in a useful form, 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 completely determines 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 \( \eta \)-region transport equation, we make use of the decomposition

\[
\langle c \rangle_q = \langle \langle c \rangle_q \rangle^\eta + \langle c \rangle_\eta
\]

in order to express the inter-region flux as

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle \langle c \rangle_q \rangle^\eta - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle^\eta \right) \, dA
\]

\[
= \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle \langle c \rangle_q \rangle - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle \right) \, dA + \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle c \rangle_q - \mathbf{D} \nabla \langle c \rangle_q \right) \, dA
\]

(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 \( \langle \psi \rangle_q \) and \( \mathbf{D} \). 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:

\[
\mathbf{D}_\eta = \{ \mathbf{D} \}^\eta + \tilde{\mathbf{D}}^\eta
\]

(13)

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

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle \langle c \rangle_q \rangle^\eta - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle^\eta \right) \, dA
\]

\[
= \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle \langle c \rangle_q \rangle - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle \right) \, dA + \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \tilde{\mathbf{D}} \nabla \langle \langle c \rangle_q \rangle \, dA
\]

(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

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \left( \langle \psi \rangle_q \langle \langle c \rangle_q \rangle^\eta - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle^\eta \right) \, dA
\]

\[
= \left[ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dA \right] \langle \langle c \rangle_q \rangle^\eta
\]

\[
- \left[ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \mathbf{D} \nabla \langle \langle c \rangle_q \rangle \, dA \right]
\]

\[
- \left[ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \tilde{\mathbf{D}} \nabla \langle \langle c \rangle_q \rangle \, dA \right]
\]

(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,

\[
\text{Periodicity:} \quad \langle \psi \rangle_q (\mathbf{r} + \ell) = \langle \psi \rangle_q (\mathbf{r}), \quad i = 1, 2, 3
\]

(16)

allows us to write

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dA = \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dA
\]

\[
+ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dA
\]

(17)

in which \( A_\omega \) represents the area of entrances and exits for the \( \eta \)-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

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dA = \frac{1}{\nu} \int_{\partial \omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \, dV = 0
\]

(18)

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

\[
\frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \langle \psi \rangle_q \langle \langle c \rangle_q \rangle^\eta - \mathbf{D} \nabla \langle \langle c \rangle_q \rangle^\eta \, dA
\]

\[
= - \left[ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \cdot \mathbf{D} \nabla \langle \langle c \rangle_q \rangle \, dA \right]
\]

\[
- \left[ \frac{1}{\nu} \int_{A_\omega} \mathbf{n}_\omega \tilde{\mathbf{D}} \nabla \langle \langle c \rangle_q \rangle \, dA \right]
\]

(19)

Considering the first term on the right-hand side of this
result, we make use of the averaging theorem to obtain
\[- \left( \frac{1}{V_\infty} \int_{A_\infty} n_{\omega} \, dA \right) \cdot \left\{ \left( \nabla \langle \epsilon \rangle \right)^n \right\} \]
\[= \nabla \varphi_\infty \left\{ \left( \nabla \langle \epsilon \rangle \right)^n \right\} \]
(20)
For a spatially periodic system, \( \nabla \varphi_\infty \) is zero and eqn (20) allows us to express eqn (19) as
\[- \left( \frac{1}{V_\infty} \int_{A_\infty} n_{\omega} \, dA \right) \cdot \left\{ \left( \nabla \langle \epsilon \rangle \right)^n \right\} \]
\[= - \left( \frac{1}{V_\infty} \int_{A_\infty} n_{\omega} \cdot \nabla \langle \epsilon \rangle \, dA \right) \]
(21)
We are now ready to return to eqn (12) and express that inter-region flux according to
\[- \left( \frac{1}{V_\infty} \int_{A_\infty} n_{\omega} \cdot \left\{ \langle \epsilon \rangle \right\} \, dA \right) \]
\[= \left( \frac{1}{V_\infty} \int_{A_\infty} n_{\omega} \cdot \left\{ \langle \epsilon \rangle \right\} \, dA \right)
\[= \nabla \cdot \left\{ \left( \nabla \langle \epsilon \rangle \right)^n \right\} \]
(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.

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, \( \nabla \langle \epsilon \rangle \). 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 \( q \)-region can be obtained from eqn (9b) and is given by
\[\begin{align*}
&\text{accumulation and adsorption} \\
&\text{large-scale convection} \\
&\text{large-scale diffusion} \\
&\text{large-scale dispersion} \\
&\text{inter-region flux}
\end{align*}
\]
\[\begin{align*}
&\text{accumulation and adsorption} \\
&\text{large-scale convection} \\
&\text{large-scale diffusion} \\
&\text{large-scale dispersion} \\
&\text{inter-region flux}
\end{align*}
\]
\[\begin{align*}
&\text{accumulation and adsorption} \\
&\text{large-scale convection} \\
&\text{large-scale diffusion} \\
&\text{large-scale dispersion} \\
&\text{inter-region flux}
\end{align*}
\]
\[\begin{align*}
&\text{accumulation and adsorption} \\
&\text{large-scale convection} \\
&\text{large-scale diffusion} \\
&\text{large-scale dispersion} \\
&\text{inter-region flux}
\end{align*}
\]
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 \( \bar{c}_v \) and \( \bar{c}_w \). The governing differential equation for \( \bar{c}_v \) can be obtained by subtracting the intrinsic form of eqn (23a) from the Darcy-scale equation for \( \bar{c}_v \) that is given by eqn (3). We develop the intrinsic form of eqn (23a) by dividing that result by \( \varphi_n \), 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, \( \varphi_n \), in the development of the closure problem, and this means that the intrinsic form of eqn (23a) can be expressed as

\[
\epsilon \left( 1 + \mathcal{K}_c \right) \frac{\partial \left( \bar{c}_v \right)}{\partial t} + \nabla \cdot \{ \bar{c}_v \} = \nabla \cdot \left( \bar{c}_v \bar{v} \right) + \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

Subtraction of this result from eqn (3) leads to

\[
\epsilon \left( 1 + \mathcal{K}_c \right) \frac{\partial \left( \bar{c}_v \right)}{\partial t} + \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

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

\[
\langle \bar{v}_b \rangle = \langle \bar{v}_b \rangle + \bar{v}_b \nonumber
\]

and write

\[
\langle \bar{v}_b \rangle = \langle \bar{v}_b \rangle + \bar{v}_b \Rightarrow \nonumber
\]

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

\[
\langle \bar{v}_b \rangle = \langle \bar{v}_b \rangle + \bar{v}_b \Rightarrow \nonumber
\]

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

\[
\nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

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

\[
\nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

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

\[
\epsilon \left( 1 + \mathcal{K}_c \right) \frac{\partial \left( \bar{c}_v \right)}{\partial t} + \nabla \cdot \left( \bar{c}_v \bar{v} \right) + \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right) - \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

and since we are ignoring variations of \( \varphi_n \), the continuity equation for the intrinsic regional average velocity takes the form

\[
\nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right) = \nabla \cdot \left( \bar{c}_v \bar{v} \right)
\]

