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# Hierarchical Structure in Nano Transport

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Transportation Energy Center 8300

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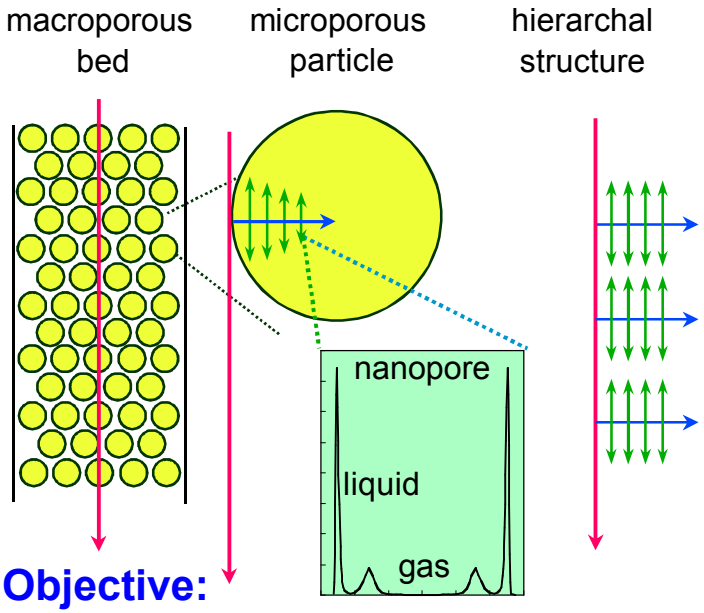
# Multi-scale Modeling of Transport in Hierarchical Nanoporous Materials




## Objective:

- Identify material structures that optimize the storage capacity and discharge/recharge rates of hierarchical materials comprised of --
  - nanopores for surface area & functionality
  - micropores for rapid transport
- Optimization is required because transport channels reduce volume available for nanopore storage

## Applications:

- Hydrogen and $CH_4$ storage
- Super capacitors and batteries
- Membrane filtration/water purification
- Catalytic beds and membranes

## Approach:

- Use Density Functional Theory (DFT) and MD to understand atomistic physics in nanopores
- Incorporate DFT and MD results into tractable continuum-like models of multiphase transport in complex hierarchical materials
  - widely disparate time & length scales
- Use models to design optimal gas-storage and super-capacitor materials

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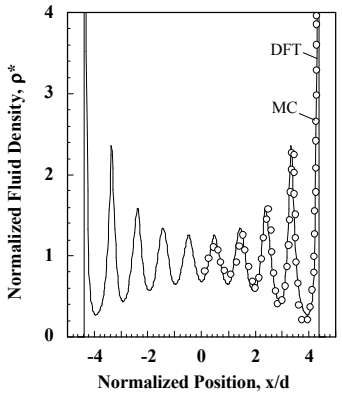
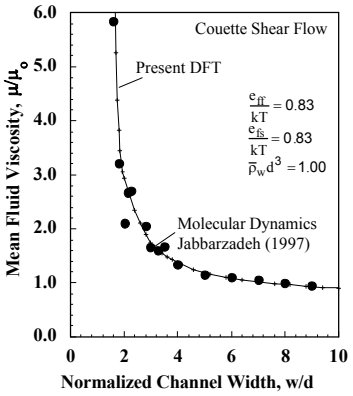
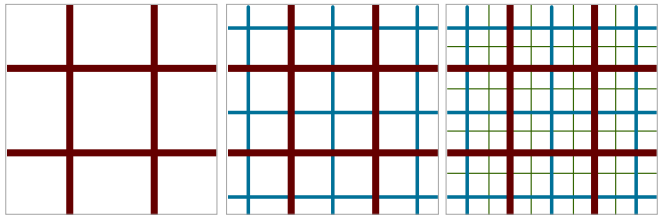
# Outline

- **Density Functional Theory**
  - equilibrium density distributions
  - gas storage materials
  - charge storage materials

