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

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Mechanical Engineering

Outline

(1) Motivation

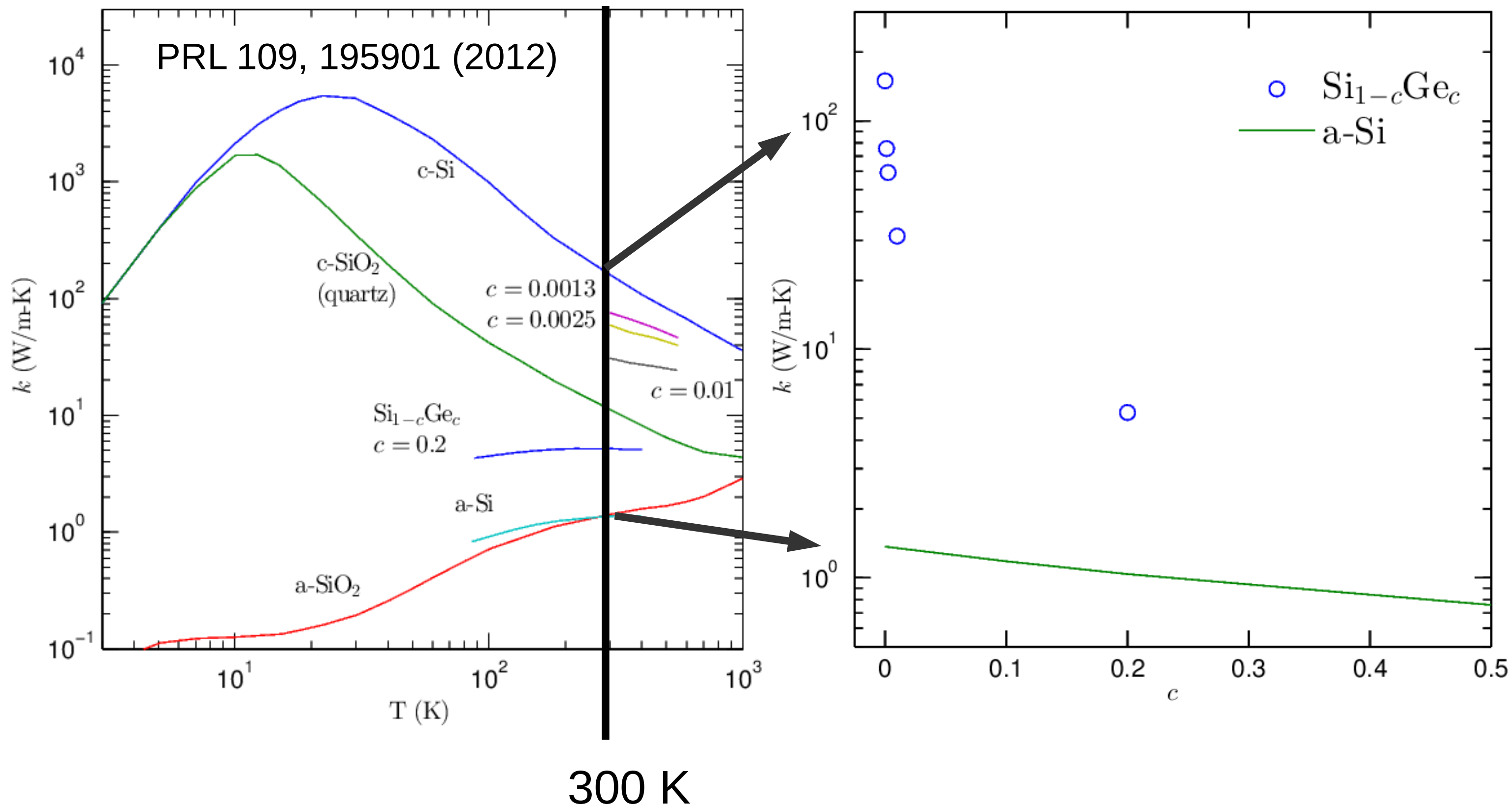
(2) Mode-level vs. System-level

(3) Alloys

(4) Amorphous

(5) Overview/Future Work

Motivation: Crystal, Alloys, Amorphous

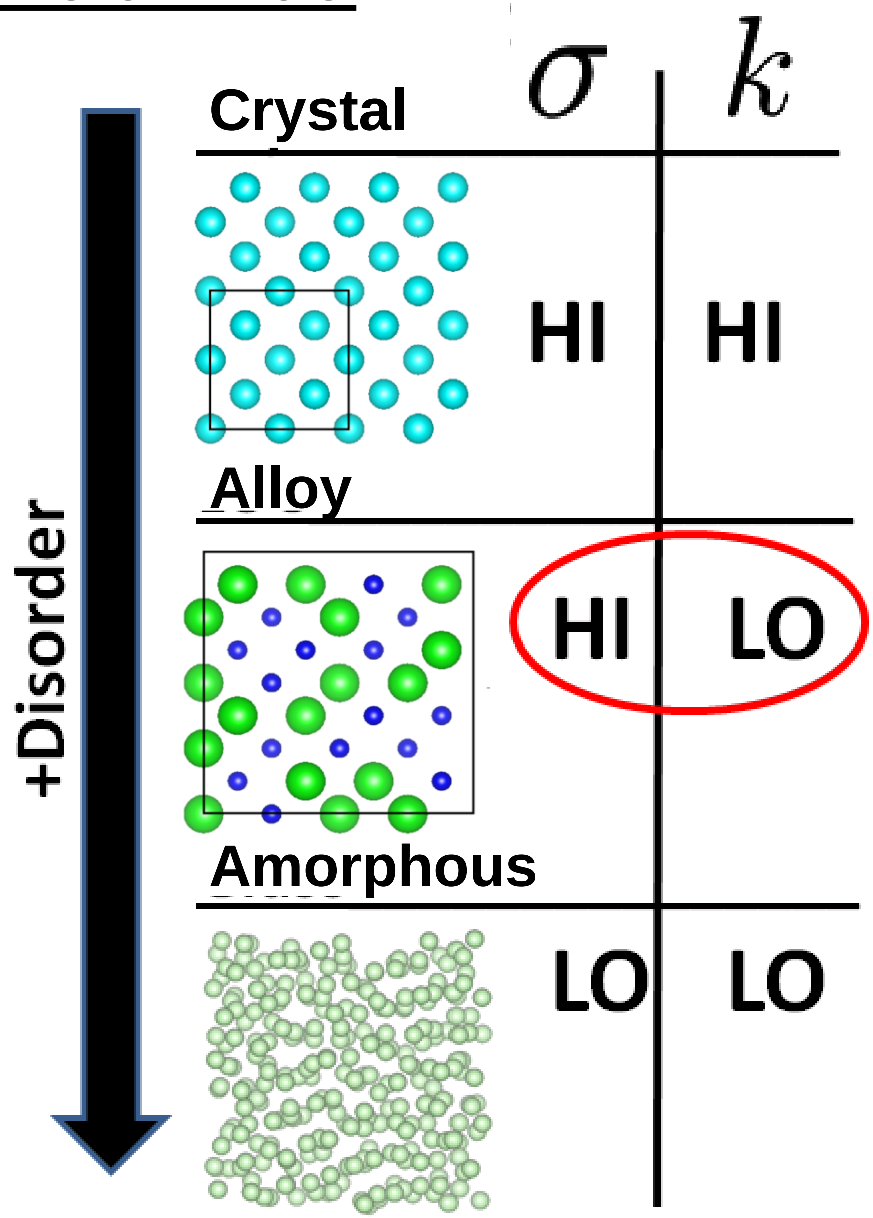


onstraints: chemistry, electron transport, operating emperature, etc.

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

Motivation: Thermoelectrics

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



Mode-level Properties:

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

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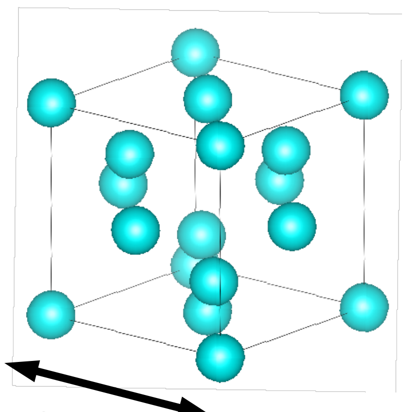
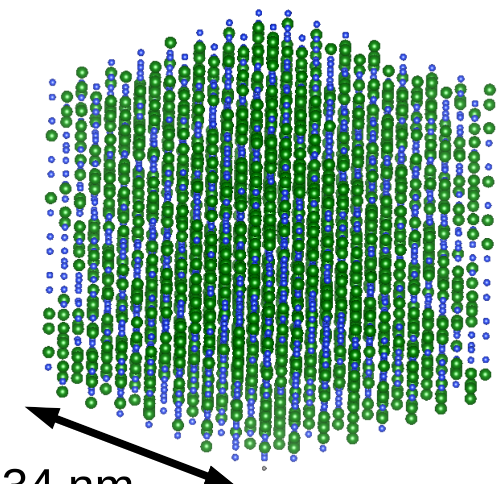
Mode-level vs. System-level