(28)
As a final simplification of this closure problem, we make use of the averaging theorem to write
\[
\{ \nabla \tilde{c}_\eta \} = \nabla \{ \tilde{c}_\eta \} + \frac{1}{\gamma_a} \int_{A_w} n_{\text{ref}} \tilde{c}_\eta \, dA
\] (33)
and setting the average of the deviation equal to zero allows us to express this result as
\[
\frac{\varphi_y}{\varphi_a} \int_{A_w} n_{\text{ref}} \tilde{c}_\eta \, dA = \{ \nabla \tilde{c}_\eta \}^p
\] (34)
Multiplication by \( \{ D_\eta^* \}^p \) provides
\[
\frac{\varphi_y}{\varphi_a} \int_{A_w} n_{\text{ref}} \tilde{c}_\eta \, dA = \{ \{ D_\eta^* \}^p \nabla \tilde{c}_\eta \}^p
\] (35)
and this allows us to express eqn (32) in the slightly more compact form given by
\[
\epsilon_\eta \left( 1 + \kappa_a \right) \frac{\partial \tilde{c}_\eta}{\partial t} + \nabla \cdot \left( \langle v_\beta \rangle \tilde{c}_\eta \right) + \frac{\tilde{v}_{B\eta}}{\epsilon_\eta} \nabla \{ \langle c_\eta \rangle \}^\eta - \nabla \cdot \left( \tilde{v}_{B\eta} \langle c_\eta \rangle \right) =
\]
\[
= \nabla \cdot \left( D_\eta^{*} \nabla \tilde{c}_\eta \right) + \nabla \cdot \left( \tilde{D}_\eta^{*} \nabla \{ \langle c_\eta \rangle \}^\eta \right) - \nabla \cdot \left( D_\eta^{*} \nabla \{ \langle c_\eta \rangle \}^\eta \right)
\]
\[
+ \frac{\varphi_a}{\varphi_y} \int_{A_w} n_{\text{ref}} \left( \langle v_\beta \rangle \tilde{c}_\eta - D_\eta^{*} \nabla \tilde{c}_\eta - \tilde{D}_\eta^{*} \nabla \{ \langle c_\eta \rangle \}^\eta \right) \, dA
\] (36)
If we estimate the accumulation and diffusive terms according to
\[
\epsilon_\eta \left( 1 + \kappa_a \right) \frac{\partial \tilde{c}_\eta}{\partial t} = O \left[ \epsilon_\eta \left( 1 + \kappa_a \right) \tilde{c}_\eta \right]
\] (37)
\[
\nabla \cdot \left( D_\eta^{*} \nabla \tilde{c}_\eta \right) = O \left[ \frac{D_\eta^{*}}{\ell_a} \right]
\] (38)
the closure equation for \( \tilde{c}_\eta \) will be quasi-steady when the following constraint is satisfied:
\[
\frac{D_\eta^{*}}{\ell_a^2 \tilde{c}_\eta} \gg 1
\] (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 \( D_\eta^{*} \) will increase with increasing values of \( \ell_a \). The convective transport term and the large-scale dispersive transport term in eqn (36) can be estimated according to
\[
\nabla \cdot \left( \langle v_\beta \rangle \tilde{c}_\eta \right) = O \left[ \langle v_\beta \rangle \tilde{c}_\eta \ell_a \right]
\] (40)
\[
\nabla \cdot \left( \tilde{v}_{B\eta} \langle c_\eta \rangle \right) = O \left[ \tilde{v}_{B\eta} \langle c_\eta \rangle \ell_a \right]
\] (41)
and this allows us to neglect the large-scale dispersive transport whenever the length scales of the heterogeneities are constrained by
\[
\ell_a \ll \ell_a
\] (42)
Moving on to the diffusive terms, we keep eqn (38) in mind and estimate the non-local term as
\[
\nabla \cdot \left( D_\eta^{*} \nabla \tilde{c}_\eta \right) = O \left[ \frac{D_\eta^{*}}{\ell_a^2 \tilde{c}_\eta} \right]
\] (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:
\[
\nabla \cdot \left( \langle v_\beta \rangle \tilde{c}_\eta \right) + \frac{\tilde{v}_{B\eta}}{\epsilon_\eta} \nabla \{ \langle c_\eta \rangle \}^\eta = \nabla \cdot \left( D_\eta^{*} \nabla \tilde{c}_\eta \right) + \nabla \cdot \left( \tilde{D}_\eta^{*} \nabla \{ \langle c_\eta \rangle \}^\eta \right)
\]
\[
+ \frac{\varphi_a}{\varphi_y} \int_{A_w} n_{\text{ref}} \left( \langle v_\beta \rangle \tilde{c}_\eta - D_\eta^{*} \nabla \tilde{c}_\eta - \tilde{D}_\eta^{*} \nabla \{ \langle c_\eta \rangle \}^\eta \right) \, dA
\] (44)
Here we note that our closure equation will be homogeneous in \( \hat{c}_q \) 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 \( \hat{c}_q \)-field. An analogous form can be derived for the \( \omega \)-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

\[ B.C.1 \quad \langle c_q \rangle^n = \langle c_q \rangle^w, \quad \text{at } A_{nw} \] (45)

\[ B.C.2 \quad n_{nw} \cdot D_q \cdot \nabla \langle c_q \rangle^w = n_{nw} \cdot D_q \cdot \nabla \langle c_q \rangle^w, \quad \text{at } A_{nw} \] (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, \( \hat{c}_q \) and \( \hat{c}_\omega \). This leads us to the closure problem as follows.

2.2 Closure problem

**Perioidicity:**

\[ \hat{c}_q (r + \ell_i) = \hat{c}_q (r), \quad \hat{c}_\omega (r + \ell_i) = \hat{c}_\omega (r), \quad i = 1, 2, 3 \]

(47e)

**Average:**

\[ \{ \hat{c}_q \}^n = 0, \quad \{ \hat{c}_\omega \}^w = 0 \]

(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.

\[ \text{Sources : } \nabla \{ \langle c_q \rangle^n \}, \quad \nabla \{ \langle c_q \rangle^w \}, \]

\[ \{ \{ \{ c_q \}^w \}^w - \{ \{ c_q \}^n \}^n \} \]

(47g)

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.

\[ \text{Sources : } \nabla \{ \langle c_q \rangle^n \}, \quad \nabla \{ \langle c_q \rangle^w \}, \]

\[ \{ \{ \{ c_q \}^w \}^w - \{ \{ c_q \}^n \}^n \} \]

(47h)

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.

\[ \text{Sources : } \nabla \{ \langle c_q \rangle^n \}, \quad \nabla \{ \langle c_q \rangle^w \}, \]

\[ \{ \{ \{ c_q \}^w \}^w - \{ \{ c_q \}^n \}^n \} \]

