

Vibrational mode properties of disordered solids from high-performance atomistic simulations and calculations

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08/29/2013

Outline

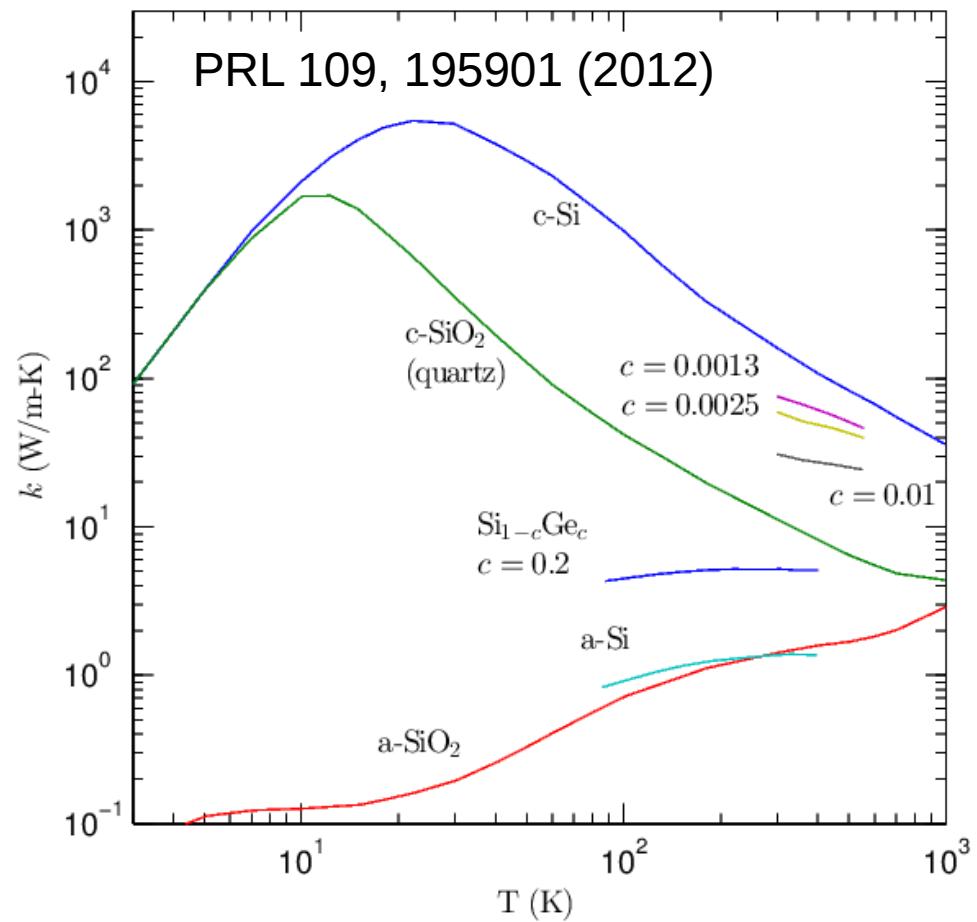
- (1) Motivation**
- (2) Mode-level vs. System-level
- (3) Alloys
- (4) Amorphous
- (5) Overview/Future Work

Motivation: Optimization

High Thermal Conductivity

Constraints: chemistry,
electron transport,
operating temperature,
etc.

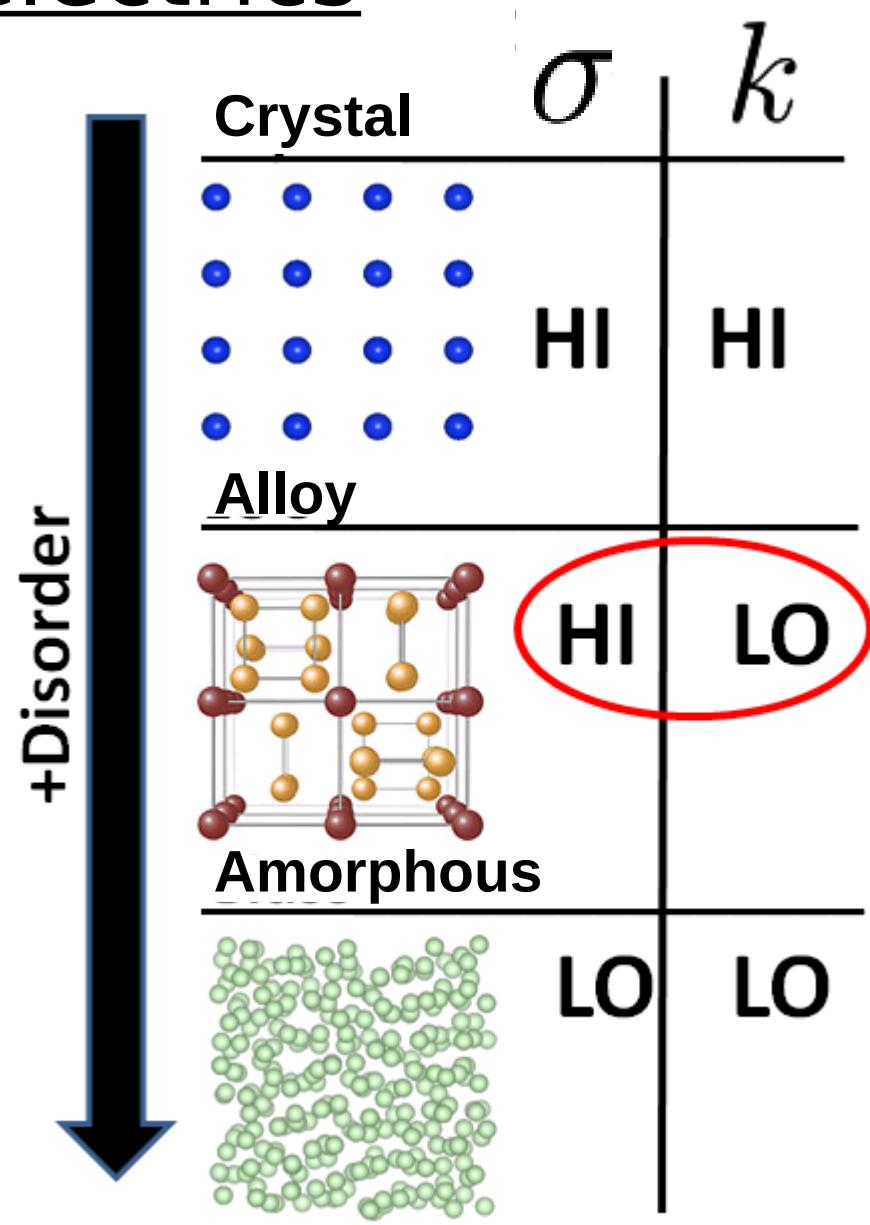
Low Thermal Conductivity



$$k_{\text{thermal}} = k_e + k_{\text{vib}} \approx k_{\text{vib}}$$

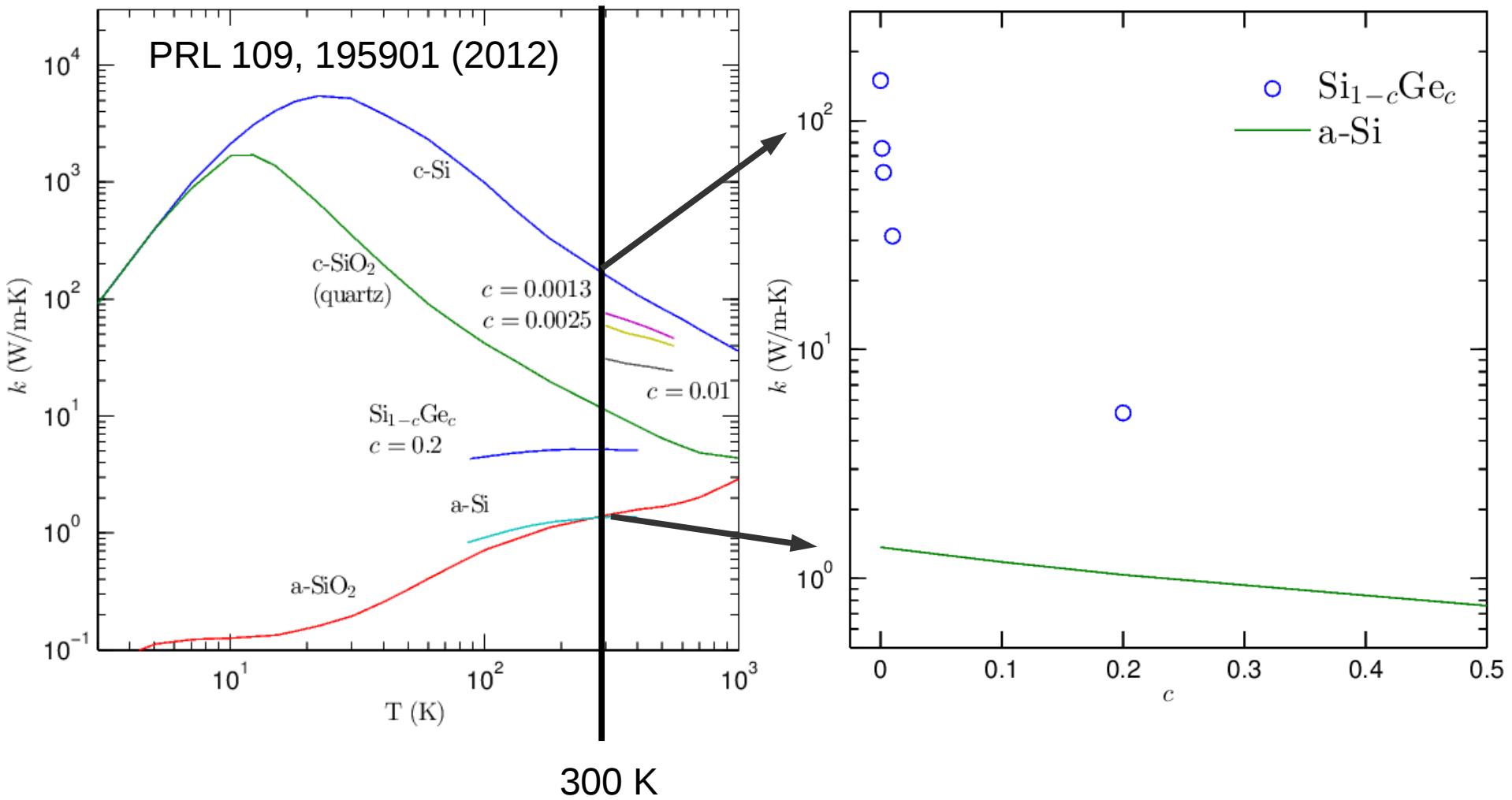
Motivation: Thermoelectrics

$$ZT = \frac{S^2 \sigma T}{k_{\text{thermal}}}$$

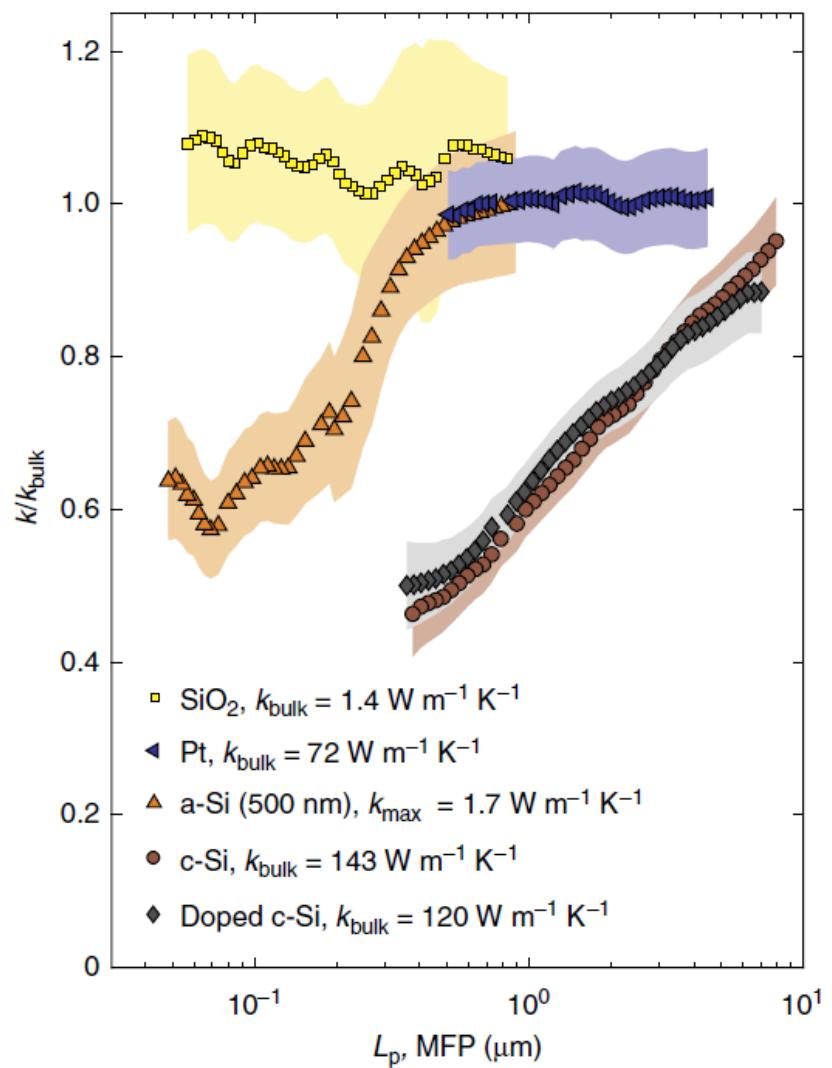


$$k_{\text{thermal}} = k_e + k_{vib} \approx k_{vib}$$

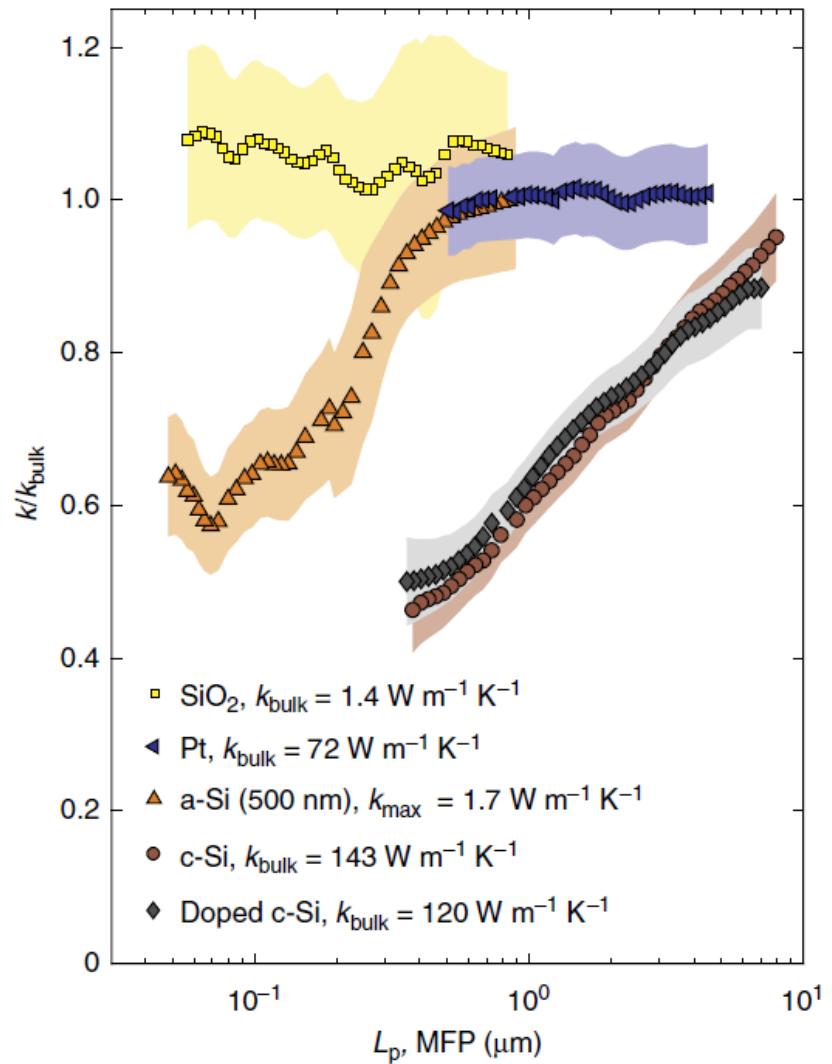
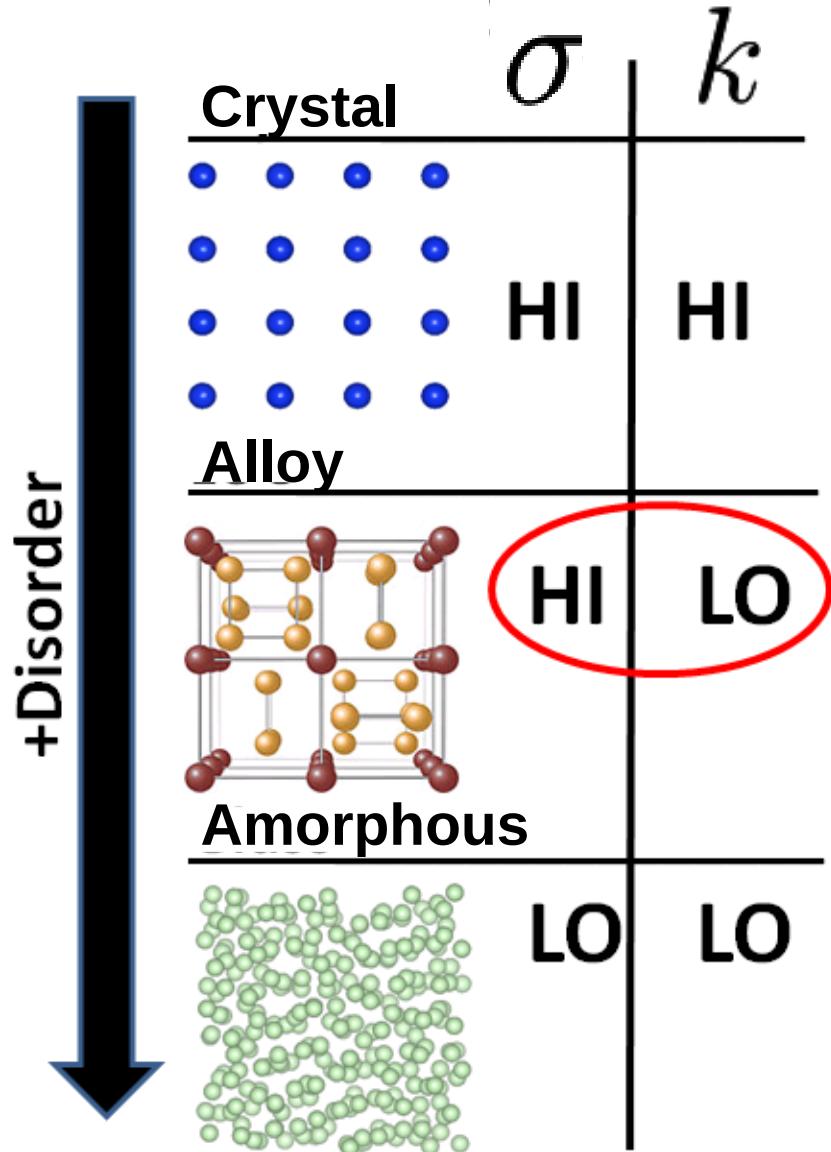
Motivation: Alloys vs. Amorphous



