This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2022-8408C

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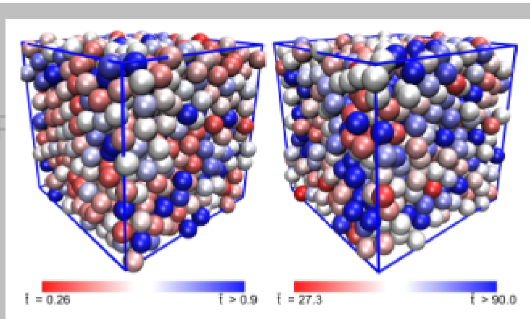

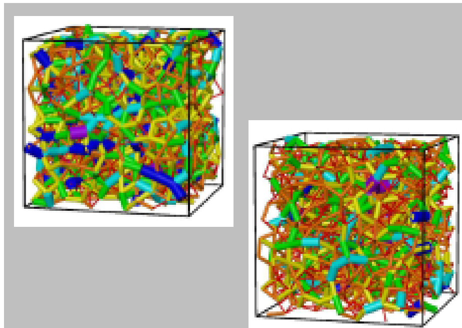

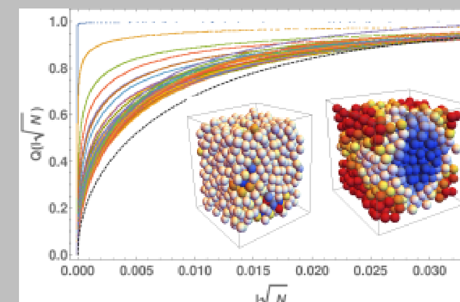

Thermal Runaway in Jammed Networks

Jeremy B. Lechman et al.

Fluid and Reactive Processes

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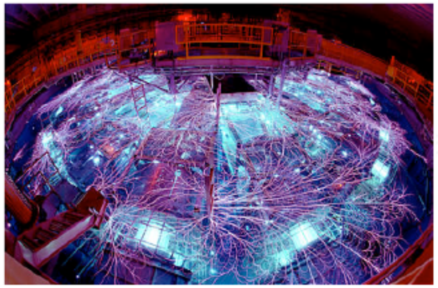
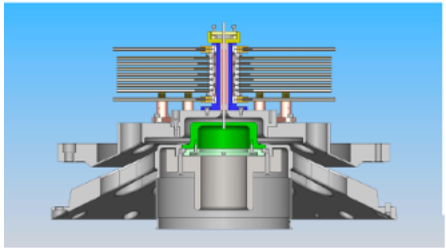
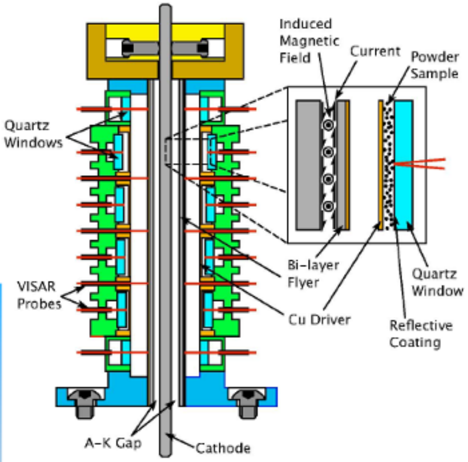
Granular Materials are Ubiquitous

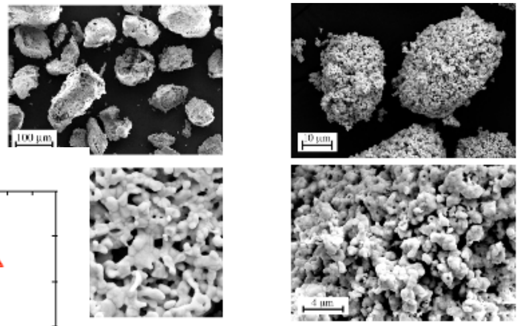
- Porous & granular materials important for many applications in HEDP
  - Iron oxide studied in context of planetary formation/impact
  - silica aerogel used to mimic liquid deuterium and impedance match target materials
  - New materials from extreme states of matter
  - New energy sources – ICF
- Shocked porous material reach higher temperatures at a given density – gives flexibility in accessing phase space

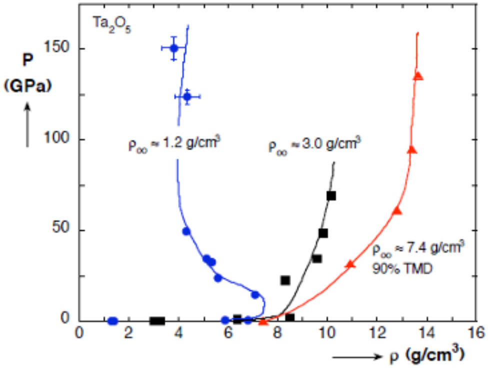






V = 9.9-10.3 and 11.2-11.4 km/s





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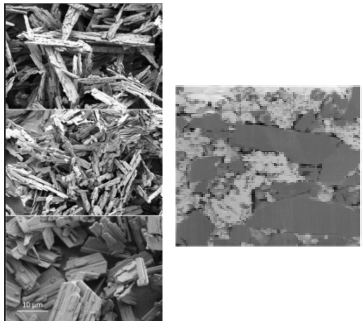
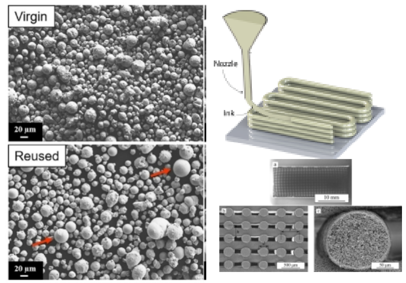
More Particulate Materials at SNL

Energetic materials

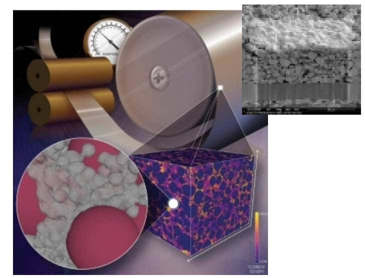


Additive manufacturing (metal, polymer powder, pastes)



Spray coating

Battery manufacturing



Ceramic piece parts, glass ceramics

.. and more!

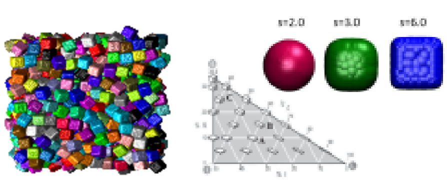
Processing operations: re-crystallization, spray drying, milling, mixing/blending, granulation, die-filling, compaction, sintering, …

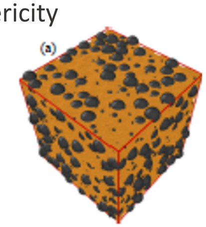
Approaches to particle/powder characterization and specification vary widely across these areas.
How do we get beyond "magic barrels" and design feedstocks/process to optimize device performance?

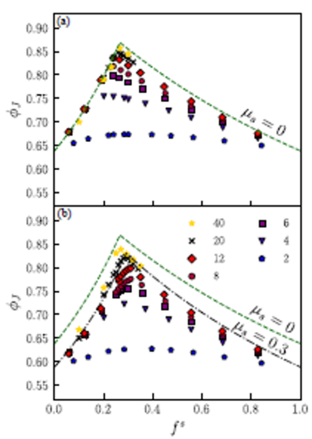
Examples:

<u>Metal additive manufacturing powders</u>

- Chemical composition: min and max for desired elements, max weight percent for other elements (contaminants)
- Particle size: min and max D10, D50, D90
- Particle shape: min and max aspect ratio, sphericity
- Flowability: max. Hausner ratio

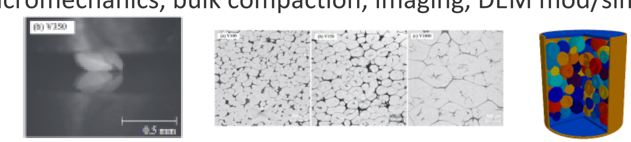






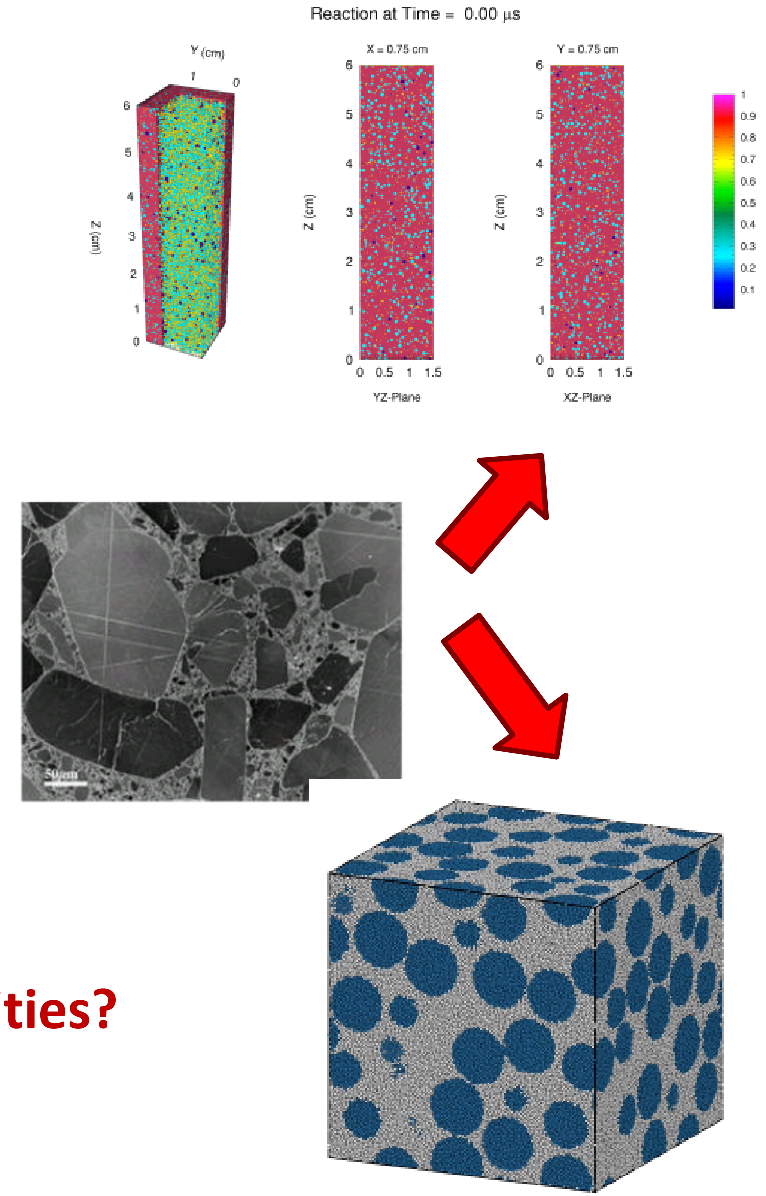
<u>Energetic materials</u>

- Small scale/high consequence
- Specifications often based on empirically matching legacy materials
- Extensive characterization efforts on-going: single-particle micromechanics, bulk compaction, imaging, DEM mod/sim



Process, Property, Performance Nexus: Role of Microstructure

- Need better prediction and control of performance, reliability and safety of, e.g.,
  - Energetic components
  - Energy storage devices
- Heterogeneous materials
  - "discontinuous" properties and discrete microstructure
    - multi-phase, multi-material → interfaces
- Heterogeneous "dynamics"
  - Spatial distribution of (relaxation) timescales
    - "Anomalous" stochastic behavior
    - Generalized Stochastic Models
- **How do fluctuations couple to nonlinearities?**



Safety: Thermal Runaway/Cookoff

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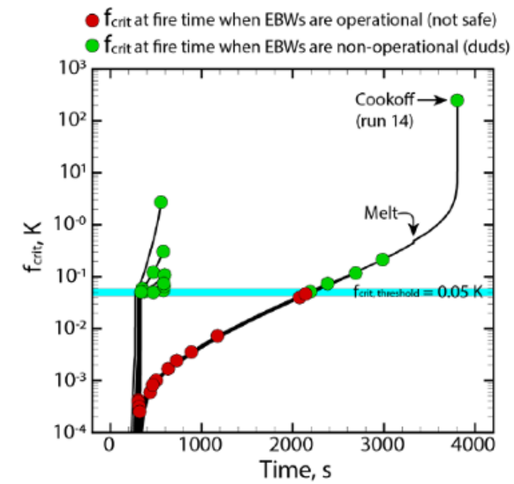
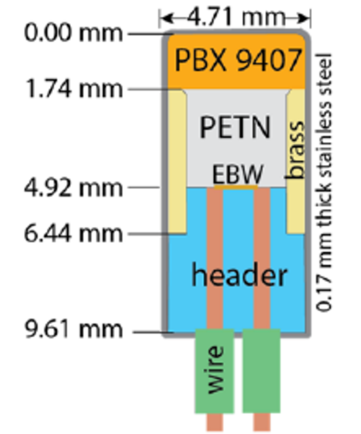
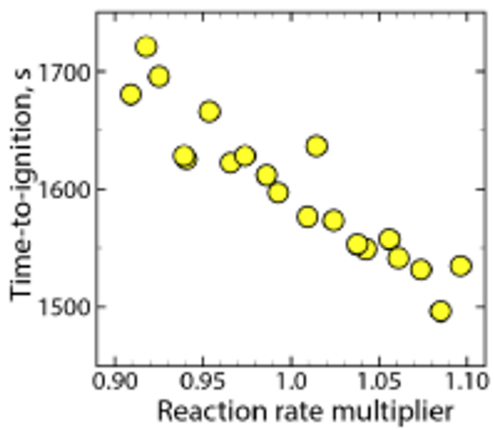
- Performance questions
  - How effective is it?
  - How reliable is it?
- Safety questions
  - Given conditions, go or no-go?
  - How certain are you?