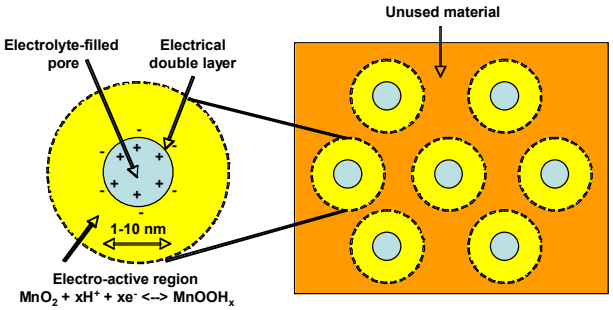


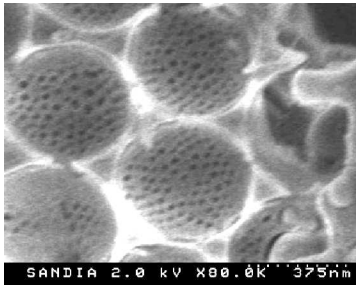




- **Optimal pore sizes and spacing**
  - lattice-like hierarchies



- **Related experimental studies**

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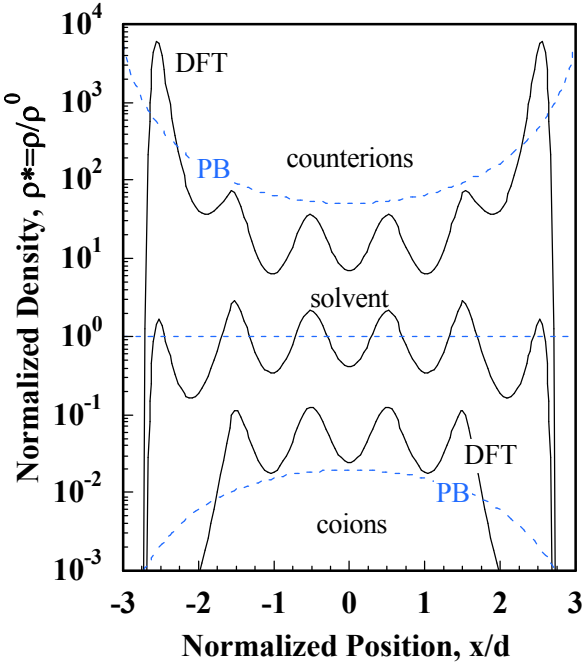
# Density Functional Theory (DFT) yields density distributions minimizing free energy

- **DFT ion density profiles are structured by adjacent solid surface**
  - DFT agrees well with MD but is much faster
  - Classical Poisson-Boltzmann (PB) model incurs large errors for typical UltraCap charge densities

- **DFT free energy functional is based on molecular pair-potentials**
  - $\rho$ = fluid density
  - V = external "field" of solid
  - $\mu$ = chemical potential
  - U = L-J fluid/fluid interaction
  - $\Delta\psi$ = hard sphere repulsion
  - $\Phi$ = electrical interactions




$$\Omega[\rho(r)] = \int \rho(r)\left(F[\rho(r)] + V(r) - \mu\right) dr$$

$$F[\rho(r)] = kT\ \ln\left[\Lambda^3\rho(r)\right] + \frac{1}{2}U(r) + \Delta\psi(r) + \Phi$$

$$U(r) = -4\varepsilon_{LJ}\int \rho(r')\left[\left(\frac{\sigma}{r'}\right)^6 - \left(\frac{\sigma}{r'}\right)^{12}\right] dr'$$

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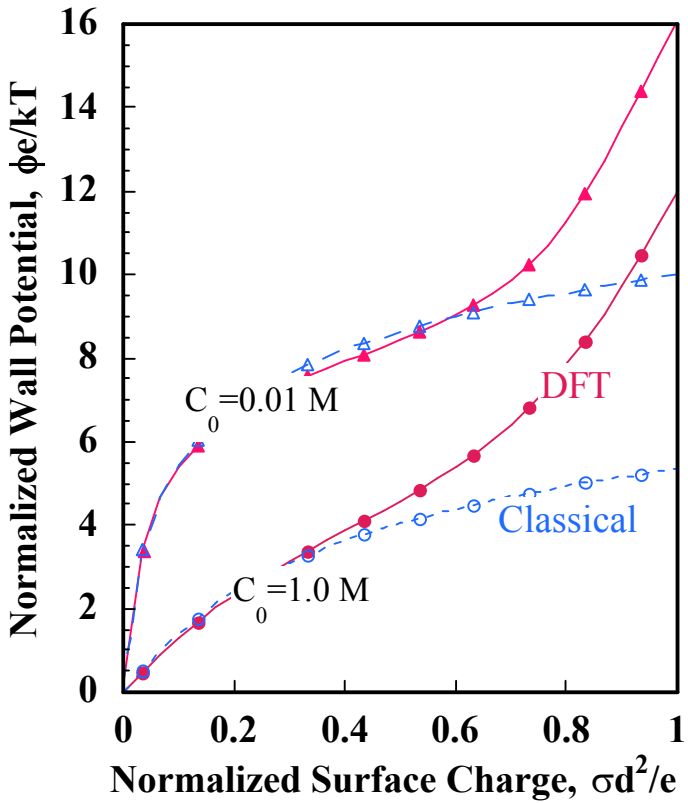
# DFT provides electrochemical potential for use in transport equations

