Macroscopic equations for vapor transport in a multi-layered unsaturated zone

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Using the method of homogenization, we present a systematic derivation of the macroscopic equations for air flow and chemical vapor transport in an unsaturated zone with a periodic structure of heterogeneity. The effective specific discharge and hydrodynamic dispersion coefficient are expressible in terms of some cell functions, whose analytical solutions are sought for the simple case of alternate stacking of two strictly plane layers of different properties. For this kind of bi-layered composite, the effects of convection velocity and layer property contrasts on the longitudinal and transverse components of the hydrodynamic dispersion coefficient are investigated. © 1999 Elsevier Science Limited. All rights reserved

Key words: vapor transport, layered porous media, dispersion, homogenization theory.

1 NOMENCLATURE

- $C$ vapor concentration
- $C_0$ characteristic vapor concentration
- $d$ layer thickness
- $D$ isotropic bulk molecular diffusion coefficient
- $D'$ macroscopic hydrodynamic dispersion coefficient tensor
- $E$ cell function introduced in (47)
- $f_E$ function defined in (82)
- $f_M$ vector function defined in (77)
- $f_Z$ vector function defined in (99)
- $I$ second-order identity tensor
- $k$ isotropic permeability
- $k'$ permeability tensor
- $K_d$ macroscopic permeability tensor
- $K_{\text{HI}}$ Henry's law constant
- $\ell$ mesoscopic length scale
- $\ell'$ macroscopic length scale
- $M$ cell vector function introduced in (47)
- $M^d$ dynamic component of $M$
- $M^s$ static component of $M$
- $M_e$ molecular weight
- $\rho$ absolute air pressure
- $P_e$ mesoscale Péclet number
- $P_e'$ macroscale Péclet number
- $R_g$ universal gas constant
- $s$ cell vector function introduced in (27)
- $t$ time
- $T_1$ short time scale
- $T_2$ long time scale
- $u$ air specific discharge = ($u,v,w$)
- $u'$ velocity fluctuation across the layers
- $U$ effective specific discharge
- $x$ air velocity scale
- $x'$ mesoscale coordinates = ($x',y',z'$)
- $Z$ function introduced in (85)
- $\beta$ retardation factor
- $\delta_{ij}, \delta_D, \delta_k, \delta_y$ ratios of layer properties as defined in Eq. (111)

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\[ \delta_{ij} \quad \text{Kronecker delta} \]

\[ \epsilon \quad \text{small perturbation parameter} = \epsilon/\epsilon' \]

\[ \eta_1, \eta_2, \eta_3 \quad \text{relation defined in (78) and (79)} \]

\[ \eta'_c \quad \text{relation defined in (83)} \]

\[ \gamma_1, \gamma_2, \gamma_3 \quad \text{relations defined in (100) and (101)} \]

\[ \nabla, \nabla' \quad \text{nabla operators} \]

\[ \Omega \quad \text{a unit cell} \]

\[ \rho \quad \text{air density} \]

\[ \rho_s \quad \text{solid density of soil grain} \]

\[ \theta_g, \theta_s, \theta_w \quad \text{volume fractions of air, solid and water in soil} \]

\[ \Theta \quad \text{absolute temperature} \]

\[ \hat{z}_1, \hat{z}_2, \hat{z}_3, \hat{z}_4 \quad \text{relations defined in (92)-(94) and (96)} \]

\[ \langle \cdot \rangle \quad \text{a normalized quantity} \]

\[ \langle \cdot \rangle^{(m)} \quad \text{the mth perturbation expansion of a quantity} \]

## 2 INTRODUCTION

The spread of vapor in the unsaturated zone often plays an important role in the contamination or decontamination of an aquifer, if the contaminants are volatile enough. Soil vapor extraction, which works simply by creating air ventilation in the contaminated soil, is a proven effective method to clean up unsaturated soils contaminated with volatile organic compounds (e.g., see Pedersen and Curtis\textsuperscript{23}). The clean-up rate however depends on the soil properties such as permeability which controls the air flow-rate, and retardation factor and dispersion coefficient which affect the vapor transport rate. Very often, the contaminated zone is stratified; layers of soil with different properties are embedded in one-another. For modeling purposes, it is desirable if effective equations can be developed for the vapor transport in such a multi-layered heterogeneous system, where advantage is taken of the fact that the layer thickness is usually much smaller than the global length scale for the transport.

So far in studies on vapor transport in heterogeneous soils, the focus has been limited to the effects due to a small number of layers or regions\textsuperscript{12,13,20}. The effects of multi-layered heterogeneity on vapor transport are yet to be investigated in detail. Typically, solute transport in a stratified medium can be studied with stochastic models, which invariably involve a number of statistical site characterization parameters such as variances, correlation lengths and distribution coefficients for various material and chemical properties (e.g., see Dagan\textsuperscript{7} and Gelhar\textsuperscript{9} and the references therein).

A different approach which allows more exact mathematical analysis can be taken when an idealized form, namely periodicity, is assumed of the medium heterogeneity. In the presence of two or more contrasting length scales, the macroscopic description of the problem can then be deduced formally with the multiple-scale method of homogenization\textsuperscript{15,22}. In contrast to many other averaging techniques, the homogenization method derives phenomenological equations on the basis of micromechanics, in a general and rigorous manner without any closure hypothesis. Despite the idealization, the resultant effective equation can often contain information that lead to a better insight into the mechanisms of the problem. See Mei et al.\textsuperscript{18} for a review of some of the applications of this method.

The application of averaging methods to convection–dispersion transport in porous media has received much attention in the past, but the focus has mainly been on the effects of heterogeneity at the microscopic (i.e., pore or grain level) scale. Typical works, among others, include the method of moments by Brenner\textsuperscript{5}, the volume averaging method by Whitaker\textsuperscript{27} and Carbonell and Whitaker\textsuperscript{1}, and the homogenization method by Mauri\textsuperscript{14}, Mei\textsuperscript{15} and Auriault and Adler\textsuperscript{1}. Clearly it is desirable if similar techniques can be applied to study effects due to field scale heterogeneity.

Over the past decade, much theoretical work has been devoted to the development of so called homogenized models for convection–diffusion in heterogeneous porous media (see a treatise on this subject by Panfilov and Panfilova\textsuperscript{21}, and the references therein). For instance, Fannjiang and Papanicolaou\textsuperscript{8} discussed proofs of convergence for linear diffusion in an oscillating velocity field. All such works however emphasize more on mathematical formalism or proofs than on physical applications. There indeed remains work to be done to utilize these theoretical developments to generate direct and explicit formulations readily applicable for specific problems.

In this paper, we extend the homogenization method to develop macroscopic equations for the air flow and the transport of chemical vapor in a multi-layered unsaturated zone (Fig. 1(a)). We emphasize the direct up-scaling from the mesoscopic or formation scale (i.e., starting governing equations are already homogenized over the pore scale). To enable the analysis, we shall assume an ideal soil structure in which the heterogeneity is periodic. Macroscopic description of the heterogeneous system is then obtained upon averaging over a unit cell of periodicity. On further assuming each cell being composed of two horizontal layers each with distinct properties (Fig. 1(b)), we may determine the effective coefficients which appear in the macroscopic equations analytically in terms of the basic flow variables and soil properties. No calibration or statistical parameters need to be introduced. In short, the major contribution of this study lies in the systematic derivation, using a versatile asymptotic method of homogenization, of the macroscale equation for vapor transport.
in a multi-layered porous medium; the results can be of potential great practical interest to water resources engineers.