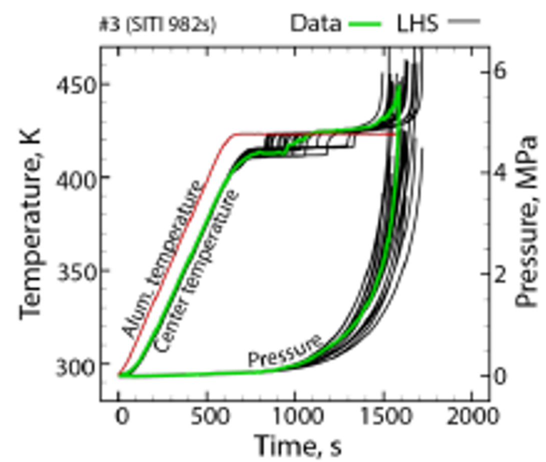




$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + h_{rxn} r$$

$$r = A \lambda_m \lambda_b T^m \exp\left(\frac{-E+\xi\sigma}{RT}\right)[\mathrm{PETN}]$$





- Sources of uncertainty
  - Epistemic
    - Model parameters
  - Aleatoric
    - Model form

Theory: Frank-Kamenetskii/Semenov

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- Reaction-Diffusion equation
  - Homogenous, isotropic material
  - Thermal conduction
  - Arrhenius type chemistry

$$\frac{\partial\theta}{\partial t} = \frac{1}{t_F}\nabla^2\theta + \frac{1}{t_{ad}}e^{\theta/(1+\varepsilon\theta)}$$

$$t_F = \frac{\varrho C_p L^2}{\kappa} \qquad \delta = \frac{t_F}{t_{ad}}$$

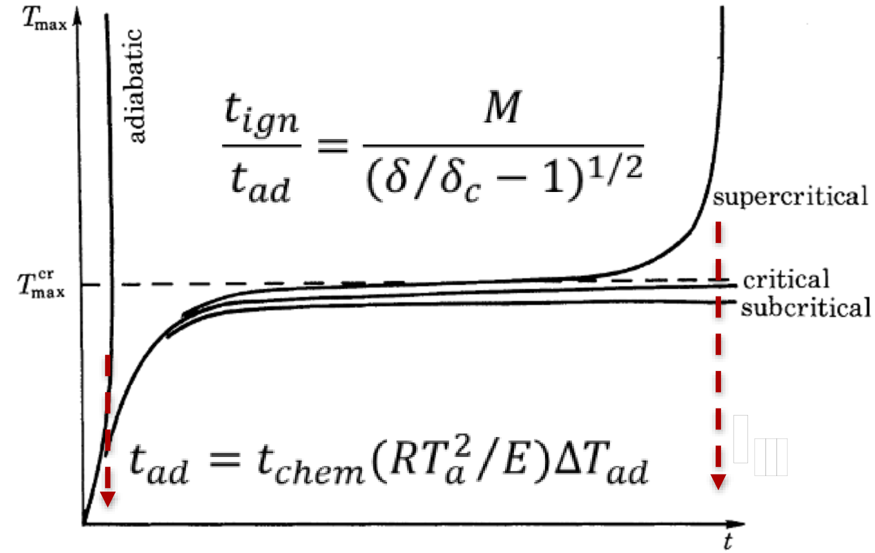
shape & size

  - BC's

$$\kappa\left(\frac{d\theta}{d\mathbf{n}}\right) + \chi\theta = 0$$

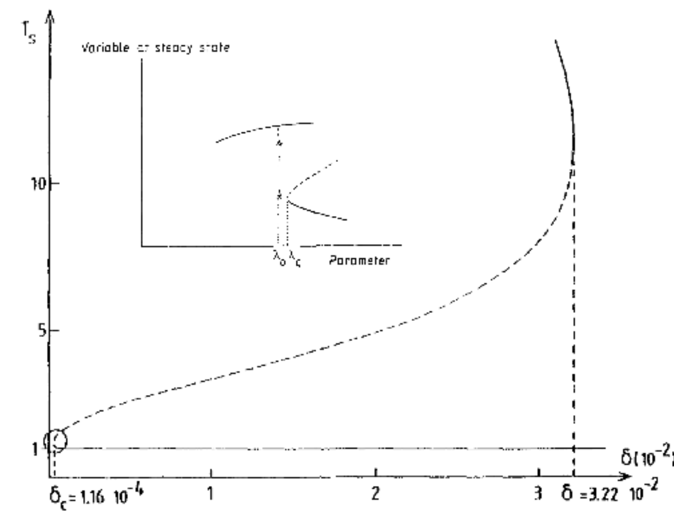
    - Biot Number, $\beta = \chi L/\kappa$
      - Frank-Kamenetzkii, $\beta \to \infty$

$$\frac{t_F}{t_N} \sim \frac{\chi}{\kappa}$$



$$\frac{t_{ign}}{t_{ad}} = \frac{M}{(\delta/\delta_c - 1)^{1/2}}$$

$$t_{ad} = t_{chem}(RT_a^2/E)\Delta T_{ad}$$



The Multi-scale Transport *through* Particulate Media

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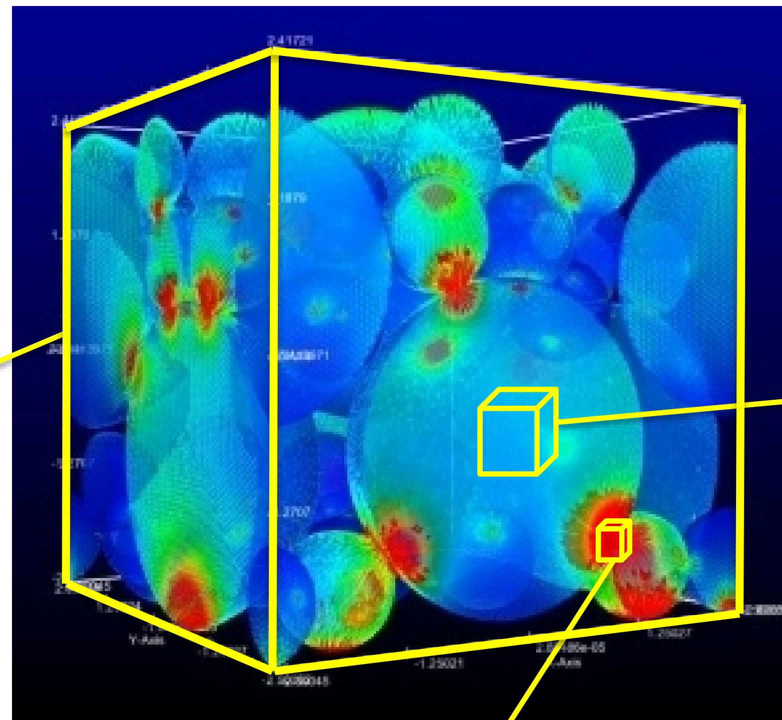
(1) Bulk, Macroscale
- Homogeneous
- "Continuum"
- Constant transport coef.

$$0 = \nabla \cdot \mathbf{q}(\mathbf{x}) = K_{eff} \nabla \cdot \langle \nabla T(\mathbf{x}) \rangle$$

bridging

(2) Particle-Particle (Meso-structure) Scale
- Inhomogeneous
- "Discrete"; Disordered
- "Anomalous" transport

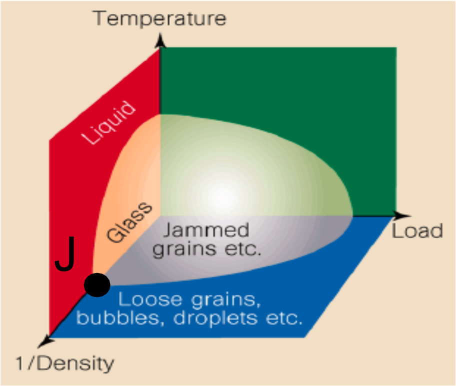
$$0 = \nabla \cdot \mathbf{q}(\mathbf{x}) = \nabla \cdot \big(K(\mathbf{x}) \nabla T(\mathbf{x})\big)$$



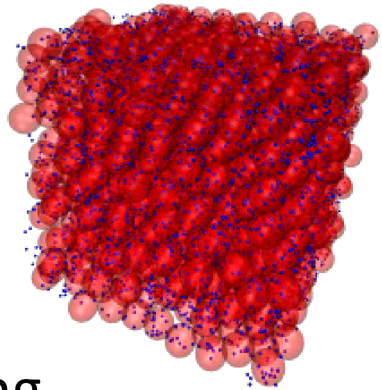
(3) Sub-particle materials structure
- Crystal structure
  - Anisotropy
  - defects, impurities, etc.
- Polycrystalline
  - Grain boundaries

(4) Interfacial Scale
- Contact area, roughness, inter-diffusion
- Material types (e.g., phonon, electron dominated)

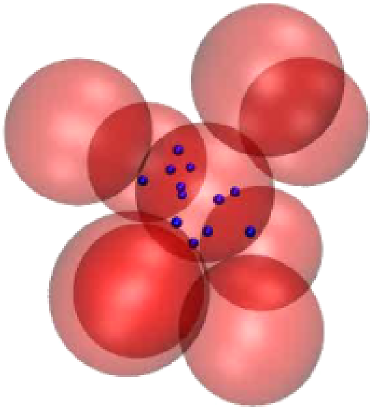
Background: Random Walks in Particle Packs



- Jammed particles near "Point J"
  - Critical-like "point" of marginal mechanical stability
    - Control of apparent microstructural length scale
  - Well defined process for creating packs
    - Remove "rattlers"

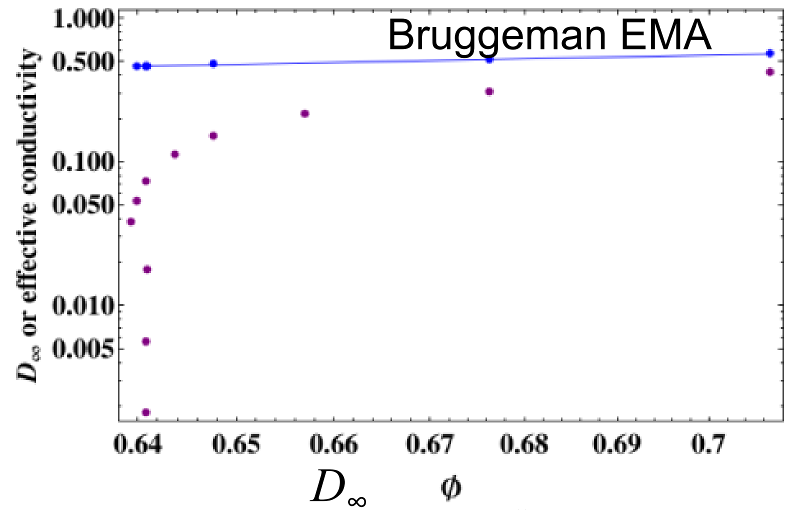


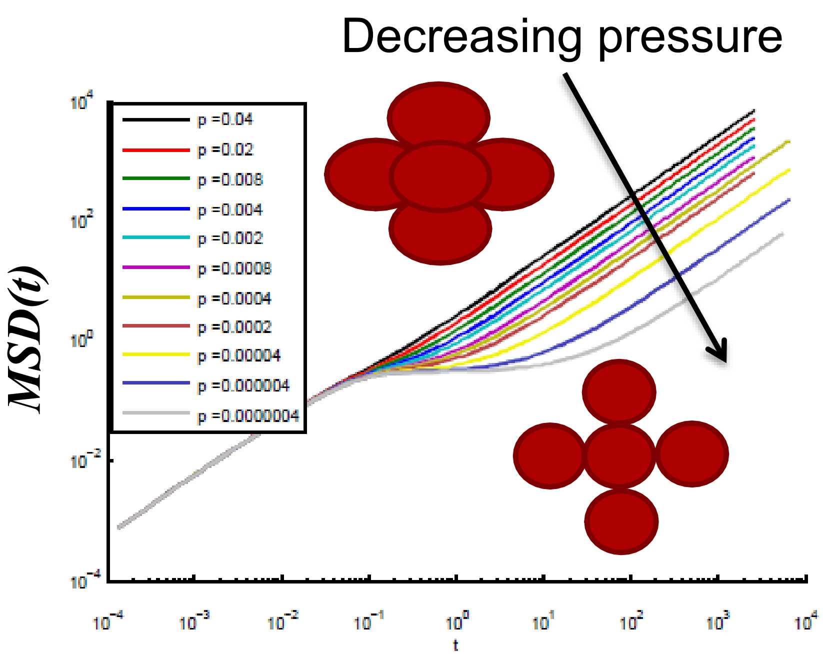
- Random Walker Simulations
  - Random walkers initially uniformly distributed within particles
  - Particles conducting; voids insulating
    - Reflecting (specular) BC at interface
      - Neumann-like, no-flux
  - Global periodic simulation domain

