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# *Multiscale Transport in Heterogeneous Materials*

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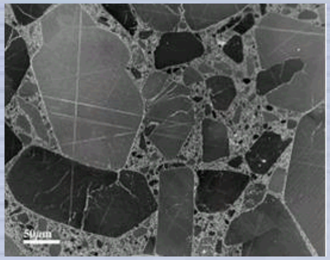
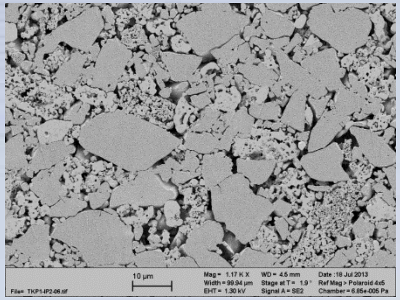
# Background and Introduction

- **Need better prediction and design-control of, e.g.,**
  - Formation of critical ignition kernel in energetic materials
  - Yield and fracture in solid mechanics



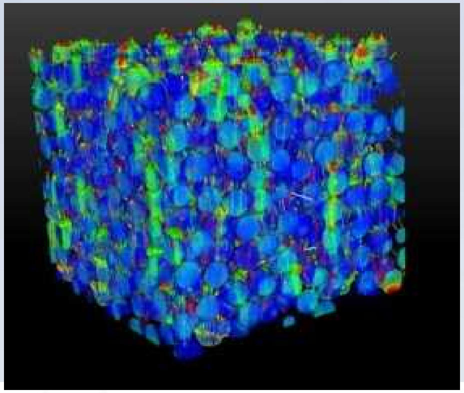
HMX micrograph

- **Complex-structured Materials**
  - Inhomogeneous, “discontinuous”, disordered
    - Microstructure varies in space and time: multi-scale
      - multi-crystalline, multi-phase, multi-component → interfaces

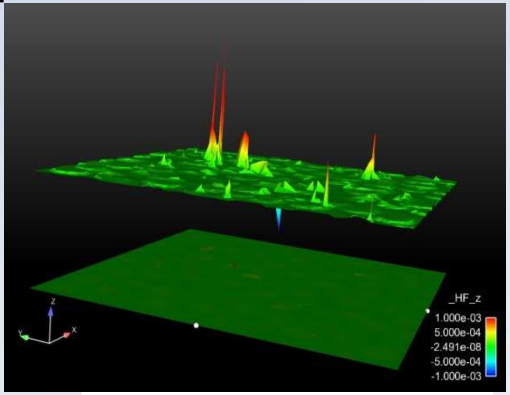


Pyro micrograph

- **Complex Multi-physics processes**
  - **Coupled matter, momentum, energy balances in complex materials driven far from equilibrium**
    - Transport processes vary across space and time *scales*
    - Generalized Stochastic Processes



Heat flux *in* granular material




Heat flux across plane

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# Transport in Complex Structured Materials: Interface of Materials and Engineering Sciences

- **Diffusion underlies all irreversible, non-equilibrium transport processes**

$$\frac{\partial f}{\partial t} = k\nabla^2 f$$

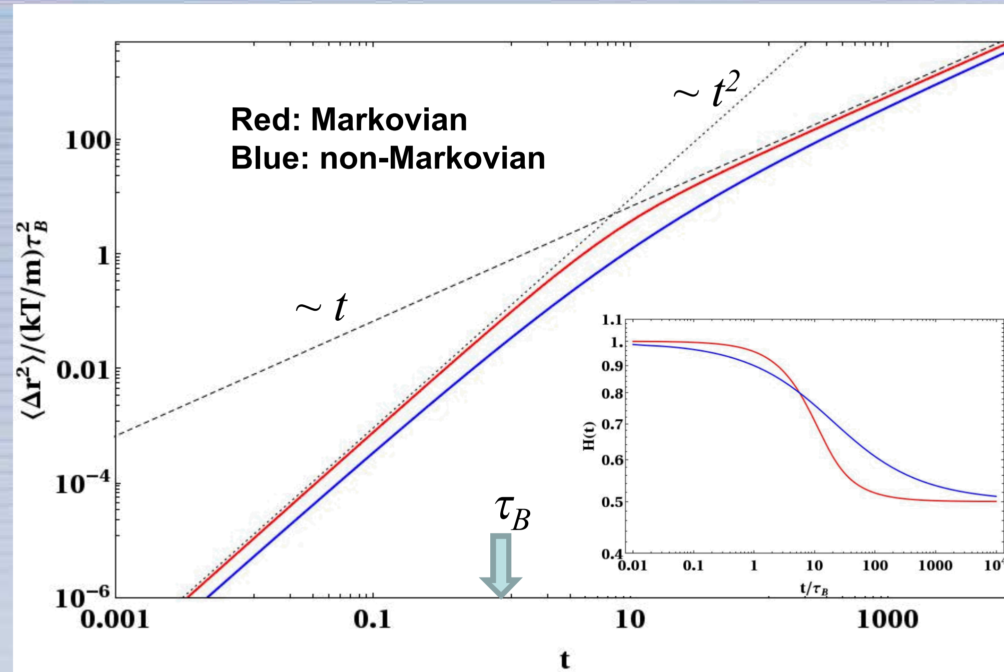
$$\frac{\partial f}{\partial t} = \nabla \cdot [\mathbf{j}]$$

  - Linear, phenomenological constitutive relations
    - Fick's (Second) Law (mass transport)
    - Fourier's Law (thermal conduction)
    - Hooke's and Newton's Laws (momentum transport)

$$\mathbf{j} = k\nabla f$$

  - Valid in long length/time limit (beyond correlation length/time scales)
- **Where do these break down?**
  - Complex-structured materials: multiple, competing length/time scales
    - Inhomogeneities: fluctuations about macroscale, homogeneous response
    - No clear scale separation: "meso-*scale*"
      - How to handle these regions where correlations still present?
  - Systems far from equilibrium
    - fluctuations and instabilities: cascade processes → "Complexity" and "Emergent Phenomena"

# When does scale matter?
# Ans: When you have one




- **Cannot measure absolute length**
  - only scale ratios have physical meaning
- **Diffusion is "scale free"**
  - $MSD \sim t$
- **Introduce a time scale**
  - Momentum relaxation timescale, $\tau_B$
  - consistent with classical, Newtonian particle dynamics on small time increments
- **Solve and obtain mean-squared displacement vs. time**
  - Defines long-time limit, $t >> \tau_B$
    - $MSD \sim t^{\alpha(t)}$; $\alpha = 2,\ t << \tau_B$ and $\alpha = 1,\ t >> \tau_B$
  - Introduces "meso" region, $t \sim \tau_B$

# The Multi-scale Transport Picture *through* Particulate Media

(2) Sub-particle materials structure

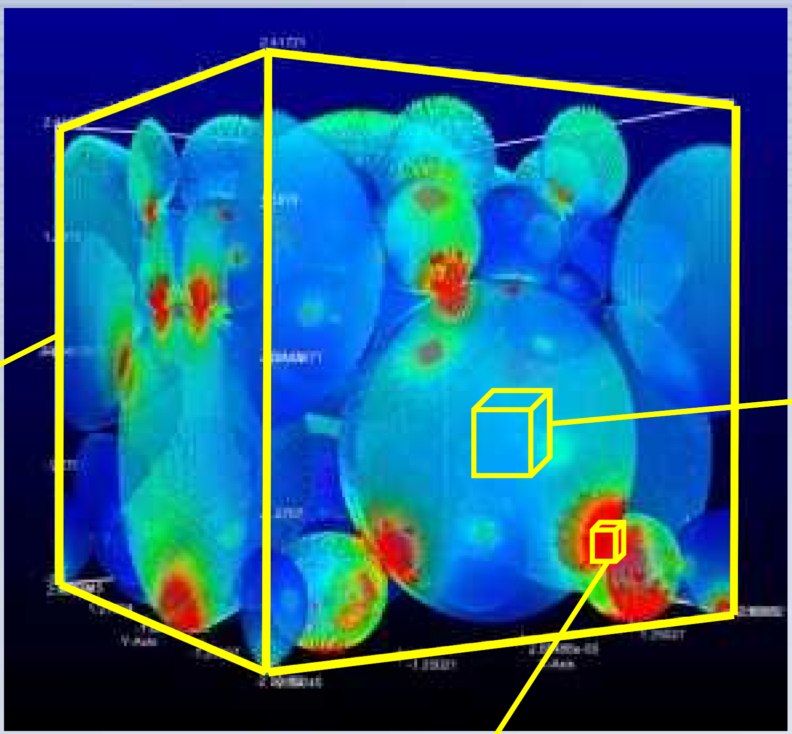
- Crystal structure
- Anisotropy
- Polycrystallinity
- Grain boundaries, defects, impurities (disorder)

(4) Homogeneous Macroscale

- "Continuum"
- "Smoothly" varying fields
- Constant transport coef.

$$\frac{\partial f}{\partial t} = K_{eff} \nabla^2 f = \nabla \cdot \mathbf{j}$$

$$\mathbf{j} = K_{eff} \nabla f$$



(3) Particle-Particle Microstructure Scale

- Inhomogeneous, "discontinuous"