The assumptions and the method of analysis are further described in Section 3, which is followed by a deduction of the perturbation equations in Section 4. The effective equations for air flow and vapor transport, up to second-order accuracy, are then found formally in terms of some cell functions in Sections 5 and 6 respectively. These equations are generally good for all kinds of periodic heterogeneity. In Section 7, the particular case of periodic bi-layered formation is considered. Solving the cell functions, the macroscopic equations are obtained with coefficients explicitly expressed in terms of flow velocity and medium parameters. It will be seen that the second-order correction to the specific discharge arises because of air compressibility, and that the macrodispersion caused by the layers is of Taylor type, i.e., the mechanical dispersion coefficient is proportional to the square of the flow velocity. Following a normalization in Section 8, the factors of the longitudinal and transverse components of the hydrodynamic dispersion coefficient are investigated in Section 9.

3 ASSUMPTIONS

A soil system can in general be described by three vastly different length scales. The microscopic or pore scale is the order of size of solid grains, while the mesoscopic scale measures the formation heterogeneity, and the macroscopic or regional scale is the global dimension to be affected by the chemical transport. In the present work, our focus is to study the effect of stratification on the vapor transport at the regional scale, and we shall start from governing equations already averaged over the microscale. No reference to the microscale will therefore be needed in this study.

For the development in Sections 4–6, it is sufficient to assume that the soil heterogeneity is purely periodic, no matter what exact form it is. The special case of alternate stacking of two kinds of horizontal layers, in each of which the material is homogeneous and isotropic, will be considered in Section 7. In any case, the thickness of a layer is assumed to be much smaller than the regional length scale.

We consider an unsaturated zone where the moisture is at the residual level. Water with dissolved and sorbed chemicals is held immobilized in the micropores, while air with chemical vapor can flow readily in the macropore space. It is also assumed that residual non-aqueous phase liquid (NAPL) is not present in the soil matrix, or has already been volatilized into vapor phase. Equilibrium chemical phase partitioning on the pore scale is assumed. That is, the local phase exchange among the aqueous, vapor and sorbed phases occurs much faster than the transport on the formation scale. It also means that rate-limiting effects such as aqueous diffusion in aggregates are minimal at the microscopic scale. We argue that this local equilibrium assumption is not necessarily a limiting one, since the primary time scale in this study is that of global transport which is usually long enough to render any non-equilibrium phase partitioning on the pore level to appear less significant on the macroscale.

In the subsequent analysis, only reference to the formation (mesoscopic) scale ($\ell$) and the regional (macroscopic) scale ($\ell'$) will be required. The small ratio $\epsilon = \ell/\ell' \ll 1$ will be used as the ordering parameter in the analysis. The coordinates at the formation and regional scales are denoted by $x \equiv (x_1, x_2, x_3) \equiv (x, y, z)$ and $x' \equiv (x'_1, x'_2, x'_3) \equiv (x', y', z')$ respectively. The medium heterogeneity is periodic so that it can be divided into unit cells $\Omega$. The average over $\Omega$ of a quantity $f(x, x')$ is defined by

$$\langle f \rangle \equiv \frac{1}{|\Omega|} \int \int f \, d\Omega.$$  

Fig. 1. (a) A multi-layered unsaturated zone contaminated with a volatile organic chemical; (b) Blow-up of the periodic structure showing a unit cell $\Omega$ containing one Layer A ($0 < z < d_a$) and one layer B ($d_a < z < d_a + d_b$).
We further assume that the mesoscale Péclet number is of order unity:

$$\text{Pe} \equiv \frac{U \ell_p}{D} = O(1),$$  \hspace{1cm} (2)

where $U$ and $D$ are respectively the characteristic air velocity and molecular diffusion coefficient of chemical vapor in pore air. Physically eqn (2) means that over the formation scale vapor diffusion is as important as advection. It also implies that the regional Péclet number is much greater than unity:

$$\text{Pe}^* \equiv \frac{U \ell_p}{D} = O(1/e) \gg 1,$$  \hspace{1cm} (3)

or the vapor advection dominates at this upper scale. Two time scales are therefore required. While the global advection time scale $T_1 = \ell_p/U$ is the primary time scale for the transport, the longer time scale $T_2 = \ell_p^2/D$ is for the global diffusion/dispersion:

$$T_2 = \frac{\ell_p^2}{D} = \frac{\left(U \ell_p/D\right)}{(U/U)} = \text{Pe}^* T_1 = O(e^{-1} T_1) \gg T_1.$$  \hspace{1cm} (4)

4 BASIC GOVERNING EQUATIONS

Let us start from the governing equations for the air flow and vapor transport on the formation scale. Assuming steady air flow, the continuity states that

$$\nabla \cdot (\rho \mathbf{u}) = 0,$$  \hspace{1cm} (5)

where $\rho$ is the air density, and $\mathbf{u}$ is the specific discharge (i.e., flow per unit area of soil) which can be found by Darcy’s law:

$$\mathbf{u} = -k \cdot \nabla p,$$  \hspace{1cm} (6)

where $k$ is the second-order tensor of air conductivity divided by the air specific weight, and $p$ is the absolute air pressure. In eqn (6), the gravity effect has been ignored. Since the pressure change can be appreciable in soil vapor extraction, we need to consider the corresponding air density change. Modeling air as an ideal gas, the equation of state is

$$\frac{pM_e}{R_e \Theta} = \rho,$$  \hspace{1cm} (7)

where $M_e$ is the molecular weight of the air mixture, $R_e$ is the universal gas constant and $\Theta$ is the absolute temperature. While the air flow can be compressible, we assume that both $\Theta$ and $M_e$ are constant so that the air density is linearly proportional to the pressure.

For the vapor transport, we invoke the advection–diffusion equation:

$$\beta \frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{u} C) = \nabla \cdot (\mathbf{D} \cdot \nabla C) = 0,$$  \hspace{1cm} (8)

where $C$ is the vapor concentration (i.e., mass of chemical in vapor phase per unit volume of pore air), $\mathbf{D}$ is the second-order tensor of bulk molecular diffusion coefficient in the pore air, and $\beta$ is the retardation factor. Note that by virtue of the high vapor diffusivity in air, the mechanical dispersion is relatively unimportant over the mesoscale when eqn (2) is true, as shown by Ng and Mei.

Therefore $\mathbf{D}$ depends only on the soil microstructure (typically given by the product of the tortuosity tensor and the molecular diffusion coefficient in pure air), but not the flow kinematics. Also, the retardation effect arises from the local equilibrium partitioning among the vapor, aqueous and sorbed phases. Hence, the retardation factor, a function of soil and chemical parameters, may be expressed as follows:

$$\beta = \theta_e + (\theta_w + K_d \theta_s \rho_s)/K_H$$  \hspace{1cm} (9)

where $\theta_e$, $\theta_w$ and $\theta_s$ are respectively the air-filled porosity, water and solid volume fractions, $\rho_s$ is the solid density, $K_d$ is the sorption partition coefficient and $K_H$ is the Henry’s law constant.