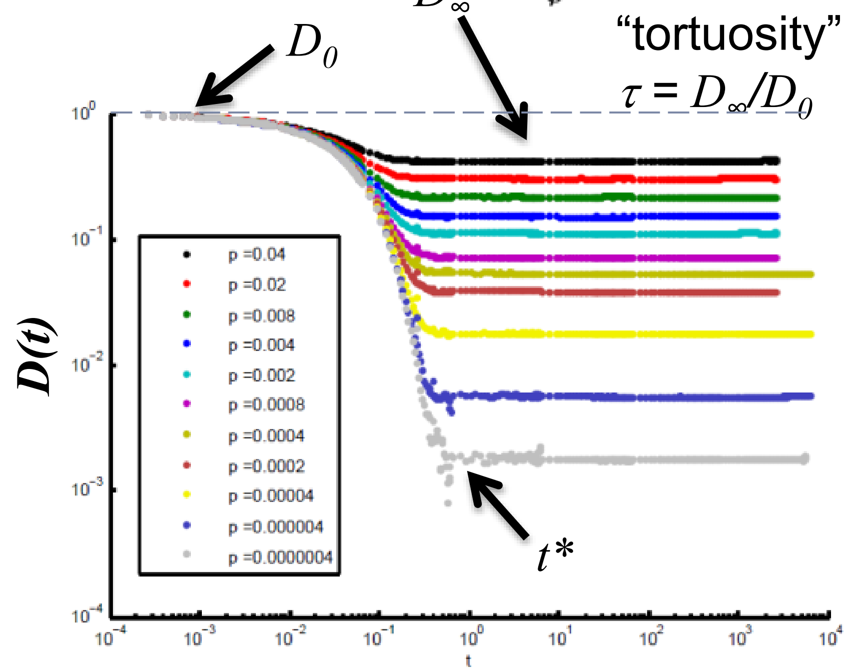


Conductivity of Particulate Microstructures

- Results
  - Late-time D_∞ function of pressure
  - Controlled by particle contact radius
  - Apparently, single relevant timescale

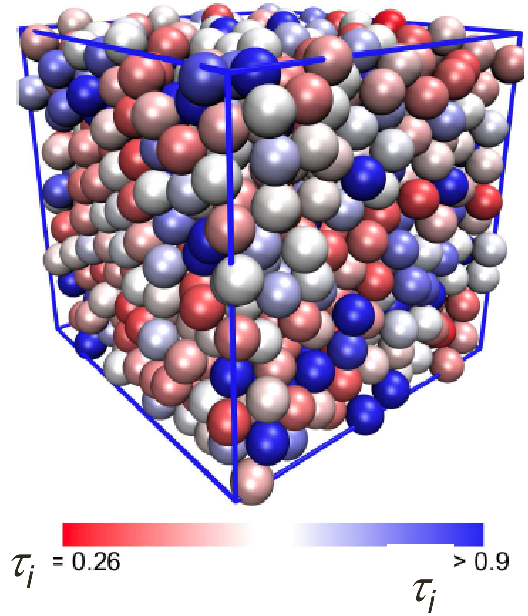




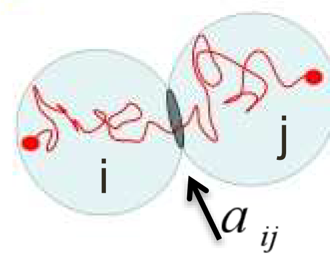


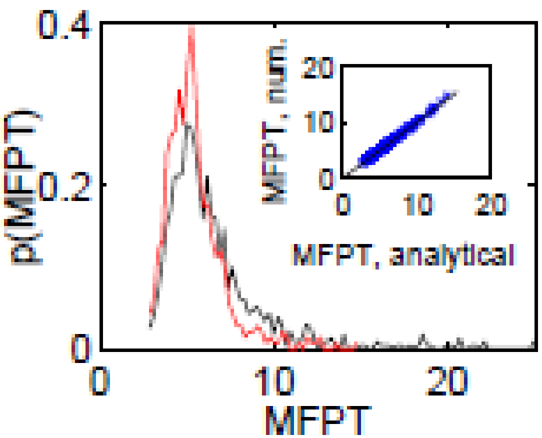
Bulk Thermal Conductivity

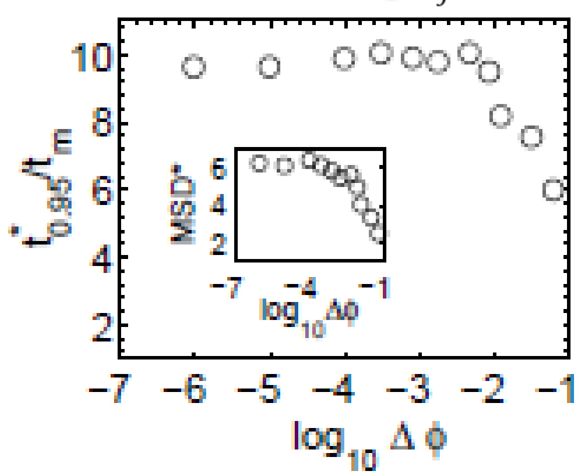
- Volume averaged MFPT per particle
  - Narrow Escape
    - **Small, well separated contacts** ($a_{ij} << d$, $r_{ij} << d$)
  - Largest Eigen value of Laplace operator in sphere with mixed BC's



Cheviakov et al. (2010), Multiscale Model. Simul., v.8, pp.836–870







$$\lambda_i = \frac{1}{\tau_i} \approx \sum_{j=1}^{z_i} \frac{4 D_i a_{ij}}{V_i}$$

$$\bar{\tau} = \frac{1}{N_p} \sum_{i=1}^{N_p} \tau_i$$

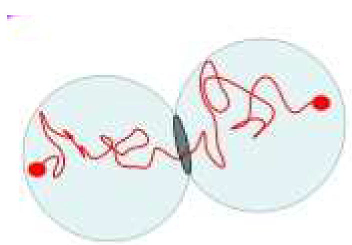
- Particle averaged, volume averaged MFPT ~ bulk conductivity

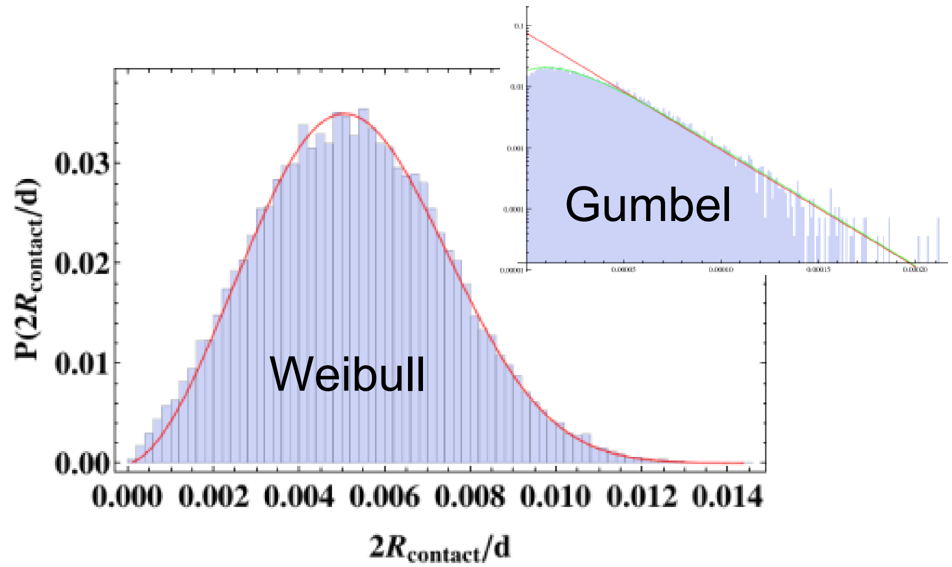
Microstructural Details: Particle-Particle Interfaces

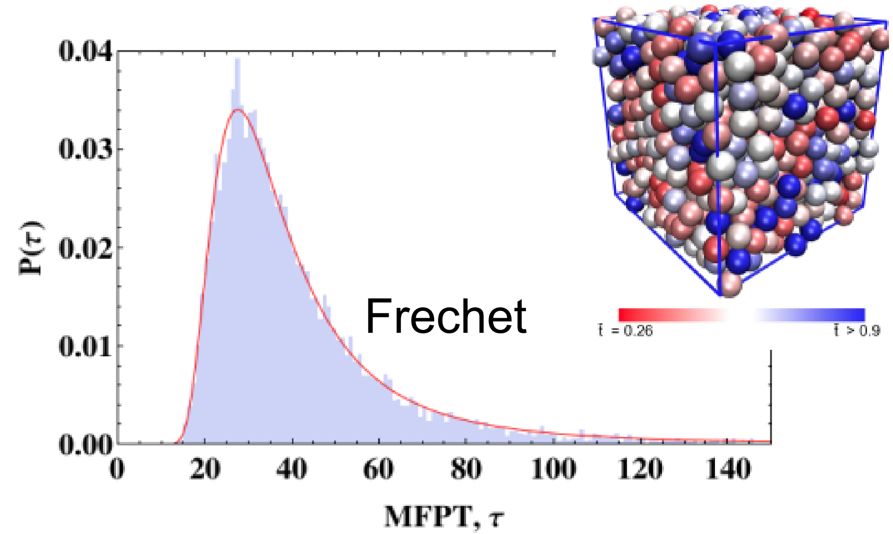
- **Difference from, say, SC lattice – disordered graph**
  - Distribution of coord. #'s
  - Distribution of forces/"overlaps"
    - Distribution of contact radii
    - Distribution of volume-averaged MFPT
      - Narrow Escape
        - » Multiple, well separated ($a << d$) contacts
        - » Largest Eigen value of Laplace Operator in spherical domain with mixed (Dirichlet and Neumann) BC's

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

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







Discretizing the Mesoscale

- Reduced-order, network modeling based on random walk simulations/analysis for thermal conduction in particle packs

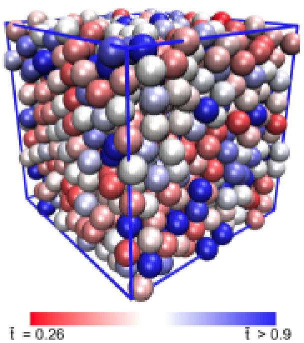
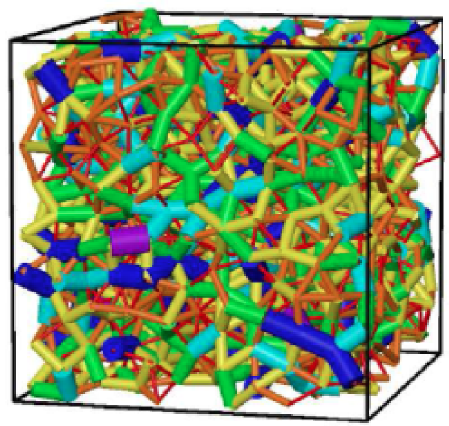
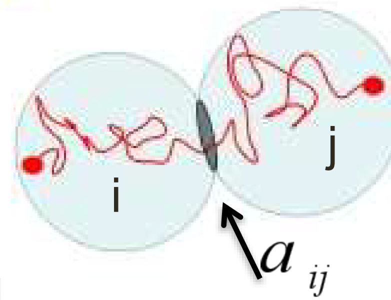