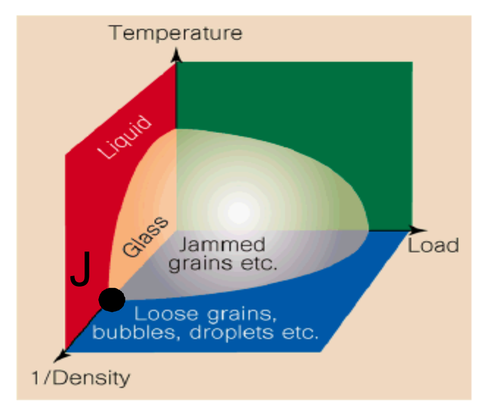
$$\frac{\partial f(x,t)}{\partial t} = \nabla \cdot \left[ K(x,t) \nabla f(x,t) \right]$$

- Disordered
- "Anomalous" transport

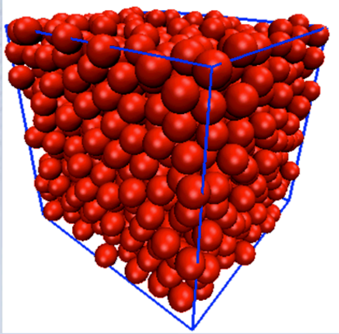
(1) Interfacial Scale

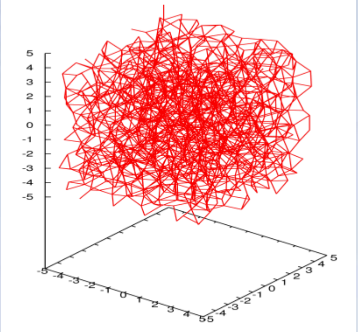
- Contact area, roughness, interdiffusion (disorder)
- Material types (phonon, electron transport dominated)

# Bridging the Particle-particle Microstructural to Homogeneous Macro scales

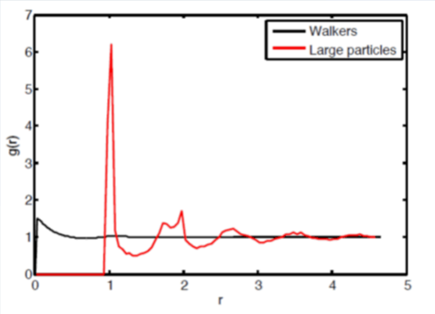


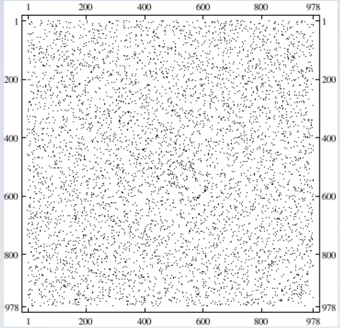

- **Transport near "Point J"**
  - Critical-like "point" of marginal mechanical stability
    - Control of microstructural length scale
  - Random walks on particle microstructures near "J"
    - Model for "failure" with respect to transport





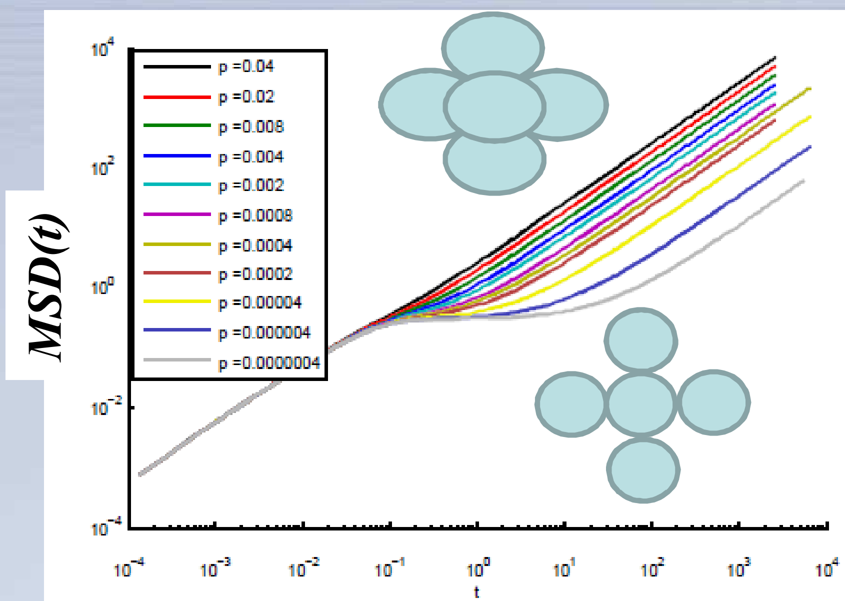
- **Random Walker Simulations**
  - Random walkers initially uniformly distributed within particles
  - Particles conducting; voids insulating
    - Reflecting (specular) BC at interface
      - Neumann-like
  - Global periodic simulation domain
    - Fluctuating homogeneous system
      - Size of fluctuations related to number of walkers

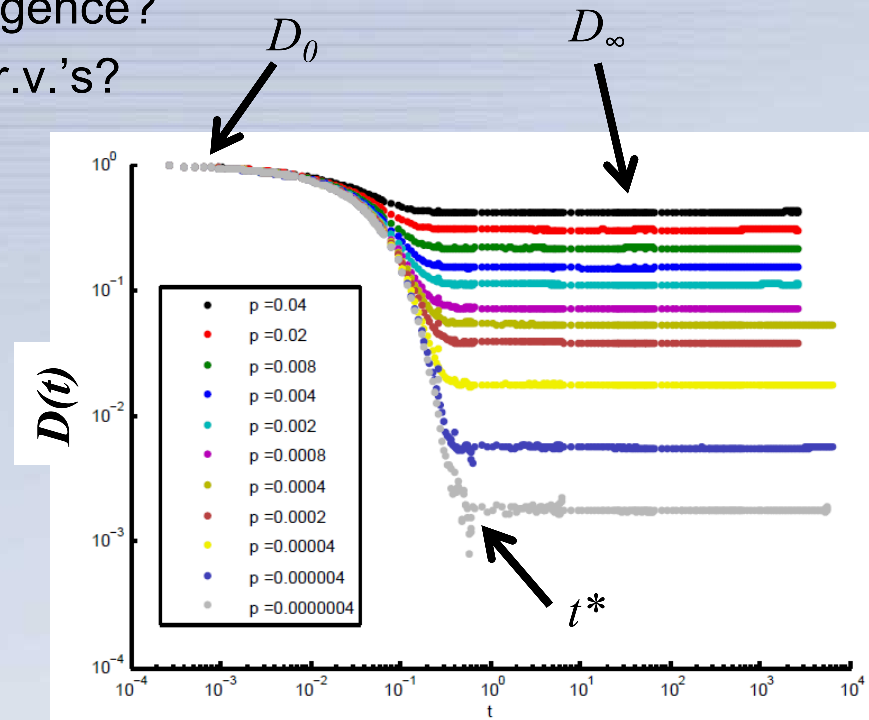


# Conduction in Inhomogeneous Microstructure

- **Random Walk in a Random Environment**
  - Law of large numbers?
  - CLT (Homogenization)?
    - Convergence? Rate of convergence?
    - Sums of non-i. and/or non-i.d. r.v.'s?



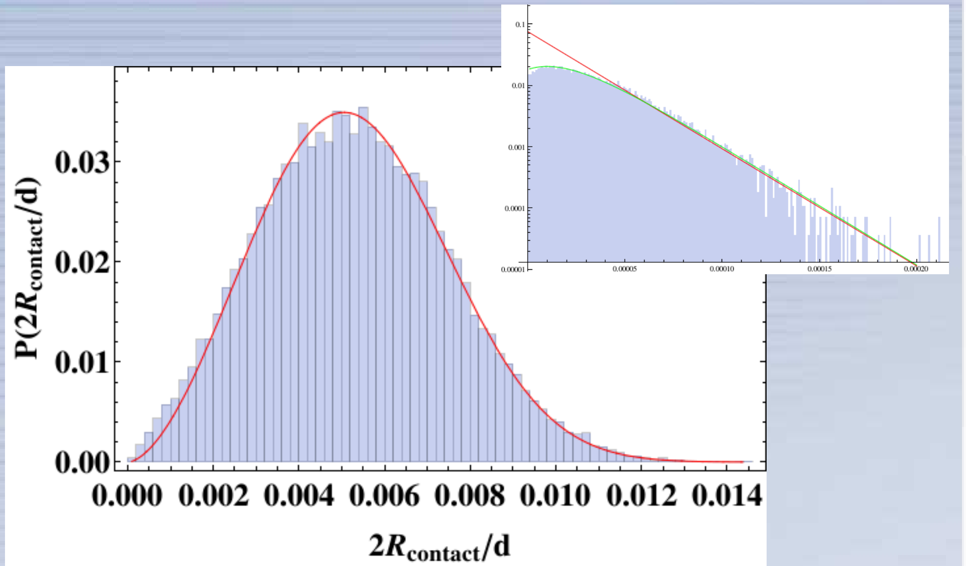



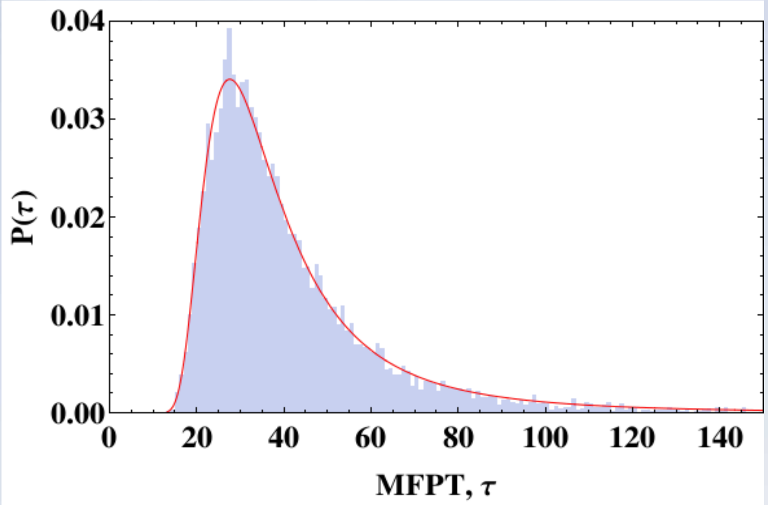
# Microstructural Details: Interfaces

- **Difference from, say, SC lattice: "Disorder"/Inhomogeneity**
  - Distribution of "overlaps"
  - Distribution of contact radii
  - Distribution of volume-averaged MFPT
    - Narrow Escape
      - Single and multiple contacts in well separated limit ($a << d$)