- **Classical prediction of electrode voltage versus surface charge density is very poor**
  - 10X error at 1 volt
  - must include atomistic physics
- **Currently working on --**
  - incorporation of atomistic physics
  - into continuum-like transport equations
  - based on DFT adjustments to chemical potentials, $\mu_i$

$$\frac{d\rho_i}{dt} = \nabla \cdot \left( \rho_i \mathbf{u} - \upsilon_i \rho_i \nabla \mu_i \right)$$

$$\mu = \mu_0 + ze\phi + kT \ln \rho + \Delta\mu_{DFT}$$

$$\Delta\mu_{DFT} = U_{L-J} + V_{wall} + \Delta\psi_{hardsphere} + \Delta\Phi_{elec}$$

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# Modeling multiphase fluid flow in nanopores

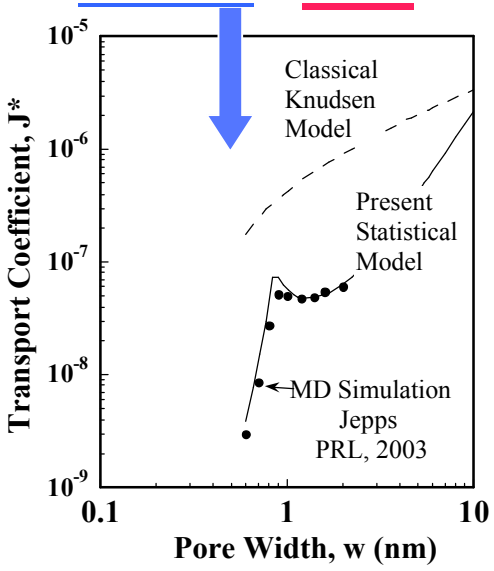
- Quasi-1D model of gas/liquid flow based on DFT inputs:

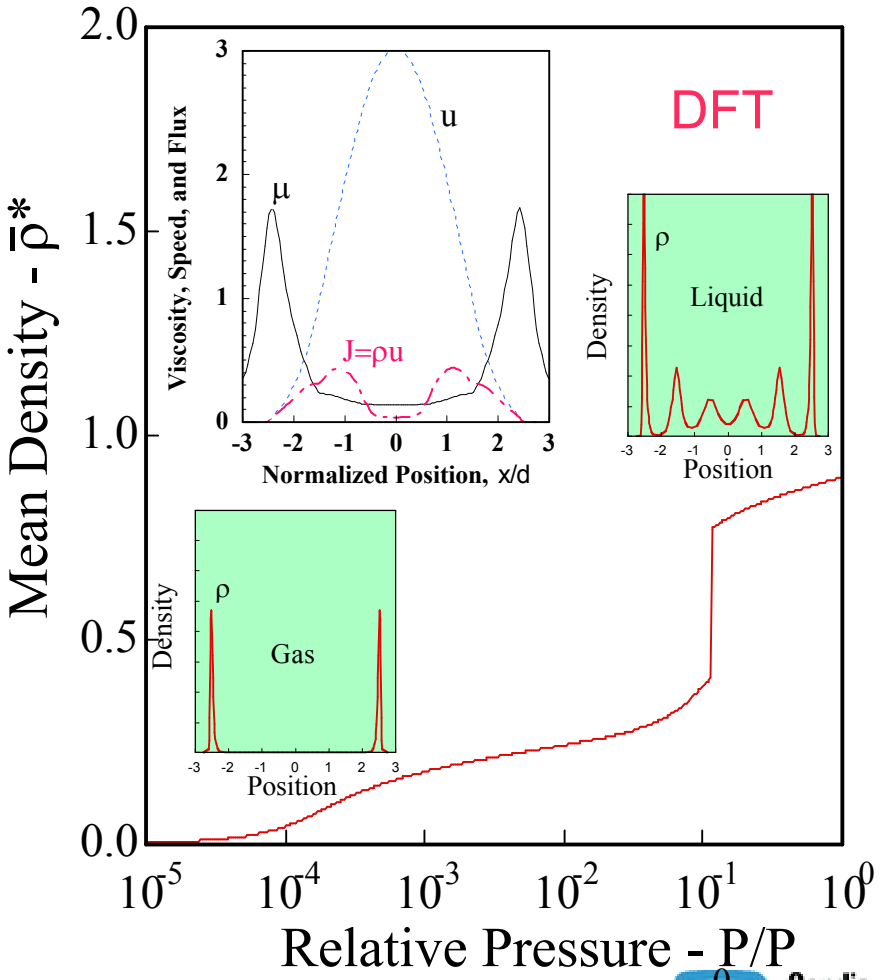
$$\frac{d\bar{\rho}}{dt} = -\frac{d}{dx}(\overline{\rho u})$$