(47i)

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.

\[ \text{Sources : } \nabla \{ \langle c_q \rangle^n \}, \quad \nabla \{ \langle c_q \rangle^w \}, \]

\[ \{ \{ \{ c_q \}^w \}^w - \{ \{ c_q \}^n \}^n \} \]

(47j)
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\textsuperscript{27–34}, or in dealing with the flow of a slightly compressible fluid in a heterogeneous porous medium\textsuperscript{33–34}, this suggests representations for the spatial deviation concentrations of the form

\[
\tilde{c}_q = b_{wq} \nabla \left( \left\langle c_q \right\rangle \right) + b_{wq} \nabla \left( \left\langle c_q \right\rangle \right) + \nabla \left( \left\langle c_q \right\rangle \right)
\]

in which we refer to \( b_{eq} \), \( b_{eq} \), \( r_{eq} \), 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**

\[
\nabla \left( \left\langle y_q \right\rangle \right) b_{eq} + \tilde{v}_q = \nabla \left( \left\langle D_q^* \nabla b_{eq} \right\rangle \right) + \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(49a)

B.C.1 \( b_{eq} = b_{eq} \) at \( A_{eq} \)

(49b)

B.C.2 \( n_{eq} D_q^* \nabla b_{eq} + n_{eq} D_q^* = n_{eq} D_q^* \nabla b_{eq} \) at \( A_{eq} \)

(49c)

\[
\nabla \left( \left\langle y_q \right\rangle \right) b_{eq} = \nabla \left( \left\langle D_q^* \nabla b_{eq} \right\rangle \right) - \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(49d)

Periodicity : \( b_{eq}(r + \ell) = b_{eq}(r), \)

\( b_{eq}(r + \ell) = b_{eq}(r), \) \( i = 1, 2, 3 \)

(49e)

Average : \( \left\{ b_{eq} \right\} = 0, \left\{ b_{eq} \right\} = 0 \)

(49f)

Here we have used the vectors \( c_{eq} \) and \( c_{eq} \) to represent the inter-region flux terms according to

\[
e_{eq} = -\frac{1}{V_{eq}} \int_{A_{eq}} \nabla \left( \left\langle y_q \right\rangle \right) b_{eq} - \nabla \left( \left\langle y_q \right\rangle \right) b_{eq} \) \( dA \)

(50a)

and these are related by

\[
e_{eq} = -e_{eq}
\]

(50c)

The second closure problem is related to the source, \( \nabla \left( \left\langle c_q \right\rangle \right) \), and it is given by

**Problem II**

\[
\nabla \left( \left\langle y_q \right\rangle \right) b_{eq} + \tilde{v}_q = \nabla \left( \left\langle D_q^* \nabla b_{eq} \right\rangle \right) + \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(51a)

B.C.1 \( b_{eq} = b_{eq} \) at \( A_{eq} \)

(51b)

B.C.2 \( n_{eq} D_q^* \nabla b_{eq} = n_{eq} D_q^* \nabla b_{eq} + n_{eq} D_q^* \) at \( A_{eq} \)

(51c)

\[
\nabla \left( \left\langle y_q \right\rangle \right) b_{eq} + \tilde{v}_q = \nabla \left( \left\langle D_q^* \nabla b_{eq} \right\rangle \right) + \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(51d)

Periodicity : \( b_{eq}(r + \ell) = b_{eq}(r), \)

\( b_{eq}(r + \ell) = b_{eq}(r), \) \( i = 1, 2, 3 \)

(51e)

Average : \( \left\{ b_{eq} \right\} = 0, \left\{ b_{eq} \right\} = 0 \)

(51f)

In this case the two constant vectors are defined by

\[
e_{eq} = -\frac{1}{V_{eq}} \int_{A_{eq}} \nabla \left( \left\langle y_q \right\rangle \right) b_{eq} - \nabla \left( \left\langle y_q \right\rangle \right) b_{eq} \) \( dA \)

(52a)

\[
e_{eq} = -\frac{1}{V_{eq}} \int_{A_{eq}} \nabla \left( \left\langle c_q \right\rangle \right) b_{eq} - \nabla \left( \left\langle c_q \right\rangle \right) b_{eq} \) \( dA \)

(52b)

and they are related by

\[
e_{eq} = -e_{eq}
\]

(52c)

The third closure problem originates with the exchange source, \( \left\{ \left\langle c_q \right\rangle \right\} - \left\{ \left\langle c_q \right\rangle \right\} \), and it takes the form

**Problem III**

\[
\nabla \left( \left\langle y_q \right\rangle \right) \nabla r_q = \nabla \left( \left\langle D_q^* \nabla r_q \right\rangle \right) - \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(53a)

B.C.1 \( r_q = r_q + 1 \) at \( A_{eq} \)

(53b)

B.C.2 \( n_{eq} D_q^* \nabla r_q = n_{eq} D_q^* \nabla r_q \) at \( A_{eq} \)

(53c)

\[
\nabla \left( \left\langle y_q \right\rangle \right) \nabla r_q = \nabla \left( \left\langle D_q^* \nabla r_q \right\rangle \right) - \nabla \left( \left\langle c_q \right\rangle \right) \nabla \left( \left\langle c_q \right\rangle \right)
\]

(53d)

Periodicity : \( r_q(r + \ell) = r_q(r), \)

\( r_q(r + \ell) = r_q(r), \) \( i = 1, 2, 3 \)

(53e)

Average : \( \left\{ r_q \right\} = 0, \left\{ r_q \right\} = 0 \)

(53f)

Here the mass transfer coefficient, \( \alpha^* \), is defined by

\[
\alpha^* = -\frac{1}{V_{eq}} \int_{A_{eq}} \nabla \left( \left\langle y_q \right\rangle \right) r_q - \nabla \left( \left\langle y_q \right\rangle \right) r_q \) \( dA \)

(54)
Rather than work directly with the closure variables, \( r_q \) and \( r_w \), it is convenient to define new variables according to
\[
s_q = r_q, \quad s_w = r_w + 1
\]
(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'**

\[
\nabla \cdot \left( \langle y_q \rangle \frac{\partial s_q}{\partial t} \right) = \nabla \cdot \left( D_q^s \nabla s_q \right) - \varphi_q^{-1} \alpha^s
\]
(56a)

**B.C.1**

\[
s_q = s_w, \quad \text{at } A_q^{sw}
\]
(56b)

**B.C.2**

\[
n_{qw} D_q^s \nabla s_q = n_{qw} D_w^s \nabla s_w, \quad \text{at } A_w^{qw}
\]
(56c)

\[
\nabla \cdot \left( \langle y_q \rangle \frac{\partial s_w}{\partial t} \right) = \nabla \cdot \left( D_w^s \nabla s_w \right) + \varphi_q^{-1} \alpha^w
\]
(56d)

