

Vibrational Mode Properties of Disordered Solids from High-Performance Atomistic Simulations and Calculations

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

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Committee:

Alan McGaughey (chair), Jonathan Malen, Craig Maloney, Michael Widom

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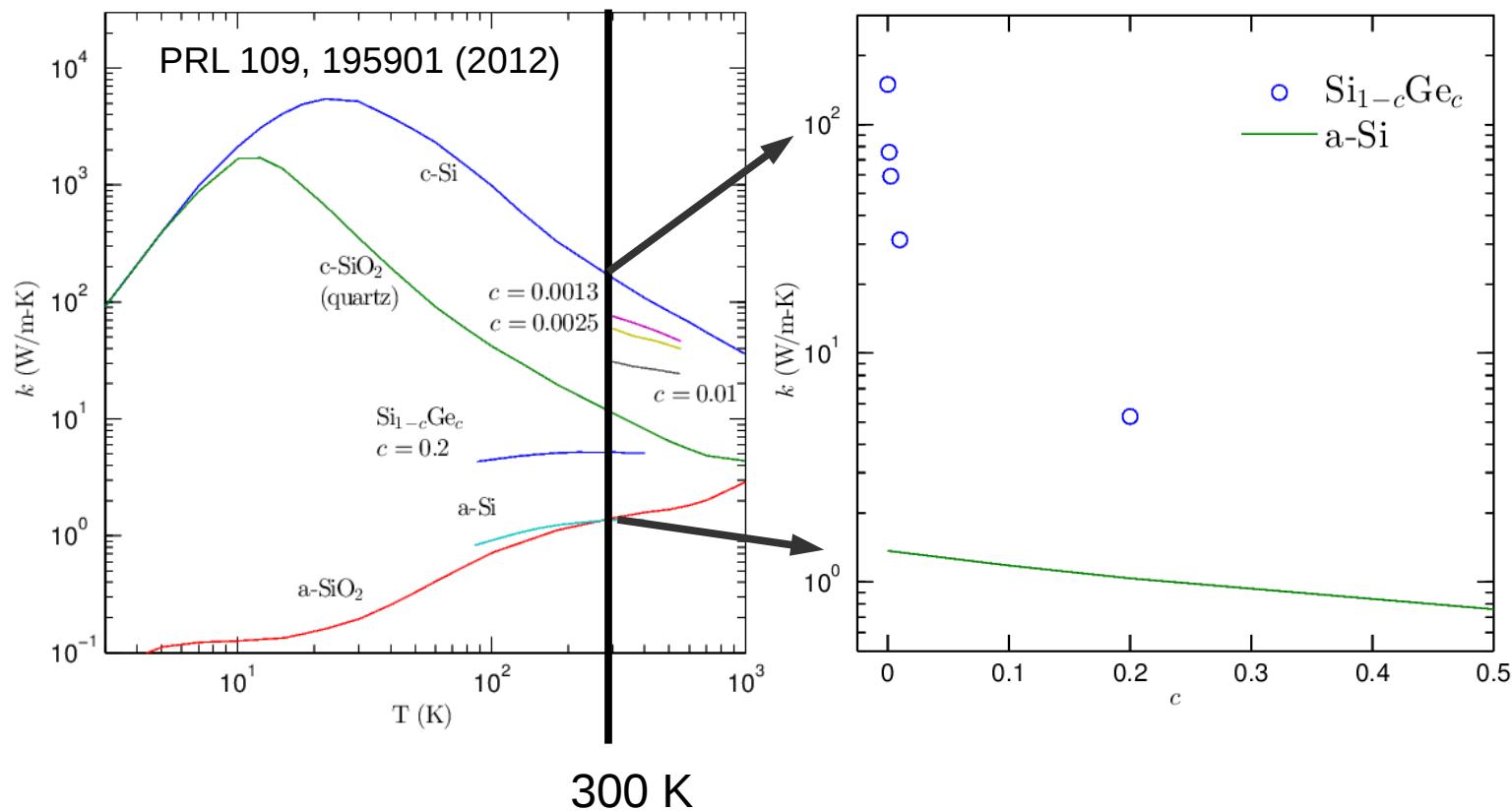
Special Thanks: Normand Mousseau for amorphous silicon samples.
PRB 62 4985–4990 (2000).

Special Thanks: Julian Gale (author of General Utility Lattice Program GULP).

Outline

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

Motivation: Crystal, Alloys, Amorphous

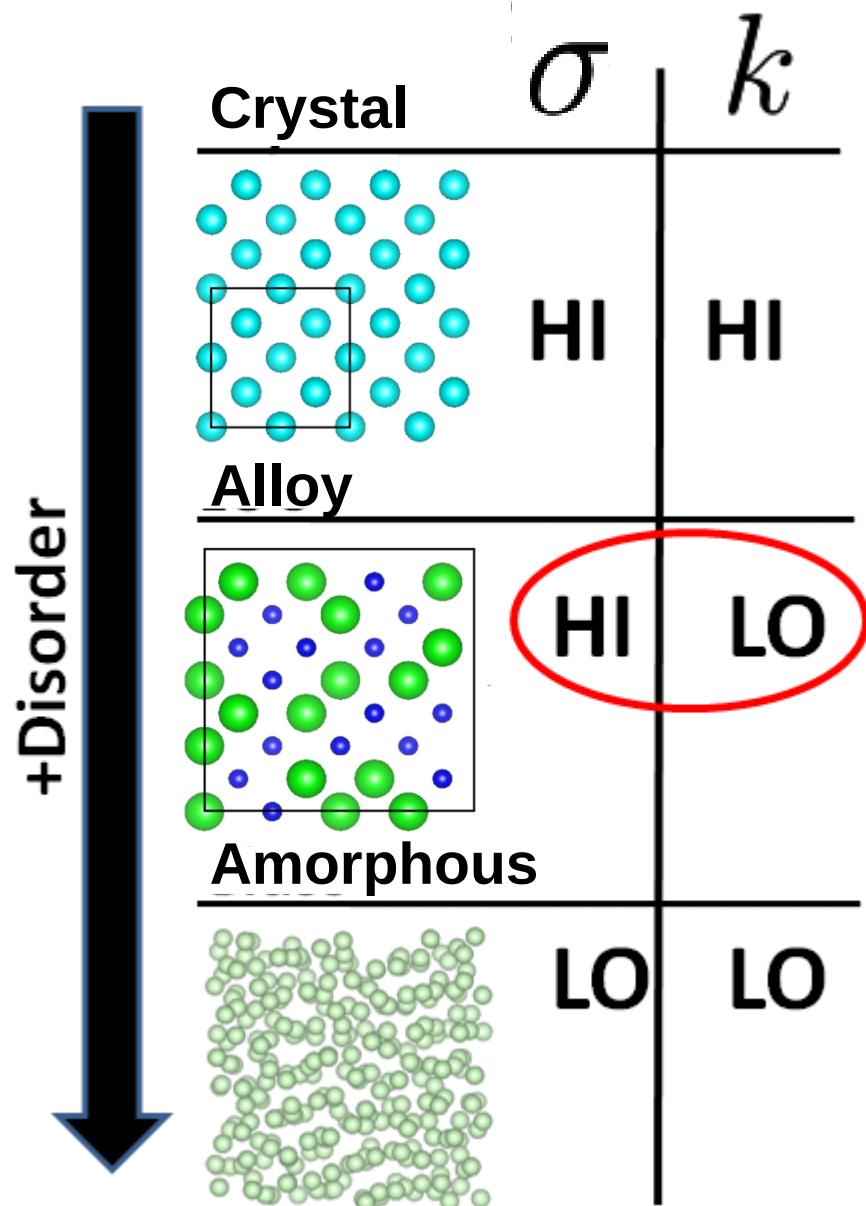


Constraints: chemistry, electron transport, operating temperature, etc.

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

Motivation: Alloys as Thermoelectrics

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



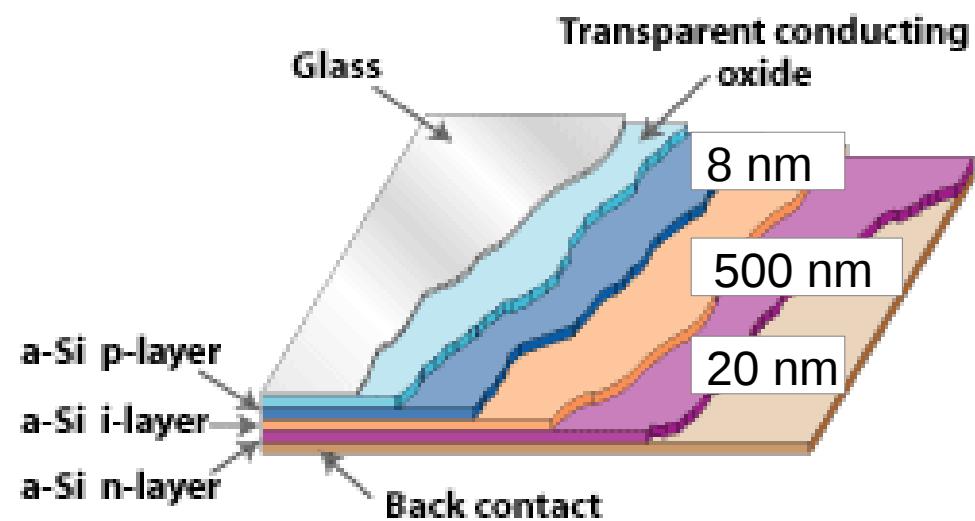
Mode-level Properties:

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

Motivation: Amorphous

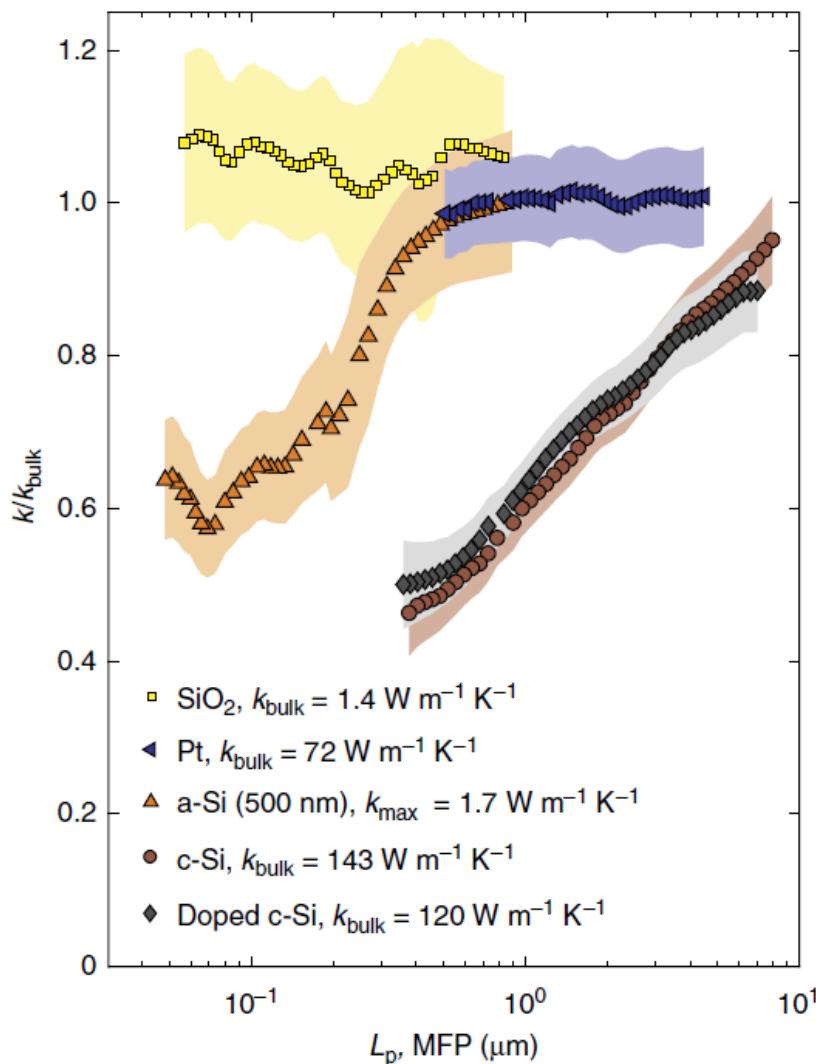
Regner et al., *Nat. Comm.* **4**, 1640 (2013)

Solar cells:



http://www.eere.energy.gov/basics/renewable_energy/types_silicon.html

http://www1.eere.energy.gov/solar/sunshot/pv_asi.html

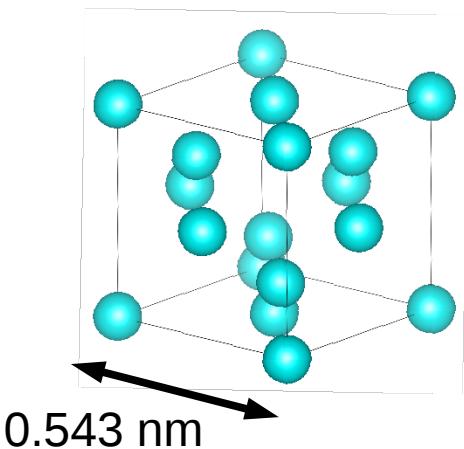


Outline

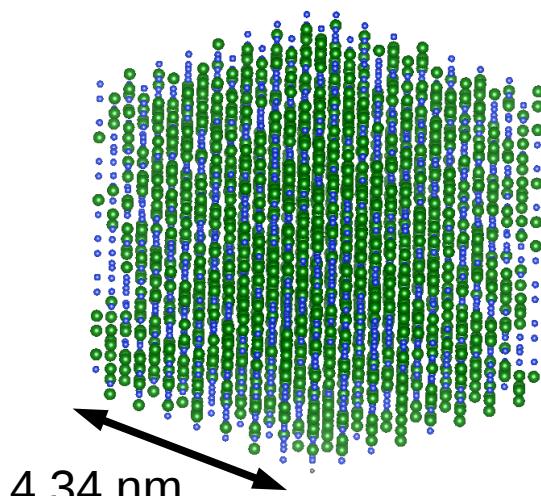
- (1) Motivation
- (2) Mode-level vs. System-level**
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Mode-level vs. System-level

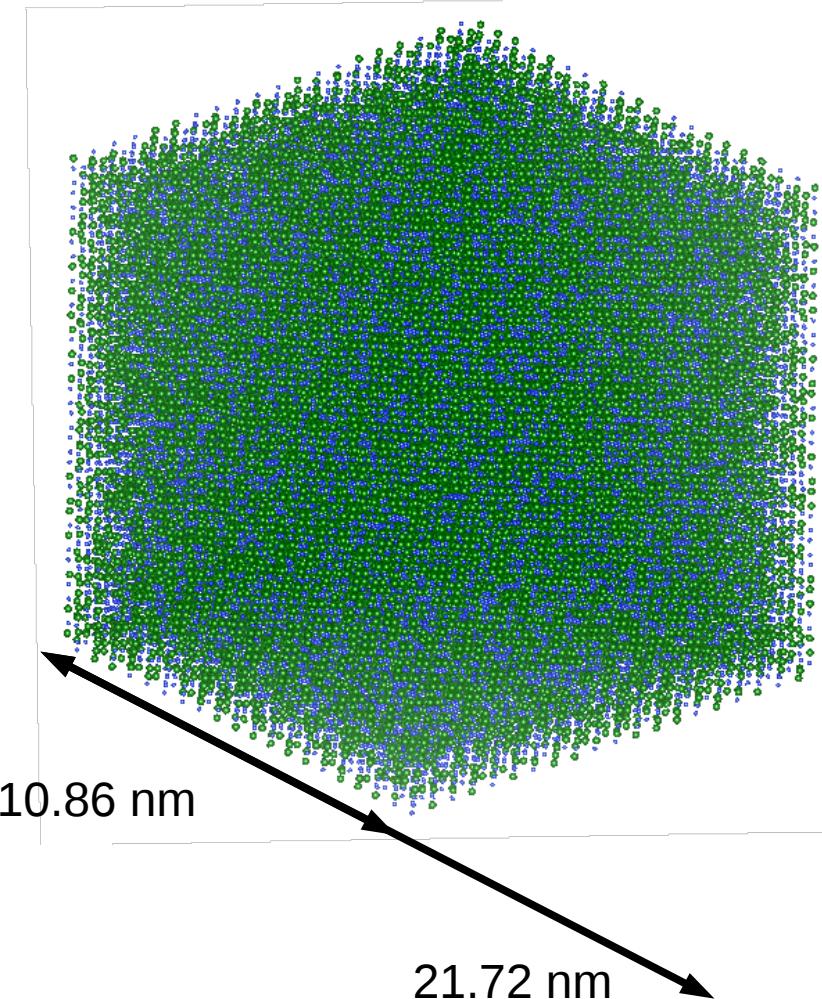
Mode-level:
8 atoms



Mode-level:
~4000 atoms



System-level:
~1E6 atoms



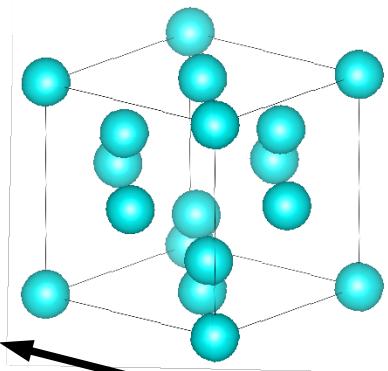
10.86 nm

21.72 nm

Mode-level: Perturbation vs. Explicit

Phonons (ph):

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



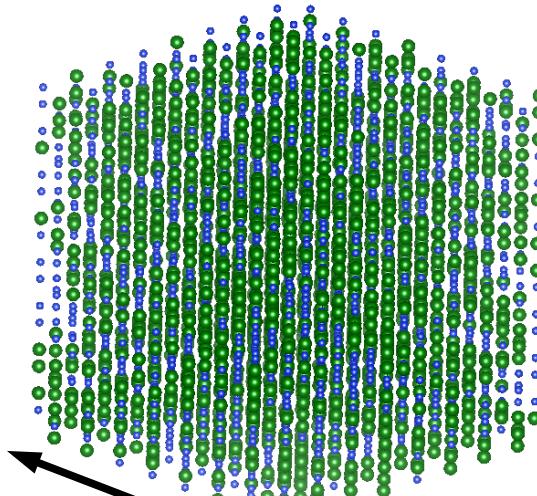
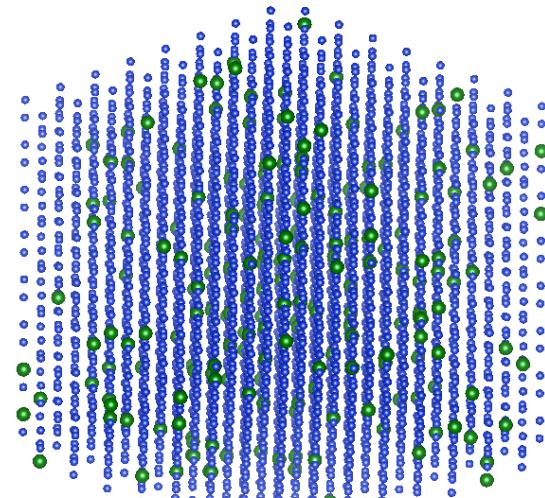
0.543 nm



?