Image stack, or simulated μstructure

Determine connectivity



graph of contact network

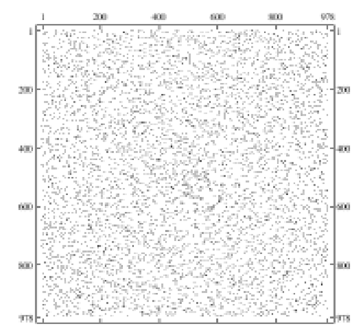


$$L_{ij} = \frac{1}{\tau_{ij}} \approx \frac{4 D_i a_{ij}}{V_i}$$

Determine: edge weights (interfacial resolution and physics models)

$$\frac{\partial T}{\partial t} = \nabla \cdot (\kappa(\mathbf{r}) \nabla T)$$

$$\frac{\partial T_i(t)}{\partial t} = \sum_{j \neq i} L_{ij} T_j(t)$$



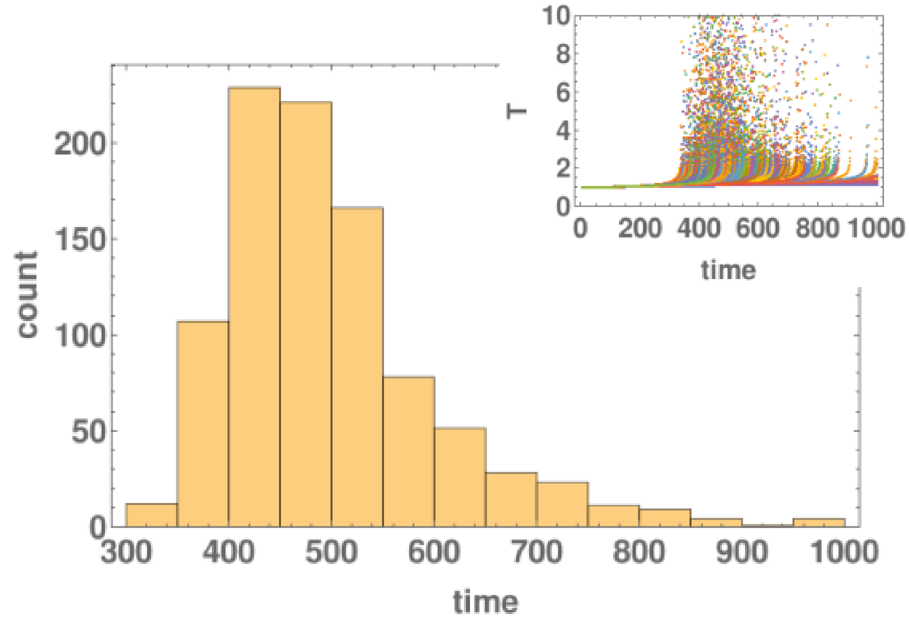
Transition Rate Matrix, Graph Laplacian …

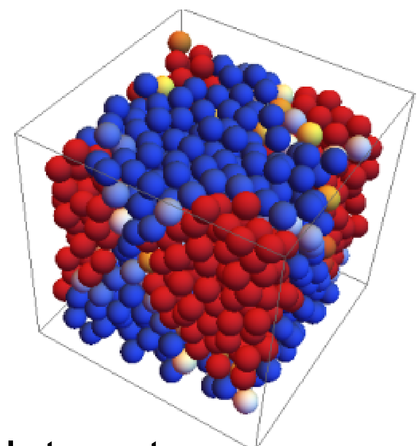
Thermal Runaway

- Add nonlinearity
  - 1st order, irreversible reactions

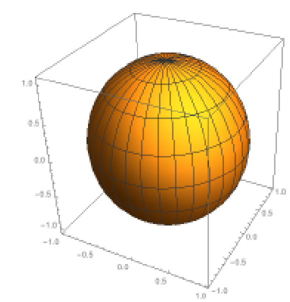
$$\frac{\partial T_i(t)}{\partial t} = \sum_{j \neq i} L_{ij} T_j(t) + \frac{Q}{\rho C_V} k c_0 \exp\left[-U/RT_i\right]$$

  - Periodic BC's (adiabatic)
  - IC: unit impulse to particle i
- Time to thermal runaway depends on particle, i
  - Varying "sensitivity" for different particles
  - Stochastic problem due to disorder in pack
- Interaction of fluctuations (due to disordered mesostructure) and nonlinearity





Hot spot



Evolution of Temperature Fluctuations

- Calculate distribution of temperature fluctuations based on Eigen decomposition

$$\boldsymbol{\delta}\mathbf{T}(t) = \mathbf{T}(t) - \boldsymbol{T}_{eq} = \sum_{j=2}^{N} e^{-\lambda_j t}\,\mathbf{v}_\mathrm{j} \qquad \delta T_i(t) = \sum_{j=2}^{N} e^{-\lambda_j t}\left(\mathbf{v}_\mathrm{j}\right)_i$$

- Autocorrelation of fluctuations decay in time as system homogenizes
  - Consistent with Effective conductivity

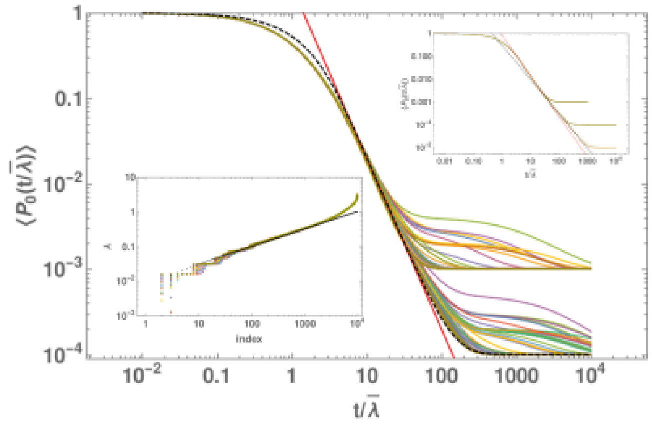
$$\frac{\partial T}{\partial t} = \alpha_{eff}\nabla^2 T$$

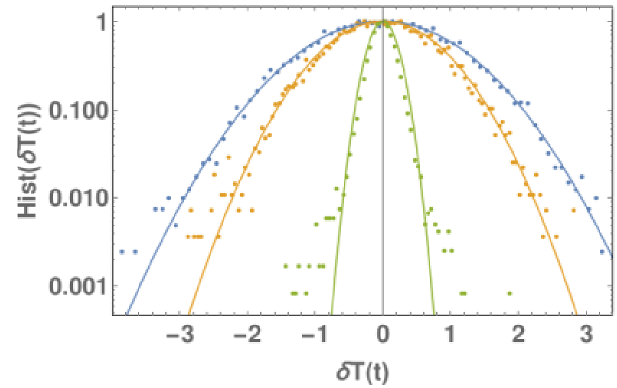
- For sum of IID Gaussian random variables, a large deviation (LD) approximation can be obtained

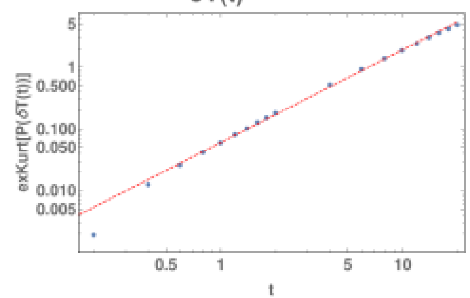
$$\mathrm{P}(\delta T_i = \delta T\,) \sim \exp\left[-\frac{1}{2}N\left(\frac{\delta T}{\sigma(t)}\right)^2\right]$$

  - Initially, Gaussian seems to work
  - However, scaling of excess Kurtosis does not follow Gaussian behavior
    - Fluctuations decay but slower

$\langle \delta T_i\,(0)\delta T_i\,(t)\rangle$







Eigenvector Statistics

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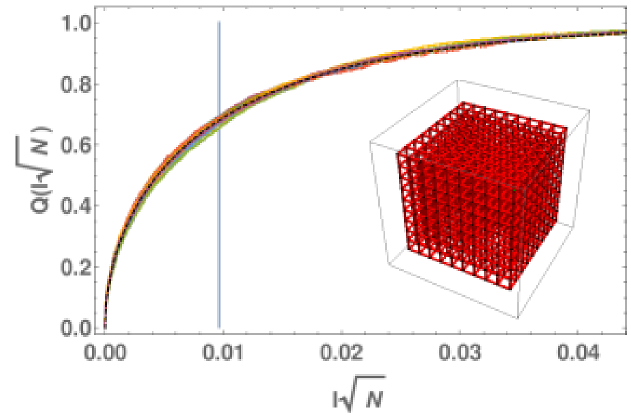
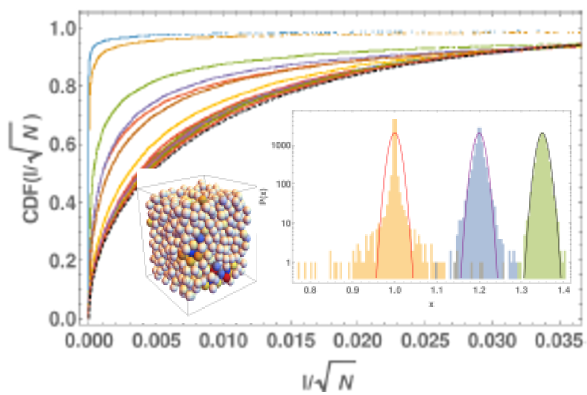
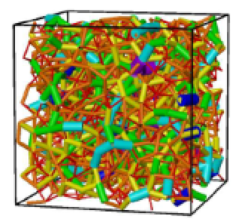
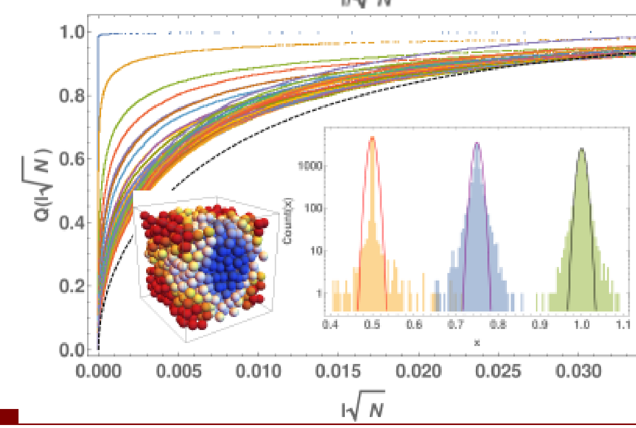
- For ordered structure, each particle contributes like an independent, gaussian-distributed random quantity for each of the N-1 eigenvectors associated with each eigenvalue
- For disordered structure, each particle contributes in a more complicated manner
- Ordered packs are locally and globally homogeneous; disorder packs are globally homogeneous but locally not so
- Statistical runaway time for disordered systems related to anomalous statistics in spectral properties of network transport operator









Stat. Mech of Trajectories: Large Deviations

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- Thermo. formalism for Markovian dynamics

$$\frac{\partial \mathbf{T}(t)}{\partial t} = \mathbf{L}\mathbf{T}(t)$$

  - Define time integrated observable

$$A(t) = \sum_{n=1}^{K-1} \alpha(C_n, C_{n+1}) \qquad = 1$$

  - Write master equation for the Laplace Transform

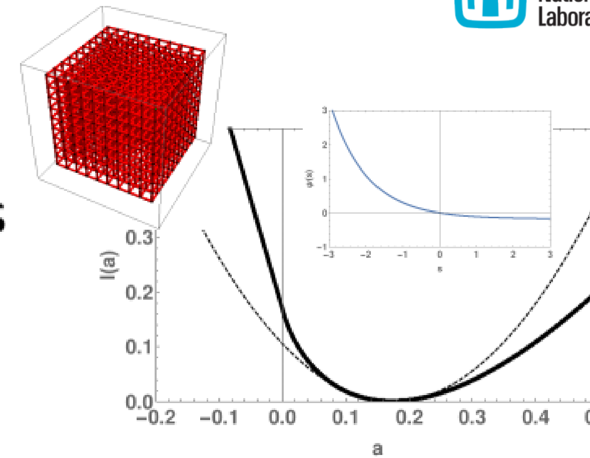
$$\widehat{T_A}(i,s,t) = \sum e^{-sA} T_A(i,A,t)$$