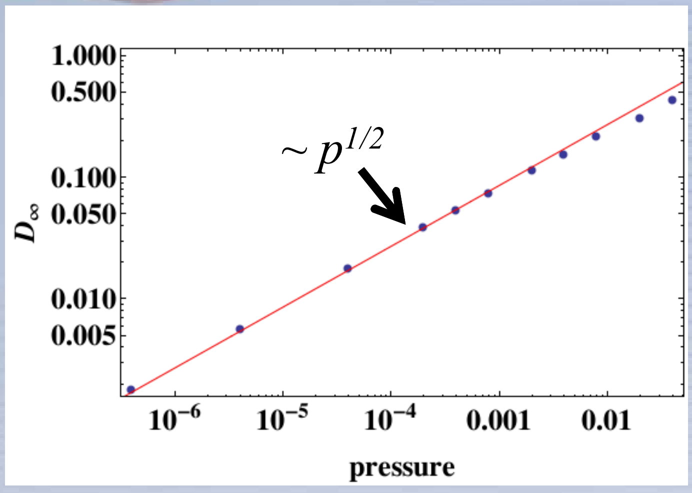
$$\bar{\tau} \sim \frac{1}{a}$$

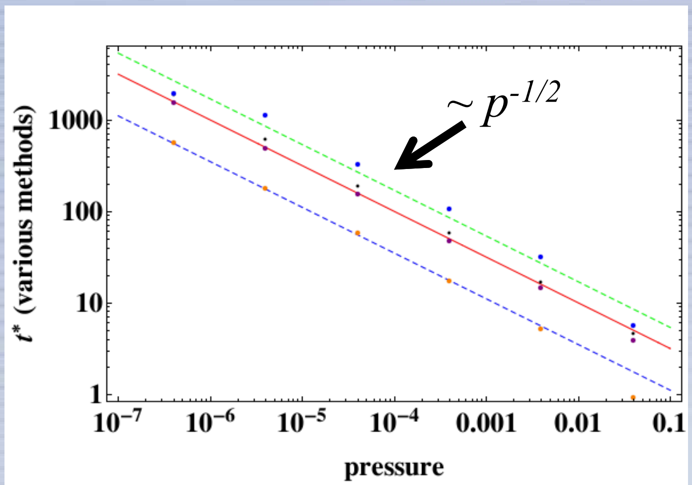
$$\bar{\tau}_{z_i} \sim \sum_{j=1}^{z_i} \frac{1}{a_{ij}}$$

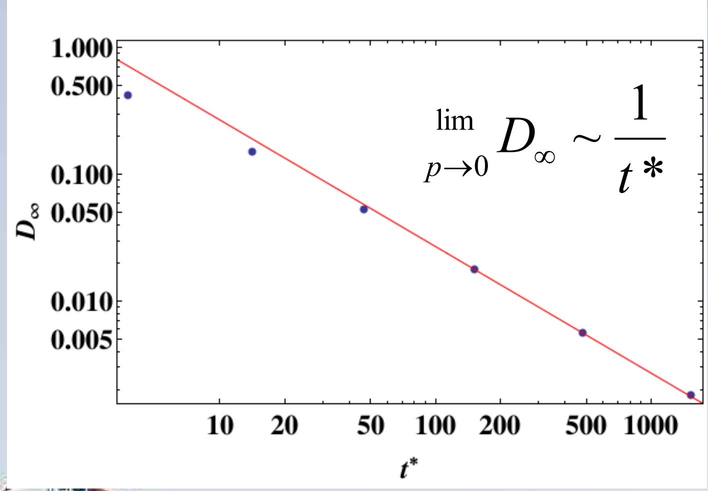


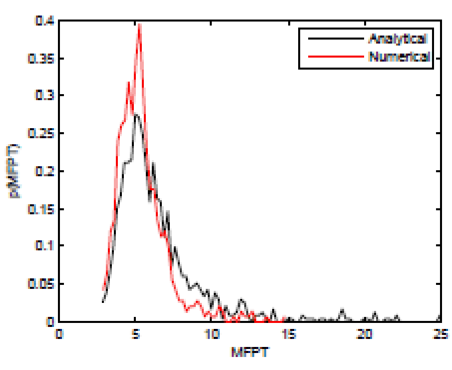



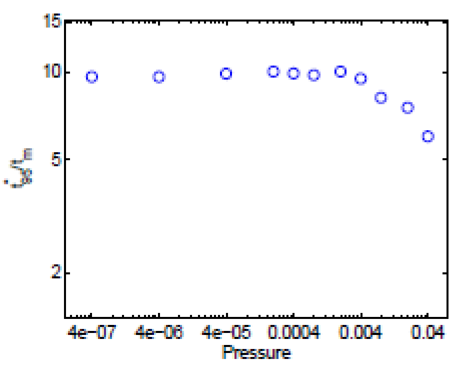
# Scaling Results



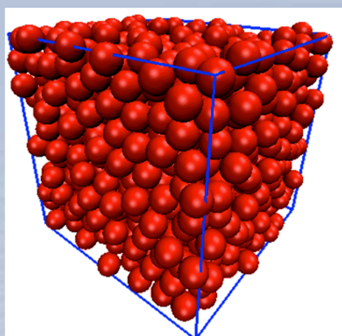



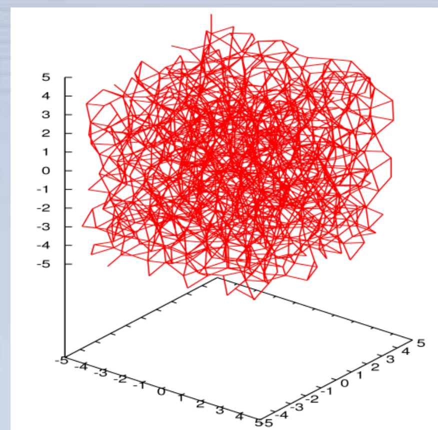
# "Coarse-graining" Workflow: Discretizing the Mesoscale

- **Continuum percolation-type viewpoint + Spectral Graph Theory**



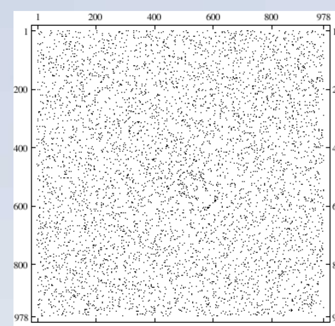
Determine segmentation: clustering (similarity relation, e.g., greyscale) & connectivity (distinction relation, e.g., proximity relation)

Image stack, or simulated μstructure




graph of contact network

Determine: edge weights (interfacial resolution and physics models)




Graph Laplacian, Transition Probability Matrix, Transition Rates, etc.

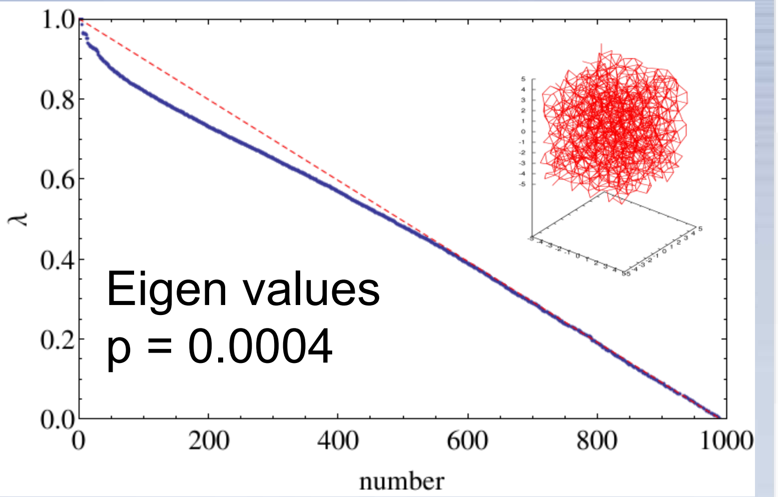
# "Coarse-grained" Equation on Contact Network

- **Transition Probability Matrix**

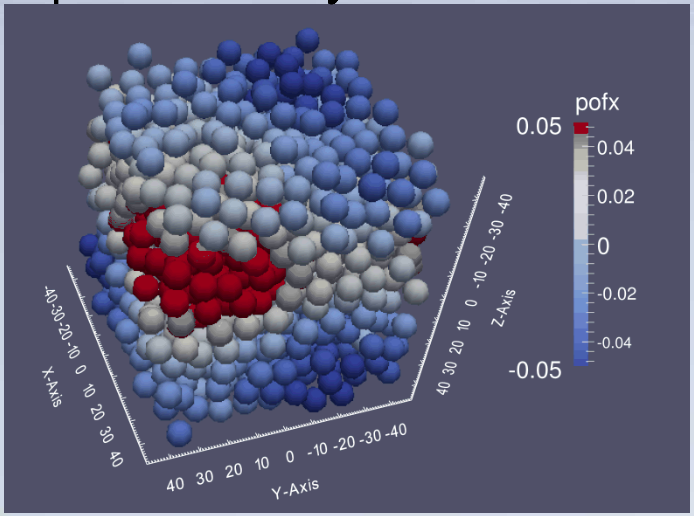
$$M_{ij} = \begin{cases} \dfrac{3D\Delta t}{\pi R^2}\sqrt{\delta_{ij}/R} & i \neq j \\ 1 - \sum_{j \neq i} M_{ij} & i = j \end{cases}$$