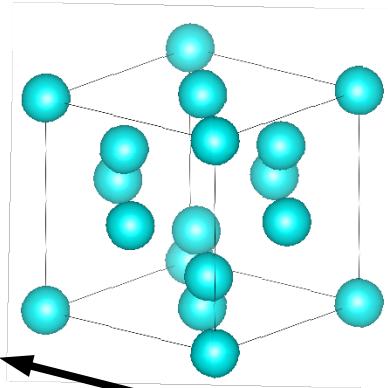
4.34 nm



Mode-level: Explicit

Phonons (ph):

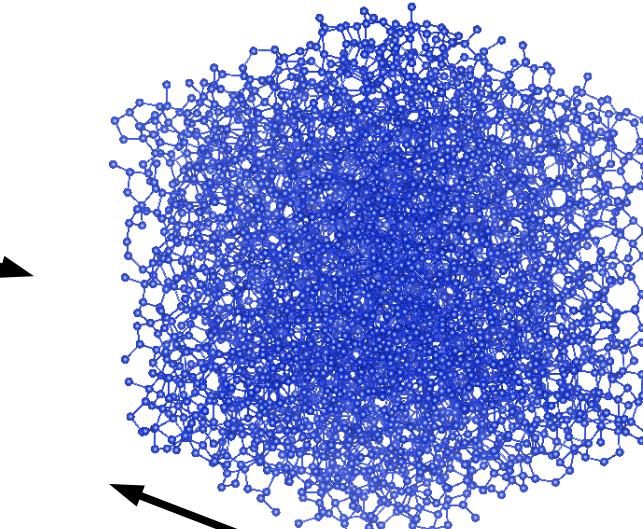
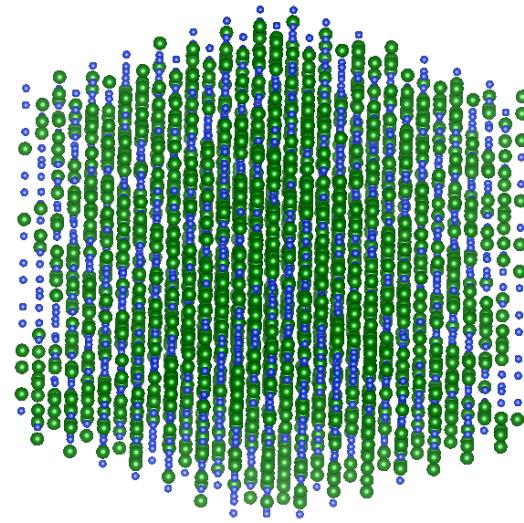
$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$



0.543 nm

?

No



4.34 nm

Disordered Modes: Vibrons

Propagons:

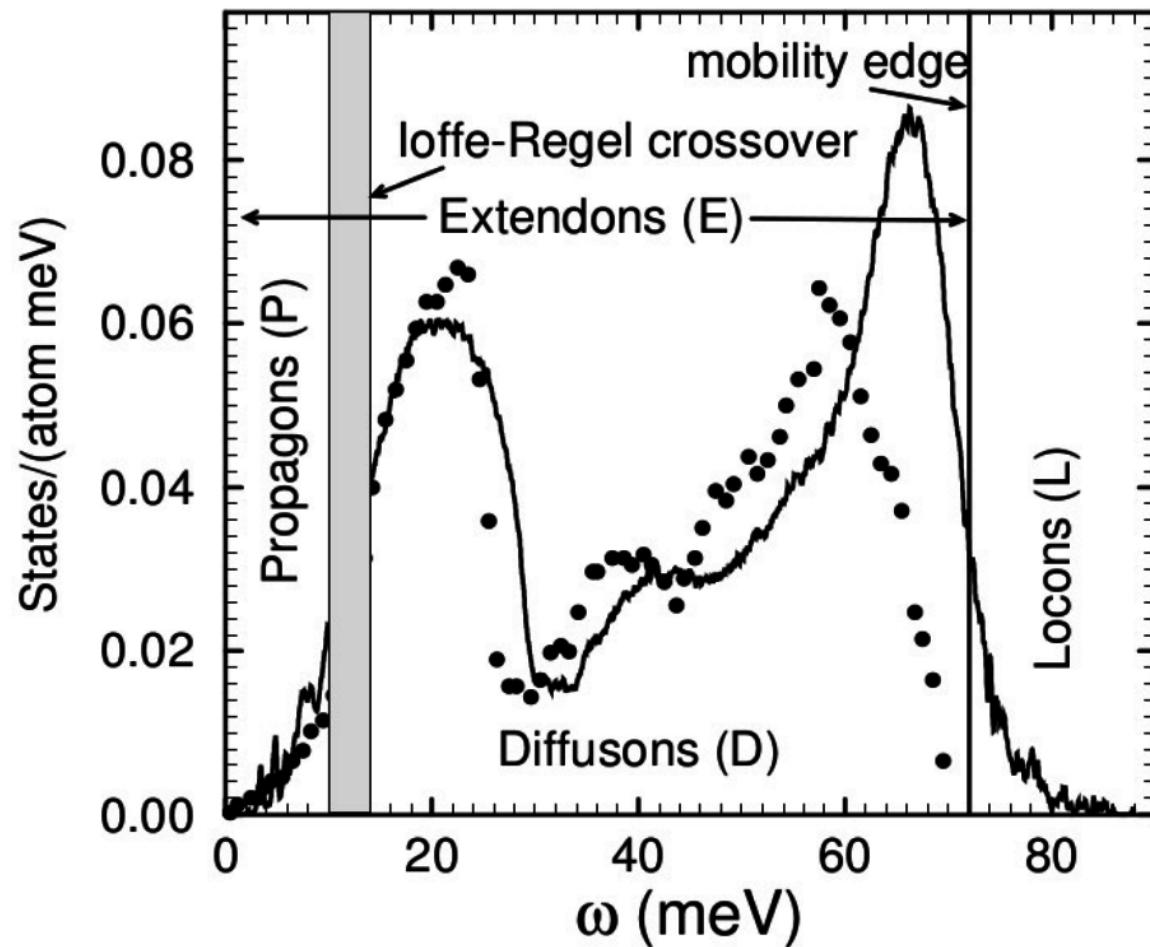
Phonon-like,
propagating,
de-localized

Diffusons:

non-propagating,
de-localized

Locons:

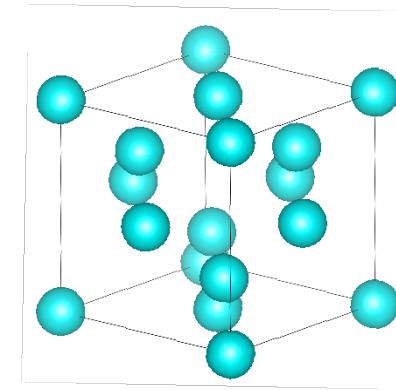
non-propagating,
localized



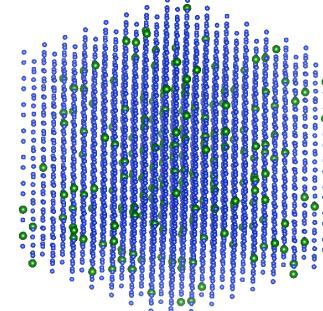
Thermal Conductivity: Mode-level

Phonons (ph):

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

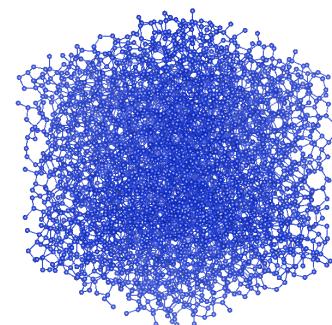
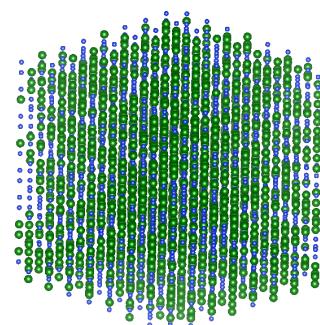


Propagons (phonon-like)



Diffusons:

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



Allen-Feldman Theory:

Phys. Rev. B, 48 12581-12588 (1993)

Mode-level and System-level Methods

Lattice Dynamics Calculations

Harmonic and Anharmonic Lattice Dynamics (**HLD, ALD**):
Mode-level (Phonons, Propagons?)

Allen-Feldman (**AF**) Diffuson Theory (HLD):
Mode-level (Diffusons)

Molecular Dynamics Simulation

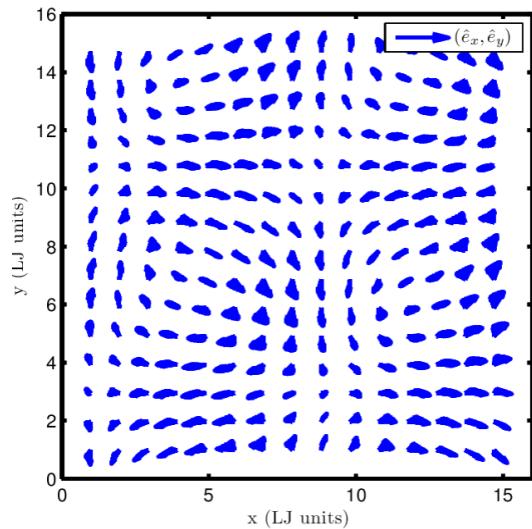
Green-Kubo (**GK**): System-level

Normal Mode Decomposition (**NMD**): Mode-level (Vibrons)

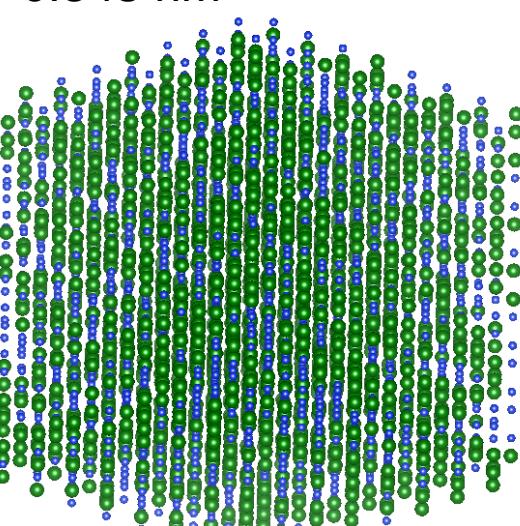
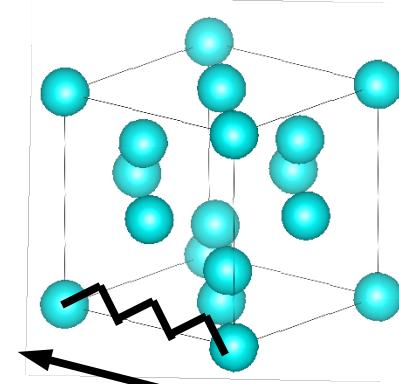
Thermal Conductivity: Mode-level

Propagons (phonon-like):

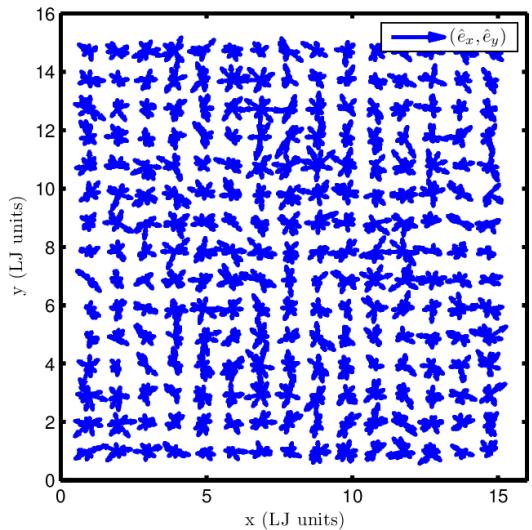
Harmonic Lattice Dynamics



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

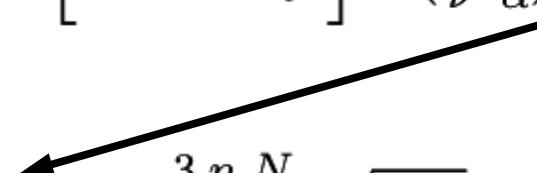


Diffusons:

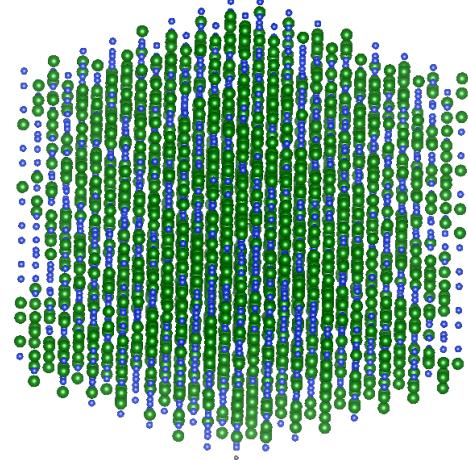


Vibrational Properties: Molecular Dynamics

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



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



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):

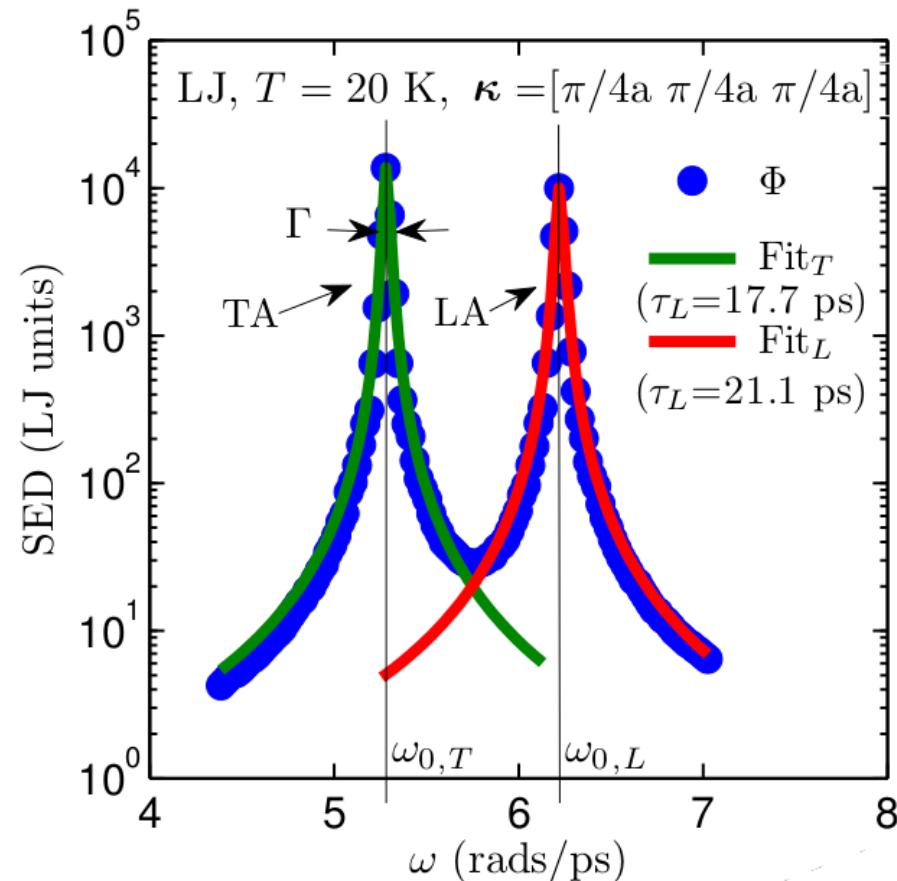
$$E(\kappa; t) = \frac{\omega(\kappa)^2}{2} q(\kappa; t)^* q(\kappa; t) + \frac{1}{2} \dot{q}(\kappa; t)^* \dot{q}(\kappa; t)$$

