

Mass Transfer Limitations and Non-Locality in Large Scale Reactive Transport

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Abstract

The correct characterization of large scale reactive transport dynamics is an important issue for modeling reactive transport on the Darcy scale, specifically in situations in which reactions are localized, that is when different reactions occur in different portions of the porous medium. We consider here reactive transport in a porous medium that is characterized by mass transfer between a mobile and a suite of immobile regions. Chemical and physical heterogeneities are reflected by distributions of kinetic reaction rate constants and residence times in the immobile zones. We derive an effective reactive transport equation for the mobile solute that is characterized by non-local physical mass transfer and reaction terms. Mass transfer limitations due to physical heterogeneity yield effective kinetic rate coefficients that can be much smaller than the volumetric average of the local scale coefficients. These results help to explain and quantify the often reported discrepancy between observed field reaction rate constants and the ones obtained under well mixed laboratory conditions. Furthermore, these results indicate that transport under physical and chemical heterogeneity cannot be upscaled separately.

Well-Mixed Condition

Physical Equilibrium

- Species concentration: $c(\mathbf{x}, t) = \frac{\Delta m(\mathbf{x}, t)}{\Delta V}$
- Support volume: $\Delta V \sim \ell^d$
- Relaxation time: $\tau_D^{mic} = \frac{\ell^2}{D}$

For $|\mathbf{x}| < \ell$ and $\Delta t > \tau_D^{mic}$, concentration gradients are zero $\nabla c(\mathbf{x}, t) = \mathbf{0}$. The system is locally well mixed and system dynamics are **Markovian**.

Mass conservation

$$\phi \frac{\partial c(\mathbf{x}, t)}{\partial t} = -\nabla \cdot [\mathbf{q} - D\nabla]c(\mathbf{x}, t).$$

Reactive Transport

- Well-mixed reactor: $\frac{dc(t)}{dt} = r\{c(t)\}$
- Reaction time scale τ_r

Reaction and transport: support volume ΔV is a well-mixed reactor if $Da^{mic} = \tau_D^{mic}/\tau_r < 1$

Mass conservation

$$\phi \frac{\partial c(\mathbf{x}, t)}{\partial t} = -\nabla \cdot [\mathbf{q} - D\nabla]c(\mathbf{x}, t) + r\{c(\mathbf{x}, t)\}.$$

We assume that a microscale ℓ exists for which this is true

Spatial Heterogeneity

Degrees of Freedom

Distribution of values of heterogeneous field $k(\mathbf{x})$

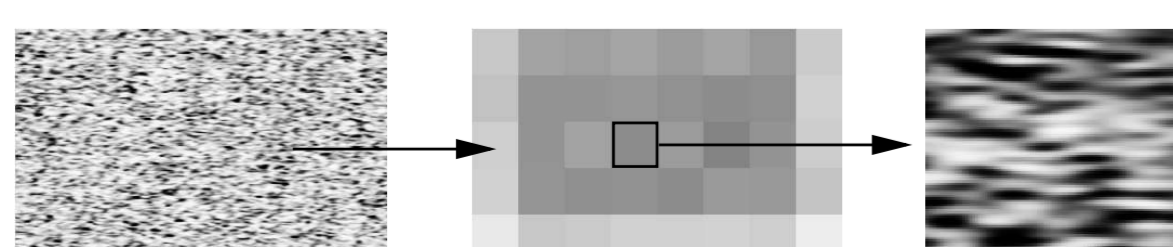
$$p_k(k) = \frac{1}{V} \int_V d\mathbf{r} \delta[k - k(\mathbf{x} + \mathbf{r})]$$

Information content of $k(\mathbf{x})$: $E = - \int dk p_k(k) \ln p_k(k)$

In practice: $E_{characterization} < E_{system}$

Physical Non-Equilibrium

- Local physical non-equilibrium depends on the support scale
- Mesoscopic support scale L gives a large relaxation time $\tau_D^{mac} = L^2/D$



- Mesoscopic support volume cannot be considered a well-mixed reactor because $Da^{mac} = \tau_D^{mac}/\tau_r > 1$

Support Scale

Microscopic support scale: processes in local equilibrium, many degrees of freedom

Mesoscopic support scale: processes in local non-equilibrium, fewer degrees of freedom