$$\left[\frac{d\bar{\rho}}{dP}\right]_{DFT} \frac{dP}{dt} = \frac{d}{dx}\left(J^* \frac{dP}{dx}\right)$$

$$J^*(P,T;w) = J^*_{\text{free molecular}} + J^*_{\text{viscous}}$$

Statistical model of free molecular flow between adsorbent walls



# Simplified model for optimization of pore networks

- **Two storage mechanisms**
  - $\rho_{surf}$ = surface density
  - $\rho_{bulk}$ = bulk density
  - $\Gamma$ = channel perimeter
  - $\delta$ = surface layer thickness
  - a = channel width
- **Transport coefficient, D, often increases with channel width**
- **Diffusivity, $\alpha=D/(1+\gamma)\sim a^m$**
  - m=0 simple diffusion (ions)
  - m=1 Knudsen diffusion
  - m=2 viscous flow
  - m=m+1 (when $\gamma$ ~$1000\delta/a>>1$)

$$(1+\gamma)\frac{\partial \rho_{bulk}}{\partial t} \approx \frac{\partial}{\partial x}\left(D\frac{\partial \rho_{bulk}}{\partial x}\right)$$

$$\gamma \approx \frac{\rho_{surf}}{\rho_{bulk}}\frac{\delta}{a} \approx 1000\frac{\delta}{a}$$

$$D = \frac{a^2}{12\mu}\rho\left(\frac{dP}{d\rho}\right)_T \approx \frac{a^2 P_0}{12\mu} \quad \text{viscous flow}$$

$$D = \upsilon_{molecular}\, a \quad \text{Knudsen diffusion}$$

$$\frac{\partial \rho_b}{\partial t} = \frac{\partial}{\partial x}\left(\alpha\frac{\partial \rho_b}{\partial x}\right)$$

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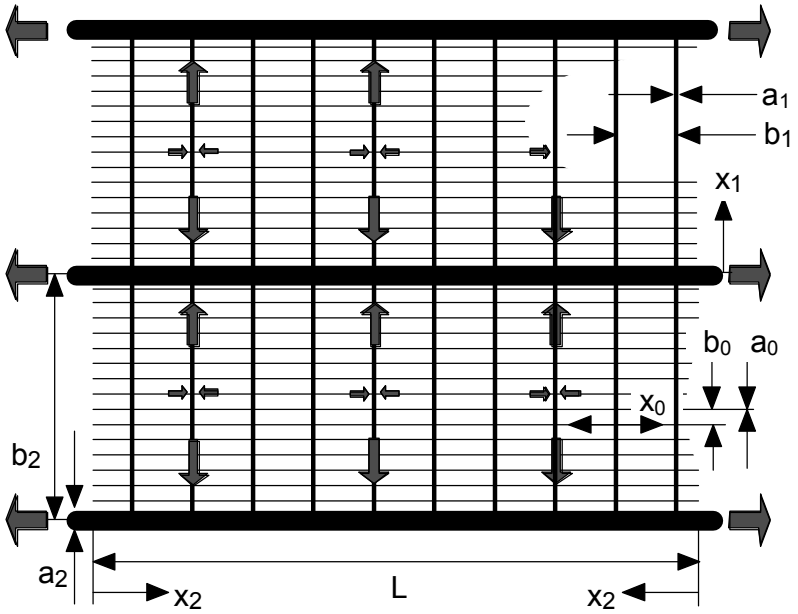
# Optimization problem for materials having several scales of porosity