**Periodicity**:

\[
 s_q(r + \ell) = s_q(r), \quad s_w(r + \ell) = s_w(r),
\]
\[
i = 1, 2, 3
\]
(56e)

**Average**:

\[
\frac{\langle s_q \rangle}{\mathcal{A}} = 0, \quad \frac{\langle s_w \rangle}{\mathcal{A}} = 1
\]
(56f)

In this case the mass transfer coefficient takes the form
\[
\alpha^s = -\frac{1}{B_{qw}} \int_{A_w^{qw}} n_{qw} \left( \langle y_q \rangle s_q - D_q^s \nabla s_q \right) d\mathcal{A}
\]
(57)

These closure problems are similar to those that have been solved previously by Quintard and Whitaker, Fabrie et al., and Quintard et al., 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 \( \tilde{e}_w \) given by eqn (48a) and make use of the change of variable indicated by eqn (55) to obtain
\[
e_q \left( 1 + \hat{x}_q \right) \frac{\partial \langle e_q \rangle}{\partial t} = \nabla \cdot \left( \varphi_q \left( \langle y_q \rangle \varepsilon \right) \nabla \langle e_q \rangle \right)
\]
\[
- \nabla \cdot \left[ \left( \langle e_q \rangle \right)^w - \left( \langle e_q \rangle \right)^w \right] - \varphi_q \nabla \left( \langle e_q \rangle \right)^w
\]
\[
+ \nabla \cdot \left( D_{qw} \nabla \langle e_q \rangle \right) - \alpha_q \left( \left( \langle e_q \rangle \right)^w - \left( \langle e_q \rangle \right)^w \right)
\]
(58)

Here the various coefficients are defined by
\[
d_q = \varphi_q \left( \langle y_q \rangle - D_q^s \nabla s_q \right)
\]
(59a)

\[
u_{qw} = -\frac{1}{B_{qw}} \int_{A_w^{qw}} n_{qw} \left( \langle y_q \rangle b_{qw} - D_q^s \nabla b_{qw} - \tilde{D}_q^s \right) d\mathcal{A}
\]
(59b)

\[
u_{qw} = -\frac{1}{B_{qw}} \int_{A_w^{qw}} n_{qw} \left( \langle y_q \rangle b_{qw} - D_q^s \nabla b_{qw} \right) d\mathcal{A}
\]
(59c)

\[
D_{qw}^s = \varphi_q \left( D_q^s \left( 1 + \nabla b_{qw} \right) - \tilde{v}_{qw} b_{qw} \right)
\]
(59d)

\[
D_{qw}^s = \varphi_q \left( D_q^s \nabla b_{qw} - \tilde{v}_{qw} b_{qw} \right)
\]
(59e)

\[
\alpha_q = -\frac{1}{B_{qw}} \int_{A_w^{qw}} n_{qw} \left( \langle y_q \rangle s_q - D_q^s \nabla s_q \right) d\mathcal{A}
\]
(59f)

In order to obtain the closed form of the \( \omega \)-region transport equation, we follow the above development from eqn (23b) to arrive at
\[
e_w \left( 1 + \hat{x}_w \right) \frac{\partial \langle e_w \rangle}{\partial t} = \nabla \cdot \left( \varphi_w \left( \langle y_w \rangle \varepsilon \right) \nabla \langle e_w \rangle \right)
\]
\[
- \nabla \cdot \left[ \left( \langle e_w \rangle \right)^w - \left( \langle e_w \rangle \right)^w \right] - \varphi_w \nabla \left( \langle e_w \rangle \right)^w
\]
\[
+ \nabla \cdot \left( D_{ww}^w \nabla \langle e_w \rangle \right) - \alpha_w \left( \left( \langle e_w \rangle \right)^w - \left( \langle e_w \rangle \right)^w \right)
\]
(60)

The coefficients in this case are analogous to those given by eqns (59), and for completeness we list them as
\[
d_w = \varphi_w \left( \langle y_w \rangle s_w - D_w^s \nabla s_w \right)
\]
(61a)

\[
u_{ww} = -\frac{1}{B_{ww}} \int_{A_w^{ww}} n_{ww} \left( \langle y_w \rangle b_{ww} - D_w^s \nabla b_{ww} - \tilde{D}_w^s \right) d\mathcal{A}
\]
(61b)

\[
u_{ww} = -\frac{1}{B_{ww}} \int_{A_w^{ww}} n_{ww} \left( \langle y_w \rangle b_{ww} - D_w^s \nabla b_{ww} \right) d\mathcal{A}
\]
(61c)
In this section, we present a complete analysis of the stratified system. 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 \( \eta \) and \( \omega \)-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 is not valid. 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 described below.

\[
\begin{align*}
\mathbf{D}^{*\omega} = \varphi_s \left( \mathbf{D}^{\omega} \mathbf{q} - \left( \mathbf{v}_b \right)_b \right) \quad (61d) \\
\mathbf{D}^{*\eta} = \varphi_s \left( \mathbf{D}^{\eta} \mathbf{n}_b \mathbf{q} - \left( \mathbf{v}_b \right)_b \right) \quad (61e) \\
\alpha = - \frac{1}{\varphi_s} \int_{\mathcal{A}} n_{qw} \left( \left( \mathbf{v}_b \right)_\omega \mathbf{q} - \mathbf{D}^{\omega} \nabla \mathbf{b}_w \right) \, d\mathcal{A} \quad (61f)
\end{align*}
\]

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

\[
\mathbf{v} \cdot \mathbf{v} \mathbf{q} = - \frac{K_{b\eta}}{\mu_b} \left( \nabla \left( p_b \right)_\eta - \partial_t \mathbf{b} \right) \quad (62c)
\]

B.C.1 \( n_{qw} \left( \mathbf{v}_b \right)_\omega = n_{qw} \left( \mathbf{v}_b \right)_\omega \) at \( A_{yw} \)

B.C.2 \( \left( p_b \right)_\omega = \left( p_b \right)_\omega \) at \( A_{yw} \)

B.C.3 \( \left( c_q \right)_\omega = \left( c_q \right)_\omega \) at \( A_{yw} \)

B.C.4 \( - n_{qw} \left( \mathbf{v}_b \right)_b \left( \left( c_q \right)_\omega \right) - \mathbf{D}^{\omega} \nabla \left( c_q \right)_\omega \right)

\[
\begin{align*}
\mathbf{v} \cdot \left( \left( \mathbf{v}_b \right)_\omega \left( \left( c_q \right)_\omega \right) - \mathbf{D}^{\omega} \nabla \left( c_q \right)_\omega \right) \\
= - n_{qw} \left( \mathbf{v}_b \right)_b \left( \left( c_q \right)_\omega \right) - \mathbf{D}^{\omega} \nabla \left( c_q \right)_\omega \right) \quad (62g)
\end{align*}
\]

\[
\begin{align*}
\eta & \quad \frac{\partial \left( c_q \right)_\omega}{\partial t} + \nabla \left( \left( \mathbf{v}_b \right)_\omega \left( c_q \right)_\omega \right) = \nabla \cdot \left( \mathbf{D}^{\omega} \nabla \left( c_q \right)_\omega \right) \quad (62h)
\end{align*}
\]

Here we note that all the concentrations are now dimensionless, so \( \left( c_q \right)_\omega \) represents a concentration made dimensionless by some reference concentration, \( c^s \). 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$^4$.2.