Let us now introduce the following normalized quantities (distinguished by a hat):

$$x = \hat{x}, \quad t = (\ell_p/U)\hat{t}, \quad \mathbf{u} = U \hat{\mathbf{u}},$$  \hspace{1cm} (10)

$$C = C_0 \hat{C}, \quad p = (U \ell_p/k)\hat{p}, \quad k = k\hat{k},$$

where $C_0$ is a characteristic vapor concentration and $k$ is a scale for the air conductivity. In terms of these normalized quantities, the above governing equations can now be expressed as follows.

$$\hat{\nabla} \cdot (\hat{\rho} \hat{\mathbf{u}}) = 0,$$  \hspace{1cm} (11)

$$\hat{\mathbf{u}} = -\hat{k} \cdot \hat{\nabla} \hat{p},$$  \hspace{1cm} (12)

$$\hat{\varepsilon}\beta \frac{\partial \hat{C}}{\partial \hat{t}} + \hat{\nabla} \cdot (\hat{\mathbf{u}} \hat{C}) = \hat{\nabla} \cdot (\hat{\mathbf{D}} \cdot \hat{\nabla} \hat{C}) = 0.$$  \hspace{1cm} (13)

From here on let us return to physical variables but keep the ordering parameter for identification. We further introduce the following multiple-scale expansions:

$$f = f(0) + \varepsilon f(1) + \varepsilon^2 f(2) + \varepsilon^3 f(3) + \cdots,$$  \hspace{1cm} (14)

$$\nabla \rightarrow \nabla + \varepsilon \nabla' \quad (i.e., \partial/\partial \hat{x}_i \rightarrow \partial/\partial \hat{x}_i + \varepsilon \partial/\partial x'_i),$$  \hspace{1cm} (15)

$$\partial/\partial \hat{t} \rightarrow \partial/\partial t + \varepsilon \partial/\partial t' ,$$  \hspace{1cm} (16)

where $f(x, x')$ stands for $u, p$ or $C$. Upon substituting these expansions, we may obtain the following perturbation equations, which form the basis of subsequent deductions:

From eqn (11), O(1):

$$\nabla \cdot (\rho(0) u(0)) = 0,$$  \hspace{1cm} (17)

O($\varepsilon$):

$$\nabla \cdot (\rho(0) u(0)) + \nabla \cdot (\rho(0) u(1) + \rho(1) u(0)) = 0.$$  \hspace{1cm} (18)

From eqn (12), O(1):

$$0 = -k \cdot \nabla p(0),$$  \hspace{1cm} (19)

O($\varepsilon$):

$$u(0) = -k \cdot (\nabla p(1) + \nabla p(0)),$$  \hspace{1cm} (20)

O($\varepsilon^2$):

$$u(1) = -k \cdot (\nabla p(2) + \nabla p(1)).$$  \hspace{1cm} (21)
From eqn (13), O(1):
\[ \nabla \cdot (u^0 C^{(0)}) - \nabla \cdot (D \cdot \nabla C^{(0)}) = 0, \tag{22} \]

O(\varepsilon):
\[ \beta \frac{\partial C^{(0)}}{\partial t} + \nabla \cdot (u^{(1)} C^{(0)} + u^0 C^{(1)}) + \nabla' \cdot (u^0 C^{(0)}) \\
- \nabla \cdot [D \cdot (\nabla C^{(1)} + \nabla') C^{(0)}] - \nabla' \cdot (D \cdot \nabla C^{(0)}) = 0, \tag{23} \]

or the leading order pressure is independent of \( x \), and hence from eqn (17)
\[ \nabla \cdot u^0 = 0. \tag{26} \]

By linearity let us put the following formal expression for \( p^{(1)} \) into eqn (20):
\[ p^{(1)} = s \cdot \nabla p^0 + p^{(1)}(x'), \tag{27} \]
where \( s(x, x') \) is a vector, and get
\[ u^0 = -k \cdot \nabla p^0, \tag{28} \]
where
\[ k = k(\nabla s + I) \tag{29} \]
in which \( I \) is the second-order identity tensor. Further substituting eqn (28) into eqn (26) will give the cell governing equation for \( x' \):
\[ \nabla \cdot [k \cdot (\nabla s + I)] = 0 \text{ in } \Omega, \tag{30} \]
which is subject to the boundary condition that \( s \) is \( \Omega \)-periodic. For uniqueness, we also require \( \langle s \rangle = 0 \). Finally we obtain the leading order macroscopic equations for the continuity and specific discharge by taking \( \Omega \)-average of eqns (18) and (28) respectively:
\[ \nabla' \cdot (p^{(0)}(u^0)) = 0, \tag{31} \]
\[ (u^0) = -k' \cdot \nabla p^0, \tag{32} \]
where \( k' \) is the effective conductivity given by
\[ k' = \langle k \rangle = \langle k(\nabla s + I) \rangle. \tag{33} \]

For the O(\varepsilon) air flow problem, we put eqns (28) and (27) into eqn (18) to get
\[ \nabla \cdot u^{(1)} = (\nabla' \cdot \hat{k}) \cdot \nabla p^0 + \nabla \cdot (\hat{k}s) \]
\[ + \hat{k} \cdot (\nabla' (p^{(0)})(\nabla' p^0)/p^0 + k'(\nabla' (p^{(0)})/p^0), \tag{34} \]
which suggests the following representation for \( u^{(1)} \):
\[ u^{(1)} = K_1 \cdot \nabla p^0 + K_2 \cdot (\nabla' p^0)(\nabla' p^0)/p^0 \]
\[ + K_3 \cdot \nabla'(p^0) \tag{35} \]
where \( K_1 \) is a second-order tensor, and \( K_2 \) and \( K_3 \) are third-order tensors. Note that eqn (35) gives nonlinear corrections to Darcy’s law. Plugging eqn (35) into eqn (34) and matching the coefficients, we obtain the following \( \Omega \)-cell problems:
\[ \nabla \cdot K_1 = \nabla' \cdot \hat{k}, \tag{36} \]
\[ \nabla \cdot K_2 = \nabla \cdot (\hat{k}s) + \hat{k}, \tag{37} \]
\[ \nabla \cdot K_3 = \hat{k}, \tag{38} \]
and \( K_1, K_2 \) and \( K_3 \) are \( \Omega \)-periodic. On taking \( \Omega \)-average of eqn (35), the O(\varepsilon) effective specific discharge is expressible by
\[ \langle u^{(1)} \rangle = \langle K_1 \rangle \cdot \nabla p^0 + \langle K_2 \rangle \cdot (\nabla' p^0)(\nabla' p^0)/p^0 \]
\[ + \langle K_3 \rangle \cdot \nabla'(p^0). \tag{39} \]

Note that the O(\varepsilon) effective specific discharge \( \langle u^{(1)} \rangle \) is identically equal to zero for the particular case that the medium properties remain constant macroscopically (i.e., independent of \( x' \)), and the material is isotropic and homogeneous within each region of soil. This is because when the properties do not change with respect to \( x' \), the forcing term on the right-hand side of eqn (36) will be zero, which implies the vanishing of \( K_1 \) and the first term in eqn (39). Further by isotropy and homogeneity the \( \Omega \)-averaged third-order tensors \( K_2 \), \( \langle K_3 \rangle \) are proportional to the permutation tensor, whose double-dot product with a symmetrical second-order tensor is always equal to zero\(^{17} \). Consequently the second and the third terms in eqn (39) will also vanish. Therefore in such case the correction to Darcy’s law is of O(\varepsilon\(^2\)).