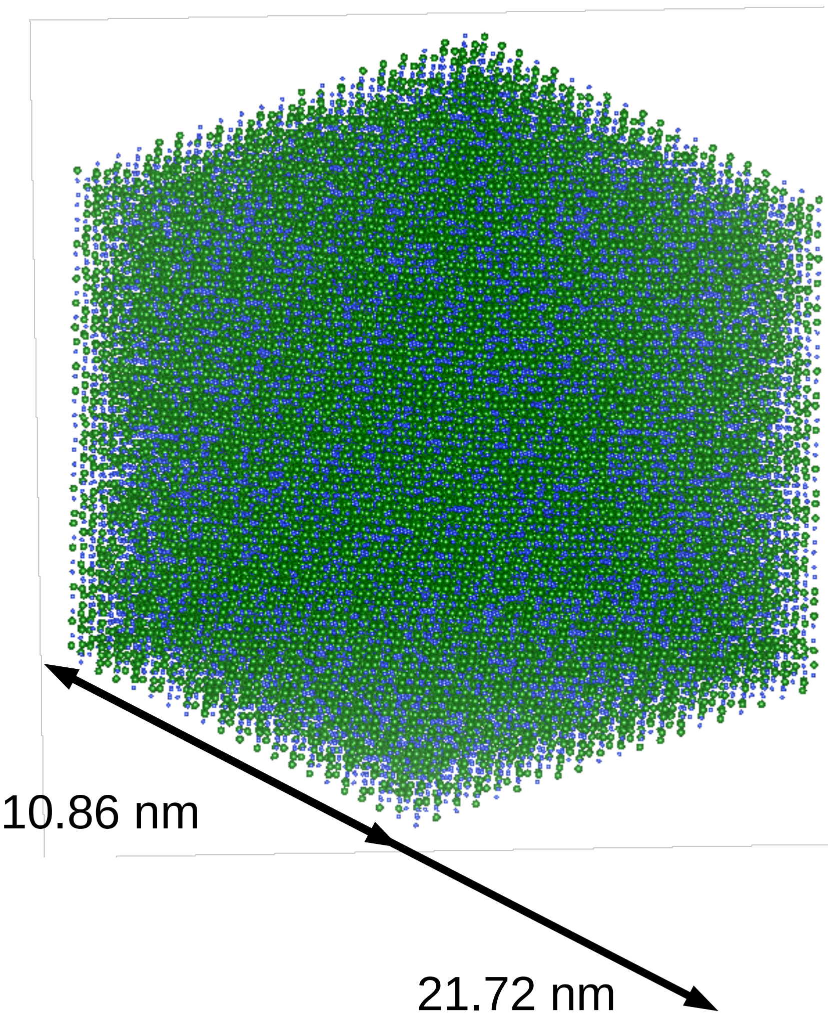
Mode-level:
8 atoms



Mode-level:
~4000 atoms



System-level:
~1E6 atoms



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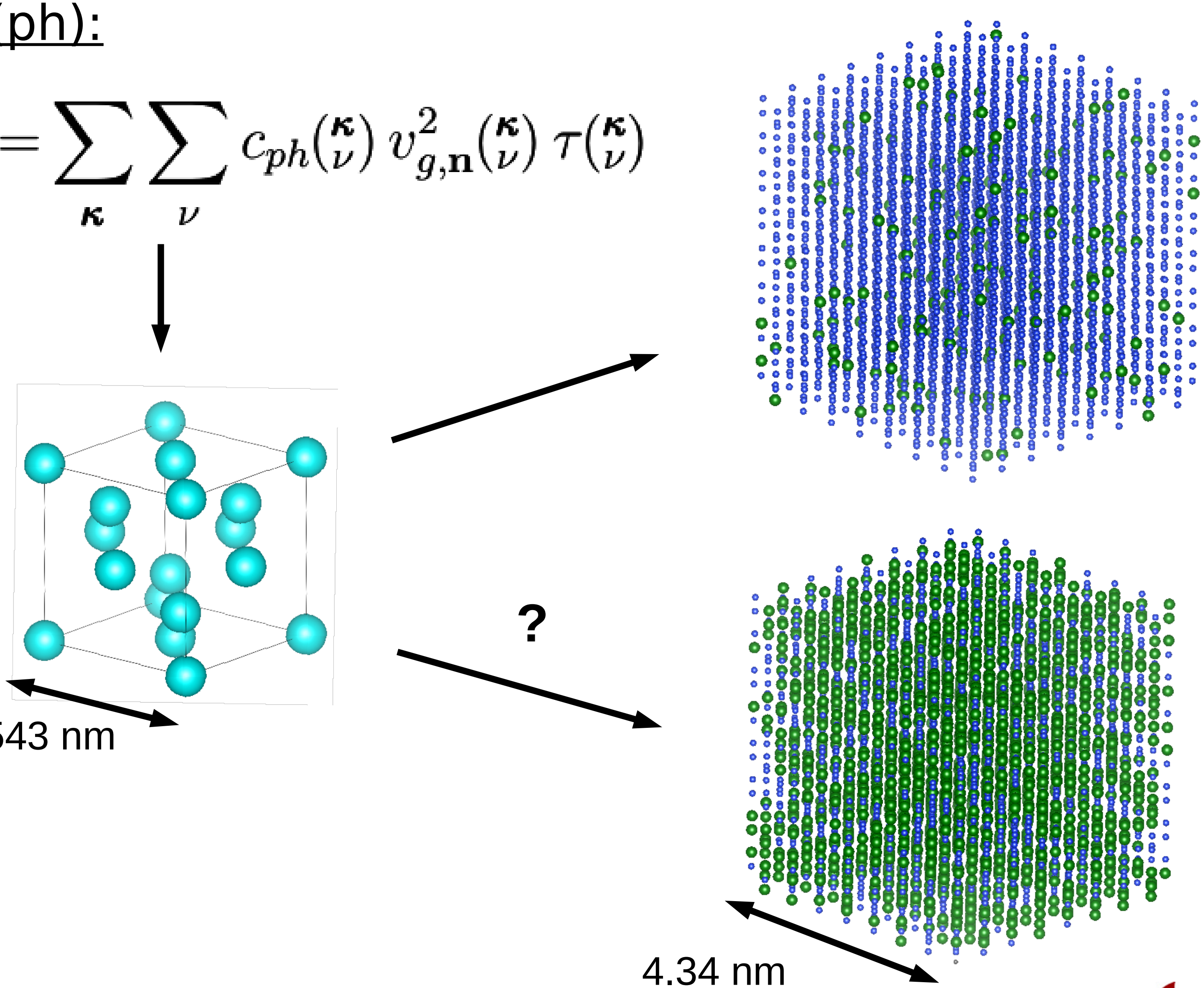
Mode-level: Perturbation vs. Explicit

Phonons (ph):

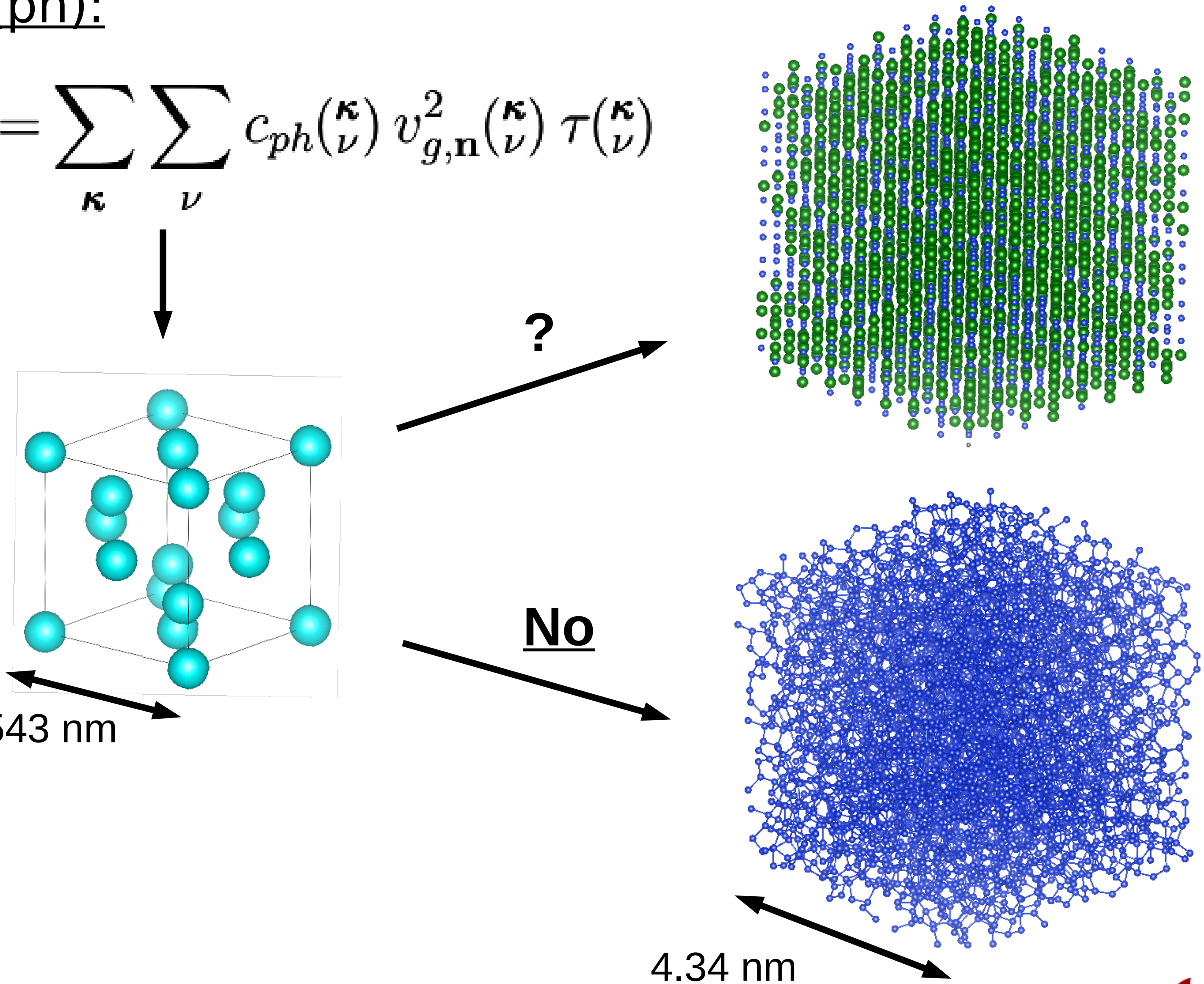
$$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} c_{ph}\binom{\boldsymbol{\kappa}}{\nu}\, v_{g,\mathbf{n}}^2\binom{\boldsymbol{\kappa}}{\nu}\, \tau\binom{\boldsymbol{\kappa}}{\nu}$$



Mode-level: Explicit

Phonons (ph):

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



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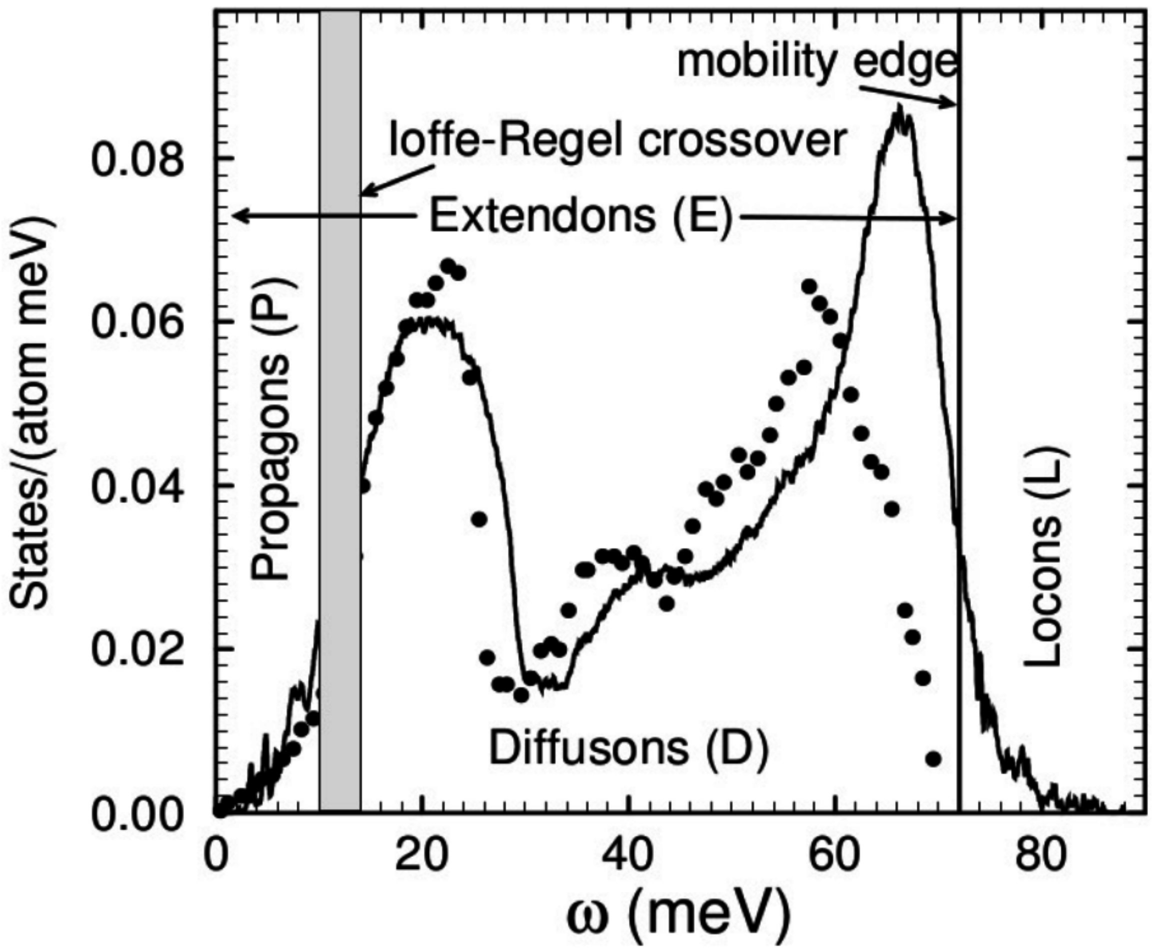
Disordered Modes: Vibrons

ropagons:
honon-like,
ropagating, de-localized

iffusons:
on-propagating,
e-localized

ocons:
on-propagating,
ocalized



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

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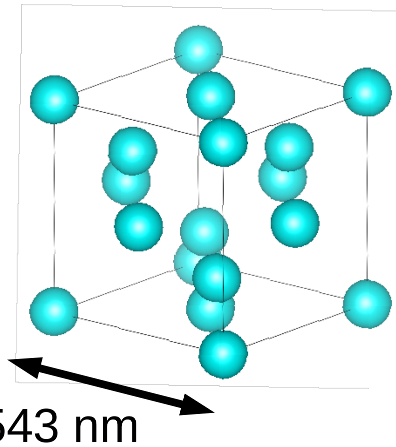
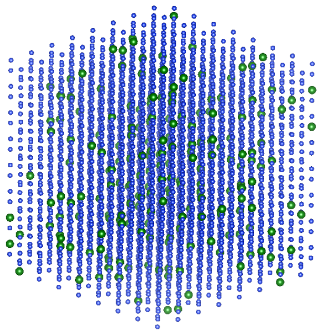
Thermal Conductivity: Mode-level

Phonons (ph):

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

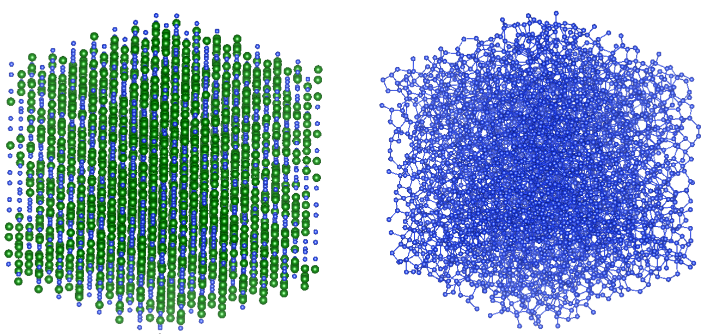


Propagons (phonon-like)



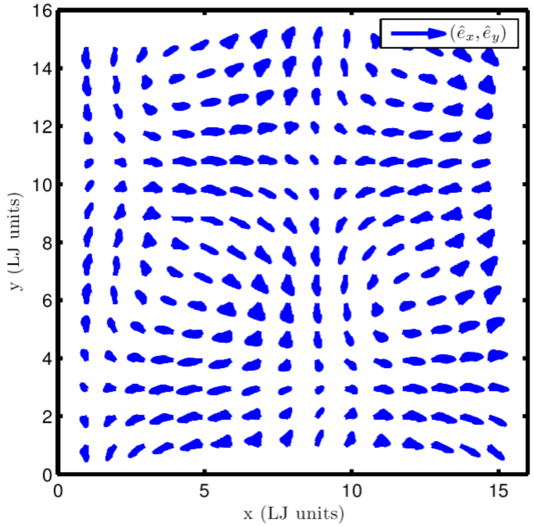
Diffusons:

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



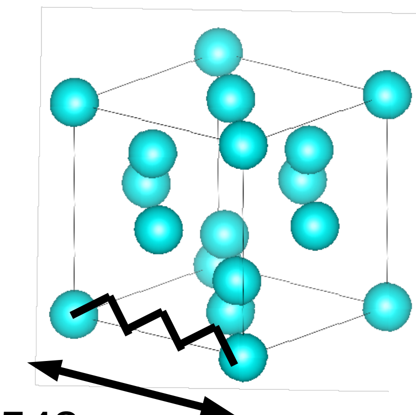
Thermal Conductivity: Mode-level

ropagons (phonon-like):