PE **KE**

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

Anharmonic Lattice Dynamics:

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



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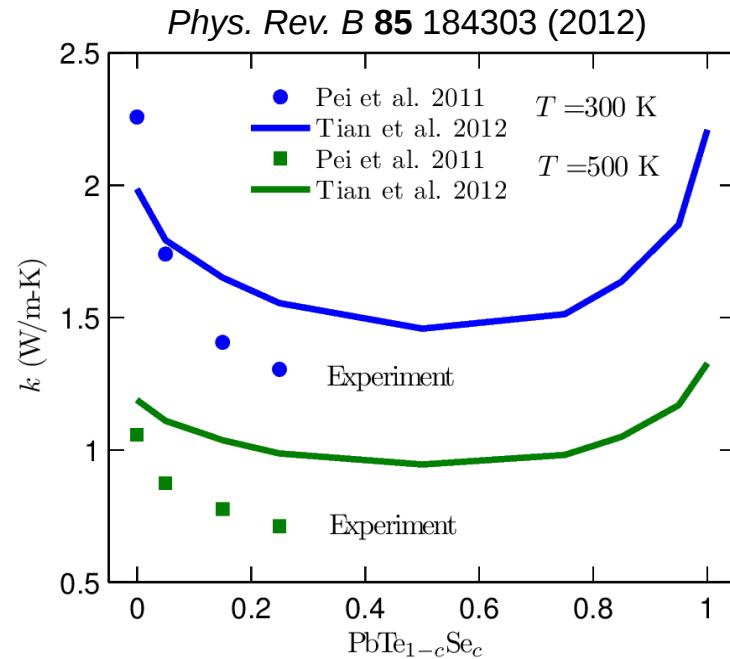
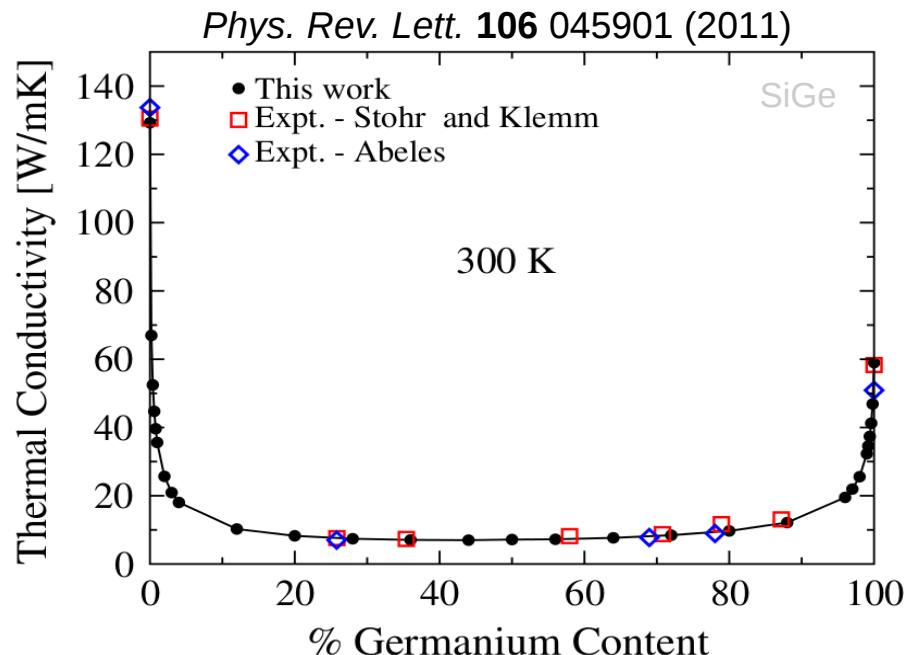
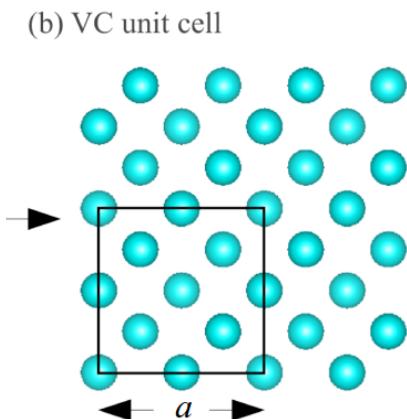
Alloys: experimental accuracy

Expensive Density Functional Theory (DFT) calculations

+

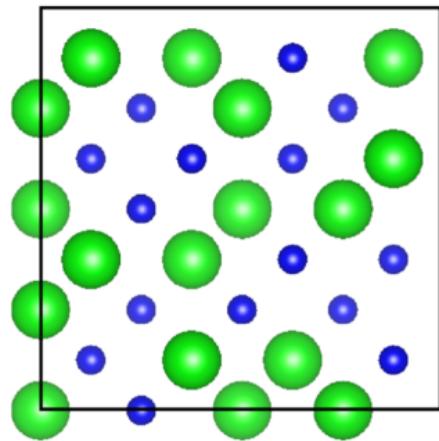
Virtual Crystal (VC) approximation &
Anharmonic Lattice Dynamics (ALD) (**VC-ALD**)

Alloys: isotopic effects, thermoelectric materials

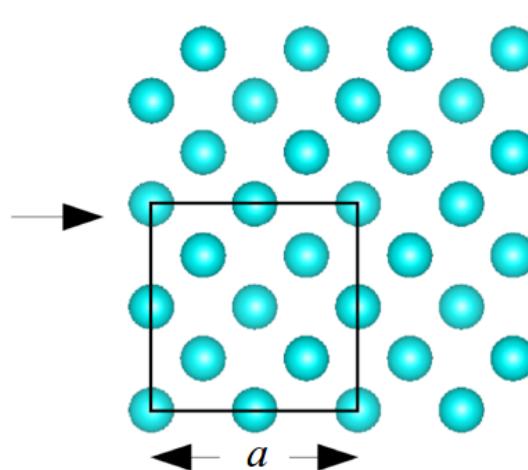


Alloys: Virtual Crystal Approximation

(a) disordered supercell



(b) VC unit cell



Computationally inexpensive empirical potential: Lennard-Jones argon

Thermal conductivity:

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

Thermal diffusivity:

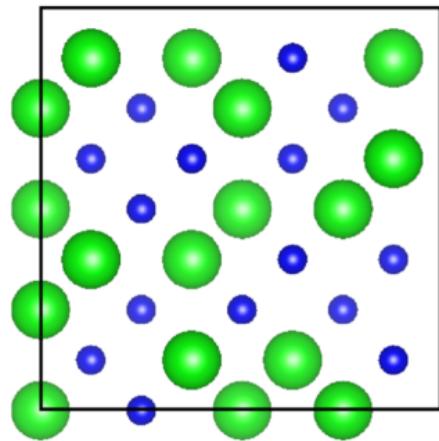
$$D_{ph,\mathbf{n}}(\kappa_{\nu}) = v_{g,\mathbf{n}}^2(\kappa_{\nu}) \tau(\kappa_{\nu})$$

Diffusons:

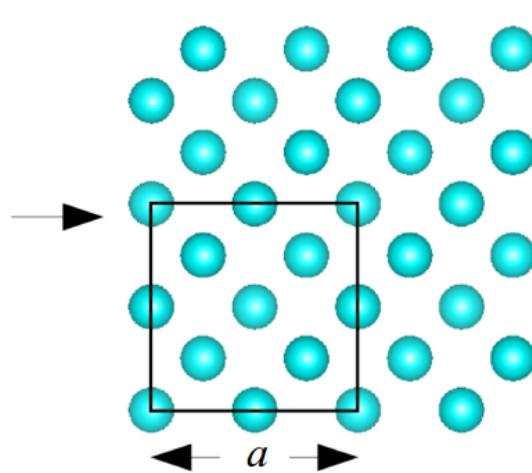
$$k_{AF} = \sum_{diffusons} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

VC-ALD: Group Velocity

(a) disordered supercell



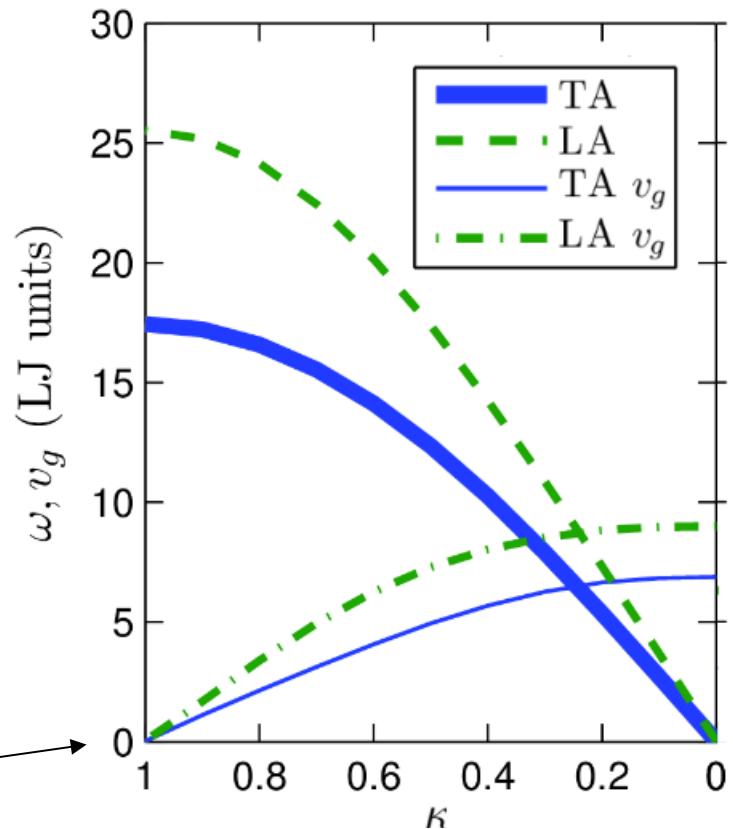
(b) VC unit cell



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

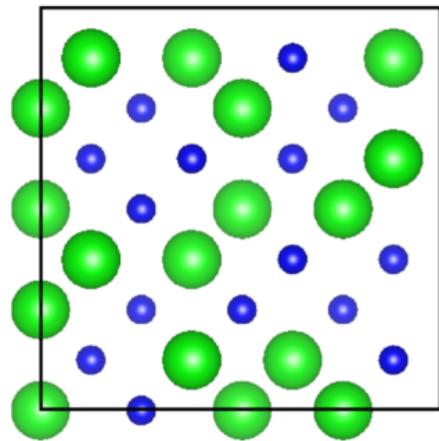
$$D_{ph}(\kappa_\nu) \approx 0$$

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

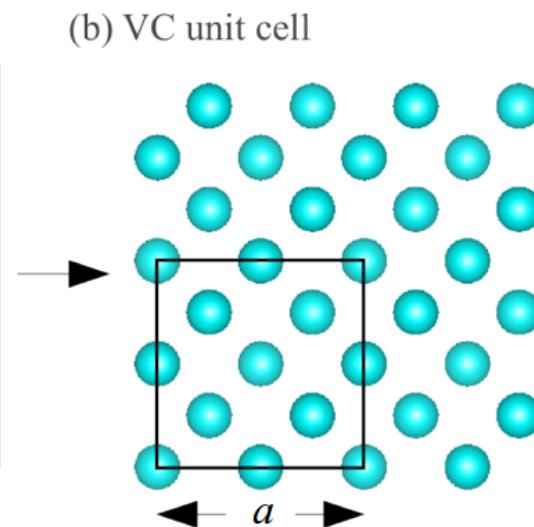


VC-ALD: Lifetimes

(a) disordered supercell

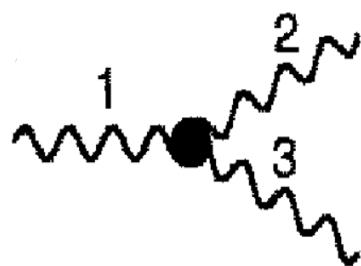


(b) VC unit cell



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

ALD:



Tamura:

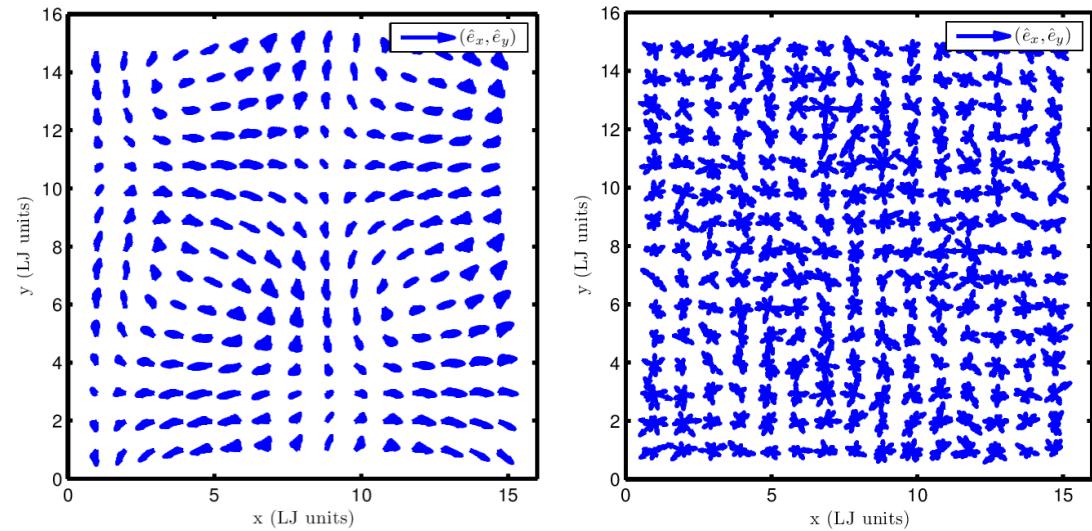


Matthiessen's Rule:

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

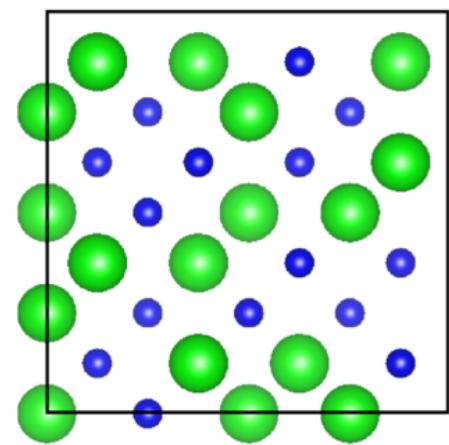
Tamura: PRB 27 858–866 (1983)

