ROCKY MOUNTAIN
JOURNAL OF MATHEMATICS
Volume 21, Number 2, Spring 1991

MISCIBLE DISPLACEMENT IN POROUS MEDIA INFLUENCED BY MOBILE AND IMMOBILE WATER

ULRICH HORNUNG

1. Introduction. In this paper we present a new model for miscible displacement in porous media. The most commonly used model assumes that transport of solutes is governed by diffusion and/or dispersion and in addition by convection and/or advection. This results in an equation of the type of Model A (see Section 2); a discussion can be found in [**2**]. Assuming that the soil consists of both slowly and rapidly conducting pores one is led to the concept of aggregated or sorbing media. The equations describing Model B (see Section 2) have been studied in detail [**5**]. These ideas have been applied recently [**8**] to transport and exchange of ions.

Here we introduce the mathematical technique of homogenization to the process of modeling. This machinery starts from a micro-model and allows one to derive a macro-model as the limit in a certain sense; the result is Model C (see Section 2). This technique is the mathematical counterpart of what is known as averaging [**3**]. The mathematical model of homogenization was used in [**9**] for chromatography, and in [**6**] for heterogeneous catalysis. In forthcoming papers homogenization will also be used in the context of double porosity models for fractured media [**1**] and in connection with heat conduction in fractured rocks [**7**]. A mathematical comparison of Models A, B, and C is given in Section 3, a numerical comparison is contained in Section 4. A derivation of the new Model C is presented in Section 5.

2. Three Models. Before we present the models in question we introduce some notations.

Notations

$\vec{u}[ms^{-1}]$	= Darcy's velocity of the mobile water
$v[kgm^{-3}]$	= concentration of the solute in the mobile water
$w[kgm^{-3}]$	= concentration of the solute in the immobile water

$\Theta[m^3m^{-3}]$	= relative water content
$\Theta_1, \Theta_0[m^3m^{-3}]$	= relative water contents of mobile and immobile water, resp.
$D[m^2m^{-1}]$	= diffusivity of the solute
$\alpha[s^{-1}]$	= exchange coefficient
$\rho(t)$	$= \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2}\exp(-\pi^2k^2\alpha t) =$ auxiliary function for model C

Model A

$$\Theta\partial_t v = D\Delta v - \vec{u}\cdot\nabla v$$

Model B

$$\Theta_1\partial_t v + \Theta_0\partial_t w = D\Delta v - \vec{u}\cdot\nabla v, \qquad \partial_t w = \alpha(v-w)$$

Model C

$$\Theta_1\partial_t v + \Theta_0\partial_t w = D\Delta v - \vec{u}\cdot\nabla v, \qquad \partial_t w = -\left(\tfrac{d}{dt}\rho\right) * \partial_t v.$$

Remarks. (a) The symbol "$*$" in Model C denotes convolution with respect to time, i.e.,

$$(f*g)(t) = \int_0^t f(t-s)g(s)\,ds.$$

(b) The second equation of Model B can also be written using a convolution, namely

$$\partial_t w = -\left(\frac{d}{dt}\sigma\right) * \partial_t v$$

where $\sigma(t) = \exp(-\alpha t)$.

(c) A surprisingly good approximation of the function ρ used in Model C is

$$\tilde{\rho}(t) = 1 - (1 - \exp(-\pi^2\alpha t))^{1/2}.$$

Numerical calculations show that

$$|\rho(t) - \tilde{\rho}(t)| \le 0.022 \quad \text{for all } t \ge 0;$$

furthermore one has

$$\rho(t) - \tilde{\rho}(t) \to 0 \quad \text{for } t \to 0 \quad \text{and} \quad \text{for } t \to \infty;$$

in addition, the limits are

$$\frac{\rho(t)}{\tilde{\rho}(t)} \to \frac{12}{\pi^2} \approx 1.22 \quad \text{for } t \to \infty$$

and

$$\frac{1-\rho(t)}{1-\tilde{\rho}(t)} \to \frac{6}{\pi^{3/2}} \approx 1.08 \quad \text{for } t \to 0.$$

The latter result is not trivial; it can be shown using Poisson's summation formula (this fact was pointed out to the author by M. Freier/Munich). Figure 2.1 shows ρ and σ as functions of time t. For a reasonable comparison we have chosen

$$\alpha \approx 13.15 \quad \text{for } \sigma \qquad \text{and} \qquad \alpha = 1.0 \quad \text{for } \rho.$$

This choice was made since then one has

$$\int_0^\infty \sigma(t)\,dt = \int_0^\infty \rho(t)\,dt.$$

Figure 2.2 shows ρ (solid lines) and $\tilde{\rho}$ (dotted lines) as functions of $z = \exp(-\pi^2 \alpha t)$.

