

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

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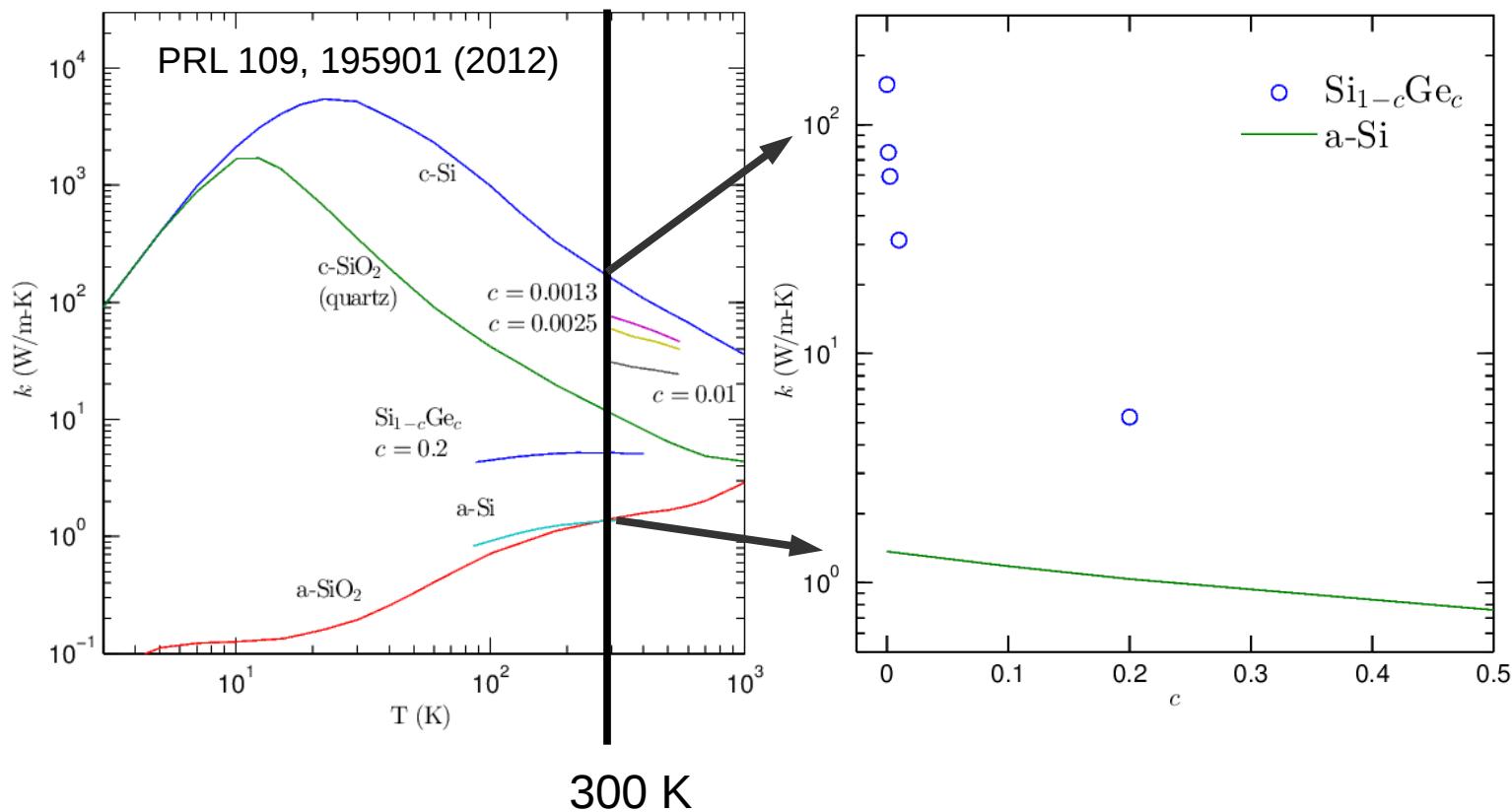
**<http://ntpl.me.cmu.edu/>**

08/29/2013

# Outline

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

# Motivation: Crystal, Alloys, Amorphous

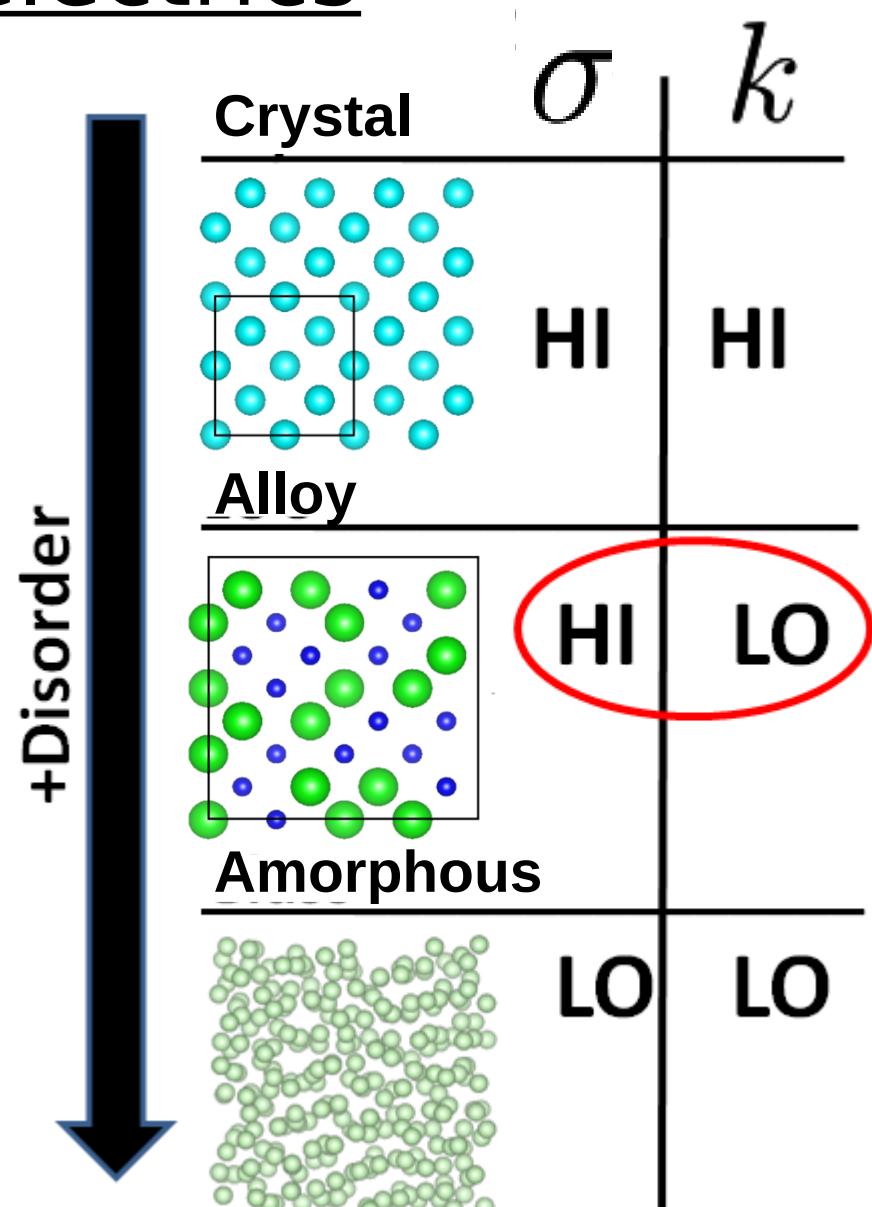


constraints: chemistry, electron transport, operating temperature, etc.

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

# Motivation: Thermoelectrics

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



## Mode-level Properties:

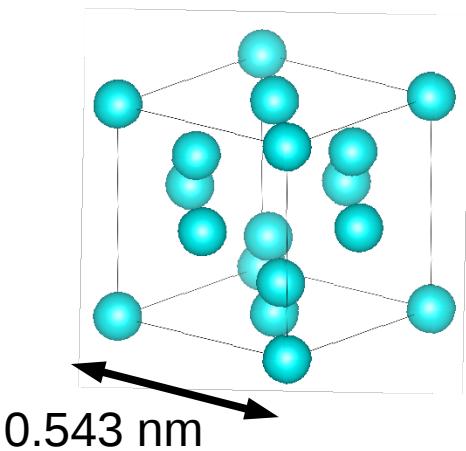
$$k_{\text{thermal}} = k_e + k_{\text{vib}} \approx k_{\text{vib}}$$

# Outline

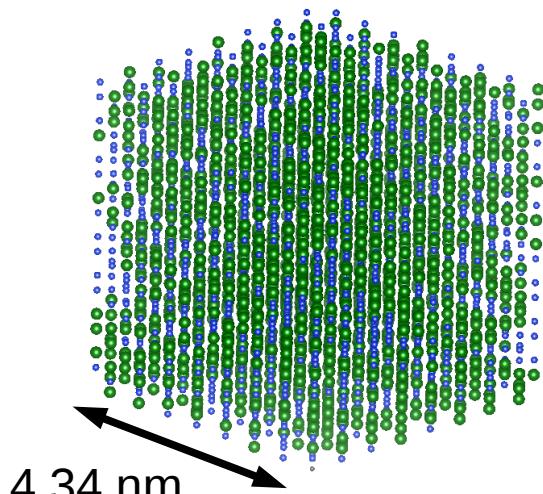
- (1) Motivation
- (2) Mode-level vs. System-level**
- (3) Alloys
- (4) Amorphous
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# Mode-level vs. System-level

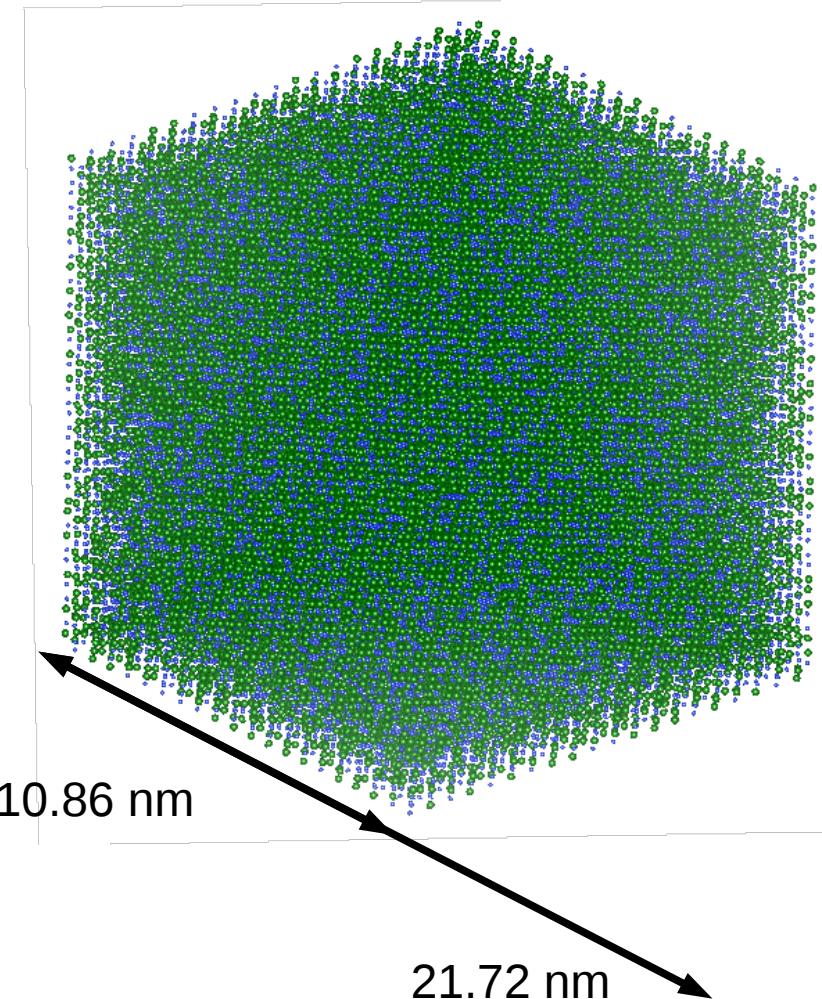
Mode-level:  
**8 atoms**



Mode-level:  
**~4000 atoms**



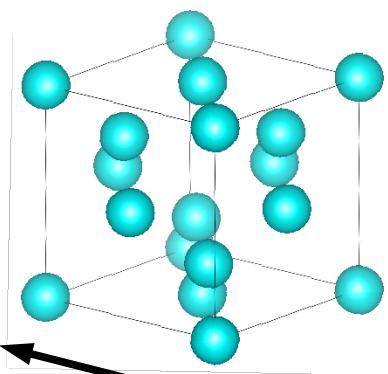
System-level:  
**~1E6 atoms**



# Mode-level: Perturbation vs. Explicit

Phonons (ph):

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



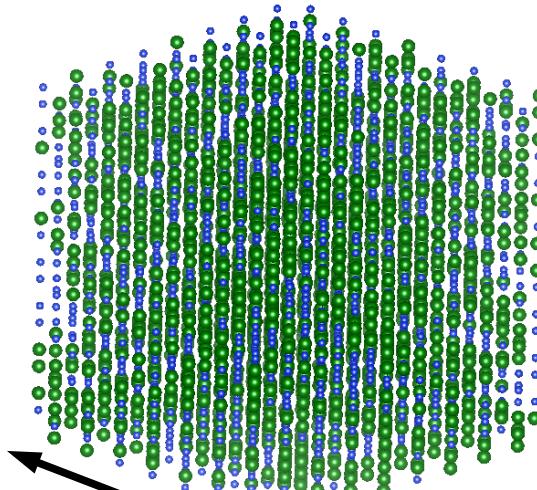
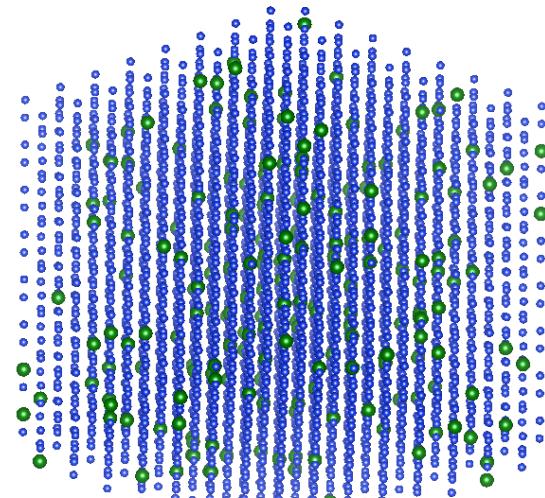
0.543 nm



?