### 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

\[
\left\langle \psi \right\rangle_x = \text{constant} \quad (63a)
\]

\[
\epsilon_v \varphi_v \frac{\partial \left\langle \psi\right\rangle^v_x}{\partial t} + \varphi_v \left\langle \psi \right\rangle^v_x \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial x} = \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2} + \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2}
\]

\[
\equiv \alpha^v \left( \left\langle \psi \right\rangle^v_x - \left\langle \psi \right\rangle^v_x \right)
\]

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:

**B.C.1** \( x = 0 \), \( \left\langle \psi \right\rangle^v_x = \left\langle \psi \right\rangle^v_x = 1 \) \quad (64a)

**B.C.2** \( x = L \), \( \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial x} = \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial x} = 0 \) \quad (64b)

**I.C.** \( t = 0 \), \( \left\langle \psi \right\rangle^v_x = \left\langle \psi \right\rangle^v_x = 0 \) \quad (64c)

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

\[
\left( D^v_{\psi} \right)_x = \varphi_v \left( D^v \right)_x \quad (65a)
\]

\[
\left( D^v_{\psi} \right)_x = \left( D^v_{\psi} \right)_x = 0 \quad (65b)
\]

\[
\left( D^v_{\psi} \right)_x = \varphi_v \left( D^v \right)_x \quad (65c)
\]

\[
\alpha^v = \frac{12}{\left( \ell_x + \ell_y \right)^2} \varphi_v \left( D^v \right)_x \quad (65d)
\]

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 \( \eta \)-region equation:

\[
\epsilon_v \varphi_v \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial t} + \varphi_v \left\langle \psi \right\rangle^v_x \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial x} = 0 \quad (66a)
\]

\[
\epsilon_v \varphi_v \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial t} = \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2} + \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2} + \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2} + \left( D^v_{\psi} \right)_x \frac{\partial^2 \left\langle \psi \right\rangle^v_x}{\partial x^2}
\]

\[
\equiv -\alpha^v \left( \left\langle \psi \right\rangle^v_x - \left\langle \psi \right\rangle^v_x \right) \quad (66b)
\]

\[
\epsilon_v \varphi_v \frac{\partial \left\langle \psi \right\rangle^v_x}{\partial t} = -\alpha^v \left( \left\langle \psi \right\rangle^v_x - \left\langle \psi \right\rangle^v_x \right) \quad (66c)
\]

Equations like eqn (66a) are solved by using an explicit second-order scheme\(^{41,44}\), while diffusion equations like eqn (66b) are solved by using a second-order implicit scheme. Finally, eqn (66c) and the similar equation for the \( \omega \)-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 \( t = 8 \times 10^8 \) 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
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 \( \eta \)-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:

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

![Image](image_url)

**Fig. 4.** Concentration at \( t = 8 \times 10^{-6} \) s, case 1.

<table>
<thead>
<tr>
<th>Unit Cell</th>
<th>( \ell_{\eta} = \ell_u ) (m)</th>
<th>( \varphi_{\eta} )</th>
<th>( \ell_u/\ell_{\eta} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
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<th>( K_{\varphi} )</th>
<th>( \epsilon_{\eta} )</th>
<th>( \epsilon_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10(^{-12}) m(^2))</td>
<td>(10(^{-12}) m(^2))</td>
<td>0.38</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.38</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>0.</td>
<td>0.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Properties</th>
<th>( \delta h ) (m)</th>
<th>( \langle v_{\eta} \rangle_{\eta} )</th>
<th>( \langle v_{\varphi} \rangle_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3 ( 10^{-7} )</td>
<td>0.3 ( 10^{-7} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effective Properties (Dispersion)</th>
<th>( \langle D_{\eta} \rangle_{\eta} )</th>
<th>( \langle D_{\varphi} \rangle_{\varphi} )</th>
<th>( \langle D_{\eta} \rangle_{\varphi} / \langle D_{\varphi} \rangle_{\eta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td>(10(^{-9}) m(^2) s(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>0.</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>( \alpha^* ) (10(^{-9}) s(^{-1}))</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

Note: All properties are taken equal to zero unless they are cited in the Table.

\( \frac{\varphi \xi}{\mu \varphi} = 7.7 \ 10^{-6} \) (m s\(^{-1}\))

\( \frac{\varphi \xi}{\mu \varphi} = 7.7 \ 10^{-6} \) (m s\(^{-1}\))
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\(^4\)\(^5\) that the theory underestimates 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\(^6\)\(^7\)\(^8\)\(^9\)\(^10\); 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.\(^2\)\(^4\)\(^5\) that for sufficiently large times the average concentration obeys rather closely a dispersion equation given by

\[
\frac{\partial \langle c \rangle}{\partial t} + \langle v \rangle \frac{\partial \langle c \rangle}{\partial x} = \left( \frac{\partial^2 \langle c \rangle}{\partial x^2} \right)_{\langle c \rangle} - \frac{\partial^2 \langle c \rangle}{\partial x^2} \quad (67)
\]

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

**Fig. 6.** Concentration at t = 8 × 10\(^{-6}\) s (case 2).

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

**Fig. 8.** Concentration at t = 8 × 10\(^{-6}\) s (case 3).
The dispersion coefficient in this equation is given by

\[ D_{pp} = J_{hh} D_{hh} + J_{qq} D_{qq} + J_{hq} D_{hq} + J_{qh} D_{qh} \]

The derivation of this result makes use of the method of moments in a manner similar to the work of Aris, and these results have been extended to more general, random stratified systems. The estimate of the large-scale asymptotic dispersion coefficient given by eqn (68) was found to agree very well with experimental data. 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

\[ \{c\} \frac{\delta^2 \{c\}}{\delta x^2} + \{\langle c \rangle \} = \{D_{xx} \} \frac{\delta^2 \{c\}}{\delta x^2} \]

This equation is restricted by the approximation

\[ \{\langle c \rangle \} = \{\langle c \rangle \} = \{c\} \]

The predicted dispersion coefficient takes the form

\[ (D_{xx}^*) = \varphi_x (D_{xx}^*) + \varphi_h (D_{hh}^*) + \varphi_q (D_{qq}^*) \]

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. obtained rather good agreement between theory and