3. Fundamental Solutions. The objective of this chapter is to point out the essential difference of the three models. To this end we simplify by neglecting the spatial derivatives in the equations and study the fundamental solutions of the resulting ordinary differential equations. Thus, we arrive at the following three problems:

Case A

$$\theta \partial_t v = \delta_0$$

Case B

$$\theta_1 \partial_t v + \theta_0 \partial_t w = \delta_0, \qquad \partial_t w = \alpha(v - w)$$

Case C

$$\theta_1 \partial_t v + \theta_0 \partial_t w = \delta_0, \qquad \partial_t w = -\left(\frac{d}{dt}\rho\right) * \partial_t v.$$

FIGURE 2.1.

FIGURE 2.2.

Here, δ_0 is the Dirac's delta-function supported at $t = 0$.

The following result is easy to establish.

Case A. The fundamental solution is

$$v(t) = \frac{1}{\theta} \quad \text{for } t > 0.$$

The Fourier-transform is

$$\hat{v}(\tau) = \frac{1}{i\tau\theta}.$$

Case B. The fundamental solution is

$$v(t) = \frac{1}{\theta_1}\left(1 - \frac{\theta_0}{\theta_0 + \theta_1}\left(1 - \exp\left(\frac{\theta_0 + \theta_1}{\theta_1}\alpha t\right)\right)\right).$$

The Fourier-transform is

$$\hat{v}(\tau) = \frac{1}{i\tau\left(\theta_1 + \frac{\alpha}{\alpha + i\tau}\theta_0\right)}.$$

Case C. The Fourier-transform of the fundamental solution is

$$v(\tau) = \frac{1}{i\tau(\theta_1 - i\tau\theta_0\hat{\rho}(\tau))}$$

where

$$\hat{\rho}(\tau) = \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2(k^2\pi^2\alpha + i\tau)}$$

is the Fourier-transform of the auxiliary function ρ.

Figure 3.1 shows the fundamental solutions in the cases B and C as functions of time t. The latter was calculated numerically using a scheme based on the trapezoidal rule, see section 4 for details. Figure 3.2 shows the factors

$$\frac{1}{\theta_1 + \frac{\alpha}{\alpha + i\tau}\theta_0} \quad \text{and} \quad \frac{1}{\theta_1 - i\tau\theta_0\hat{\rho}(\tau)}$$

as orbits in the complex plane. For figures 3.1 and 3.2, the values $\theta_1 = 0.4$, $\theta_0 = 0.2$, were chosen and the same factors α as in section 2.

4. Break-through curves. We have performed numerical calculations that give approximate solutions for the three models. The basic idea was to use methods that generalize the Crank-Nicholson scheme.

For Model A Crank-Nicholson's method can be described as follows. If the differential equation is of the form

$$\partial_t v = Av + b$$

and a step-size $h > 0$ is chosen, one defines

$$t_j = j \cdot h, \qquad j = 0, 1, 2, \ldots$$

and uses v_j, v'_j as approximations for

$$v(t_j) \quad \text{and} \quad \partial_t v(t_j), \text{ resp.}$$

Combining the two equations

$$v_{j+1} = v_j + \frac{h}{2}(v'_j + v'_{j+1})$$

and

$$v'_{j+1} = Av_{j+1} + b$$

one obtains

$$\left(1 - \frac{h}{2}A\right) v'_{j+1} = A\left(v_j + \frac{h}{2}v'_j\right) + b.$$

In order to apply this procedure to Model B, we write the differential equations in the form

$$\theta_1 \partial_t v + \theta_0 \partial_t w = Av + b, \qquad \partial_t w = \alpha(v - w).$$

Using similar notations we get

$$v_{j+1} = v_j + \frac{h}{2}(v'_j + v'_{j+1}), \qquad w_{j+1} = w_j + \frac{h}{2}(w'_j + w'_{j+1})$$

FIGURE 3.1.

FIGURE 3.2.

and

$$\theta_1 v'_{j+1} + \theta_0 w'_{j+1} = Av_{j+1} + b, \qquad w'_{j+1} = \alpha(v_{j+1} - w_{j+1}).$$

From these equations one deduces immediately

$$\left(\theta_1 + \frac{h}{2}(\lambda - A)\right) v'_{j+1} = \lambda\left(w_j + \frac{h}{2}w'_j\right) - (\lambda - A)\left(v_j + \frac{h}{2}v'_j\right) + b$$

and

$$\left(1 + \frac{h}{2}\alpha\right) w'_{j+1} = \alpha\left(v_{j+1} - w_j - \frac{h}{2}w'_j\right)$$

with

$$\lambda = \frac{\theta_0\alpha}{(1 + \frac{h}{2}\alpha)}.$$

The derivation of a numerical scheme for Model C starts from the equation

$$\theta_1 \partial_t v(t) - \theta_0 \int_0^t \frac{d}{dt}\rho(t-s)\partial_t v(s)\, ds = Av(t) + b.$$

Integration by parts gives

$$\theta_1 \partial_t v(t) - \theta_0 \int_0^t \rho(t-s)\partial_{tt} v(s)\, ds + \theta_0\rho(0)\partial_t v(t) - \theta_0\rho(t)\partial_t v(0) = Av(t) + b.$$

