Transport in Porous Media

1. Conduction

In the previous lecture, we considered conduction of electricity (or heat conduction or mass diffusion) in a composite medium, where each component has a nonzero conductivity. In a porous medium, we focus on one “pore phase” and assign zero conductivity to the “matrix phase”. From the notation of the previous lecture,

$$\phi_1 = \epsilon_p = porosity$$

$$\sigma_1 = \sigma_p = pore\ phase\ conductivity$$

$$\sigma_i = 0, for\ i > 1$$

Note: the Hashin-Shtrikman and Wiener **lower** bounds are zero, since any volume fraction of nonconductive material can be distributed so as to completely block conduction through the porous medium (i.e. if there is no percolating path of the conductive phase). The **upper** bounds are

$$\bar{\sigma}_{max}^{Wiener} = \phi_1\sigma_1 = \epsilon_p\sigma_p \qquad anisotropic\ pores$$

$$\bar{\sigma}_{max}^{HS} = \phi_1\sigma_1 - \frac{\sigma_1^2\phi_1\phi_2}{\phi_2\sigma_1 + \sigma_1} = \sigma_p\left(\epsilon_p - \frac{\epsilon_p(1-\epsilon_p)}{2-\epsilon_p}\right) = \sigma_p\left(\frac{\epsilon_p}{2-\epsilon_p}\right) \qquad isotropic\ pores$$

Percolation model (which assumes isotropic media) gives

$$\bar{\sigma}_{perc} \sim (\epsilon_p - \epsilon_c)^t$$

For ϵ_p just above the critical point ϵ_c, where the exponent t=2 is believed to have a universal value for any 3D model.

A simple form which captures this effect is

$$\bar{\sigma}_{perc} \cong \begin{cases} \sigma_p\left(\frac{\epsilon_p - \epsilon_c}{1-\epsilon_c}\right)^2 & , \epsilon_c \le \epsilon_p \le 1 \\ 0 & ,0 \le \epsilon_p \le \epsilon_c \end{cases}$$

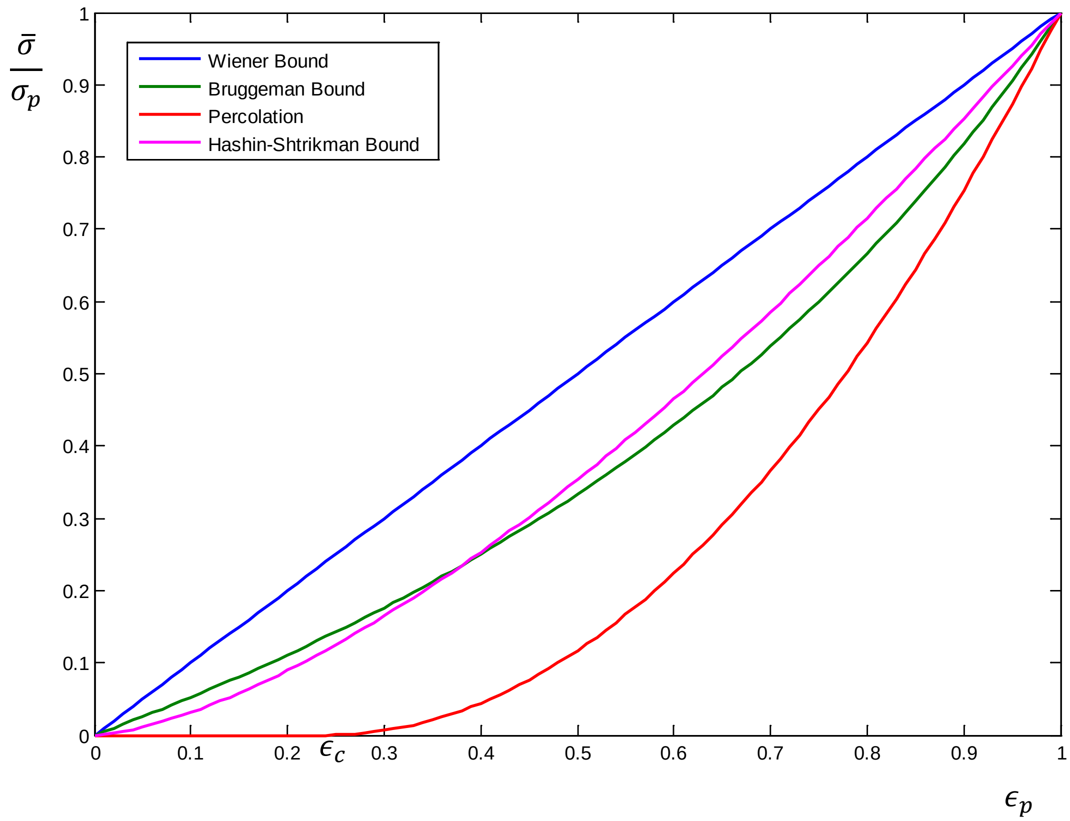
since $\bar{\sigma}_{perc} \to \sigma_p$ as $\epsilon_p \to 1$.