- **Smallest scale nanopores have prescribed --**
  - widths $a_0$
  - spacing $b_0$
- **Transport channels have**
  - widths $a_1, a_2, a_3, \ldots, a_N$
  - spacing $b_1, b_2, b_3, \ldots, b_N$
- **Optimization: choose $a_1$ - $a_N$ and $b_1$ - $b_N$ to maximize integrated inflow/outflow for given --**
  - fixed total system volume
  - fixed discharge/recharge time, $\tau$
  - prescribed variation in surface potential
    - sinusoidal variation ($\tau = 1/\omega$)
    - step change

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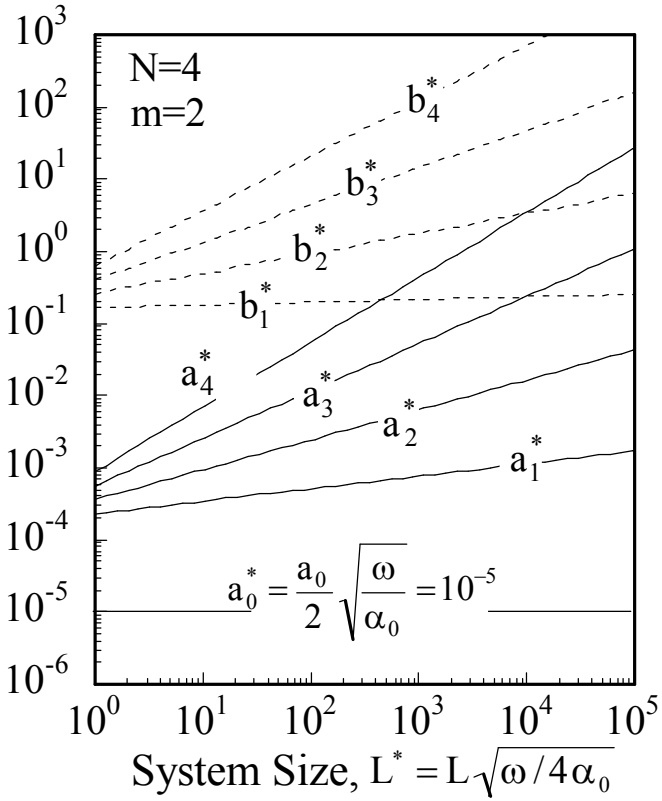
# Optimum channel dimensions increase with system scale

- **Optimization criterion**
  - maximum outflow from fixed volume
  - wider & closer transport channels
    - improve response time
    - reduce storage capacity
- **All length dimensions are scaled by range of diffusion along a nanopore in a time period of $\tau=1/\omega$**
- **Power scaling of channel widths and spacing persists over many decades**

$$a_1^* = A\,L^{*q} \qquad b_1^* = B\,L^{*p}$$

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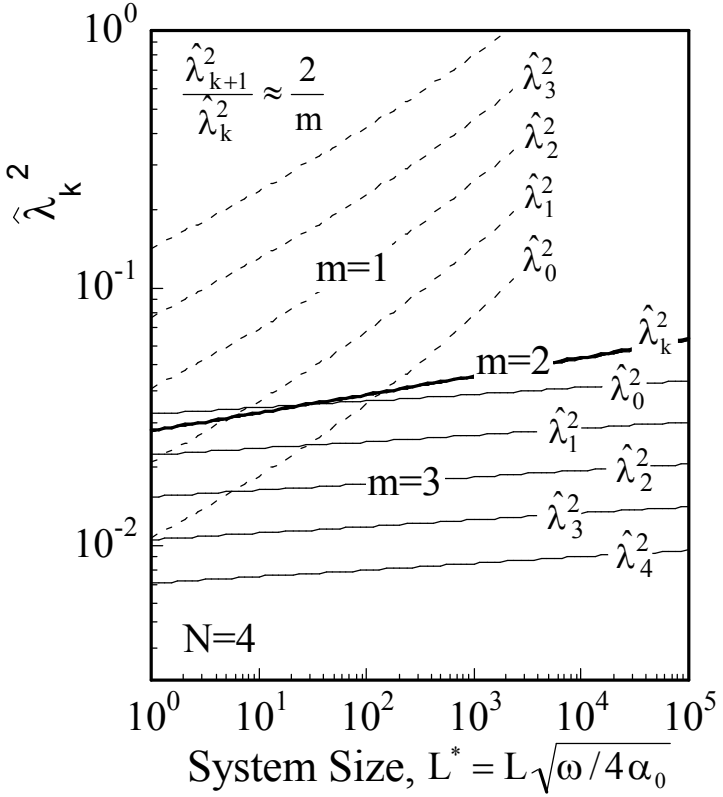
# Equality of Fourier moduli indicates matching of impedance between scales