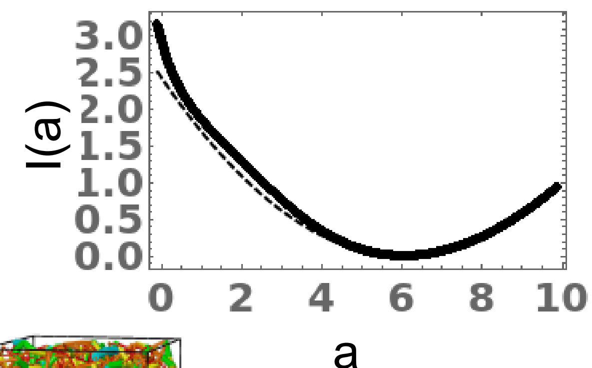
    - At large times

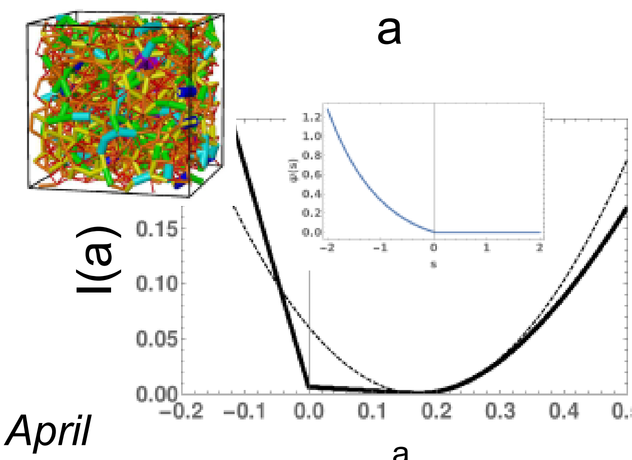
$$\hat{T}_A\,(i,s,t) \sim \psi_0\, e^{t\lambda_A(s)}$$

$$\lambda_A(s) = \max_a [I(a) - sa] \qquad I(a) = \min_s [\lambda_A(s) + sa]$$

$$\left.\frac{d\lambda_A}{ds}\right|_{s=0} = \frac{1}{N}\sum_i \lambda_i = \frac{1}{N}\mathrm{Tr}[\mathbf{L}] = \bar{\lambda}$$







Lecomte et al., Journal of Statistical Physics, Vol. 127, No. 1, April 2007

Localization Theory: landscape function

- Define landscape function

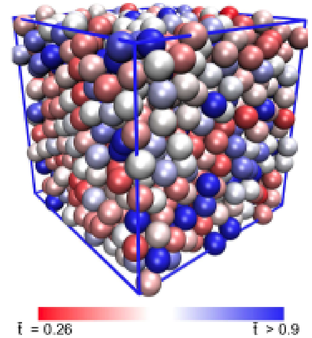
$$u(x) = \int_{\Omega} |G(x, y)| dy$$

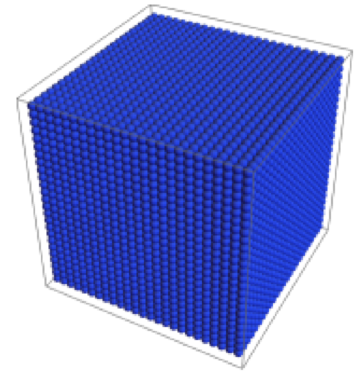
where G is the Green's function, (,) = ( )

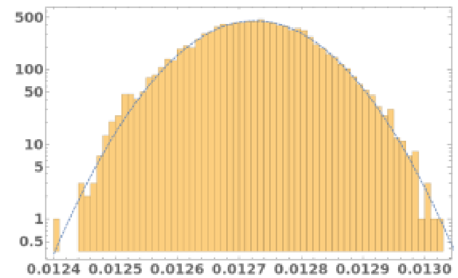
- Modes localized to regions where $u(x) < {}^{1}/_{\lambda}$

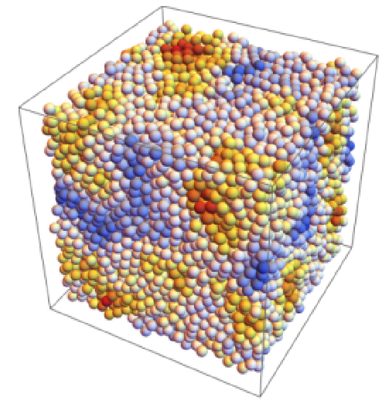
$$\mathcal{H}_t(x, y) = \sum_{i=1}^{N} e^{-\lambda_i t} \psi_i(x) \psi_i(y)$$

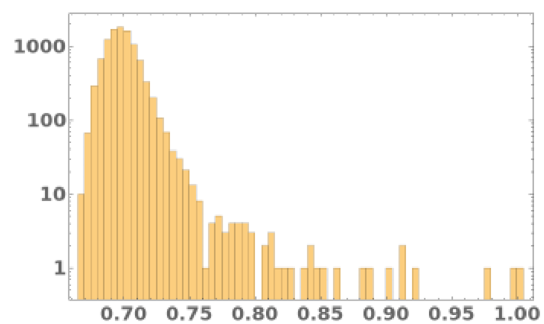
$$G(x, y) = \int_0^{\infty} \mathcal{H}_t dt = \sum_{i=2}^{N} \frac{\psi_i(x) \psi_i(y)}{\lambda_i}$$

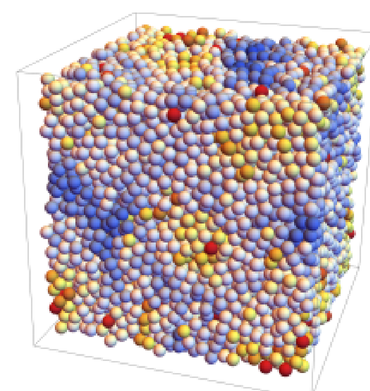












Summary & Conclusions

- Reduced-order, network-type model of thermal transport on particulate materials is possible
  - Spectral analysis of conduction matrix allows for development of macro-scale models and analysis of thermal fluctuations due to disordered microstructure
- Addition of nonlinearity due to chemical reactions can be accomplished
  - Comparison to classical Frank-Kamenetskii problem shows similar critical slowing down near critical point
  - However, details of thermal runaway time show statistical characteristics due to disorder of microstructure
  - DMD-type analysis allows for possibility of extending spectral analysis from linear to nonlinear equations through approximation of (linear) Koopman Operator

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- Mike Hobbs
- Joe Monti, Joel Clemmer, Ishan Srivastava, Dan Bolintineanu, Leo Silbert, Mike Salerno, Gary S. Grest
- Industrial collaborators
- LDRD and ASC/P&EM programs at Sandia

Backup Slides

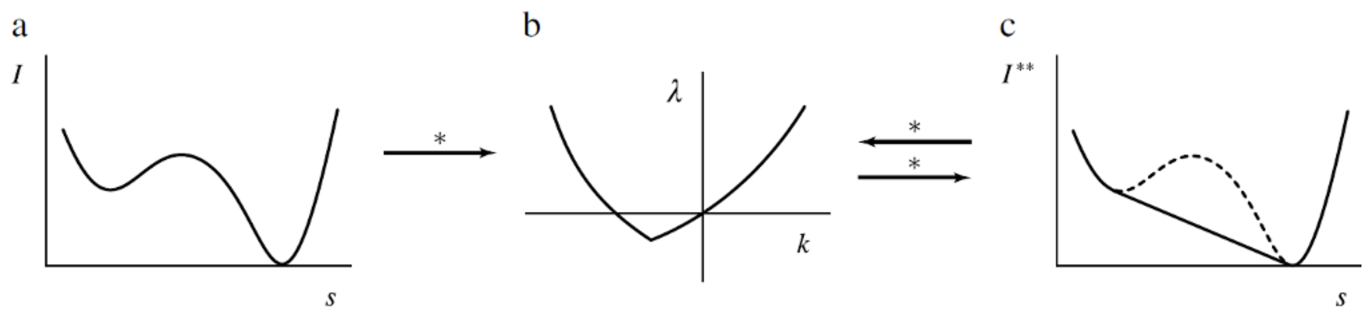


Fig. 9. Legendre–Fenchel transforms connecting (a) a nonconvex rate function $I(s)$, (b) its associated scaled cumulant generating function $\lambda(k)$, and (c) the convex envelope $I^{**}(s)$ of $I(s)$. The arrows illustrate the relations $I^* = \lambda$, $\lambda^* = I^{**}$ and $(I^{**})^* = \lambda$.

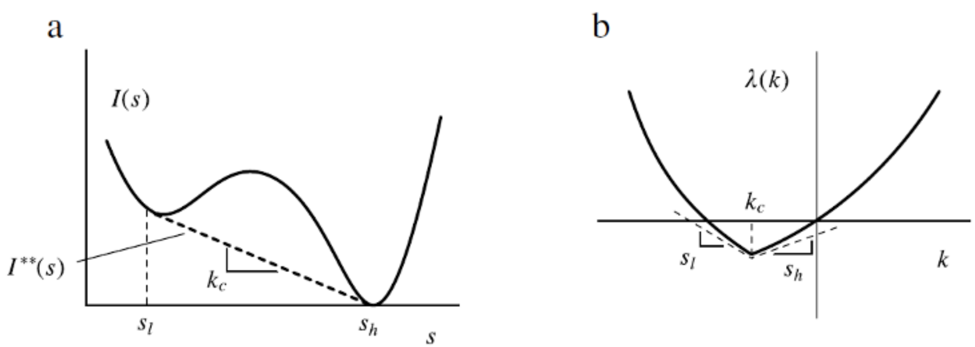


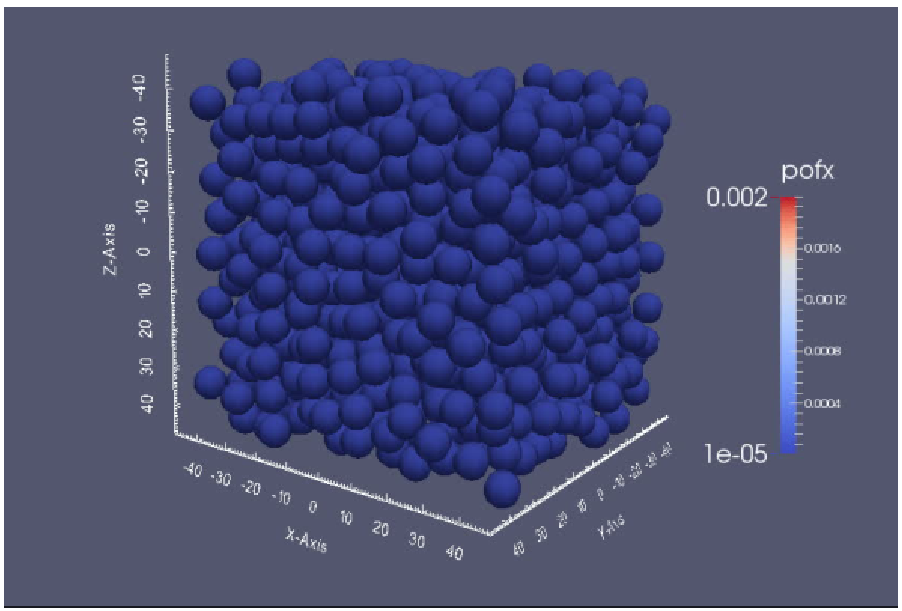
Fig. 10. (a) Nonconvex rate function I and its convex envelope I^{**}. (b) Associated scaled cumulant generating function $\lambda(k)$ having a nondifferentiable point at k_c.