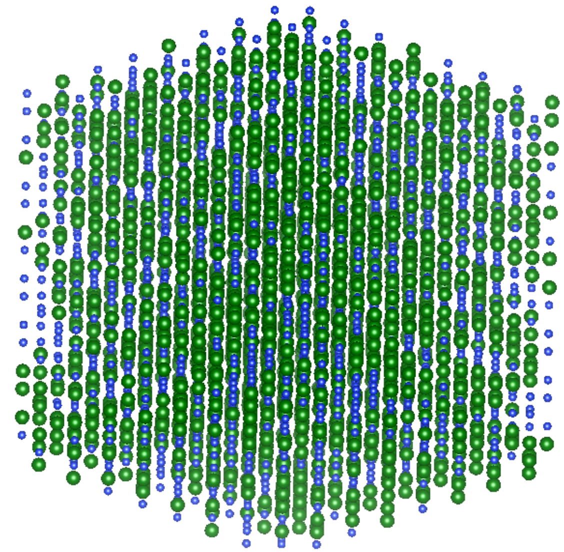


$$e^{*}\begin{pmatrix} \boldsymbol{\kappa} & b \\ \nu & \alpha \end{pmatrix}$$

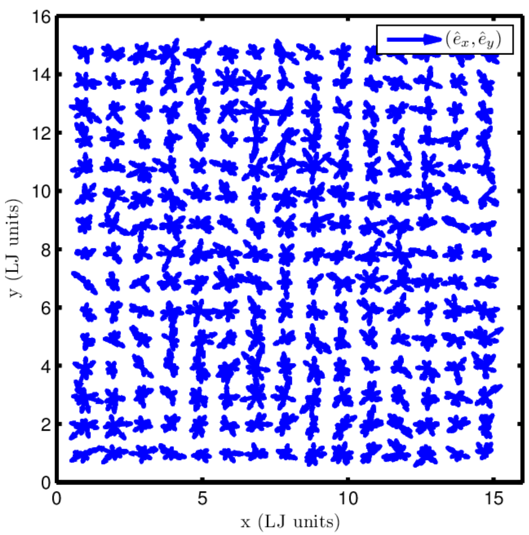
Harmonic Lattice Dynamics



0.543 nm

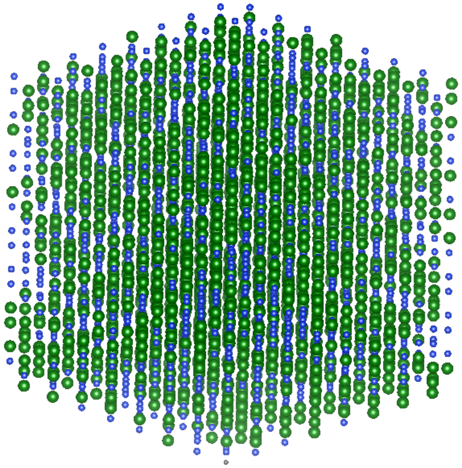


iffusons:



Vibrational Properties: Molecular Dynamics

$$\dot{u}_\alpha\left(\begin{smallmatrix} l \\ b \end{smallmatrix}; t\right) = \sum_{\boldsymbol{\kappa},\nu}^{N,3n} \frac{1}{\sqrt{m_b N}} \exp\left[i\boldsymbol{\kappa} \cdot \mathbf{r}_0\left(\begin{smallmatrix} l \\ 0 \end{smallmatrix}\right)\right] e^*\left(\begin{smallmatrix} \boldsymbol{\kappa} & b \\ \nu & \alpha \end{smallmatrix}\right) \dot{q}\left(\begin{smallmatrix} \boldsymbol{\kappa} \\ \nu \end{smallmatrix}; t\right)$$



$$\dot{q}\left(\begin{smallmatrix} \boldsymbol{\kappa} \\ \nu \end{smallmatrix}; t\right) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} \dot{u}_\alpha\left(\begin{smallmatrix} l \\ b \end{smallmatrix}; t\right) e^*\left(\begin{smallmatrix} \boldsymbol{\kappa} & b \\ \nu & \alpha \end{smallmatrix}\right) \exp\left[i\boldsymbol{\kappa} \cdot \mathbf{r}_0\left(\begin{smallmatrix} l \\ 0 \end{smallmatrix}\right)\right]$$

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**):

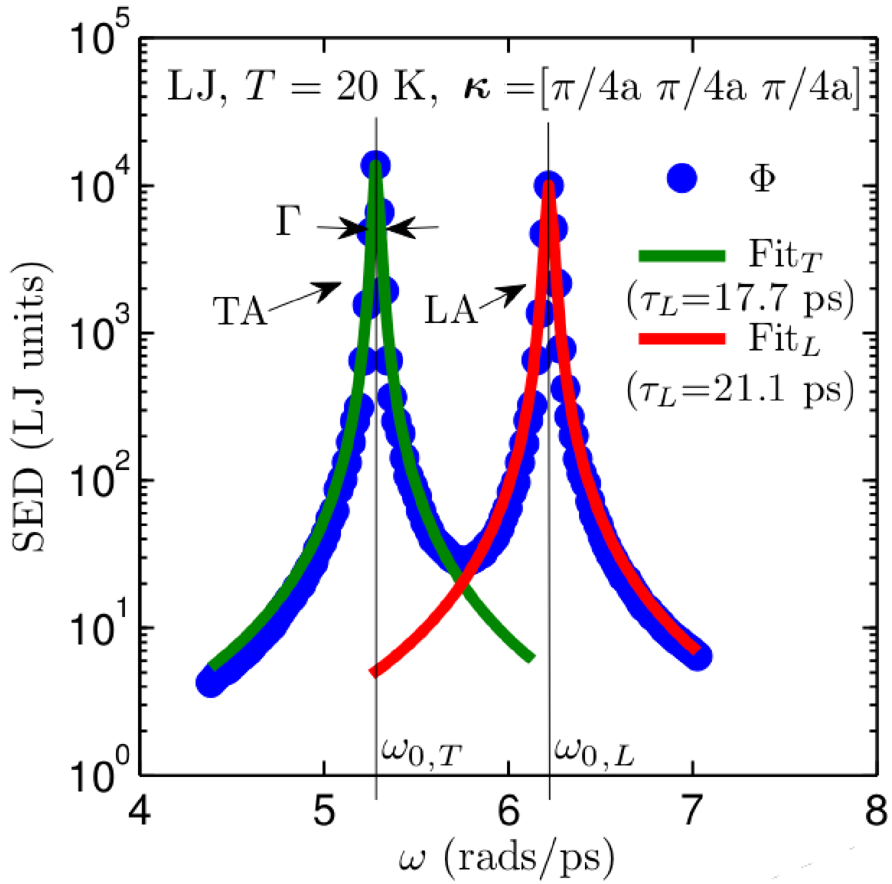
$$E(\tbinom{\boldsymbol{\kappa}}{\nu};t) = \frac{\omega(\tbinom{\boldsymbol{\kappa}}{\nu})^2}{2} q(\tbinom{\boldsymbol{\kappa}}{\nu};t)^* \, q(\tbinom{\boldsymbol{\kappa}}{\nu};t) + \frac{1}{2}\dot{q}(\tbinom{\boldsymbol{\kappa}}{\nu};t)^* \, \dot{q}(\tbinom{\boldsymbol{\kappa}}{\nu};t)$$

PE **KE**

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

nharmonic Lattice Dynamics:

$$\tau(\tbinom{\boldsymbol{\kappa}}{\nu}) = 1/[2\Gamma(\tbinom{\boldsymbol{\kappa}}{\nu})]$$



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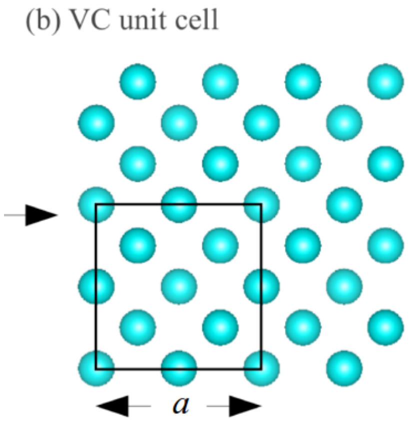
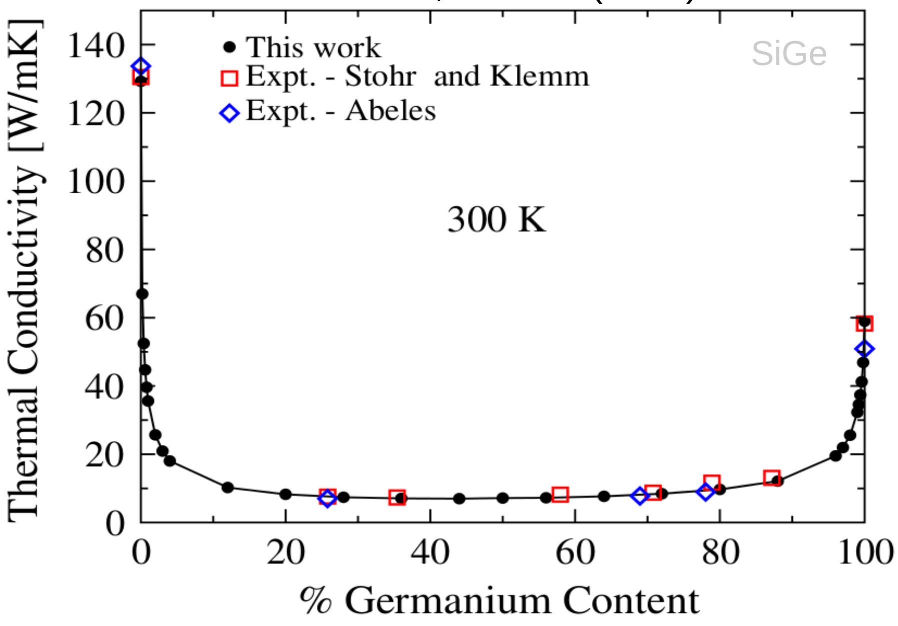
Alloys: experimental accuracy

Expensive Density Functional Theory (DFT) calculations
+
Virtual Crystal (VC) approximation &
Anharmonic Lattice Dynamics (ALD) (**VC-ALD**)

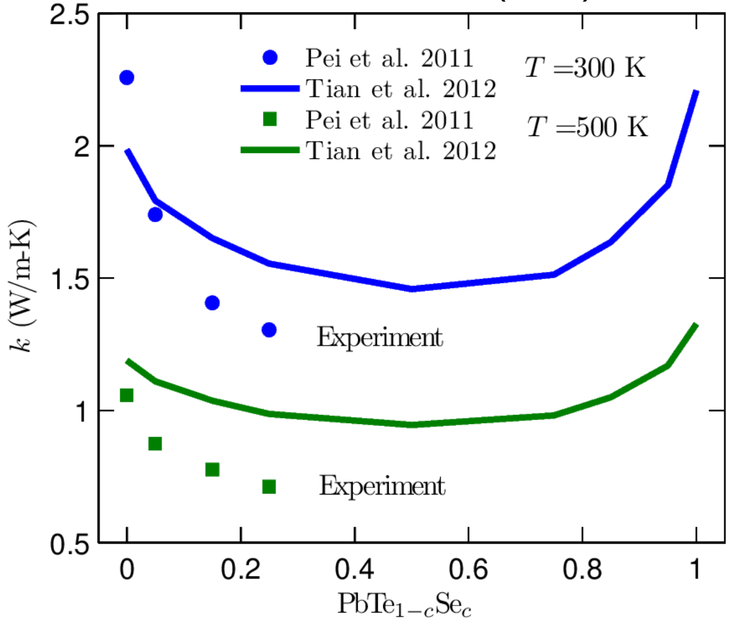
Alloys: isotopic effects, thermoelectric materials



PRL 106, 045901 (2011)



PRB 85, 184303 (2012)