- **Fourier moduli indicate ratio of --**
  - diffusion time $\tau_{diff} = b_{k+1}^2 / \alpha_k$
  - to cycle time $\tau_{cycle} \sim 1/\omega$

$$\hat{\lambda}_k = \frac{b_{k+1}}{2}\sqrt{\frac{\omega}{\alpha_k}} \sim \sqrt{\frac{\tau_{diff}}{\tau_{cyc}}}$$

- **Pressure drops along channels depend only on λ's**

- **λ's are identically the same only for m=2**

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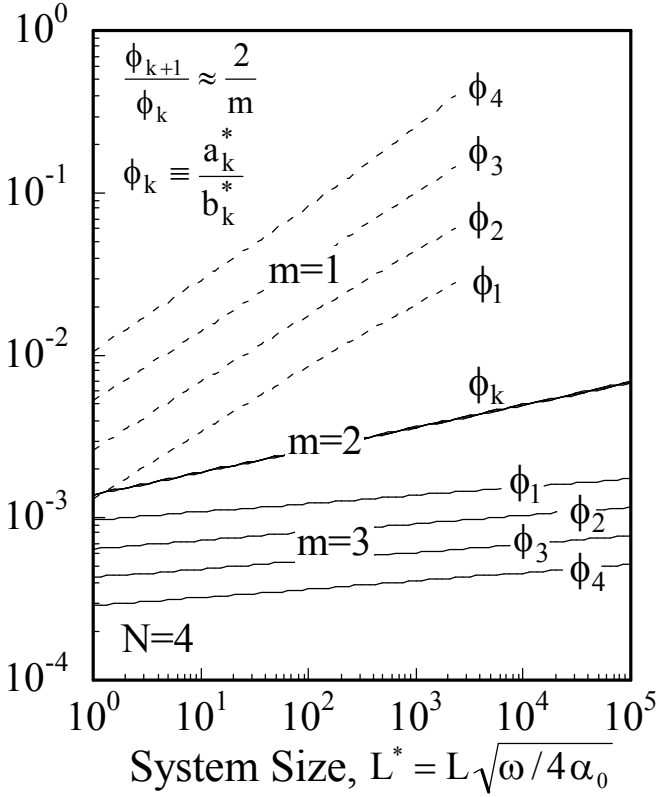
# Network has a fractal structure only for quadratic dependence of diffusivity on pore size

- **Porosities indicate ratio of channel width to channel spacing**
- **Uniformity across all scales --**
  - indicates fractal structure
  - holds only for m=2
- **m=2 is the only case where equality of time constants is consistent with equality of porosities across all scales**

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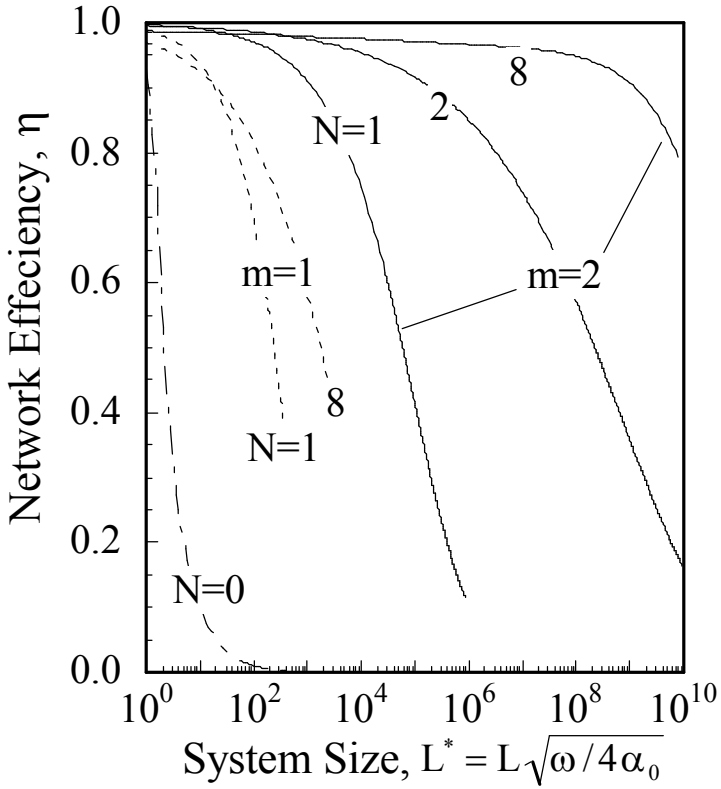
# Benefits of hierarchical networks