Motivation: Phonons in Amorphous



Motivation: Mode-level Properties



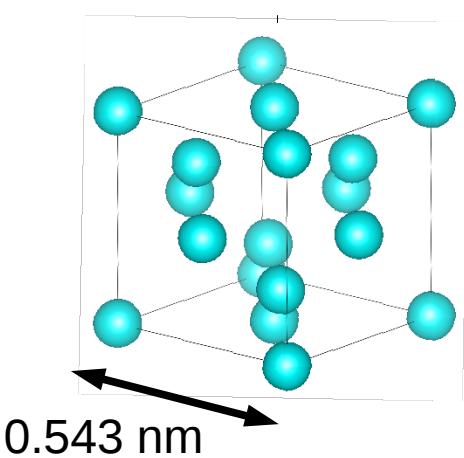
Regner et al., *Nat. Comm.* **4**, 1640 (2013)

Outline

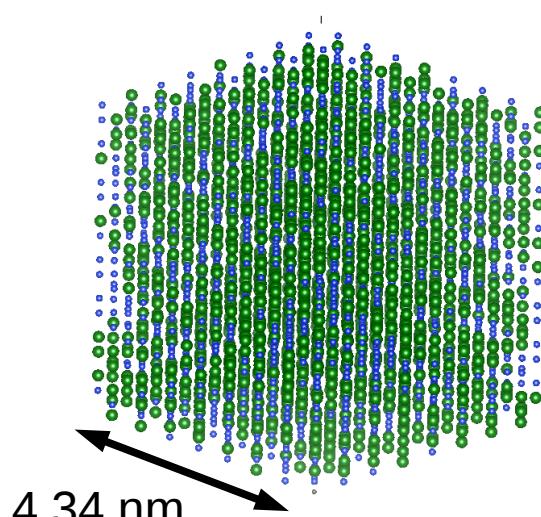
- (1) Motivation
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Mode-level vs. System-level

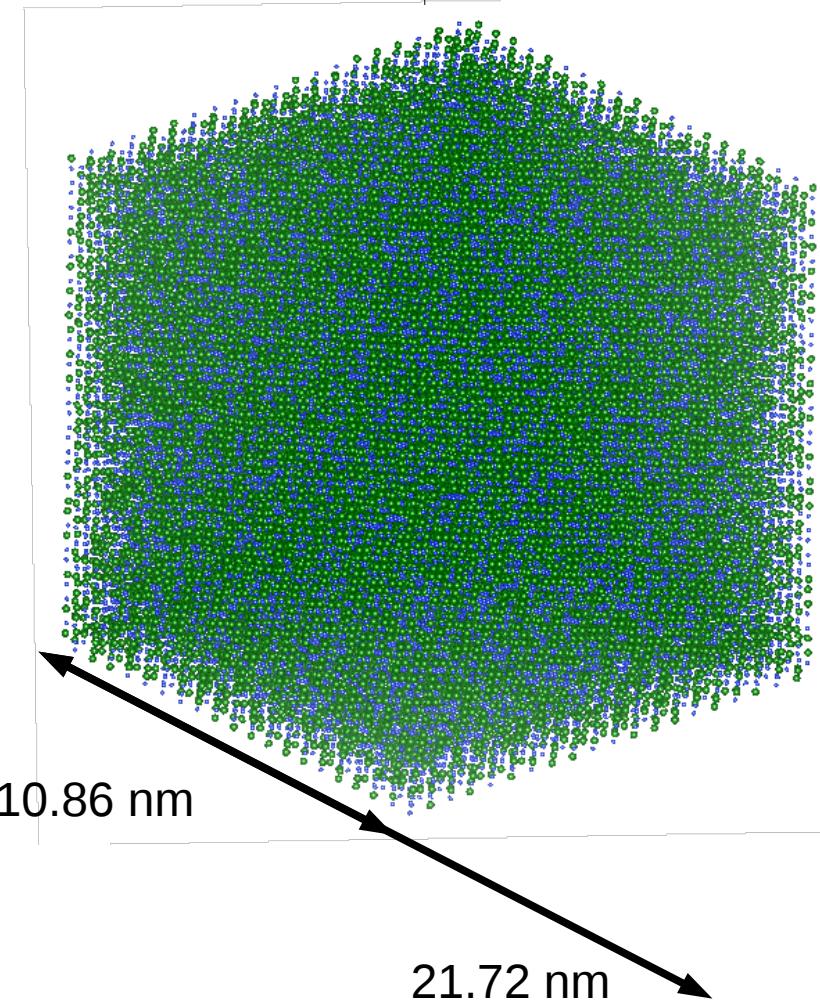
Mode-level:
8 atoms



Mode-level:
~4000 atoms



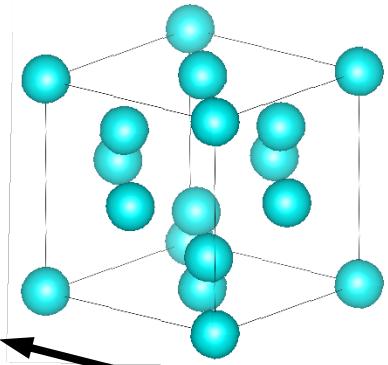
System-level:
~1E6 atoms



Mode-level: Perturbation vs. Explicit

Phonons (ph):

$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$



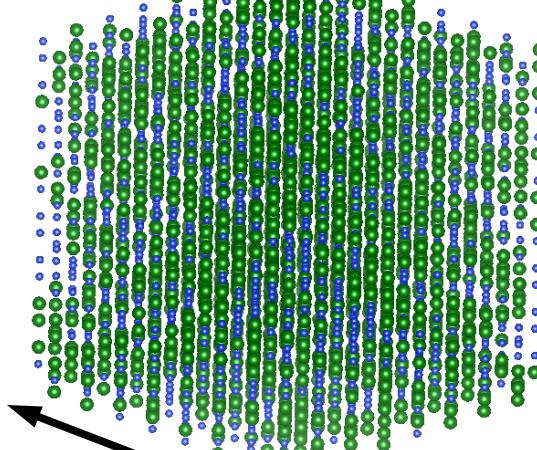
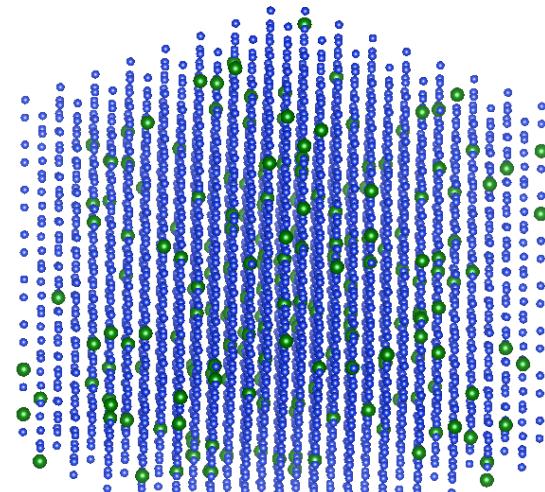
0.543 nm



?



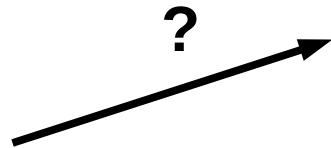
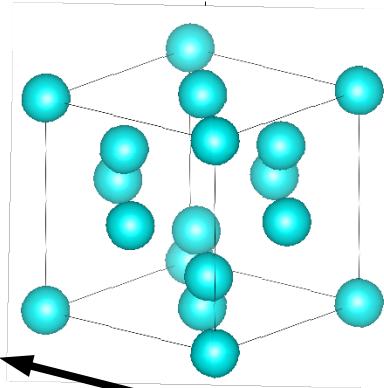
4.34 nm



Mode-level: Explicit

Phonons (ph):

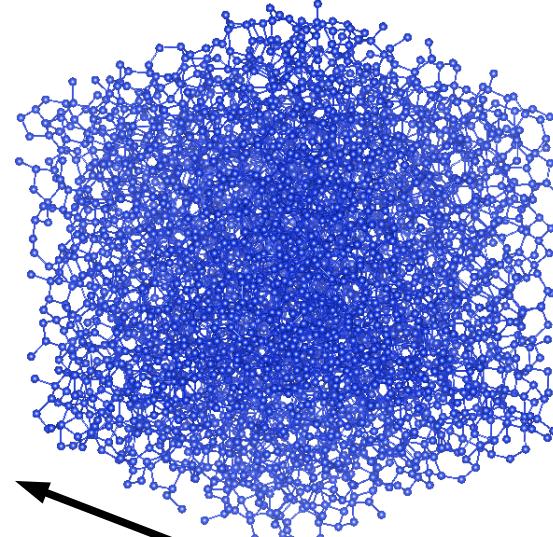
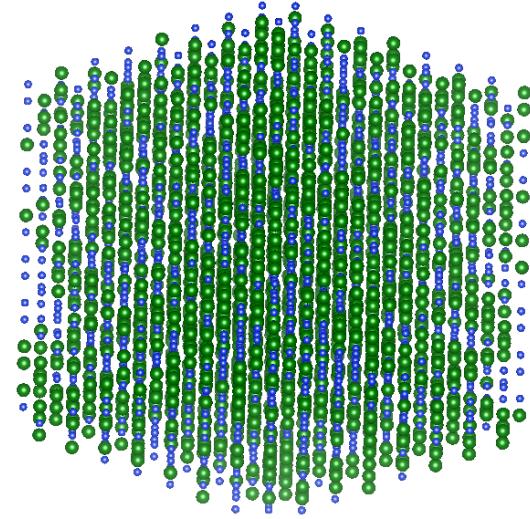
$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$



No



4.34 nm



Disordered Modes: Vibrons

Propagons:

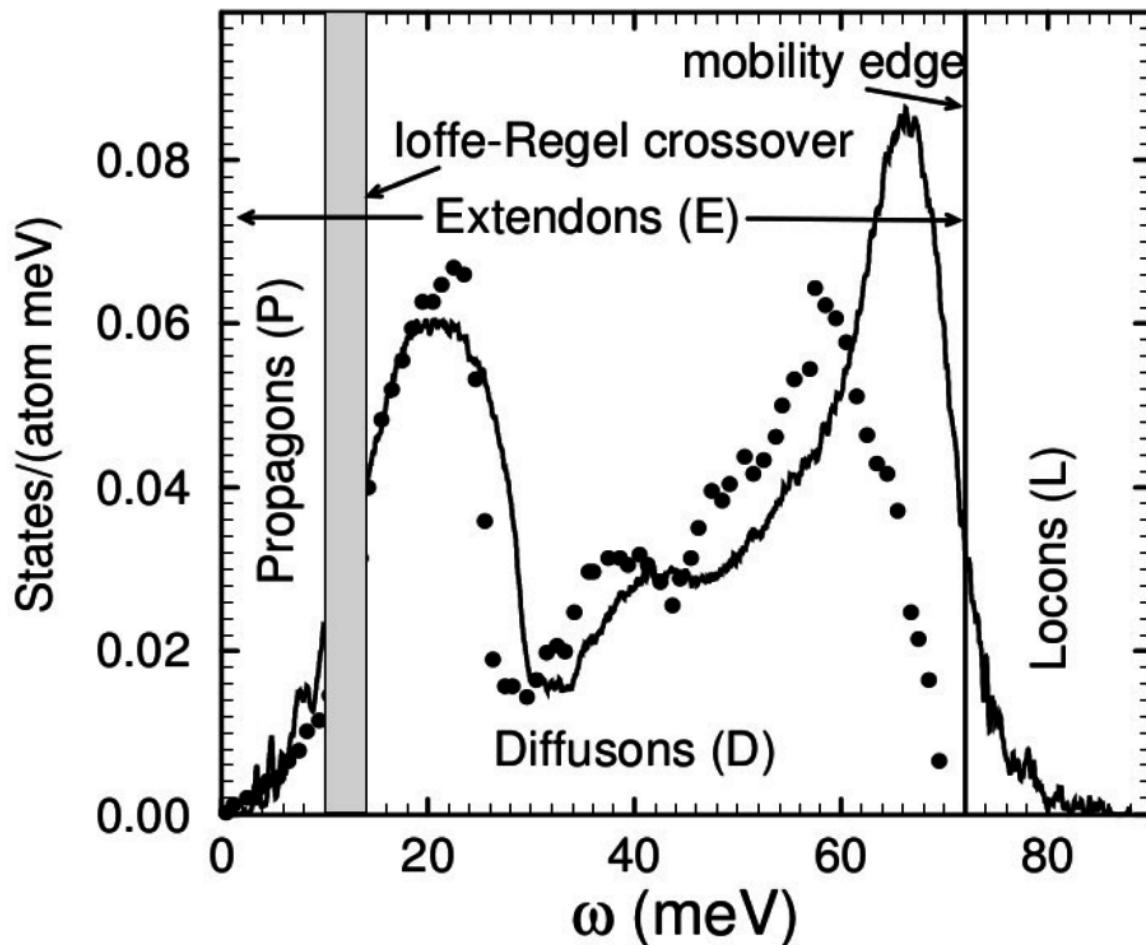
Phonon-like,
propagating,
de-localized

Diffusons:

non-propagating,
de-localized

Locons:

non-propagating,
localized

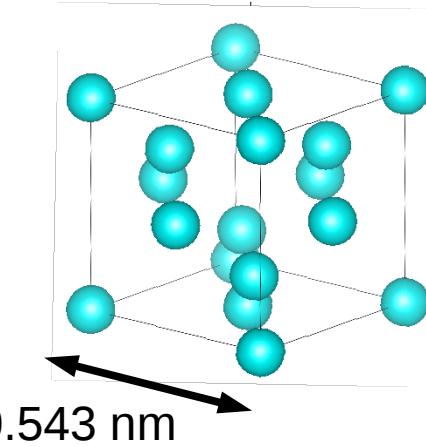


Phil. Mag. B, 79 (1999) 1715-1731

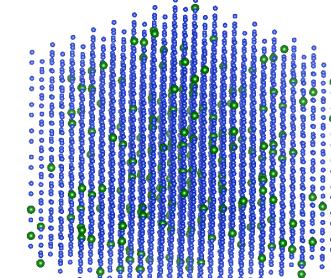
Thermal Conductivity: Mode-level

Phonons (ph):

$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$

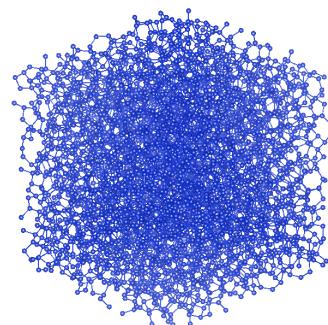
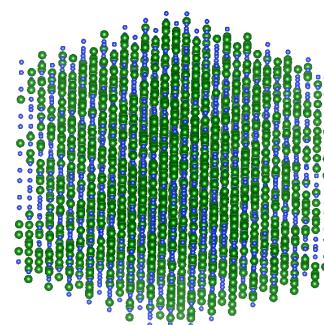