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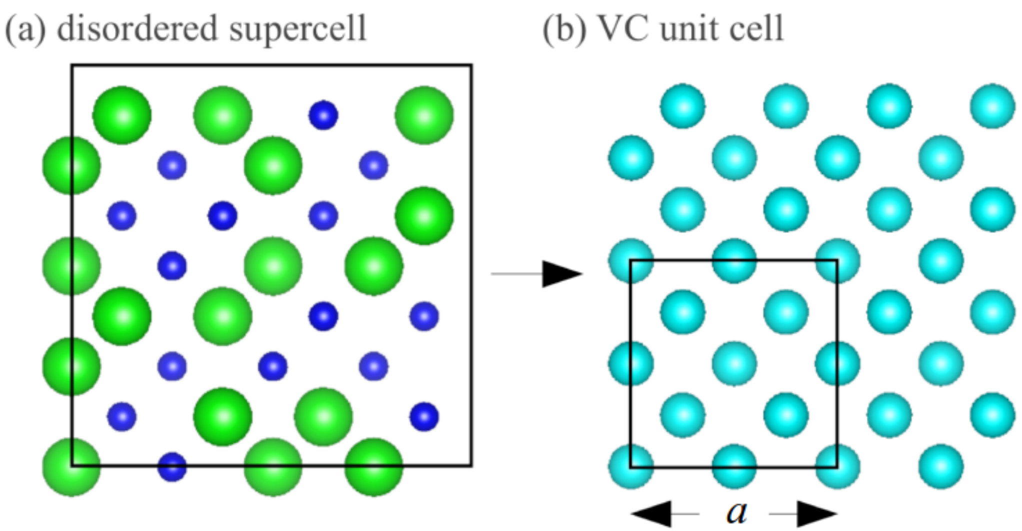
Alloys: Virtual Crystal Approximation



$$c^{\mu}, m^{\mu}$$

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

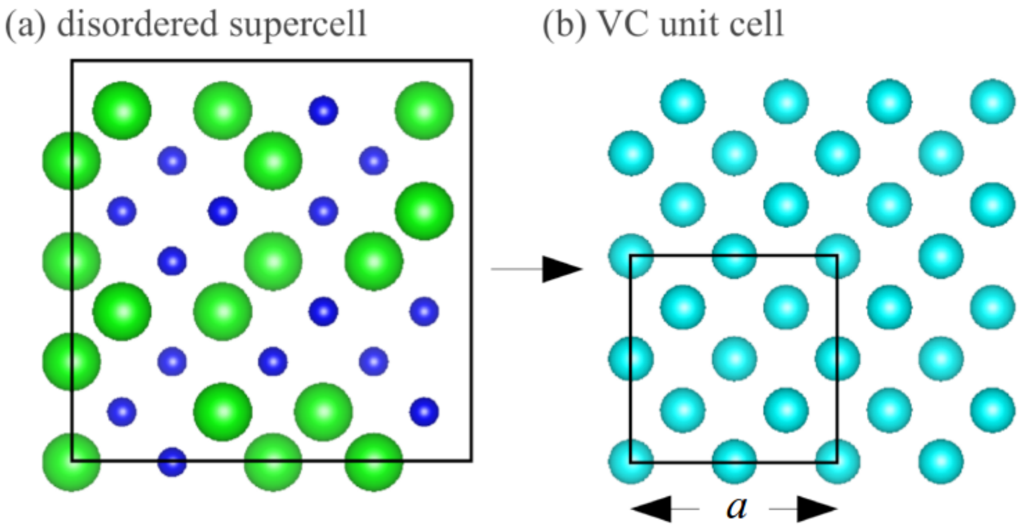
Thermal conductivity: $$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} \frac{k_B}{V} D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu}$$

Thermal diffusivity: $$D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = v^2_{g,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu}\, \tau\binom{\boldsymbol{\kappa}}{\nu}$$

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

PRB 48, 12581-12588 (1993)

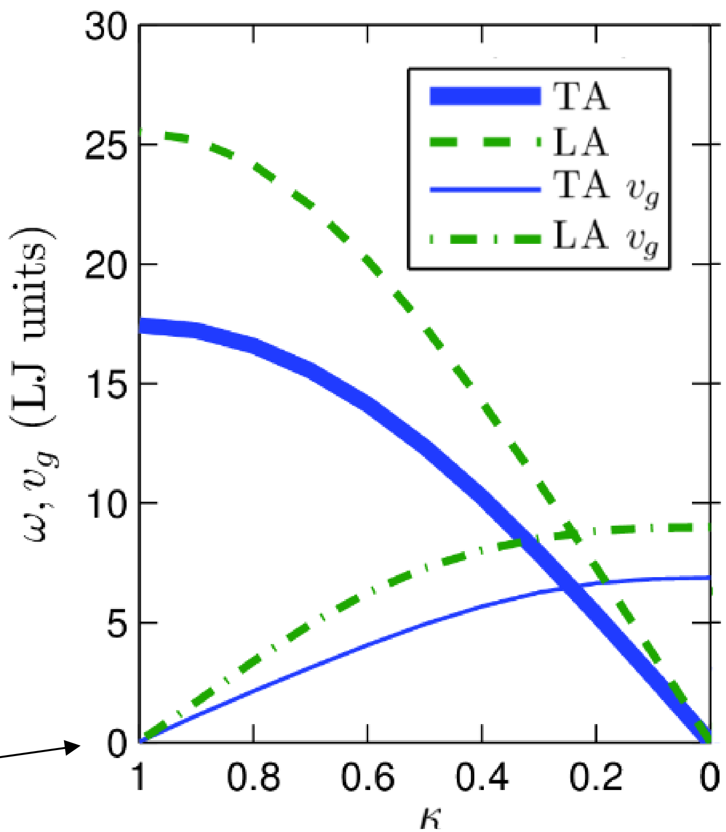
VC-ALD: Group Velocity



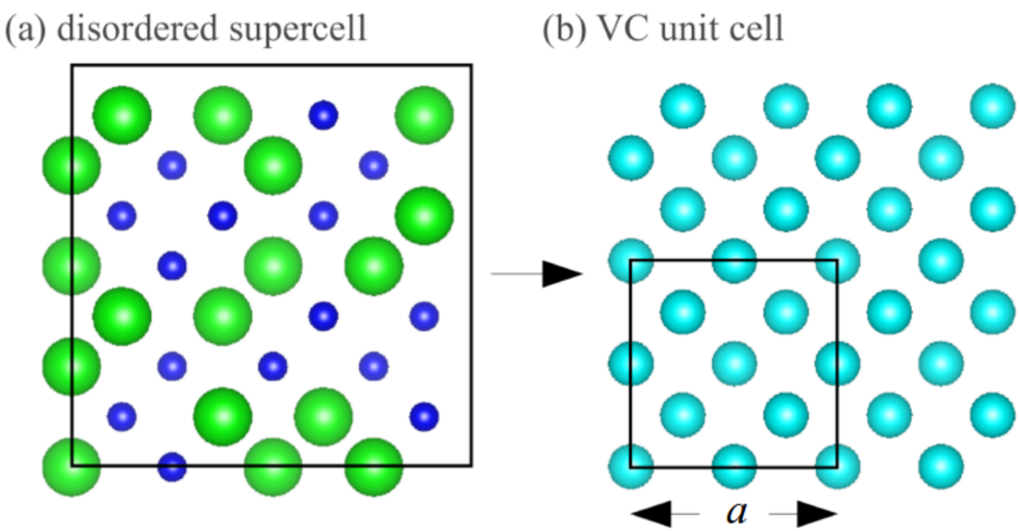
$$D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = v_{g,\mathbf{n}}^2\binom{\boldsymbol{\kappa}}{\nu}\,\tau\binom{\boldsymbol{\kappa}}{\nu}$$

$$v_{g,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = \frac{\partial\omega\binom{\boldsymbol{\kappa}}{\nu}}{\partial\boldsymbol{\kappa}}$$

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} \approx 0$$



VC-ALD: Lifetimes



$$D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = v^2_{g,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu}\,\tau\binom{\boldsymbol{\kappa}}{\nu}$$

ALD

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

Tamura

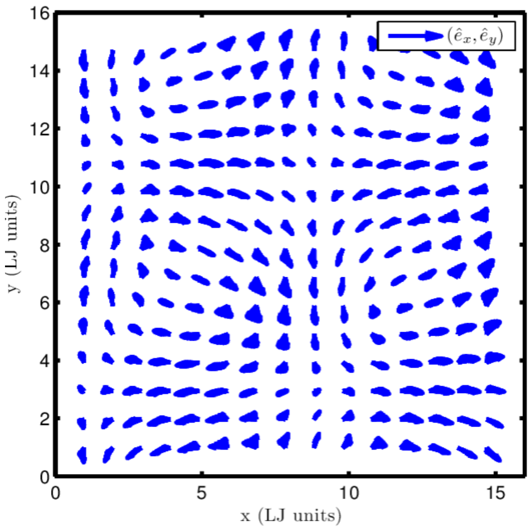
$\tau_{p-d}\binom{\boldsymbol{\kappa}}{\nu} \sim 1/\omega^4$

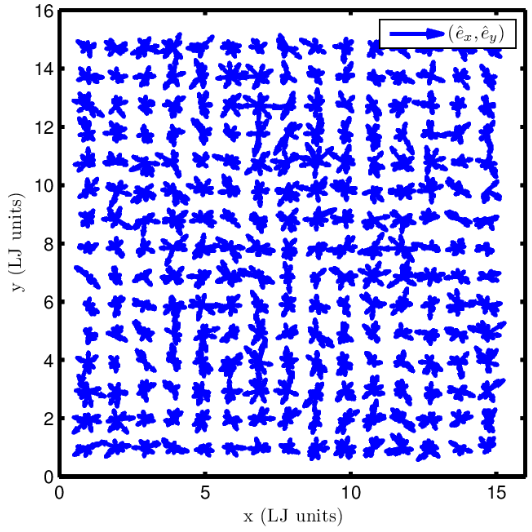
Matthiessen's Rule:

$$\frac{1}{\tau\binom{\boldsymbol{\kappa}}{\nu}} = \frac{1}{\tau_{p-p}\binom{\boldsymbol{\kappa}}{\nu}} + \frac{1}{\tau_{p-d}\binom{\boldsymbol{\kappa}}{\nu}}$$

Tamura, PRB 27, 858–866 (1983)

Structure Factor: Effective Dispersion

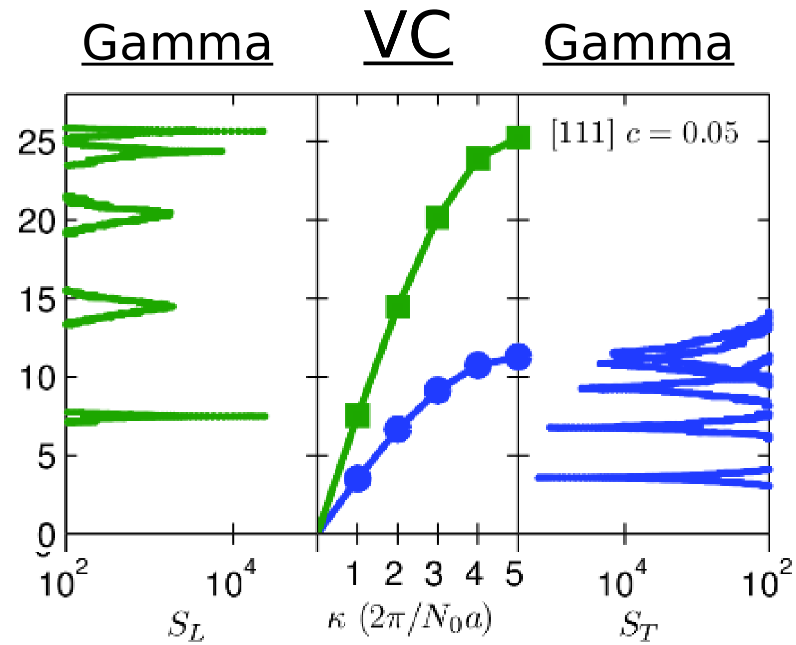




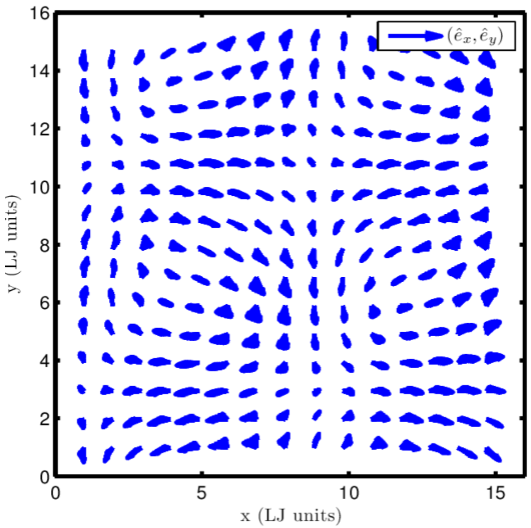
$$e^*\binom{\boldsymbol{\kappa}\ \ b}{\nu\ \ \alpha}$$

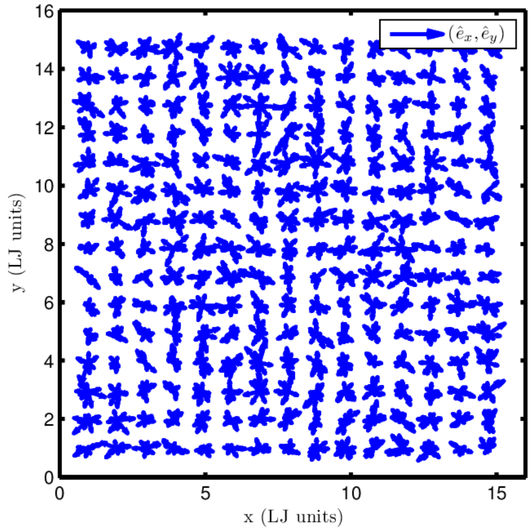
$$E^T\binom{\boldsymbol{\kappa}_{VC}}{\nu} = \left| \sum_b \hat{\boldsymbol{\kappa}}_{VC} \times e\binom{\boldsymbol{\kappa}=\mathbf{0}\ \ b}{\nu\ \ \alpha} \exp[i\boldsymbol{\kappa}_{VC} \cdot \boldsymbol{r}_0\binom{l=0}{b}] \right|^2$$