- **Transport efficiency is figure of merit**

$$\eta \equiv \frac{\text{actual discharge}}{\text{maximum possible}}$$

- **When diffusivity depends weakly on aperture (e.g. m=1)**
  - maximum benefit is:
    - ~ $10^2$ larger size
    - ~ $10^4$ faster response

- **Benefit increases dramatically when diffusivity depends more strongly on aperture**
  - may be even greater when physics change with scale

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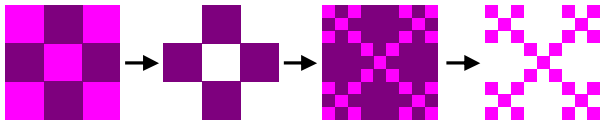
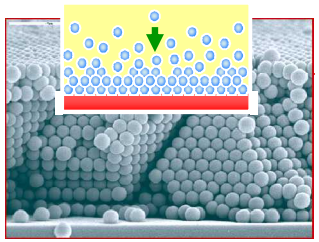
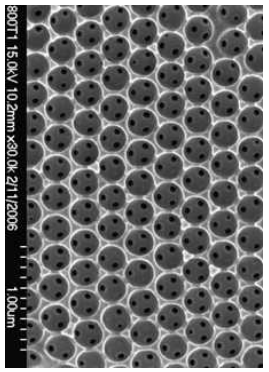
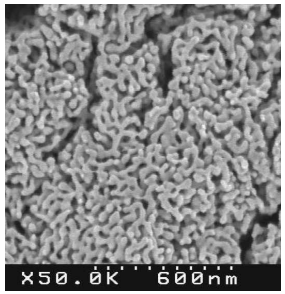
# Sandia & UIUC are developing methods for fabrication of hierarchal nanoporous materials

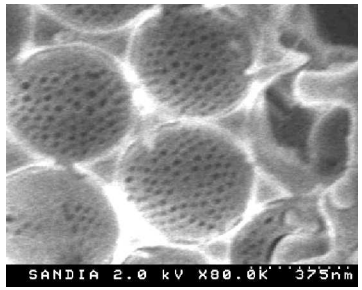
- **Approach:**
  - iterative templating
  - phase separation
  - removal and replacement
- **Larger scale**
  - polymer spheres are assembled on conducting substrate
  - silica is formed between spheres and spheres are removed
- **Smaller scale**
  - bottom left: gold-silver alloy is electroplated into template and silver is chemically removed to form pores
  - bottom right: Block copolymers are infused in template, annealed, and chemically stripped of one block