Note that this lies between the Hashin-Shtrikman bound and the lower bound.

In electrochemical engineering, it is common to use the empirical Bruggeman formula

$$\sigma_B = \epsilon_p^{3/2}\sigma_p$$

As shown in the figure below (where ϵ_c is assumed to be 0.24), this lies above the Hashin-Shtrikman upper bound for large ϵ_p, so it is inconsistent to as for isotropic media. It also neglects percolation transition at small ϵ_p. However, it is fairly close to the Hashin-Shtrikman upper bound, so it may be reasonable for a continuous porous phase with isolated solid matrix particles (as in the core-shell model for the HS upper bound model).



2. Diffusion

The effective conductivity determines the macroscopic current density $\bar{J} = -\bar{\sigma}\nabla\phi$. In the case of diffusion, the net flux is $\bar{F} = -\bar{\sigma}_d\nabla c$, where c is the concentration in the pores (which is constant in equilibrium, even if the porosity varies in space). Macroscopic conservation of mass requires

$$\frac{\partial \bar{c}}{\partial t} + \nabla \cdot \vec{F} = 0$$

Where $\bar{c} = \epsilon_p c$ is the volume-averaged concentration.

$$\frac{\partial \bar{c}}{\partial t} = \bar{\sigma}_d \nabla^2 c = \bar{D} \nabla^2 \bar{c}$$

$$or \;\; \frac{\partial c}{\partial t} = \bar{D} \nabla^2 c$$

Where $\bar{D} = \frac{\bar{\sigma}_d}{\epsilon_p}$ is the effective diffusivity in the porous medium.

Note: the Wiener upper bound implies $\bar{D} \leq D_p$, since $\bar{\sigma} \leq \epsilon_p \sigma$. Therefore, we can interpret the reduction of D in the pores via an effective extension of the path length for diffusion by a factor called tortuosity τ_p.

$$L_p = \tau_p L$$

$$\nabla = \tau_p \nabla_p \to \frac{\partial c}{\partial t} = D_p \nabla_p^2 c$$

$$\bar{D} = \frac{D_p}{\tau_p^2}$$

So we can recover the same diffusion equation as in the free solution only with a stretched spatial coordinate system.

Thus, we arrive at the following interpretation of the diffusive mean conductivity.

$$\bar{\sigma}_d = \frac{D_p \epsilon_p}{\tau_p^2}$$

Note: if $\bar{\sigma}_d$is a tensor, then tortuosity is also a tensor given by $\tau_p = \left(D_p \epsilon_p \bar{\sigma}_d^{-1}\right)^{1/2}$.

For the models and bounds above, we have the following tortuosity (noting that $\tau_p = 1$ when $\epsilon_p = 1$):

$\tau_p^{Wiener} = 1$ (**lower** bound, attained by aligned stripes);

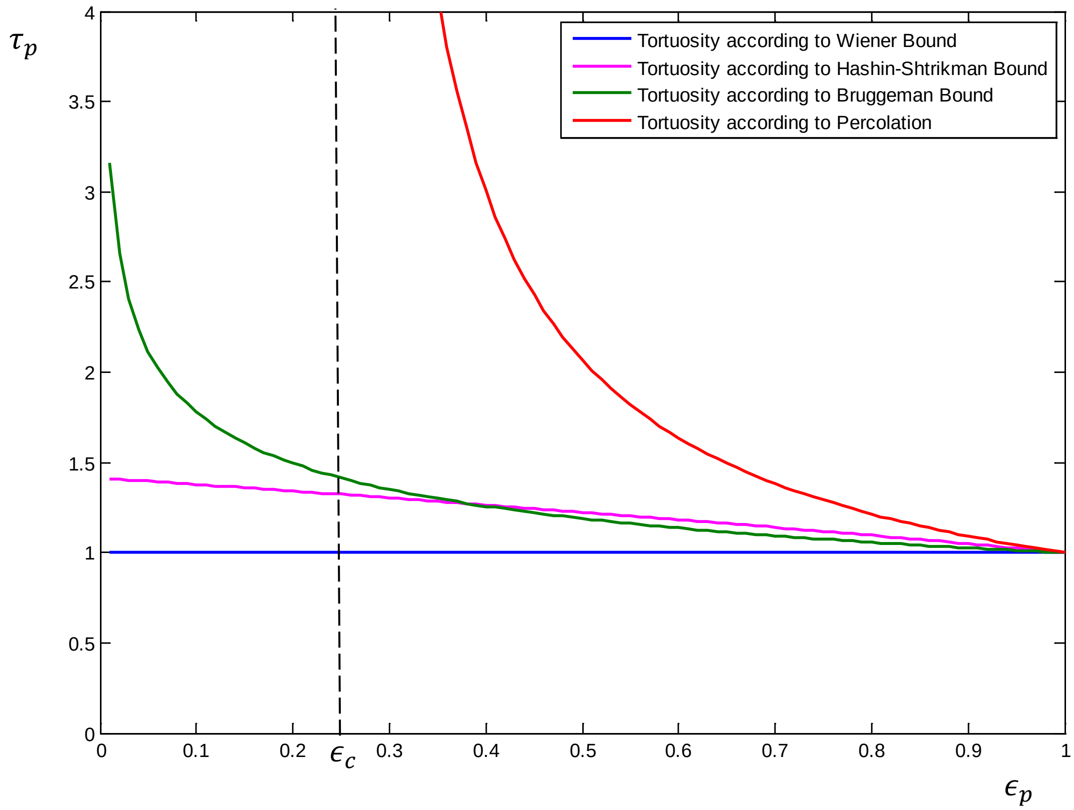
$\tau_p^{HS} = \sqrt{2 - \epsilon_p}$ (**lower** bound for isotropic pores);