Thermo-mechanical nonlinearity

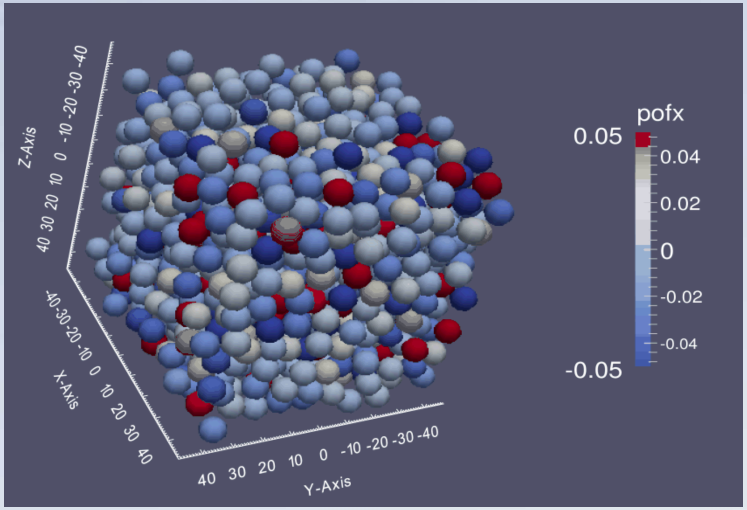
$$\delta_{ij} = 2R - \left\| \mathbf{r}_j - \mathbf{r}_i \right\| \geq 0$$




- Spectral analysis




Eigen mode for large λ



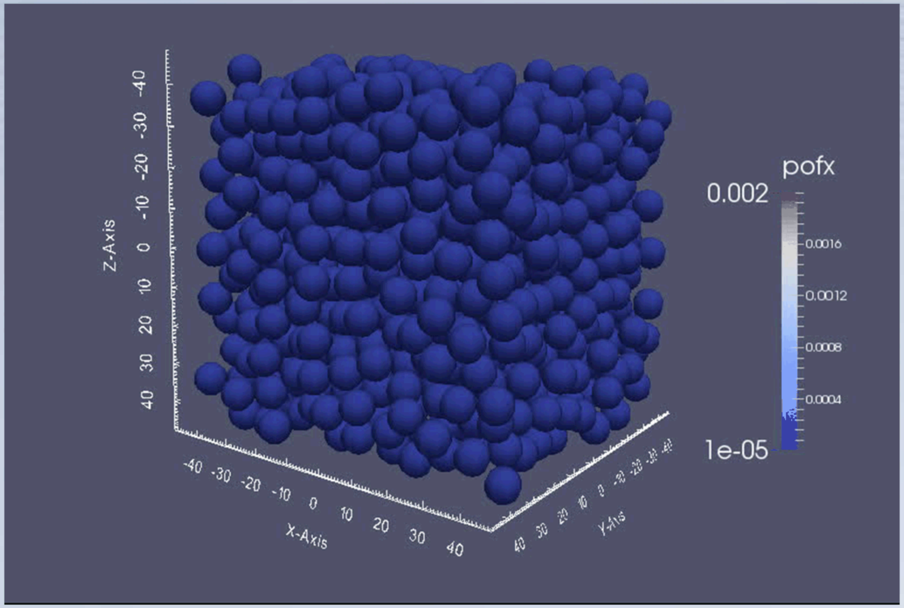

Eigen mode for small λ

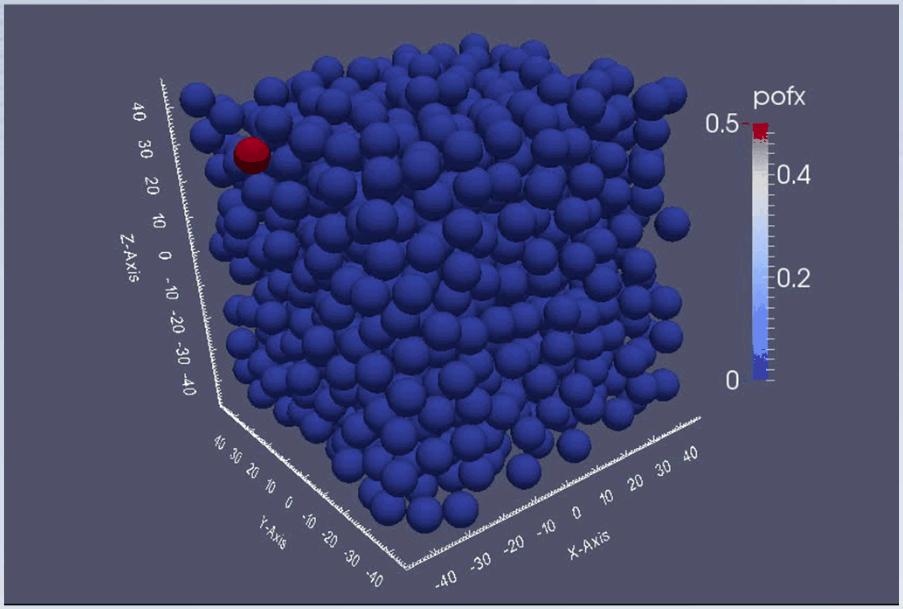
# Discrete Master Equation (RW) on Contact Network

- **Markov Process on contact network**

$$\mathbf{P}_{n+1} = \mathbf{M}\mathbf{P}_n$$

  - I.C. $\mathbf{P}_0 = \hat{\mathbf{e}}_1 \qquad \left\|\hat{\mathbf{e}}_1\right\| = 1$



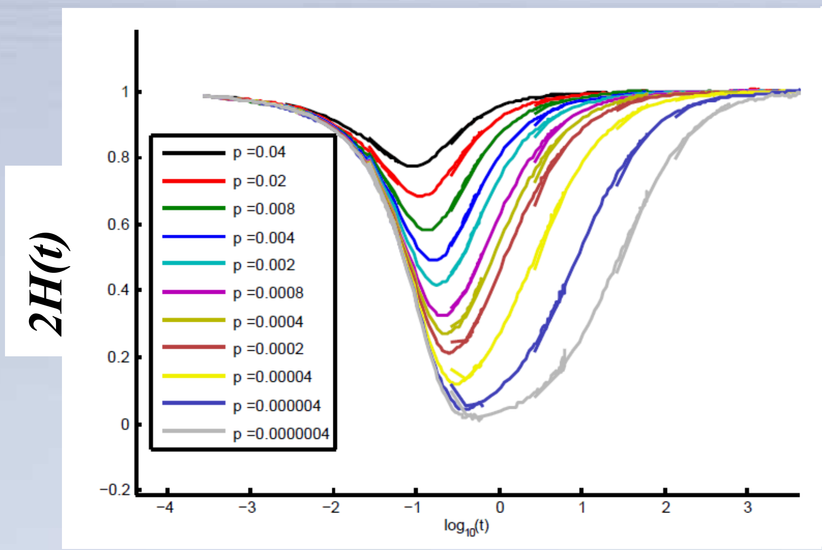

p = 0.0004

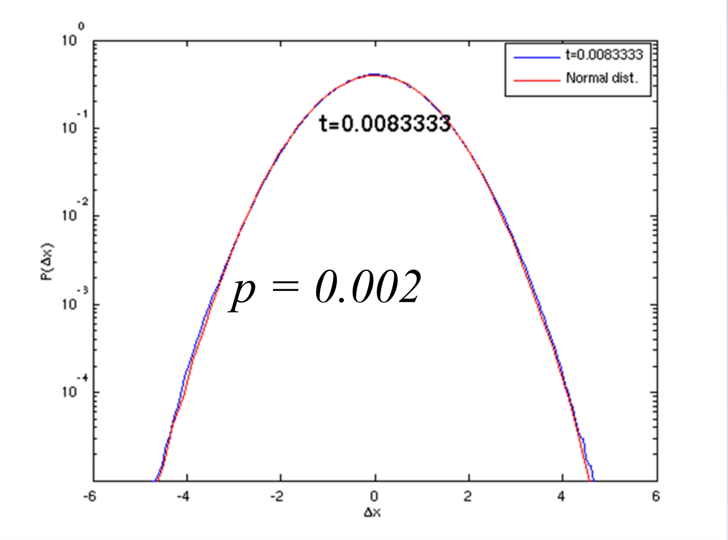
p = 0.00004

# Non-Fickian and Non-Gaussian Transport

- **Fickian** → $MSD \sim t$
  - Here $MSD \sim t^{2H(t)}$

- **Gaussian** → $P(\Delta x, \Delta t) = \frac{1}{\sqrt{2\pi D \Delta t}} \exp\left[ -\frac{\Delta x^2}{4D\Delta t} \right]$