6 VAPOR TRANSPORT

Let us first show that \( C^{(0)} \) is independent of the mesoscale. On multiplying eqn (22) with \( C^{(0)} \) and using the product rule of differentiation, we obtain
\[ \frac{1}{2} \nabla \cdot (u^0 C^{(0)} - C^{(0)} u^0) \]
\[ = \nabla \cdot [D \cdot \nabla C^{(0)}] - D \cdot \nabla C^{(0)} \nabla C^{(0)}. \tag{40} \]
The second term on the left-hand side vanishes by virtue of eqn (26). Further taking \( \Omega \)-average of eqn (40) and invoking the \( \Omega \)-periodicity, we finally obtain
\[
\int_\Omega \nabla C^{(0)} \nabla C^{(0)} \, d\Omega = 0. \tag{41}
\]

Since \(D\), a diffusion coefficient, is positive definite, eqn (41) must imply that \(\nabla C^{(0)}\) is zero and \(C^{(0)}\) is constant with respect to \(x\). Hence we can write that
\[
C^{(0)} = C^{(0)}(x', t_1, t_2). \tag{42}
\]

We next derive the leading order effective transport equation. With eqns (42) and (23) reduces to
\[
\beta \frac{\partial C^{(0)}}{\partial t_1} + \nabla \cdot (u^{(1)} C^{(1)} + u^{(0)} C^{(1)}) + \nabla' \cdot (u^{(0)} C^{(0)}) = 0.
\tag{43}
\]

On taking \(\Omega\)-average of eqn (43) and using Gauss theorem, we obtain the macroscopic transport equation at the leading order:
\[
\langle \beta \frac{\partial C^{(0)}}{\partial t_1} + \nabla' \cdot (u^{(0)} C^{(0)}) \rangle = 0. \tag{44}
\]

We may now find a representation for \(C^{(1)}\). By eliminating the unsteady term \(\partial C^{(0)}/\partial t_1\) from eqns (43) and (44), we obtain
\[
\nabla \cdot [u^{(0)} C^{(1)} - D \cdot \nabla C^{(1)}] = \left[ \nabla \cdot D - \bar{u}^{(0)} \right] \cdot \nabla C^{(0)} + \left[ -\nabla \cdot u^{(1)} - \nabla' \cdot \bar{u}^{(0)} + (\beta/\langle \beta \rangle) \nabla' \cdot (u^{(0)}) \right] C^{(0)},
\tag{45}
\]
where
\[
\bar{u}^{(0)} = u^{(0)} - \langle \beta/\langle \beta \rangle \rangle (u^{(0)})
\tag{46}
\]
is the velocity fluctuation on the mesoscale. By linearity, we may put
\[
C^{(1)} = M \cdot \nabla C^{(0)} + E C^{(0)} + \tilde{C}(x', t_1, t_2), \tag{47}
\]
where \(M(x, x')\) is a vector, \(E(x, x')\) is a scalar. The mesoscale problems for these functions follow from eqn (45):
\[
\nabla \cdot [\bar{u}^{(0)} M - D \cdot (I + \nabla M)] = -\bar{u}^{(0)}, \tag{48}
\]
\[
\nabla \cdot [\bar{u}^{(0)} E - D \cdot \nabla E] = -\nabla \cdot \bar{u}^{(1)} - \nabla' \cdot \bar{u}^{(0)} + (\beta/\langle \beta \rangle) \nabla' \cdot (u^{(0)}), \tag{49}
\]
and \(M\) and \(E\) are \(\Omega\)-periodic. For uniqueness, we further require these functions to satisfy
\[
\langle \beta M \rangle = \langle \beta E \rangle = 0. \tag{50}
\]

Note that eqn (50) implies \(\langle \beta C^{(1)} \rangle = \langle \beta \tilde{C} \rangle\); the rationale is to ultimately combine \(C^{(1)}\) with \(C^{(0)}\) in the final effective transport equation. Physically eqn (47) gives corrections to \(C^{(0)}\) owing to mesoscale spatial variation in advection velocity as in the first term, and in air compressibility as in the second term. Obviously for incompressible flows \(E\) will be identically zero.

Finally we may derive the \(O(\varepsilon)\) effective transport equation as follows. Using Gauss theorem and the uniqueness condition (50), we obtain the \(\Omega\)-average of eqn (24):
\[
\langle \beta \rangle \frac{\partial C^{(0)}}{\partial t_2} + \langle \beta \rangle \frac{\partial C^{(1)}}{\partial t_2} + \nabla' \cdot [\langle u^{(1)} \rangle C^{(0)} + \langle u^{(0)} C^{(1)} \rangle] - \nabla' \cdot [(D \cdot \nabla C^{(1)}) + (D \cdot \nabla' C^{(0)})] = 0. \tag{51}
\]

On further substituting eqn (47), the above equation becomes
\[
\langle \beta \rangle \frac{\partial C^{(0)}}{\partial t_2} + \langle \beta \rangle \frac{\partial C^{(1)}}{\partial t_2} + \nabla' \cdot \left( \langle u^{(1)} \rangle C^{(0)} + \langle u^{(0)} \rangle \tilde{C} \right) - \nabla' \cdot (D' \cdot \nabla' C^{(0)}) = 0, \tag{52}
\]
where
\[
\tilde{u}^{(1)} = \langle u^{(1)} \rangle - D \cdot \nabla E + u^{(0)} E
\tag{53}
\]
is the \(O(\varepsilon)\) correction to the specific discharge, and
\[
D' = \langle D \cdot (I + \nabla M) \rangle - u^{(0)} M
\tag{54}
\]
is the effective hydrodynamic dispersion coefficient.

Finally we may add eqn (52) multiplied by \(\varepsilon\) to eqn (44) to get the macroscopic effective transport equation which is valid up to \(O(\varepsilon)\):
\[
\langle \beta \rangle \frac{\partial C}{\partial t_2} + \nabla' \cdot (\tilde{u} C) - \varepsilon \nabla' \cdot (D' \cdot \nabla C) = 0, \tag{55}
\]
where
\[
C = C^{(0)} + \varepsilon \tilde{C}^{(1)}, \quad \tilde{u} = \langle u^{(0)} \rangle + \varepsilon \tilde{u}^{(1)}
\tag{56}
\]
are the combined concentration and effective specific discharge respectively. Note that while advection is dominant at the leading order, dispersion is significant only over a long time scale comparable to \(T_2\). Also note that mechanical dispersion now emerges on the macro-scale owing to the mesoscale heterogeneity. The \(\varepsilon\) parameter in eqns (55) and (56) serves only to indicate the order of the associated term, and can be discarded when the physical terms are computed.