Propagons (phonon-like)



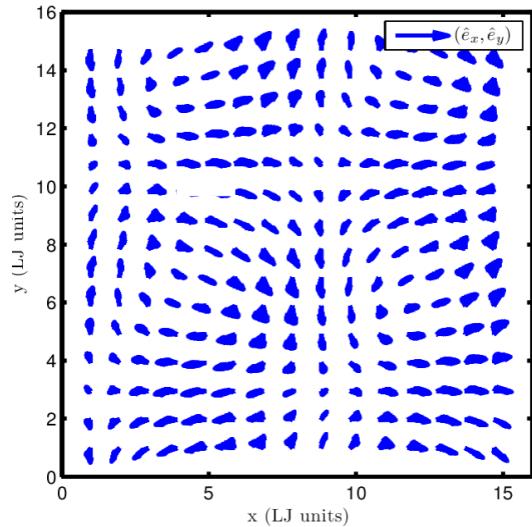
Diffusons:

$$k_{AF} = \sum_{diffusons} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

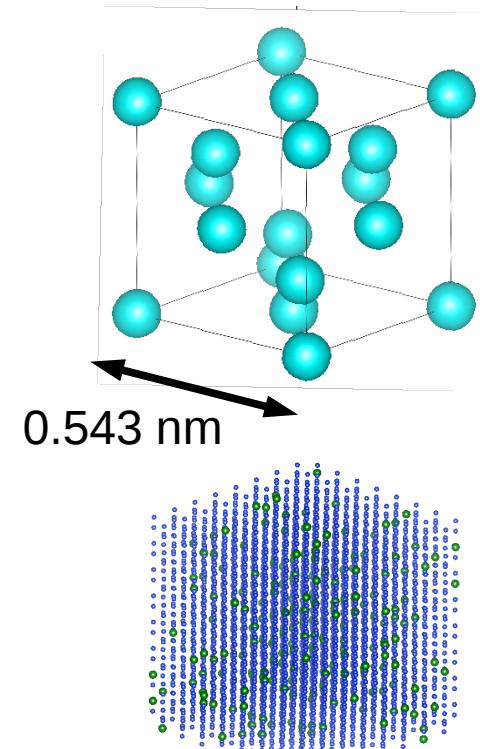


Thermal Conductivity: Mode-level

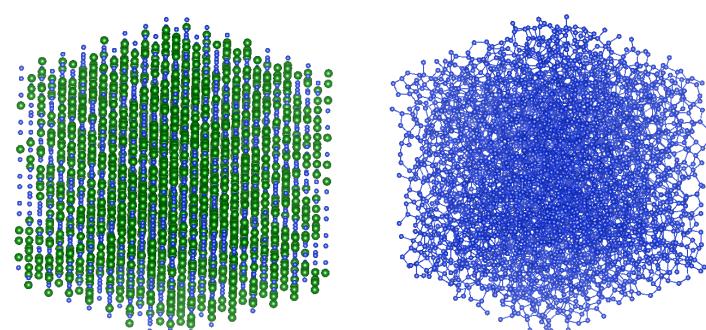
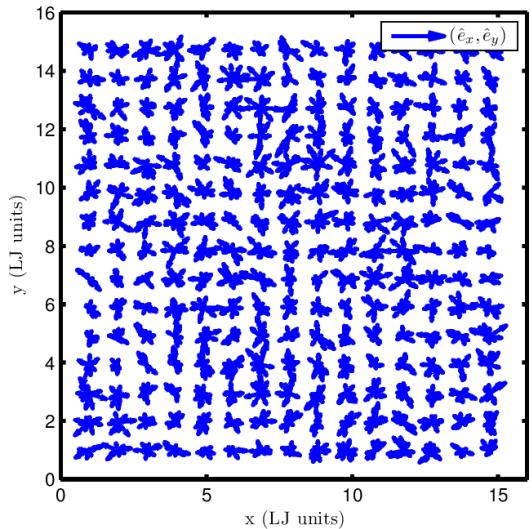
Propagons (phonon-like):



$$e^*(\kappa_{\nu} b_{\alpha})$$

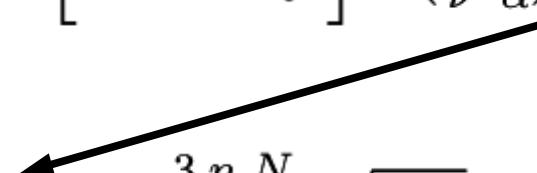


Diffusons:

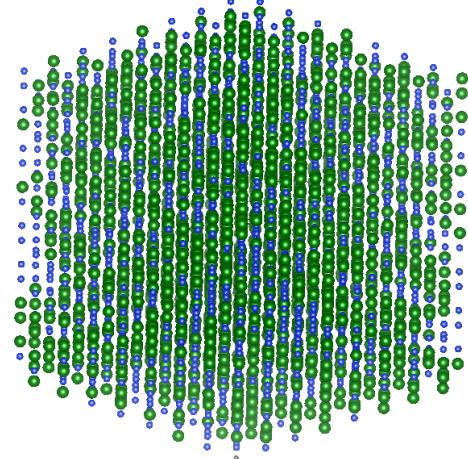


Vibrational Properties: Molecular Dynamics

$$\dot{u}_\alpha(b; t) = \sum_{\kappa, \nu}^{N, 3n} \frac{1}{\sqrt{m_b N}} \exp[i\kappa \cdot \mathbf{r}_0(l)] e^*(\kappa_\nu b_\alpha) \dot{q}(\kappa_\nu; t)$$



$$\dot{q}(\kappa_\nu; t) = \sum_{\alpha, b, l}^{3, n, N} \sqrt{\frac{m_b}{N}} \dot{u}_\alpha(b; t) e^*(\kappa_\nu b_\alpha) \exp[i\kappa \cdot \mathbf{r}_0(l)]$$



J. M. Larkin, J. E. Turney, A. D. Massicotte, C. H. Amon, and A. J. H. McGaughey, "Comparison and evaluation of spectral energy methods for predicting phonon properties." To appear in Journal of Computational and Theoretical Nanoscience.

A. J. H. McGaughey and J. M. Larkin, "Predicting phonon properties from equilibrium molecular dynamics simulations." To appear in Annual Reviews of Heat Transfer, Volume 17.

J. M. Larkin and A. J. H. McGaughey, "Predicting alloy vibrational mode properties using lattice dynamics calculations, molecular dynamics simulations, and the virtual crystal approximation." Journal of Applied Physics 114 (2013) 023507.

J. M. Larkin and A. J. H. McGaughey, "Thermal Conductivity Accumulation in Amorphous Materials", Physical Review B (submitted).

S. C. Huberman, J. M. Larkin and A. J. H. McGaughey, C. H. Amon, "Disruption of Superlattice Phonons by Interfacial Mixing", Physical Review B (submitted).

Vibrational Properties: Molecular Dynamics

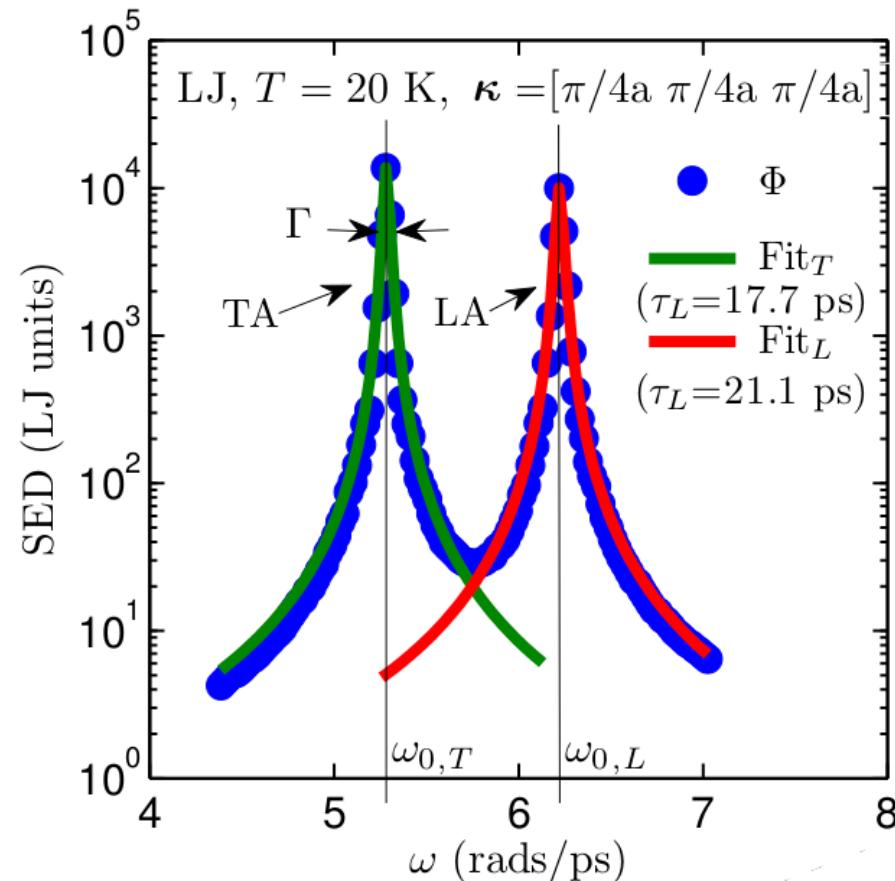
Normal Mode Decomposition (NMD):

$$E(\kappa; t) = \frac{\omega(\kappa)^2}{2} q(\kappa; t)^* q(\kappa; t) + \frac{1}{2} \dot{q}(\kappa; t)^* \dot{q}(\kappa; t)$$

PE **KE**

$$\Phi(\kappa, \omega) = \sum_{\nu}^{3n} C_0(\nu) \frac{\Gamma(\nu)/\pi}{[\omega_0(\nu) - \omega]^2 + \Gamma^2(\nu)}$$

$$\tau(\nu) = 1/[2\Gamma(\nu)]$$



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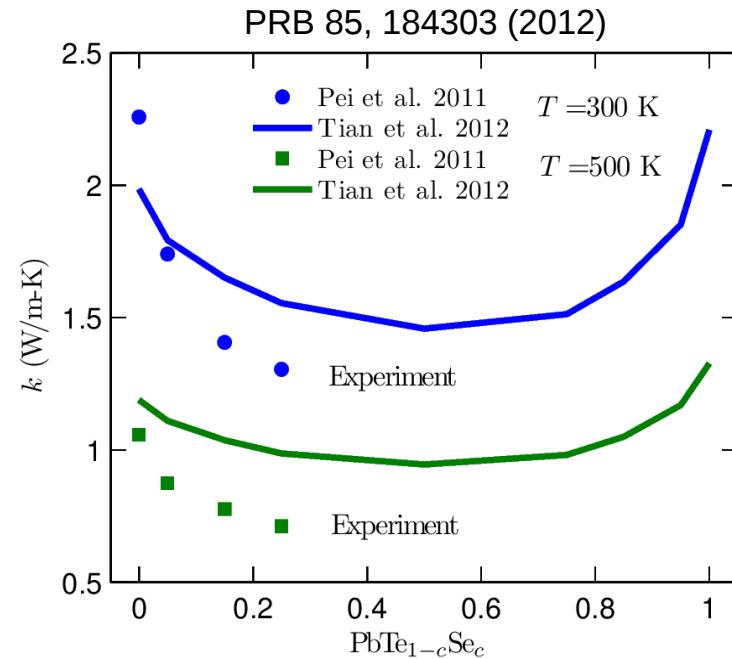
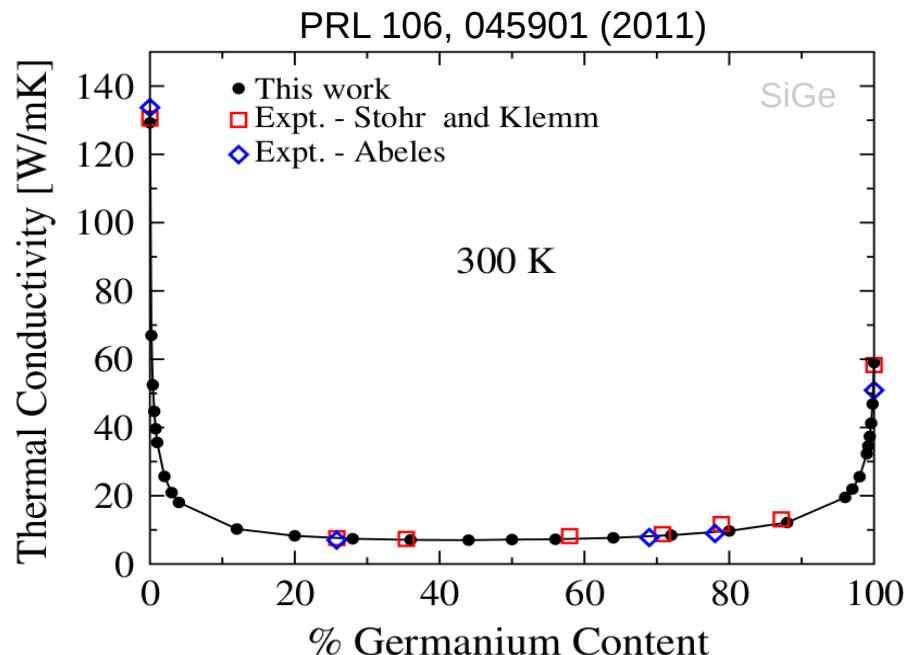
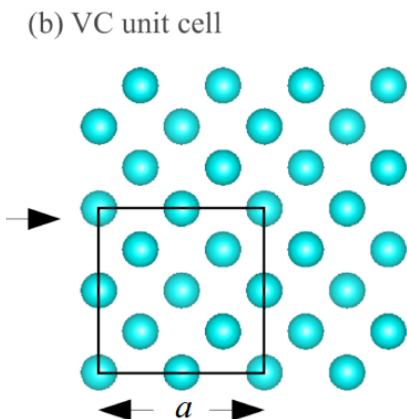
Alloys: experimental accuracy

Expensive Density Functional Theory (DFT) calculations

+

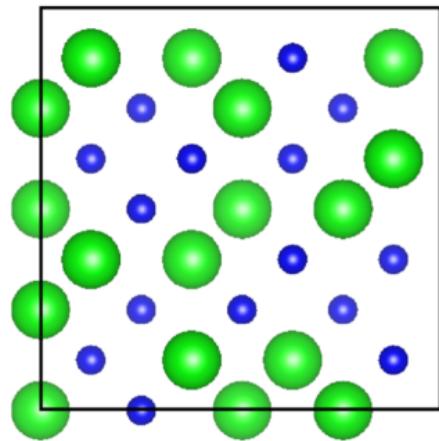
Virtual Crystal (VC) approximation &
Anharmonic Lattice Dynamics (ALD) (**VC-ALD**)

Alloys: isotopic effects, thermoelectric materials

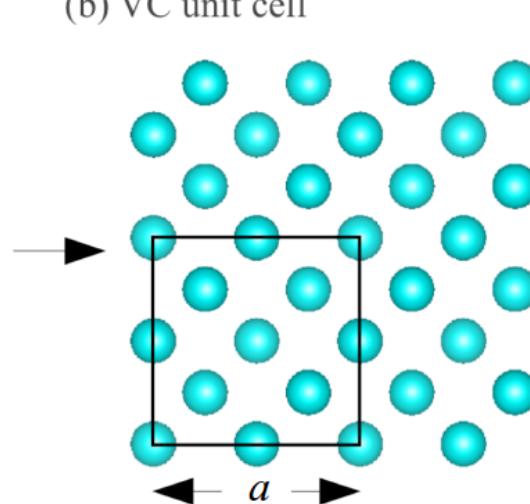


Alloys: Virtual Crystal Approximation

(a) disordered supercell



(b) VC unit cell



$$c^\mu, m^\mu$$

$$\bar{m}^\mu = (1 - c)m^i + cm^j$$

Thermal conductivity:

$$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} \frac{k_B}{V} D_{ph,\mathbf{n}}(\boldsymbol{\nu})$$

Thermal diffusivity:

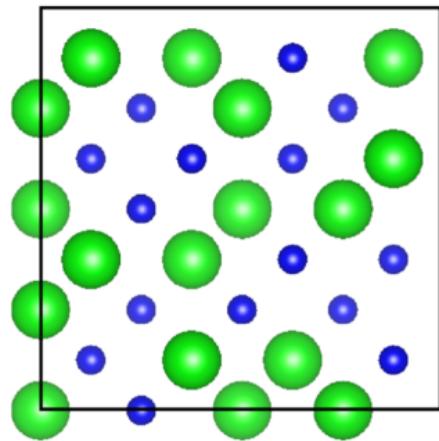
$$D_{ph,\mathbf{n}}(\boldsymbol{\nu}) = v_{g,\mathbf{n}}^2(\boldsymbol{\nu}) \tau(\boldsymbol{\nu})$$

Diffusons:

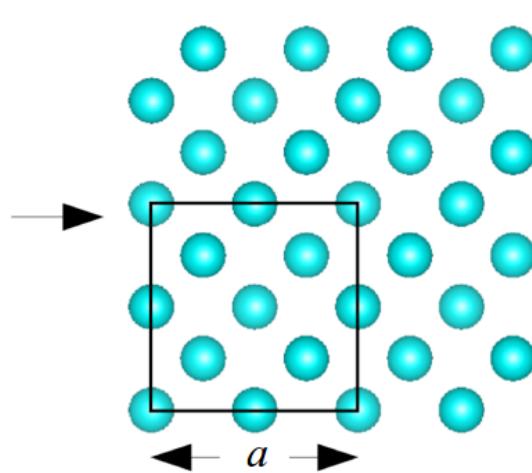
$$k_{AF} = \sum_{diffusons} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

VC-ALD: Group Velocity

(a) disordered supercell



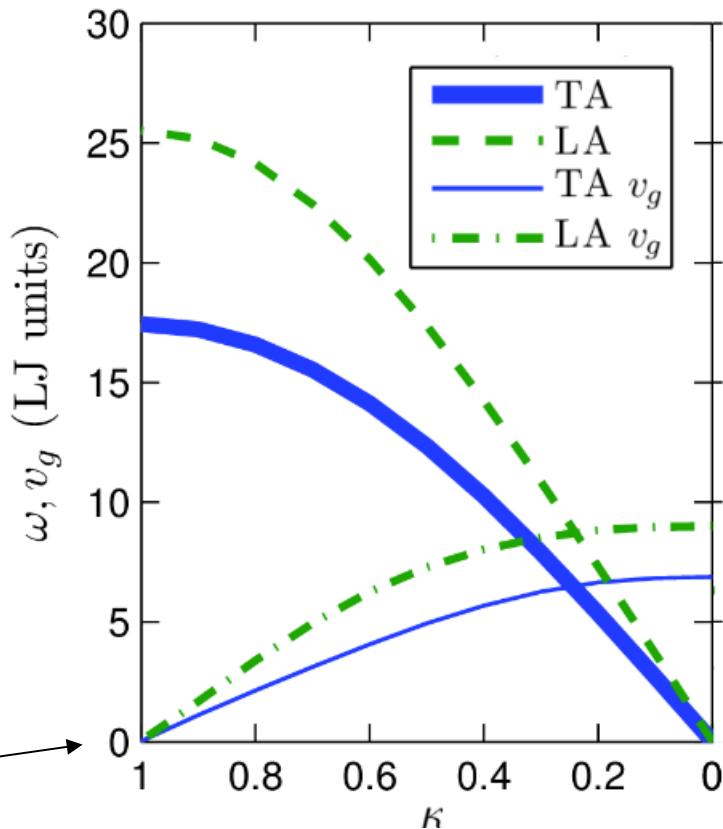
(b) VC unit cell



$$v_{g,\mathbf{n}}(\kappa) = \frac{\partial \omega(\kappa)}{\partial \kappa}$$

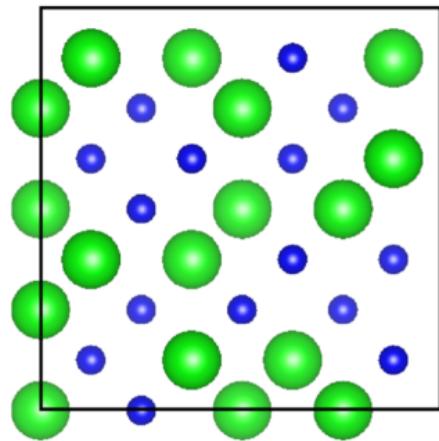
$$D_{ph}(\kappa) \approx 0$$

$$D_{ph,\mathbf{n}}(\kappa) = v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$

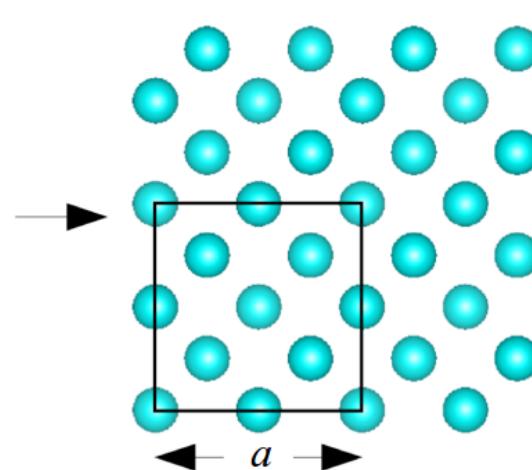


VC-ALD: Lifetimes

(a) disordered supercell



(b) VC unit cell



$$D_{ph,\mathbf{n}}(\kappa_\nu) = v_{g,\mathbf{n}}^2(\kappa_\nu) \tau(\kappa_\nu)$$

ALD

$$\tau_{p-p} \sim 1/\omega^2$$



Tamura

$$\tau_{p-d}(\kappa_\nu) \sim 1/\omega^4$$

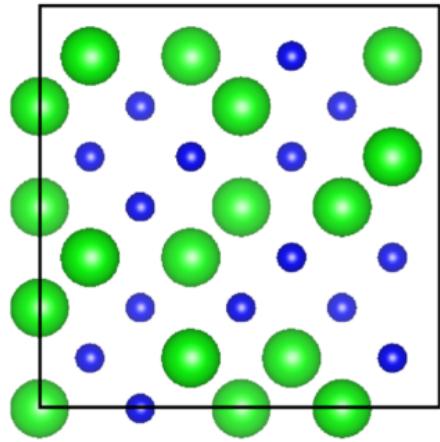


Matthiessen's Rule:

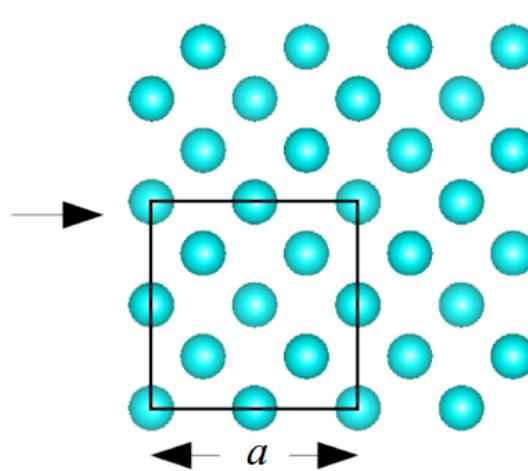
$$\frac{1}{\tau(\kappa_\nu)} = \frac{1}{\tau_{p-p}(\kappa_\nu)} + \frac{1}{\tau_{p-d}(\kappa_\nu)}$$

Explicit disorder: VC vs Gamma

(a) disordered supercell



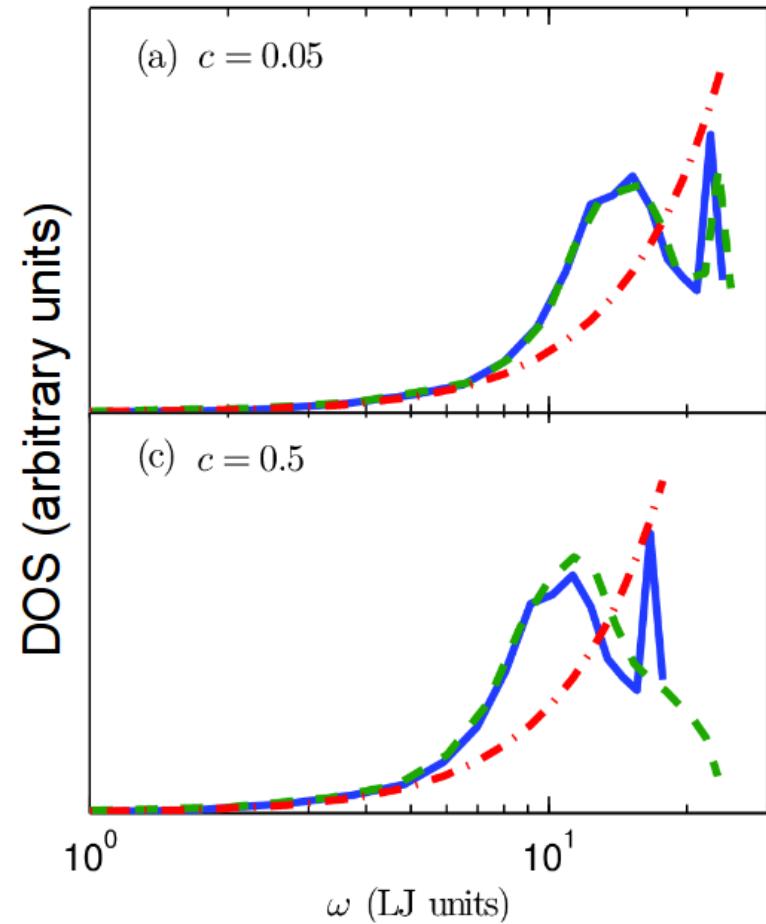
(b) VC unit cell



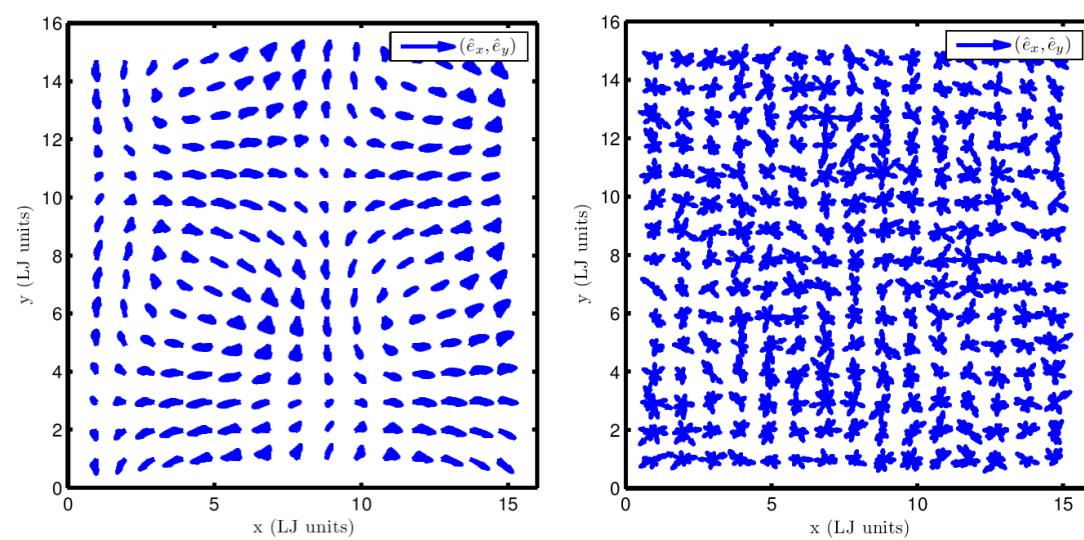
Gamma

Computationally-inexpensive
empirical potential:
Lennard-Jones argon

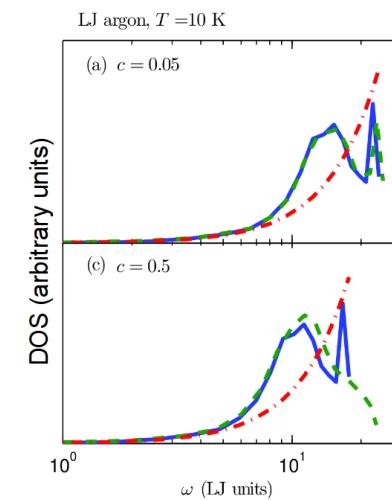
LJ argon, $T = 10$ K



Structure Factor: Effective Dispersion



$$e^*(\kappa'_\nu b_\alpha)$$

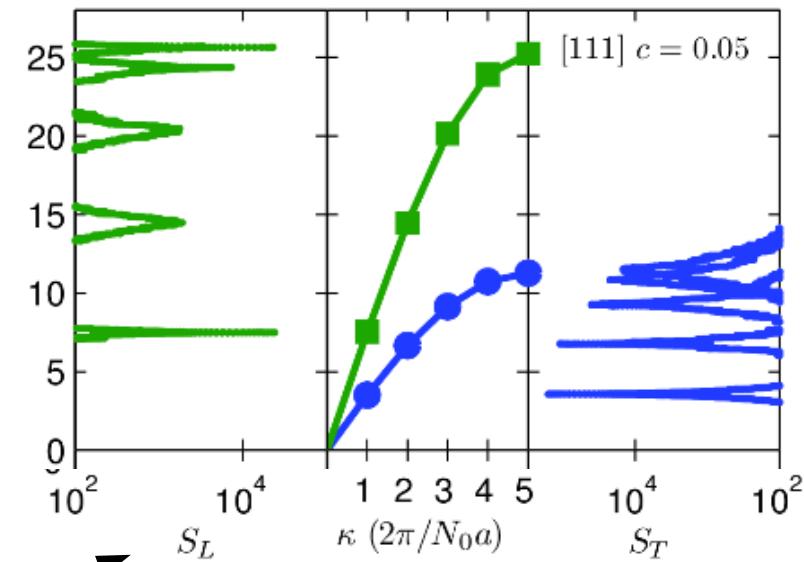


$$v_{g,\mathbf{n}}(\kappa_\nu) = \frac{\partial \omega(\kappa_\nu)}{\partial \kappa}$$

$$E^T(\kappa_{\nu}^{VC}) = \left| \sum_b \hat{\kappa}_{VC} \times e(\kappa_\nu = 0 b) \exp[i\kappa_{VC} \cdot \mathbf{r}_0(l=0)] \right|^2$$

$$E^L(\kappa_{\nu}^{VC}) = \left| \sum_b \hat{\kappa}_{VC} \cdot e(\kappa_\nu = 0 b) \exp[i\kappa_{VC} \cdot \mathbf{r}_0(l=0)] \right|^2$$

Gamma VC Gamma

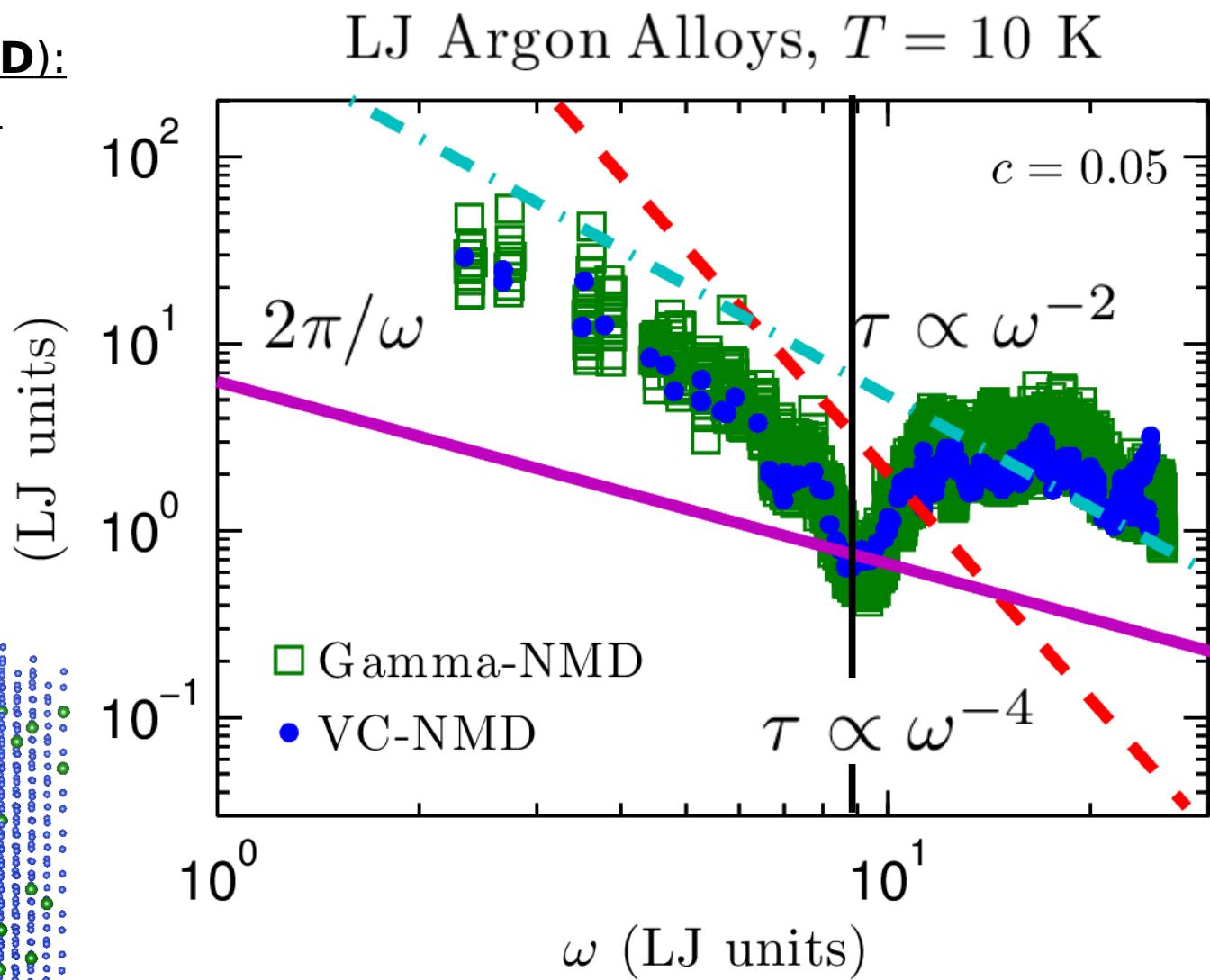
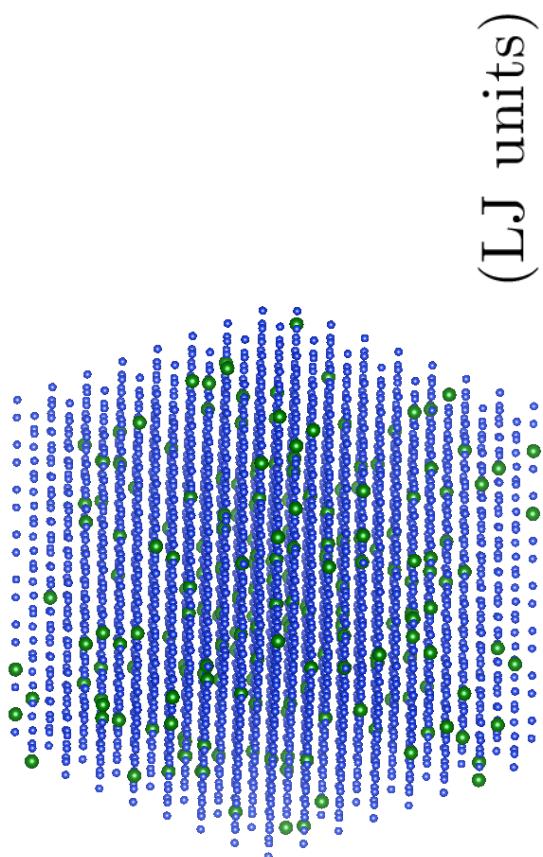


$$S^{L,T}(\omega) = \sum_\nu E^{L,T}(\kappa_\nu^{VC}) \delta[\omega - \omega(\kappa_\nu = 0)]$$