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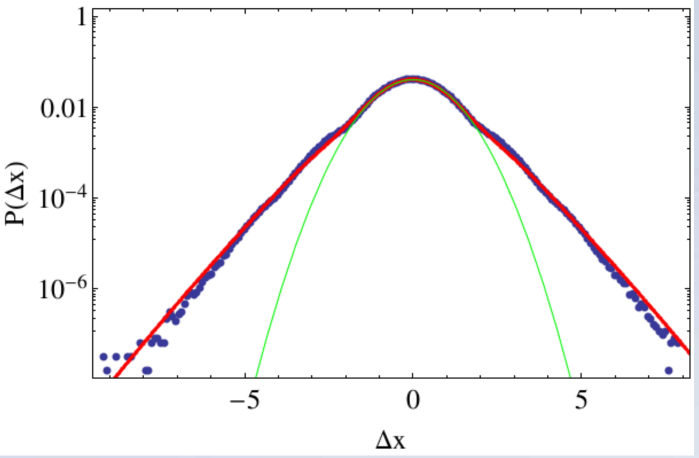
# CTRW and GME

- **Consider CTRW a la Montroll and Wiess (cf. Chaudhuri et al. (2010) PRL, v.99 , p.060604 )**
  - Conditional probability of walker being at position $r$ at time $t$ (van Hove function)

$$G_s(k,s) = f_{vib}(k)\left[\frac{1-\phi_1(s)+f(k)\big(\phi_1(s)-\phi_2(s)\big)}{s(1-\phi_2(s)f(k))}\right]$$

$$f(k) = f_{vib}(k) f_{jump}(k)$$




$$f_{vib}(k) = \left(2\pi\ell^2\right)^{-3/2}\exp\left(-r^2/2\ell^2\right)$$

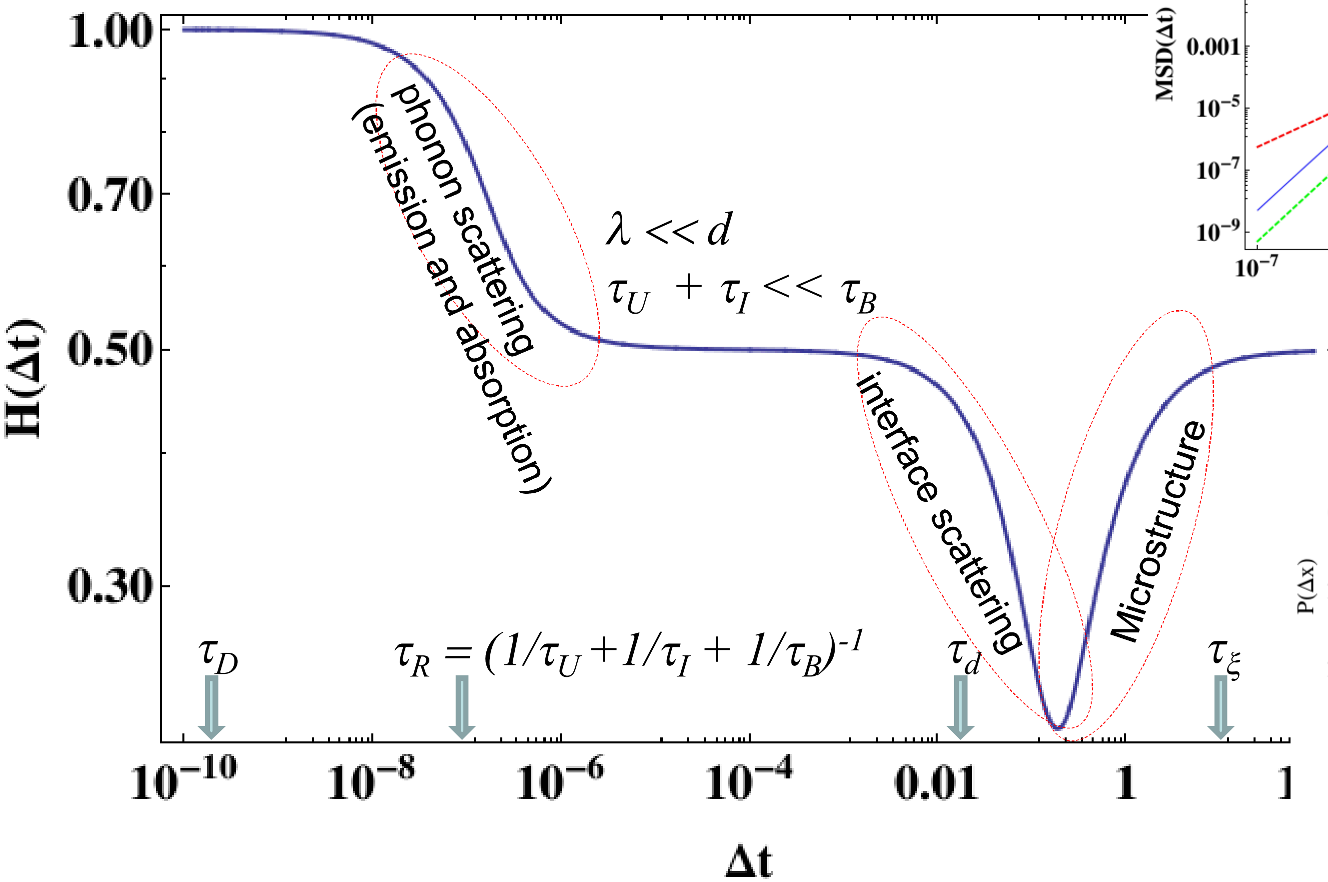
$$f_{jump}(k) = \left(2\pi\lambda^2\right)^{-3/2}\exp\left(-r^2/2\lambda^2\right)$$

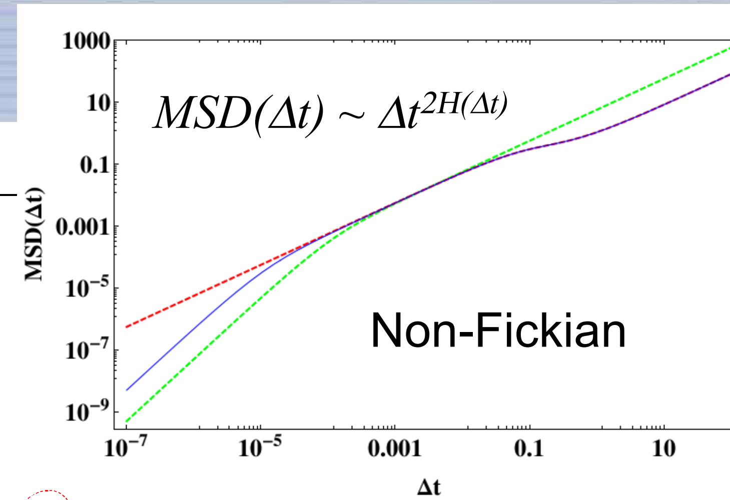
$$\phi_1 = \tau_1^{-1}\exp\left(-t/\tau_1\right)$$

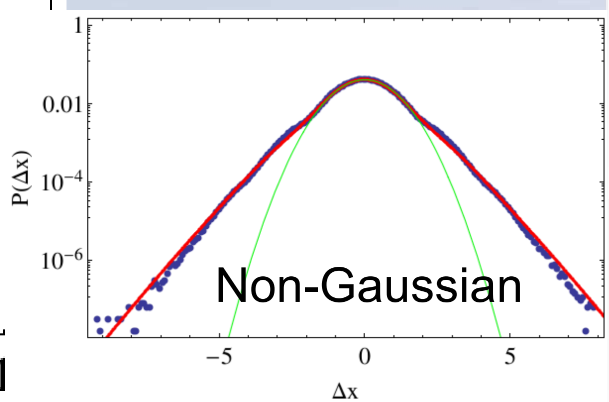
$$\phi_2 = \tau_1^{-1}\exp\left(-t/\tau_2\right)$$

  - Equivalent to GME

# Summary: Bridging Scales…




cf. K. Razi Naqvi and S. Waldenstrom (2005) *PRL* **95**, 065901

# Conclusions

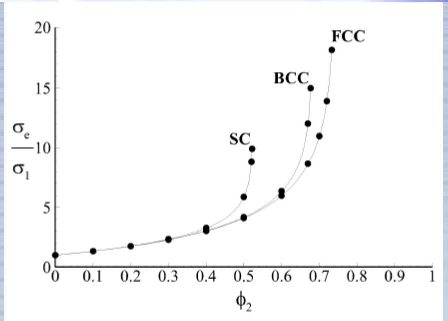
- **Transport in inhomogeneous/heterogeneous materials can manifest multiple scales**
- **GME/CTRW approaches can be applied to bridge scales**
  - Non-Fickian
  - Non-Gaussian
- **Coarse-graining approaches are possible on discrete material structure**

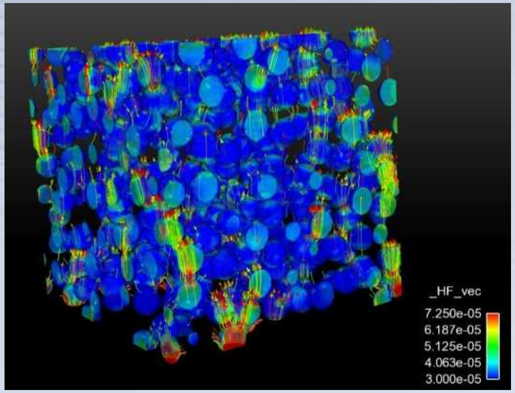
# Acknowledgements

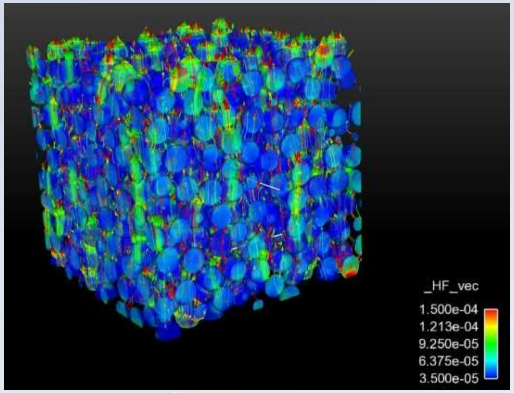
- P. R. Schunk
- Leo Silbert, Gary S. Grest
- Stephen Bond, Rich Lehoucq