At $t + h$ instead of t this reads

$$\theta_1 \partial_t v(t+h) - \theta_0 \int_0^{t+h} \rho(t+h-s)\partial_{tt} v(s)\, ds + \theta_0\partial_t v(t+h) - \theta_0\rho(t+h)\partial_t v(0) = Av(t+h) + b,$$

where we have used $\rho(0) = 1$. The same discretization as before gives

$$\begin{aligned}\theta_1 v'_{j+1} &- \theta_0 \sum_{i=1}^{j} \frac{v'_i - v'_{i-1}}{h} \int_{t_{i-1}}^{t_i} \rho(t_{j+1} - s)\, ds \\ &- \theta_0 \frac{v'_{j+1} - v'_j}{h} \int_{t_j}^{t_{j+1}} \rho(t_{j+1} - s)\, ds \\ &+ \theta_0 v'_{j+1} - \theta_0\rho_{j+1} v'_0 = Av_{j+1} + b.\end{aligned}$$

Using

$$\int_{t_{i-1}}^{t_i} \rho(t_{j+1} - s)\, ds = \int_{t_{j-i-1}}^{t_{j-i+2}} \rho(s)\, ds,$$

$$v_{j+1} = v_j + \frac{h}{2}(v'_j + v'_{j+1}),$$

and rearranging terms one obtains the formula

$$\begin{aligned}
&\left(\theta_1 + \theta_0 - \frac{\theta_0}{h}\int_{t_0}^{t_1} \rho(s)\, ds - \frac{h}{2}A\right) v'_{j+1} \\
&\quad = A\left(v_j + \frac{h}{2}v'_j\right) \\
&\qquad + \left((1 - \delta_{0j})\frac{\theta_0}{h}\int_{t_1}^{t_2} \rho(s)\, ds - \frac{\theta_0}{h}\int_{t_0}^{t_1} \rho(s)\, ds\right) v'_j \\
&\qquad - \frac{\theta_0}{h}\sum_{i=1}^{j-1}\left(\int_{t_{j-1}}^{t_{j-i+1}} \rho(s)\, ds - \int_{t_{j-i+1}}^{t_{j-i+2}} \rho(s)\, ds\right) v'_i \\
&\qquad + \left(\theta_0\rho_{j+1} - (1 - \delta_{0j})\frac{\theta_0}{h}\int_{t_j}^{t_{j+1}} \rho(s)\, ds\right) v'_0 + b.
\end{aligned}$$

Here δ_{0j} is 1 if $j = 0$ and 0 else. Since a constant step-size h is used, the quantities involving ρ and the integrals thereof can be calculated once and for all. The discretization of time described so far has to be combined with a spatial discretization of the differential operator

$$D\Delta v - \vec{u} \cdot \nabla v.$$

On a $1 - D$ interval $\Omega = [0, L]$ with constant flow rate u and boundary conditions

$$-D\partial_x v + uv = f(t) \quad \text{at } x = 0, \qquad v = 0 \quad \text{at } x = L$$

we have used the standard finite difference approximation as follows: Let $\Delta x = L/(n + \frac{1}{2})$ and $x_i = \left(i + \frac{1}{2}\right)\Delta x$ for $i = 0, \ldots, n$. Then one defines

$$\begin{aligned}
(Av + b)(x_i) = &\frac{D}{(\Delta x)^2}(v(x_{i+1}) - 2v(x_i) + v(x_{i-1})) \\
&- \frac{u}{2\Delta x}(v(x_{i+1}) - v(x_{i-1})) \quad \text{for } i = 1, \ldots, n
\end{aligned}$$

and

$$(Av+b)(x_0) = \left(\frac{D}{(\Delta x)^2} - \frac{u}{2\Delta x}\right) v(x_1) - \left(\frac{D}{(\Delta x)^2} + \frac{u}{2\Delta x}\right) v(x_0) + \frac{1}{\Delta x} f(t).$$

Figure 4.1 shows the numerical approximations of the concentration v at an interior point $x = x^*$ as a function of time for the models B and C. The initial conditions were

$$v = 0 \quad \text{and} \quad w = 0 \quad \text{for } t = 0.$$

The exchange coefficients α were the same as in Section 2 and the values of the parameters (after making the equations dimensionless) were chosen to be

$$L = 10,\ n = 20,\ \theta_1 = 0.4,\ \theta_0 = 0.2,\ D = 0.1,\ u = 0.5,\ \text{and } h = 0.1.$$

The injection rate at $x = 0$ was

$$f(t) = \begin{cases} 1, & t < 2 \\ 0, & t > 2. \end{cases}$$

Figure 4.2 shows the values of w versus those of v.

5. Justification of Model C. In this paragraph we discuss the asymptotic expansion for a micro-model describing diffusion and convection of a solute under the influence of mobile and immobile water. The basic reference of the technique used is [**4**].