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Unit Cell & \( \ell \) & \( \Phi \) & \( L_{0}/\ell \) \\
\hline
1 & 0.5 & 10 & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Physical Properties & \( K_{pp} \) & \( K_{pp0} \) & \( \varepsilon \) \\
(10^{-12} m^3) & (10^{-12} m^3) & & \\
\hline
1 & 0.1 & 0.38 & 0.30 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Flow Properties & \( \delta h \) & \( \langle v_p \rangle \) \\
(m) & (m/s) & & \\
\hline
0.4 & 3.10^7 & 0.3 10^7 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Effective Properties & \( \langle D_{xx}^* \rangle \) & \( \langle D_{xx}^* \rangle \) \\
(10^{-9} m^3/s) & (10^{-9} m^3/s) & \\
\hline
0.19 & 0.135 & 0.0 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|}
\hline
\( \alpha \) \\
(10^{-9} s) \\
\hline
0.947 \\
\hline
\end{tabular}
\end{table}

Note: All properties are taken equal to zero unless they are cited in the Table.
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 \(1 + \{K\}\) 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 \(L_o\) 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 \(L_o / \gamma\), 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.\textsuperscript{24}. The results from the two-equation model indicate that the concentration profile for the \(\phi\)-region lies below that for the \(\psi\)-region, and this is required since the velocity in the \(\phi\)-region is a factor of ten less than the velocity in the \(\psi\)-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.\textsuperscript{24} clearly over-predicts the concentration. The average concentration predicted by the two-equation model is given by

\[
\langle \psi \rangle = \frac{\langle \psi \rangle_h}{C_{1o}} + \frac{\langle \psi \rangle_q}{C_{1o}}
\]

in which \(\langle \psi \rangle_h / C_{1o}\) and \(\langle \psi \rangle_q / C_{1o}\) are not constrained by eqn (70). We consider this average concentration to be the

<table>
<thead>
<tr>
<th>Unit Cell</th>
<th>(\ell_\eta = \ell_u) (m)</th>
<th>(\varphi_\eta)</th>
<th>(L_o/\ell_\eta)</th>
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<tr>
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<td>10</td>
</tr>
</tbody>
</table>

<table>
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<th>Physical Properties</th>
<th>(K_{\eta \eta})</th>
<th>(K_{\eta \psi})</th>
<th>(\varepsilon_\eta)</th>
<th>(\varepsilon_u)</th>
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<tr>
<td></td>
<td>((10^{12} m^2))</td>
<td>((10^{12} m^2))</td>
<td>0.38</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\langle \psi \rangle_h)</td>
<td>(\langle \psi \rangle_q)</td>
<td>(\varphi_\eta / \varepsilon_\eta)</td>
<td>(\varphi_q / \varepsilon_u)</td>
</tr>
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<td>3</td>
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<table>
<thead>
<tr>
<th>Flow Properties</th>
<th>(\delta \gamma)</th>
<th>(\langle \psi \rangle_h)</th>
<th>(\langle \psi \rangle_q)</th>
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<td>(3 \times 10^{-7})</td>
<td>(0.3 \times 10^{-7})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effective Properties</th>
<th>(\langle \psi \rangle_h)</th>
<th>(\langle \psi \rangle_q)</th>
<th>(\langle \psi \rangle_{1o})</th>
</tr>
</thead>
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<tr>
<td>(Dispersion)</td>
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<td>((10^{9} m^2 s^{-1}))</td>
<td>((10^{9} m^2 s^{-1}))</td>
</tr>
<tr>
<td></td>
<td>15.</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>(\alpha^*)</td>
<td>((10^{9} s^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.64</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All properties are taken equal to zero unless they are cited in the Table.

\(Q_\psi / \mu_\psi = 7.7 \times 10^{4} \text{ (m s)}^{-1}\)

Table 3. Properties of the stratified system (case 3)
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 \( \frac{\partial c}{\partial t} \), 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.\textsuperscript{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

\[
(D_{pp}^*)_{ax} = (D_{pp}^*)_{xx} + (D_{pp}^*)_{xx} + (D_{pp}^*)_{xx} + (D_{pp}^*)_{xx} + (D_{pp}^*)_{xx} + \frac{\left( \epsilon_\omega \varphi_\omega \langle \langle v \rangle \rangle_\omega - \epsilon_\omega \varphi_\omega \langle \langle v \rangle \rangle_\omega \right)^2}{\alpha^2 (\epsilon_\omega \varphi_\omega + \epsilon_\omega \varphi_\omega)}
\]

Introducing the expression for \( \alpha^* \) given by eqn (73), we obtain an expression for the asymptotic longitudinal dispersion coefficient equal to the one proposed by Marle et al.\textsuperscript{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 \( \alpha^* \). 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.\textsuperscript{24} shows that the proposed theory gives an exact result.

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
stratified systems has demonstrated the ability of the

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

<table>
<thead>
<tr>
<th>Unit Cell</th>
<th>( \ell_\eta = \ell_\omega ) (m)</th>
<th>( \varphi_\eta )</th>
<th>( L_0/\ell_\eta )</th>
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</thead>
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<td>1</td>
<td>0.5</td>
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</table>

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<th>Physical Properties</th>
<th>( K_{\eta \eta} ) (10^{12} m^2)</th>
<th>( K_{\eta \omega} ) (10^{12} m^2)</th>
<th>( \varepsilon_\eta )</th>
<th>( \varepsilon_\omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.38</td>
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</table>

<table>
<thead>
<tr>
<th>Flow Properties</th>
<th>( \delta \eta ) (m)</th>
<th>( \langle \nu_\eta \rangle_\eta )</th>
<th>( \langle \nu_\omega \rangle_\omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3 \times 10^{-7}</td>
<td>0.3 \times 10^{-7}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effective Properties (Dispersion)</th>
<th>( \langle D_\eta^- \rangle_\eta ) (10^{-9} m^2 s^{-1})</th>
<th>( \langle D_\omega^- \rangle_\omega ) (10^{-9} m^2 s^{-1})</th>
<th>( \langle D_\eta^- \rangle_\eta / \langle D_\omega^- \rangle_\omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150.</td>
<td>15</td>
<td>0.0</td>
</tr>
</tbody>
</table>

| \( \alpha^* \) (10^{-6} s^{-1}) | 16.4 |

Note: All properties are taken equal to zero unless they are cited in the Table.

\( \varrho_\eta \ g / \mu_\eta = 7.7 \times 10^{48} \) (m s)\(^{-1}\)

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 numerical experiments can be considered as a reliable verification of the essential features of the two-equation model.
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\cite{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. 12.** Asymptotic behaviour of the different large-scale models: concentration fields (case 4; \(x = 20\) m).

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

This work was completed while Stephen Whitaker was a visitor at the Laboratoire Energétique et Phénomène de Transfert in 1994 and 1996. The support of L.E.P.T. and the Société de Secours des Amis des Sciences is greatly appreciated. Partial support for Michel Quintard from INSU/PRH is gratefully acknowledged.