### 7 Layered Formation

To obtain analytical solutions for the cell functions, we further consider the simple yet practically important composite meso-structure; the medium is composed of two types of horizontal layers, A and B, stacking alternately in the vertical direction \(x_3\) or \(z\). As shown in Fig. 1(b), a periodic unit cell \(\Omega\) consists of one Layer A \((0 < z < d_a)\) and one Layer B \((d_a < z < d_a + d_b)\) where \(d_a\) and \(d_b\) are the respective layer thicknesses. Within each layer the medium is isotropic and homogeneous, and the material properties are known. Specifically, the conductivity and diffusion tensors are
\[
k_{ij} = k \delta_{ij}; \quad D_{ij} = D \delta_{ij}
\tag{57}
\]
where \(\delta_{ij}\) is the Kronecker delta, and
\[
(k, D, \beta) = \begin{cases} (k_a, D_a, \beta_a) & \text{in Layer A,} \\ (k_b, D_b, \beta_b) & \text{in Layer B,} \end{cases}
\tag{58}
\]
where \( k_a, k_b, D_a, D_b, \beta_a \) and \( \beta_b \) are all constants. Since strictly horizontal layers are considered, the dependence on the horizontal coordinates \((x, y)\) on the mesoscale can be omitted. The definition of an \( \Omega \)-average (1) is now reduced to

\[
\langle f \rangle \equiv (d_a + d_b)^{-1} \left[ \int_0^{d_a} f \, dz + \int_{d_a}^{d_a + d_b} f \, dz \right].
\]  

With dependence on \( z \) only, the vector \( s \) in eqn (30) has been found by Mei and Auriault\(^16\):

\[
\frac{ds_1}{dz} = \frac{ds_2}{dz} = 0, \quad \frac{ds_3}{dz} = -1 + \frac{k^{-1}}{k^{-1}}.
\]  

Also, the macroscale permeability tensor follows readily from eqn (33):

\[
k'_{11} = k'_{22} = \langle k \rangle = \frac{k_a d_a + k_b d_b}{d_a + d_b},
\]  

\[
k'_{33} = \langle k (1 + \frac{ds_3}{dz}) \rangle = \langle k^{-1} \rangle^{-1} = \frac{k_a k_b (d_a + d_b)}{k_a d_b + k_b d_a}
\]  

where \( d_a \) and \( d_b \) are the thicknesses of layers A and B respectively. As expected, the equivalent longitudinal and transverse permeabilities are respectively the arithmetic mean and the harmonic mean of the individual permeabilities. From eqns (28) and (32), the following relations are also obtained:

\[
u^{(00)} = -k \frac{\partial p^{(0)}}{\partial x} = \frac{k}{\langle k \rangle} \langle u^{(00)} \rangle,
\]  

\[
u^{(0)} = -k \frac{\partial p^{(0)}}{\partial y} = \frac{k}{\langle k \rangle} \langle v^{(0)} \rangle,
\]  

\[
\omega^{(0)} = -k \left( 1 + \frac{ds_3}{dz} \right) \frac{\partial p^{(0)}}{\partial z} = -k \frac{\partial p^{(0)}}{\partial z} = \langle w^{(0)} \rangle
\]  

where we have denoted \((u_1, u_2, u_3)\) by \((u, v, w)\). Therefore while the horizontal components of the specific discharge are discontinuous across the layers, the vertical component is continuous and equal to that of the macroscale. Unless stated otherwise, we shall from here on omit the leading order superscript, and use subscripts \( a \) and \( b \) to distinguish medium properties in layers A and B respectively.

Let us now consider the problem eqn (48) for \( M(z) \). We first decompose the function into static and dynamic components (i.e., the former is not, but the latter is a function of convection velocity):

\[
M_i = M_i^d + M_i^s \quad (i = 1, 2, 3)
\]  

such that

\[
\frac{d}{dz} \left[ D \left( \delta_{3i} + \frac{dM_i^s}{dz} \right) \right] = 0,
\]  

\[
\frac{d}{dz} \left[ w M_i^d - D \frac{dM_i^s}{dz} \right] = -\bar{u}_i - \frac{d}{dz} (w M_i^s),
\]  

and

\[
\langle \beta M_i^s \rangle = \langle \beta M_i^s \rangle = 0.
\]  

We anticipate that the static component in eqn (66) is giving rise to the bulk effective diffusion coefficient, while the dynamic component will lead to the mechanical dispersion coefficient of vapor in the layered medium.

The static component \( M_i^s \) can be found in a manner similar to \( s \):

\[
\frac{dM_i^s}{dz} = \frac{dM_i^s}{dz} = 0
\]  

\[
\frac{dM_i^s}{dz} = -1 + \frac{D^{-1}}{(D^{-1})} = \begin{cases} -d_b f_M, & \text{Layer A}, \\ d_a f_M, & \text{Layer B} \end{cases}
\]  

where

\[
f_M = \frac{D_a - D_b}{D_a d_b + D_b d_a}.
\]  

On further integrating for separate layers as shown in Fig. 1(b), and making use of continuity of \( M^s \) across an interface and the uniqueness condition eqn (69), we obtain

\[
M_i^s(z) = M_i^s(z) = 0 \quad \text{in both layers}
\]  

and

\[
M_i^s(z) = \begin{cases} -d_b f_M z + d_b d_b f_M / 2, & 0 \leq z < d_a, \\ d_a f_M z - d_a (2d_a + d_b) f_M / 2, & d_a \leq z < d_a + d_b. \end{cases}
\]  

Note \( M_i^s \) also satisfies

\[
\int_{\text{Layer A}} M_i^s \, dz = \int_{\text{Layer B}} M_i^s \, dz = 0.
\]  

With regard to eqn (68), we may use the relations eqns (63)–(65) and eqns (70) and (71) to write its right-hand side as

\[
\text{RHS}(68) = -\bar{u}_i - w \frac{dM_i^s}{dz} = -\begin{bmatrix} \beta \langle \frac{1}{\beta} \rangle \langle u \rangle, & \beta \langle \frac{1}{\beta} \rangle \langle v \rangle, & \\ \beta \langle \frac{1}{\beta} \rangle \langle w \rangle, & D^{-1} \langle w \rangle \end{bmatrix} = \begin{cases} d_a f_M, & \text{Layer A}, \\ -d_a f_M, & \text{Layer B} \end{cases}
\]  

where

\[
f_M = (\eta_1, \eta_2, \eta_3)(w),
\]  

and

\[
\eta_1 = \eta_2 = \frac{\beta_a - \beta_b}{\beta_a d_a + \beta_b d_b} - \frac{k_a - k_b}{k_a d_a + k_b d_b},
\]  

\[
\eta_3 = \frac{\beta_a - \beta_b}{\beta_a d_a + \beta_b d_b} + \frac{D_a - D_b}{D_a d_b + D_b d_a}.
\]  

Hence the problem for \( M^d \) can be written as
\[ \frac{d}{dz} \left[ \langle w \rangle M^d - D \frac{dM^d}{dz} \right] = \begin{cases} d_a f_M & \text{Layer A,} \\ -d_a f_M & \text{Layer B} \end{cases} \quad (80) \]