FIGURE 4.1.

FIGURE 4.2.

Geometry of the Micro-Model.

$\vec{e}_j = j$-th unit vector in $\mathbf{R}^3$

$Z = \left\{ \sum_{j=1}^{3} \lambda_j \vec{e}_j : 0 \le \lambda_j \le 1 \right\} =$ unit cell in $\mathbf{R}^3$

$X^m = m_j \vec{e}_j + X$ for $m = (m_1, m_2, m_3)$ and $X \subset Z$

$Y_0 (\subset\subset Z) =$ representative fraction of immobile water

$Y_1 = Z \backslash Y_0 =$ representative fraction of mobile water

$\Gamma = \partial Y_0 =$ representative interface

$\nu =$ inner normal on Γ with respect to Y_0

$\varepsilon (> 0)[m] =$ scale parameter

$\Omega =$ bounded domain in $\mathbf{R}^3 =$ porous medium

$\Omega_1^\varepsilon = \Omega \cap \bigcup \left\{ \varepsilon Y_1^m : m \in \mathbf{R}^3 \right\} =$ fraction of mobile water

$\Omega_0^\varepsilon = \Omega \cap \bigcup \left\{ \varepsilon Y_0^m : m \in \mathbf{R}^3 \right\} =$ fraction of immobile water

$\Gamma^\varepsilon + \Omega \cap \bigcup \left\{ \varepsilon \Gamma^m : m \in \mathbf{R}^3 \right\} =$ interface

$\nu^\varepsilon =$ inner normal on Γ^ε with respect to Ω_0^ε.

Variables of the Micro-Model.

$\vec{u}^\varepsilon : \overline{\Omega_1^\varepsilon} \to \mathbf{R}^3 [m s^{-1}] =$ Darcy's velocity of the mobile water

$p^\varepsilon : \Omega_1^\varepsilon \to \mathbf{R}[m] =$ pressure head of the mobile water

$v^\varepsilon : [0, T] \times \overline{\Omega}_1^\varepsilon \to \mathbf{R}[kg m^{-3}] =$ concentration of the solute in the mobile water

$w^\varepsilon : [0, T] \times \overline{\Omega}_0^\varepsilon \to \mathbf{R}[kg m^{-3}] =$ concentration of the solute in the immobile water

Coefficients of the Micro-Model.

$k[m^2 s^{-1}] =$ hydraulic conductivity in the mobile fraction

$\theta_1 [m^3 m^{-3}] =$ relative water content in the mobile fraction

$\theta_0 [m^3 m^{-3}] =$ relative water content in the immobile fraction

$d[m^2 s^{-1}] =$ diffusivity of the solute in the mobile fraction

$\varepsilon^2 \alpha [m^2 s^{-1}] =$ diffusivity of the solute in the immobile fraction

The Micro-Model.

$$\vec{u}^{\varepsilon}(x) = -k\nabla p(x), \qquad x \in \Omega_1^{\varepsilon} \tag{5.1}$$

$$\nabla \cdot \vec{u}^{\varepsilon}(x) = 0, \qquad x \in \Omega_1^{\varepsilon} \tag{5.2}$$

$$\nu^{\varepsilon} \cdot \vec{u}^{\varepsilon}(x) = 0, \qquad x \in \Gamma^{\varepsilon} \tag{5.3}$$

$$\theta_1 \partial_t v^{\varepsilon}(t,x) = d\Delta v^{\varepsilon}(t,x) - \vec{u}^{\varepsilon} \cdot \nabla v^{\varepsilon}(t,x), \quad t > 0, x \in \Omega_1^{\varepsilon} \tag{5.4}$$

$$w^{\varepsilon}(t,x) = v^{\varepsilon}(t,x), \qquad t > 0, x \in \Gamma^{\varepsilon} \tag{5.5}$$

$$\varepsilon^2 \alpha \nu^{\varepsilon} \cdot \nabla w^{\varepsilon}(t,x) = d\nu^{\varepsilon} \cdot \nabla v^{\varepsilon}(t,x), \qquad t > 0, x \in \Gamma^{\varepsilon} \tag{5.6}$$

$$\theta_0 \partial_t w^{\varepsilon}(t,x) = \varepsilon^2 \alpha \Delta w^{\varepsilon}(t,x), \qquad t > 0, x \in \Omega_0^{\varepsilon}. \tag{5.7}$$

Variables of the Macro-Model.

$\vec{u} : \overline{\Omega} \to \mathbf{R}^3[ms^{-1}] =$ Darcy's velocity of the mobile water

$p : \Omega \to \mathbf{R}[m] =$ pressure head of the mobile water

$v : [0,T] \times \overline{\Omega} \to \mathbf{R}[kgm^{-3}] =$ concentration of the solute in the mobile water

$w : [0,T] \times \Omega \to \mathbf{R}[kgm^{-3}] =$ concentration of the solute in the immobile water

Auxiliary functions and constants of the macro-model.