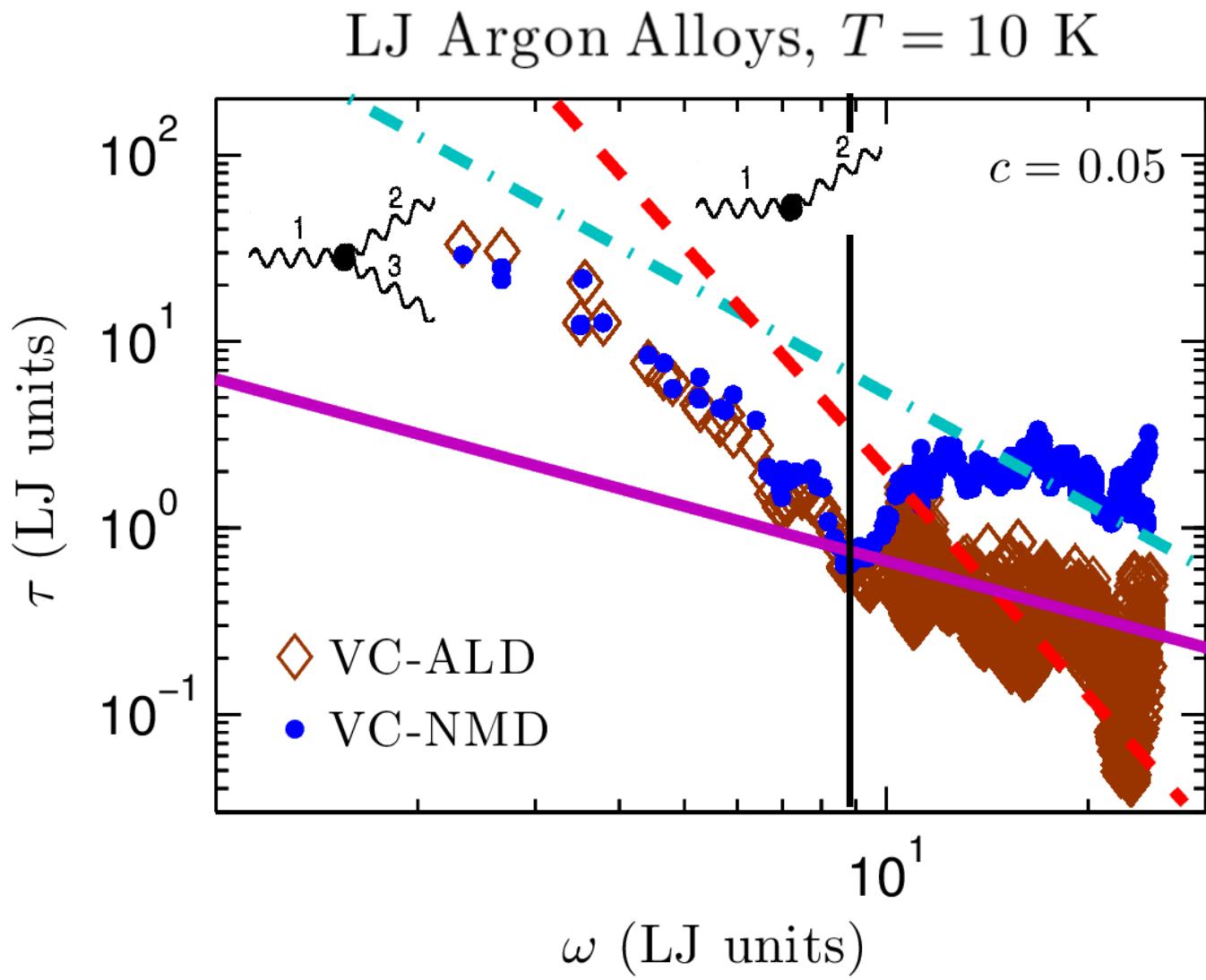


Explicit disorder: NMD

- Normal Mode Decomposition (NMD): Molecular Dynamics



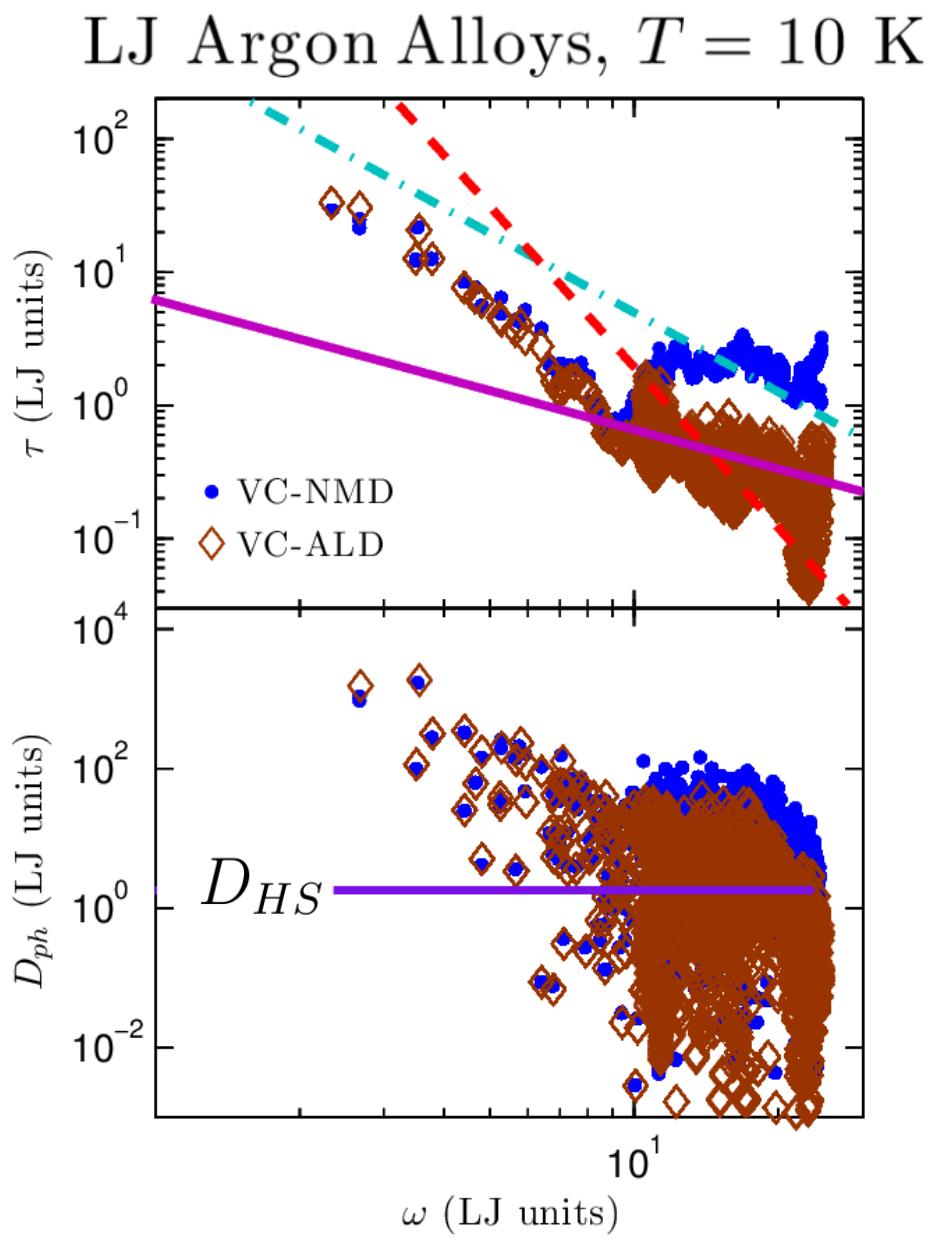
VC-NMD vs VC-ALD



VC Diffusivities

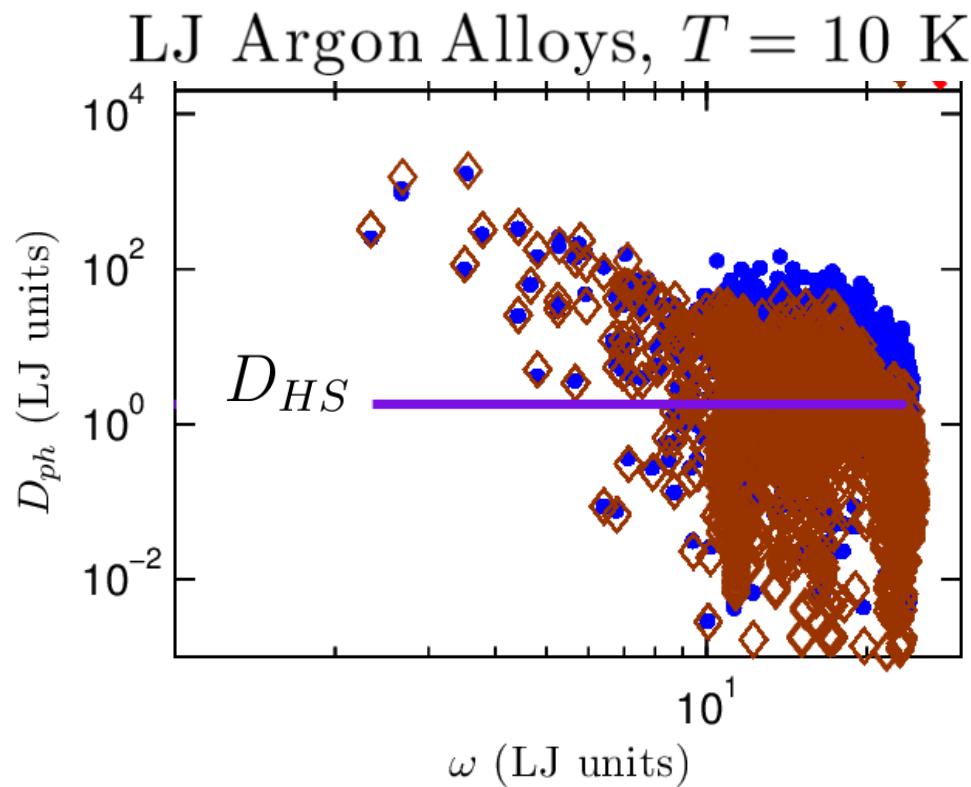
$$D_{ph}(\kappa_\nu) \approx 0$$

$$D_{HS} = \frac{1}{3} v_s a$$

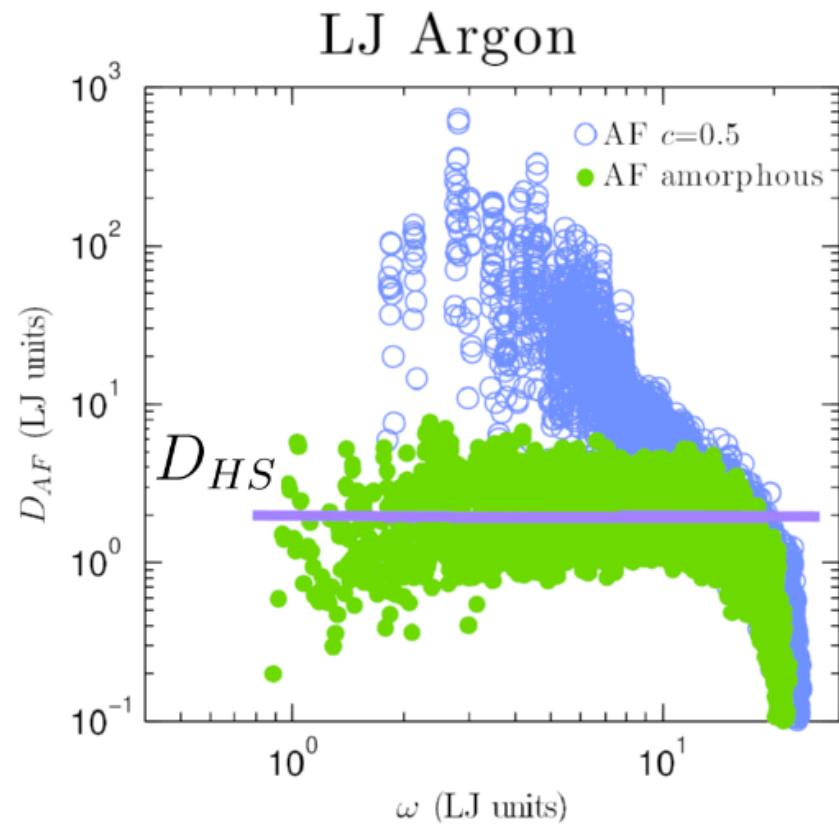


AF and VC Diffusivities

Phonons



Diffusons

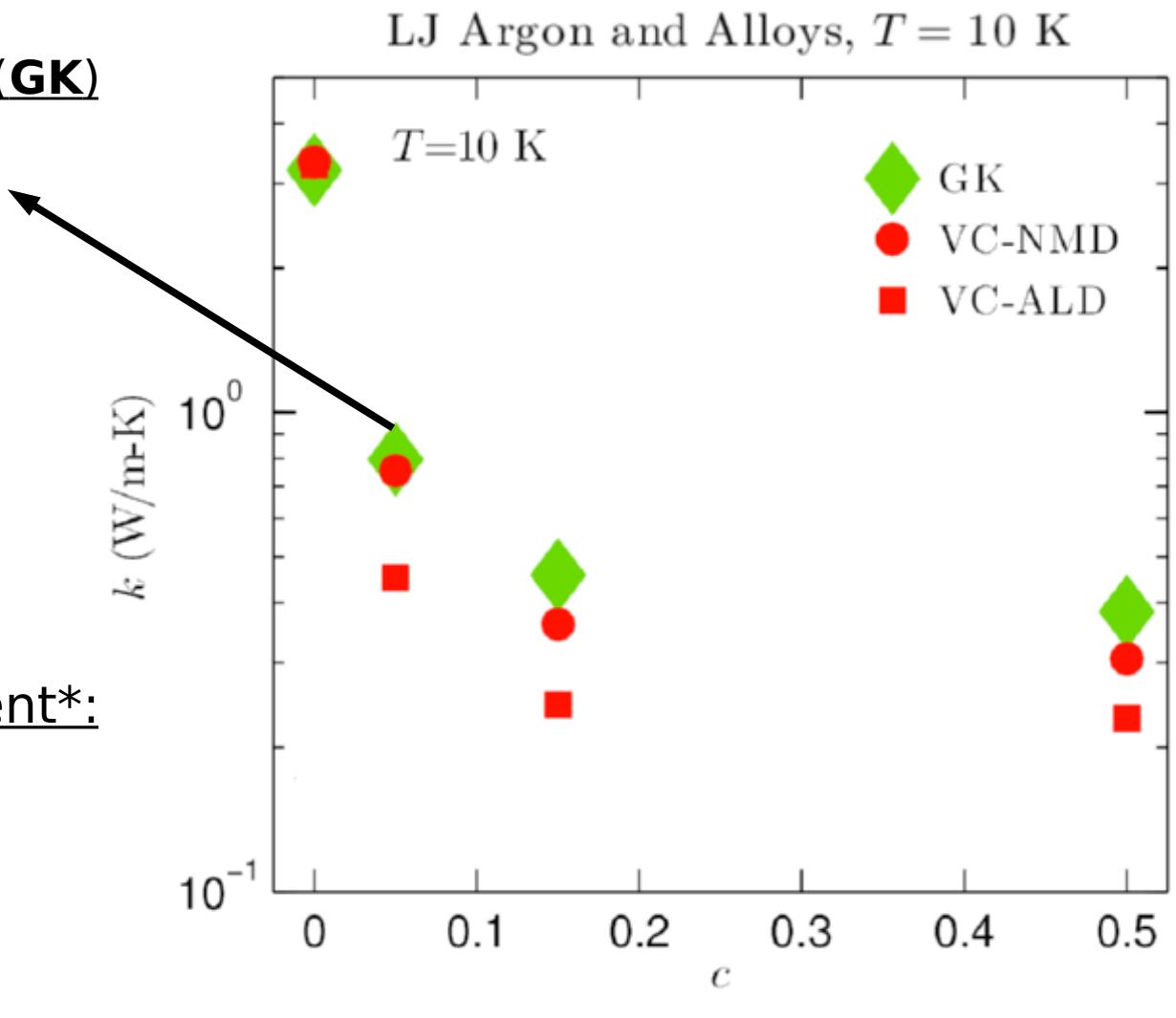


PRB 48, 1258112588 (1993)

$$k_{AF} = \sum_{\text{diffusons}} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

