

VI. Porous Media

Lecture 34: Transport in Porous Media

4/29/2011 (corrected 5/4/12 MZB)

Notes by MIT Student

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,

$$\phi_1 = \epsilon_p = \text{porosity}$$

$$\sigma_1 = \sigma_p = \text{pore phase conductivity}$$

$$\sigma_i = 0, \text{ for } i > 1$$

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

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

$$\bar{\sigma}_{max}^{HS} = \phi_1 \sigma_1 - \frac{\sigma_1^2 \phi_1 \phi_2}{\phi_2 \sigma_1 + \sigma_1 (d-1)} = \sigma_p \left(\frac{(d-1)\epsilon_p}{d-\epsilon_p} \right) = \sigma_p \left(\frac{2\epsilon_p}{3-\epsilon_p} \right) \quad \text{isotropic pores}$$

where the last equation is for d=3 dimensions. Percolation model (which assumes isotropic media) gives the following scaling for ϵ_p just above the critical point ϵ_c ,

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

where the exponent t=2 is believed to have a universal value for any 3D model.

A simple form which captures this effect is

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

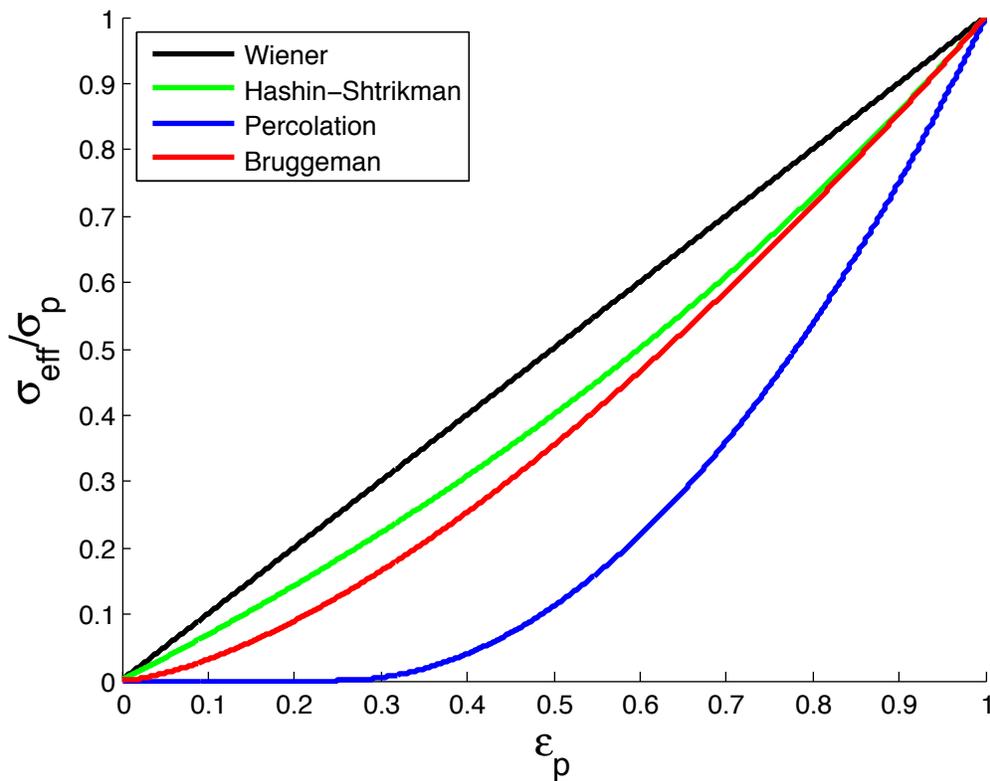
since $\bar{\sigma}_{perc} \rightarrow \sigma_p$ as $\epsilon_p \rightarrow 1$.

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, this lies close to the Hashin-Shtrikman upper bound, especially for large ϵ_p . Therefore, the Bruggeman formula could represent an isotropic medium with ample percolating pathways of unblocked pores, similar to the core-shell microstructure (composed of spheres with conducting shells and non-conducting cores) that attains the HS upper bound. This makes sense in porous electrodes, since they are often fabricated from grains and powders soaked in a liquid electrolyte, which effectively coats the particles and percolates through the system. Where this approximation breaks down is at low porosity, where percolation effects can become important with an increasing number of blocked “dead end” pores, and this is reflected in the lower Bruggeman conductivity compared to the HS upper bound (which is attained by microstructures without any blocked pores).



[Figure credit: Todd Ferguson] Conductivity bounds and models in d=3 dimensions.

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

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

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

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

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

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 .

$$L_p = \tau_p L$$

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

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

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 $\tau_p = (D_p \epsilon_p \bar{\sigma}_d^{-1})^{1/2}$.