Let us next consider the \( E \) problem eqn (49). Using the relationships eqns (18), (27) and (31), we may also write the right-hand side as

\[ \text{RHS}(49) = |\nabla p \cdot \hat{u} + (\nabla s \cdot \nabla' p) \cdot \hat{u}|p^{-1} = \begin{cases} d_a f_E & \text{Layer A,} \\ -d_a f_E & \text{Layer B,} \end{cases} \quad (81) \]

where

\[ f_E = -\left[ \eta_1(w) \frac{\partial p}{\partial x} + \eta_2(w) \frac{\partial p}{\partial y} + \eta_3(w) \frac{\partial p}{\partial z} \right] p^{-1} \]

in which \( \eta_1 \) and \( \eta_2 \) are given by eqn (78) and

\[ \eta_3 = \left( \frac{\beta_a - \beta_b}{\beta_a d_a + \beta_b d_b} + \frac{k_a - k_b}{k_a d_a + k_b d_b} \right). \quad (82) \]

Hence the problem for \( E \) can be written as

\[ \frac{d}{dz} \left[ \langle w \rangle E - D \frac{dE}{dz} \right] = \begin{cases} d_a f_E & \text{Layer A,} \\ -d_a f_E & \text{Layer B} \end{cases} \quad (84) \]

By now it is clear that in eqns (80) and (84) for \( M^d \) and \( E \), the same spatial operations are applied on the left-hand sides, while the right-hand sides differ only by a factor which is independent of \( z \). Therefore the \( z \)-dependence for the two functions will be the same, and the solutions are in the form

\[ (M^d, E) = Z(z) \times (f_M, f_E), \quad (85) \]

and

\[ M(z) = Z(z) f_M + (0, 0, M_z'), \quad (86) \]

where \( Z(z) \) is to be found from the following boundary value problem:

\[ \frac{d}{dz} \left[ \langle w \rangle Z - D \frac{dZ}{dz} \right] = \begin{cases} d_a & 0 < z < d_a, \\ -d_a & d_a < z < d_a + d_b, \end{cases} \quad (87) \]

with boundary conditions derived from the continuity of concentration and flux at the layer interfaces:

\[ Z(z = d_a^-) = Z(z = d_a^+), \quad Z(z = 0) = Z(z = d_a + d_b). \quad (88) \]

\[ (wZ - D_a \frac{dZ}{dz})_{z=d_a^-} = (wZ - D_a \frac{dZ}{dz})_{z=d_a^+}, \quad (89) \]

and the uniqueness condition

\[ \langle \beta Z \rangle = \beta_a \int Z \, dz + \beta_b \int Z \, dz = 0. \quad (90) \]

When \( \langle w \rangle \) is not zero, the solution to the above problem is

\[ Z(z) = \begin{cases} \zeta_1 e^{w/z_d} + \frac{d_a}{d_a - d_b} \left( z - \frac{d_a}{2} + \frac{d_a}{w} \right) - \frac{\beta_a D_a - \beta_b D_b}{\beta_a D_a + \beta_b D_b} \zeta_1, & 0 < z < d_a, \\ \zeta_2 e^{w/z_d} - \frac{d_a}{d_a + d_b} \left( z - d_a - \frac{d_a}{2} + \frac{d_a}{w} \right) - \frac{\beta_a D_a - \beta_b D_b}{\beta_a D_a + \beta_b D_b} \zeta_1, & d_a < z < d_a + d_b, \end{cases} \quad (91) \]

where

\[ \zeta_1 = \frac{d_a d_b}{\langle w \rangle^2} \left( \frac{\langle w \rangle}{\langle w \rangle} \right) \left( \frac{\langle w \rangle}{\langle w \rangle} \right) - 1 \right) \langle w \rangle^3, \quad (92) \]

\[ \zeta_2 = \frac{e^{(w)} - (w)}{\langle w \rangle} \left( \frac{\langle w \rangle}{\langle w \rangle} \right) - 1 \right) \langle w \rangle^2, \quad (93) \]

and

\[ \zeta_3 = \frac{e^{(w)} - (w)}{\langle w \rangle} \left( \frac{\langle w \rangle}{\langle w \rangle} \right) - 1 \right) \langle w \rangle^2. \quad (94) \]

In the case when the flow is horizontal, or \( \langle w \rangle \) is equal to zero, the solution is reduced to

\[ Z(z) = \begin{cases} -\frac{d_a}{d_a - d_b} z^2 + \frac{d_a}{d_a - d_b} z, & 0 < z < d_a, \\ \frac{d_a}{d_a - d_b} z^2 - \frac{2d_a d_b}{d_a + d_b} z + \frac{d_a^2 d_b}{d_a + d_b} \zeta_4, & d_a < z < d_a + d_b, \end{cases} \quad (95) \]

where

\[ \zeta_4 = \frac{d_a d_b (\beta_a D_a - \beta_b D_b)}{12D_a D_b (\beta_a d_a + \beta_b d_b)}. \quad (96) \]

Note also the limit

\[ \zeta_1 \to \frac{d_a d_b}{12D_a D_b} \] as \( \langle w \rangle \to 0. \quad (97) \]

Before further substitutions, let us first obtain the following cell average:

\[ \langle uZ - D \cdot \nabla Z \rangle = -f_Z \quad (98) \]

where

\[ f_Z = (\gamma_1 w, \gamma_2 w, \gamma_3 w) \]. \quad (99) \]

in which

\[ \gamma_1 = \gamma_2 = \frac{(\beta_a D_a + \beta_b D_b)(k_a \beta_a - k_b \beta_b)}{(\beta_a d_a + \beta_b d_b) k_a d_a + k_b d_b) \zeta_1}, \quad (100) \]

\[ \gamma_3 = \left( \frac{\beta_a D_a - \beta_b D_b}{\beta_a d_a + \beta_b d_b} \right) \zeta_1. \quad (101) \]

On decomposing \( M \) according to eqn (66), and using eqns (85) and (98), the hydrodynamic dispersion tensor (54) may now be developed as follows.

\[ \mathbf{D}' = \langle \mathbf{D} \cdot (I + \nabla' \mathbf{M'} + \mathbf{M}') - \mathbf{u}[\mathbf{M'} + \mathbf{M}'] \rangle \]

\[ = \langle \mathbf{D} \cdot (I + \nabla' \mathbf{M'}) \rangle - \langle \mathbf{u}[\mathbf{M'} - \mathbf{D} \cdot \nabla' \mathbf{M'}] \rangle - \langle \mathbf{u}[\mathbf{M'} - \mathbf{D} \cdot \nabla' \mathbf{M'}] \rangle \]

\[ = \mathbf{D}' + \langle \mathbf{u}Z - \mathbf{D} \cdot \nabla Z \rangle f_M \]

\[ = \mathbf{D}' + f_z f_M \], \quad (102) \]

where the last term in the second line is zero because of eqns (73) and (75), and \( \mathbf{D}' \) is the effective diffusion coefficient given by
\[ D_{11}^* = D_{22}^* = \langle D \rangle = \frac{D_1 d_1 + D_2 d_2}{d_1 + d_2} \text{,} \]
\[ D_{33}^* = (D^{-1})^{-1} = \frac{D_1 d_0 + D_2 d_0}{D_1 d_0 + D_2 d_0} \text{,} \]
\[ D_{ij}^* = 0 \text{ for } i \neq j. \text{ (105)} \]