$\sigma_j : \mathbf{R}^n \to \mathbf{R}$ $(j = 1, \ldots, n)$ is a Z-periodic solution of the cell problem

$$\begin{cases} \Delta_y \sigma_j(y) = 0, & y \in Y_1 \\ \nu \cdot \nabla_y \sigma_j(y) = -\nu \cdot \vec{e}_j, & y \in \Gamma. \end{cases}$$

The tensor S has the coefficients

$$s_{ij} = |Y_1|\delta_{ij} + \int_{Y_1} \partial_i \sigma_j(y)\, dy.$$

The tensors K and D are defined by

$$K = kS, \qquad D = dS.$$

$r : [0,\infty) \times \overline{Y}_0 \to \mathbf{R}$ is the solution of the cell problem

$$\begin{cases} \theta_0 \partial_t r(t,y) = \alpha \Delta_y r(t,y), & t > 0, y \in Y_0 \\ r(t,y) = 0, & t > 0, y \in \Gamma \\ r(t,y) = 1, & t = 0, y \in Y_0. \end{cases}$$

$\rho : [0,\infty) \to \mathbf{R}$ is the average

$$\rho(t) = \fint_{Y_0} r(t,y)\, dy = \frac{1}{|Y_0|} \int_{Y_0} r(t,y)\, dy.$$

The constants Θ_1, Θ_0 are

$$\Theta_1 = |Y_1|\theta_1, \qquad \Theta_0 = |Y_0|\theta_0.$$

Remark. It is easily seen that the tensor S, and thus also K and D, are symmetric and positive definite. If Y_0 is a ball, centered at the origin with radius R, the function r is known to be

$$r(t,y) = \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k} e^{-k^2\pi^2\alpha t} \sin\left(k\pi \frac{|y|}{R}\right),$$

and therefore ρ is the same as the function given in Section 2.

The Macro-Model

(5.8)
$$\vec{u}(x) = -K\nabla p(x), \qquad x \in \Omega$$

(5.9)
$$\nabla \cdot \vec{u}(x) = 0, \qquad x \in \Omega$$

(5.10)
$$\Theta_1 \partial_t v(t,x) + \Theta_0 \partial_t w(t,x) = \nabla(D\nabla v(t,x)) - \vec{u}(x) \cdot \nabla v(t,x), \qquad t > 0, x \in \Omega$$

(5.11)
$$\partial_t w(t,x) = -\left(\frac{d}{dt} \rho * \partial_t v(\cdot,x)\right)(t), \qquad t > 0, x \in \Omega.$$

If appropriate boundary and initial conditions are specified one can show the following result.

Theorem. *$p^\varepsilon \to p$ in $L^2(\Omega)$ and $v^\varepsilon \to v$ in $L^2(0,T,L^2(\Omega))$ strongly.*

We don't give the exact mathematical proof here; instead, we show how the macro-model can be derived formally from the micro-model. The rigorous proof will be published elsewhere.

The starting point of the formal asymptotics is the assumption that the variables of the micro-model can be represented as

$$\begin{aligned}
p^\varepsilon(x) &= p^0(x,y) + \varepsilon p^1(x,y) + \varepsilon^2 p^2(x,y) + \dots \\
\vec{u}^\varepsilon(x) &= \vec{u}^0(x,y) + \varepsilon \vec{u}^1(x,y) + \varepsilon^2 \vec{u}^2(x,y) + \dots \\
v^\varepsilon(t,x) &= v^0(t,x,y) + \varepsilon v^1(t,x,y) + \varepsilon^2 v^2(t,x,y) + \dots \\
w^\varepsilon(t,x) &= w^0(t,x,y) + \varepsilon w^1(t,x,y) + \varepsilon^2 w^2(t,x,y) + \dots
\end{aligned}$$

where the functions $p^i(x,y)$, $\vec{u}^i(x,y)$, $v^i(t,x,y)$, and $w^i(t,x,y)$ are Z-periodic with respect to the variable $y = \frac{x}{\varepsilon}$. Then one applies the rules

$$\nabla = \frac{1}{\varepsilon}\nabla_y + \nabla_x, \qquad \Delta = \frac{1}{\varepsilon^2}\Delta_y + \frac{2}{\varepsilon}\nabla_y \cdot \nabla_x + \Delta_x.$$

For simplicity of notation we drop the variable t. After plugging (5.1) into (5.2) we have

$$\Delta p^\varepsilon(x) = 0, \qquad x \in \Omega_1^\varepsilon. \tag{5.12}$$

From this we get

$$\begin{aligned}
\varepsilon^{-2}\Delta_y p^0(x,y) + \varepsilon^{-1}(\Delta_y p^1(x,y) + 2\nabla_y \cdot \nabla_x p^0(x,y)) \\
+ \varepsilon^0(\nabla_y \cdot (\nabla_y p^2(x,y) + \nabla_x p^1(x,y)) \\
+ \nabla_x \cdot (\nabla_y p^1(x,y) + \nabla_x p^0(x,y)) + \varepsilon^1 \cdots = 0, \qquad y \in Y_1.
\end{aligned} \tag{5.13}$$