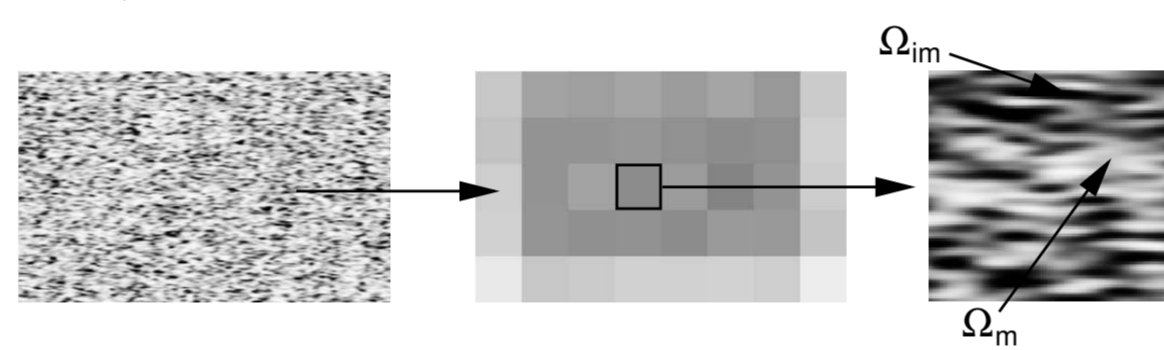
Upscaling

Heterogeneous advection dispersion reaction equation

$$\phi(\mathbf{x}) \frac{\partial c(\mathbf{x}, t)}{\partial t} + \nabla \cdot [\mathbf{q}(\mathbf{x}) - D(\mathbf{x})] \nabla c(\mathbf{x}, t) = -\phi(\mathbf{x})k(\mathbf{x}) [c(\mathbf{x}, t) - c^{eq}]$$

Multicontinuum approach

Define continuous sub-regions with uniform spatial properties (ϕ, k, D) .



(e.g., Lichtner and Kang, 2007)

Multicontinuum Model

Average concentration in the mobile region

$$\begin{aligned} \phi_m \bar{c}_m(\mathbf{x}, t) &= \frac{1}{\Delta V} \int_{\Delta V_m} d\mathbf{r} \phi(\mathbf{x} + \mathbf{r}) c(\mathbf{x} + \mathbf{r}, t), \\ \phi_m &= \frac{1}{\Delta V} \int_{\Delta V_m} d\mathbf{r} \phi(\mathbf{x} + \mathbf{r}) \end{aligned}$$

Reaction rate in the mobile region (well mixed)

$$\begin{aligned} \frac{1}{\Delta V} \int_{\Delta V_m} d\mathbf{r} k(\mathbf{x} + \mathbf{r}) \phi(\mathbf{x} + \mathbf{r}) [c(\mathbf{x} + \mathbf{r}, t) - c^{eq}] \\ = \phi_m k_m [\bar{c}_m(\mathbf{x}, t) - c^{eq}] \end{aligned}$$

Interface between mobile and immobile regions

$$c_m(\mathbf{x}, t) = c_i(\mathbf{x}, t), \quad \mathbf{n} \cdot \mathbf{D}_m \nabla c_m(\mathbf{x}, t) = \mathbf{n} \cdot D_i \nabla c_i(\mathbf{x}, t),$$

for $\mathbf{x} \in \Omega_m \cap \Omega_i$.

Average over the mobile domain

$$\begin{aligned} \phi_m \frac{\partial \bar{c}_m(\mathbf{x}, t)}{\partial t} + \nabla \cdot [\bar{\mathbf{q}} - \bar{\mathbf{D}}_m \nabla] \bar{c}_m(\mathbf{x}, t) &= \phi_m k_m [\bar{c}_m(\mathbf{x}, t) - c^{eq}] \\ - \sum_i \frac{p_i \phi_i}{\Delta V_i} \int_{\Omega_m \cap \Omega_i} d\mathbf{f} \mathbf{n} \cdot D_i \nabla c_i(\mathbf{r}, t). \end{aligned}$$

Immobile concentrations

$$\frac{\partial c_i(\mathbf{r}, t)}{\partial t} - D_i \nabla^2 c_i(\mathbf{r}, t) = -k_i [c_i(\mathbf{r}, t) - c^{eq}], \quad c_i(\mathbf{r}, t)|_{\mathbf{r} \in \partial \Omega_i} = \bar{c}_m(\mathbf{x}, t)$$

Diffusion time in the immobile regions of type i , $\tau_i = \ell_i^2/D_i$.

Effective Reactive Transport Equation

$$\begin{aligned} \phi_m \frac{\partial \bar{c}_m(\mathbf{x}, t)}{\partial t} + \frac{\partial}{\partial t} \int_0^t dt' \varphi_r(t-t') \bar{c}_m(\mathbf{x}, t') \\ + \nabla \cdot [\bar{\mathbf{q}} - \bar{\mathbf{D}}_m \nabla] \bar{c}_m(\mathbf{x}, t) = - \int_0^t dt' \kappa(t-t') [c_m(\mathbf{x}, t') - c^{eq}] \end{aligned}$$

with the kernels

$$\varphi_r(t) = \sum_i \phi_i \varphi_i(t) \exp(-k_i t), \quad \kappa(t) = k_m \delta(t) + \sum_i \phi_i k_i \varphi_i(t) \exp(-k_i t)$$