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



Structure Factor: Effective Dispersion





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

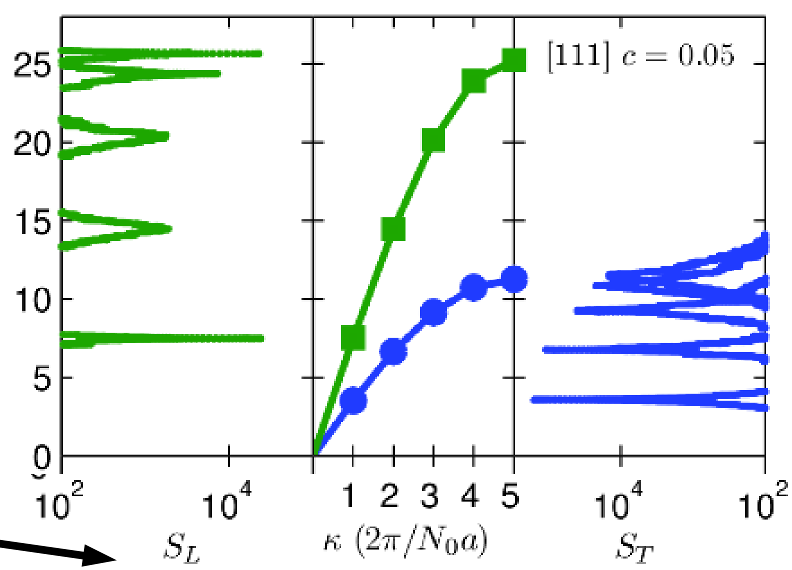
$$v_{g,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = \frac{\partial\omega\binom{\boldsymbol{\kappa}}{\nu}}{\partial\boldsymbol{\kappa}}$$

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

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

$$S^{L,T}\binom{\boldsymbol{\kappa}_{VC}}{\omega} = \sum_\nu E^{L,T}\binom{\boldsymbol{\kappa}_{VC}}{\nu}\,\delta[\omega - \omega\binom{\boldsymbol{\kappa}=\mathbf{0}}{\nu}]$$

Gamma VC Gamma



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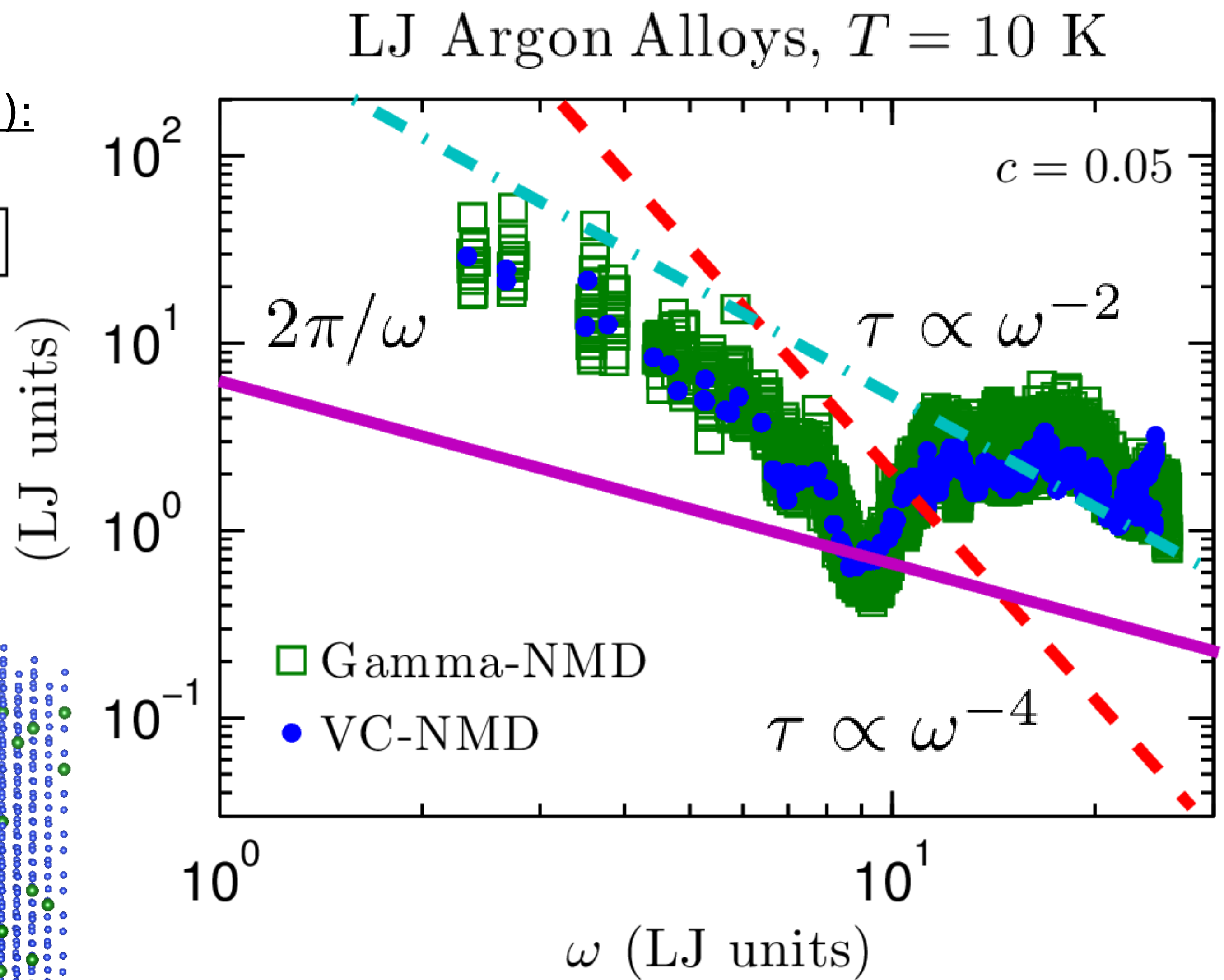
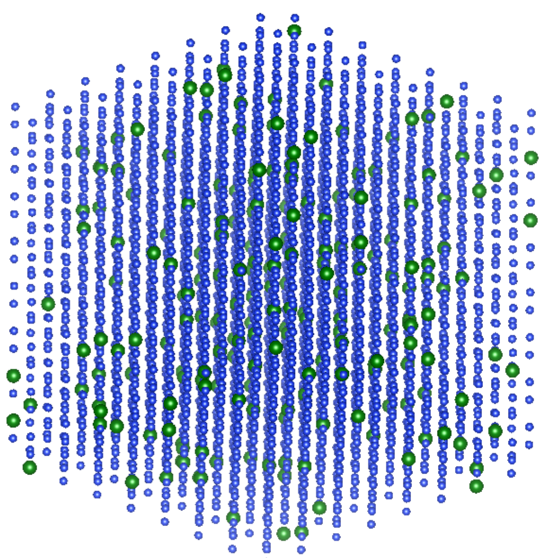
Explicit disorder: NMD $D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = v_{g,\mathbf{n}}^2\binom{\boldsymbol{\kappa}}{\nu}\tau\binom{\boldsymbol{\kappa}}{\nu}$

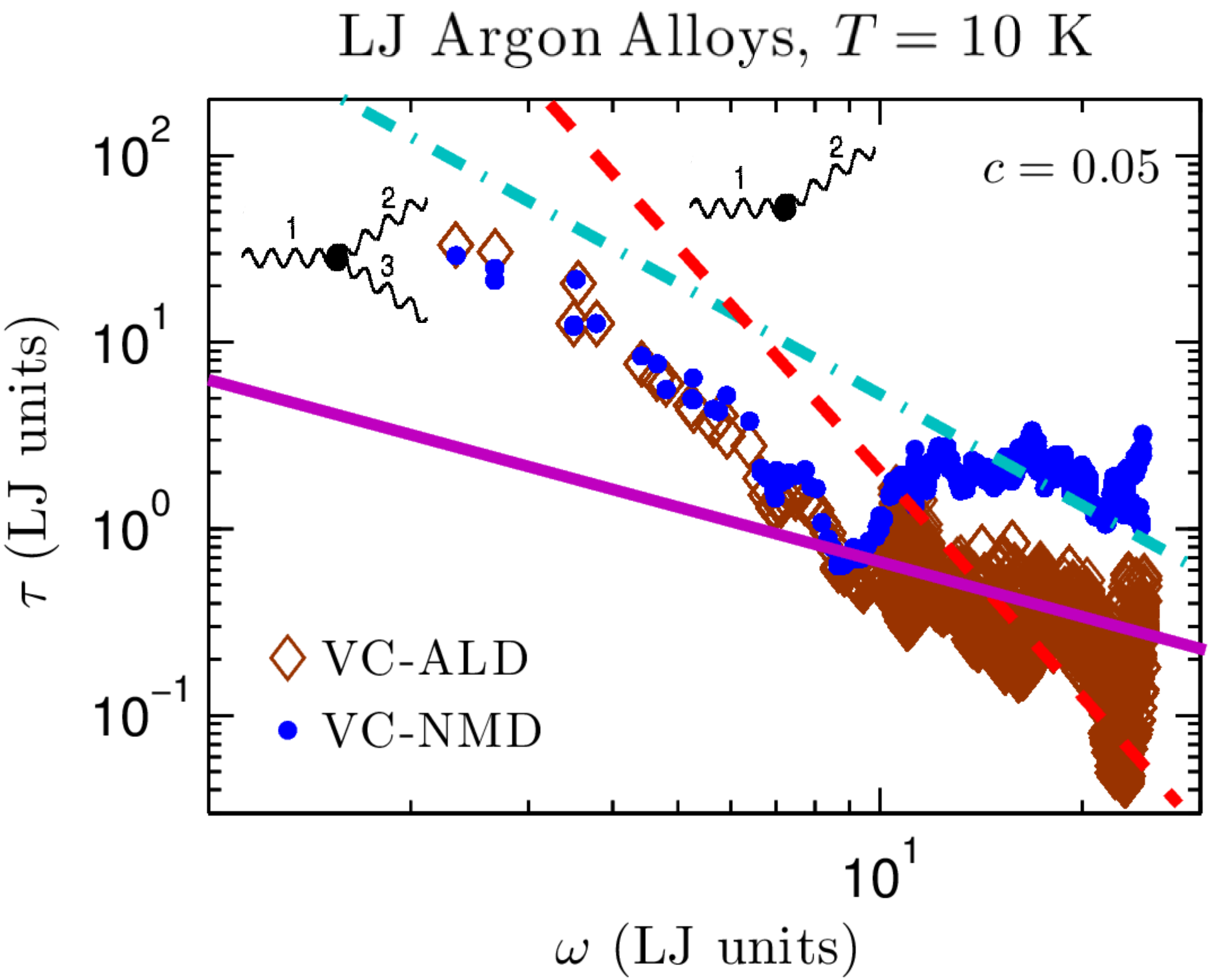
Normal Mode Decomposition (**NMD**):

$$\tau\binom{\boldsymbol{\kappa}}{\nu} = 1/[2\Gamma\binom{\boldsymbol{\kappa}}{\nu}]$$

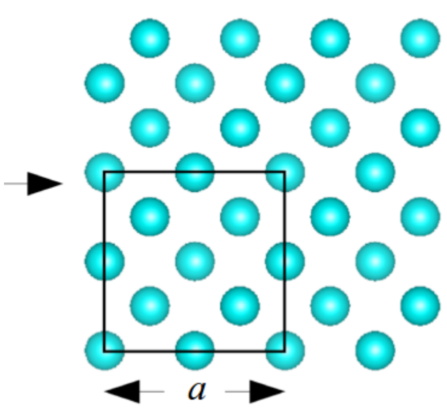




VC-NMD vs VC-ALD



(b) VC unit cell



VC Diffusivities

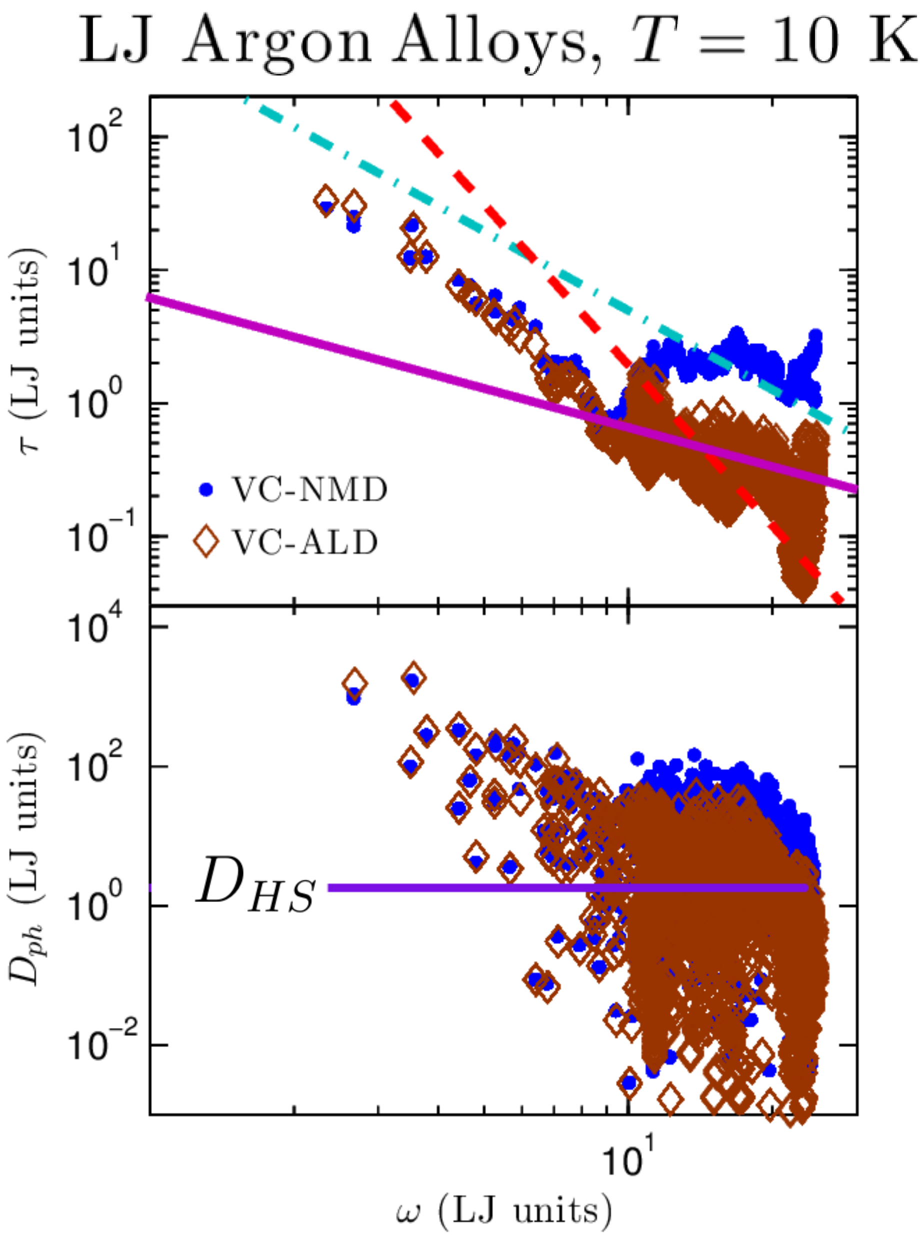
$$D_{ph,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu} = v^2_{g,\mathbf{n}}\binom{\boldsymbol{\kappa}}{\nu}\,\tau\binom{\boldsymbol{\kappa}}{\nu}$$