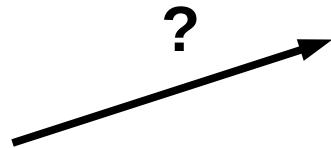
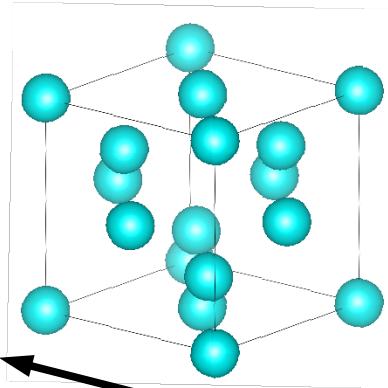
4.34 nm



# Mode-level: Explicit

Phonons (ph):

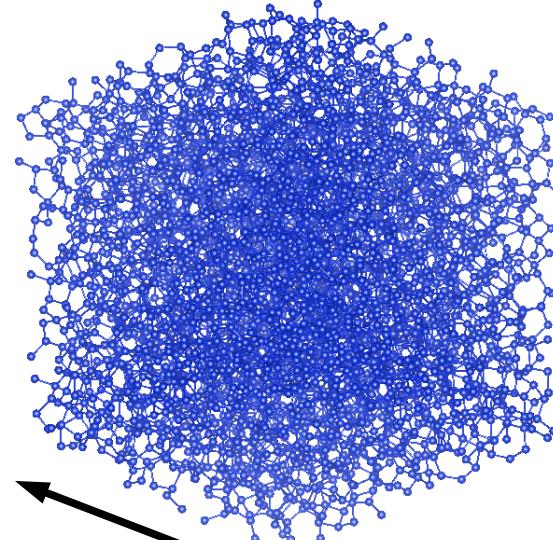
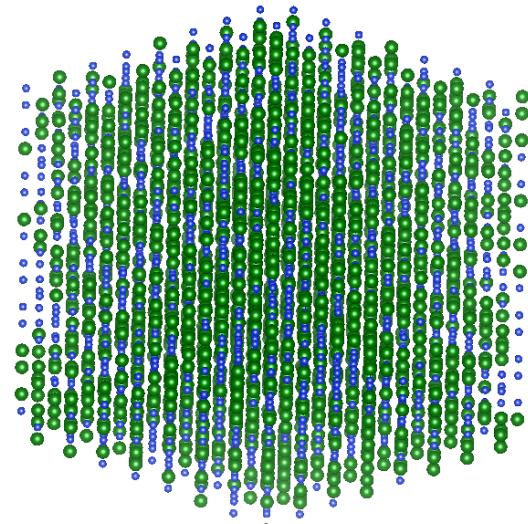
$$k_{ph,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$



No



4.34 nm



# Disordered Modes: Vibrons

## **Propagons:**

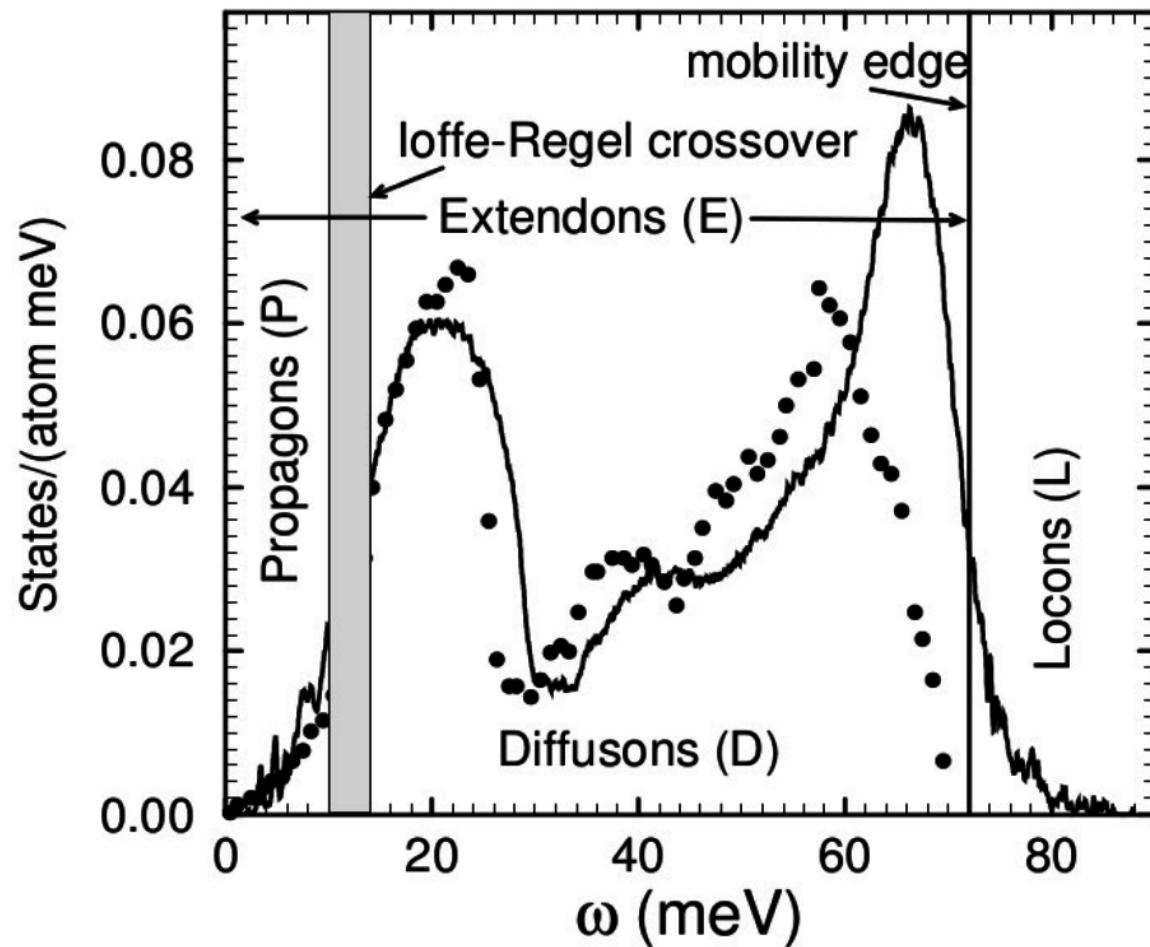
Phonon-like,  
propagating,  
de-localized

## **Diffusons:**

non-propagating,  
de-localized

## **Locons:**

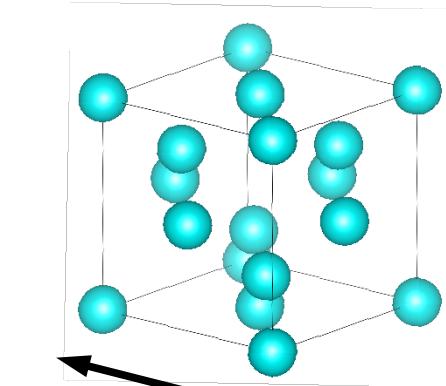
non-propagating,  
localized



# Thermal Conductivity: Mode-level

Phonons (ph):

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

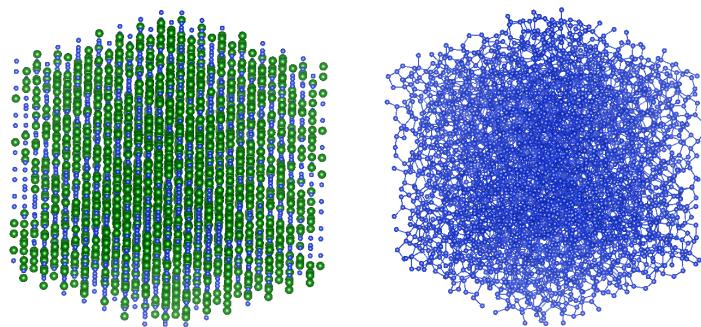


Propagons (phonon-like)

0.543 nm

Diffusons:

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



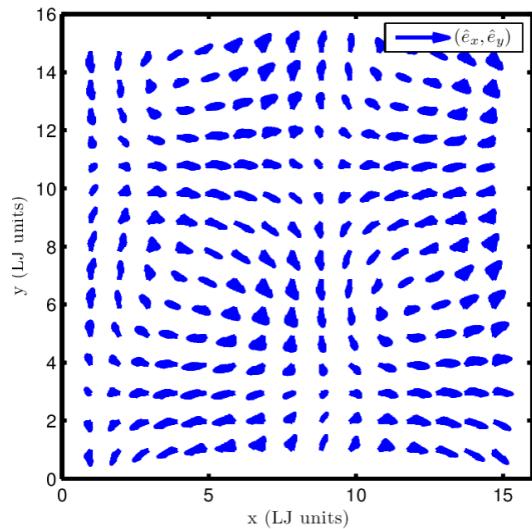
**Allen-Feldman Theory:**

PRB 48, 12581-12588 (1993)

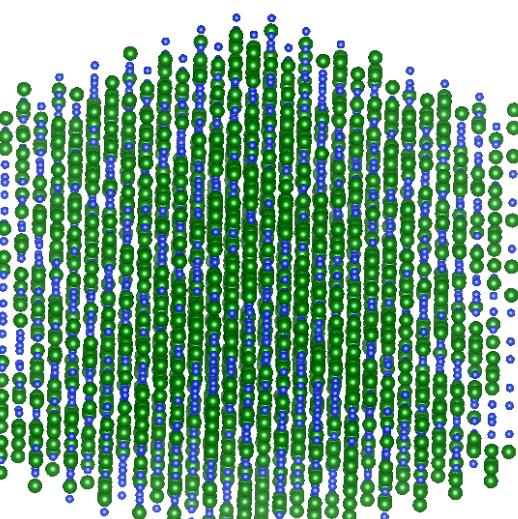
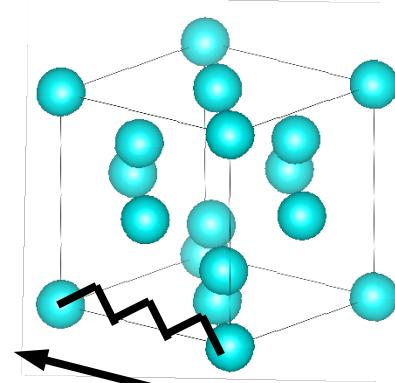
# Thermal Conductivity: Mode-level

Propagons (phonon-like):

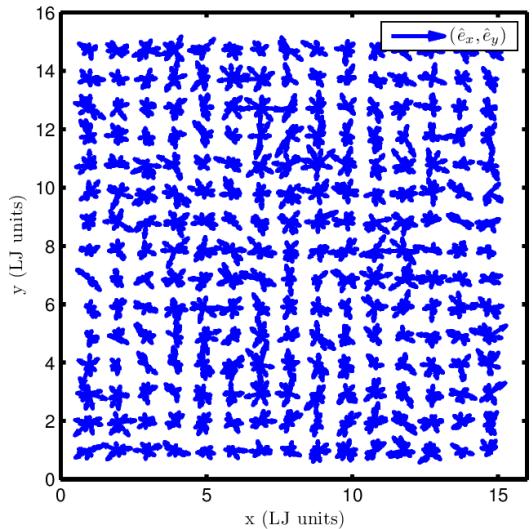
Harmonic Lattice Dynamics



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

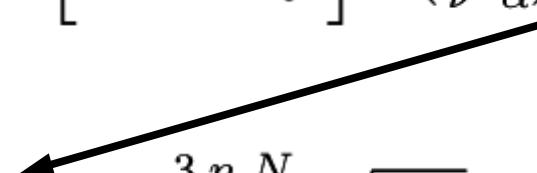


Diffusons:

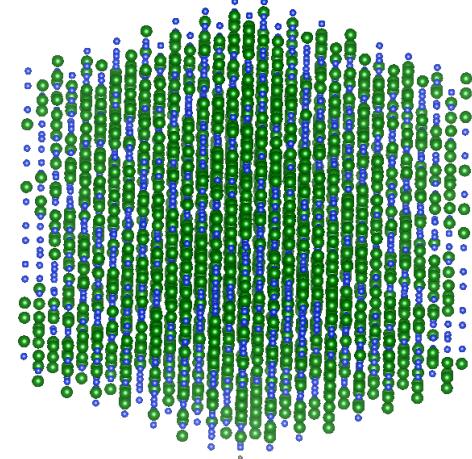


# Vibrational Properties: Molecular Dynamics

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



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



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):

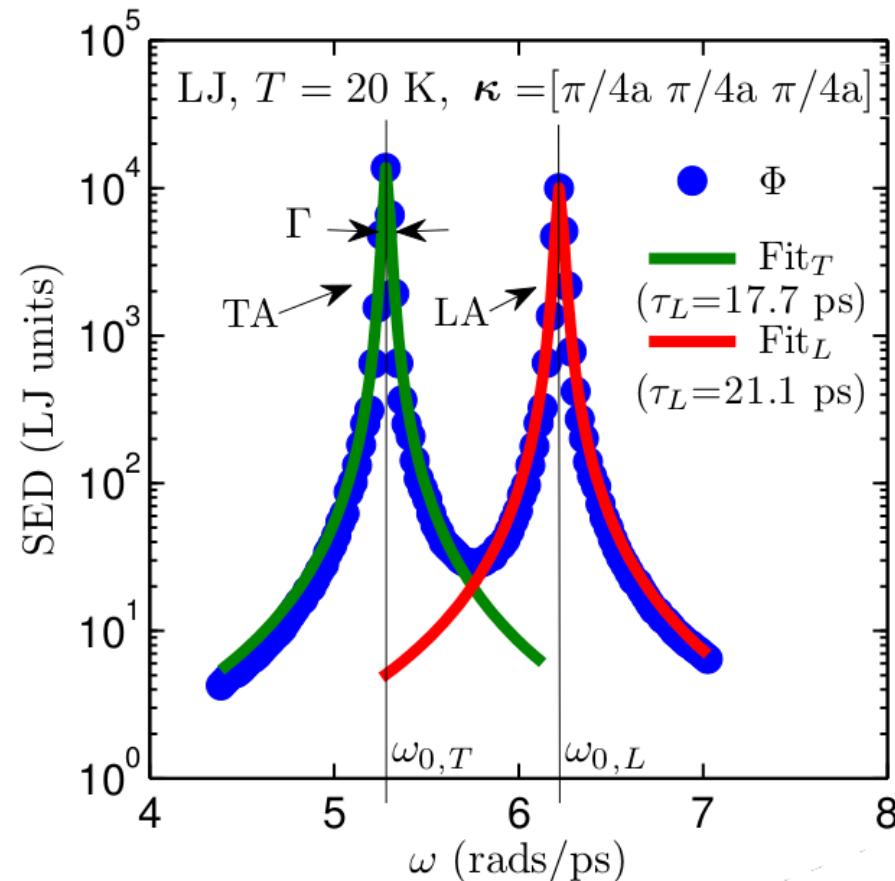
$$E(\kappa; t) = \frac{\omega(\kappa)^2}{2} q(\kappa; t)^* q(\kappa; t) + \frac{1}{2} \dot{q}(\kappa; t)^* \dot{q}(\kappa; t)$$

**PE**                           **KE**

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

Inharmonic Lattice Dynamics:

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



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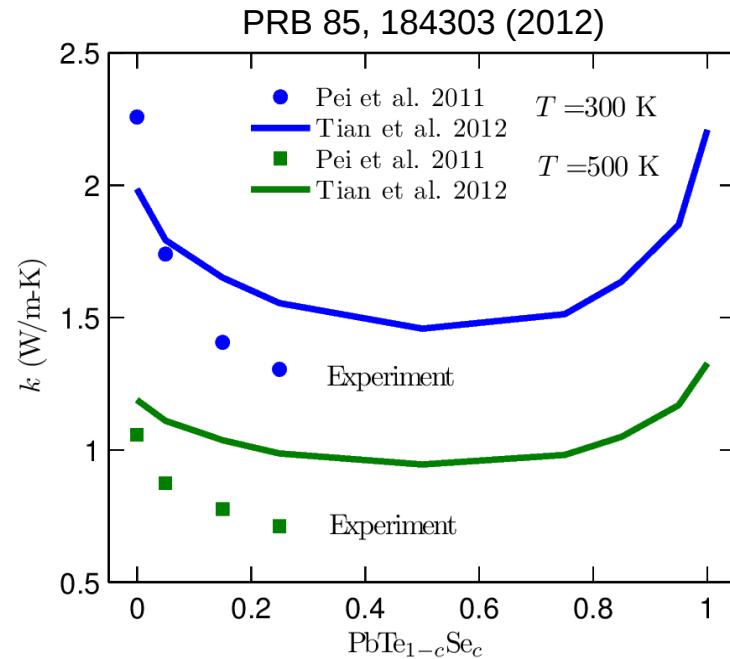
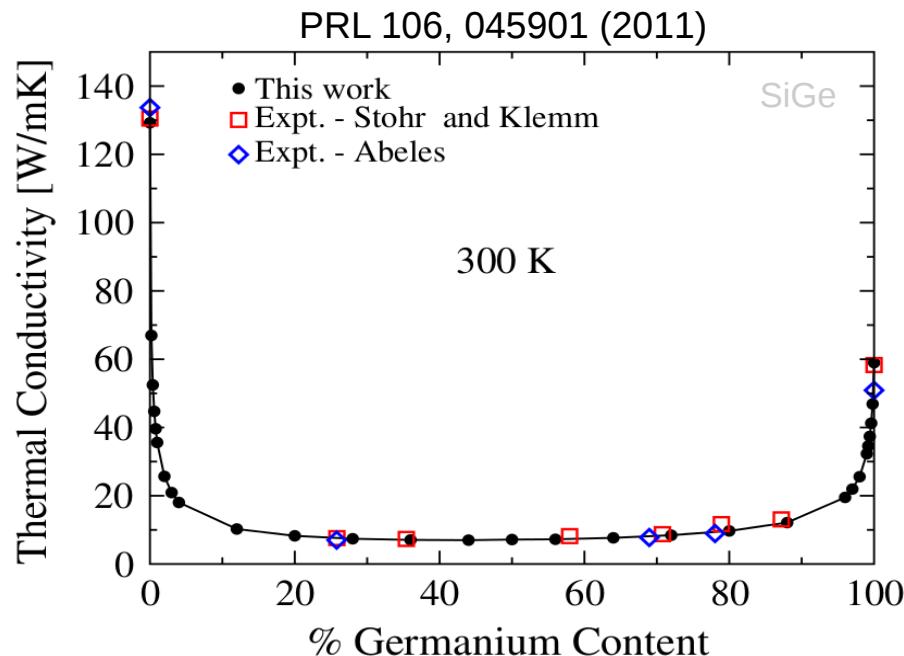
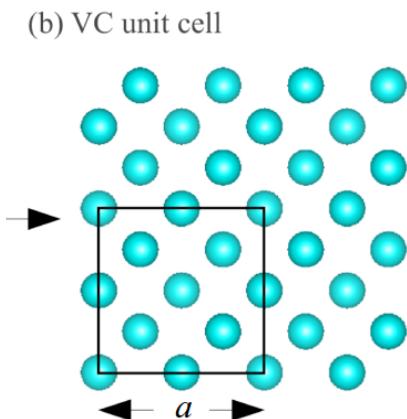
# Alloys: experimental accuracy

