DISPERSION IN POROUS MEDIA FOR MULTICOMPONENT SYSTEMS

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Introduction

In this paper we consider multicomponent mass transport in porous media for non-dilute solutions, i.e., with full diffusion matrices. This process is described by coupled, nonlinear transport equations that must be spatially smoothed in order to be useful. This spatial smoothing is achieved by the method of volume averaging for the case of negligible adsorption, desorption, and heterogeneous reaction [1]. For pure diffusion, the results demonstrate that a single tortuosity tensor applies to the transport of all species, as heuristically done in the literature [2,3, …]. When convective transport is important, the process becomes much more complex. A generalized dispersion theory is proposed. The results show that the simplifications used in the literature may be introduced in the linear dispersion case only.

We provide below a summary of the findings.

Theory

One starts with the pore-scale multicomponent mass balance equations given by

$$\frac{\partial(\rho_\gamma \omega_{A\gamma})}{\partial t} + \nabla \cdot \left(\rho_\gamma \omega_{A\gamma} \mathbf{v}_\gamma \right) = \nabla \cdot \left[\sum_{E=1}^{E=N-1} \rho_\gamma D_{AE} \nabla \omega_{E\gamma} \right], \quad A = 1,2,..,N-1$$

$$\frac{\partial \rho_\gamma}{\partial t} + \nabla \cdot \left(\rho_\gamma \mathbf{v}_\gamma \right) = 0$$

with the following boundary conditions at the liquid-solid interface

$$\text{BC.} \quad \mathbf{n}_{\gamma\kappa} \cdot \left(\rho_\gamma \mathbf{v}_\gamma \right) = 0, \quad \text{at the } \gamma - \kappa \text{ interface}$$

$$\text{BC.} \quad \mathbf{n}_{\gamma\kappa} \cdot \sum_{E=1}^{E=N-1} \rho_\gamma D_{AE} \nabla \omega_{E\gamma} = 0, \quad A = 1,2,..,N-1, \quad \text{at the } \gamma - \kappa \text{ interface}$$

Using the method of volume averaging we obtain the following equation for species A

$$\frac{\partial\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\langle\omega_{A\gamma}\rangle^\gamma\right)}{\partial t} \; + \; \nabla\cdot\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\langle\omega_{A\gamma}\rangle^\gamma\langle\mathbf{v}_\gamma\rangle^\gamma\right) \; + \; \nabla\cdot\left(\langle\rho_\gamma\rangle^\gamma\underbrace{\langle\tilde{\omega}_{A\gamma}\tilde{\mathbf{v}}_\gamma\rangle}_{filter}\right)$$

$$= \; \nabla\cdot\left[\sum_{E=1}^{E=N-1}\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\langle D_{AE}\rangle^\gamma\nabla\langle\omega_{E\gamma}\rangle^\gamma \; + \; \underbrace{\frac{\langle\rho_\gamma\rangle^\gamma\langle D_{AE}\rangle^\gamma}{V}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\tilde{\omega}_{A\gamma}\,dA}_{filter}\right], \quad A = 1,2,..,N-1$$

where the tildas refer to deviation to the intrinsic averaged values (noted with brackets).

In order to obtain a closed form of the above equation, i.e., an equation without the deviation terms, we need to obtain a representation for the deviations.
This is obtained by using the following algorithm (the development is rather lengthy, and details can be found in [1]):

1. replace concentrations by averaged values and deviations in the pore-scale equations
2. simplify the system of coupled equations (averaged and pore-scale) using the assumption of separation of scale, we obtain

$$\tilde{\mathbf{v}}_\gamma\cdot\nabla\langle\omega_{A\gamma}\rangle^\gamma \; + \; \mathbf{v}_\gamma\cdot\nabla\tilde{\omega}_{A\gamma} \; = \; \nabla\cdot\left[\sum_{E=1}^{E=N-1}\langle D_{AE}\rangle^\gamma\nabla\tilde{\omega}_{A\gamma}\right], \quad A = 1,2,..,N-1$$

$$\mathbf{n}_{\gamma\kappa}\cdot\sum_{E=1}^{E=N-1}\langle\rho_\gamma\rangle^\gamma\langle D_{AE}\rangle^\gamma\,\nabla\tilde{\omega}_{E\gamma} \; = \; -\,\mathbf{n}_{\gamma\kappa}\cdot\sum_{E=1}^{E=N-1}\langle\rho_\gamma\rangle^\gamma\langle D_{AE}\rangle^\gamma\,\nabla\langle\omega_{E\gamma}\rangle^\gamma,$$