Similar to the effective conductivity, the longitudinal and the transverse components of the effective diffusion coefficient are respectively given by the arithmetic mean and the harmonic mean of the layer values. Obviously in eqn (102) the hydrodynamic dispersion coefficient \( D' \) is the sum of the effective molecular diffusion coefficient \( D^* \) and the mechanical dispersion coefficient \( f_x f_y \) which is proportional to the square of the velocity. Substituting eqns (77) and (99) Eqn. (102) can be written in the alternative form

\[ D'_{ij} = D_0^{ij} + \gamma_i \eta_i \langle u_i \rangle \langle u_i \rangle. \text{ (106)} \]

While it is trivial to see that \( \gamma_1 \eta_2 = \gamma_2 \eta_1 \), it can also be shown after some algebra that \( \gamma_1 \eta_3 = \gamma_3 \eta_1 \) and \( \gamma_2 \eta_3 = \gamma_3 \eta_2 \). Therefore the dispersion coefficient tensor is symmetric: \( D'_{ij} = D'_{ji} \).

Finally the combined effective specific discharge eqn (56) may also be expressed as follows:

\[ u^* = \langle u^{(0)} \rangle + \langle u^{(1)} \rangle + \langle u^{(0)} E - D \cdot \nabla E \rangle = \langle u^{(0)} \rangle + f_x \langle u^{(0)} Z - D \cdot \nabla Z \rangle \]
\[ = \langle u^{(0)} \rangle - f_x f_z. \text{ (107)} \]

or, omitting the leading order superscript and using eqn (99),

\[ u_i^* = (1 - \gamma_i f_x) \langle u_i \rangle. \text{ (108)} \]

Note that use has been made of \( \langle u^{(1)} \rangle = 0 \) which is true for the present particular case (see the discussion in the last paragraph of Section 5).

8 NORMALIZED TRANSPORT EQUATION

Let us normalize the effective transport equation using the normalization introduced in eqn (10):

\[ \langle \beta \rangle \frac{\partial \tilde{C}}{\partial t} + \nabla \cdot \left( \tilde{u} \tilde{C} \right) - \text{Pe}_a' \langle \hat{u}_i \rangle \nabla \tilde{C} = 0, \text{ (109)} \]

where

\[ \tilde{u} = u' / U, \text{ } \tilde{D} = D' / D_a, \text{ } \text{Pe}_a' = U \ell / D_a. \text{ (110)} \]

Note that by eqn (3) \( \text{Pe}_c = O(1/c) \), or the dispersion is significant over a long time scale comparable to \( T_2 \).

We further introduce the following ratios of layer properties

\[ \delta_0 = d_0 / d_a, \text{ } \delta_k = k_0 / k_a, \text{ } \delta_D = D_0 / D_a, \text{ } \delta_\beta = \beta_0 / \beta_a. \text{ (111)} \]

and the following dimensionless variables and parameters:

\[ \hat{\eta}_i = d_i \eta_i = \frac{(\delta_i - \delta_k)(1 + \delta_k)}{(1 + \delta_\beta \delta_d)(1 + \delta_\beta \delta_D)} \text{ for } i = 1, 2, \text{ (112)} \]
\[ \hat{\eta}_3 = d_3 \eta_3 = \frac{(1 - \delta_\beta \delta_D)}{(1 + \delta_\beta \delta_D)}, \text{ (113)} \]
\[ \hat{\gamma}_i = \frac{(U^2)}{D_i d_a} \gamma_i = \frac{\delta_i (\delta_k - \delta_D)(\delta_d + \delta_D)}{(1 + \delta_\beta \delta_d)(1 + \delta_\beta \delta_D)} (i = 1, 2), \text{ (114)} \]
\[ \hat{\gamma}_3 = \frac{(U^2)}{D_3 d_a} \gamma_3 = \frac{\delta_d (1 - \delta_\beta \delta_D)}{(1 + \delta_\beta \delta_D)} (i = 1, 2), \text{ (115)} \]

where

\[ \hat{\xi}_i = \frac{(U^2)}{D_i d_a} \xi_i \]
\[ = \frac{1}{\langle \hat{u} \rangle^2} \left[ 1 - \frac{(\langle \hat{w} \rangle \text{Pe}_a - 1)(\langle \hat{w} \rangle \text{Pe}_b - 1)(\text{Pe}_a + \text{Pe}_b)}{(\langle \hat{w} \rangle \text{Pe}_a + \text{Pe}_b - 1)(\langle \hat{w} \rangle \text{Pe}_a \text{Pe}_b)} \right], \text{ (116)} \]

and

\[ \text{Pe}_a = U d_a / D_a, \text{ } \text{Pe}_b = U d_b / D_b = \text{Pe}_a \delta_d / \delta_D. \text{ (117)} \]

Note that \( \hat{\xi}_i \) is always greater than zero for any finite value of \( \langle \hat{w} \rangle \) and it tends to a finite limit when \( \langle \hat{w} \rangle \) becomes zero:

\[ \hat{\xi}_i \rightarrow \text{Pe}_a \text{Pe}_b / 12 \text{ as } \langle \hat{w} \rangle \rightarrow 0. \text{ (118)} \]

On substituting eqn (82), the normalized form of the specific discharge eqn (108) may now be written as (for \( i = 1, 2, 3 \)):

\[ \hat{u}_i = 1 + \left( \text{Pe}_c \hat{\rho} \right)^{-1} \hat{\eta}_i \langle \hat{u} \rangle \frac{\partial \hat{\rho}}{\partial \hat{\rho}} + \hat{\gamma}_i \langle \hat{w} \rangle \hat{\rho} \frac{\partial \hat{\rho}}{\partial \hat{\rho}} \left( \langle \hat{u} \rangle \right). \text{ (119)} \]

Also, the normalized form of the hydrodynamic dispersion coefficient (106) can be written as (for \( i, j = 1, 2, 3 \)):

\[ \hat{D}_{ij} = \hat{D}_{ij}^* + \hat{\gamma}_i \langle \hat{u}_i \rangle \langle \hat{u}_j \rangle, \text{ (120)} \]

where \( \hat{D}_{ij}^* \) is the normalized diffusion coefficient given by

\[ \hat{D}_{11} = \hat{D}_{22} = \frac{1 + \delta_\beta \delta_d}{1 + \delta_\beta \delta_D}, \text{ (121)} \]
\[ \hat{D}_{33} = \frac{\delta_D (1 + \delta_\beta)}{\delta_d + \delta_D}, \text{ (122)} \]
\[ \hat{D}_{ij} = 0 \text{ for } i \neq j. \text{ (123)} \]
9 THE DISPERSION COEFFICIENT

We stress that the dispersion coefficient given in eqn (121) is a function of both the convection velocity and the layer properties. The vapor dispersion is enhanced at the macroscopic scale because of the layered heterogeneity. In this section the factors of velocity and the layer properties. The vapor dispersion is essentially caused by the exchange of velocity and diffusion that promotes lateral transfer between layers interacting with molecular variation across the layers interacting with molecular diffusion.