Expensive Density Functional Theory (DFT) calculations

+

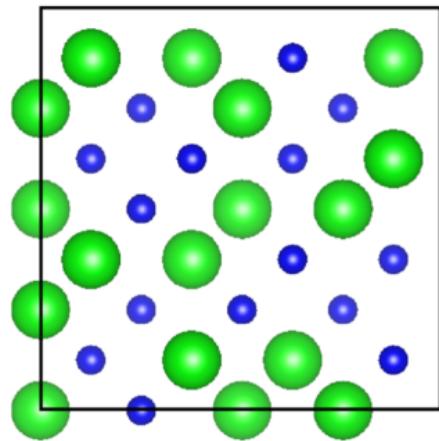
Virtual Crystal (VC) approximation &  
Anharmonic Lattice Dynamics (ALD) (**VC-ALD**)

Alloys: isotopic effects, thermoelectric materials

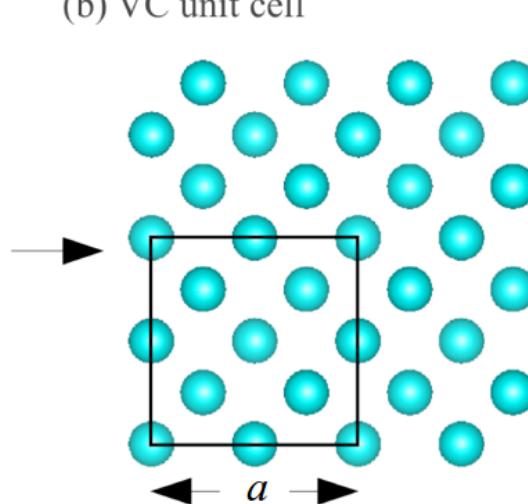


# Alloys: Virtual Crystal Approximation

(a) disordered supercell



(b) VC unit cell



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

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

Thermal conductivity:

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

Thermal diffusivity:

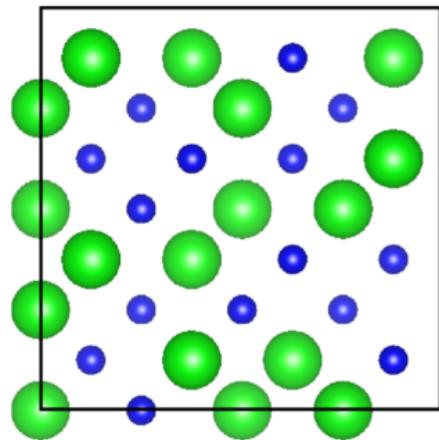
$$D_{ph,\mathbf{n}}(\boldsymbol{\nu}) = v_{g,\mathbf{n}}^2(\boldsymbol{\nu}) \tau(\boldsymbol{\nu})$$

Diffusons:

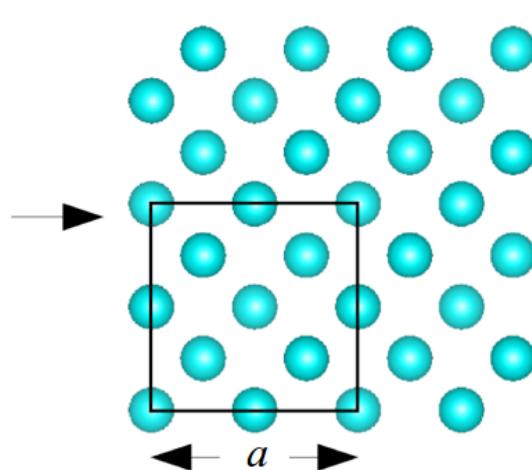
$$k_{AF} = \sum_{diffusons} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

# VC-ALD: Group Velocity

(a) disordered supercell



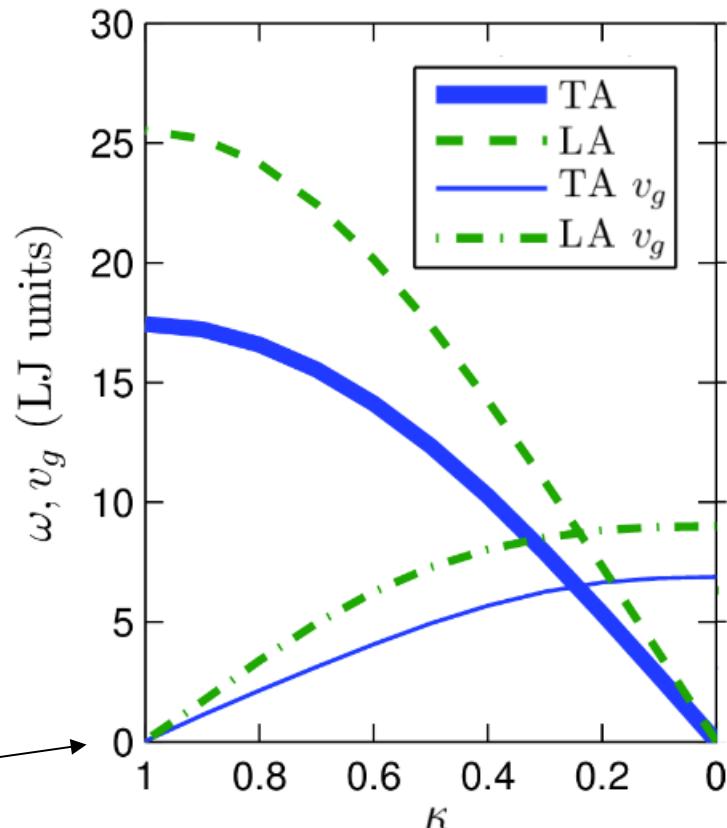
(b) VC unit cell



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

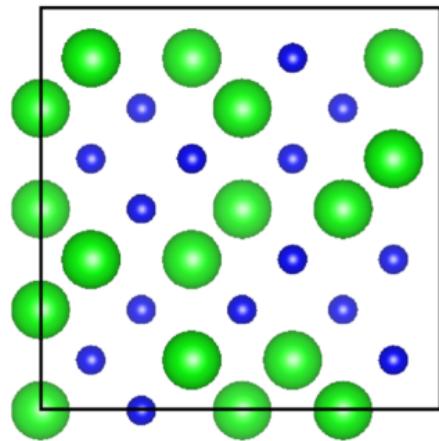
$$v_{g,\mathbf{n}}(\kappa_\nu) = \frac{\partial \omega(\kappa_\nu)}{\partial \kappa}$$

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

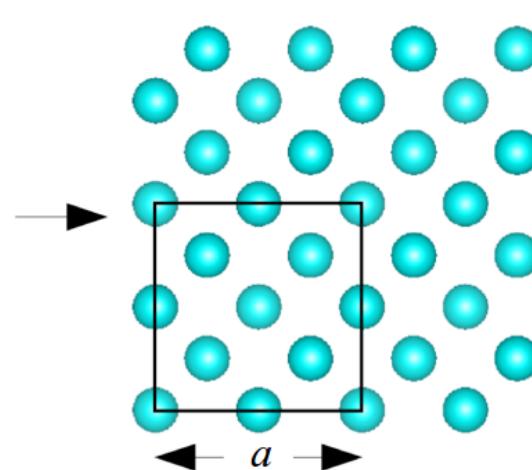


# VC-ALD: Lifetimes

(a) disordered supercell



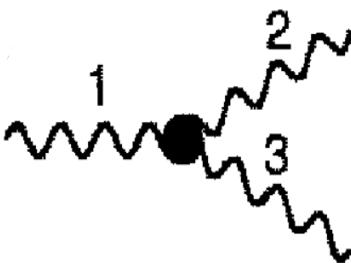
(b) VC unit cell



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

ALD

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



Tamura

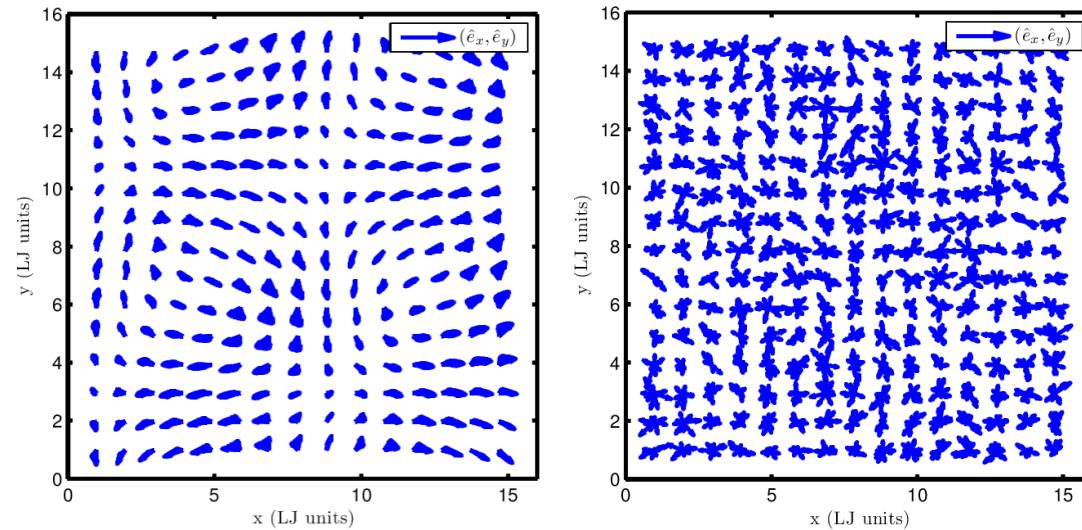
$$\tau_{p-d}(\kappa_\nu) \sim 1/\omega^4$$



Matthiessen's Rule:

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

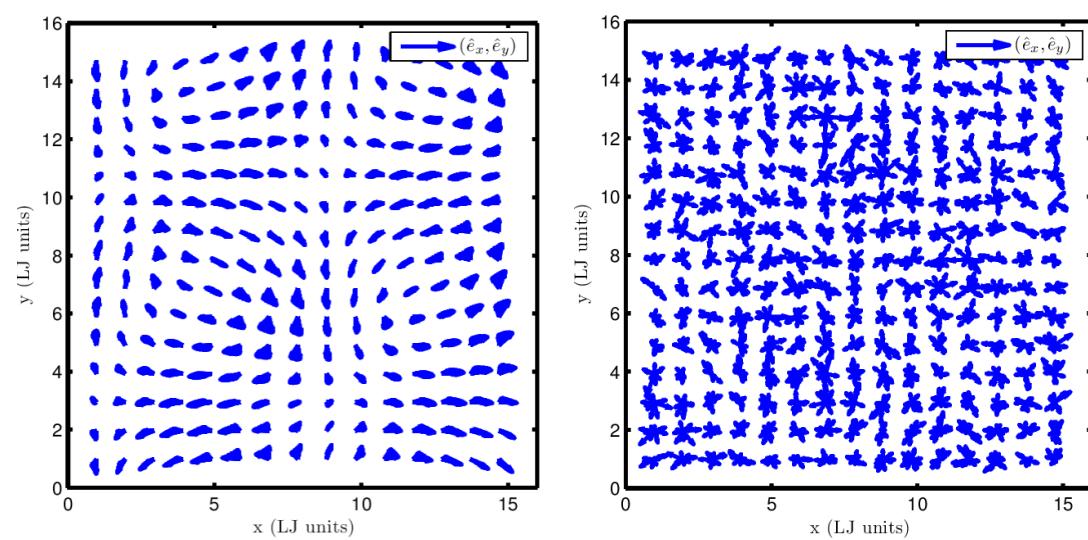
# Structure Factor: Mode Shapes



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

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

# Structure Factor: Effective Dispersion



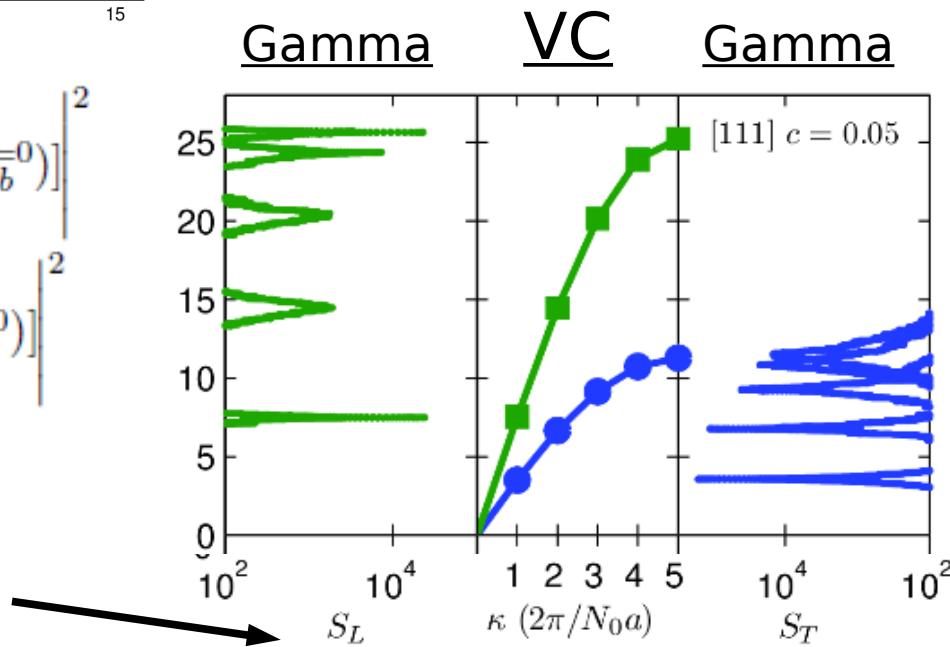
$$D_{ph,n}(\kappa_\nu) = v_{g,n}^2(\kappa_\nu) \tau(\kappa_\nu)$$

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

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

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

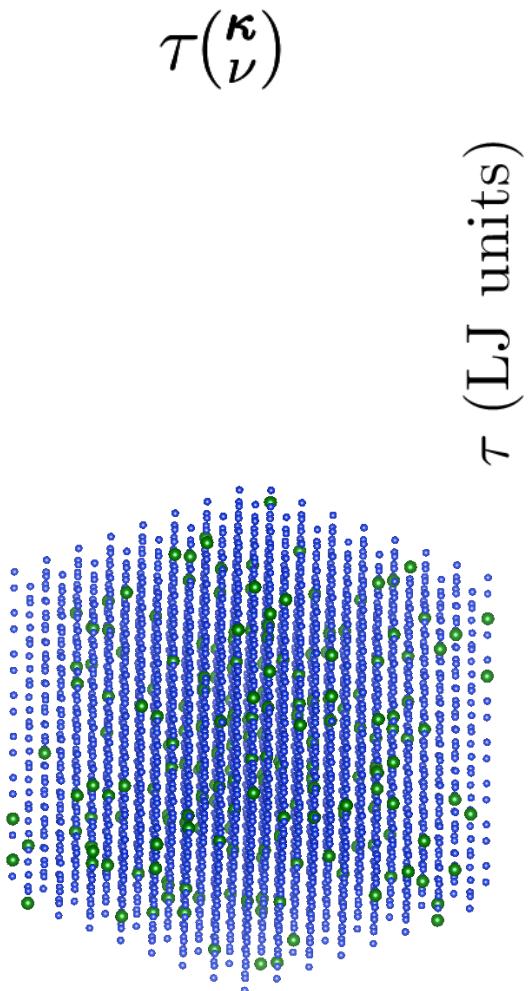
$$S^{L,T}(\omega) = \sum_\nu E^{L,T}(\kappa_{VC}) \delta[\omega - \omega(\kappa=0)]$$