After combining (5.1) and (5.3) we have

$$\nu^\varepsilon \cdot \nabla p^\varepsilon(x,y) = 0. \tag{5.14}$$

Thus we get

$$\begin{aligned}
\varepsilon^{-1}\nu \cdot \nabla_y p^0(x,y) + \varepsilon^0 \nu \cdot (\nabla_y p^1(x,y) + \nabla_x p^0(x,y)) \\
+ \varepsilon^1 \nu \cdot (\nabla_y p^2(x,y) + \nabla_x p^1(x,y)) + \varepsilon^2 \cdots = 0, \qquad y \in \Gamma.
\end{aligned} \tag{5.15}$$

Looking at (5.1) separately, we have

(5.16)
$$\varepsilon^{-1}k\nabla_y p^0(x,y)+\varepsilon^0(\vec{u}^0(x,y)+k(\nabla_y p^1(x,y)+\nabla_x p^0(x,y))+\varepsilon^1\ldots=0, \qquad y\in Y_1.$$

Equation (5.4) implies

(5.17)
$$\begin{aligned}&-\varepsilon^{-2}d\Delta_y v^0(x,y)\\ &-\varepsilon^{-1}(d\Delta_y v^1(x,y)\\ &+2d\nabla_y\cdot\nabla_x v^0(x,y)-\vec{u}^0(x,y)\cdot\nabla_y v^0(x,y))\\ &+\varepsilon^0(\theta_1\partial_t v^0(x,y)-d\nabla_y\cdot(\nabla_y v^2(x,y)+\nabla_x v^1(x,y))\\ &\qquad -d\nabla_x\cdot(\nabla_y v^1(x,y)+\nabla_x v^0(x,y))\\ &+\vec{u}^1(x,y)\cdot\nabla_y v^0(x,y)+\vec{u}^0(x,y)\cdot\nabla_x v^0(x,y))+\varepsilon^1\cdots=0, \qquad y\in Y_1.\end{aligned}$$

Next from (5.5) we get

$$\varepsilon^0(w^0(x,y)-v^0(x,y))+\varepsilon^1\cdots=0, \qquad y\in\Gamma. \tag{5.18}$$

Equation (5.6) implies

$$\begin{aligned}&\varepsilon^{-1}d\nu\cdot\nabla_y v^0(x,y)+\varepsilon^0\,d\nu\cdot(\nabla_y v^1(x,y)+\nabla_x v^0(x,y))\\ &\qquad+\varepsilon^1(d\nu\cdot(\nabla_y v^2(x,y)+\nabla_x v^1(x,y))-\alpha\nu\cdot\nabla_y w^0(x,y))\\ &\qquad+\varepsilon^2\cdots=0, \qquad y\in\Gamma.\end{aligned} \tag{5.19}$$

And finally, we get from (5.7)

$$\varepsilon^0(\theta_0\partial_t w^0(x,y)-\alpha\Delta_y w^0(x,y))+\varepsilon^1\cdots=0, \qquad y\in Y_0. \tag{5.20}$$

The next step is to compare coefficients. The powers ε^{-2} in (5.13) and ε^{-1} in (5.15) give

$$\begin{cases}\Delta_y p^0(x,y)=0, & y\in Y_1\\ \nu\cdot\nabla_y p^0(x,y)=0, & y\in\Gamma.\end{cases}$$

Therefore, we have

$$p^0(x,y)=p(x) \tag{5.21}$$

independently of y.

The powers ε^{-1} in (5.13) and ε^0 in (5.15) yield

$$\begin{cases} \Delta_y p^1(x,y) = 0, & y \in Y_1 \\ \nu \cdot \nabla_y p^1(x,y) = -\nu \cdot \nabla_x p(x), & y \in \Gamma. \end{cases}$$

One writes

$$\nabla_x p^0(x) = \sum_{j=1}^{n} \vec{e}_j \partial_j p(x)$$

and uses the functions σ_j defined earlier. Then p^1 can be written as

$$p^1(x,y) = \sum_{j=1}^{n} \sigma_j(y) \partial_i p(x) + p^1(x),$$

where $p^1(x)$ is independent of y. Looking at the ε^0-power in (5.16), we see that

$$\vec{u}^0(x,y) = -k(\nabla_y p^1(x,y) + \nabla_x p(x)), \tag{5.22}$$

and thus the i-th component is given by

$$u_i^0(x,y) = -k \sum_{j=1}^{n} (\partial_i \sigma_j(y) + \delta_{ij}) \partial_j p(x).$$