Reaction Rate Coefficients

Definitions

Volume averaged reaction coefficient

$$k_v = \phi_m k_m + \sum_i \phi_i k_i$$

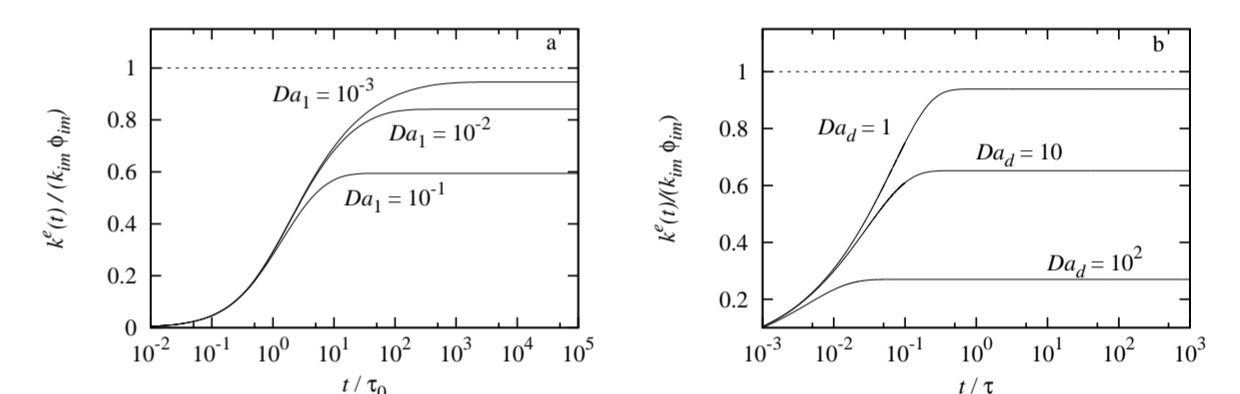
Effective reaction rate coefficient

$$k^e(t) = \phi_m k_m + \sum_i \phi_i k_i \int_0^t dt' \varphi_i(t') \exp(-k_i t')$$

Apparent reaction coefficient

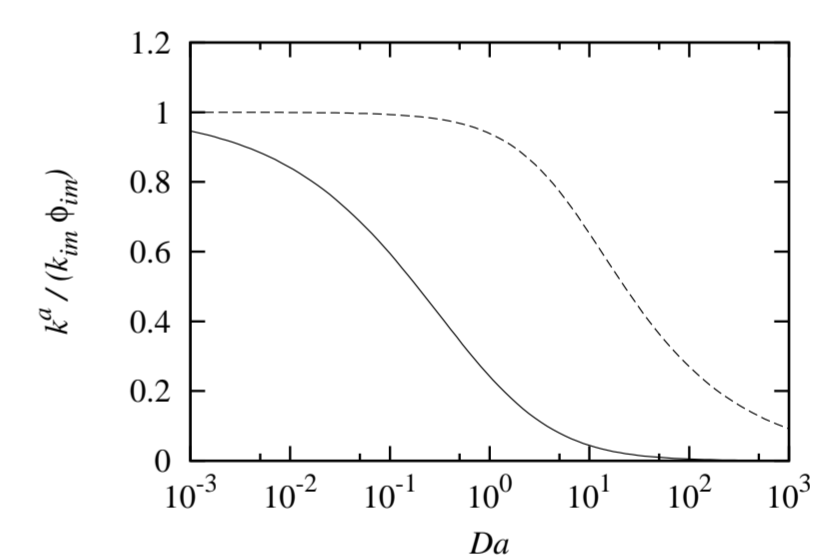
$$k^a = \lim_{t \rightarrow \infty} k^e(t) = \phi_m k_m + \sum_i \phi_i k_i \hat{\varphi}_i(k_i).$$

Effective Reaction Rate Coefficient



Effective reaction rate coefficients for $k_m = 0$ and $k_i = k_{im}$ and (a) power-law distribution of diffusion times $p(\tau) \propto \exp(-\tau_0/\tau) \tau^{-5/2}$, (b) $p(\tau) = \delta(\tau - \tau_0)$ and different $Da = \tau_0 k_{im}$.

Apparent Reaction Rate Coefficient



Apparent reaction rate coefficients for $k_m = 0$ and $k_i = k$ and (solid line) $p(\tau) \propto \exp(-\tau_0/\tau) \tau^{-5/2}$, and (dashed line) $p(\tau) = \delta(\tau - \tau_0)$.

Summary

- Changing the support scale in heterogeneous media introduces local physical non-equilibrium
- As a consequence large scale transport is non-Markovian.
- Multicontinuum model provides a useful 'hybrid' approach
- Effective reactive transport is non-local in time
- Macroscale reaction rates decreases with increasing Damköhler number.

References:

Dentz, M., Guouze, P. and Carrera, J., 2011, Effective non-local reaction kinetics for transport in physically and chemically heterogeneous media, J. Contam. Hydrol., 120121, 222236.
Lichtner, P.C., Kang, Q., 2007. Upscaling pore-scale reactive transport equations using a multiscale continuum formulation. Water Resour. Res. 43, W12S15.

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