Structure Factor: Mode Shapes



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

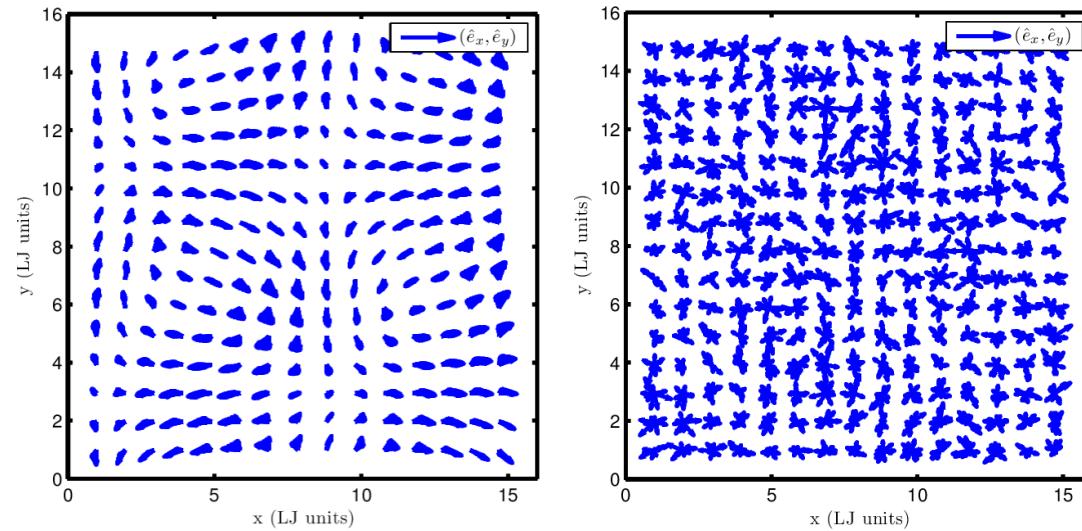
(a) disordered supercell



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

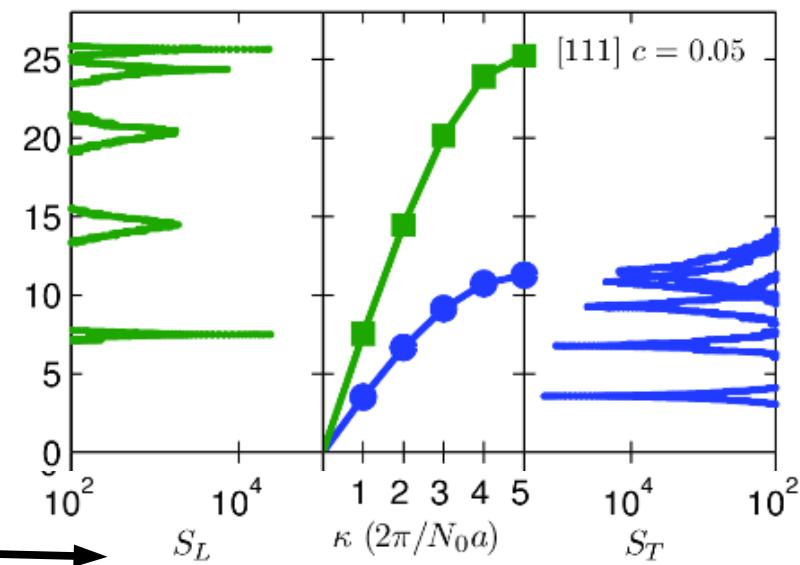
$$E^L(\kappa_{\nu C}) = \left| \sum_b \hat{\kappa}_{VC} \cdot e(\kappa_{\nu} b_{\alpha}) \exp[i\kappa_{VC} \cdot \mathbf{r}_0(l=0)] \right|^2$$

Structure Factor: Effective Dispersion



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

Gamma VC Gamma



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

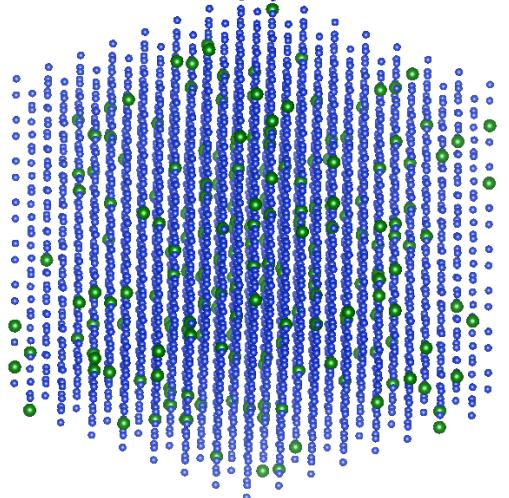


Explicit disorder: NMD

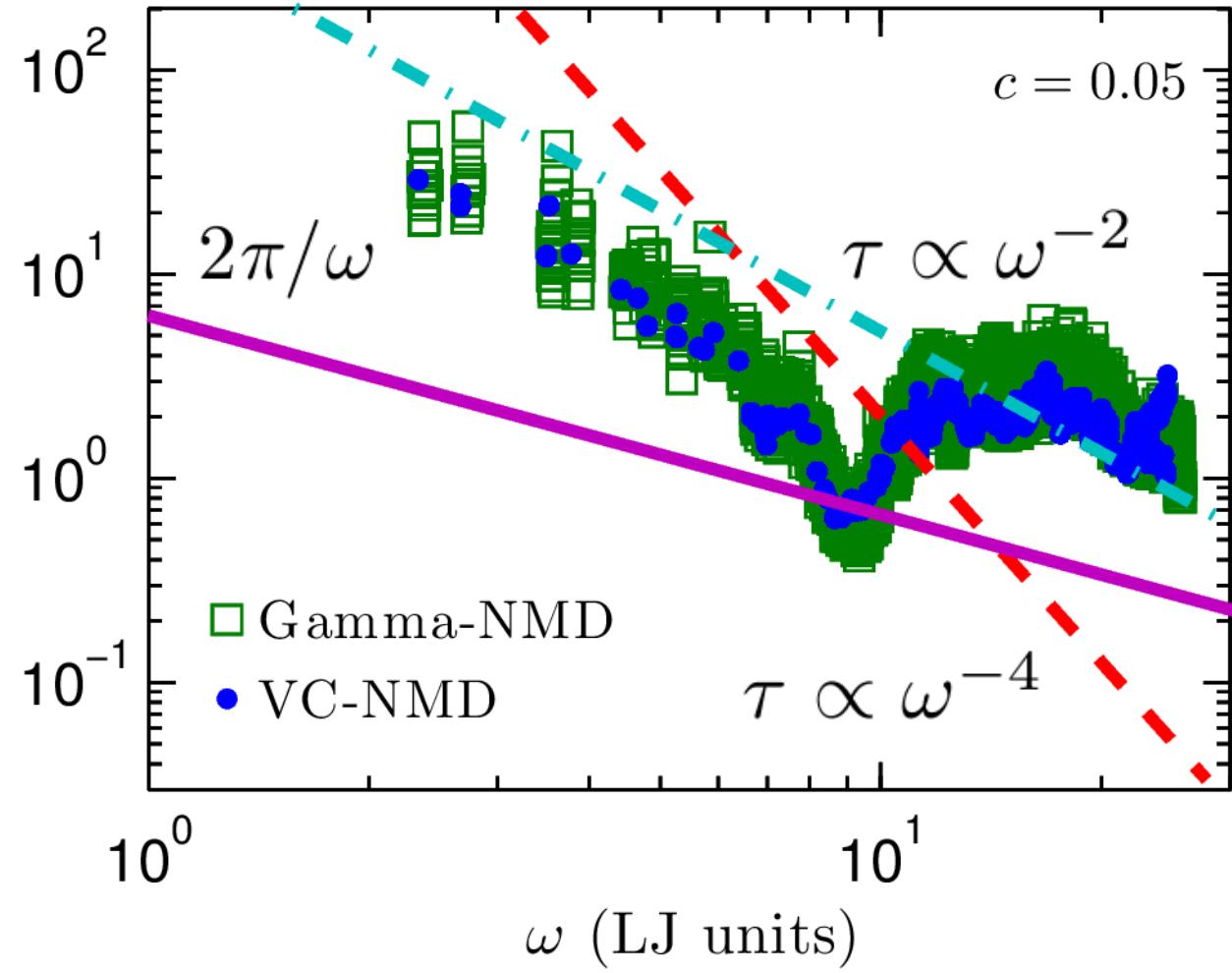
Normal Mode

Decomposition (NMD):

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

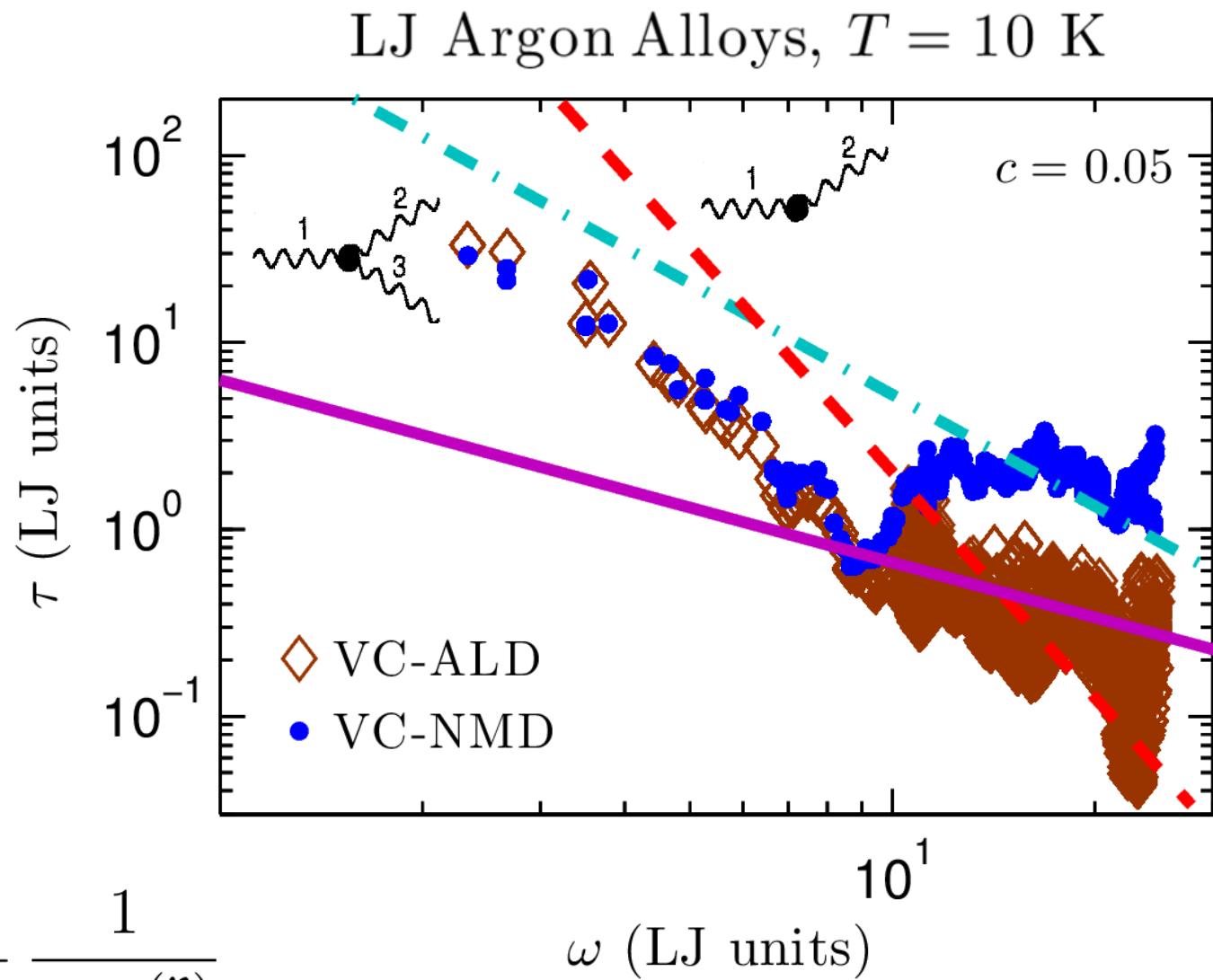
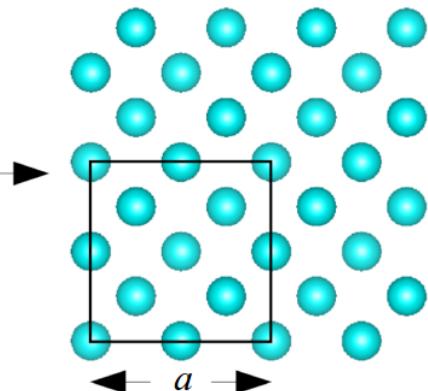


LJ Argon Alloys, $T = 10$ K



VC-NMD vs VC-ALD

(b) VC unit cell



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

VC Diffusivities

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

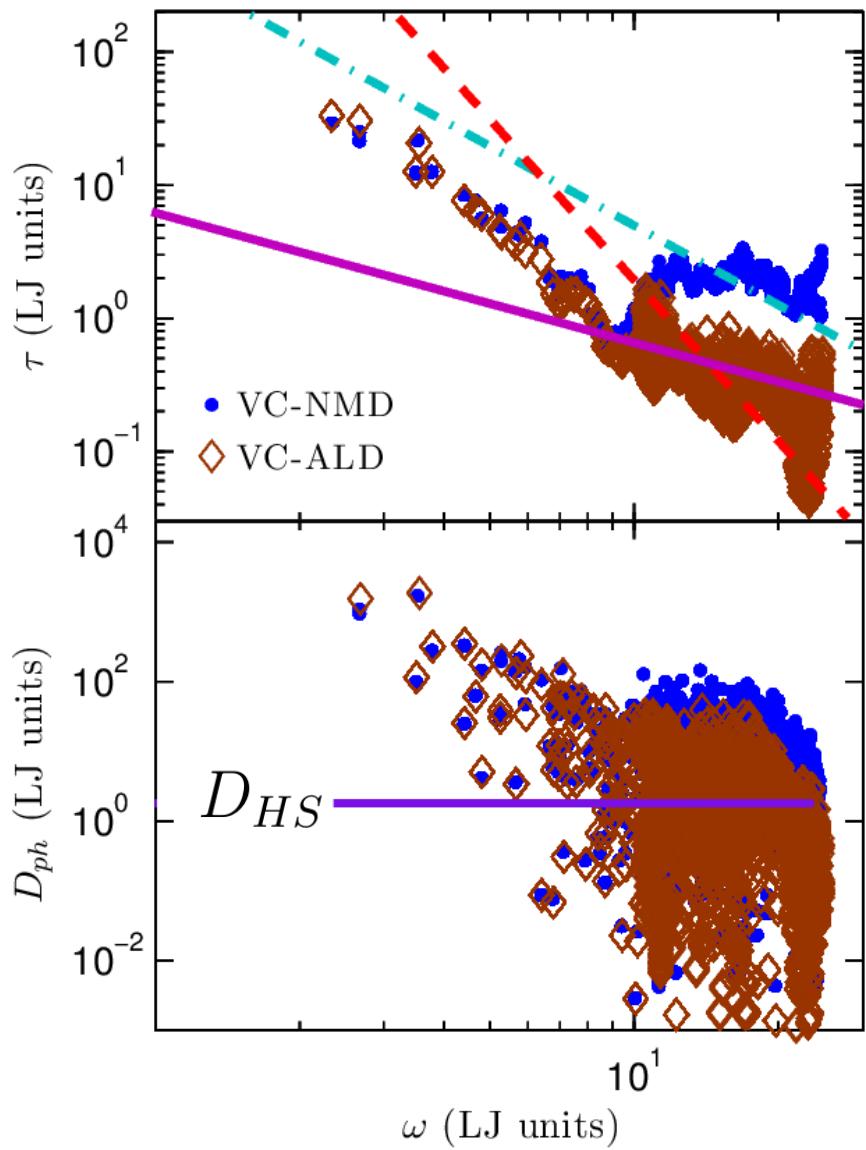
Phonon limit:

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

High-scatter limit:

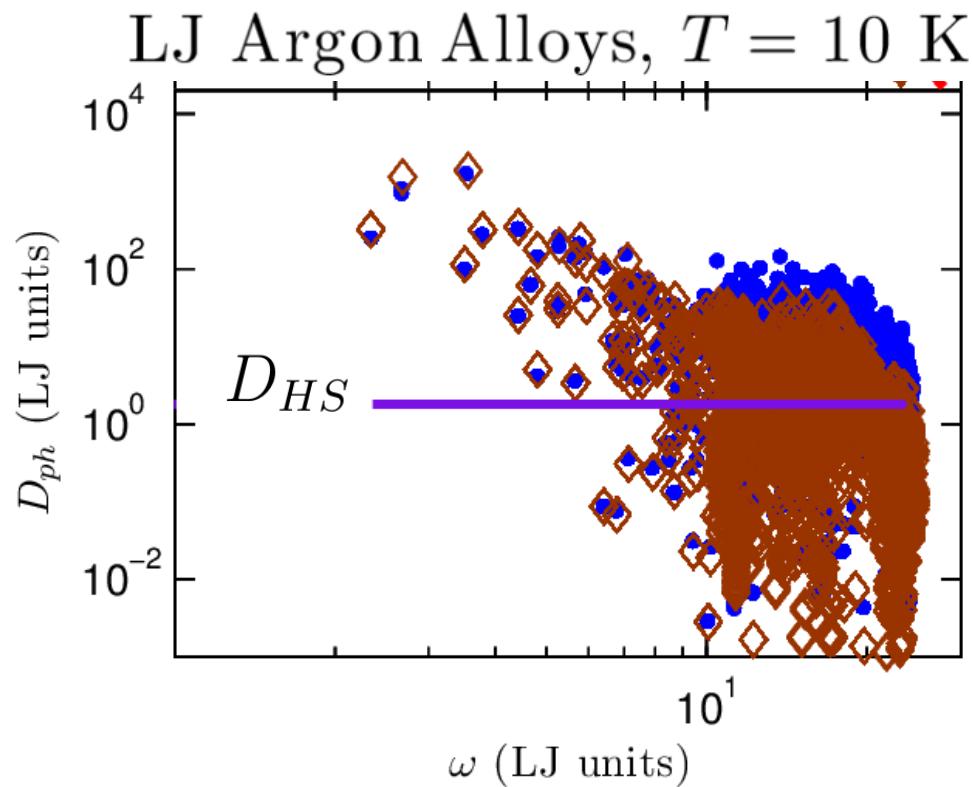
$$D_{HS} = \frac{1}{3} v_s a$$

LJ Argon Alloys, $T = 10$ K

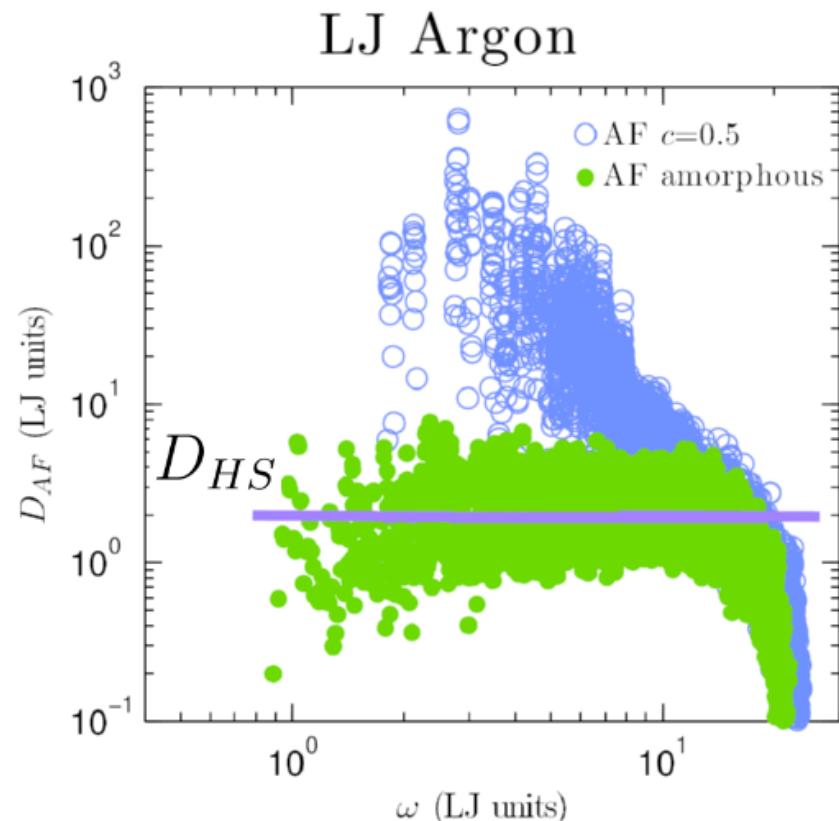


VC and AF Diffusivities

Phonons



Diffusons

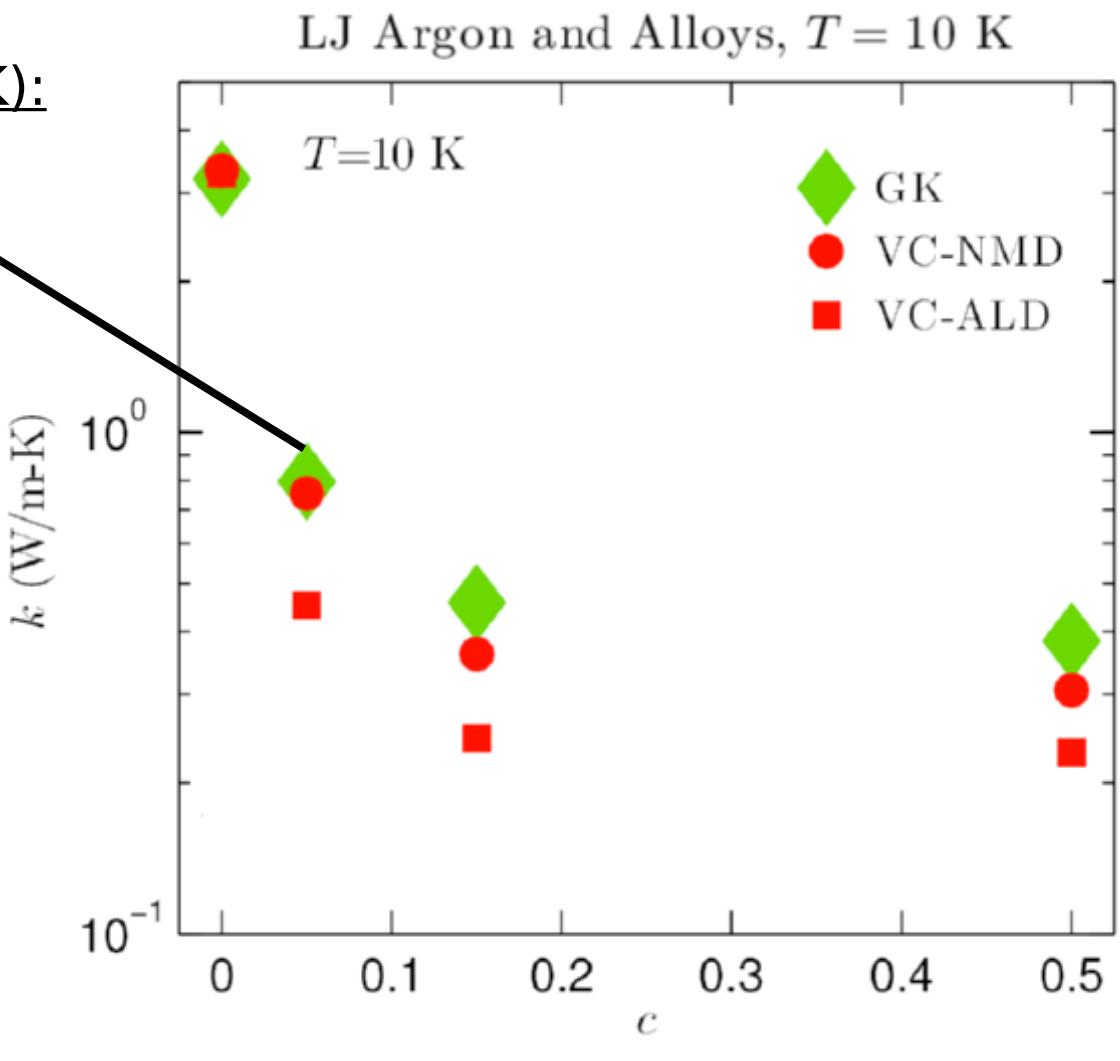
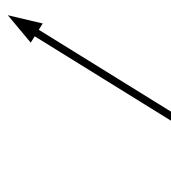


$$D_{HS} = \frac{1}{3} v_s a$$

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

Thermal conductivity: System-level

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



High-scatter adjustment*:

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

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

Thermal conductivity: System-level

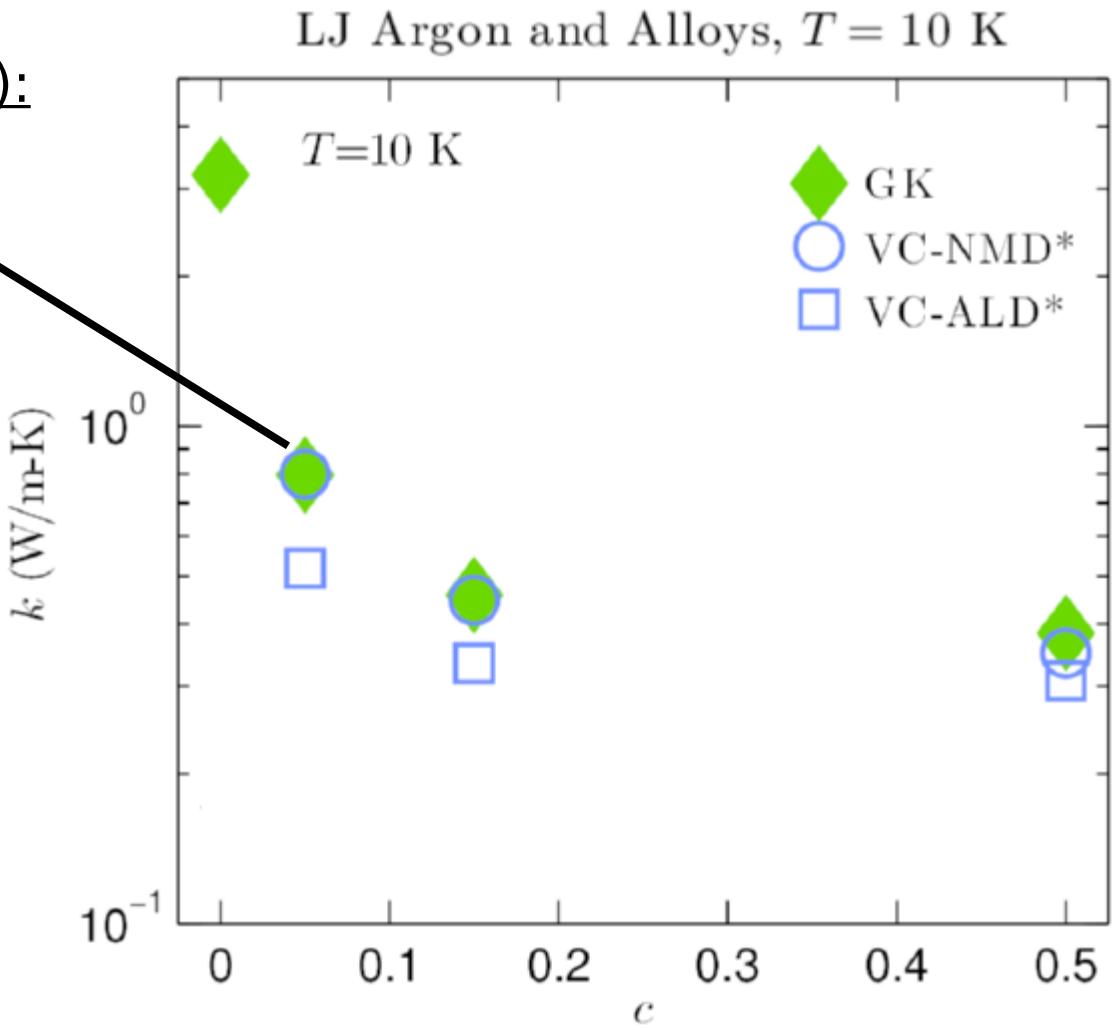
MD-based Green-Kubo (GK):
System-level



High-scatter adjustment*:

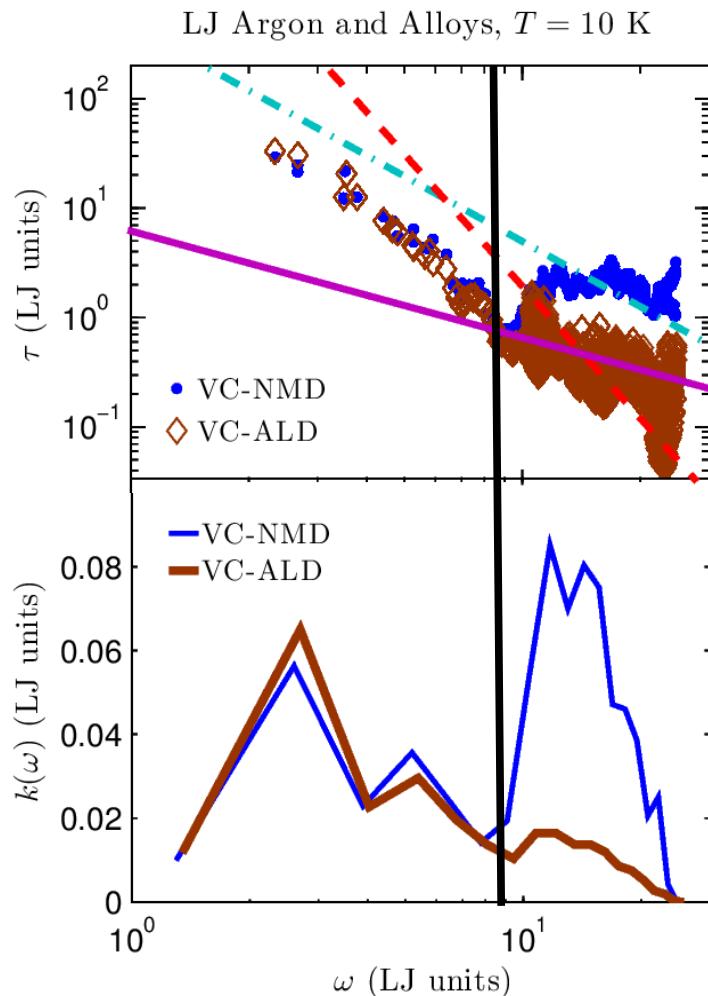
$$D_{ph}(\kappa) < D_{HS}$$

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



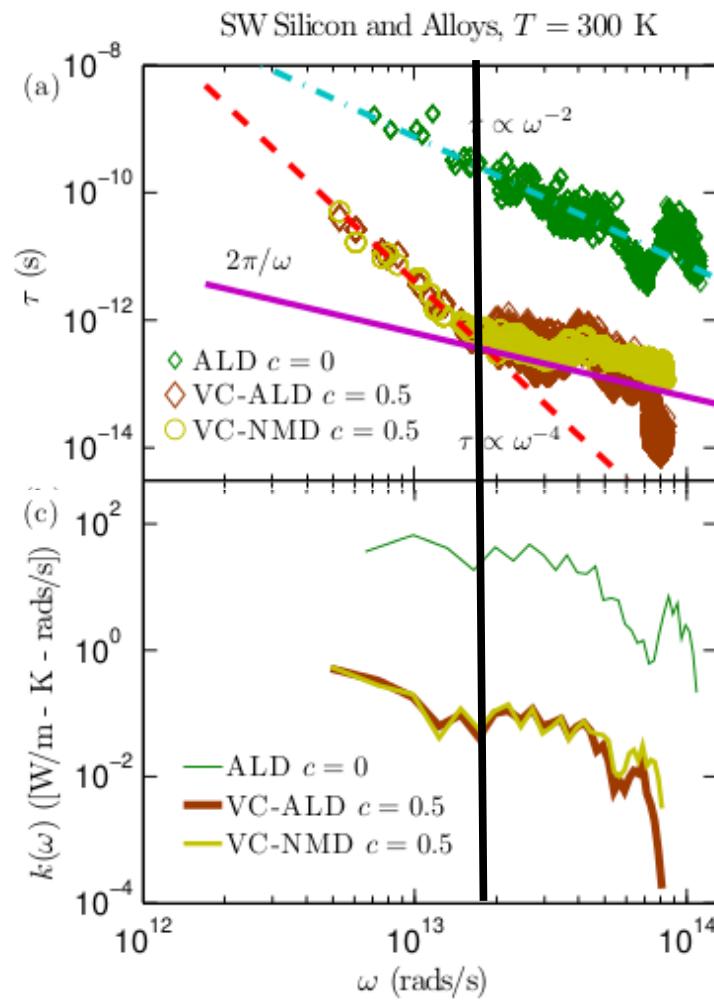
Thermal Conductivity Spectrum

Low and High Frequency



50% Propagons,
50% Diffusons

Low Frequency

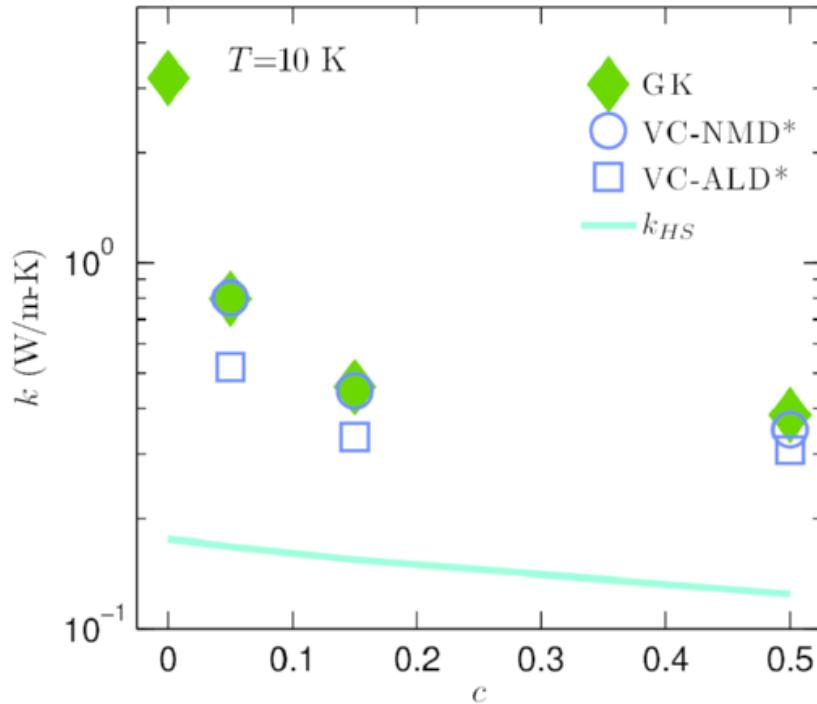


95% Propagons

Alloys: Two Classes

Full-Spectrum Alloys

LJ Argon and Alloys, $T = 10$ K

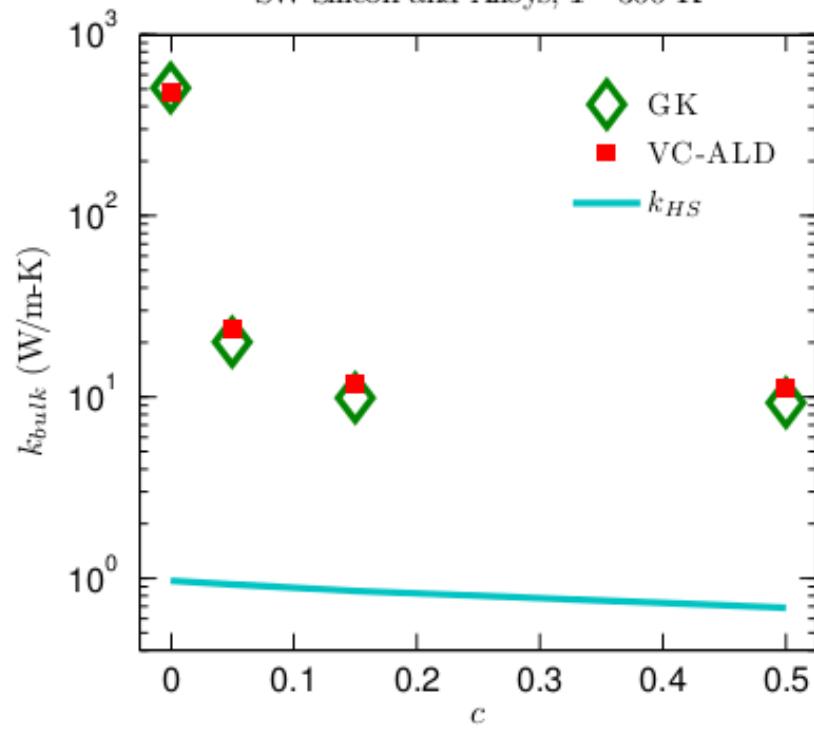


50% Propagons,
50% Diffusons

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



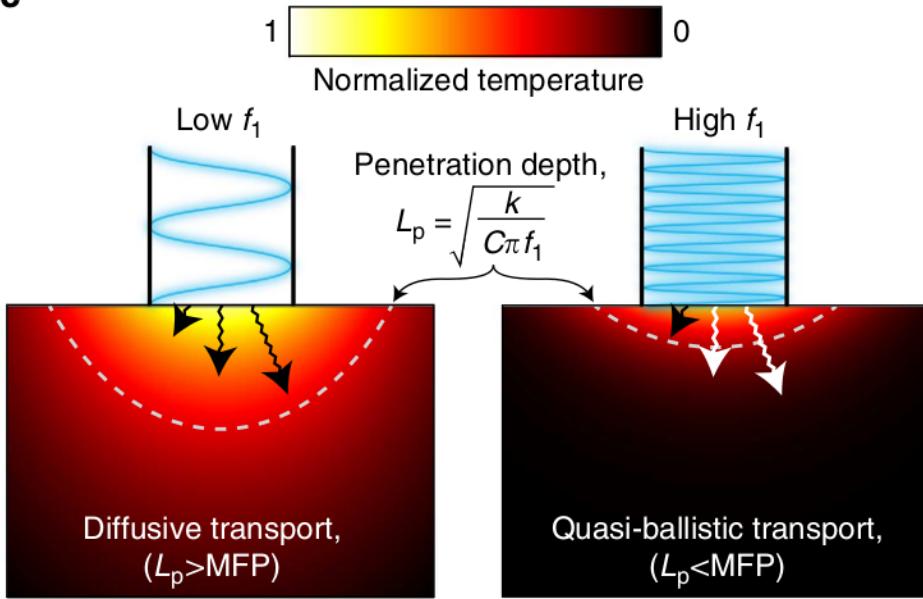
95% Propagons

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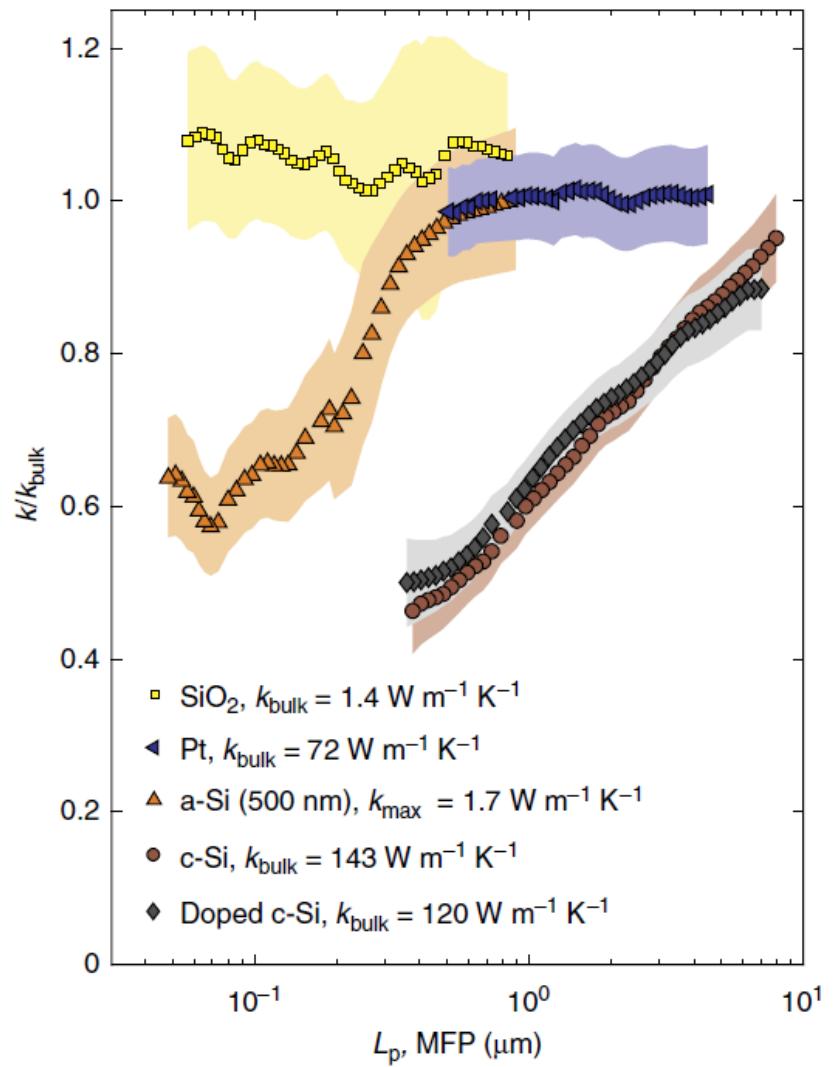
Amorphous: Motivation

c

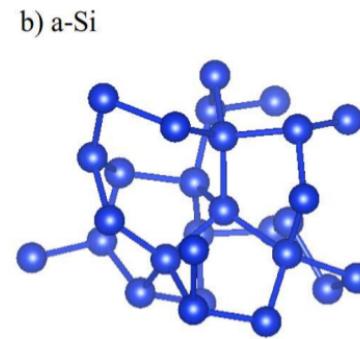
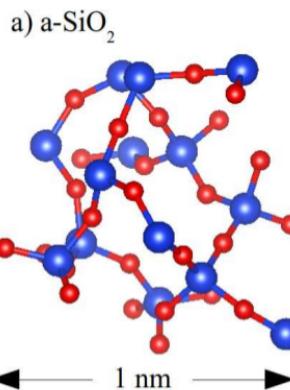
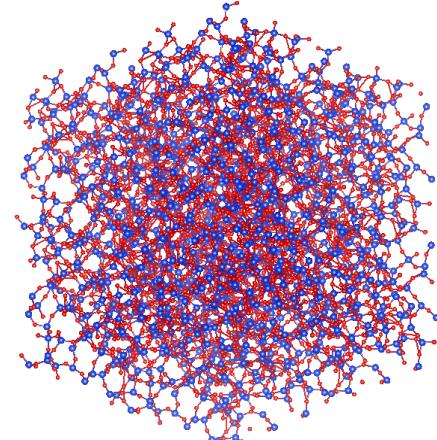


Diffusive transport,
($L_p > \text{MFP}$)

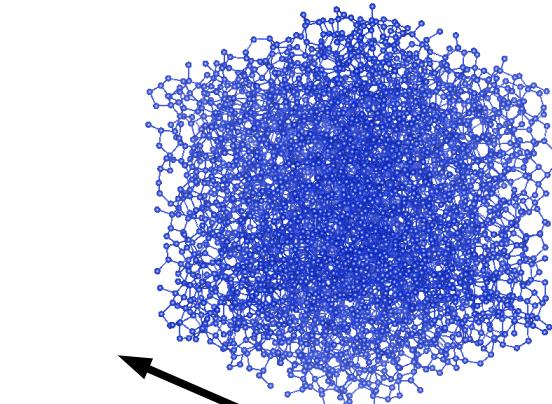
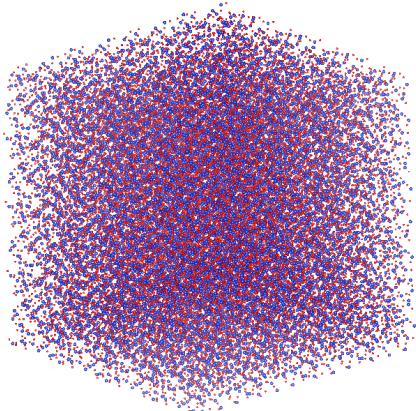
Quasi-ballistic transport,
($L_p < \text{MFP}$)



Amorphous Solids: no VC

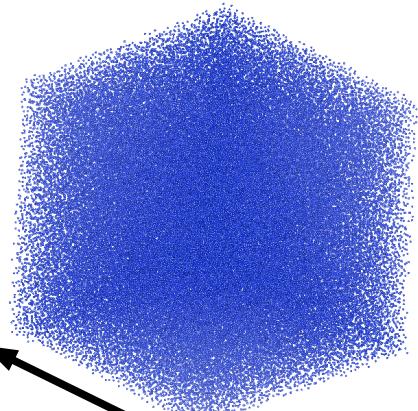


Mode-level:
~4000 atoms



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):

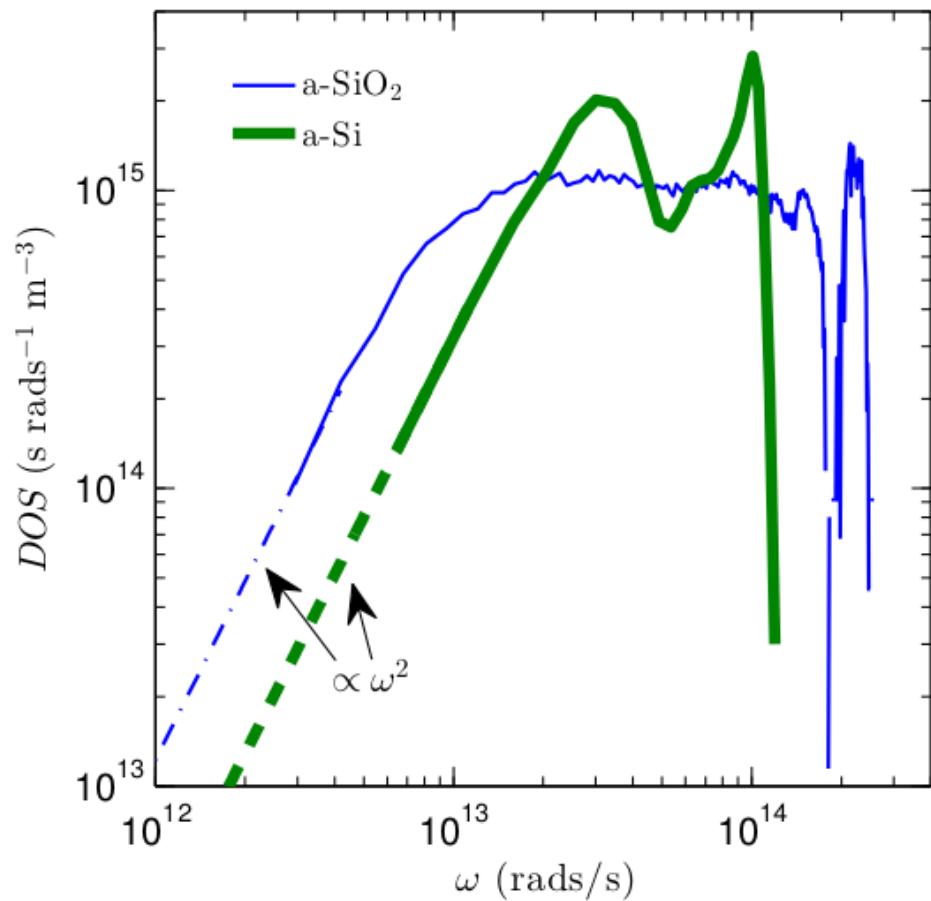
Debye-like Model: $k_{pr} = \frac{1}{V} \int_0^{\omega_{cut}} DOS(\omega) C(\omega) D_{pr}(\omega) d\omega$

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

Vibrons: Phonon character

Density of States (DOS):
Debye Model

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

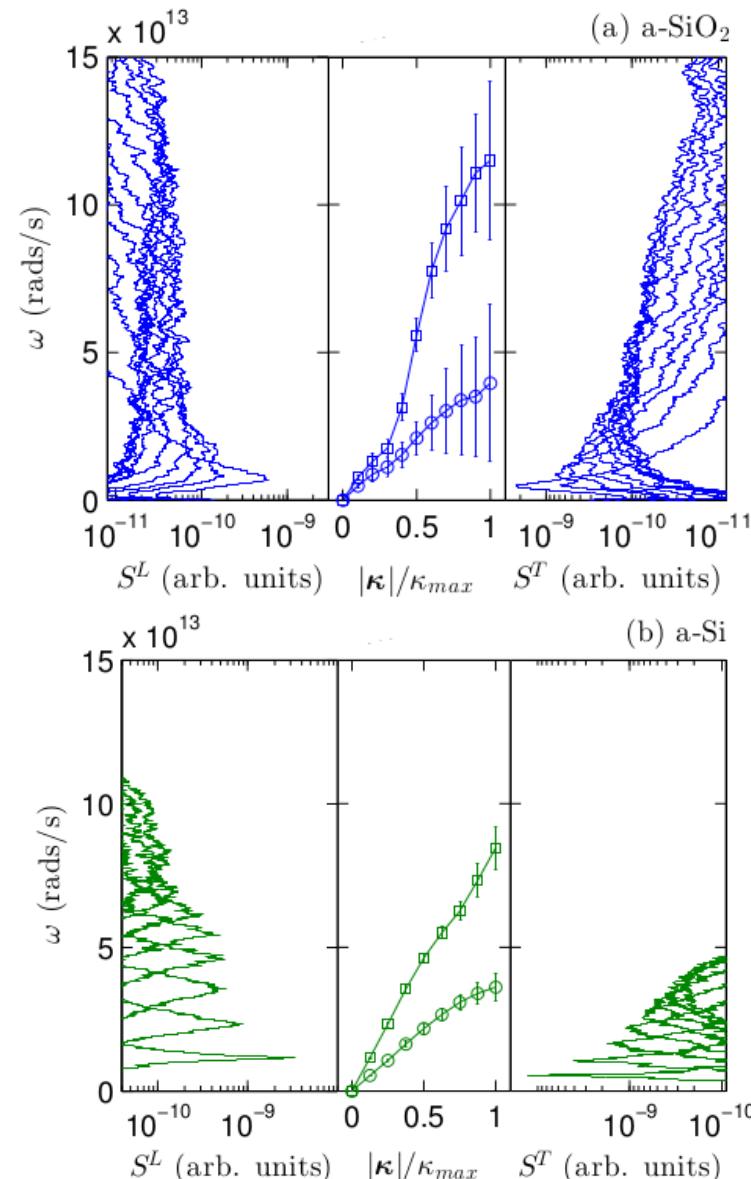


Vibrons: Phonon character

"Dispersion Law for Diffusons"
PRB 87, 134203 (2013)

Structure Factors:
Effective Dispersion

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



Vibrons: Lifetimes and Diffusivities

Diffusons (non-propagating):