$\tau_B = \epsilon_p^{-1/4}$ (Bruggeman empirical formula);

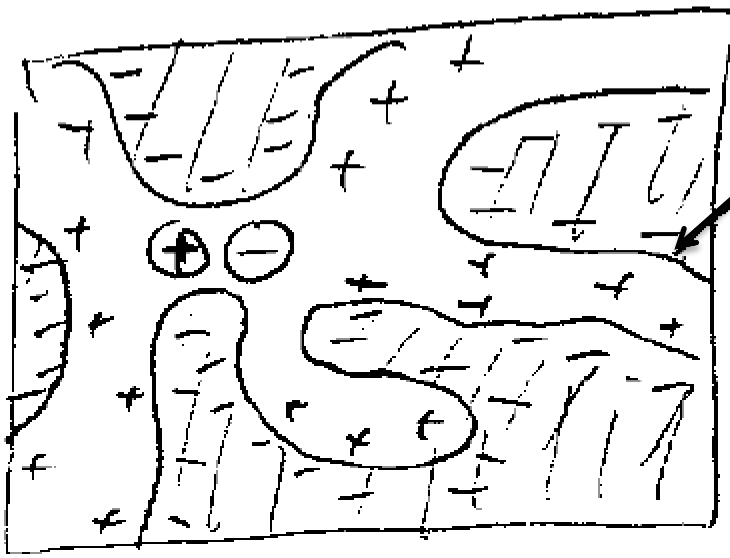
$$\tau_{perc} \cong \begin{cases} \sqrt{\epsilon_p}\left(\frac{1-\epsilon_c}{\epsilon_p-\epsilon_c}\right), \epsilon_c \leq \epsilon_p \leq 1 \\ \infty \qquad\qquad\qquad ,0 \leq \epsilon_p \leq \epsilon_c \end{cases}$$

Note: tortuosity makes no sense when conductivity becomes significantly reduced by loss of percolation, since it is not the longer path length but rather the many “dead ends” and few percolating paths that lower the conductivity.

The figure below shows the tortuosity according to the above models (note, here ϵ_c is assumed to be 0.24)



3. Ion transport (neglect convection and electroosmotic flow)



Microscopic Nernst-Planck equation in the pores (NOT Laplace's equation as before):

$$\frac{\partial c_i}{\partial t} + \nabla \cdot F_i = 0$$

$$F_i = -D_i c_i \nabla \tilde{\mu}_i$$

$$\tilde{\mu}_i = \mu_i / k_B T$$

$$\mu_i = k_B T \ln(\gamma_i c_i) + z_i e \phi$$

Poisson's equation gives: $-\varepsilon_p \nabla^2 \phi = \rho = \sum_i z_i e c_i$

Boundary condition (no reaction, fixed surface charge):

$$-\varepsilon_p \vec{n} \cdot \nabla \phi = q_s$$

$$\vec{n} \cdot F_i = 0$$

Macroscopic PNP equation:

$$\frac{\partial \bar{c}_i}{\partial t} + \nabla \cdot \bar{F}_i = 0$$

$$\bar{F}_i = -\bar{D}_i \bar{c}_i \nabla \tilde{\mu}_i$$

$\tilde{\mu}_i \cong constant, across\ pores\ and\ small\ length\ scales, even\ though\ c\ and\ \phi\ vary\ quickly.$

$$Define\ \bar{\rho} = \sum_i z_i e \bar{c}_i$$

$$-\boldsymbol{\nabla} \cdot (\bar{\varepsilon} \nabla \bar{\phi}) = \bar{\rho} + \bar{\rho}_s$$

Where $\bar{\rho}_s = a_p q_s$, $a_p = \frac{pore\ surfcae\ area}{volume}$.

In the limit of the double layer, $c_i \cong constant\ in\ the\ pore\ bulk\ solution = \bar{c}_i/\epsilon_p$, and $\bar{\phi} \cong \phi = constant\ outside\ double\ layer$ and $\bar{\varepsilon} \to 0$:

$$\bar{\rho} + \bar{\rho}_s = 0\ \ Thin\ double\ layer$$

$$\rho_s = \frac{surface\ charge}{volume}$$

This is just macroscopic neutrality condition.