APPENDIX A: CLOSURE FOR THE ONE-EQUATION MODEL

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

\[
\{e\} + \{K\} \partial_c = \frac{\partial}{\partial t} \left( \frac{v_b}{C_10/C_9} \{c\} \right) = D \nabla^2 \{c\} (A1)
\]

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

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
$$D_\text{L} = \phi_1 (D^1_v) + \phi_2 (D^2_v),$$
and the convective transport term is given by
$$\int_{\Delta t} n_{\text{m}} \cdot \bar{b}_{\text{m}} \, \text{d}\Delta t + \{ \bar{D}_v \cdot \nabla b_{\text{m}} \}.$$
and the resemblance becomes clearer when we make use of the combined closure variables defined by
\[ b_x = b_{xy} + b_{ux}, \quad b_y = b_{xy} + b_{uw} \]  
(A17)

Use of these relations in eqn (A16) leads to
\[
D_{xy} + D_{ux} + D_{uw} = \phi_x \left( D_x \right)^\mathbf{y} + \phi_y \left( D_y \right)^\mathbf{u} + \int_{A_{xy}} n_{ux} b_y \, dA + \int_{A_{xy}} n_{uy} b_x \, dA + \int_{A_{xy}} n_{ux} b_y + (\tilde{D}_x \cdot \nabla) b_x \, dA + (\tilde{D}_y \cdot \nabla) b_y \, dA + \int_{A_{xy}} n_{ux} b_y + \int_{A_{xy}} n_{uy} b_x \, dA + (\tilde{D}_x \cdot \nabla) b_x \, dA + (\tilde{D}_y \cdot \nabla) b_y \, dA + \int_{A_{xy}} n_{ux} b_y + \int_{A_{xy}} n_{uy} b_x \, dA \]  
(A18)

At this point one need only recognize that \( n_{xy} = -n_{uy} \) and make use of the two boundary conditions given by eqs (49) and (51) to conclude that
\[
D_{xy} + D_{ux} + D_{uw} = \phi_x \left( D_x \right)^\mathbf{y} + \phi_y \left( D_y \right)^\mathbf{u} + \int_{A_{xy}} n_{ux} b_x \, dA + \int_{A_{xy}} n_{uy} b_x \, dA + \int_{A_{xy}} n_{ux} b_y + (\tilde{D}_x \cdot \nabla) b_x \, dA + (\tilde{D}_y \cdot \nabla) b_y \, dA + \int_{A_{xy}} n_{ux} b_y + \int_{A_{xy}} n_{uy} b_x \, dA \]  
(A19)

Use of this result with eqn (A7) provides the more compact form of the one-equation model given by
\[
\{ e \{ 1 + \{ c \} \} \} = \nabla \cdot (\nabla \cdot \{ c \}) \]
\[ - (u_x + u_{ux} + u_{ux} + u_{uw}) \nabla \{ c \} = \nabla \cdot (D^* \cdot \nabla \{ c \}) \]  
(A20)

In order to calculate values of the dispersion tensor, \( D^* \), we need the closure problem that produces the closure variables \( b_x \) and \( b_y \). On the basis of the definitions given by eqn (A17) and the following definitions for the constants in the two-equation model closure problem:
\[
c_y = c_{xy} + c_{ux}, \quad c_x = c_{xy} + c_{uw} \]  
(A21)

we can add eqns (49) and (51) to obtain
\[
\nabla \cdot (\nabla \{ c \} b_y) + \tilde{v}_{by} = \nabla \cdot (D^* \cdot \nabla b_y) + (\nabla \cdot \tilde{D}) \cdot \nabla c_y \]  
(A22a)

\[
B.C.1 \quad b_x = b_y \text{ at } A_{xy} \]  
(A22b)

\[
B.C.2 \quad n_{ux}(D^* \cdot \nabla b_x) = n_{ux}(D^* \cdot \nabla b_y) + n_{ux}(D^* \cdot \nabla b_y) \]  
(A22c)

\[
\nabla \cdot (\nabla \{ c \} b_y) + \tilde{v}_{by} = \nabla \cdot (D^* \cdot \nabla b_y) + (\nabla \cdot \tilde{D}) \cdot \nabla c_y \]  
(A22d)

\[
\text{Periodicity} : \quad b_x(r + \ell) = b_x(r), \quad b_y(r + \ell) = b_y(r), \quad \ell = 1, 2, 3 \]  
(A22e)

\[
\text{Average} : \quad \{ b_x \}^\mathbf{y} = 0, \quad \{ b_y \}^\mathbf{u} = 0 \]  
(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
\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{ux} \left( \langle \nu \rangle_{b_y} b_x - D^* \cdot \nabla b_x - \tilde{D} \right) \, dA \]  
(A23a)

\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{ux} \left( \langle \nu \rangle_{b_y} b_x - D^* \cdot \nabla b_x - \tilde{D} \right) \, dA \]  
(A23b)

\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{uy} \left( \langle \nu \rangle_{b_y} b_x - D^* \cdot \nabla b_x - \tilde{D} \right) \, dA \]  
(A23c)

\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{uy} \left( \langle \nu \rangle_{b_y} b_x - D^* \cdot \nabla b_x - \tilde{D} \right) \, dA \]  
(A23d)

Use of the definitions of the closure variables given by eqn (A17) allows us to add pairs of these equations to obtain
\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{ux} \left( \langle \nu \rangle_{b_y} b_y - D^* \cdot \nabla b_y - \tilde{D} \right) \, dA \]  
(A24a)

\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{uy} \left( \langle \nu \rangle_{b_y} b_y - D^* \cdot \nabla b_y - \tilde{D} \right) \, dA \]  
(A24b)

On the basis of the boundary condition given by eqn (8):
\[
B.C.3 \quad n_{ux} \langle \nu \rangle_{b_y} = n_{uy} \langle \nu \rangle_{b_y} \text{ at } A_{xy} \]  
(A25)

we can add eqns (A24a) and (A24b) to obtain
\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{ux} \left( D^* \cdot \nabla b_x + \tilde{D} \right) \, dA \]  
(A26)

Integrating eqn (A22c) over the area \( A_{xy} \) indicates that the two integrals in this result sum to zero:
\[
\frac{1}{\gamma_u} \int_{A_{xy}} n_{ux} \left( D^* \cdot \nabla b_x + \tilde{D} \right) \, dA = 0 \]  
(A27)

so eqn (A20) simplifies to
\[
\{ e \} \frac{\partial \{ c \} \}}{\partial t} + \nabla \cdot \left( \nabla \{ c \} \right) = \nabla \cdot (D^* \cdot \nabla \{ c \}) \]  
(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 Carbonell29. 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

\[
\Delta \rho \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = - \nabla \cdot \rho \mathbf{a} + \rho \mathbf{b}
\]

Heterogeneous porous media V

\[
\text{Moments of order } \alpha, \beta, \gamma \text{ have been performed within SCIENTIFIC WORKPLACE}^{10} \text{ using the MAPLE}^{10} \text{ library.}
\]