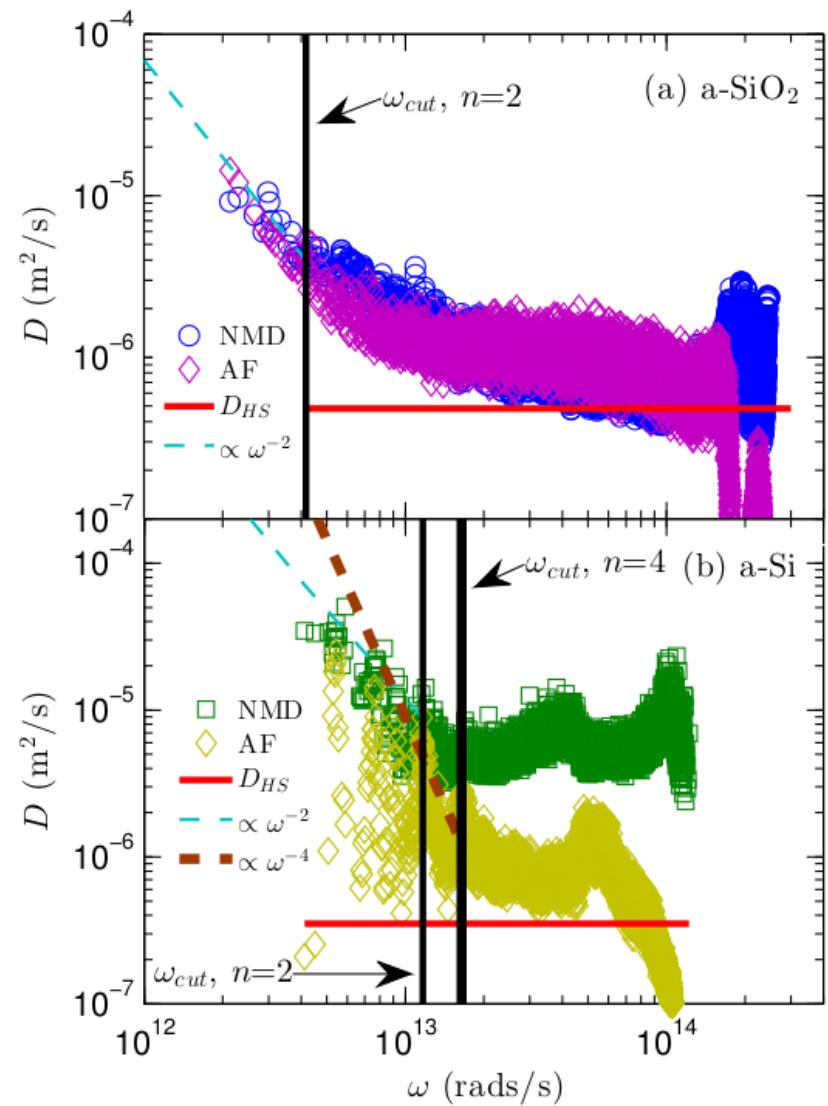
$$k_{AF} = \frac{1}{V} \sum_{i, \omega_i > \omega_{cut}} C(\omega_i) D_{AF}(\omega_i)$$

Propagons (phonon-like):

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

Normal Mode Decomposition (**NMD**):

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



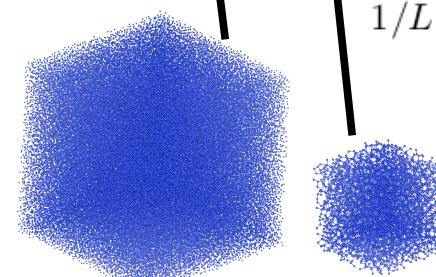
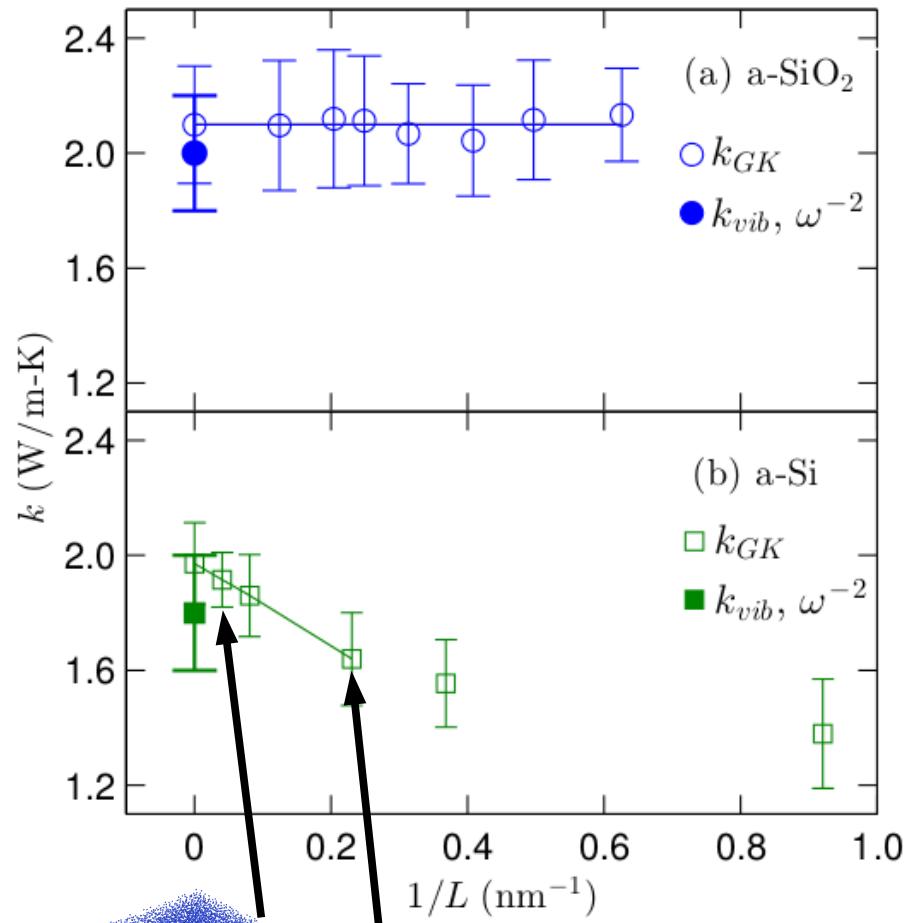
Vibrons: Mode- and System-level

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



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

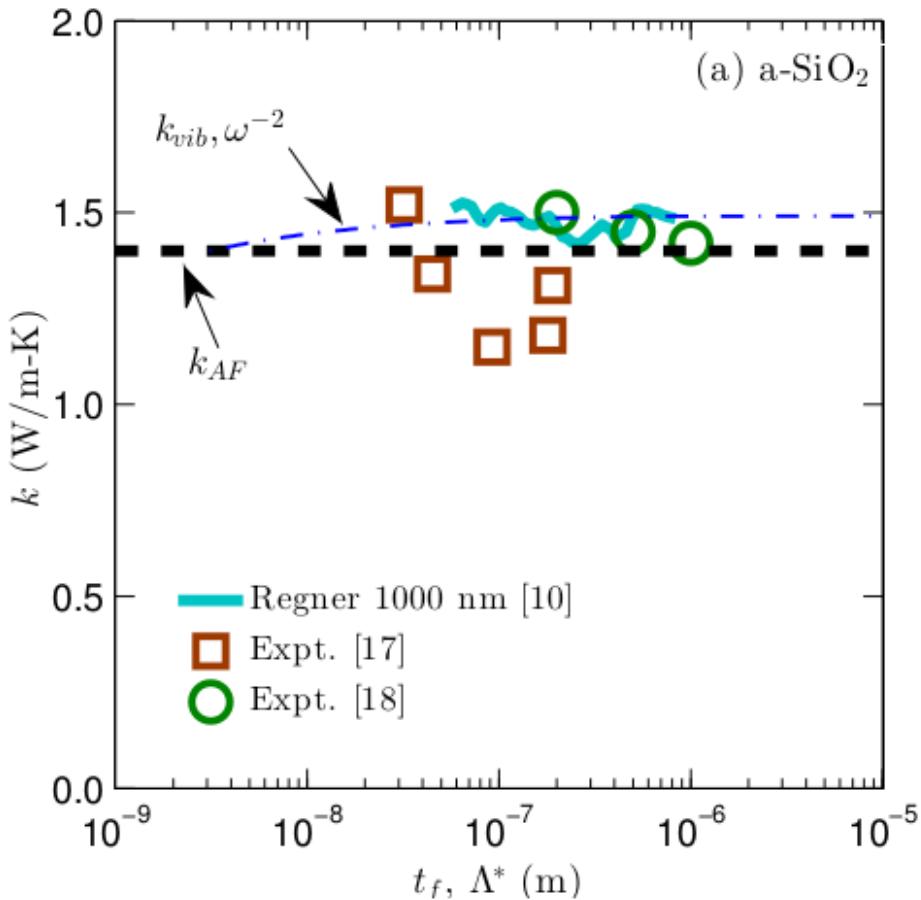
$$D_{pr}(\omega) = \frac{1}{3} v_s \Lambda(\omega)$$



System-level

Mode-level

Thermal Conductivity Accumulation



$$k(\Lambda^*) = k_{AF} + \int_{\Lambda_{cut}}^{\Lambda^*} k(\Lambda) d\Lambda$$

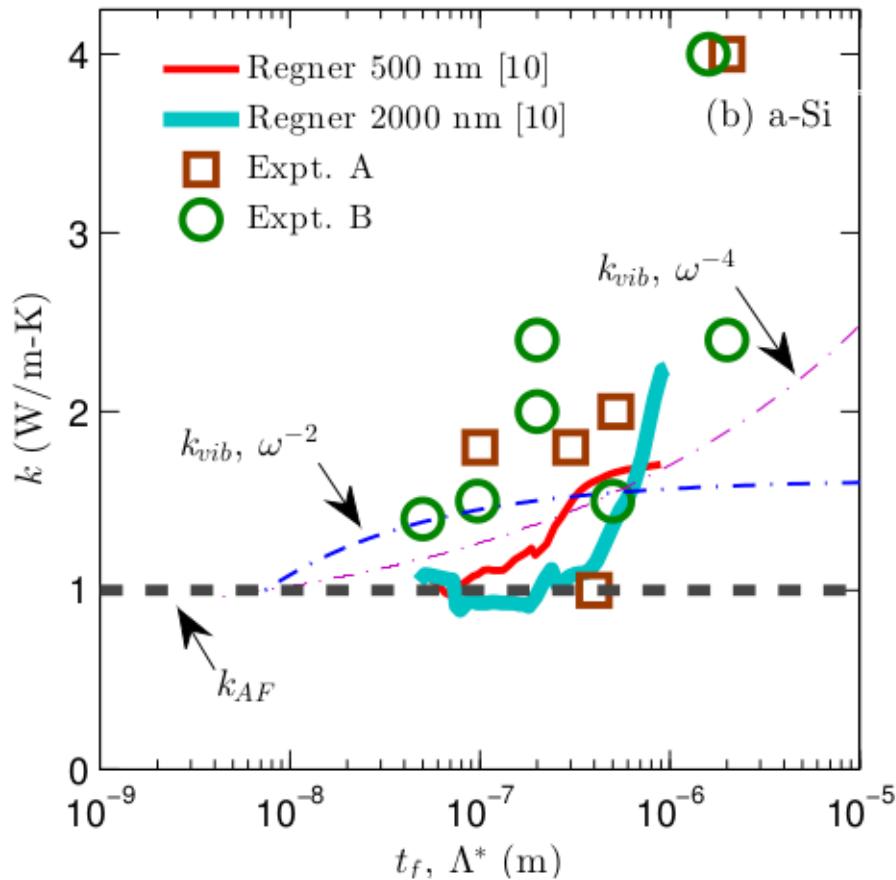
Propagating: 6% k_{pr}

Non-Propagating: 94% k_{AF}

$$C(\omega) = k_B \left[\frac{\hbar\omega/2k_B T}{\sinh(\hbar\omega/2k_B T)} \right]^2$$

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

Thermal Conductivity Accumulation



$$k(\Lambda^*) = k_{AF} + \int_{\Lambda_{cut}}^{\Lambda^*} k(\Lambda) d\Lambda$$

Propagating: 40% k_{pr}

Non-Propagating: 60% k_{AF}

$$C(\omega) = k_B \left[\frac{\hbar\omega/2k_B T}{\sinh(\hbar\omega/2k_B T)} \right]^2$$

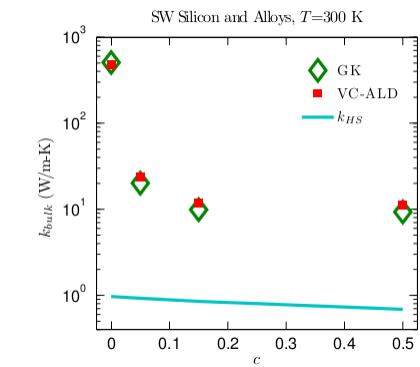
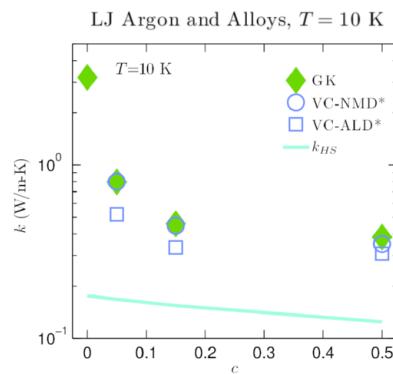
J. M. Larkin and A. J. H. McGaughey, "Thermal Conductivity Accumulation in Amorphous Materials", *Physical Review B* (submitted).

Outline

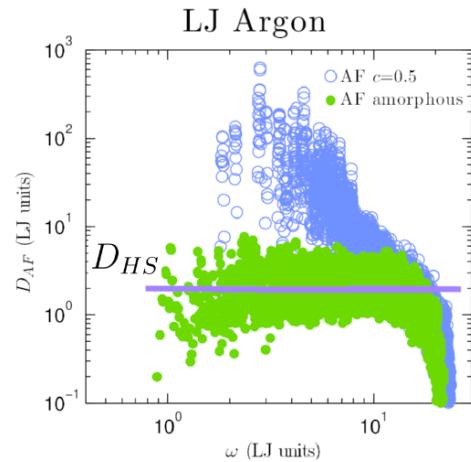
- (1) Motivation
- (2) Mode-level vs. System-level
- (3) Alloys
- (4) Amorphous
- (5) Overview/Future Work**

Overview

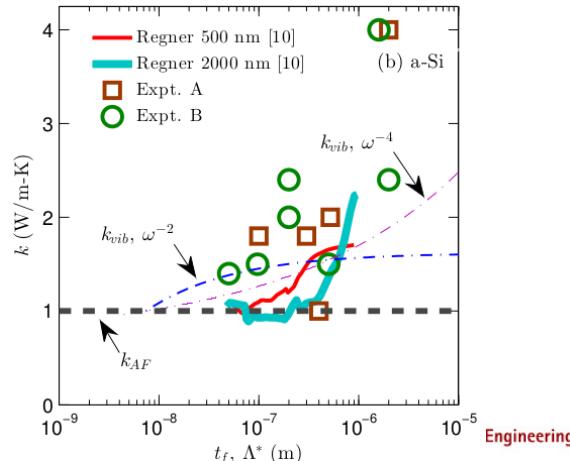
Limits of Perturbation Methods:



Alloys can behave like Amorphous:



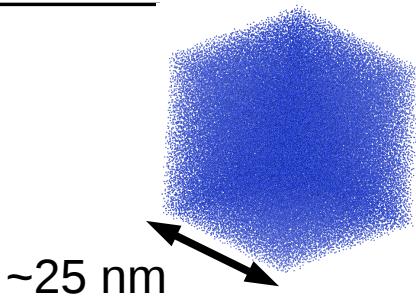
Amorphous can behave like Crystal:



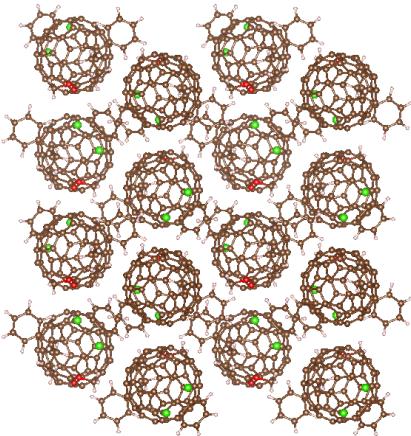
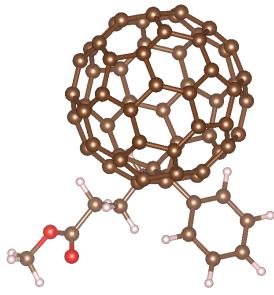
Future Work

Very Large MD-based Predictions:

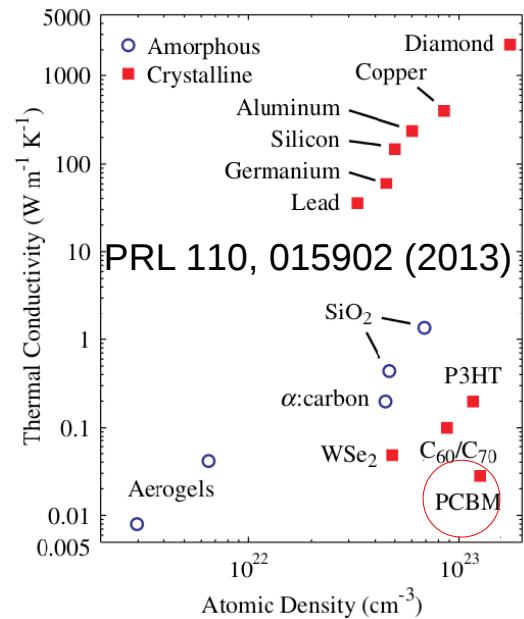
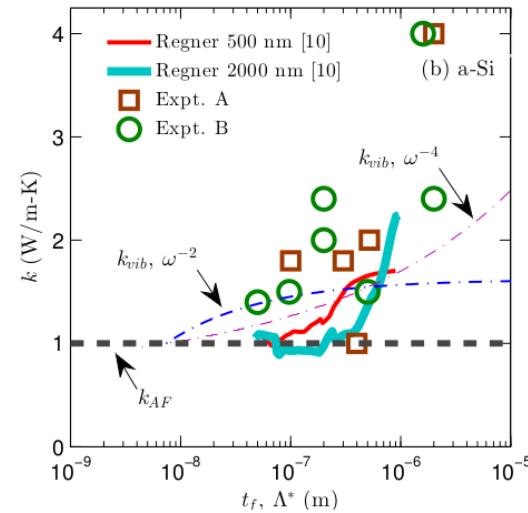
System- and Mode-level



Large Unit Cell Materials (PCBM):



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



Four Methods (+ more): A comprehensive package

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

Present and Future Work

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).