Thermal conductivity

- MD-based Green-Kubo (GK) System-level



High-scatter adjustment*:

$$D_{ph}(\kappa_\nu) < D_{HS}$$

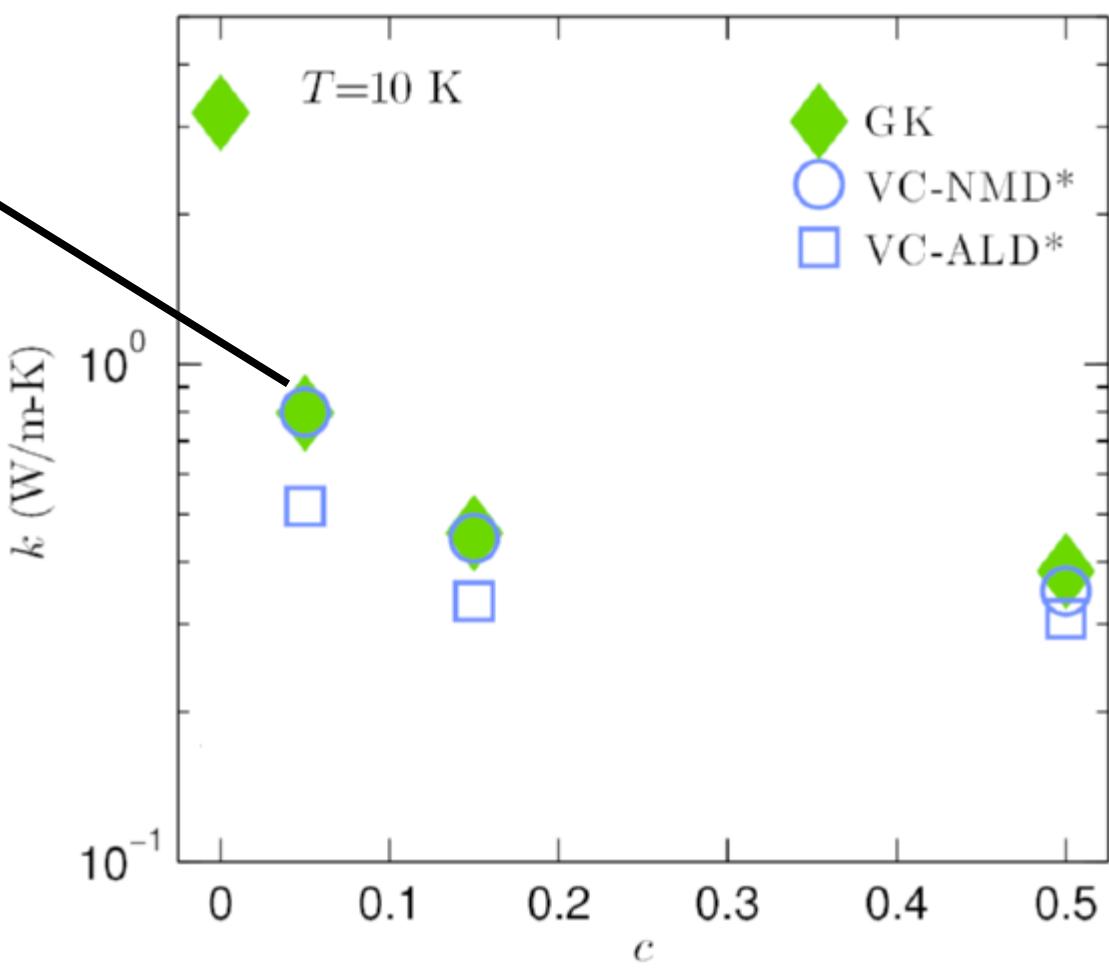
$$D_{ph}(\kappa_\nu) = D_{HS}$$

Thermal conductivity

- MD-based Green-Kubo (GK): System-level



LJ Argon and Alloys, $T = 10$ K



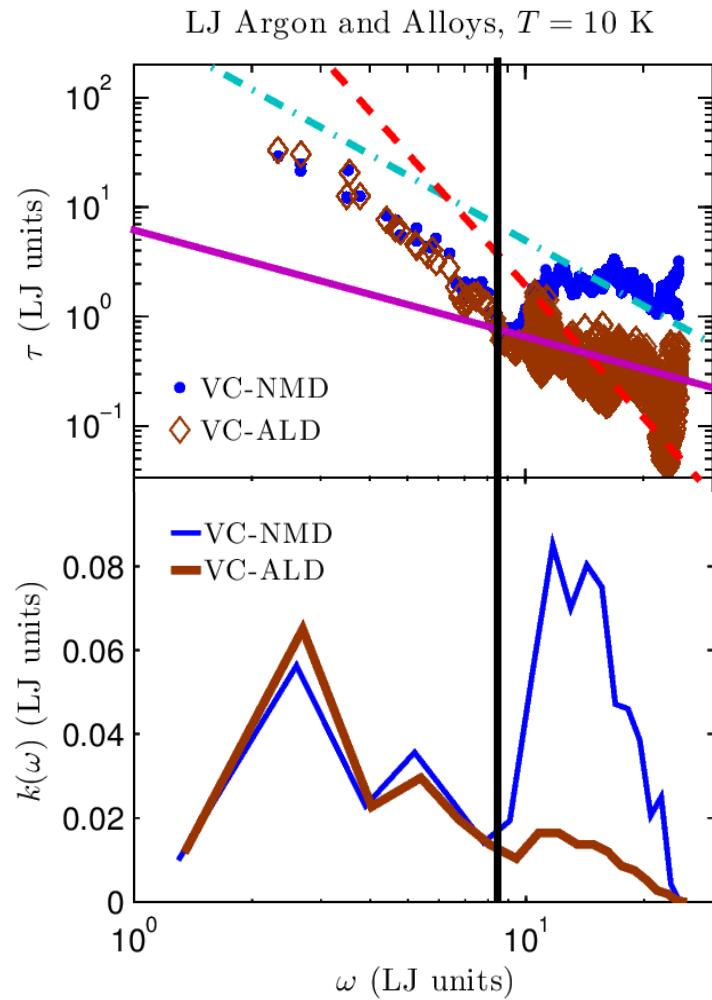
High-scatter adjustment*:

$$D_{ph}(\kappa) < D_{HS}$$

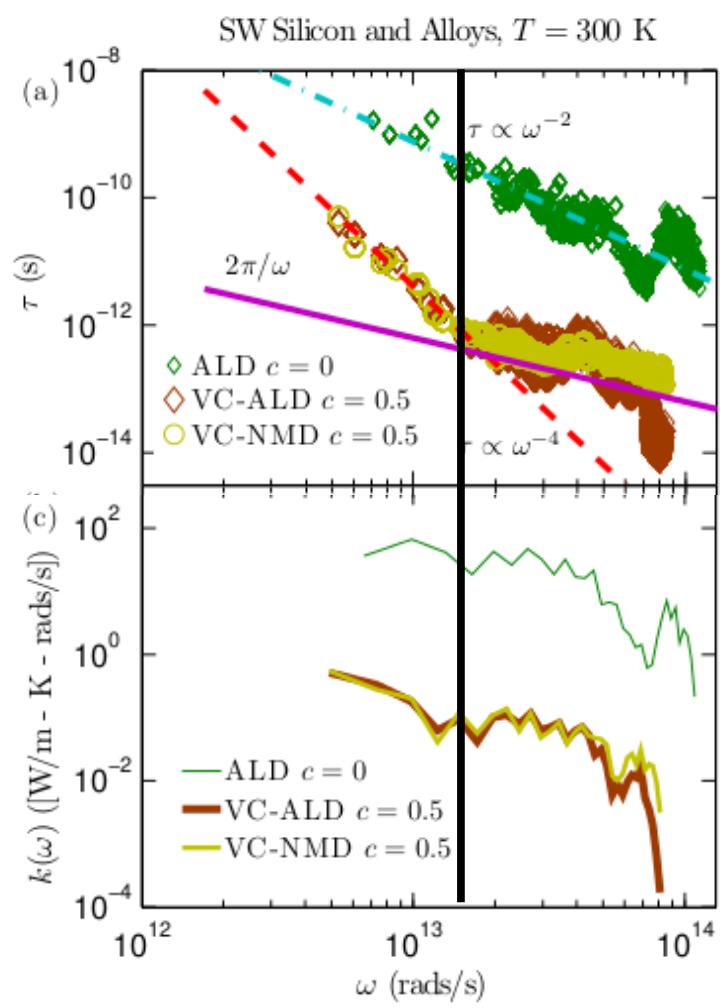
$$D_{ph}(\kappa) < D_{HS}$$

Alloys: Thermal Conductivity Spectrum

Low and High Frequency



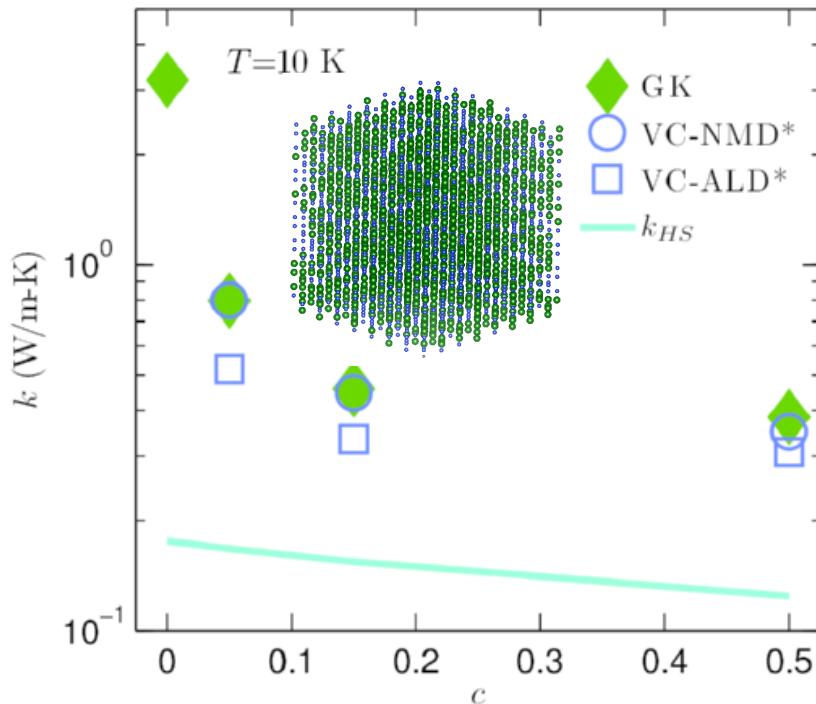
High Frequency



Alloys: Two Classes

Full-Spectrum Alloys

LJ Argon and Alloys, $T = 10$ K



High-scatter adjustment*:

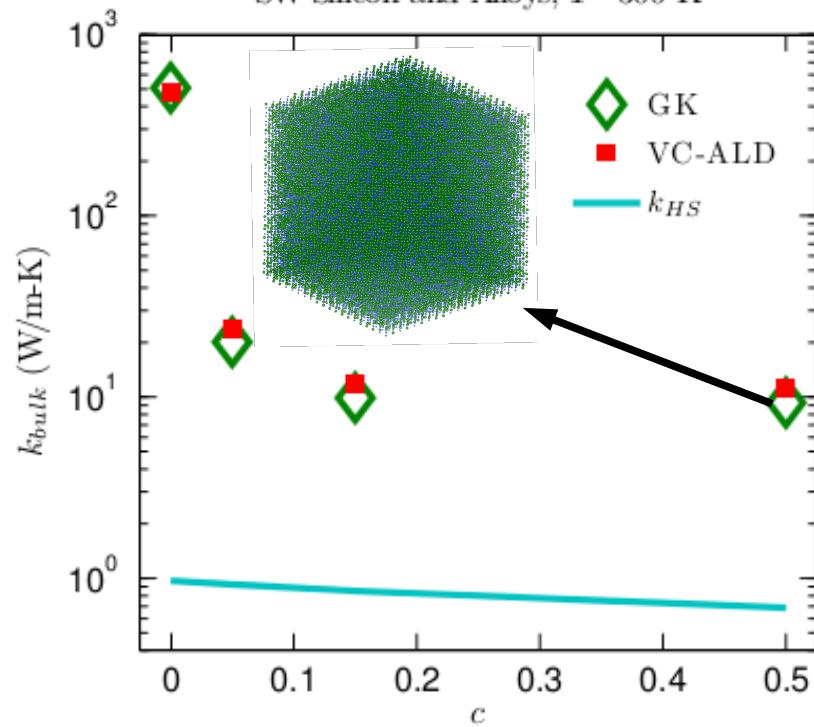
$$D_{ph}(\kappa) < D_{HS}$$

$$k_{HS} = \frac{k_B}{V_b} b v_s a$$

J. M. Larkin and A. J. H. McGaughey, "Predicting alloy vibrational mode properties using lattice dynamics calculations, molecular dynamics simulations, and the virtual crystal approximation." Journal of Applied Physics 114 (2013) 023507.

Low-frequency Alloys

SW Silicon and Alloys, $T=300$ K



$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} \frac{k_B}{V} D_{ph,\mathbf{n}}(\kappa)$$

Thermal Conductivity Accumulation in Amorphous Materials

Jason Larkin and Alan J. H. McGaughey

Department of Mechanical Engineering
Carnegie Mellon University

<http://ntpl.me.cmu.edu/>

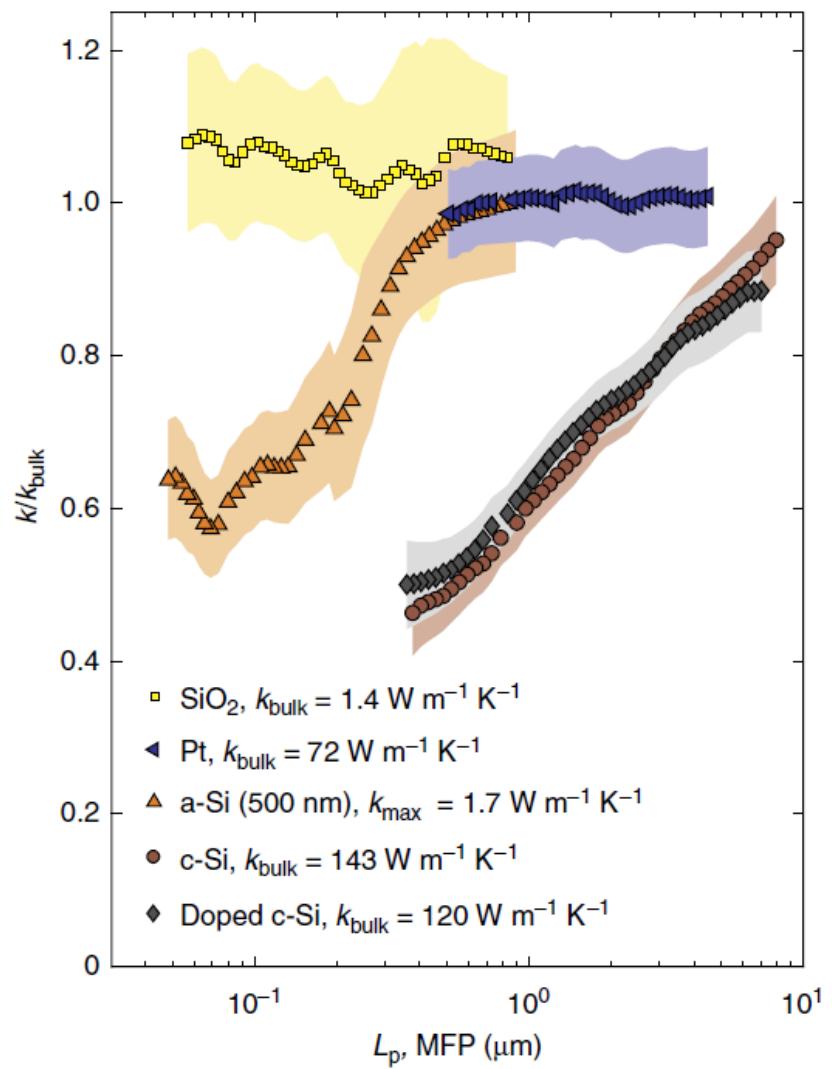
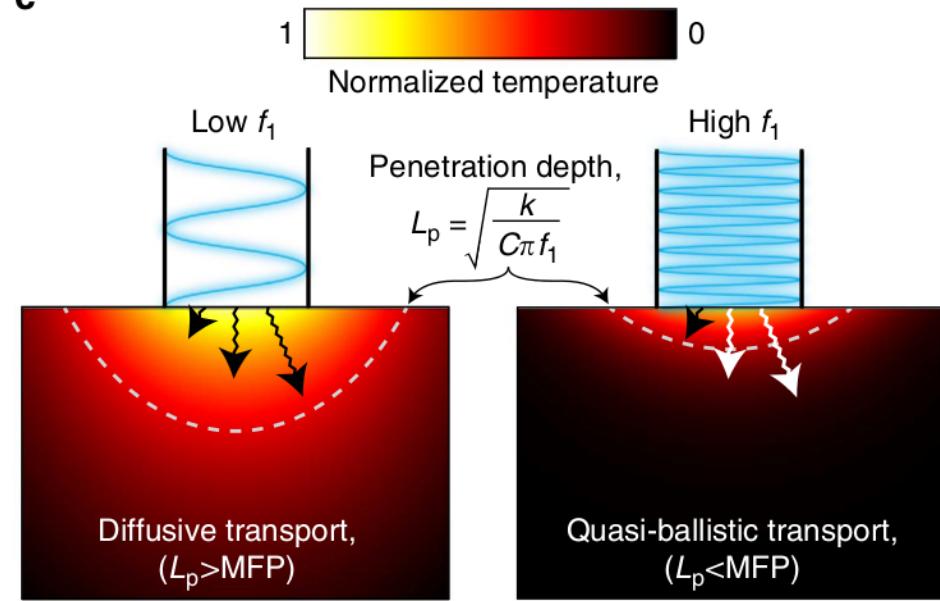
04/04/13