# Effective Thermal Conductivity of Particle Dispersions: Process to Property

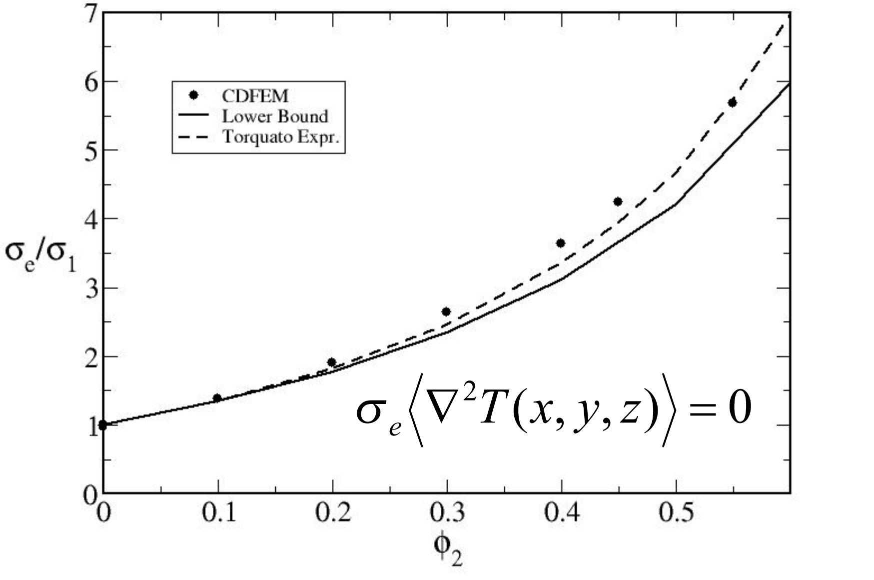
- **Verification of CDFEM for Average thermal conductivity in static random dispersions**
  - Particle configurations taken from Brownian Dynamics Simulations of Repulsive Colloids
  - Suspending fluid insulating, particles conductive (ratio of conductivities ~ 1000)




$$\left\langle \nabla \cdot \left( \sigma(x,y,z) \nabla T(x,y,z) \right) \right\rangle = 0$$




$$\sigma_e \left\langle \nabla^2 T(x,y,z) \right\rangle = 0$$

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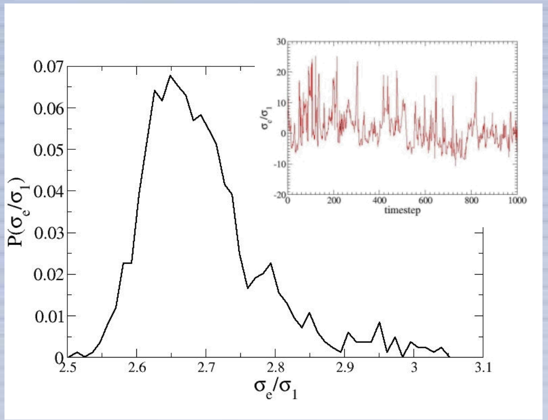
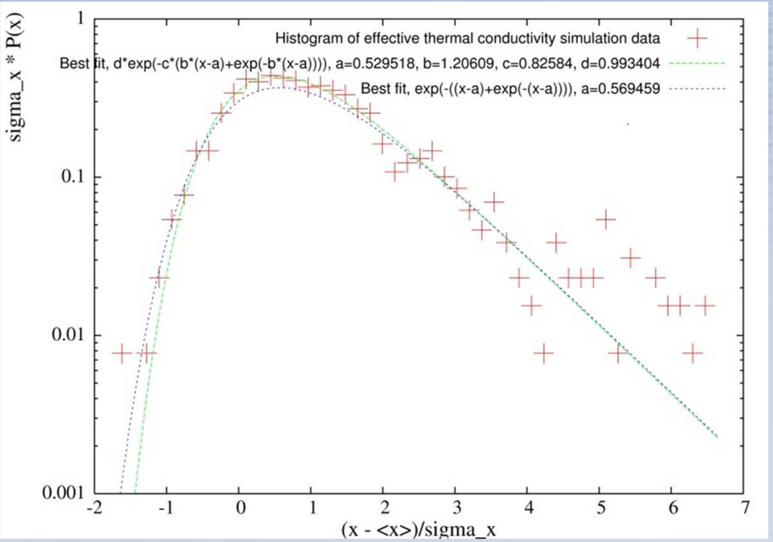
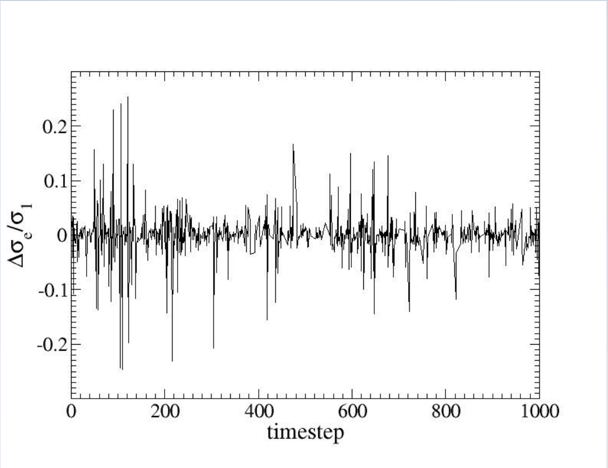
# Statistics of Effective Conductivities

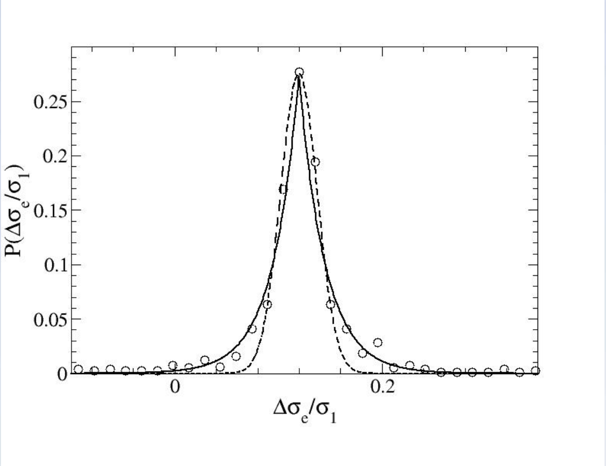
- **Distribution of conductivities**
  - Asymmetric
  - Broad tail to high values



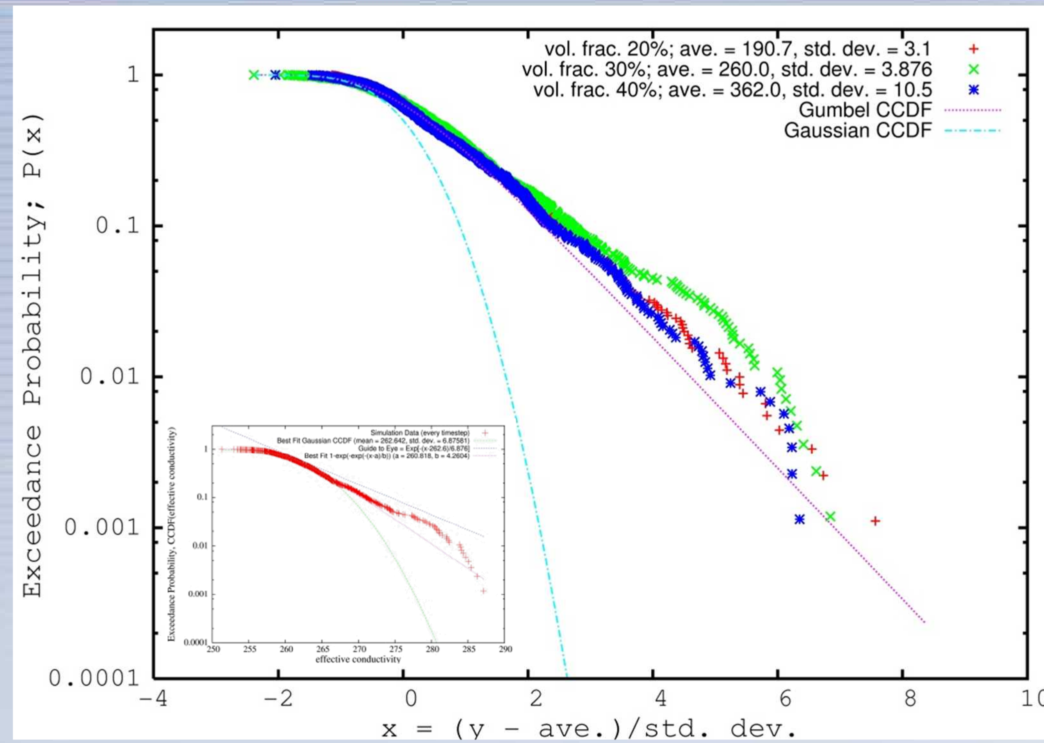




- **"Increments" and their distribution**
  - Volatile
  - Non-Gaussian



# Exceedance Probability (Survival Function)




- **Based on sampling ~1000 μstructures**
  - "Aleatory" Uncertainty only
- **What is "irreducible" about this uncertainty?**
  - Note Gumbel distrib. and extreme-value-type statistics
    - "medium tailed", between Frechet and Wiebul
- **What are sources of epistemic uncertainty?**
    - Micro-structure resolution, thermal conductivity measurement