Simulate Markov Process on Contact Network

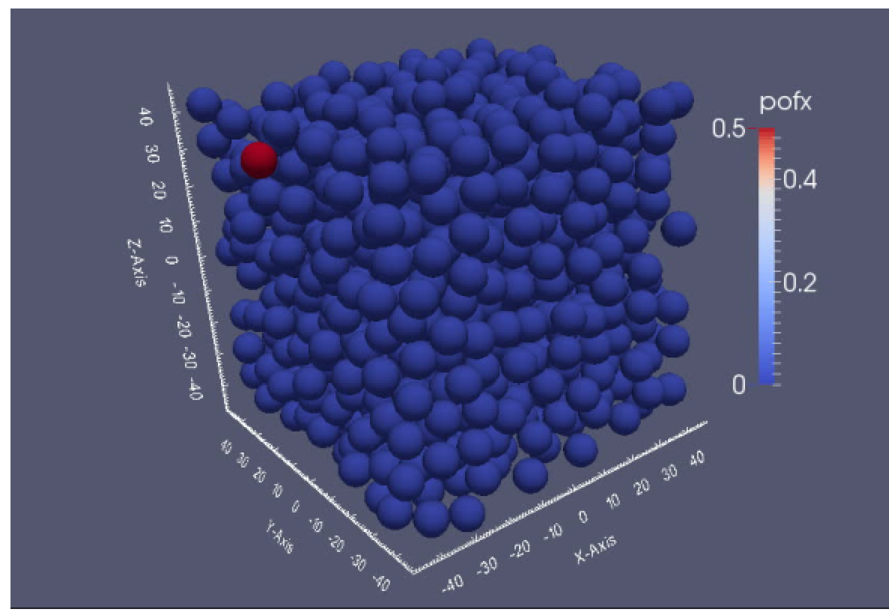
- Discretize Continuous-Time Equation

$$\frac{\partial \mathbf{T}(t)}{\partial t} = \mathbf{L}\mathbf{T}(t) \qquad L_{ij} = \begin{cases} \dfrac{3D}{\pi R^2}\sqrt{\delta_{ij}/R} & i \neq j \\ -\sum_{j \neq i} L_{ij} & i = j \end{cases} \qquad \Rightarrow \qquad \begin{aligned} \mathbf{T}_{n+1} &= \mathbf{M}\mathbf{T}_n \\ \mathbf{M} &= \mathbf{I} + \Delta t \mathbf{L} \end{aligned}$$

  - I.C. $\mathbf{T}_0 = \hat{\mathbf{e}}_1 \quad \left\| \hat{\mathbf{e}}_1 \right\| = 1$
  - Periodic B.C.'s



p = 0.0004



p = 0.00004

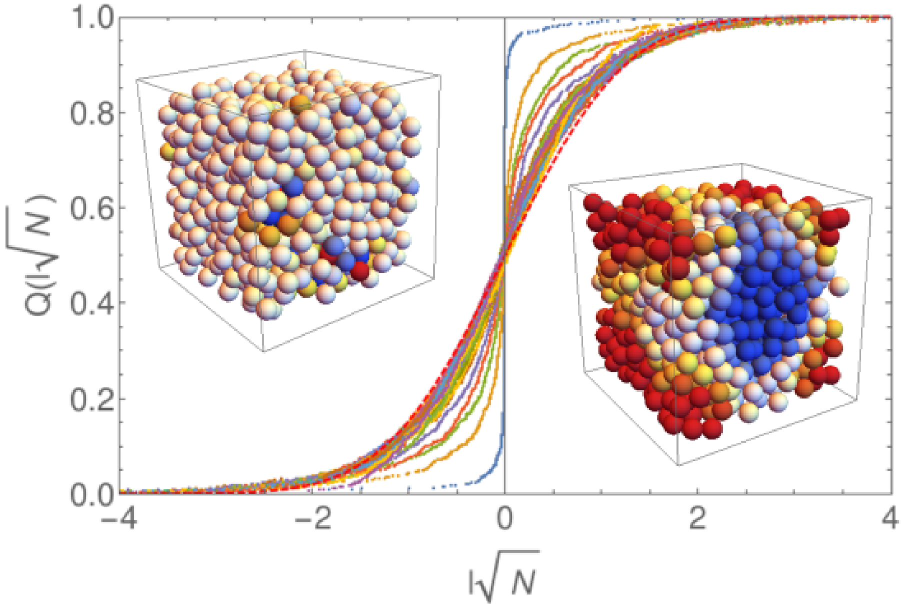
Eigenvectors and Statistics

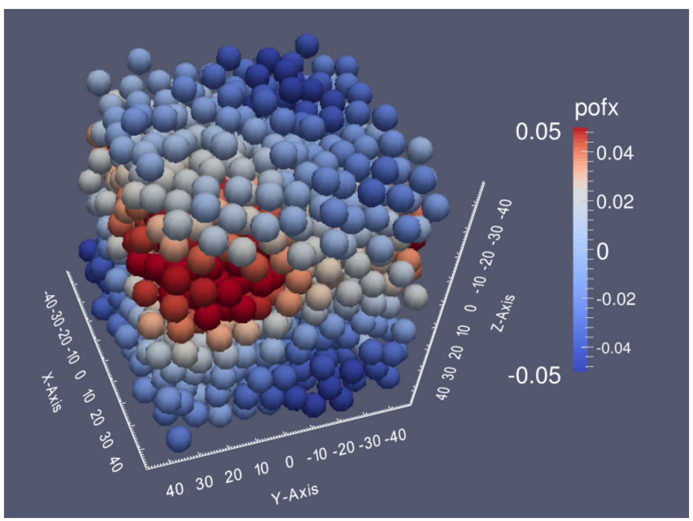
- Eigenvectors
  - small eigenvalues show plane

Cf. Silbert et al. (2009), PRE v.79, p.021308

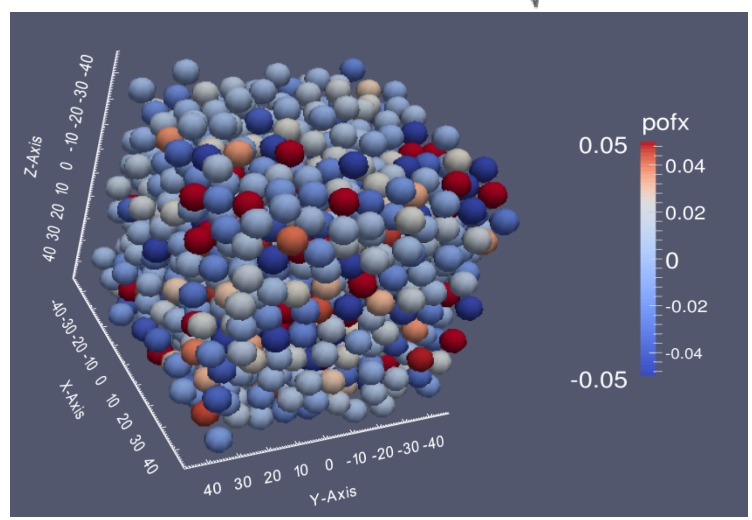
- Close to Porter-Thomas distribution
  - But, not quite

cf. Manning and Liu (2015), EPL v.109, p.36002





Eigenvector for large λ



Eigenvector for small λ

Large Deviations

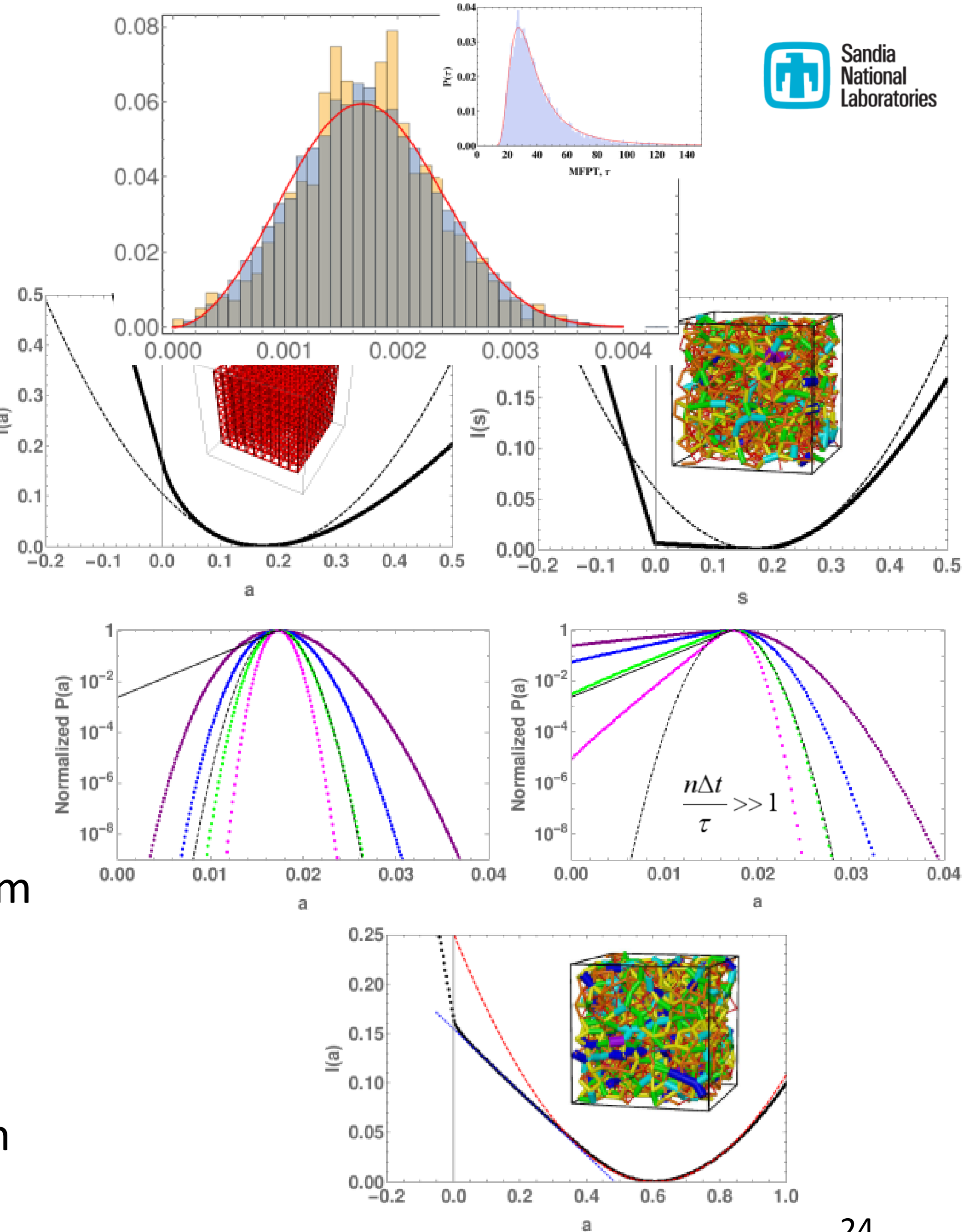
Sandia National Laboratories

- Process-structure
- Structure-property
- LD of sums of random varia

$$S_n = \frac{1}{n}\sum_n X_n$$

$$P(S_n = s) \approx e^{-nI(s)}$$

- Statistical Mechanics of "Trajectories"
  - Use thermodynamic formalism for systems with Markovian dynamics
  - Obtain convergence (in distribution) of fluctuations in diffusion coefficient
  - Distributions reminiscent of "Extreme Value Statistics" (e.g.



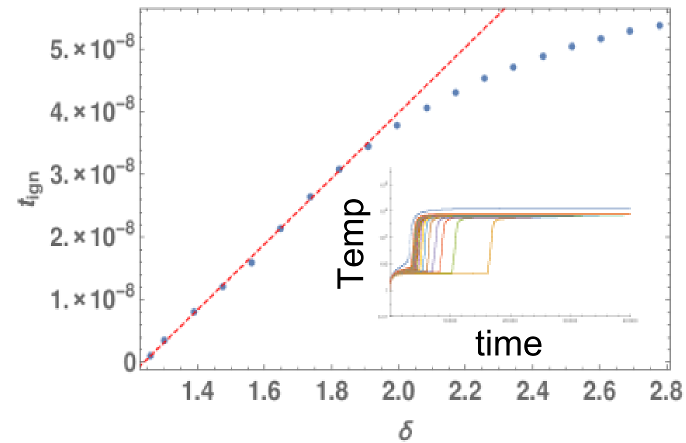
Extending spectral analysis to discrete approximation of Koopman Operator

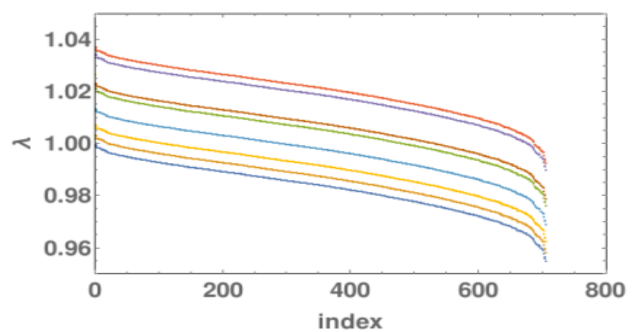
- Use homogeneous IC and Dirichlet BC's
  - Scaling of time to ignition follows classical homogeneous result; exhibiting critical slowing down

$$t_{ign} \sim (1 - \delta/\delta_c)^{-1/2}$$

where δ is the Frank-Kamenetskii parameter

- Expected that system will be sensitive to "large deviations" (i.e., fluctuations stronger than Guassian)
- DMD eigenvalues can be computed as a function of the strength of the nonlinearity
  - Interpretation and verification of analysis is ongoing