Outline

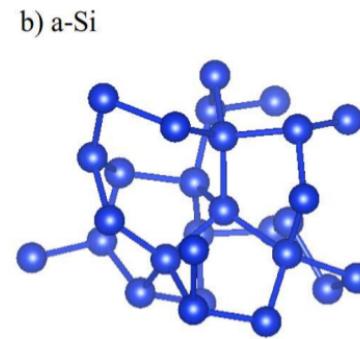
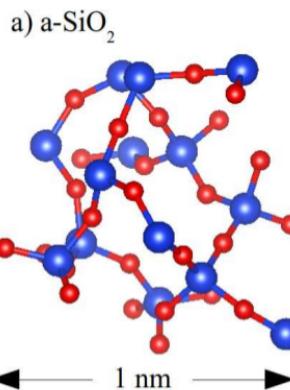
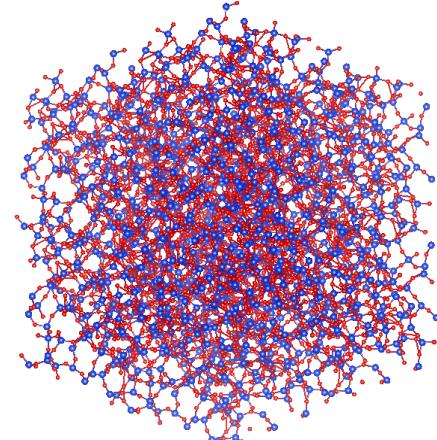
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Amorphous: Motivation

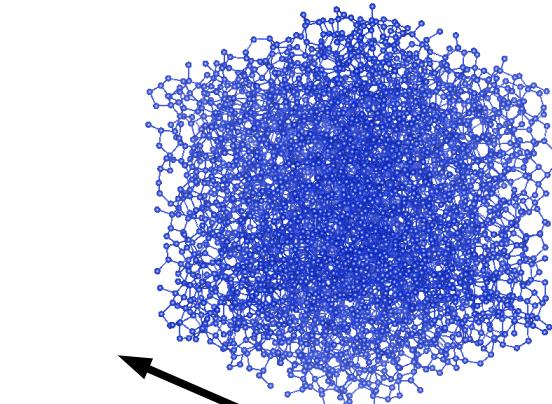
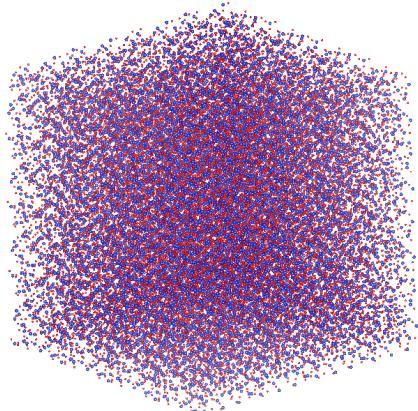
c



Amorphous Solids: no VC

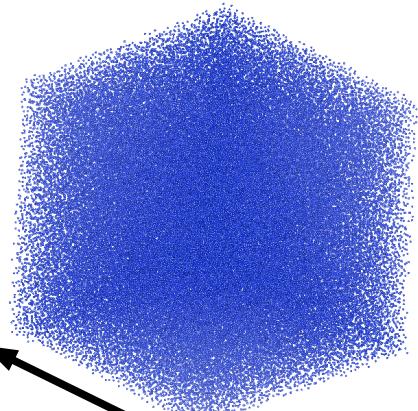


Mode-level:
~4000 atoms



System-level:
~1E6 atoms

~25 nm



Vibron Thermal Conductivity

$$k_{vib} = k_{pr} + k_{AF}$$

Diffusons (non-propagating):

$$k_{AF} = \frac{1}{V} \sum_{i, \omega_i > \omega_{cut}} C(\omega_i) D_{AF}(\omega_i)$$

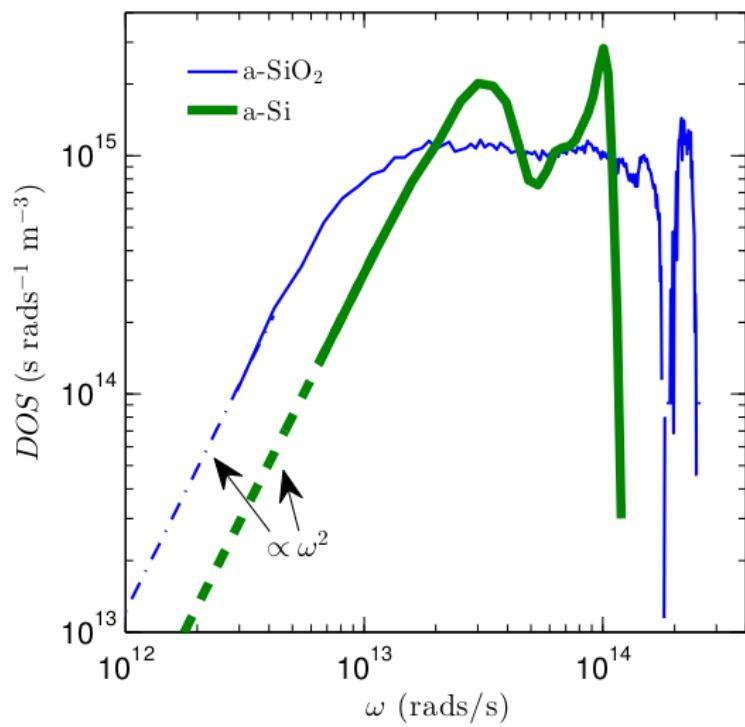
Propagons (phonon-like): $k_{pr} = \frac{1}{V} \int_0^{\omega_{cut}} DOS(\omega) C(\omega) D_{pr}(\omega) d\omega$

$$D_{pr}(\omega) = \frac{1}{3} v_s^2 \tau(\omega)$$

$$\Lambda(\omega) = v_s \tau(\omega)$$

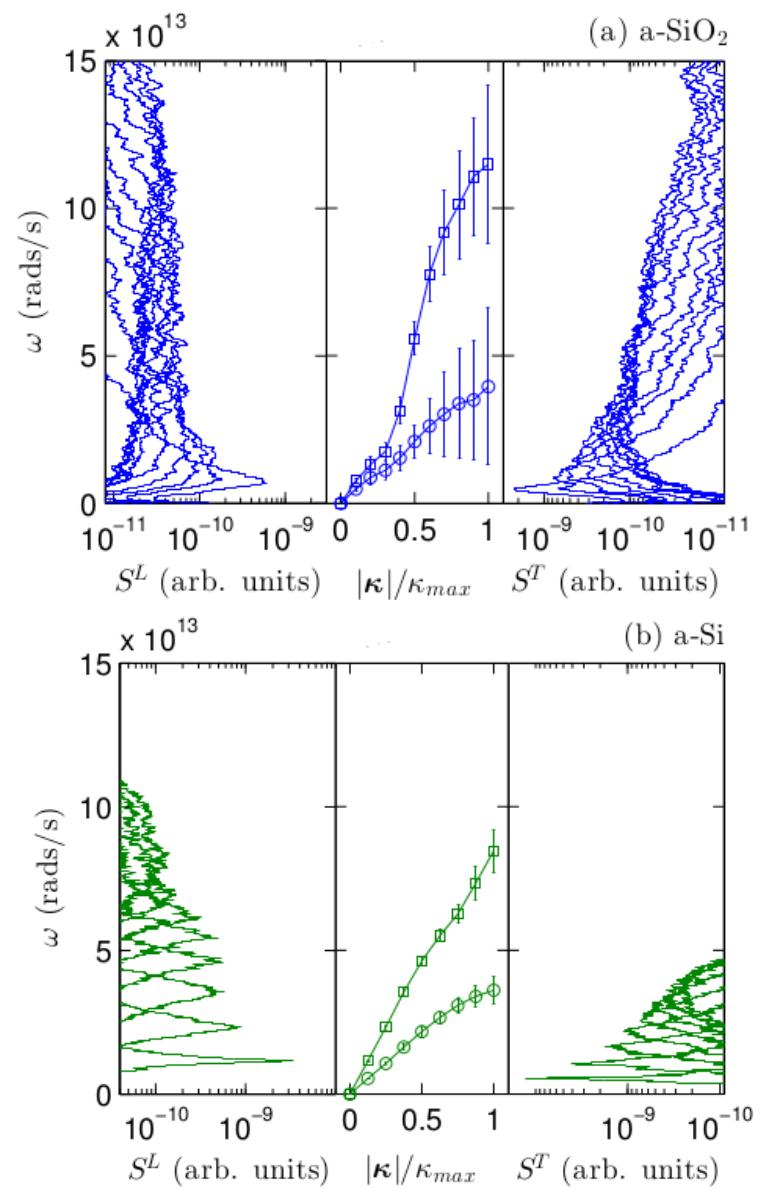
$$D_{pr}(\omega) = \frac{1}{3} v_s \Lambda(\omega)$$

Vibrons: Phonon character

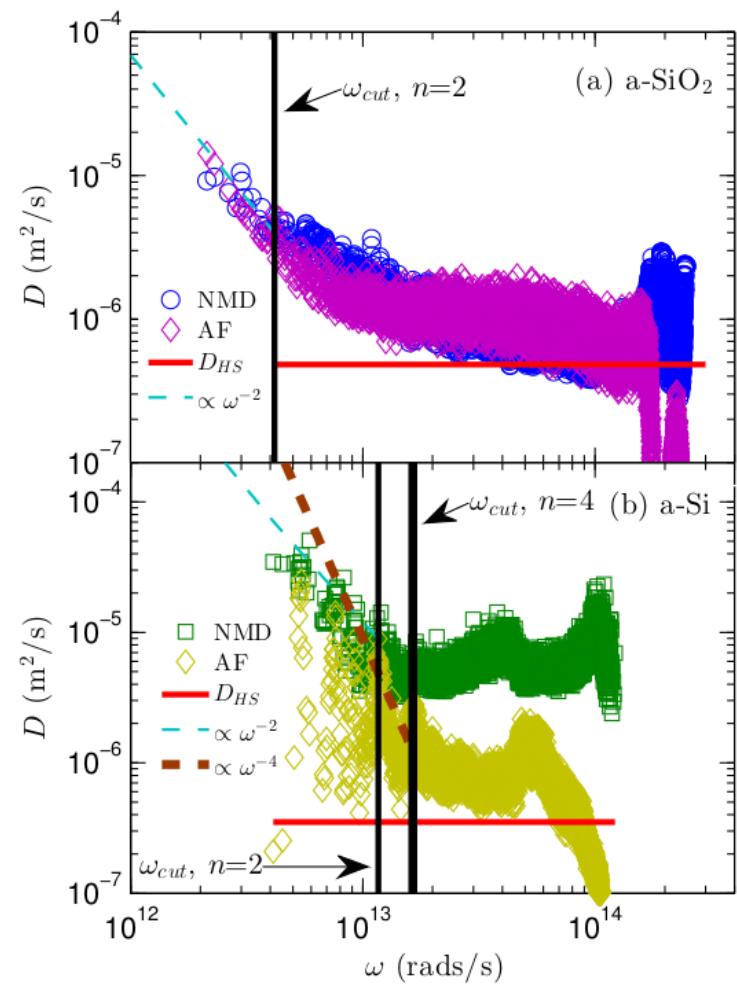
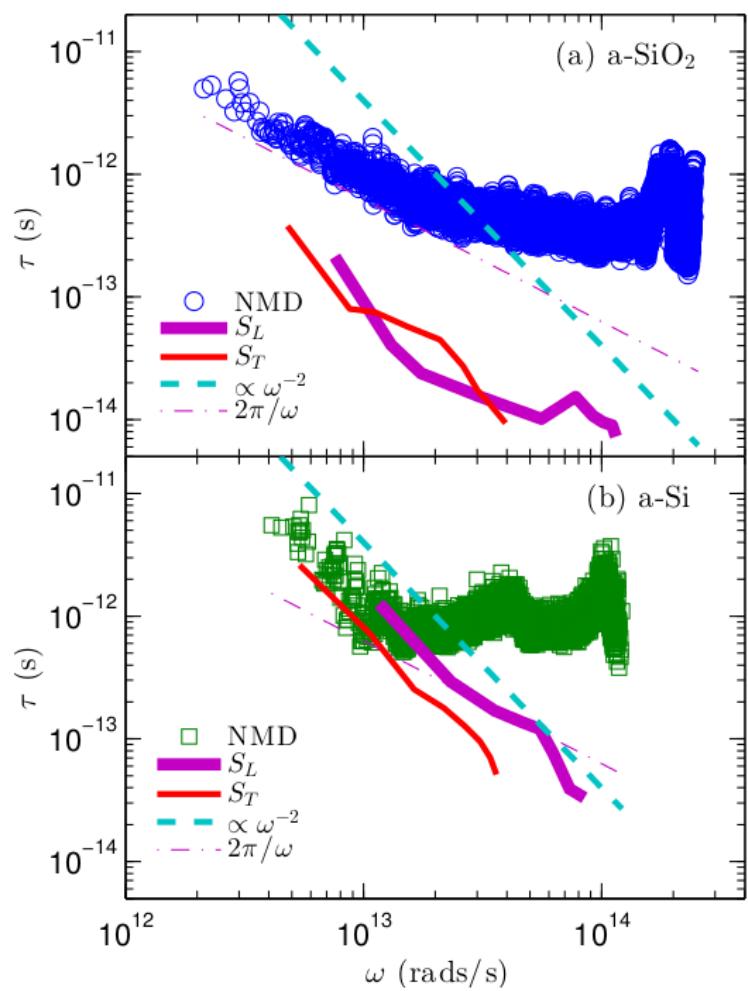


$$DOS(\omega) = \frac{3V\omega^2}{2\pi^2 v_s^3}$$

$$S^{L,T}(\kappa_{\omega}^{VC}) = \sum_{\nu} E^{L,T}(\kappa_{\nu}^{VC}) \delta[\omega - \omega(\kappa_{\nu}^{=0})]$$