Therefore, the integral

$$u_i(x) = \int_{Y_1} u_i^0(x,y)\, dy$$

satisfies

$$u_i(x) = -k \sum_{j=1}^{n} \left(\int_{Y_1} \partial_i \sigma_j(y)\, dy + |Y_1| \delta_{ij} \right) \partial_j p(x),$$

i.e.,

$$u_i(x) = -k \sum_{j=1}^{n} s_{ij} \partial_j p(x).$$

Hence, for short, the vector $\vec{u}(x) = (u_1(x), \ldots, u_n(x))$ is given by

$$\vec{u} = -K\nabla p,$$

which is exactly formula (5.8). The ε^0-power in (5.13) and the ε^1-power in (5.15) give

$$\begin{cases} \nabla_y \cdot (\nabla_y p^2(x,y) + \nabla_x p^1(x,y)) + \nabla_x \cdot (\nabla_y p^1(x,y) + \nabla_x p(x)) = 0, \\ \qquad\qquad y \in Y_1 \\ \nu \cdot (\nabla_y p^2(x,y) + \nabla_x p^1(x,y)) = 0, \\ \qquad\qquad y \in \Gamma. \end{cases}$$

We integrate the first of these equations over Y_1 and obtain by the divergence theorem

$$\int_\Gamma \nu \cdot (\nabla_y p^2(x,y) + \nabla_x p^1(x,y))\, d\Gamma(y) + \int_{Y_1} \nabla_x \cdot (\nabla_y p^1(x,y) + \nabla_x p(x))\, dy = 0.$$

The first term vanishes and using (5.22) we get from this

$$\nabla_x \cdot \vec{u}(x) = \nabla_x \cdot \int_{Y_1} \vec{u}^0(x,y)\, dy = 0,$$

i.e., we arrive at (5.9). Next, we look at the ε^{-2}-power in (5.17) and the ε^{-1}-power in (5.19) and obtain

$$\begin{cases} \Delta_y v^0(x,y) = 0, & y \in Y_1 \\ \nu \cdot \nabla_y v^0(x,y) = 0, & y \in \Gamma. \end{cases}$$

This implies

$$v^0(x,y) = v(x) \tag{5.23}$$

independently of y. The ε^{-1}-power in (5.17) and the ε^0-power in (5.19) yield

$$\begin{cases} \Delta_y v^1(x,y) = 0, & y \in Y_1 \\ \nu \cdot \nabla_y v^1(x,y) = -\nu \cdot \nabla_x v(x), & y \in \Gamma. \end{cases}$$

In the same way as for p^1 one obtains

$$v^1(x,y) = \sum_{j=1}^{n} \sigma_j(y)\partial_j v(x) + v^1(x), \tag{5.24}$$

where $v^1(x)$ is independent of y. Now we use the ε^0-power in (5.17) and the ε^1-power in (5.19) and get the equations

$$\begin{cases} \theta_1 \partial_t v(x) = d\nabla_y \cdot (\nabla_y v^2(x,y) + \nabla_x v^1(x,y)) \\ \qquad +d\nabla_x \cdot (\nabla_y v^1(x,y) + \nabla_x v(x)) - \vec{u}^0(x,y) \cdot \nabla_x v(x), & y \in Y_1 \\ d\nu \cdot (\nabla_y v^2(x,y) + \nabla_x v^1(x,y)) = \alpha\nu \cdot \nabla_y w^0(x,y), & y \in \Gamma. \end{cases}$$

We integrate the first equation over Y_1 and obtain

$$\begin{aligned} \Theta_1 \partial_t v(x) = d \int_\Gamma \nu \cdot (\nabla_y v^2(x,y) + \nabla_x v^1(x,y))\, d\Gamma(y) \\ + d \int_{Y_1} \nabla_x \cdot (\nabla_y v^1(x,y) + \nabla_x v(x))\, dy - \vec{u}(x) \cdot \nabla v(x). \end{aligned}$$

The first term on the right-hand side is

$$\alpha \int_\Gamma \nu \cdot \nabla_y w^0(x,y)\, dy = -|Y_0| \fint_{Y_0} \alpha \Delta_y w^0(x,y)\, dy.$$

The second term is, by using (5.24),

$$\begin{aligned} d \int_{Y_1} \sum_{i=1}^{n} \partial_{x_i} \left(\sum_{j=1}^{n} \partial_{y_i} \sigma_j(y) + \delta_{ij} \right) \partial_{x_j} v(x)\, dy \\ = d \sum_{i,j=1}^{n} \left(\int_{Y_1} \partial_i \sigma_j(y)\, dy + \delta_{ij} \right) \partial_{ij} v(x) \\ = d \sum_{i,j=1}^{n} s_{ij} \partial_{ij} v(x). \end{aligned}$$

Thus, we get

$$\Theta_1 \partial_t v(x) + |Y_0| \fint_{Y_0} \alpha \Delta_y w^0(x,y)\, dy = \nabla \cdot (D \nabla v(x)) - \vec{u}(x) \cdot \nabla v(x). \tag{5.25}$$