Stochastic Models

- Nicolis and Baras (1987)
  - Recall Semenov problem, $\beta \to 0$

$$\frac{d\theta}{dt} = \frac{1}{t_{ad}} e^{\theta/(1+\varepsilon\theta)} - \frac{\theta}{t_N} + F(t) \quad \sim \frac{1}{\;}$$

$$\langle F(t) \rangle = 0$$

$$\langle F(t)F(t') \rangle = (C_{chem}/t_{ad} + C_f/t_N)\delta(t - t')$$

$$\frac{d\theta}{dt} = -\frac{\theta}{t_N} + F(t)$$

$$\langle \theta(t) \rangle = 0$$

$$\langle \theta(t)\theta(t') \rangle \sim e^{-(t-t')/t_N}$$

- What about the Frank-Kamenetzkii problem, $\beta \to \infty$
  - Replace master equation for inhomogeneous material with generalized Langevin equation for homogeneous material ***with*** memory

$$\frac{d\theta}{dt} = -C \int_{-\infty}^{t} \left(\frac{(t-t')^{-\frac{3}{2}}}{2\Gamma(1/2)} + \delta(t-t') \right) \theta(t')dt' + E(t)$$

$$\langle E(t) \rangle = 0$$

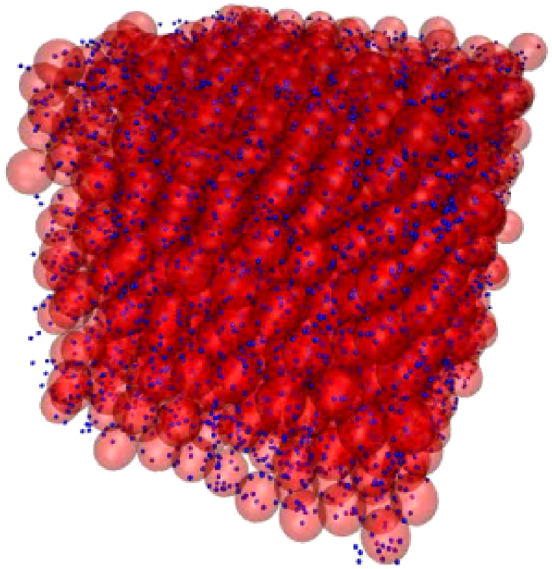
$$\langle E(t)E(t') \rangle \sim M(t - t')$$

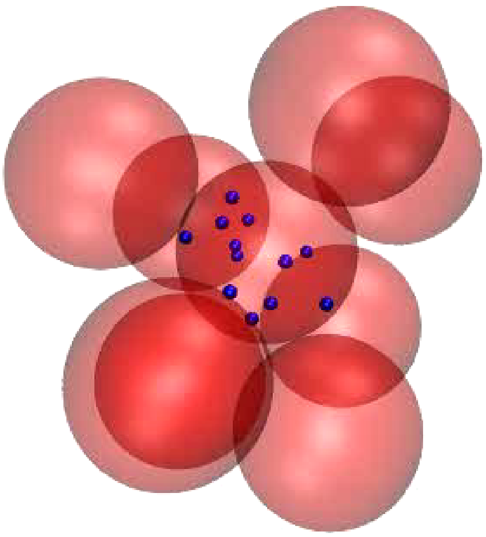
$$\langle \theta(t) \rangle = 0$$

$$\langle \theta(t)\theta(t') \rangle \sim (t - t')^{-3/2}$$

Example Simulation

- Random walk through interior of particles, where diffusion coefficient $D_0 = 1$
- Similar to method of Kim and Torquato[1](“walk on spheres”), but modified to yield time-dependent behavior
- Random walker displacement relates to material properties
- “Narrow escape” hopping between neighboring particles requires long simulation times, but accounts for small contacts explicitly and accurately





1. Kim IC and Torquato S., J. Appl. Phys. 68 (1990): 3892; Kim IC and Torquato S., J. Appl. Phys. 69 (1991): 2280

Homogenized Models: Bridging particle meso-scale to Bulk scale

- Consider Continuous-Time Random Walk 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

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

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

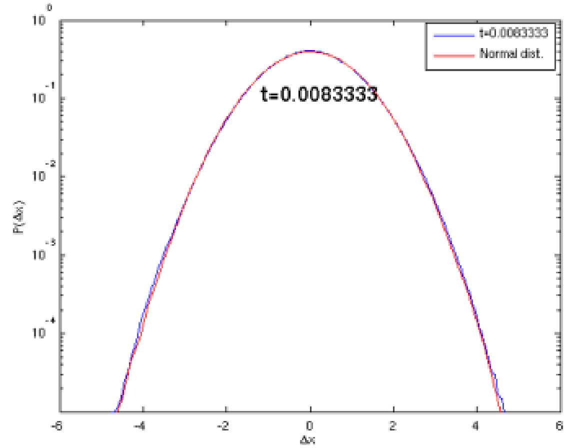
$$f_{vib}(k) = \left(2\pi l^2\right)^{-3/2}\exp\left(-r^2/2l^2\right)$$

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

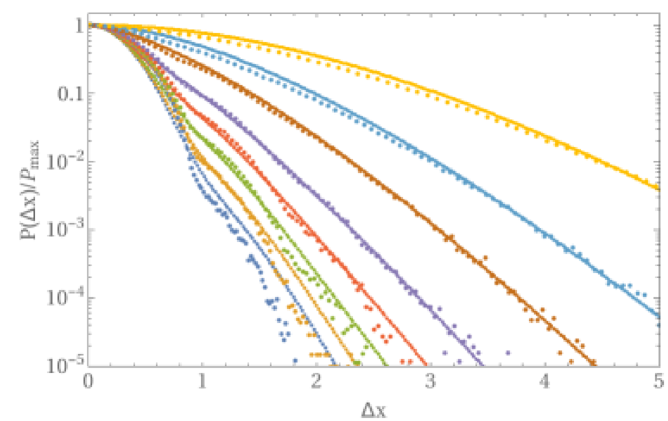
$$\phi_1 = \tau_1^{-1}\exp\left(-t/\tau_1\right)$$

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

$p = 0.002$

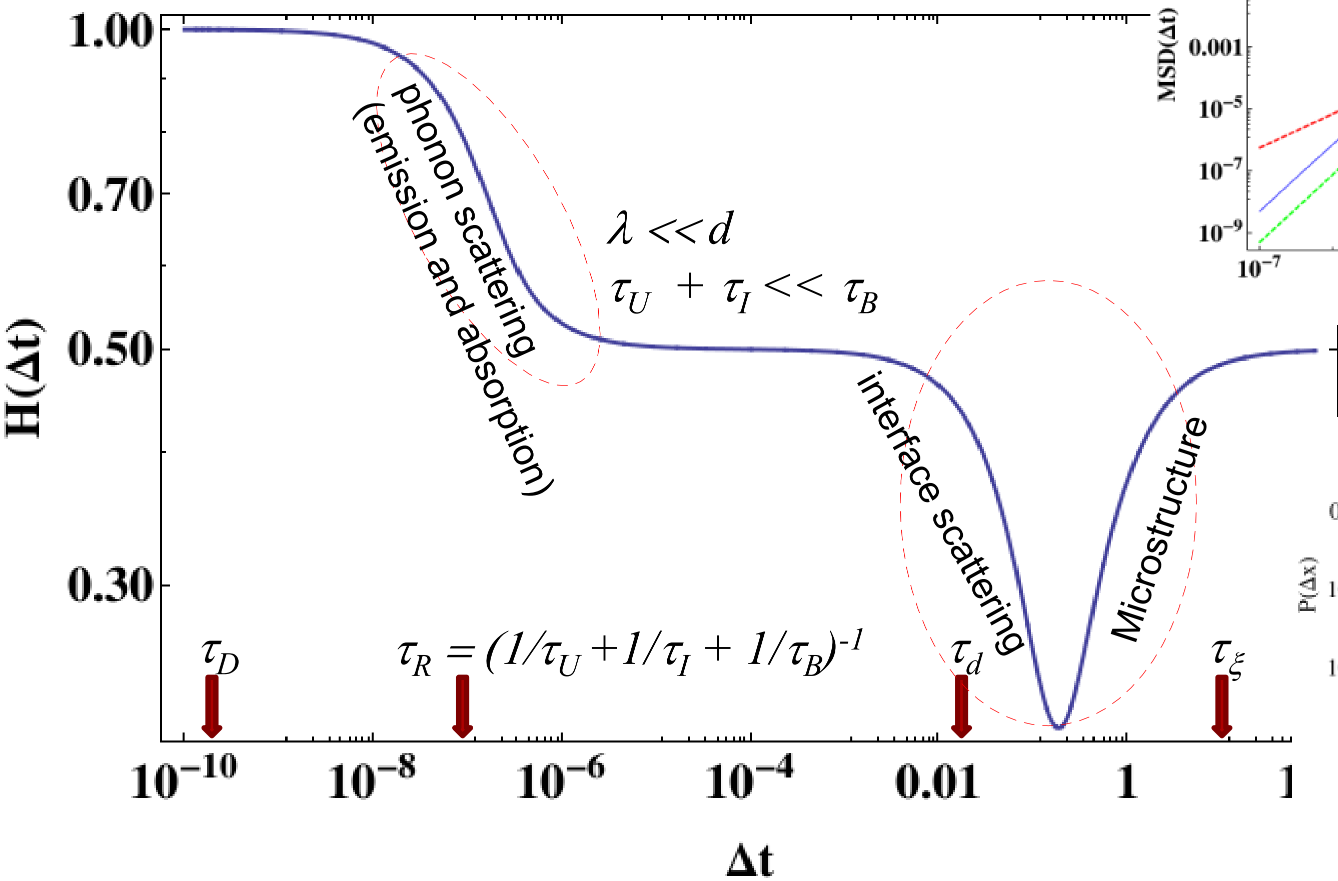


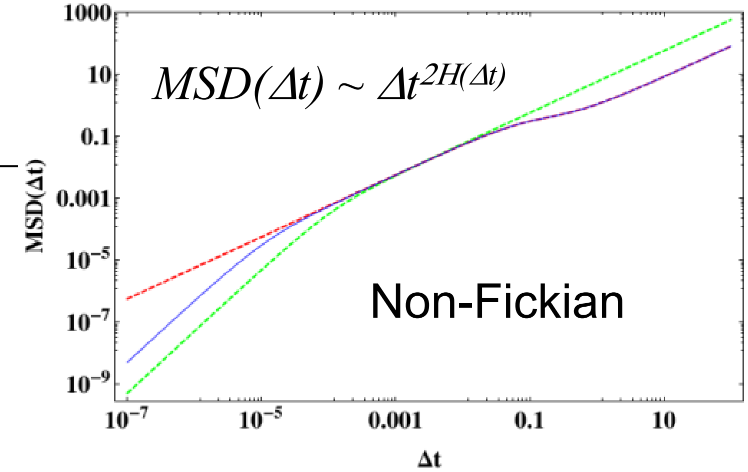
$p = 0.0004$

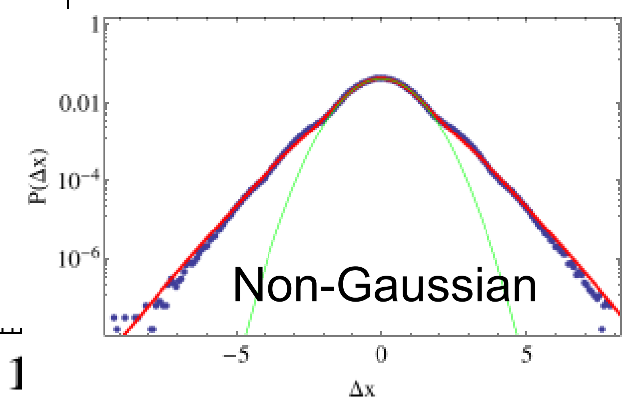


  - Equivalent to Generalized Master Equation

Transport Heterogeneity: Crossing Scales







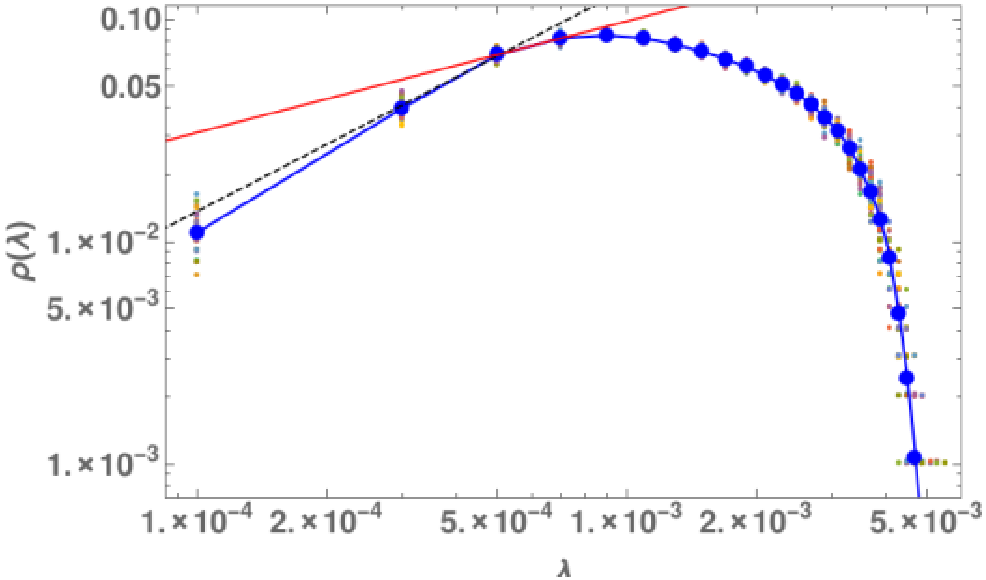
cf. K. Razi Naqvi and S. Waldenstrom (2005) *PRL* **95**, 065901