BC.
$$A \; = \; 1,2,..,N-1, \quad \text{at the } \gamma-\kappa \text{ interface}$$

3. This set of equations, called the closure problem, may be solved conveniently in the *pseudo-composition space* obtained by transforming the system with the help of the nodal matrix $[P]^{-1}$ (see [4, ,…]), i.e.

$$[\tilde{w}_\gamma] \; = \; [P]^{-1}[\tilde{\omega}_\gamma]$$

4. In the pseudo-composition space, we obtain the following mapping (in matrix form)

$$[\tilde{w}_\gamma] \; = \; [\mathbf{b}]\cdot[\nabla\langle w_\gamma\rangle^\gamma]$$

where the components of [**b**] obey *classical* dispersion closure problems for the diagonal diffusion coefficients.

5. Returning back to the normal components, we obtain a set of generalized dispersion equations such as

$$\frac{\partial\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma[\langle\omega_\gamma\rangle^\gamma]\right)}{\partial t} + \nabla\cdot\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma\langle\mathbf{v}_\gamma\rangle^\gamma[\langle\omega_\gamma\rangle^\gamma]\right)$$

$$= \nabla\cdot\left\{\langle\rho_\gamma\rangle^\gamma\left(\varepsilon_\gamma[\mathbf{D}_{eff}]+\varepsilon_\gamma[\mathbf{D}_\gamma]\right)\cdot[\nabla\langle\omega_\gamma\rangle^\gamma]\right\}$$

with

$$[\mathbf{D}_{eff}] = [\langle D\rangle^\gamma]\left\{[\mathbf{I}] + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}[P]\ [\mathbf{b}]\ [P]^{-1}\ dA\right\}$$

$$[\mathbf{D}_\gamma] = -\left\langle\tilde{\mathbf{v}}_\gamma[P]\ [\mathbf{b}]\ [P]^{-1}\right\rangle^\gamma$$

Theoretical implications

The closure problems may be solved in different cases.
In the case of *pure diffusion*, we obtain the following macroscopic equations

$$\frac{\partial\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma[\langle\omega_\gamma\rangle^\gamma]\right)}{\partial t} = \nabla\cdot\left(\varepsilon_\gamma\langle\rho_\gamma\rangle^\gamma[\mathbf{D}_{eff}]\cdot[\nabla\langle\omega_\gamma\rangle^\gamma]\right)$$

where we have the important result that the *effective diffusion matrix* features a *unique* tortuosity tensor.

$$[\mathbf{D}_{eff}] = [\langle D\rangle^\gamma]\left\{\mathbf{I} + \underbrace{\frac{1}{V_\gamma}\int_{A_{\gamma\kappa}}\mathbf{n}_{\gamma\kappa}\mathbf{b}\ dA}_{\text{tortuosity tensor}}\right\}$$

In the case of *linear dispersion regimes*, we have in the pseudo-component space

$$D^*_{AA\gamma}\Big|_{pseudo-component} = \frac{\langle D_{AA}\rangle^\gamma}{\tau} + \alpha_L\langle\mathbf{v}_\gamma\rangle^\gamma$$

for the longitudinal dispersion term.
When returning back to the original space, we obtain a set of dispersion equations, and the matrix of dispersion tensors has the important following property

$$\mathbf{i} \cdot [\mathbf{D}_\gamma^*] \cdot \mathbf{i} \;=\; \frac{1}{\tau}[\langle D \rangle^\gamma] + \alpha_L \langle v_\gamma \rangle^\gamma \begin{bmatrix} 1 & 0 & \dots & . & 0 \\ 0 & 1 & \dots & . & . \\ . & . & \dots & . & . \\ . & . & \dots & . & 0 \\ 0 & . & \dots & 0 & 1 \end{bmatrix}$$

Contrary to heuristic proposals, it is important to recognize that this form is only valid for the linear dispersion regime, and cannot be used under other conditions.

Validation by numerical experiments

In order to validate the theory, numerical experiments have been performed for a ternary system consisting of Aceton, Benzene, and CCl4. This system is interesting since it is fully non-linear. Density, viscosity, and diffusion coefficients vary significantly with the composition.