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);

$$\tau_p^{HS} = \sqrt{\frac{d - \epsilon_p}{d - 1}} = \sqrt{\frac{3 - \epsilon_p}{2}} \quad (\text{lower bound for isotropic pores});$$

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

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

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

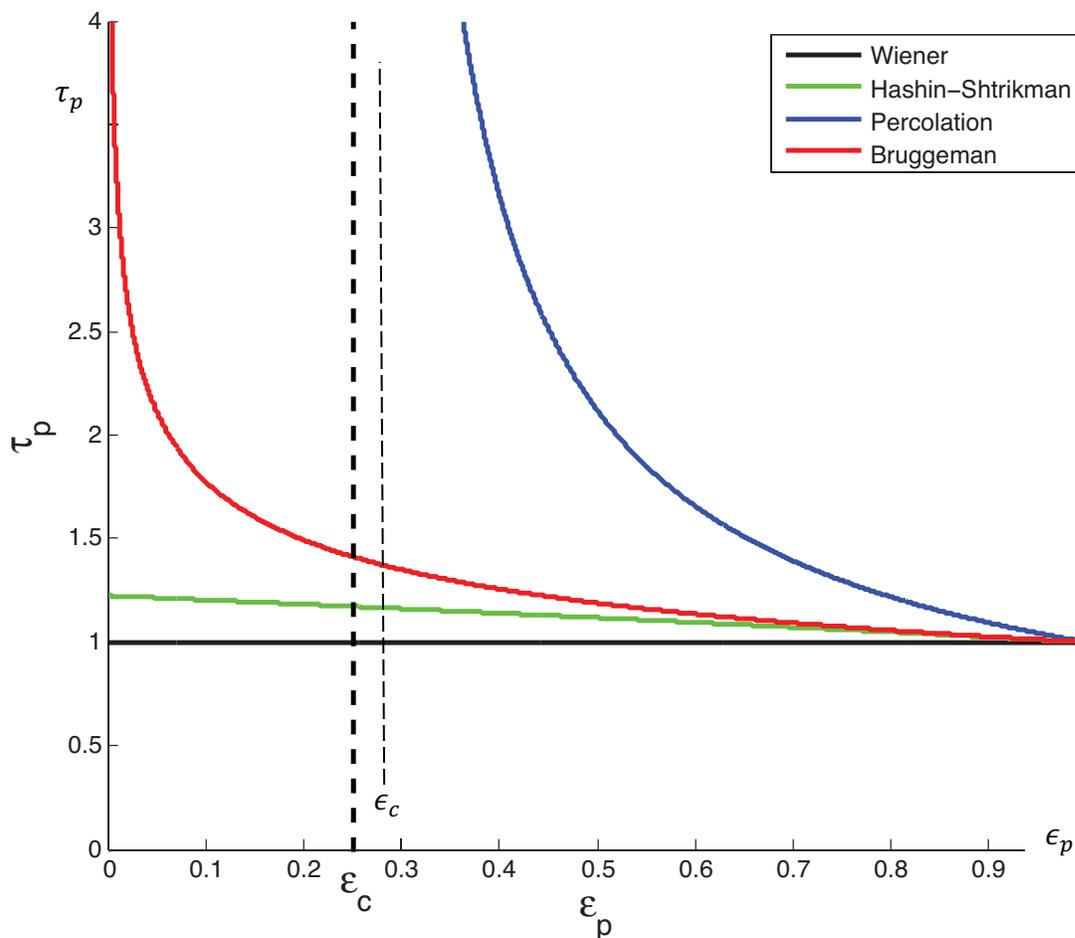
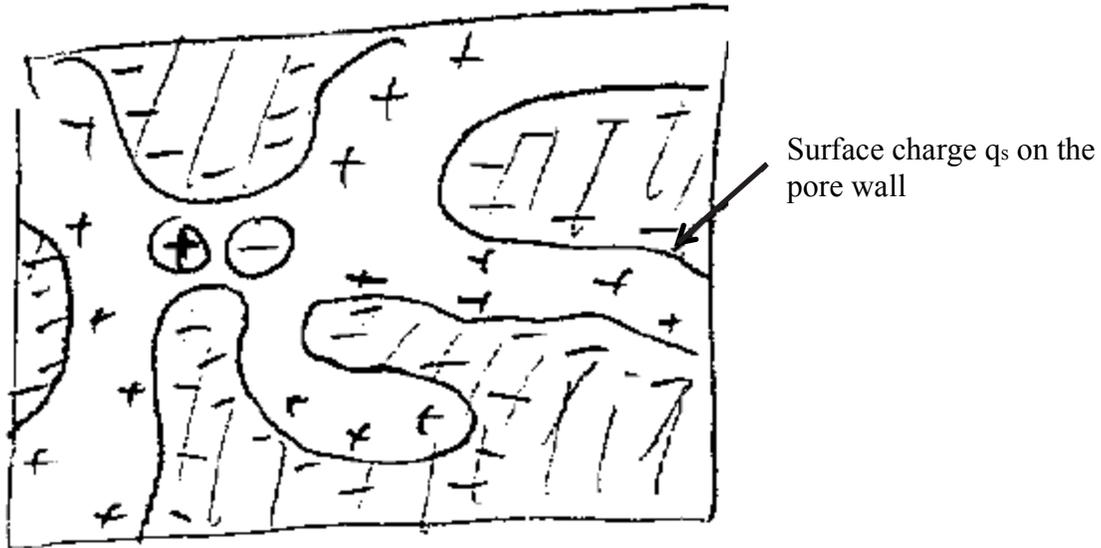


Figure: Tortuosity vs. porosity for bounds and models in d=3 dimensions [T. Ferguson]

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:

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

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

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

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

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

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

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

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

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

This is just macroscopic neutrality condition.

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