**Moments of order**

The set of differential equations to be solved is

\[
\frac{d}{dt} \mu_{\alpha, \beta, \gamma} = - \alpha \beta \gamma \mu_{\alpha - 1, \beta, \gamma} + \text{terms involving } \mu_{\alpha, \beta, \gamma}
\]

and the general solution is given by

\[
\mu_{\alpha, \beta, \gamma}(t) = \epsilon \phi \phi' \delta_{\alpha, \beta, \gamma} + \epsilon \phi \phi' \delta_{\alpha, \beta, \gamma, \mu_{\alpha, \beta, \gamma}}
\]

where \( \delta_{\alpha, \beta, \gamma} \) are the initial values. Adding eqns (B8), we obtain the following result:

\[
\{ \epsilon \} \mu_{\alpha, \beta, \gamma} = \epsilon \phi \phi' \delta_{\alpha, \beta, \gamma} + \epsilon \phi \phi' \delta_{\alpha, \beta, \gamma, \mu_{\alpha, \beta, \gamma}} = \text{constant}
\]
In addition, we get
\[
\lim_{t \to \infty} \mu_{u,0} = \lim_{t \to \infty} \mu_{u,0} = \frac{\epsilon_u \varphi u \mu_{u,0} + \epsilon_u \varphi u \mu_{u,0}}{\langle \epsilon \rangle} = \mu_u.
\]  

**Moments of order 1**

From eqns (B6) we get
\[
\epsilon_v \varphi_v \frac{\partial \mu_{v,1}}{\partial t} = \left( \langle \gamma \rangle_v \right) - \epsilon_v \varphi_v V_r \mu_{v,0} - \alpha^2 (\mu_{v,1} - \mu_{v,0}) \tag{B11a}\]
\[
\epsilon_w \varphi_w \frac{\partial \mu_{w,1}}{\partial t} = \left( \langle \gamma \rangle_w \right) - \epsilon_w \varphi_w V_r \mu_{w,0} - \alpha^2 (\mu_{w,1} - \mu_{w,0}) \tag{B11b}\]

Adding these two equations, we obtain
\[
\{ \epsilon \} \frac{\partial \mu}{\partial t} = \epsilon_v \varphi_v \frac{\partial \mu_{v,1}}{\partial t} + \epsilon_w \varphi_w \frac{\partial \mu_{w,1}}{\partial t} + \left( \langle \gamma \rangle_v \right) - \epsilon_v \varphi_v V_r \mu_{v,0} + \left( \langle \gamma \rangle_w \right) - \epsilon_w \varphi_w V_r \mu_{w,0} \tag{B12}\]

The asymptotic behaviour is such that
\[
\lim_{t \to \infty} \{ \epsilon \} \frac{\partial \mu}{\partial t} = \left( \langle \gamma \rangle_v \right) - \epsilon_v \varphi_v V_r \mu_{v,0} + \left( \langle \gamma \rangle_w \right) - \epsilon_w \varphi_w V_r \mu_{w,0} \tag{B13}\]

The reference velocity that makes the right-hand side of this equation equal to zero is
\[
V_r = \left( \langle \gamma \rangle_v \right) + \left( \langle \gamma \rangle_w \right) \tag{B14}\]

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

Using symbolic calculus, we were able to obtain the following limits:
\[
\lim_{t \to \infty} \mu_{v,1} = \epsilon_v \varphi_v f_v + \epsilon_v \varphi_v \mu_r \frac{\epsilon_v \varphi_v \left( \langle \gamma \rangle_v \right) - \epsilon_v \varphi_v V_r \left( \langle \gamma \rangle_v \right)}{\alpha^2 \langle \epsilon \rangle^2} \tag{B15a}\]
\[
\lim_{t \to \infty} \mu_{w,1} = \epsilon_w \varphi_w f_w + \epsilon_w \varphi_w \mu_r \frac{\epsilon_w \varphi_w \left( \langle \gamma \rangle_w \right) - \epsilon_w \varphi_w V_r \left( \langle \gamma \rangle_w \right)}{\alpha^2 \langle \epsilon \rangle^2} \tag{B15b}\]

where
\[
f_r = \mu_{u,1}(t = 0), \quad \alpha = \eta, \omega \tag{B15c}\]

**Moments of order 2**

The governing equations for the moments of order 2 are
\[
\epsilon_v \varphi_v \frac{\partial \mu_{v,2}}{\partial t} = 2 \left[ \langle \gamma \rangle_v \right] - \epsilon_v \varphi_v V_r \mu_{v,1} + 2 \left( D_{v,v}^{(1)} \right) \mu_{v,0} - \alpha^2 (\mu_{v,2} - \mu_{v,1}) \tag{B16a}\]
\[
\epsilon_w \varphi_w \frac{\partial \mu_{w,2}}{\partial t} = 2 \left[ \langle \gamma \rangle_w \right] - \epsilon_w \varphi_w V_r \mu_{w,1} + 2 \left( D_{w,w}^{(1)} \right) \mu_{w,0} - \alpha^2 (\mu_{w,2} - \mu_{w,1}) \tag{B16b}\]

When these two equations are added, we obtain
\[
\{ \epsilon \} \frac{\partial \mu}{\partial t} = \epsilon_v \varphi_v \frac{\partial \mu_{v,2}}{\partial t} + \epsilon_w \varphi_w \frac{\partial \mu_{w,2}}{\partial t} + 2 \left( D_{v,v}^{(1)} \right) + 2 \left( D_{w,w}^{(1)} \right) \mu_{v,0} + 2 \left( D_{v,w}^{(1)} \right) \mu_{v,1} \tag{B17}\]

The asymptotic limit is obtained by taking the limit of this equation and using eqns (B15) and (B10) to obtain
\[
\{ \epsilon \} \frac{\partial \mu}{\partial t} = 2 \left[ (D_{v,v}^{(1)}) + (D_{w,w}^{(1)}) + (D_{v,w}^{(1)}) \right] \mu_{v,0} + 2 \left( D_{v,w}^{(1)} \right) \mu_{v,1} + 2 \left( D_{w,w}^{(1)} \right) \mu_{w,1} \tag{B18}\]

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
\[
\{ \epsilon \} \frac{d^2 \langle c \rangle}{dt^2} + \langle \gamma \rangle_v \frac{d \langle c \rangle}{dt} + \langle \gamma \rangle_w \frac{d \langle c \rangle}{dt} = \left( D_{v,v}^{(1)} \right) \frac{d^2 \langle c \rangle}{dx^2} \tag{B19}\]

where the asymptotic dispersion coefficient is given by
\[
(D_{v,v}^{(1)}) = \frac{\left( D_{v,v}^{(1)} \right) + \left( D_{w,w}^{(1)} \right) + \left( D_{v,w}^{(1)} \right) + \left( D_{w,w}^{(1)} \right)}{2} \tag{B20}\]

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

**REFERENCES**

2. Sposito, G., Jury, W. A. & Gupta, V. K., Fundamental