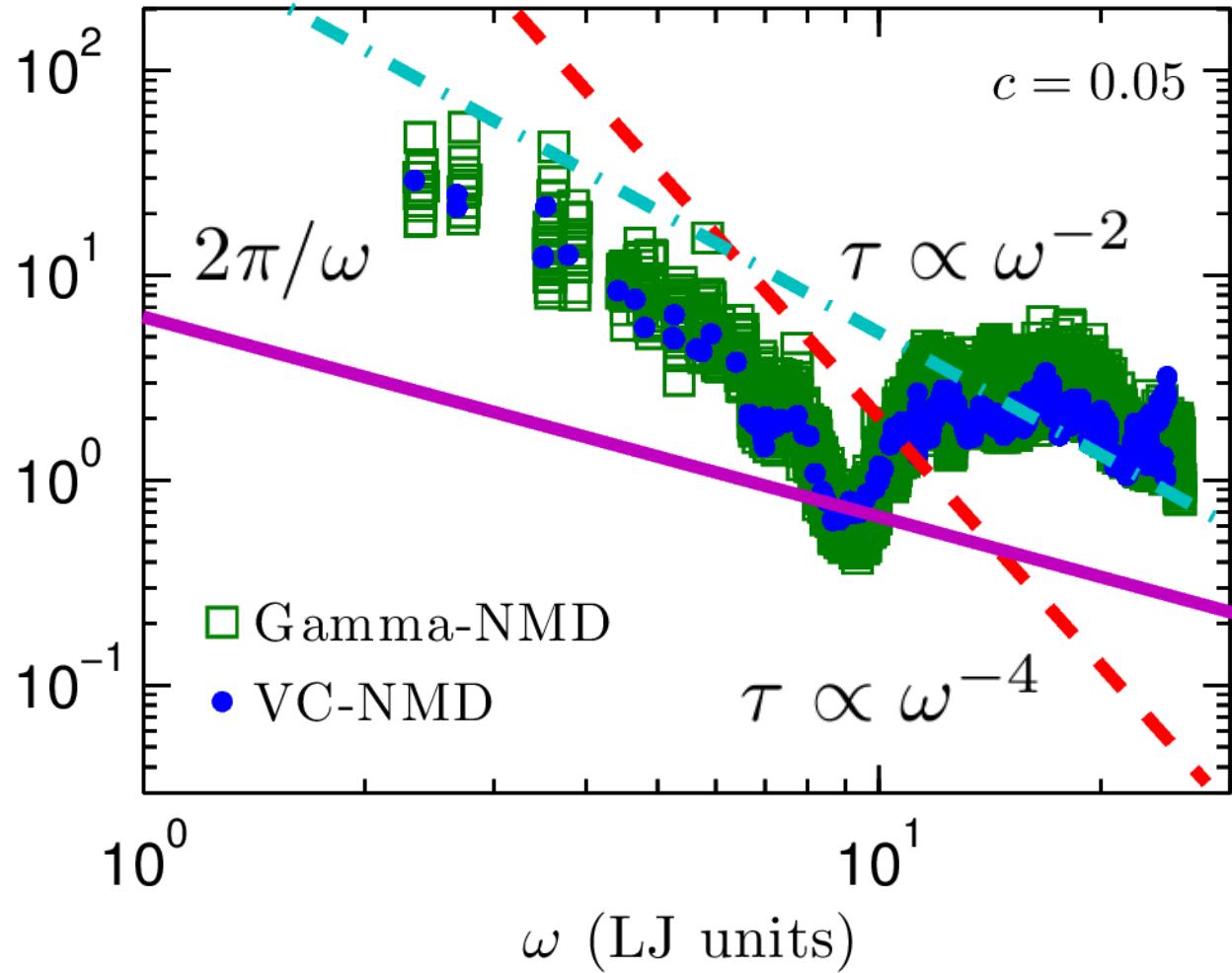
# Explicit disorder: NMD $D_{ph,\mathbf{n}}(\kappa_\nu) = v_{g,\mathbf{n}}^2(\kappa_\nu) \tau(\kappa_\nu)$

Normal Mode

Decomposition (NMD):

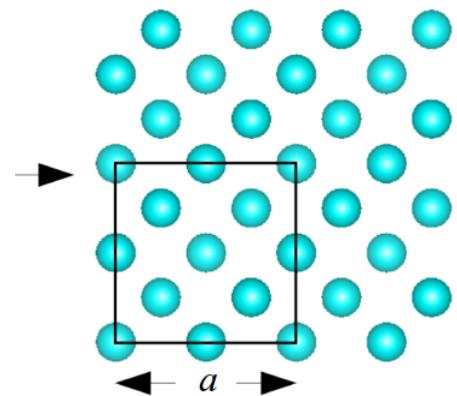


LJ Argon Alloys,  $T = 10$  K

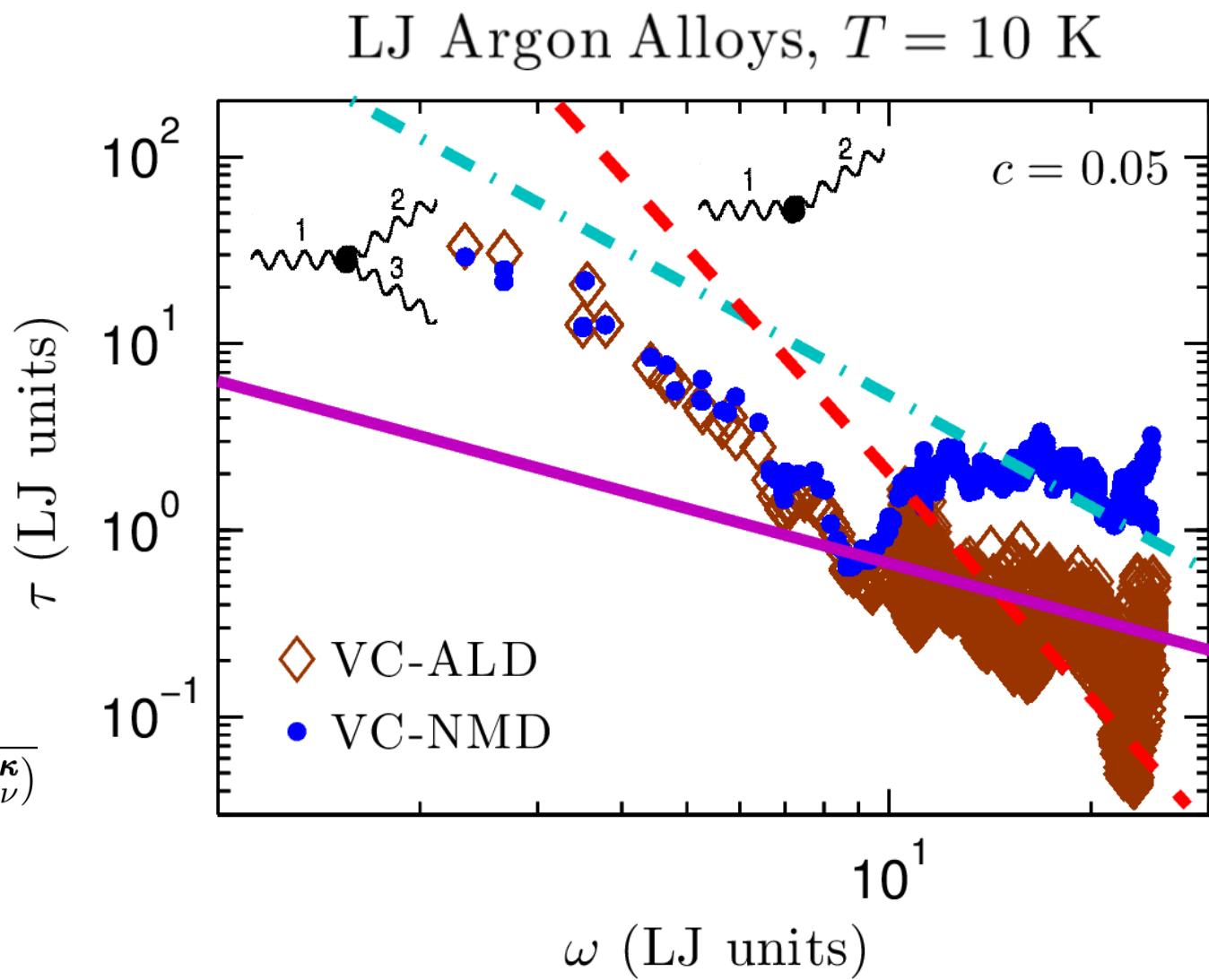


# VC-NMD vs VC-ALD

(b) VC unit cell



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



# VC Diffusivities

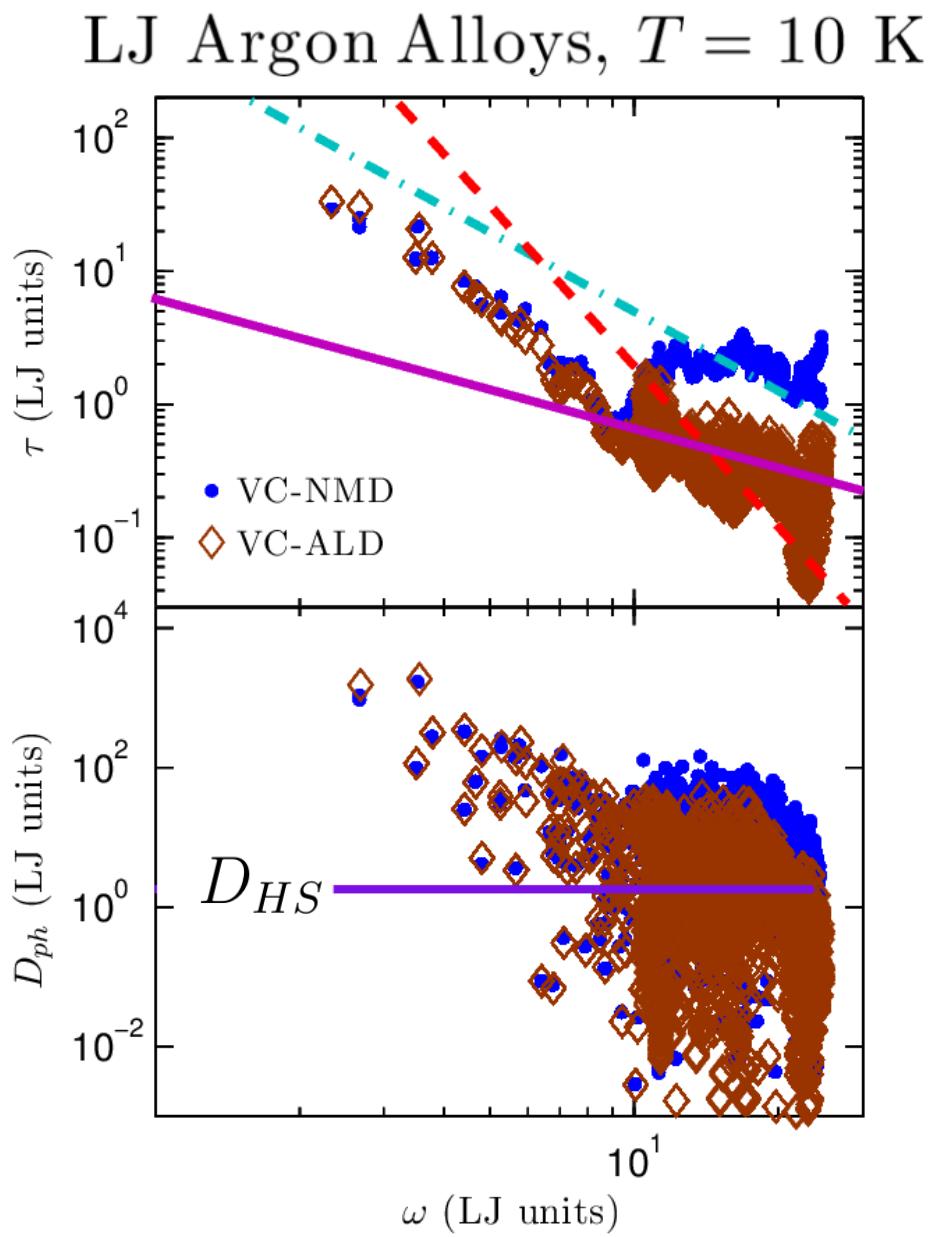
$$D_{ph,\mathbf{n}}(\kappa) = v_{g,\mathbf{n}}^2(\kappa) \tau(\kappa)$$

Phonon limit:

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

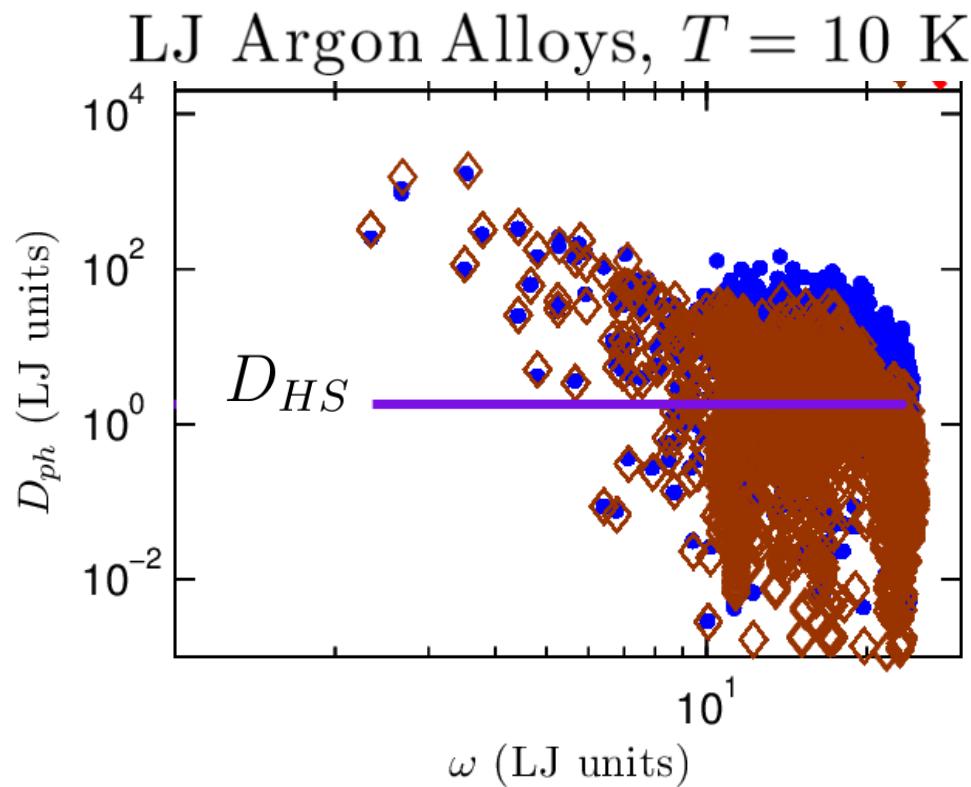
High-scatter limit:

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

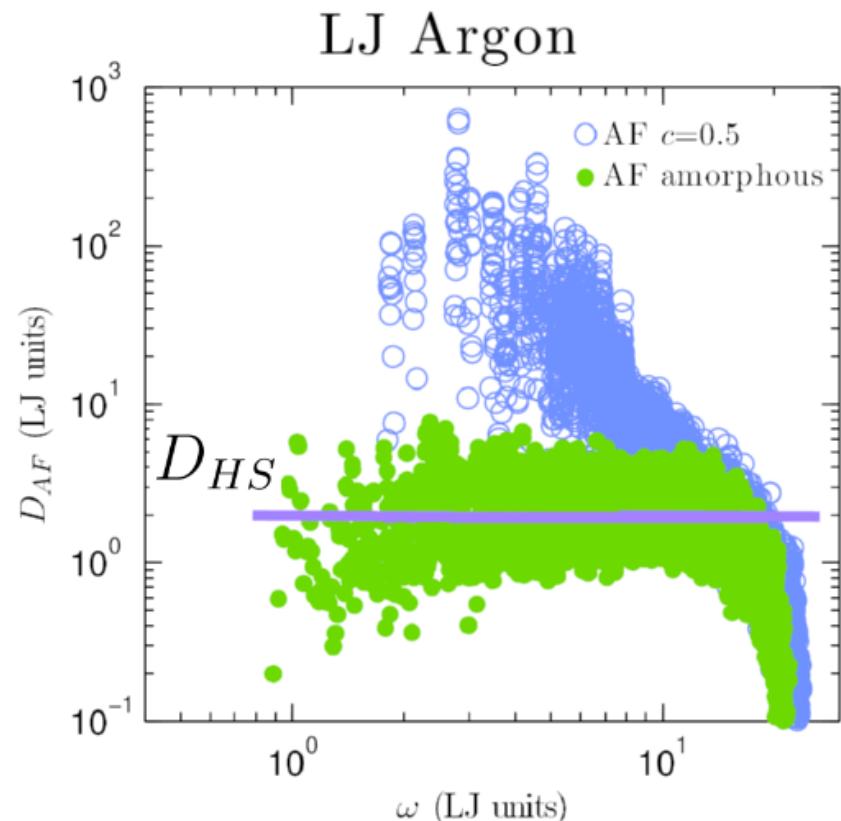


# VC and AF Diffusivities

## Phonons



## Diffusons

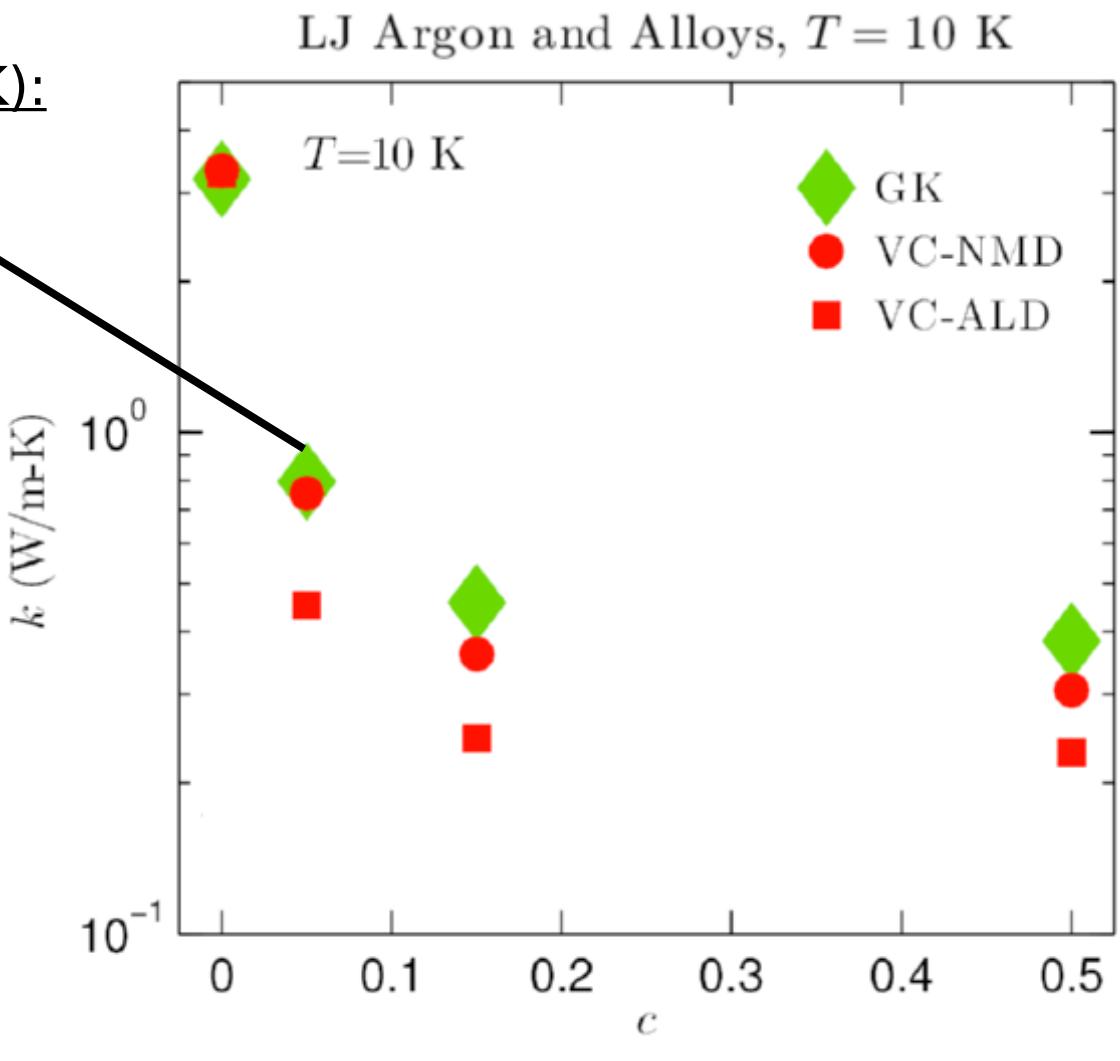
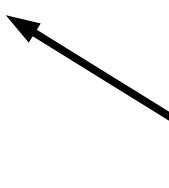


$$D_{HS} = \frac{1}{3} v_s a$$

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

# 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

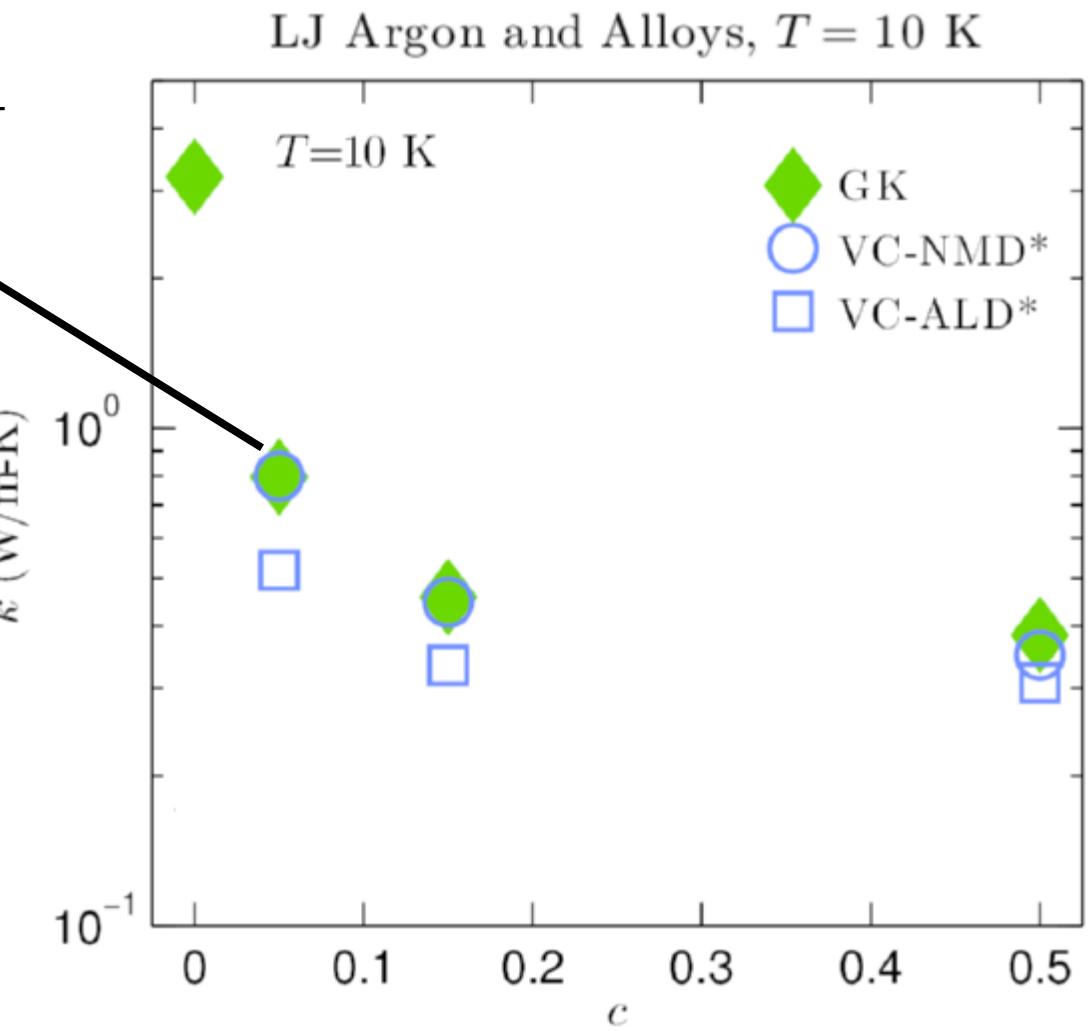
MD-based Green-Kubo (GK):  
System-level



High-scatter adjustment\*:

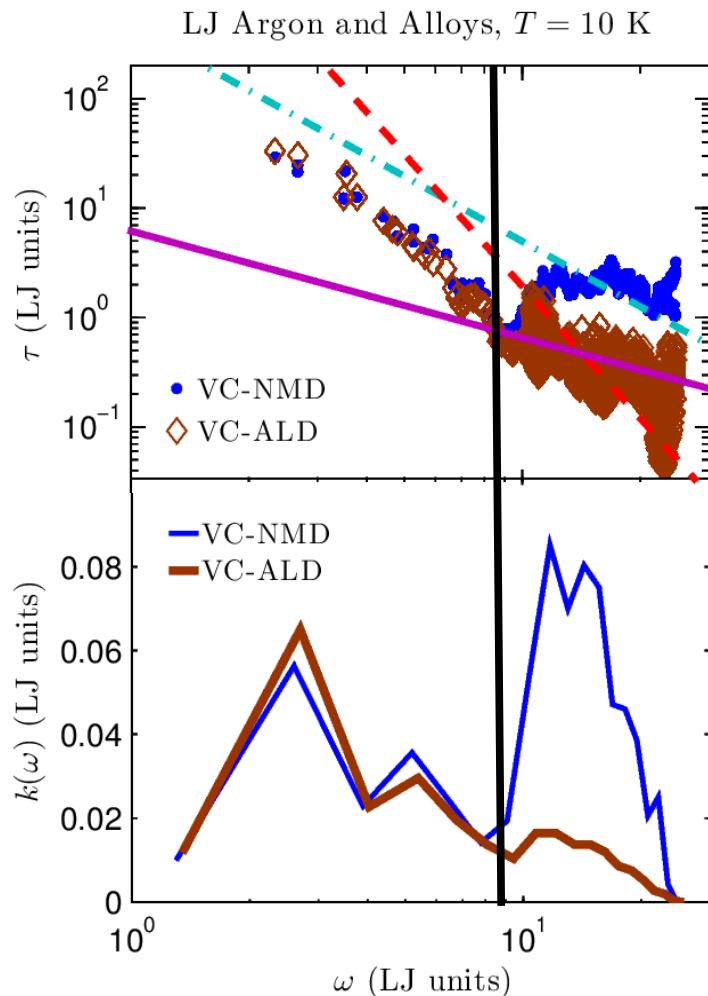
$$D_{ph}(\kappa) < D_{HS}$$

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



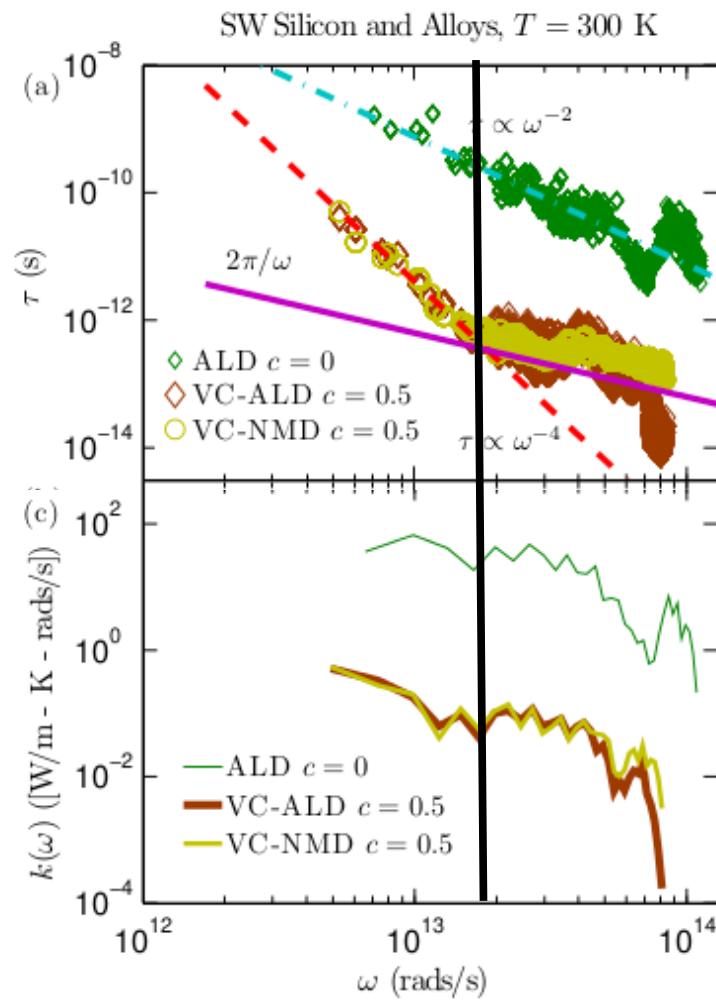
# Thermal Conductivity Spectrum

## Low and High Frequency



50% Propagons,  
50% Diffusons

## High Frequency

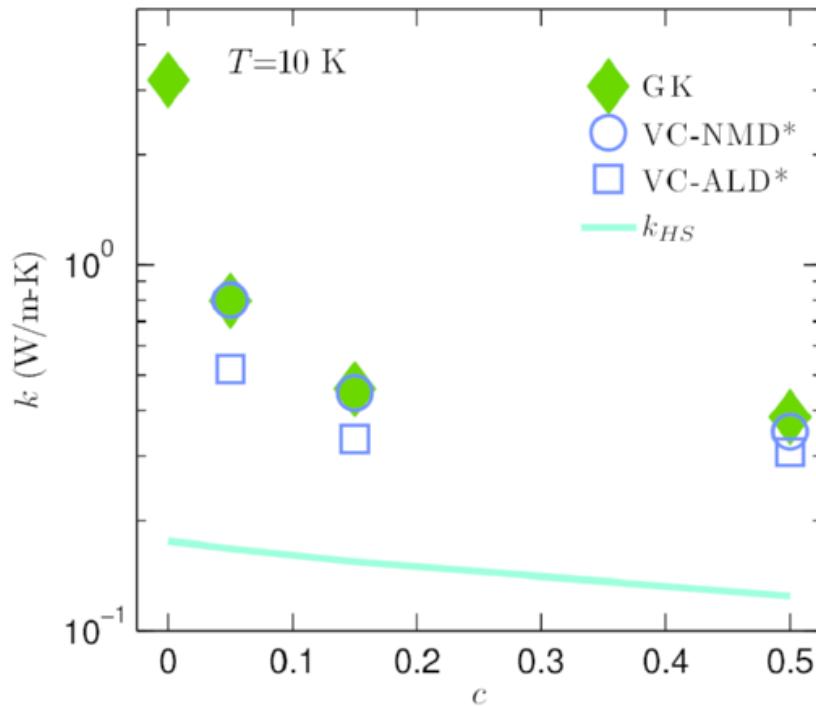


95% Propagons

# Alloys: Two Classes

## Full-Spectrum Alloys

LJ Argon and Alloys,  $T = 10$  K

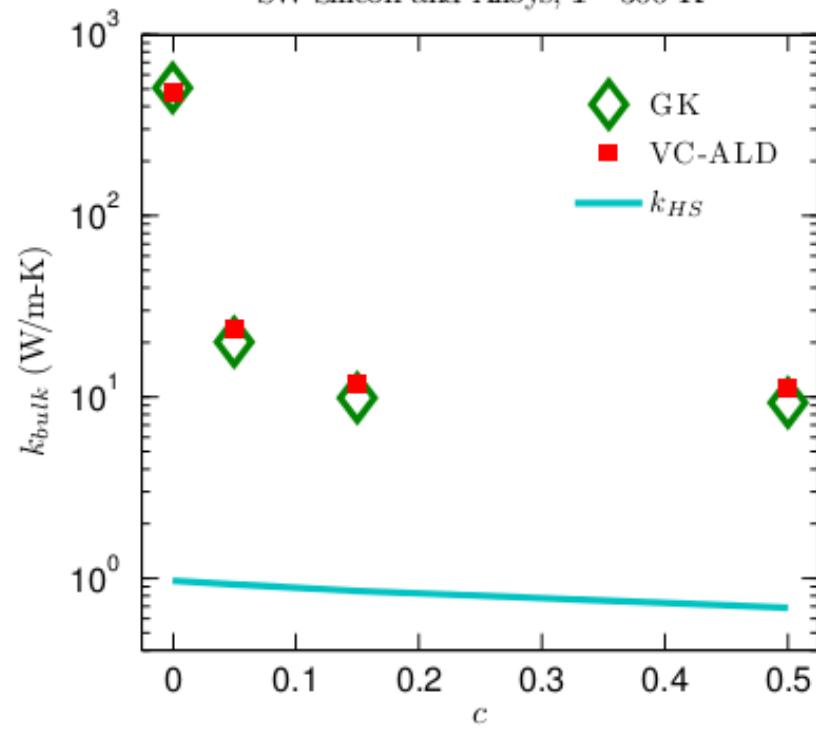


50% Propagons,  
50% Diffusons

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



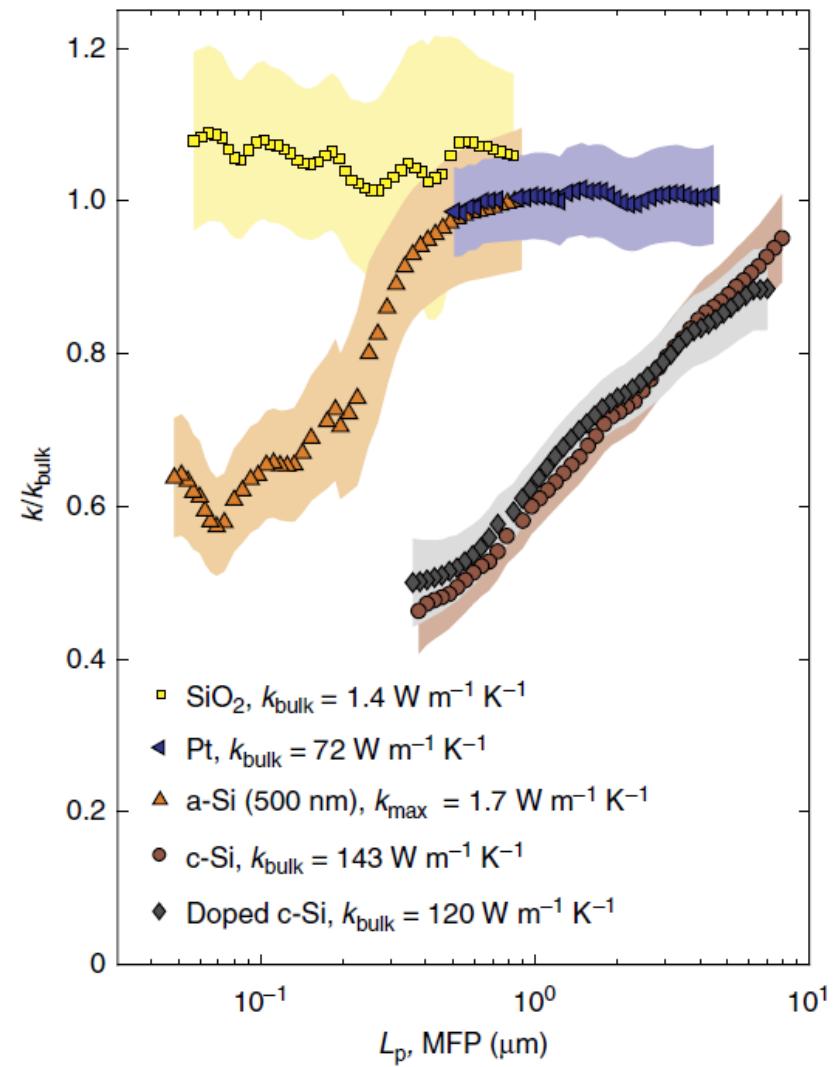
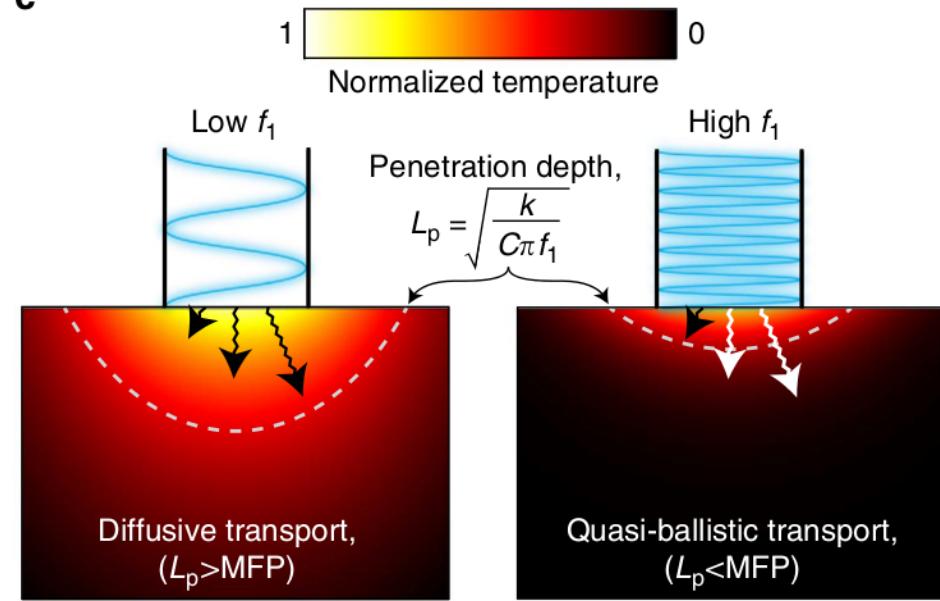
95% Propagons

# Outline

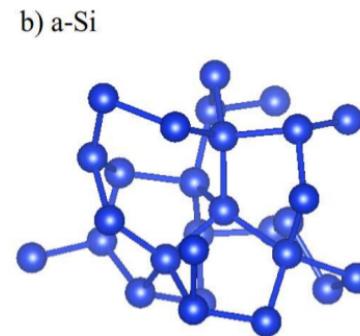
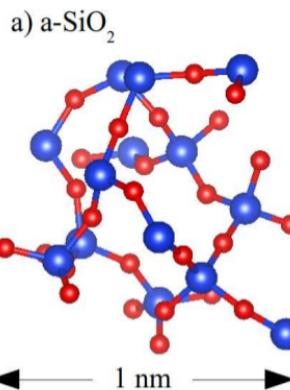
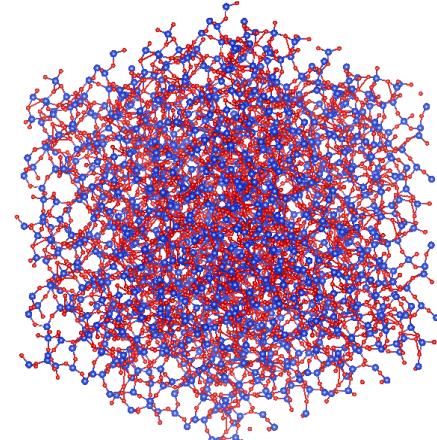
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# Amorphous: Motivation

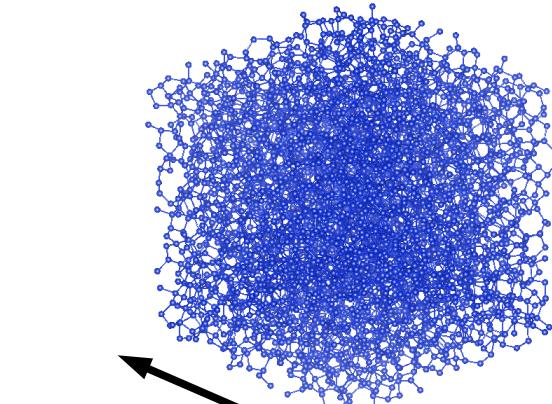
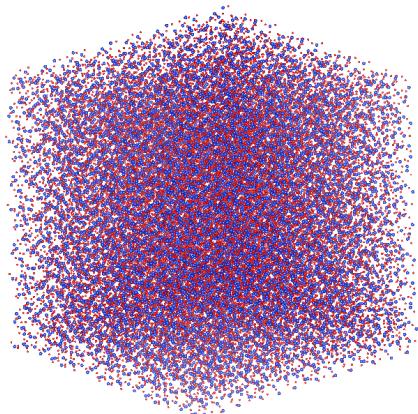
c



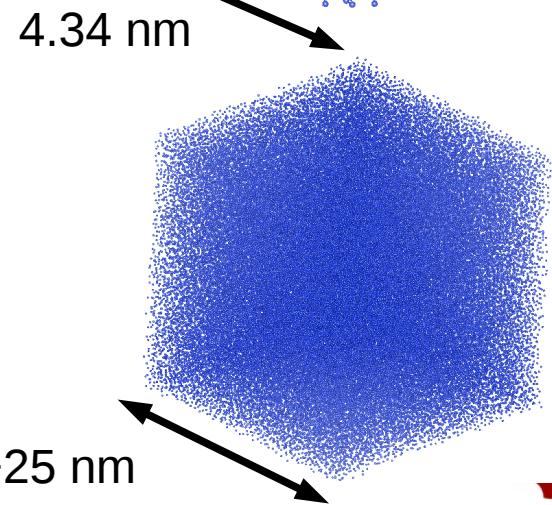
# Amorphous Solids: no VC



Mode-level:  
**~4000 atoms**



System-level:  
**~1E6 atoms**



# Vibron Thermal Conductivity

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

Diffusons (non-propagating):

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

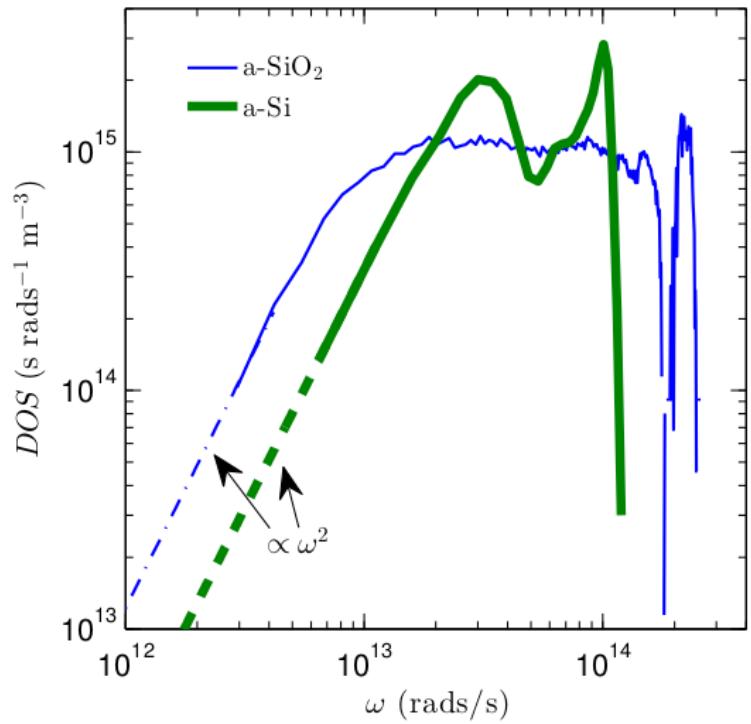
Propagons (phonon-like):

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

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

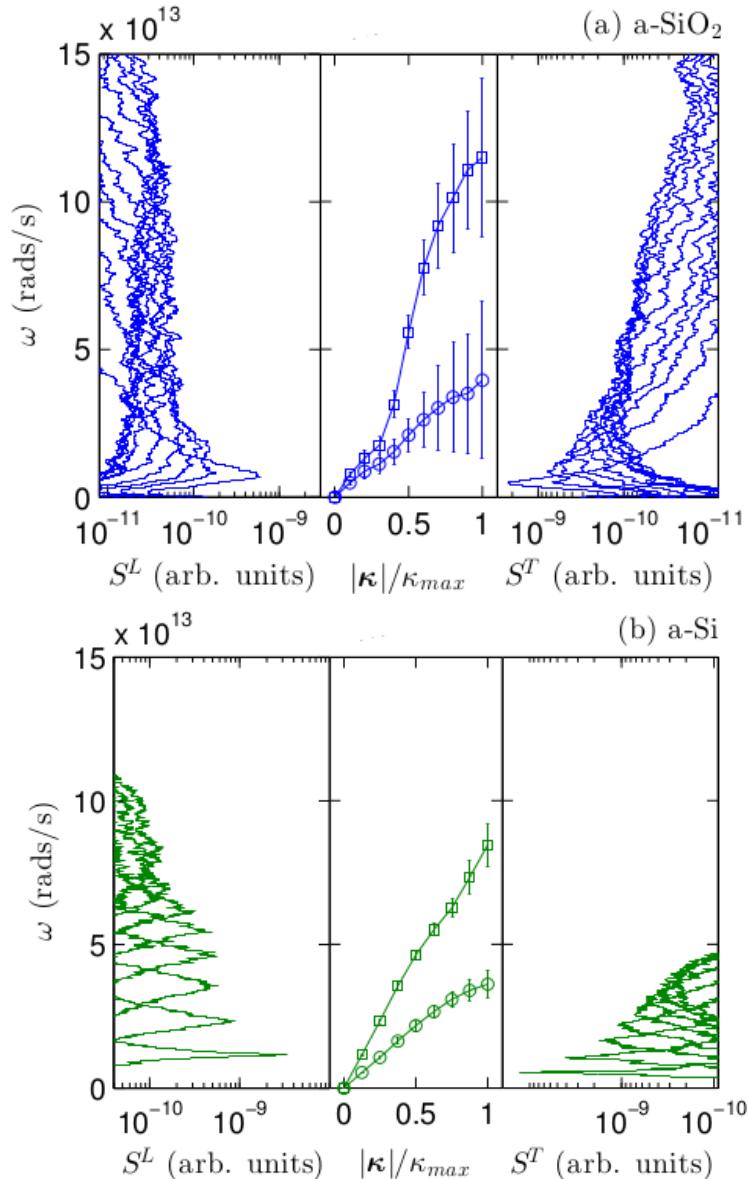
# Vibrons: Phonon character

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



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

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



# Vibrons: Lifetimes and Diffusivities

Diffusons (non-propagating):

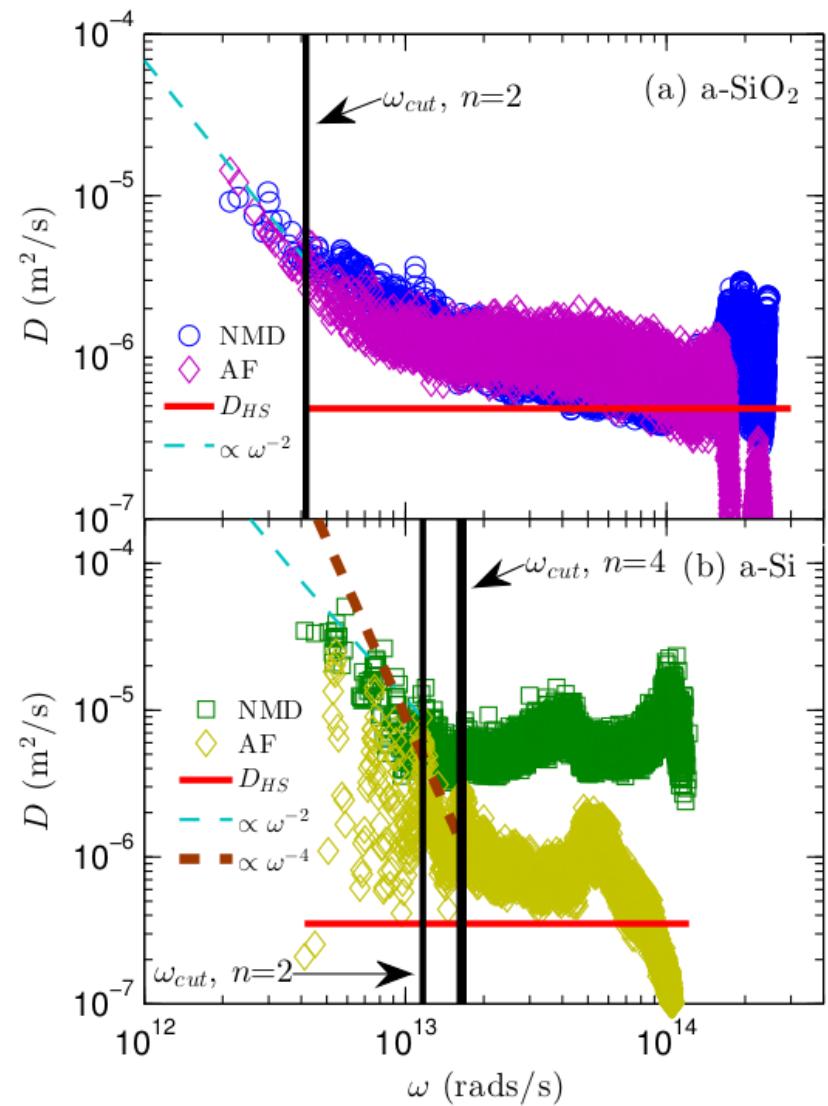
$$k_{AF} = \frac{1}{V} \sum_{i, \omega_i > \omega_{cut}} C(\omega_i) D_{AF}(\omega_i)$$