The next step is to use the ε^0-power in (5.20) and the ε^0-power in (5.18); we get

$$\begin{cases} \theta_0 \partial_t w^0(x,y) = \alpha \Delta_y w^0(x,y), & y \in Y_0 \\ w^0(x,y) = v(x), & y \in \Gamma. \end{cases} \tag{5.26}$$

Therefore, the average

$$w(x) = \fint_{Y_0} w^0(x,y)\, dy$$

satisfies

$$|Y_0| \fint_{Y_0} \alpha \Delta_y w^0(x,y)\, dy = \Theta_0 \partial_t w(x),$$

and (5.25) becomes now

$$\Theta_1 \partial_t v(x) + \Theta_0 \partial_t w(x) = \nabla \cdot (D \nabla v(x)) - \vec{u}(x) \cdot \nabla v(x),$$

which is (5.10). The final step is to express the solution w^0 of (5.26) in terms of v. If we define (now writing t again for clarification)

$$\tilde{w}(t,x,y) = v(t,x) - \int_0^t r(t-s,y) \partial_t v(s,x)\, ds,$$

then we get

$$\begin{aligned} \theta_0 \partial_t \tilde{w}(t,x,y) &= \theta_0 \partial_t v(t,x) - \theta_0 r(0,y) \partial_t v(t,x) \\ &\quad - \int_0^t \theta_0 \partial_t r(t-s,y) \partial_t v(s,x)\, ds \\ &= - \int_0^t \alpha \Delta_y r(t-s,y) \partial_t v(s,x)\, ds = \alpha \Delta_y \tilde{w}(t,x,y), \qquad y \in Y_0; \end{aligned}$$

in addition we see that

$$\tilde{w}(t,x,y) = v(t,x) \quad \text{for } y \in \Gamma.$$

Therefore, we have $w^0(t,x,y) = \tilde{w}(t,x,y)$ and we conclude

$$w(t,x) = v(t,x) - \int_0^t \rho(t-s) \partial_t v(s,x)\, ds$$

and, thus,

$$\partial_t w(t,x) = -\int_0^t \frac{d}{dt}\rho(t-s)\partial_t v(s,x)\,ds,$$

which is just (5.11). This concludes the justification of model C.

It should be emphasized that the model we have developed in this paragraph is more general than that presented in Section 2.

6. Conclusion. The material presented in the preceding paragraphs suggests the following conclusions:

- Both Models B and C contain Model A as a special case, namely by setting $\Theta_1 = \Theta$ and $\Theta_0 = 0$.
- Model B is simpler than Model C, theoretically and numerically.
- Model C has a sound basis in that it can be deduced by homogenization from a reasonable micro-model. It is the macro-model obtained as a certain limit.
- Very roughly speaking, Models B and C have comparable properties. But a careful analysis of the kinetics reveals qualitative differences. Both the fundamental solutions of ODE problems (see Section 3) and the breakthrough curves for PDE problems (see Section 4) show different behavior.
- The difference mentioned is not dramatic; but it is significant enough to be checked by laboratory measurements. Model C gives smoother breakthrough curves than Model B.

Acknowledgment. The author is grateful for the stimulus given by W. Jäger/Heidelberg, who has pointed out the relevance of homogenization. Useful hints were given by M. Freier/Munich, M. Hauhs/Göttingen, Z. Jackiewicz/Tempe and R. Schulin/Zurich.

REFERENCES

1. T. Arbogast, J. Douglas and U. Hornung, *Derivation of the double porosity model of single phase flow via homogenization theory*, SIAM J. Math. Anal. **21** (1990), 823–836.

2. J. Bear, *Dynamics of Fluids in Porous Media*, American Elsevier, New York, 1972.

3. ———, Y. Bachmat, *On the equivalence of areal and volumetric averages in transport phenomena in porous media,* Adv. Wat. Res. **6** (1983), 59–62.

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

5. M. Th. van Genuchten and P.J. Wierenga, *Mass transfer studies in sorbing porous media I. Analytical solutions,* Soil Sci. Soc. Amer. J. **40** (1976), 473–480.

6. U. Hornung, W. Jäger, *A model for chemical reactions in porous media*, J. Warnatz, W. Jäger (eds.), Complex Chemical Reaction Sysstems. Mathematical Modeling and Simulation, Chemical Physics **47**, Springer, Berlin (1987), 318–334.

7. ———, R. Showalter, *Diffusion models for fractured media*, J. Math. Anal. Appl. **147** (1990), 69 –80.

8. R. Schulin, A. Papritz, H. Flühler and H.M. Selim, *Ionentransport in Böden mit und ohne Aggregatstruktur: ein Modell-Vergleich*, Mitteilgn. Dtsch. Bodenkdl. Ges. **53** (1987), 473–478.

9. Ch. Vogt, *A Homogenization Theorem Leading to a Volterra Integro-Differential Equation for Permeation Chromatography*, Preprint #155, SFB 123, Heidelberg, 1982.

SCHI, P.O. Box 1222, W-8014 Neubiberg, Republic of Germany