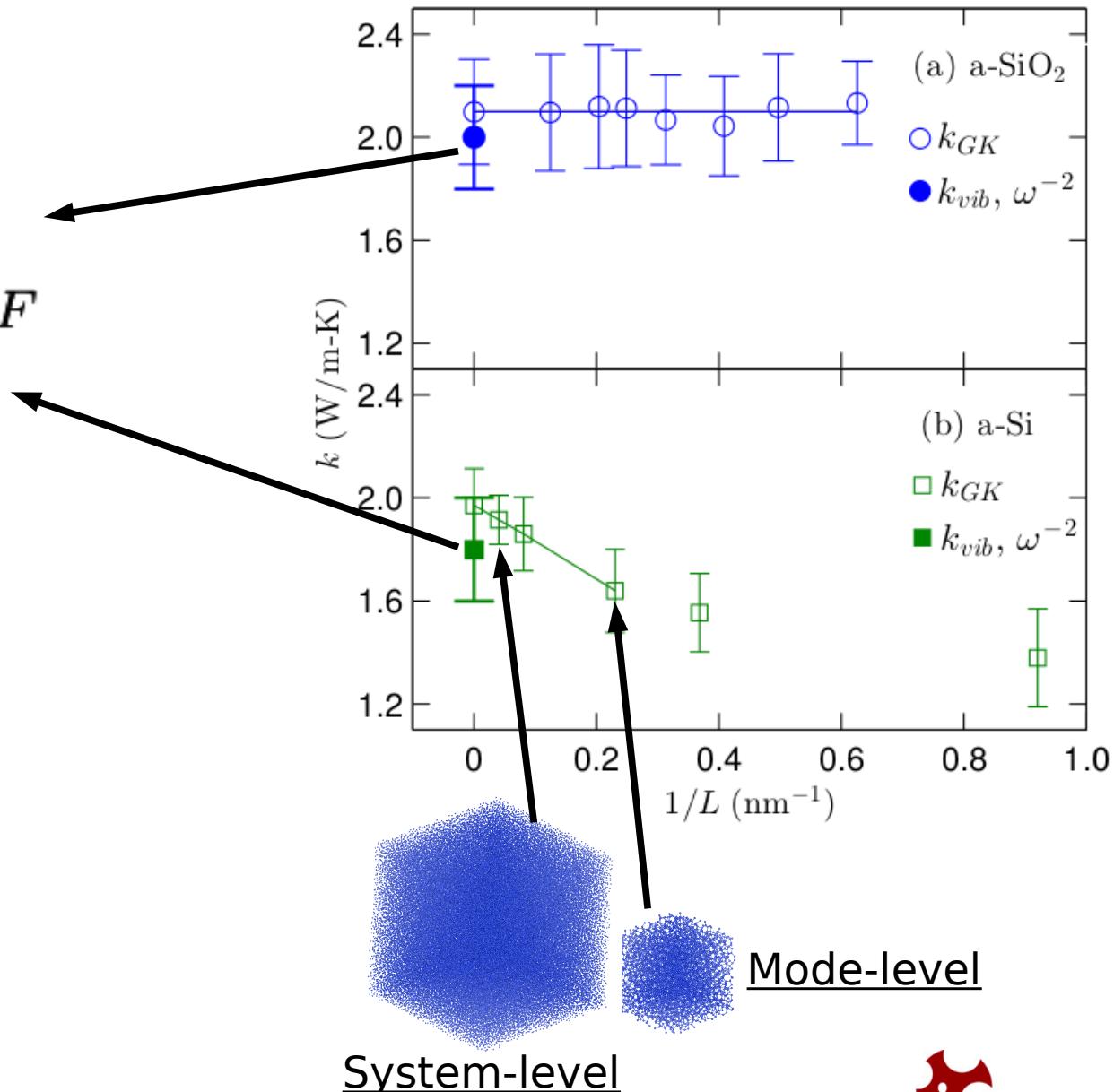


Vibrons: Lifetimes and Diffusivities

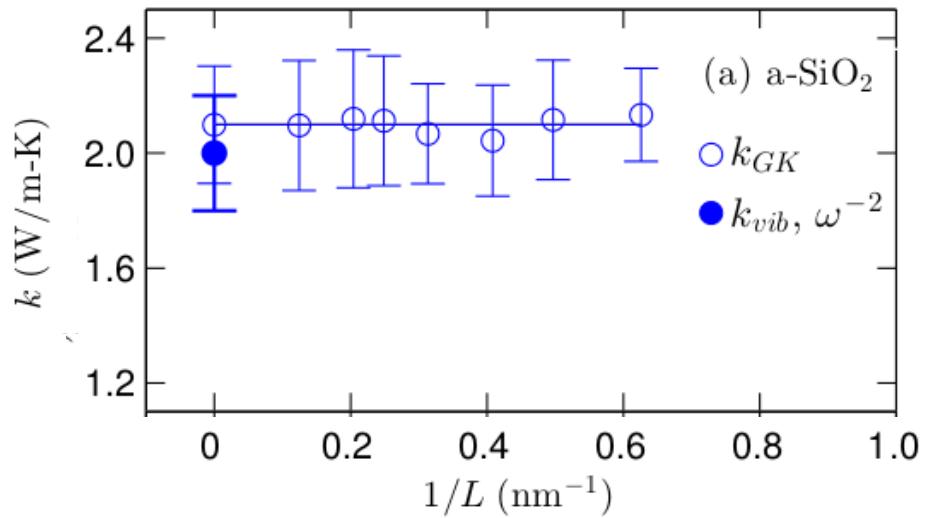
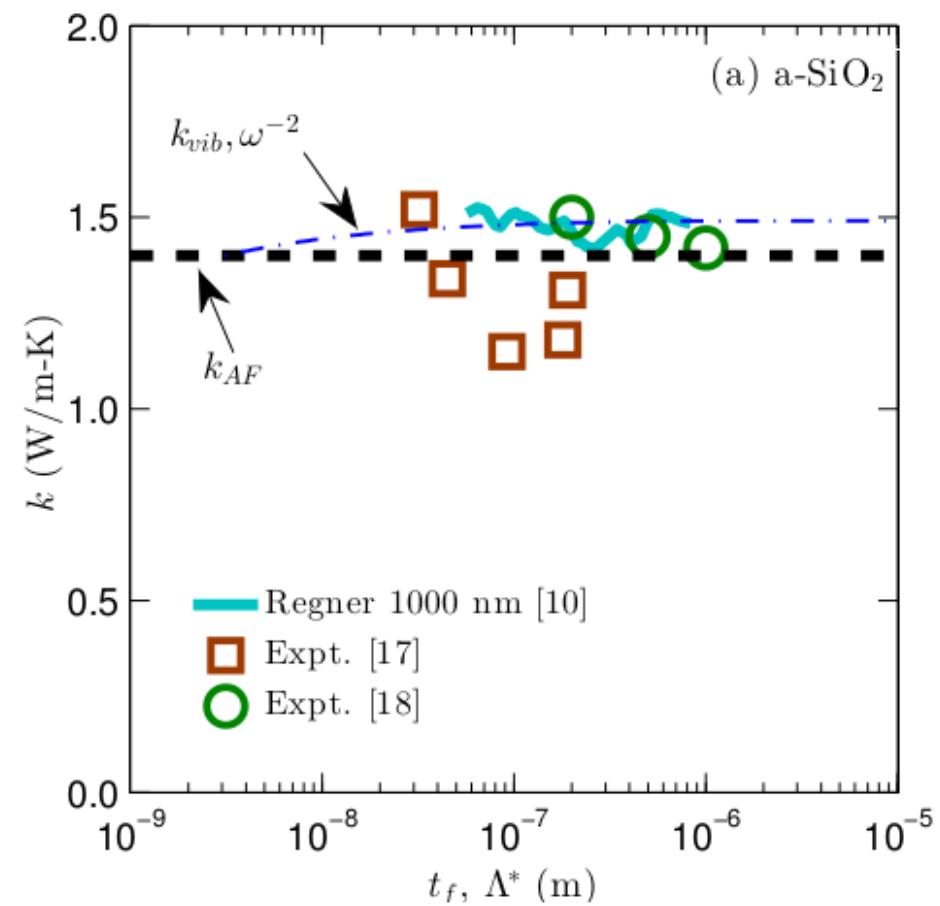


Vibrons: Mode- and System-level

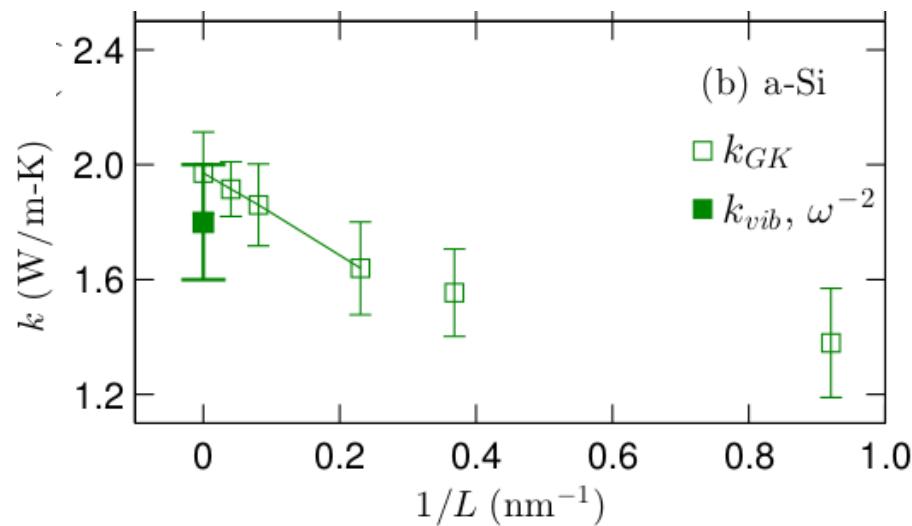
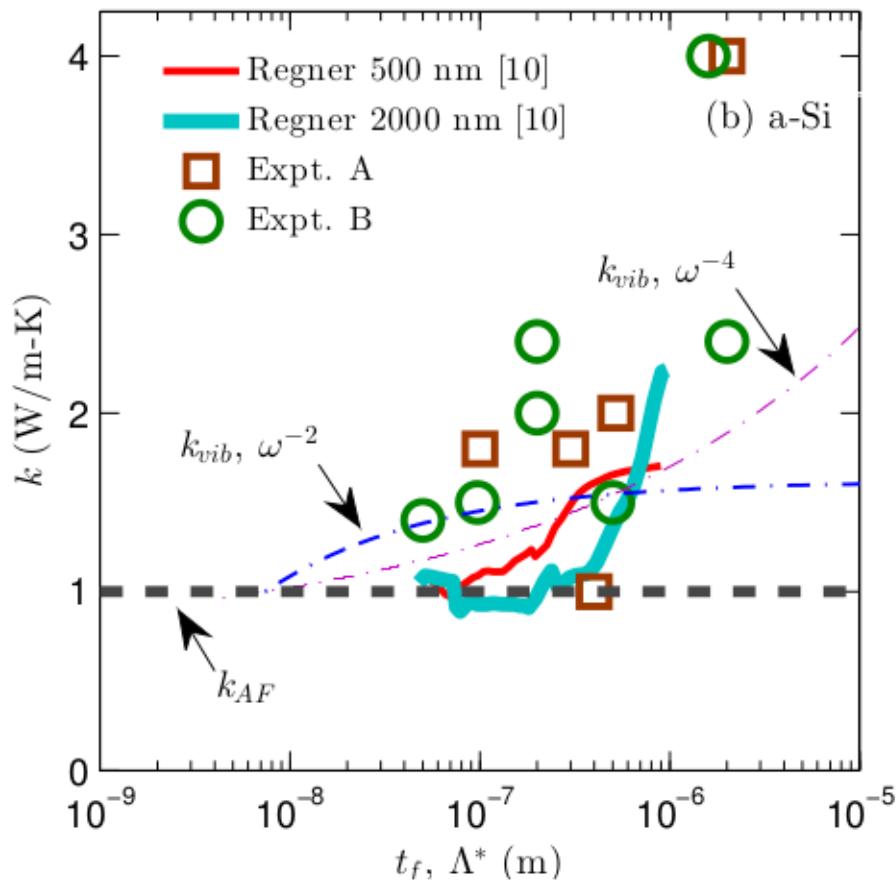
$$k_{vib} = k_{pr} + k_{AF}$$



Thermal Conductivity Accumulation



Thermal Conductivity Accumulation

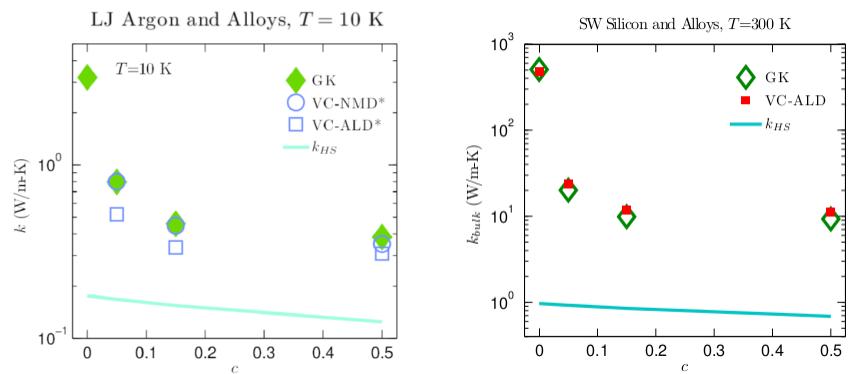


Outline

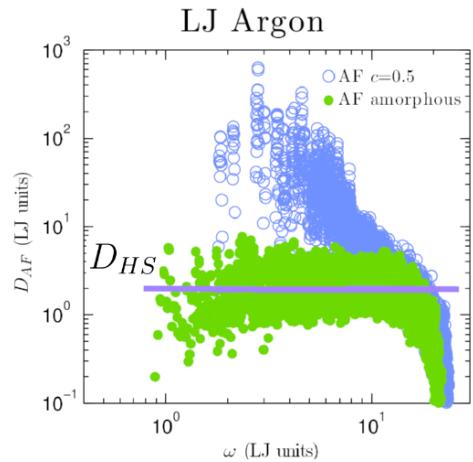
- (1) Motivation
- (2) Mode-level vs. System-level
- (3) Alloys
- (4) Amorphous
- (5) Overview/Future Work**

Overview

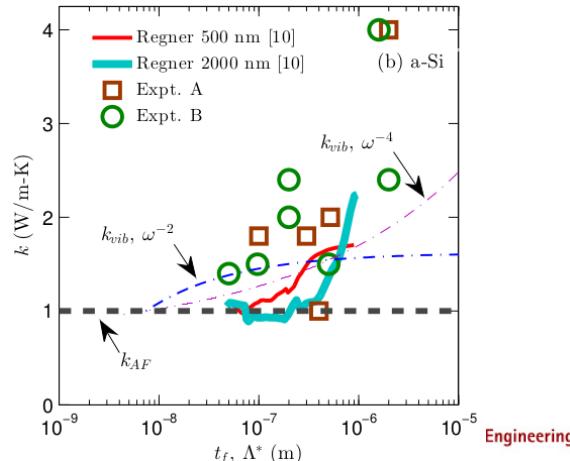
Limits of Perturbation Methods:



Alloys can behave like Amorphous:



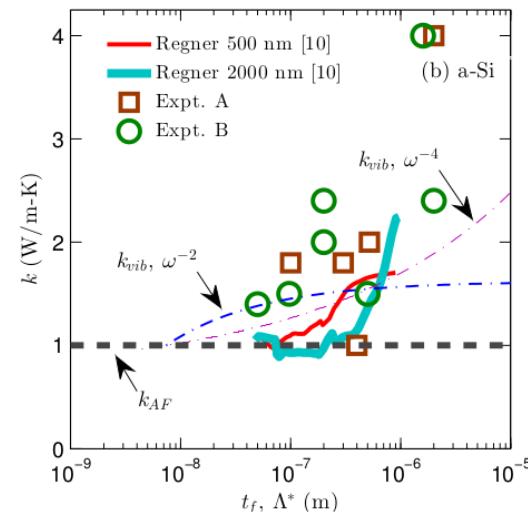
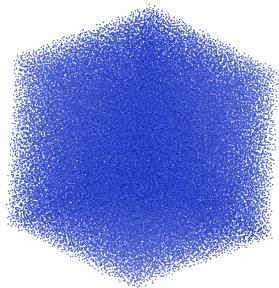
Amorphous can behave like Crystal:



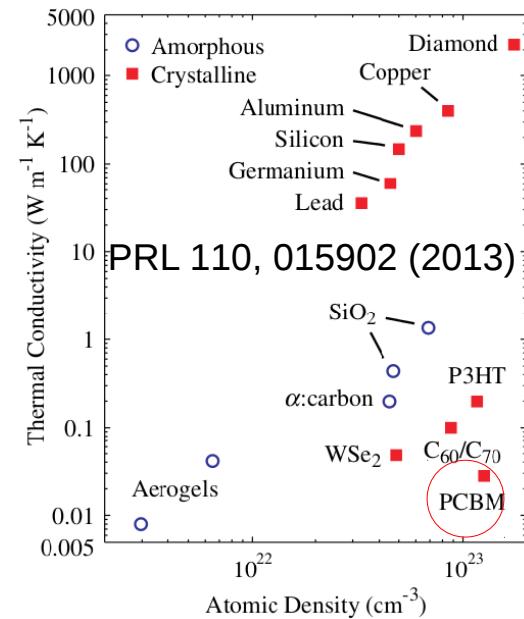
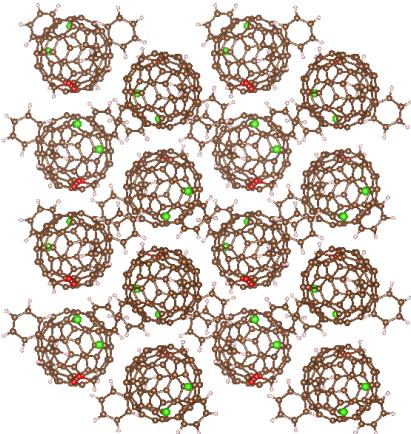
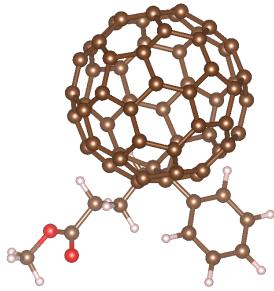
Future Work

Very Large MD-based Predictions:

System- and Mode-level



Large Unit Cell Materials (PCBM):



J. M. Larkin, W. A. Saidi, A. J. H. McGaughey, "Origin of the Exceptionally Low Thermal Conductivity in Fullerene-derived PCBM Films", Physical Review B (in progress).

Four Methods (+ more): A comprehensive package

<https://github.com/ntpl/ntpy>