The pore-scale numerical experiments were performed on systems like the one presented in Figure 1.
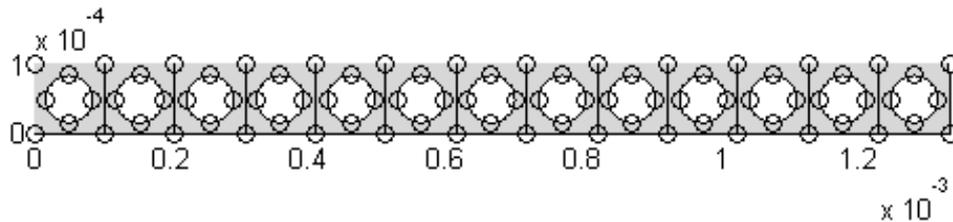

Figure 1. Pore-scale arrays of cylinders.

The pore-scale and averaged equations were solved using a special implementation in FEMLAB™, while the closure problems were solved using a proprietary finite volume code in order to obtain the tortuosity and dispersion tensors.

Typically, the pore-scale concentrations were averaged over each unit-cell and compared to the macroscopic predictions. It was found a very good agreement between the "numerical experiments" and theoretical predictions, as illustrated in Figure 2. In this figure, the circles and triangles refer to values averaged over the pore-scale numerical results. The lines referred to as "theor. nodisp" correspond to the averaged equations with only the tortuosity terms, while the others correspond to the full theory.
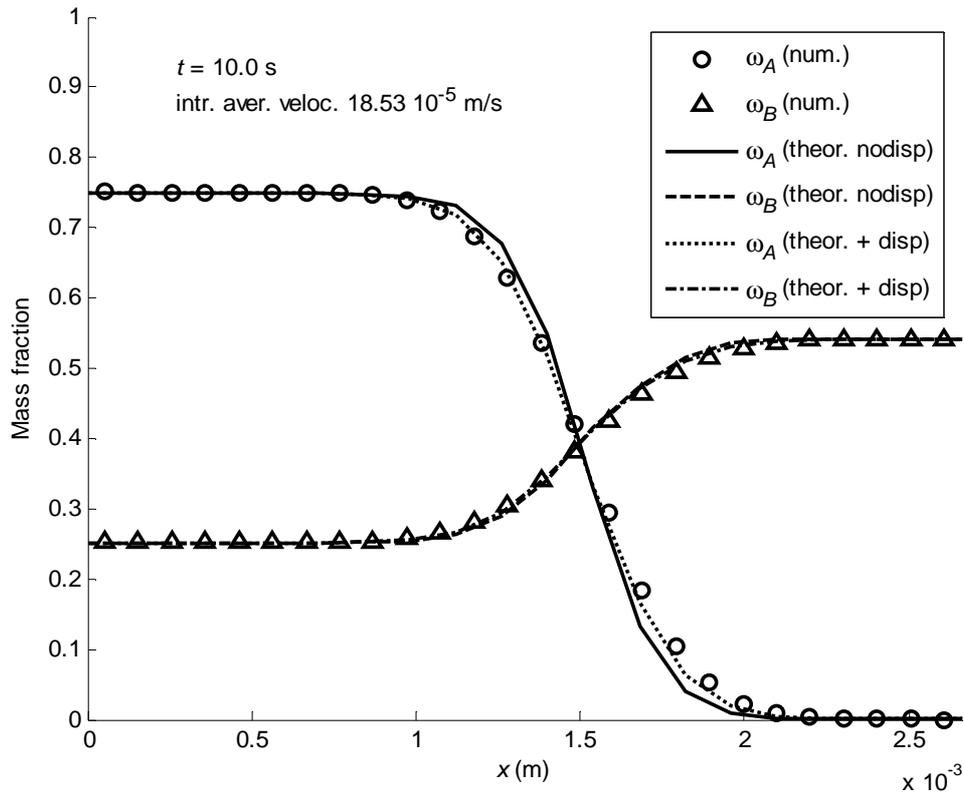
Figure 2. Example of a comparison between numerical experiments and theoretical predictions.

Conclusions

The proposed theory gives a generalized multicomponent dispersion theory. It shows that the heuristic effective dispersion tensors proposed in the literature are only valid under special circumstances, i.e., pure diffusion or linear dispersion regime. Under general conditions, the theory may be used to build a generalized dispersion matrix from available experimental data, for complex multicomponent systems.

References

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