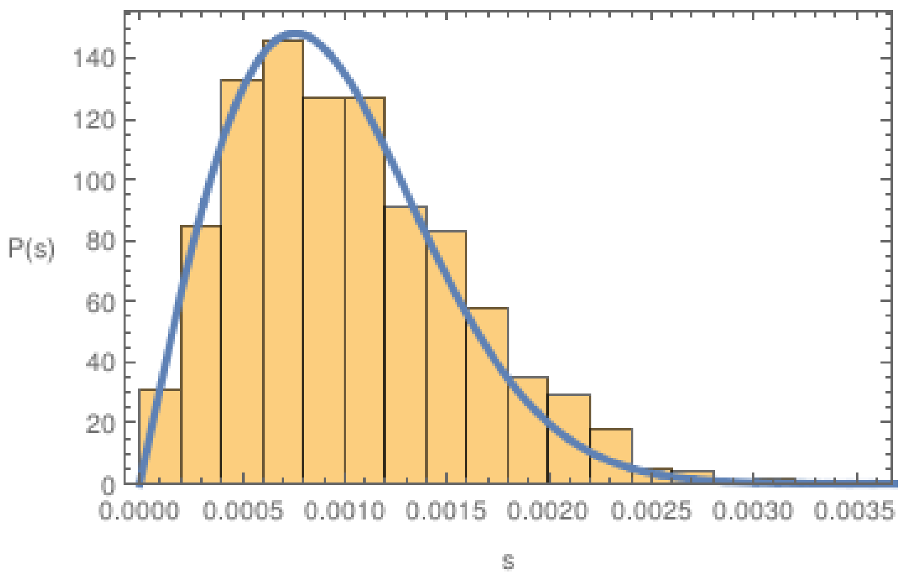
Spectral Analysis

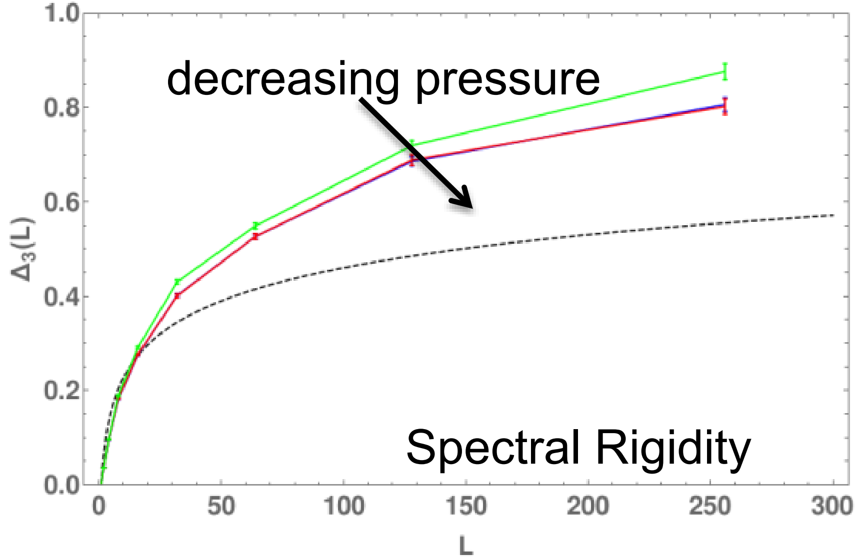
- **Transition Rate Matrix**

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

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

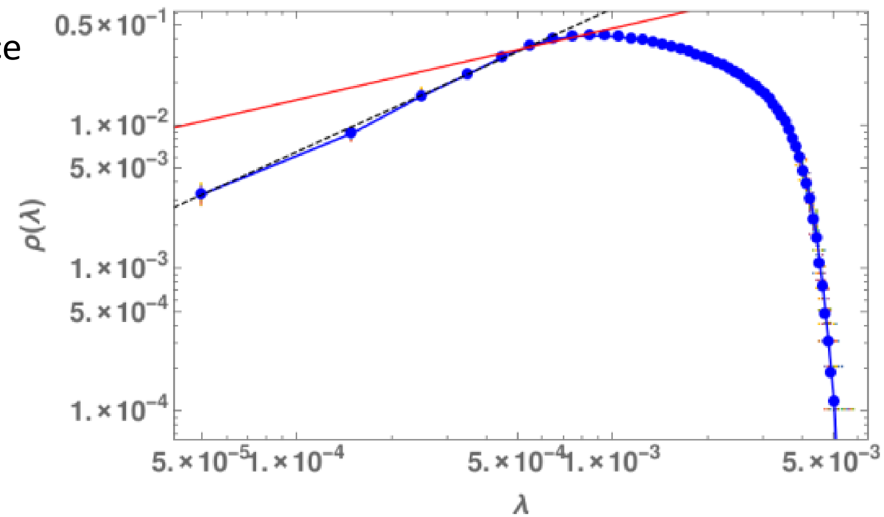


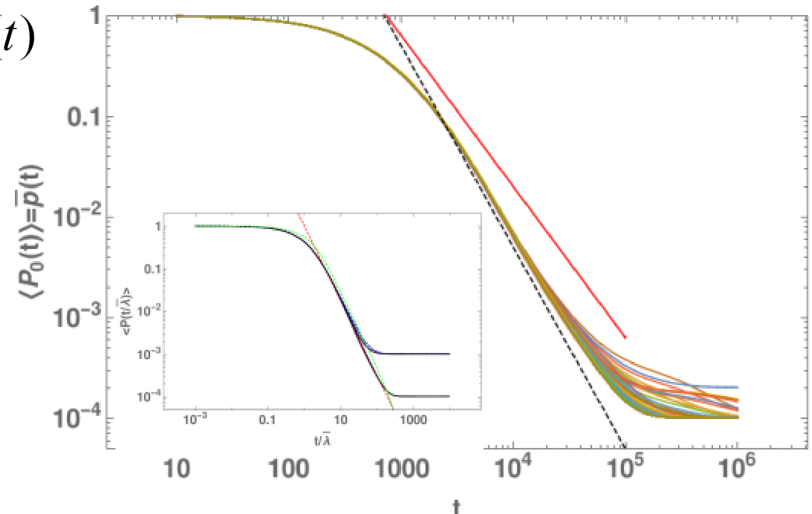




Meso-Macro Model Development

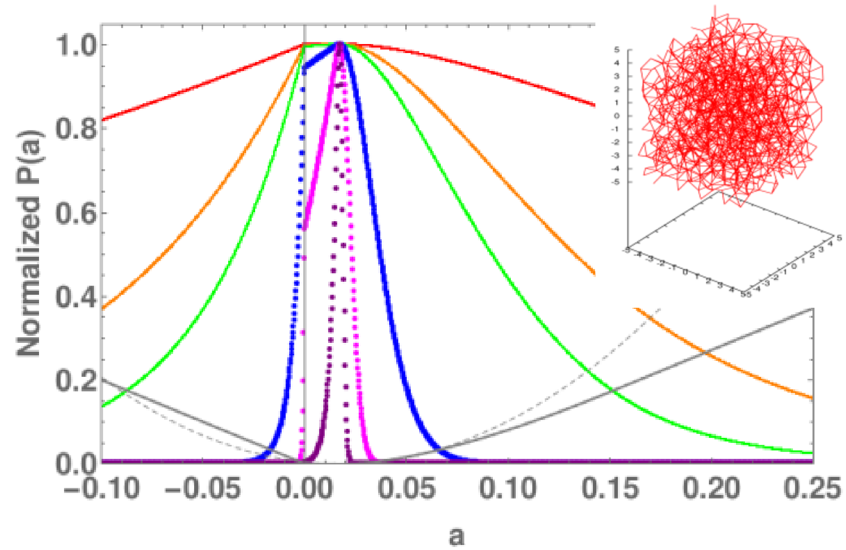
- Temperature distribution in isotropic, homogeneous, 3-dimensional, infinite medium classically modeled by heat equation; heated by an instantaneous point source at r=0
$$T(r,t) = \frac{Q\exp(-r^2/4Dt)}{8\pi\rho C(Dt)^{3/2}}$$
- Hence, T(0,t) scales as $T(0,t) \sim t^{-3/2}$
- Discrete case (transport on a graph) return probability
$$\overline{p}_{discr}(t) = \frac{1}{N}\sum_{n=1}^{N}\exp(-\lambda_n t)$$
- In "thermodynamic" (continuum) limit, N → ∞, $T(0,t) = \overline{p}(t)$
$$\overline{p}(t) = \int \rho(\lambda)\exp(-\lambda t)d\lambda$$
- Thus, if $\rho(\lambda) \sim \lambda^{\nu}$, $\overline{p}(t) \sim t^{-(1+\nu)}$ and ν = d/2-1 , with d = 3 for the homogeneous, isotropic case above
- Hence, scaling is anomalous with respect to classical descriptions
- Could be measured…

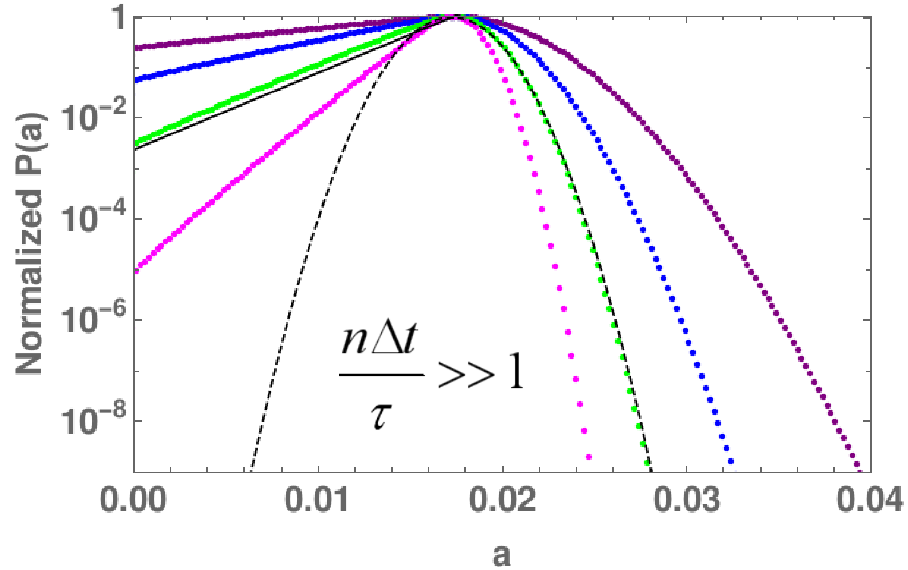




Large Deviations in Disordered Networks

- Statistical Mechanics of "Trajectories"
- Use thermodynamic formalism for systems with Markovian dynamics
  - Largest Eigen value of *modified* transition rate matrix is dynamical free energy
  - The negative of the rate function can be viewed as a dynamical entropy
- Obtain convergence (in distribution) of fluctuations in diffusion coefficient
- Distributions reminiscent of "Extreme Value Statistics" (e.g., Gumbel distribution)





$$\delta T_i(t) = \sum_{k=2}^{N} e^{-\lambda_j t} \left(\mathbf{v}_\mathrm{k}\right)_i \qquad \delta T_j(t) = \sum_{k=2}^{N} e^{-\lambda_j t} \left(\mathbf{v}_\mathrm{k}\right)_j$$

$$f(r,t) = \left\langle \frac{1}{2} \sum_{i,j} \delta T_i\,(t) \delta T_j\,(t') \delta(r_{ij} - r) \delta(t - t') \right\rangle$$

$$\boldsymbol{\delta}\mathbf{T}(t) = \mathbf{T}(t) - \boldsymbol{T}_{\boldsymbol{eq}} = \sum_{j=2}^{N} e^{-\lambda_j t}\, \mathbf{v}_\mathrm{j}$$

$$\boldsymbol{\delta}\mathbf{T}(t) \cdot \boldsymbol{\delta}\mathbf{T}^{T}(t') = \mathbf{C}(t,t') \rightarrow c_{ij} = \delta T_i(t)\ \delta T_j(t')$$

$$\langle \delta T_i\,(0) \delta T_i\,(t) \rangle = \frac{1}{N} Tr[\mathbf{C}(0,t)]$$

Large Deviation Function

- SC lattice vs. Jammed network
  - Dynamic Phase Transition?