Propagons (phonon-like):

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

Normal Mode Decomposition (**NMD**):

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



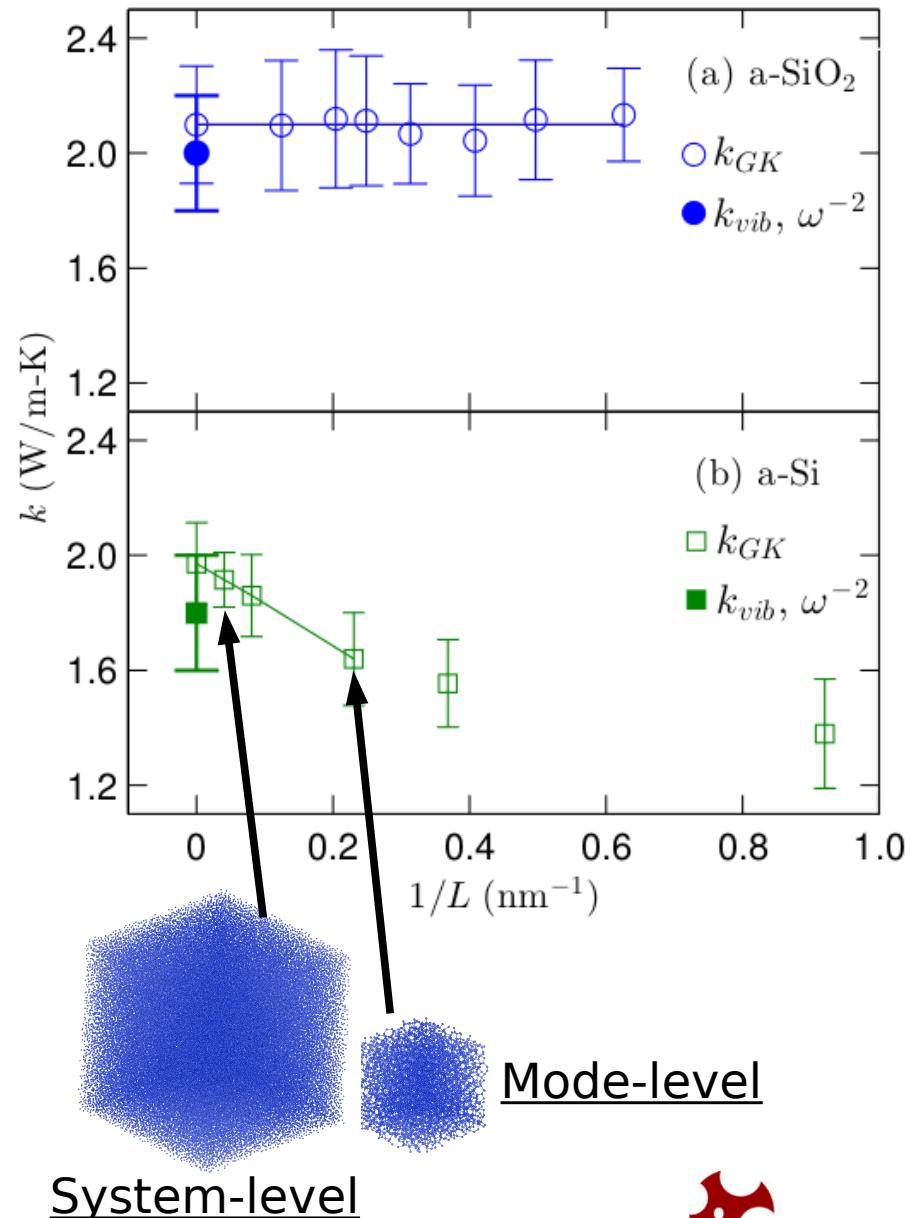
# Vibrons: Mode- and System-level

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



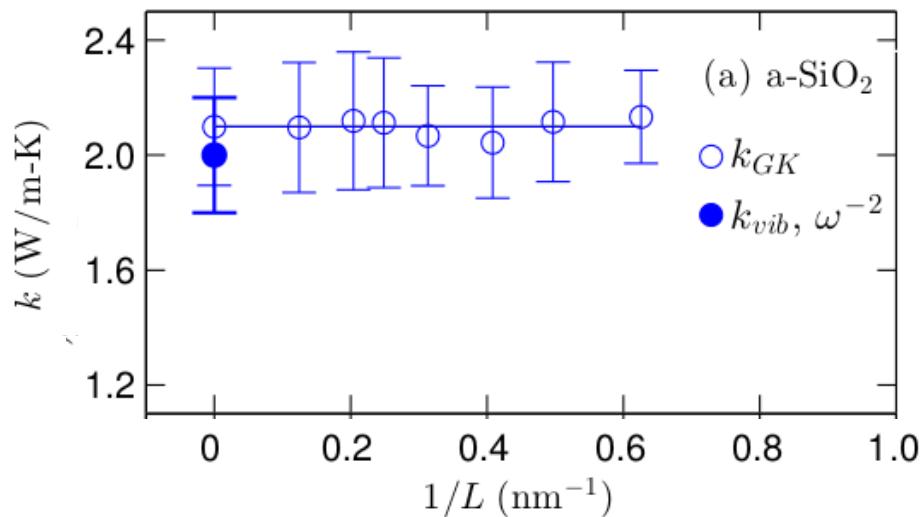
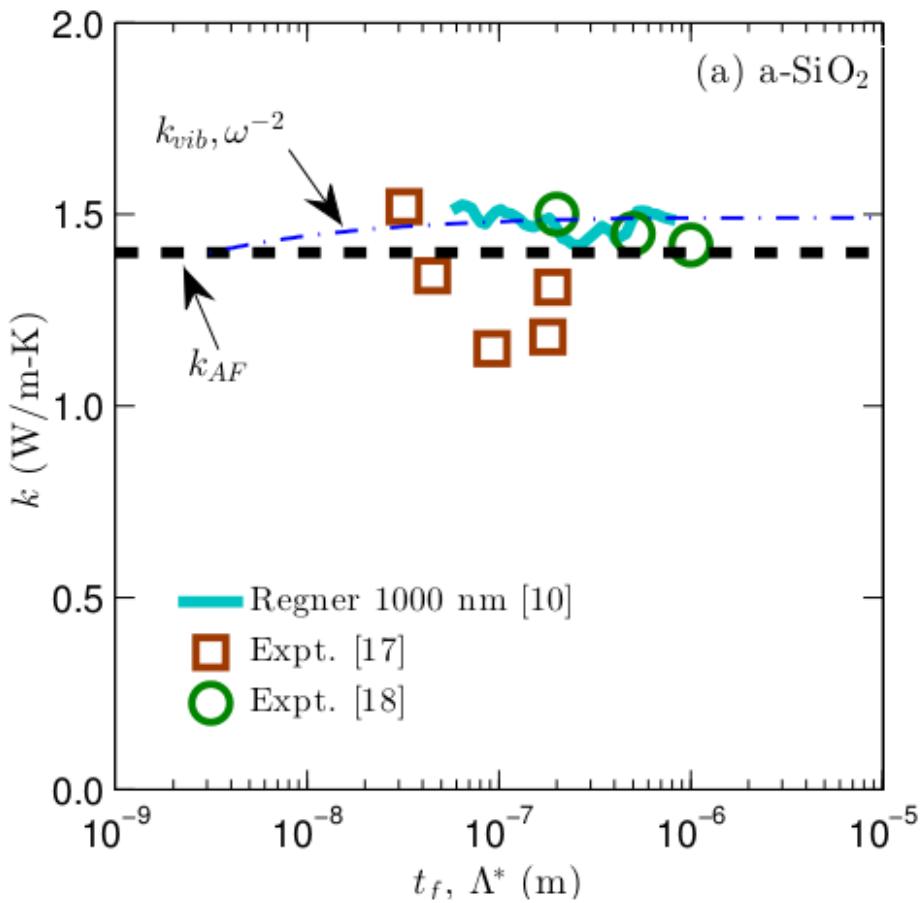
$$\Lambda(\omega) = v_s \tau(\omega)$$

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



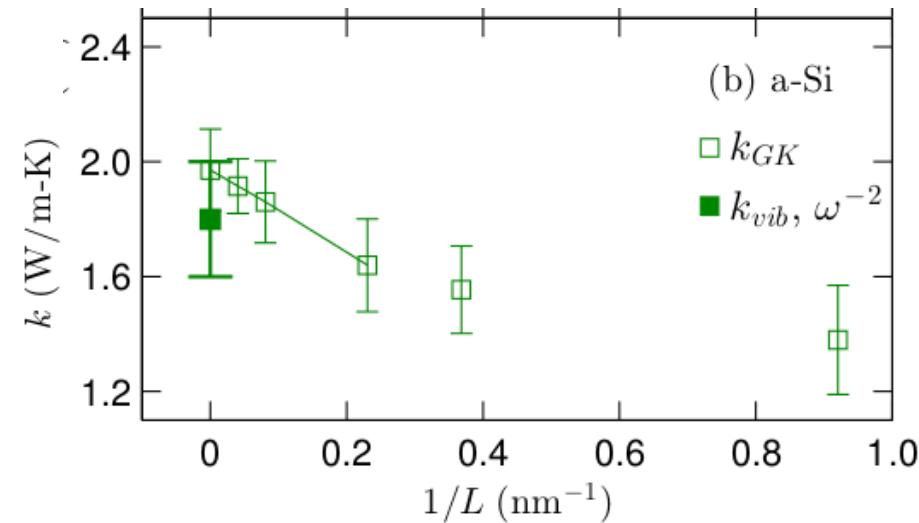
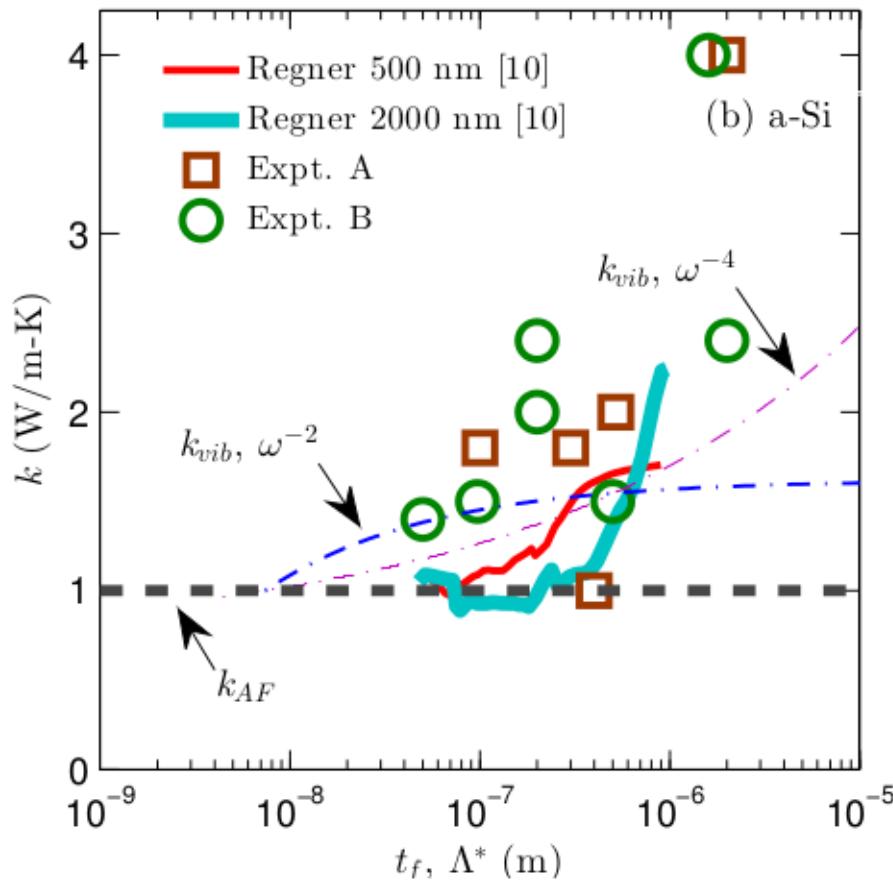
# Thermal Conductivity Accumulation

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



# Thermal Conductivity Accumulation

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

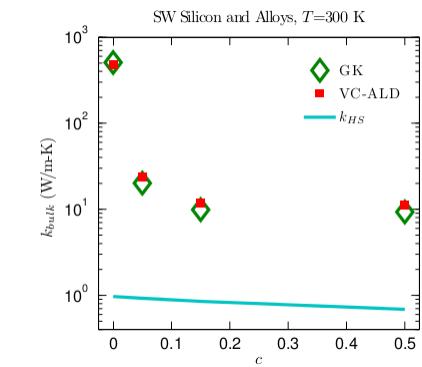
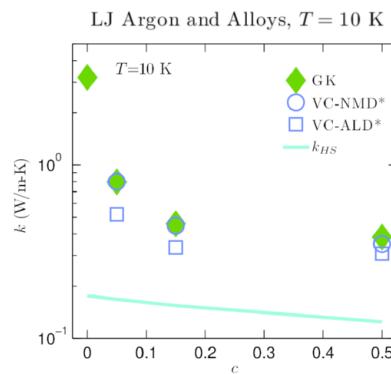


# Outline

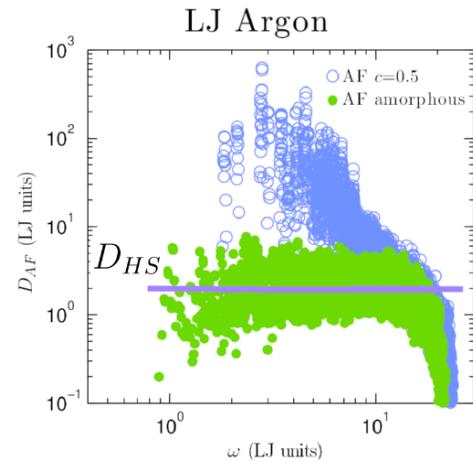
- (1) Motivation
- (2) Mode-level vs. System-level
- (3) Alloys
- (4) Amorphous
- (5) Overview/Future Work**

# Overview

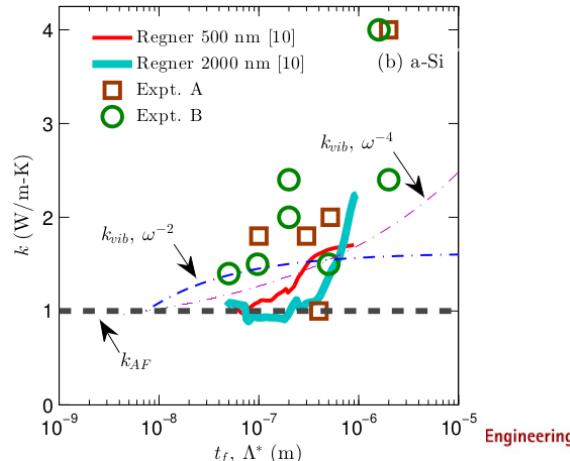
Limits of Perturbation Methods:



Alloys can behave like Amorphous:



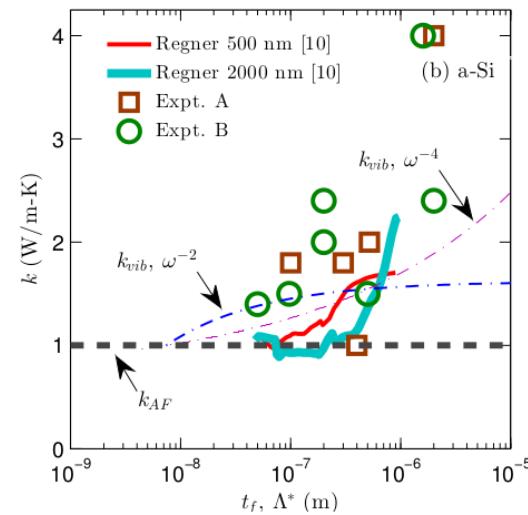
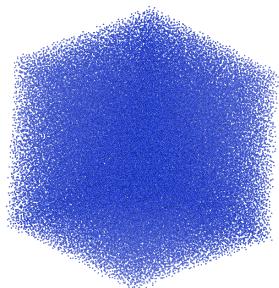
Amorphous can behave like Crystal:



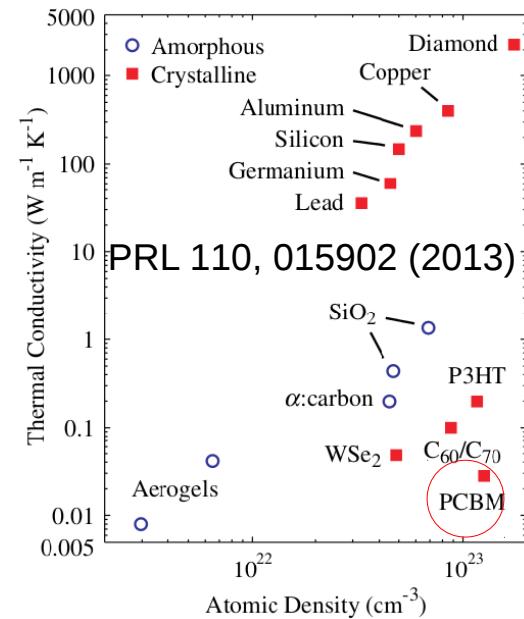
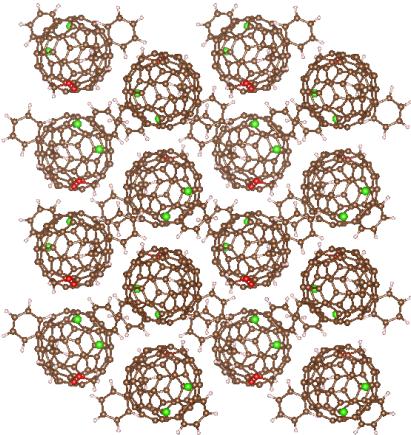
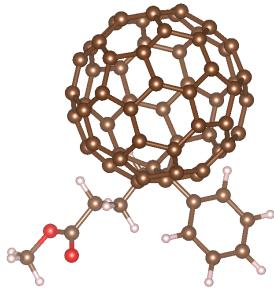
# Future Work

Very Large MD-based Predictions:

System- and Mode-level



Large Unit Cell Materials (PCBM):



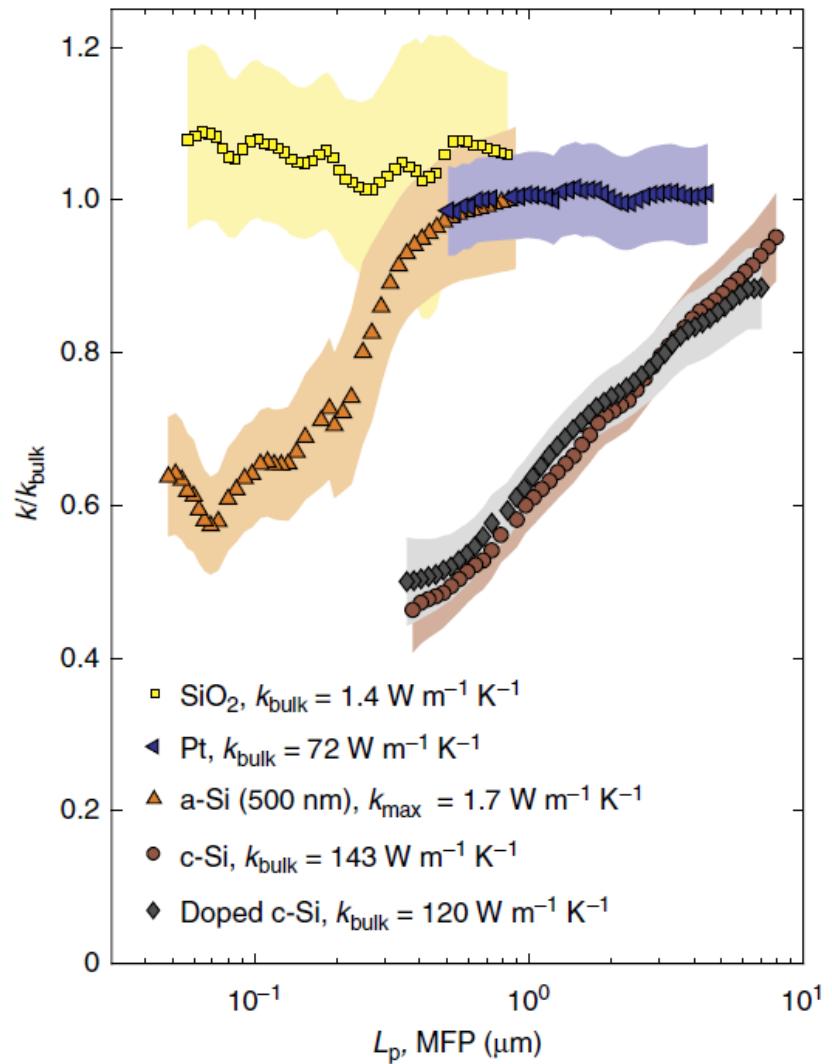
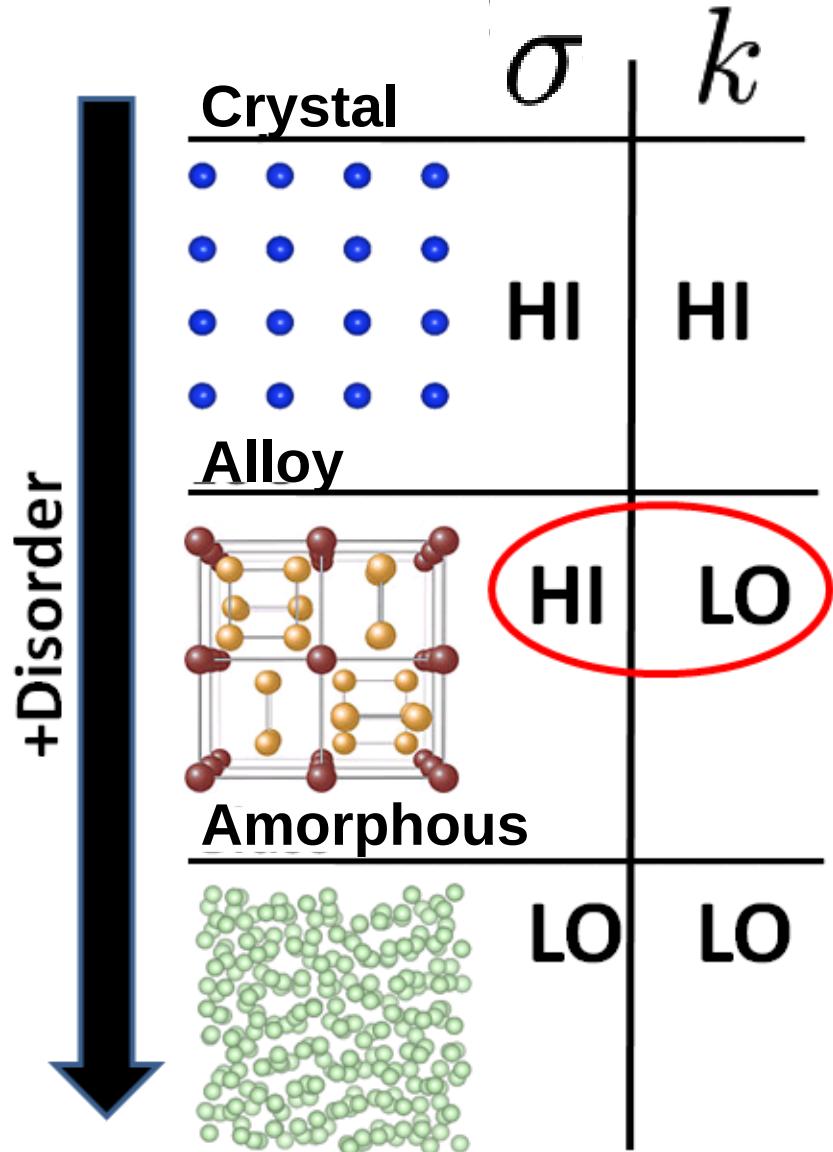
J. M. Larkin, W. A. Saidi, A. J. H. McGaughey, "Origin of the Exceptionally Low Thermal Conductivity in Fullerene-derived PCBM Films", Physical Review B (in progress).

Four Methods (+ more): A comprehensive package

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

# Supplimentary

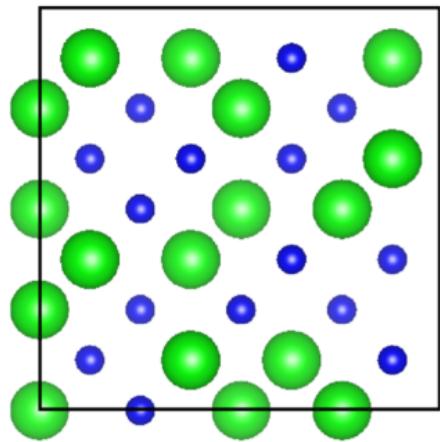
# Motivation: Mode-level Properties



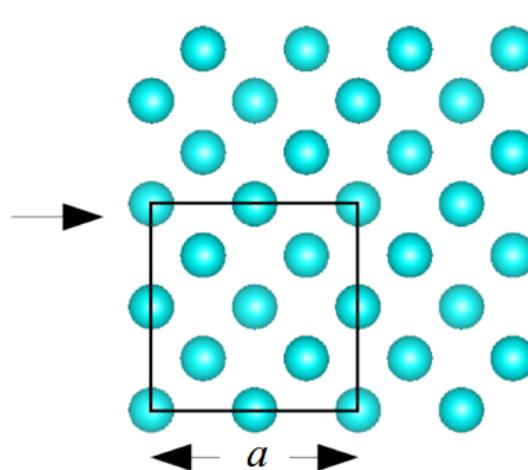
Regner et al., *Nat. Comm.* **4**, 1640 (2013)

# Explicit disorder: VC vs Gamma

(a) disordered supercell



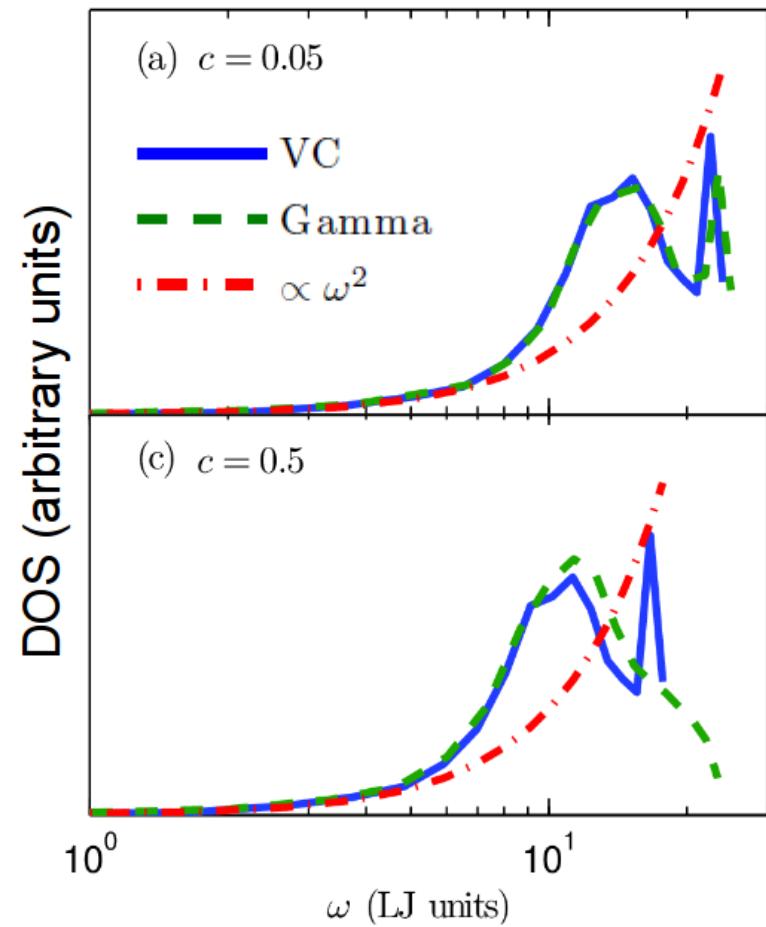
(b) VC unit cell



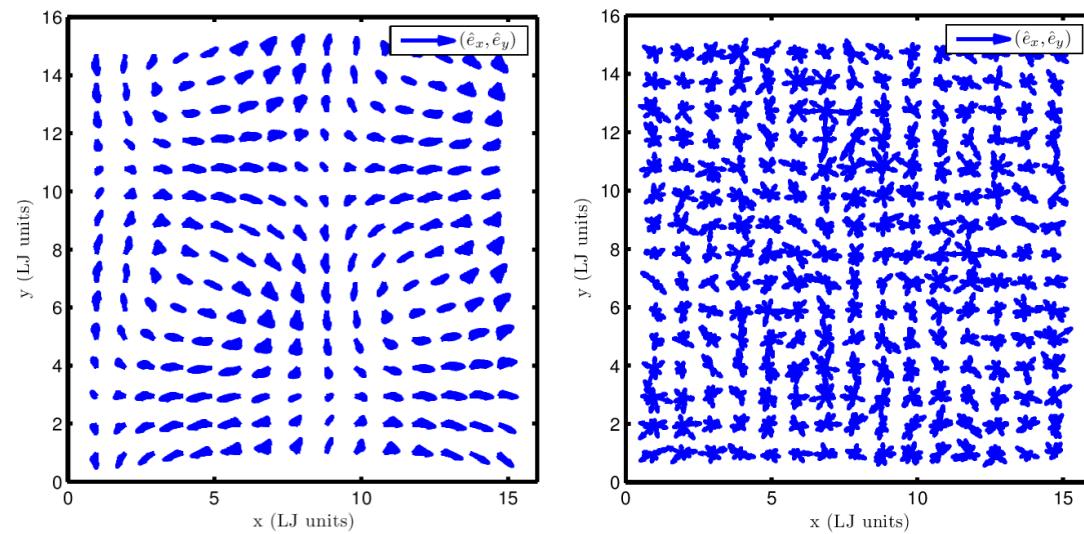
Gamma

Computationally-inexpensive  
empirical potential:  
Lennard-Jones argon

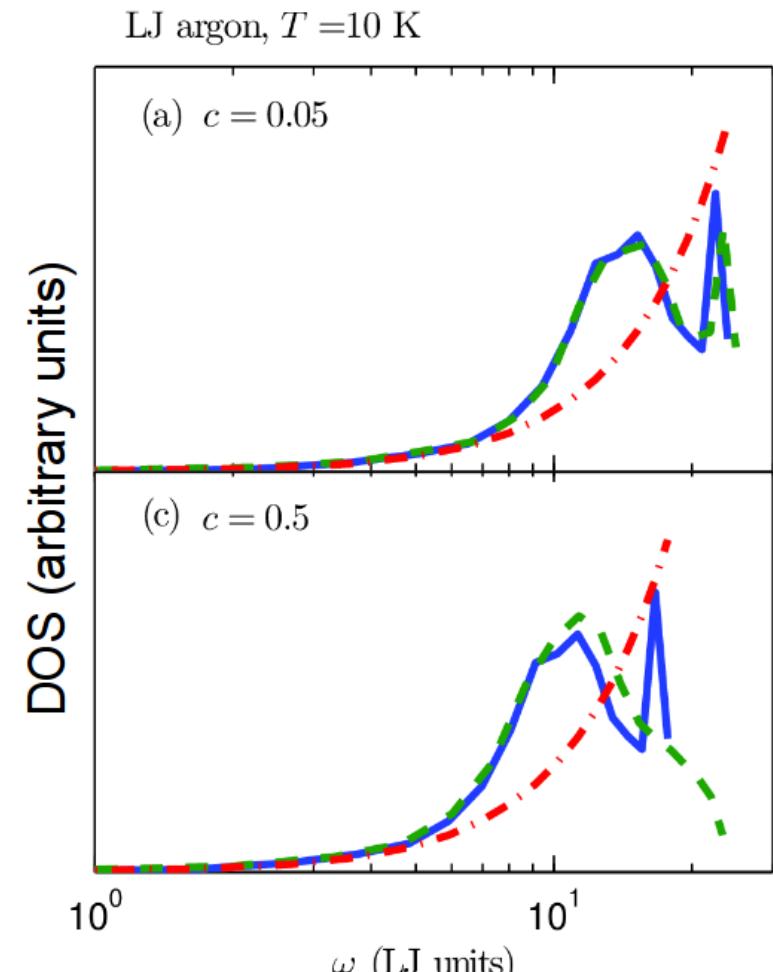
LJ argon,  $T = 10$  K



# 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