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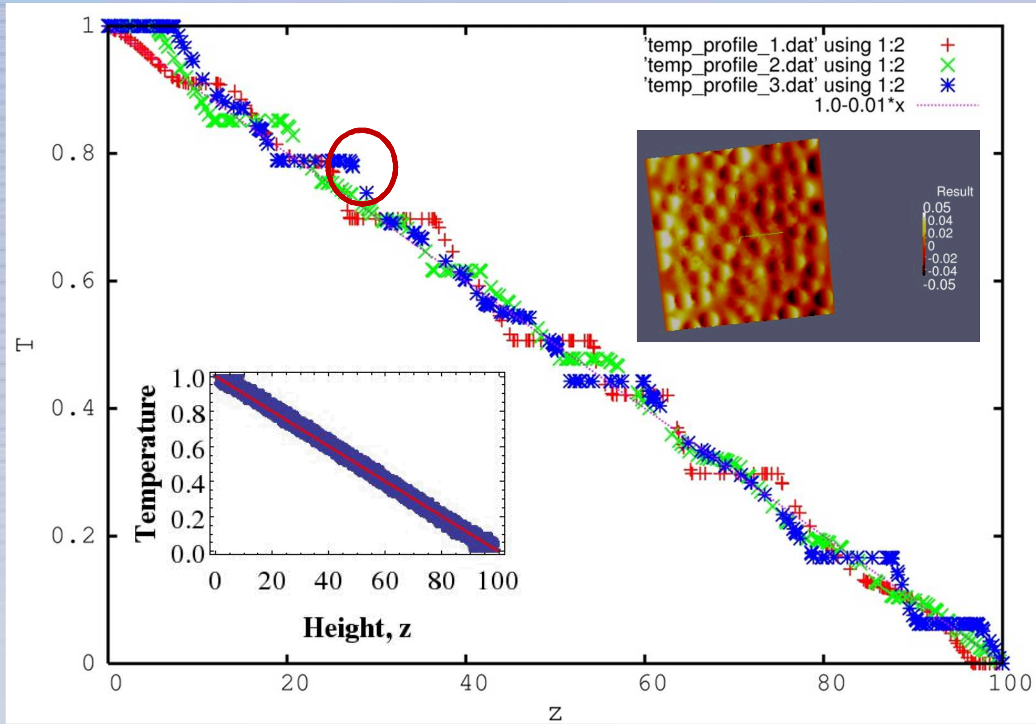
# Temperature Profiles: Thermodynamics and Fluctuations

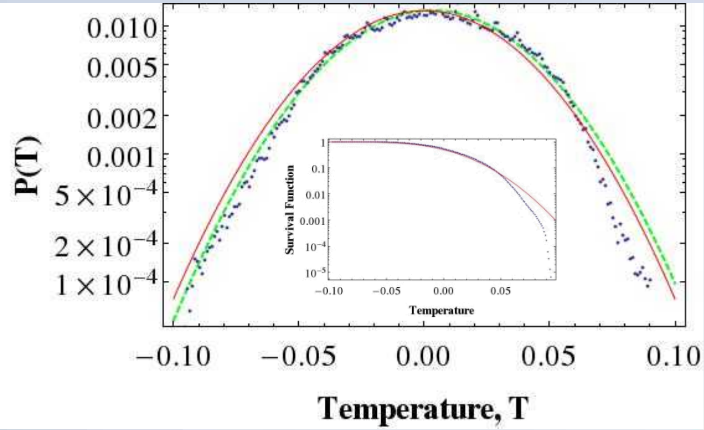
- Random "Stair-step" temperature profiles
  - Yield "fluctuating" temperature field
- A non-equilibrium thermodynamic fluctuation theory gives

$$P(\delta T) \sim \mathrm{Exp}\left[-\frac{1}{2k_B}\int \frac{c_v^0}{T_0^2}(\delta T)^2\, dV\right]$$

$$T_0(z) = 1.0 - 0.01z;\ \delta T = T - T_0$$

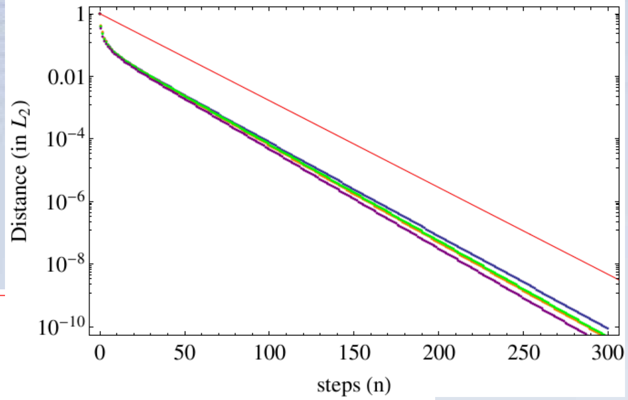
  - Fit temperature fluctuations to Gaussian Distribution
    - $\sigma \approx 0.03$

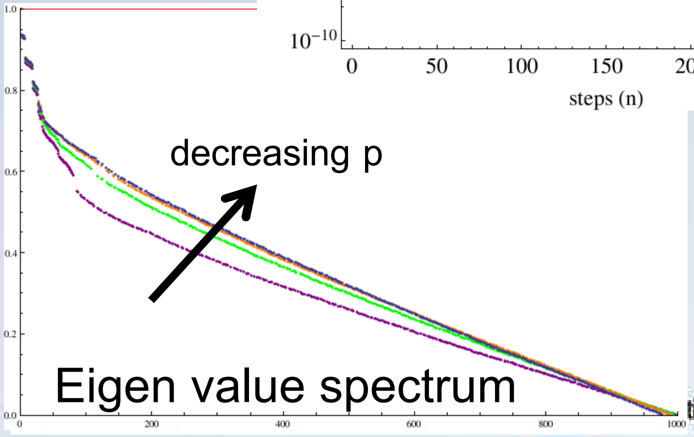


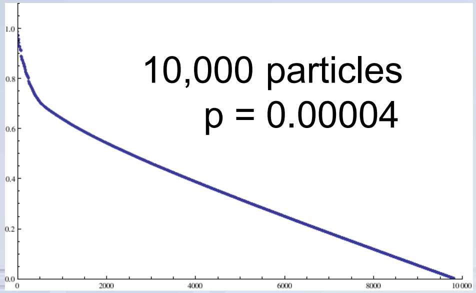



# Contact Network Properties

- **Walk on network ("myopic ant")**
  - Define master equation on contact network
    - Transition Probability Matrix
      - Primitive => Strongly connected => Ergodic
        - » Steady-state exists and is (weakly) inhomogeneous
          Conditional probability of finding a walker in a particle after long time not constant for all particles
        - » Rate of convergence given
    - *MSD ~ number of steps*
      - Relationship to homogenized limit (or CLT)?



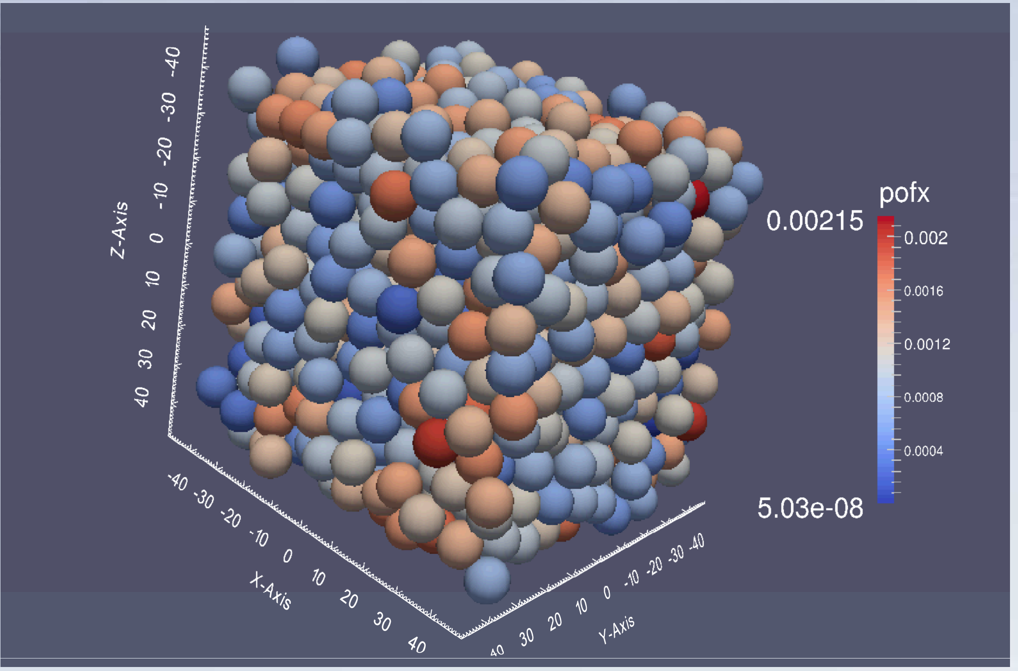



# Inhomogeneous Steady State

- **Nonequilibrium**
  - Non-zero global flux
    - Asymmetric local transitions

$$M_{ij} \neq M_{ji}$$



# Thermodynamics and Homogenization

- **Necessary but not sufficient to consider homogenization (understood in my current naïve sense)**
  - How do we know that the homogenized limit is relevant from a stability perspective?
    - Prediction and “emergent” phenomena: e.g., phase changes (first and second order) and/or dissipative structures
  - What can we say about fluctuations away from asymptotic limit?
    - Role of Law of Large Numbers and Central Limit Theorem
  - Non-equilibrium phase transition and “self-organization”