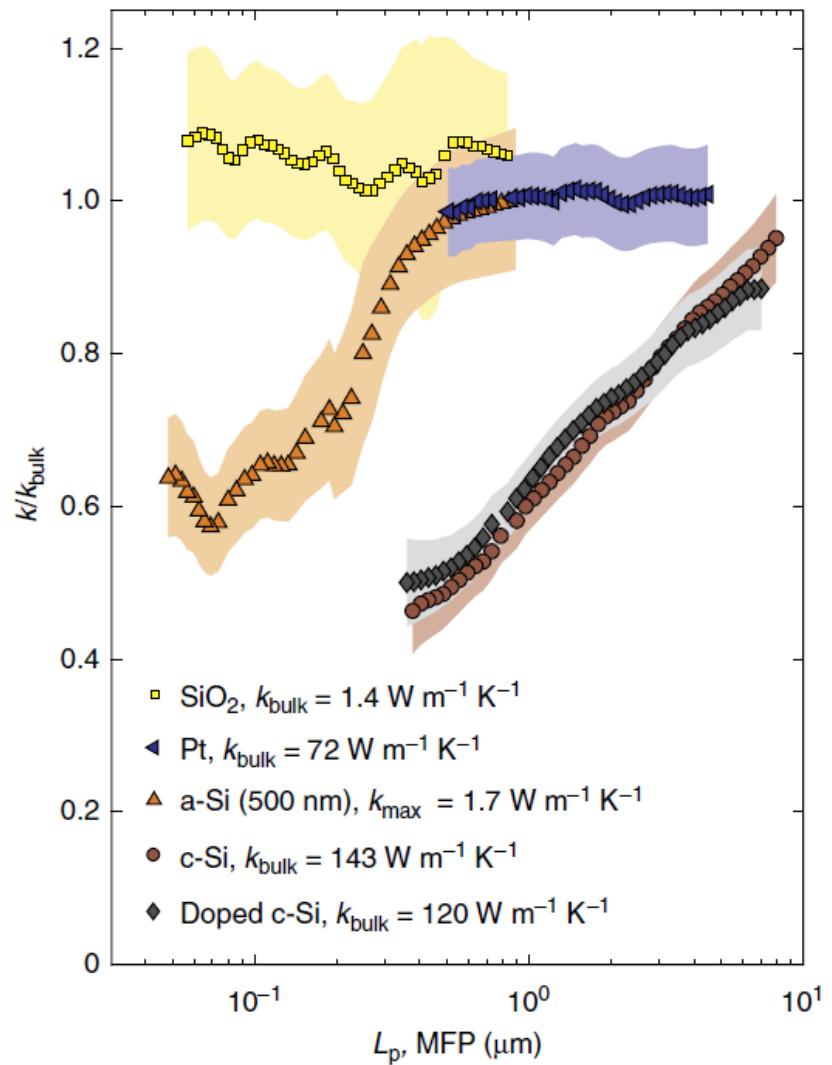
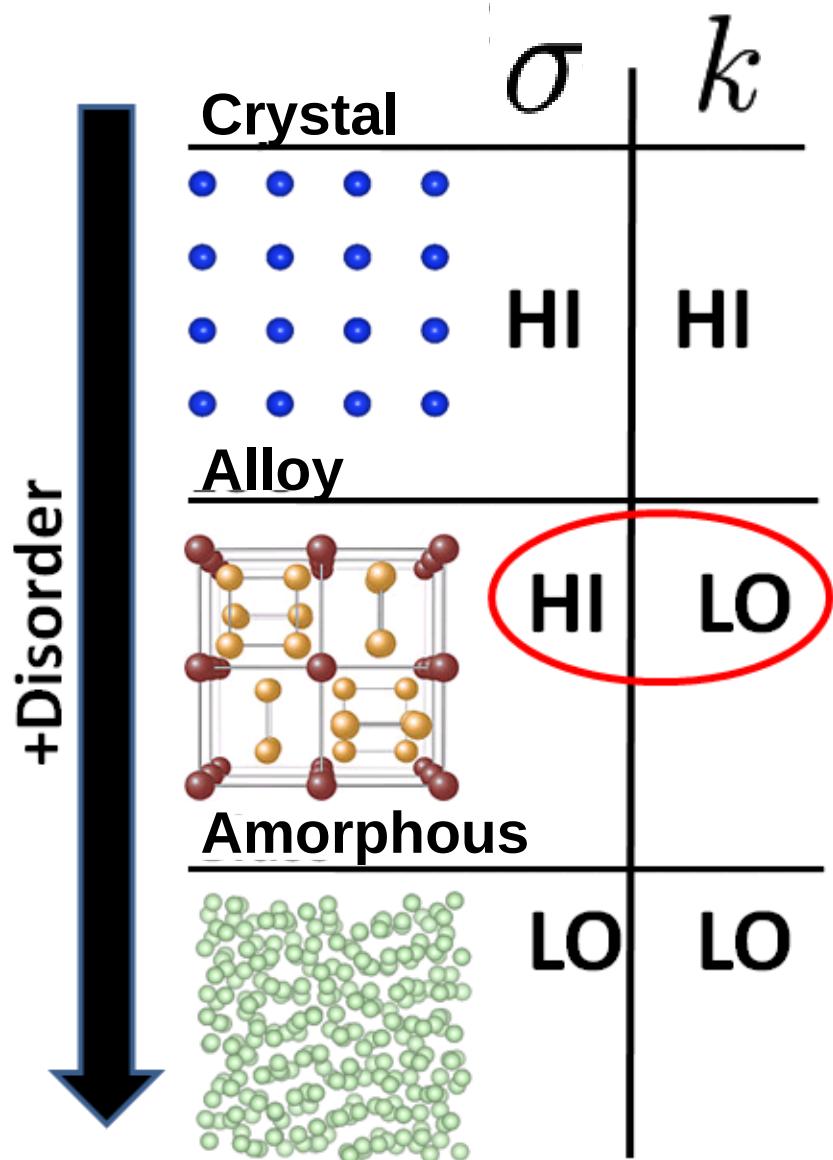
S. C. Huberman, J. M. Larkin and A. J. H. McGaughey, C. H. Amon, "Disruption of Superlattice Phonons by Interfacial Mixing", *Physical Review B* (submitted).

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

K. D. Parrish, A. Jain, J. M. Larkin, A. J. H. McGaughey, "Origins of Thermal Conductivity Changes in Strained Systems", *Journal of Applied Physics* (in progress).

Supplementary

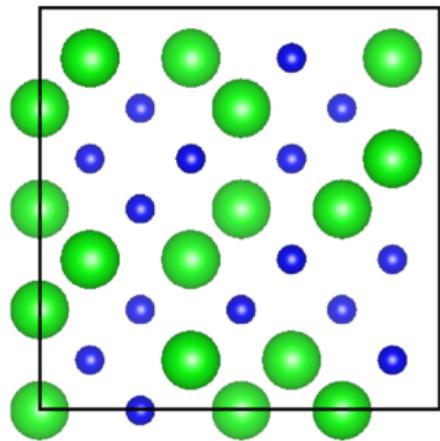
Motivation: Mode-level Properties



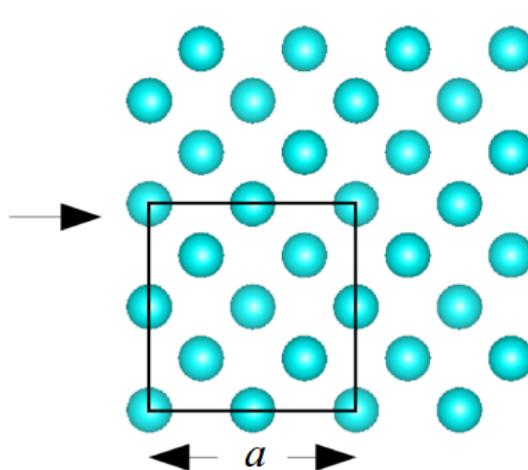
Regner et al., *Nat. Comm.* **4**, 1640 (2013)

Explicit disorder: VC vs Gamma

(a) disordered supercell



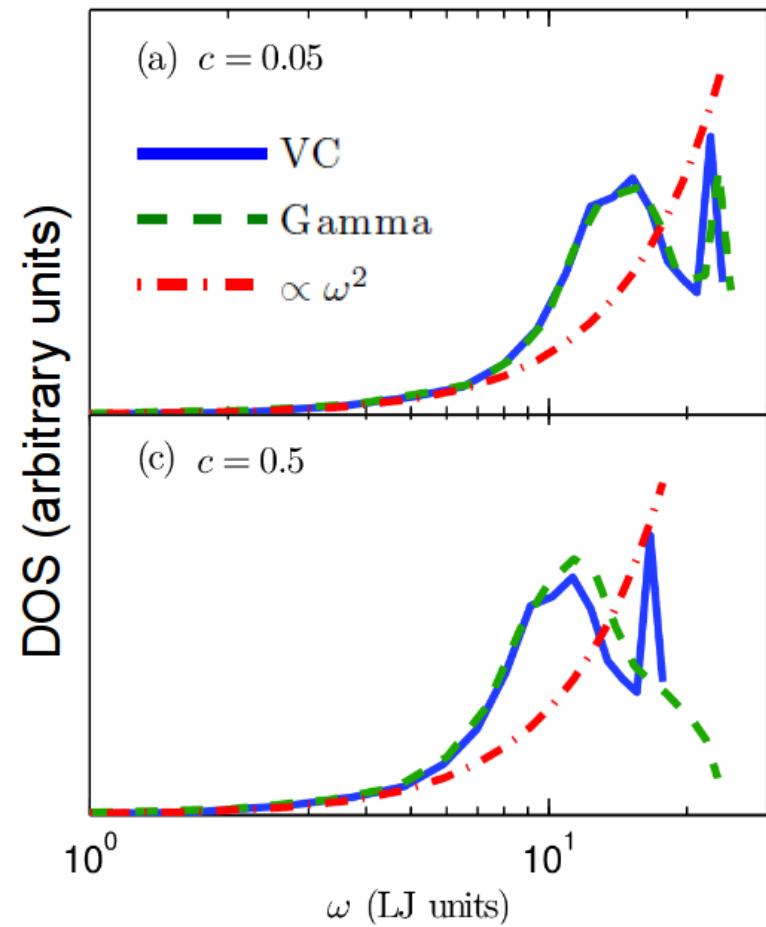
(b) VC unit cell



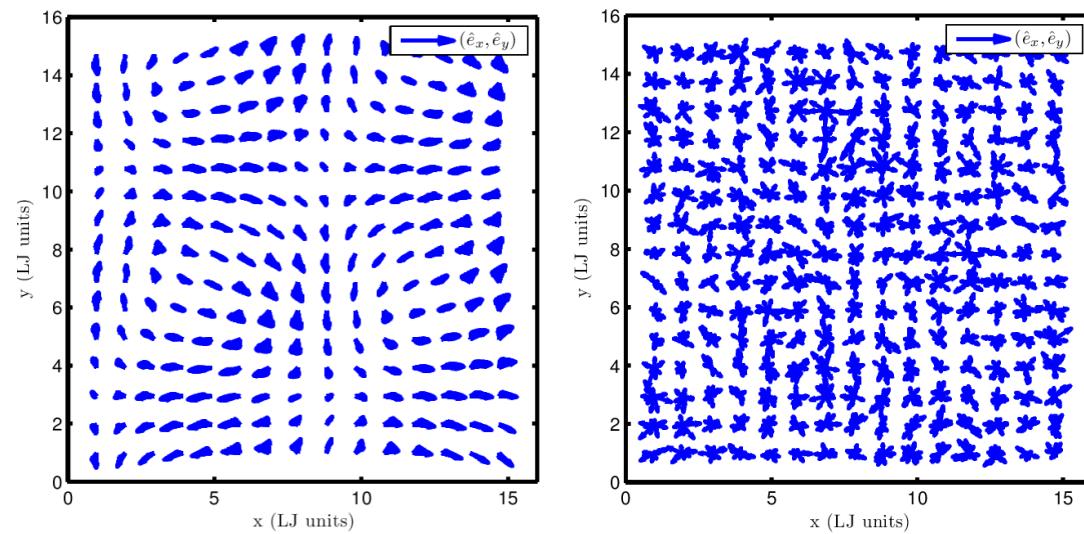
Gamma

Computationally-inexpensive
empirical potential:
Lennard-Jones argon

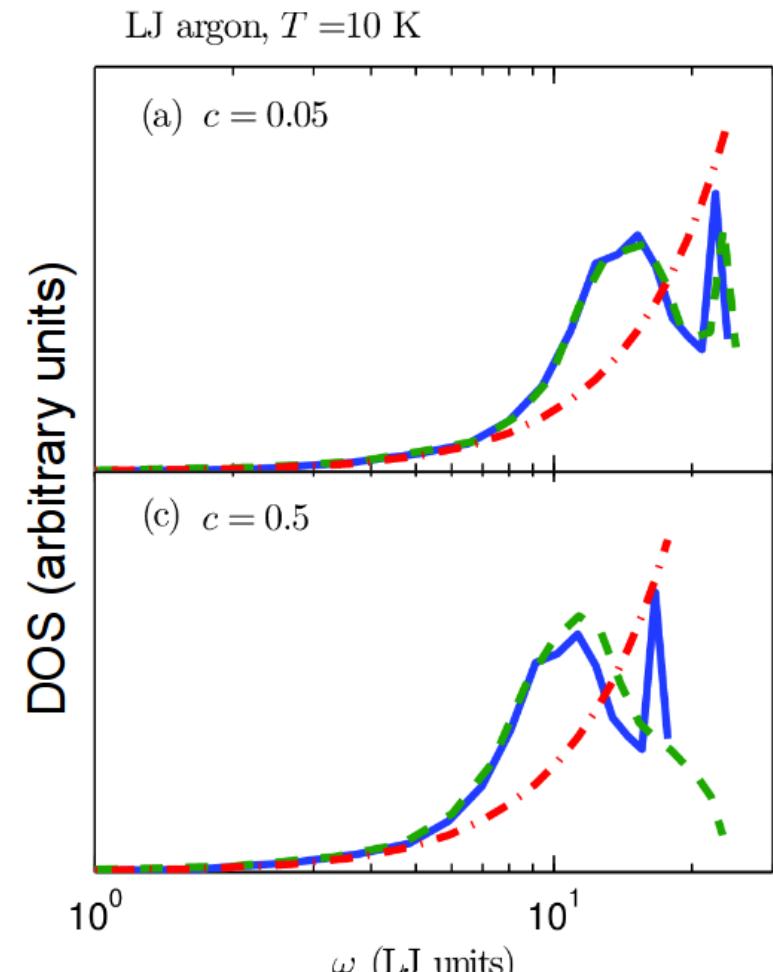
LJ argon, $T = 10$ K



Structure Factor: Effective Dispersion



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



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

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

Vibrons: Lifetimes and Diffusivities