Phonon limit:

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} \approx 0$$

High-scatter limit:

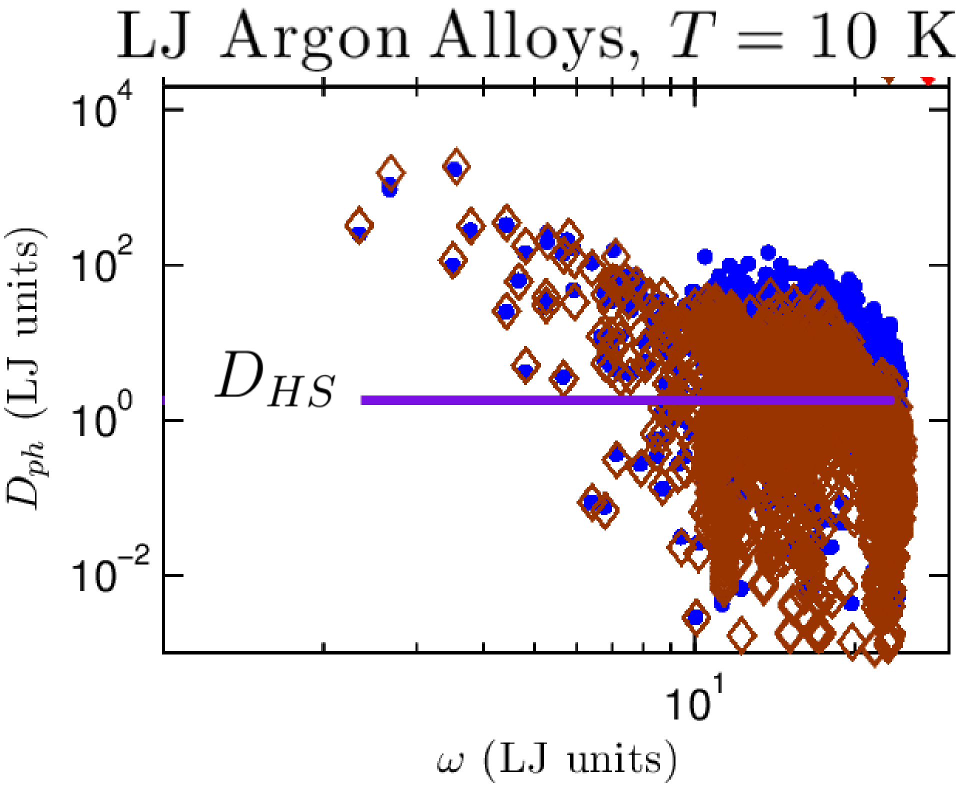
$$D_{HS} = \frac{1}{3} v_s a$$



Sol. Sta. Comm. 70, 927 – 930 (1989)

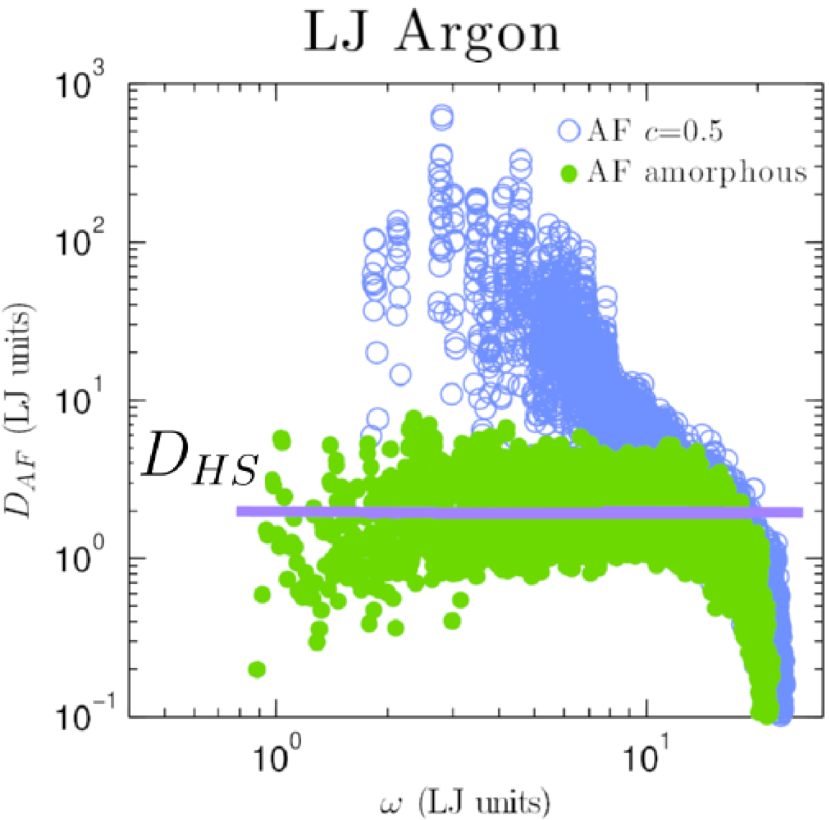
VC and AF Diffusivities

Phonons



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

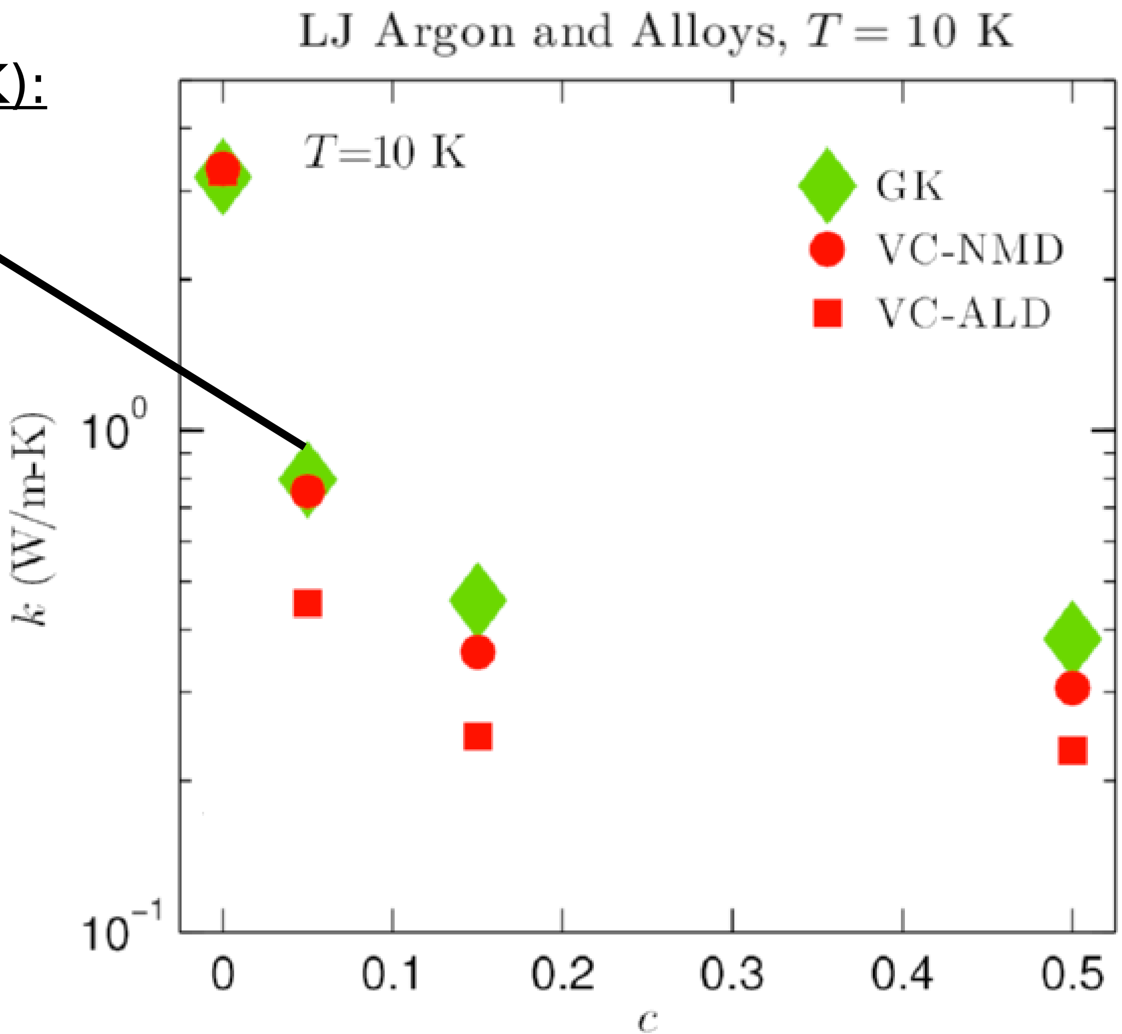
Diffusons



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

Thermal conductivity: System-level

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



High-scatter adjustment*:

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} < D_{HS}$$

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} = D_{HS}$$

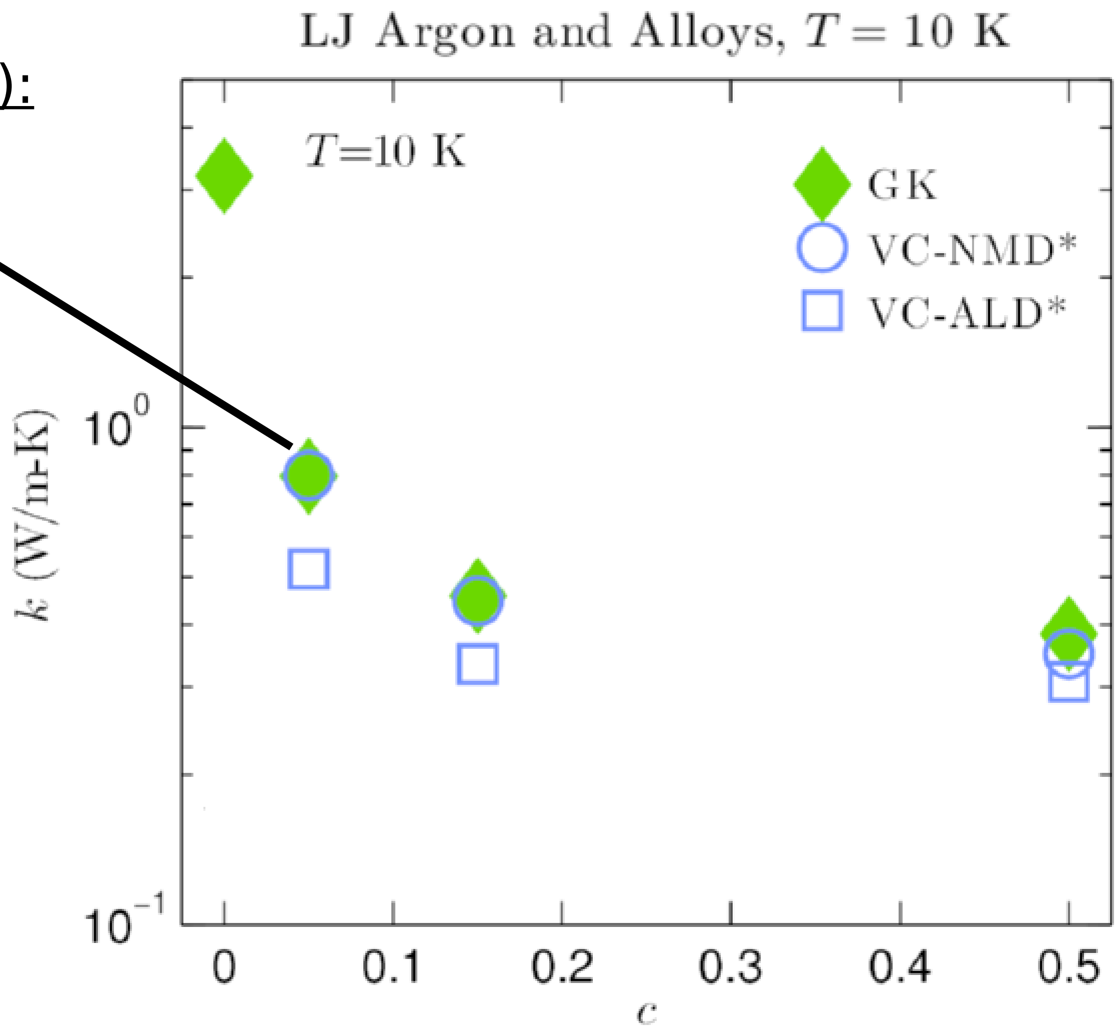
Thermal conductivity: System-level

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

High-scatter adjustment*:

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} < D_{HS}$$

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} = D_{HS}$$



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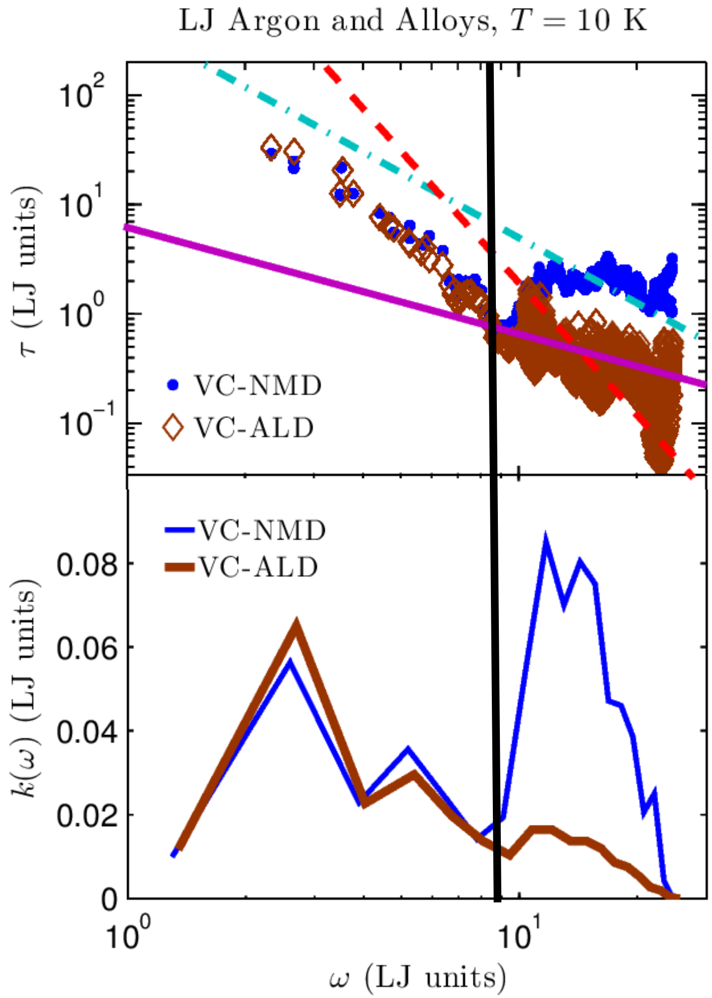
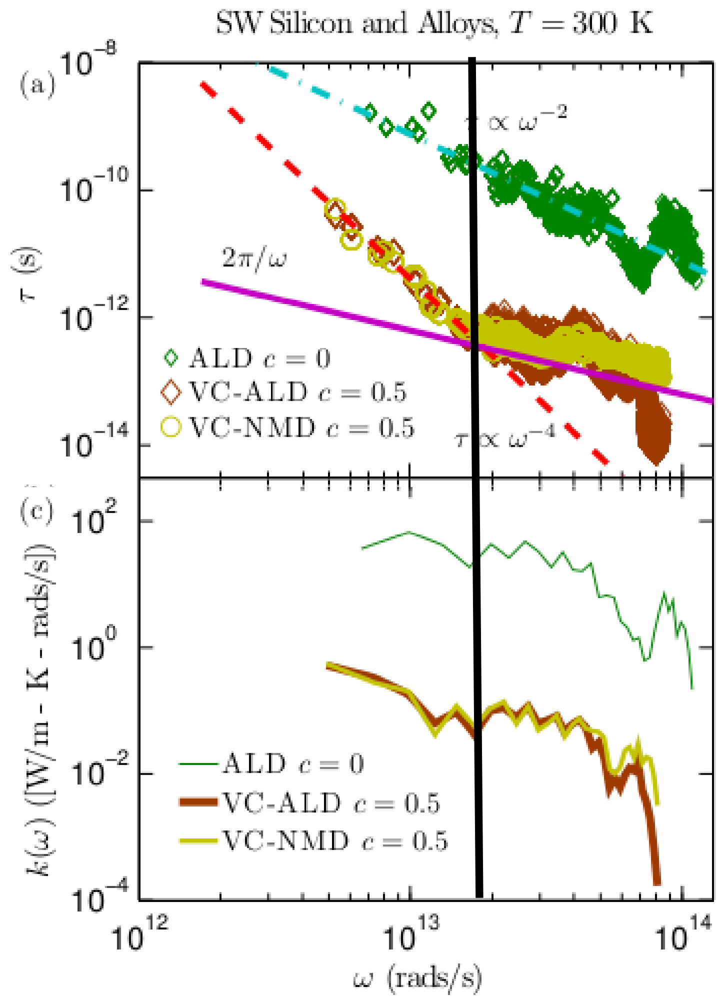
Thermal Conductivity Spectrum

Low and High Frequency



50% Propagons,
50% Diffusons

High Frequency



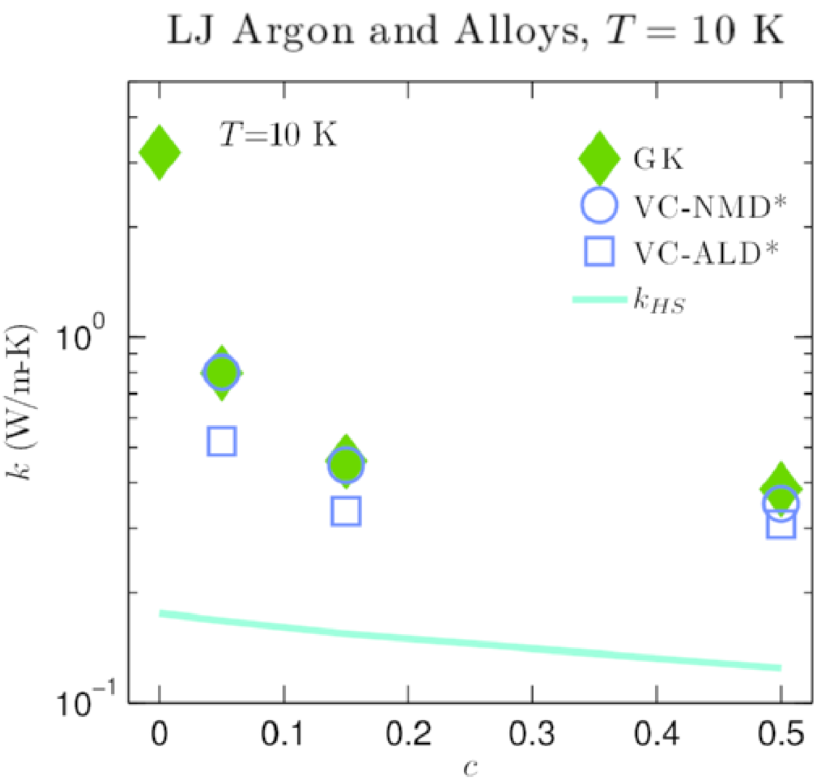
95% Propagons

Mechanical Engineering

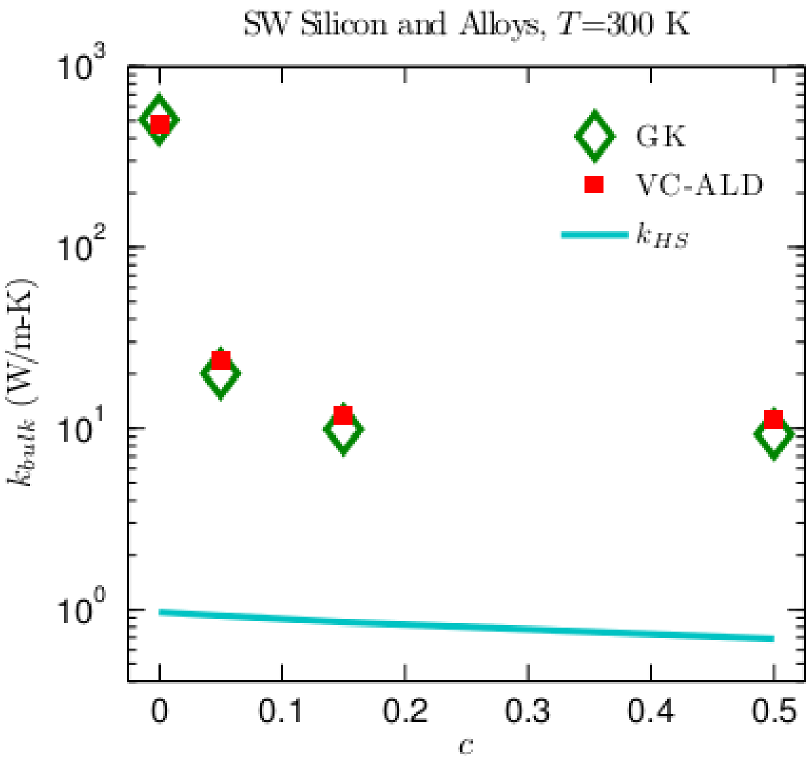
Alloys: Two Classes

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.

Full-Spectrum Alloys



Low-frequency Alloys



50% Propagons,
50% Diffusons

95% Propagons

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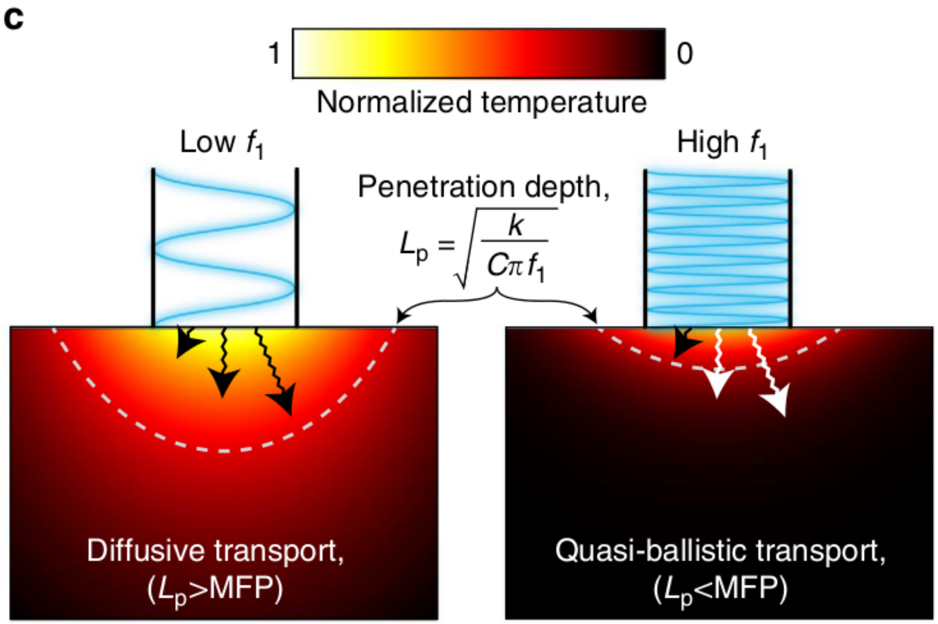
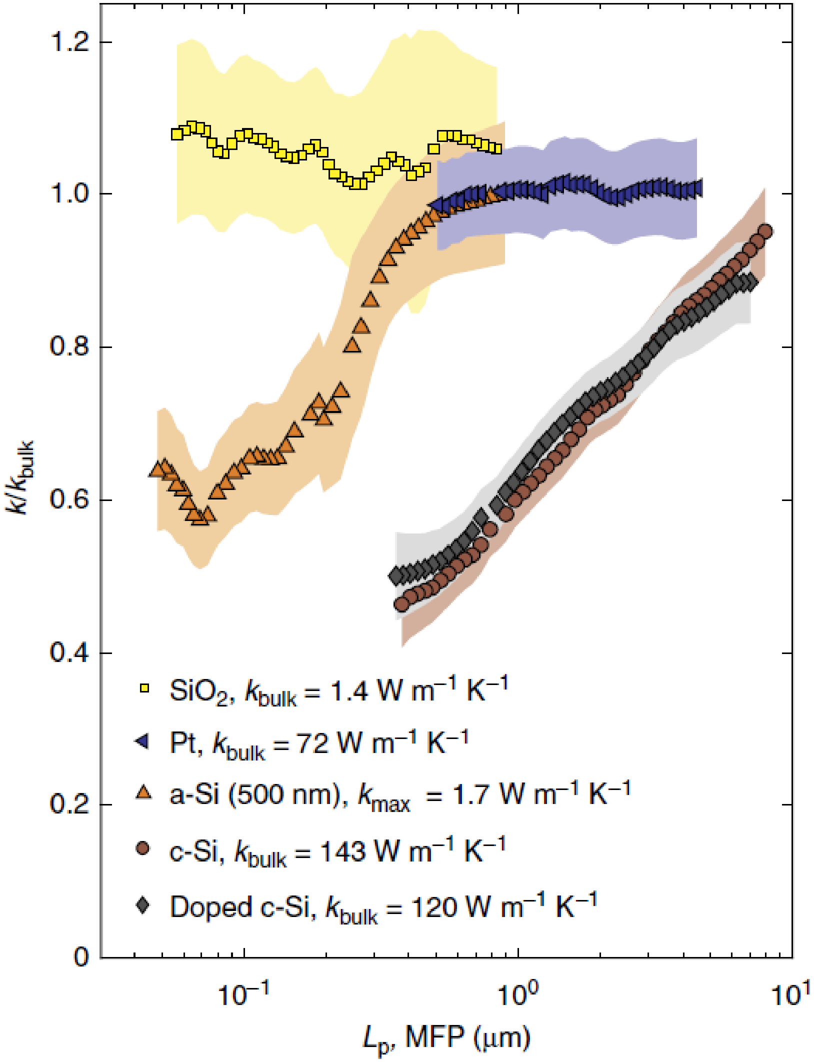
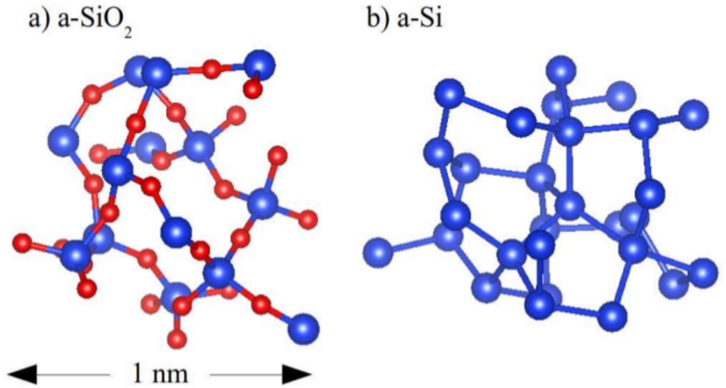
Amorphous: Motivation