- **Need non-Equilibrium Fluctuation Theory**

# Thermodynamics and Homogenization: the Local Potential

- **Consider boundary value problem**

$$\rho \frac{\partial}{\partial t} e = -W_{j,j} \qquad + B.C.\text{'s and } I.C.$$

$$W_j = \lambda(x_j) T^2 \left(T^{-1}\right)_{,j}$$

  - Following Glansdorf and Prigogine (1971)
    - Local equilibrium assumption
    - Linear irreversible processes
      - C.f., multiscale projection method of homogenization (Vogelius and Papanicolaou 1982)

$$\frac{1}{2}\frac{\partial}{\partial t}\left(\delta^2 S\right) = \frac{1}{2}\int \lambda T^2 \delta\left(T^{-1},_j\right)^2 dV \geq 0$$

  - Assume perturbation about steady state $\lambda T^2 = \lambda_0 T_0^2 + \delta\left(\lambda T^2\right)$

$$\frac{1}{2}\frac{\partial}{\partial t}\left(\delta^2 S\right) = \frac{1}{2}\int \lambda_0 T_0^2 \delta\left(T_{,j}^{-1}\right)^2 dV + \frac{1}{2}\int \delta\left(\lambda T^2\right)\delta\left(T_{,j}^{-1}\right)^2 dV$$

    - First term can be taken as a functional of $T$ and $T_0$ to be extremalized

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# Local Potential and Thermodynamic Stability

$$\frac{1}{2}\frac{\partial}{\partial t}\left(\delta^2 S\right)=\frac{1}{2}\int \lambda_0 T_0^2 \delta\left(T_{,j}^{-1}\right)^2 dV+\frac{1}{2}\int \delta\left(\lambda T^2\right)\delta\left(T_{,j}^{-1}\right)^2 dV$$

- **This is the excess entropy production**
  - Okay for thermodynamic equilibrium states or NESS near equilibrium (linear response region), but not okay far-from-equilibrium
- **First term taken as functional for variational problem**
  - Perturbation positive around reference state => absolute (global) minimum; always minimum at reference state
- **Second term *NOT* small (nor necessarily positive)**
  - When stability conditions hold, sign of local potential is same a excess entropy production; i.e., positive
  - Else reference solution given by first term is unstable
- **How can we obtain (approx.) lambda_0?**
  - periodic vs. random cell, boundary conditions, etc.

# Homogenization and the Local Potential: Approximating $\lambda_0$

- **Multiscale Projection** **following Vogelius and Papanicolaou (1982)**

$$I^{\varepsilon}(w) = \frac{1}{2}\int_{\Omega} \lambda\left(\frac{\mathbf{x}}{\varepsilon}\right)\left|w(\mathbf{x})\right|^2 d\mathbf{x} \qquad w(\mathbf{x}) = \bar{u} + \sum_{j=1}^{3} \varepsilon\chi\left(\frac{\mathbf{x}}{\varepsilon}\right)\bar{v}_j$$

  – If (1-periodic) cell functions $\chi_j(\mathbf{y})$ satisfy certain nondegeneracy conditions,

$$\bar{v}_j(\mathbf{x}) \xrightarrow{\varepsilon \to 0} \frac{\partial \bar{u}(\mathbf{x})}{\partial x_j}$$

  – And (away from boundaries),

$$\sum_{i,j=1}^{3} (\lambda_0)_{ij} \frac{\partial^2 \bar{u}_j}{\partial x_i \partial x_j} = f(\mathbf{x})$$

$$(\lambda_0)_{ij} = \int_0^1\int_0^1\int_0^1 \lambda(\mathbf{y}) \sum_{k=1}^{3} \left(\delta_{ik} + \frac{\partial \chi_i(\mathbf{y})}{\partial y_k}\right)\left(\delta_{jk} + \frac{\partial \chi_j(\mathbf{y})}{\partial y_k}\right) d\mathbf{y}$$

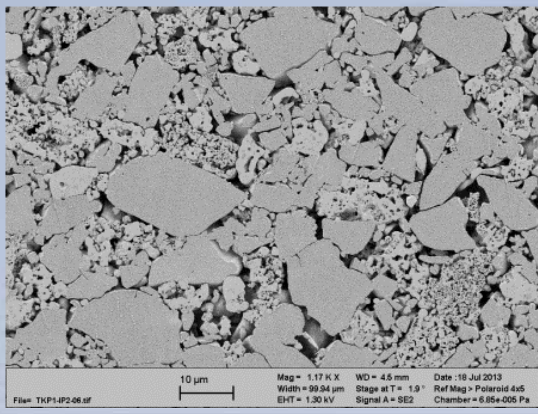
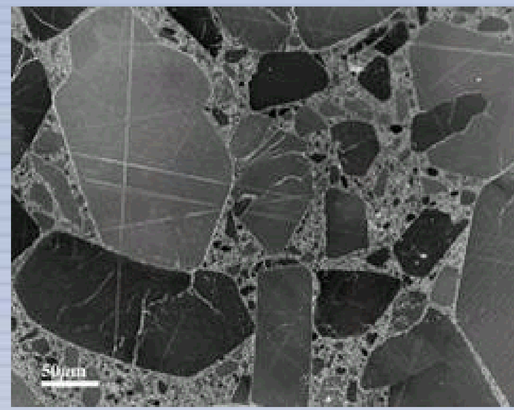
    - Again, what about stability?

# Materials Science Needs

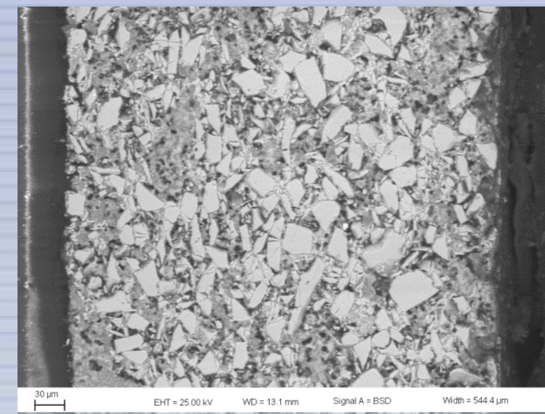
- **Multi-scale Transport**
  – Sub-particle materials structure
  – Interfacial structure and transport processes
- **Multiphysics**
  – Heterogeneous reactions
    - Multi-species nonequilibrium thermodynamic phase behavior of material constituents
      – Phase changes, melting, …
    - Role of Interfaces
  – Thermo-mechanical effects

# Meso-scale particle-based applications

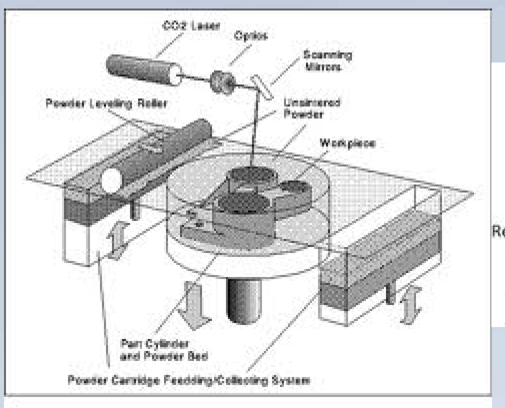
## Need particle scale mod-sim capability to predict microstructure formation and properties

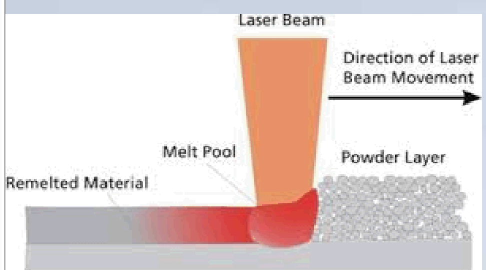



Energetic materials

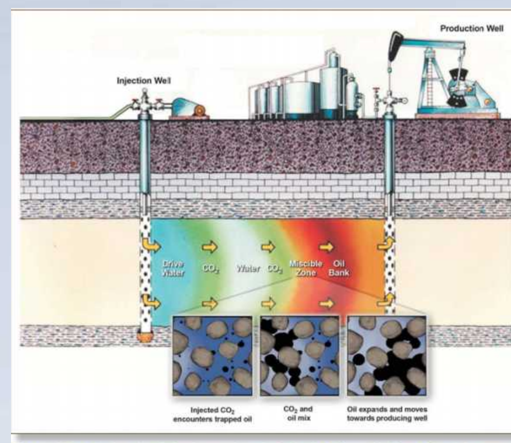


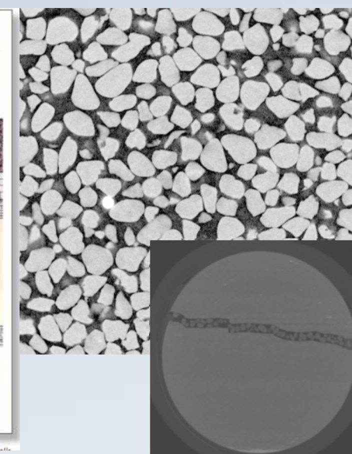
Energy storage




Additive Manufacturing: selective Laser melting/sintering



Waste repository: porous flow
Energy: fracking

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