The second (mechanical dispersion) terms in the above expressions are always non-negative; they are zero only when the corresponding velocity component vanishes or when \( \delta_k = \delta_l \) for \( D_{11} \), \( \delta_k \delta_l = 1 \) for \( D_{33} \). Therefore, as expected, in the absence of heterogeneity the mechanical dispersion of vapor in a porous medium becomes subdominant. Note also that these two dispersion components are even functions of \( \langle \hat{w} \rangle \), i.e., \( D_{11}(\langle \hat{w} \rangle) = D_{11}(-\langle \hat{w} \rangle) \) and \( D_{33}(\langle \hat{w} \rangle) = D_{33}(-\langle \hat{w} \rangle) \).

It can readily be seen from \( D_{11} \) that the longitudinal mechanical dispersion is of the magnitude \( U^2 D_{11}/D_m \), which is the form of Taylor dispersion in a capillary tube. This is reasonable since in our model the dispersion is essentially caused by the effect of velocity variation across the layers interacting with molecular diffusion that promotes lateral transfer between layers with different retardation factor and flow velocity. Similar results were also obtained for the special case of structured media composed of mobile and immobile regions. The diffusion exchange between these two regions can effectively increase the dispersion coefficient by the amount proportional to \( U^2 D_{11}/D_m \), where \( U_m \) is the velocity in the mobile region, \( d_{im} \) is a characteristic dimension of the immobile region, and \( D_m \) is the molecular diffusion coefficient in the immobile region. It suggests that the longitudinal dispersion has a strong dependence on the velocity along the more permeable layer, and the diffusion time scale across the less permeable layer.

<table>
<thead>
<tr>
<th>Case</th>
<th>( \delta_k )</th>
<th>( \delta_l )</th>
<th>( \delta_D )</th>
<th>( \delta_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.5</td>
<td>10</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>0.05</td>
<td>100</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>0.05</td>
<td>100</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>IV</td>
<td>0.05</td>
<td>100</td>
<td>0.05</td>
<td>2</td>
</tr>
</tbody>
</table>

We also remark that the transverse mechanical dispersion vanishes when the flow is strictly horizontal. This is consistent with the analysis by statistical means which yields a zero zero transverse asymptotic macrodispersivity when the heterogeneous structure of the medium does not create transverse dispersion. In the present case, transverse mechanical dispersion occurs only in the presence of transverse flow, but with a rather weak dependence on it, as will be seen shortly.

To facilitate further discussions, we assume that the vapor transport takes place slower in layer B than layer A. Physically, this can be realized when the material in layer B is more fine-grained (therefore smaller conductivity and diffusivity) and has a larger organic matter content (therefore a larger retardation factor) than that in layer A. The material contrasts are therefore \( \delta_k < 1 \), \( \delta_l < 1 \) and \( \delta_D > 1 \). Specifically four cases of parameter values given in Table 1 are considered on studying their effects on the dispersion coefficient components. In each case, \( P_{eb} \) is taken to be unity. By comparing with Case I, the effects of a larger contrast in conductivity and retardation factor can be examined in Case II. Also by comparing with Case II, the effects of a larger contrast in layer diffusivity can be examined in Case III. Again by comparing with Case III the effects of a thicker Layer B can be studied in Case IV.

Fig. 2 shows for the four cases the longitudinal dispersion coefficient \( D_{11} \) as a function of the longitudinal specific discharge \( \langle \hat{u} \rangle \) when there is no transverse flow (i.e., \( \langle \hat{w} \rangle = 0 \)). According to eqn (125) \( D_{11} \) increases with
the square of \( h^u \). The increase is relatively mild in Case I when \( h^u \) is between 0 and 1. A ten-time increase in the contrast of the conductivity and the retardation factor (Case II) only slightly increases the effect of the velocity on dispersion. However a ten-time increase in the diffusion coefficient contrast (Case III) can appreciably enhance the increase of the dispersion with velocity. The enhancement is even more dramatic when the thickness of layer B is doubled (Case IV). The results confirm our earlier statement that the longitudinal dispersion has a strong relationship with both the longitudinal velocity and the effective diffusion time scale across the less permeable layer.

Fig. 3 shows similar plots as in Fig. 2, but for \( h^w = 0.5 \). By comparing the two figures, it is clear that the vertical flow suppresses the increase of the longitudinal dispersion coefficient with the horizontal velocity, more in Cases III and IV than Cases I and II. This is reasonable because the transverse flow can reduce the rate of transport along the layers and therefore lower the extent of longitudinal dispersion.

The variations between the transverse dispersion coefficient and the transverse specific discharge are shown in Fig. 4. Over the range of \( \langle \hat{w} \rangle \) from 0 to 5, \( \hat{D}_{31} \) increases slightly in Cases I and II, but remains practically unchanged in Cases III and IV. In fact the transverse dispersion coefficient does not as strongly depend on the velocity as the longitudinal dispersion coefficient does. It is clear from eqn (126) that \( \hat{D}_{31} \) does not increase with the square of the vertical velocity, but only with the value inside the square brackets which has a maximum of unity when \( \langle \hat{w} \rangle \) becomes infinite. In addition, the effect of the velocity disappears when the product \( \delta_d \delta_D \) happens equal to unity. Therefore the enhancement of the transverse mechanical dispersion by the seepage velocity is in general very limited. The transverse dispersion is more dominated by the effective molecular diffusion normal to the layers which is controlled by \( \delta_D \) or the diffusivity in the less permeable layer.

10 CONCLUDING REMARKS

In this paper we have presented a mathematical derivation of the macroscopic equations for the transport of chemical vapor in a multi-layered unsaturated zone. Based on the assumptions of cell periodicity and a sharp contrast in length scales, the method of homogenization is applied in order to identify the range of validity of the theory. The effective transport eqn (55), in which the specific discharge and dispersion coefficient are expressed in terms of some cell functions, is good for all forms of periodic heterogeneity with a characteristic dimension much smaller than the global length scale. Analytical solutions to the cell functions have been obtained for the simple case of bi-layered unit cell. In terms of flow velocity and medium parameters, the specific discharge and the hydrodynamic dispersion coefficient are given respectively by eqns (108) and (106), or in dimensionless form, eqns (120) and (121).

For this periodic bi-layered composite, the factors of the dispersion components have been examined in some detail. The longitudinal dispersion is found to be caused by Taylor mechanism. That is, the coefficient varies with the square of the longitudinal velocity, and linearly with the diffusion time across the less permeable layer. A larger contrast in the retardation factor and conductivity can only modestly increase the dependence of the dispersion on the flow velocity. Also, an increase in the transverse flow velocity will lower the value of longitudinal dispersion coefficient. On the other hand, owing to the ideal layering structure, the transverse mechanical dispersion does not depend on the longitudinal flow, and only weakly depends on the transverse flow velocity.

Extensions of the present theory are desirable for the cases of: (i) strongly kinetic phase exchange on the pore scale so that a source term may appear in the transport eqn (8); (ii) more complex periodic layering structures;
(iii) a larger contrast in the layer properties, and (iv) vapor transport influenced by gravity.

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