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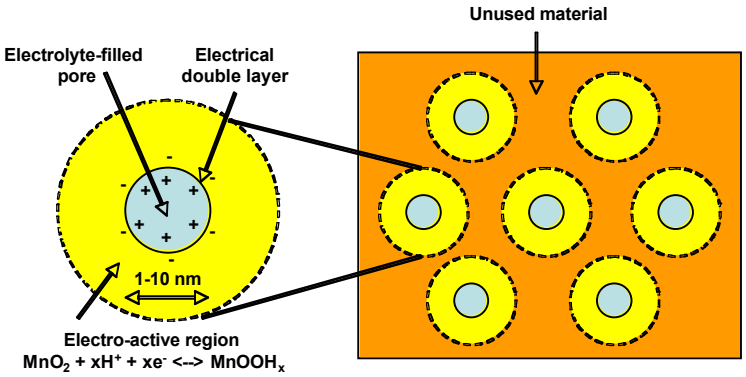
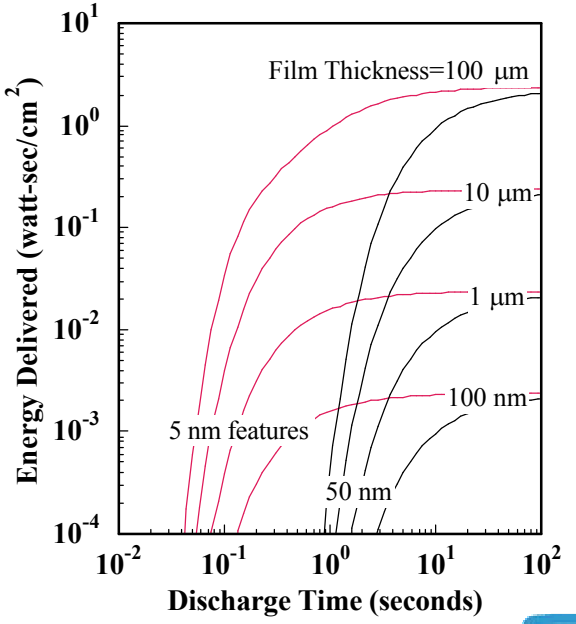
# Ultracapacitor LDRD project is exploring new classes of electroactive materials

- **Thin films in initial experiments**
- **Find a replacement for $RuO_2$**
  - more pseudo-capacitance
  - faster response
  - less cost
- **Nanometer feature scale --**
  - reduces proton diffusion distance
  - enhances participation of electroactive oxide
- **Modeling studies establish relationship between--**
  - material properties and structure
  - device energy and power density
  - cyclic voltametry studies of candidate electroactive materials

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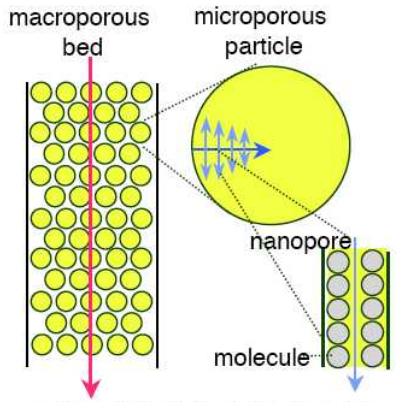
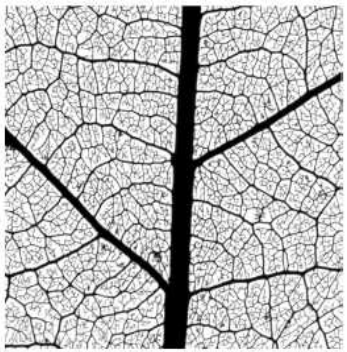
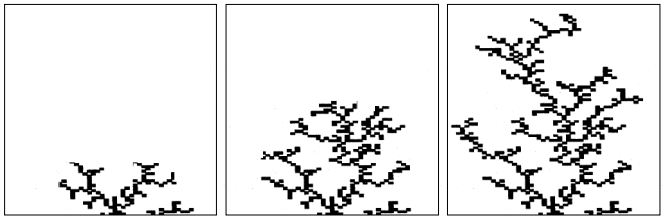
# New Directions

- **Extending modeling to include isotope exchange kinetics for storage of hydrogen species in metal hydrides (new ESRF project)**
- **Research proposal submitted to BES Office of Advanced Scientific Computing**
  - multiscale modeling
  - parallel processing
  - network evolutionary algorithms
    - vascular and dendritic
- **Comparison with experimental studies**



Laguna, PhysBio-Phys 07



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# Publications and Presentations

"Influence of atomistic physics on electroosmotic flow: an analysis based on Density Functional Theory," ***Journal of Chemical Physics***, 125 (16): No. 164510, 1-13, Oct 2006.

"Charged Species Transport, Separation and Dispersion in Nano-Scale Channels: Autogenous Electric Field-Flow Fractionation", ***Analytical Chemistry***, 78 (23): 8134-8141, Dec 2006.

"Optimizing Multiscale Networks for Transient Transport in Nanoporous Materials," R. H. Nilson and S. K. Griffiths, ***Nanotechnology 2008***, ISBN: 978-1-4200-8511-2, Vol. 3, Boston, June 2008

.

"Optimizing transport in materials having two scales of porosity," submitted to ***Phys. Rev. E***., September 2008.

"Hierarchical transport networks optimized for dynamic response," submitted to ***Phys. Rev. E***., October 2008.

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