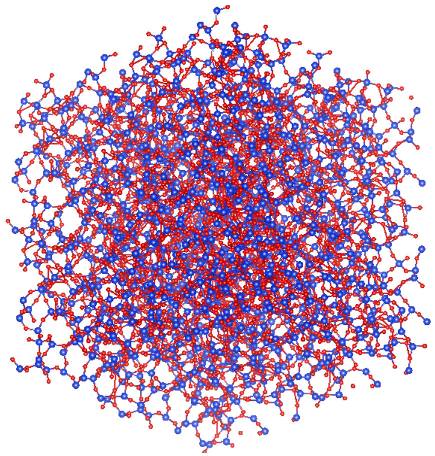




Regner et al., *Nat. Comm.* **4**, 1640 (2013)

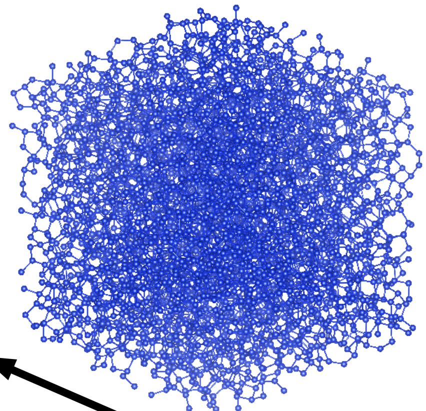
Amorphous Solids: no VC



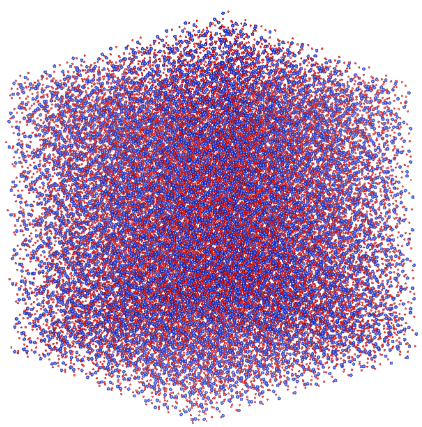


Mode-level:

~4000 atoms

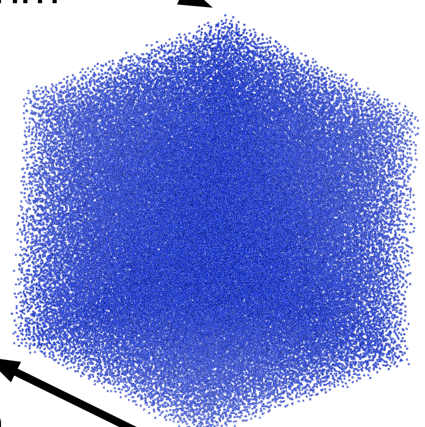


4.34 nm



System-level:

~1E6 atoms



~25 nm

Mechanical Engineering

Vibron Thermal Conductivity

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

ffusons (non-propagating):

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

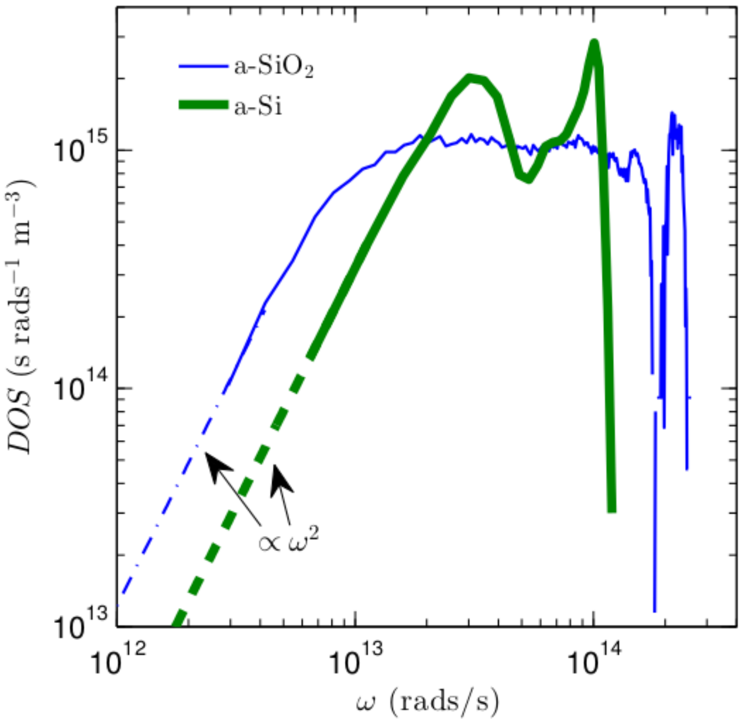
opagons (phonon-like):

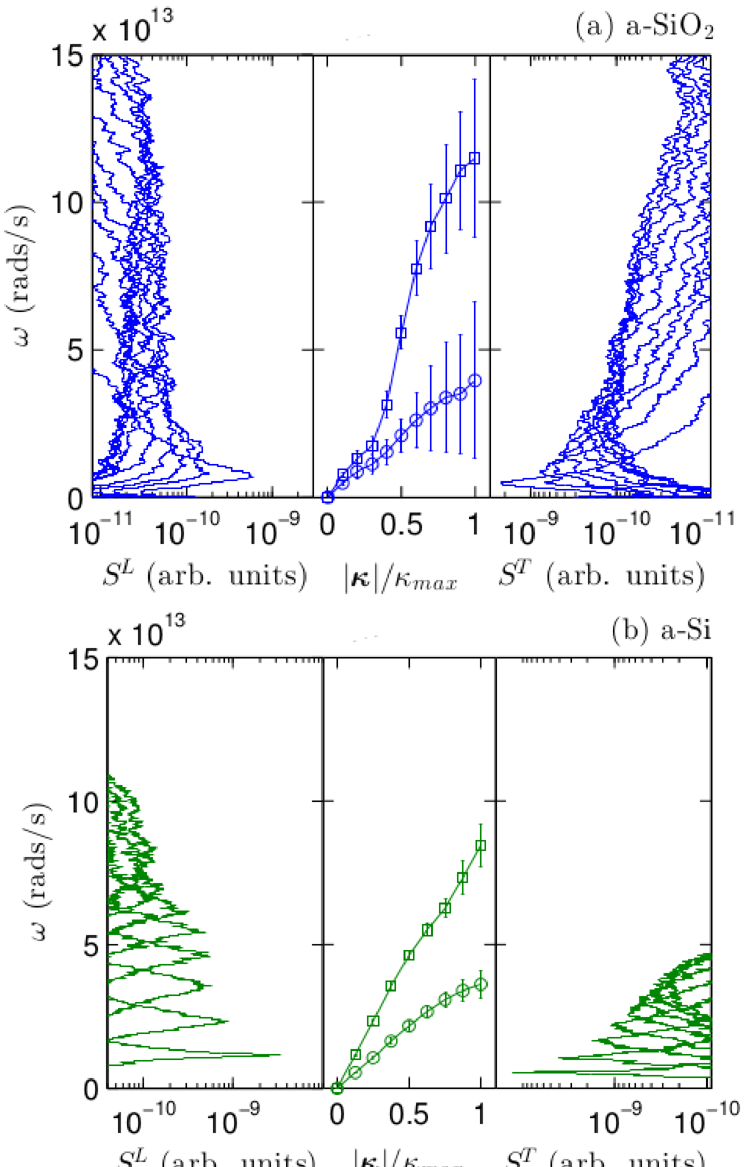
$$k_{pr} = \frac{1}{V} \int_0^{\omega_{cut}} DOS(\omega) C(\omega) D_{pr}(\omega) d\omega$$

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

Mechanical Engineering

Vibrons: Phonon character





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

$$S^{L,T}\left(\begin{smallmatrix}\boldsymbol{\kappa}_{VC}\\ \omega\end{smallmatrix}\right) = \sum_{\nu} E^{L,T}\left(\begin{smallmatrix}\boldsymbol{\kappa}_{VC}\\ \nu\end{smallmatrix}\right)\delta\left[\omega - \omega\left(\begin{smallmatrix}\boldsymbol{\kappa}=0\\ \nu\end{smallmatrix}\right)\right]$$

Vibrons: Lifetimes and Diffusivities

Diffusons (non-propagating):

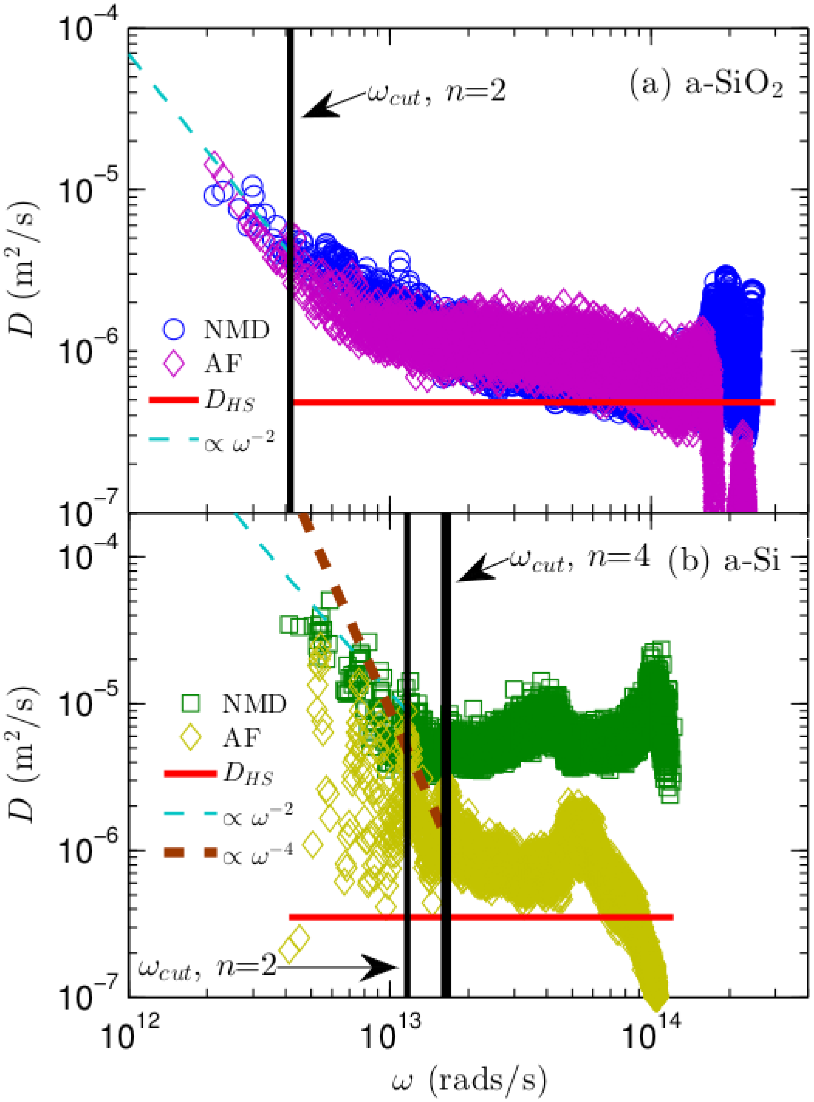
$$k_{AF} = \frac{1}{V} \sum_{i,\omega_i > \omega_{cut}} C(\omega_i) D_{AF}(\omega_i)$$

Propagons (phonon-like):

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

Normal Mode Decomposition (**NMD**):

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



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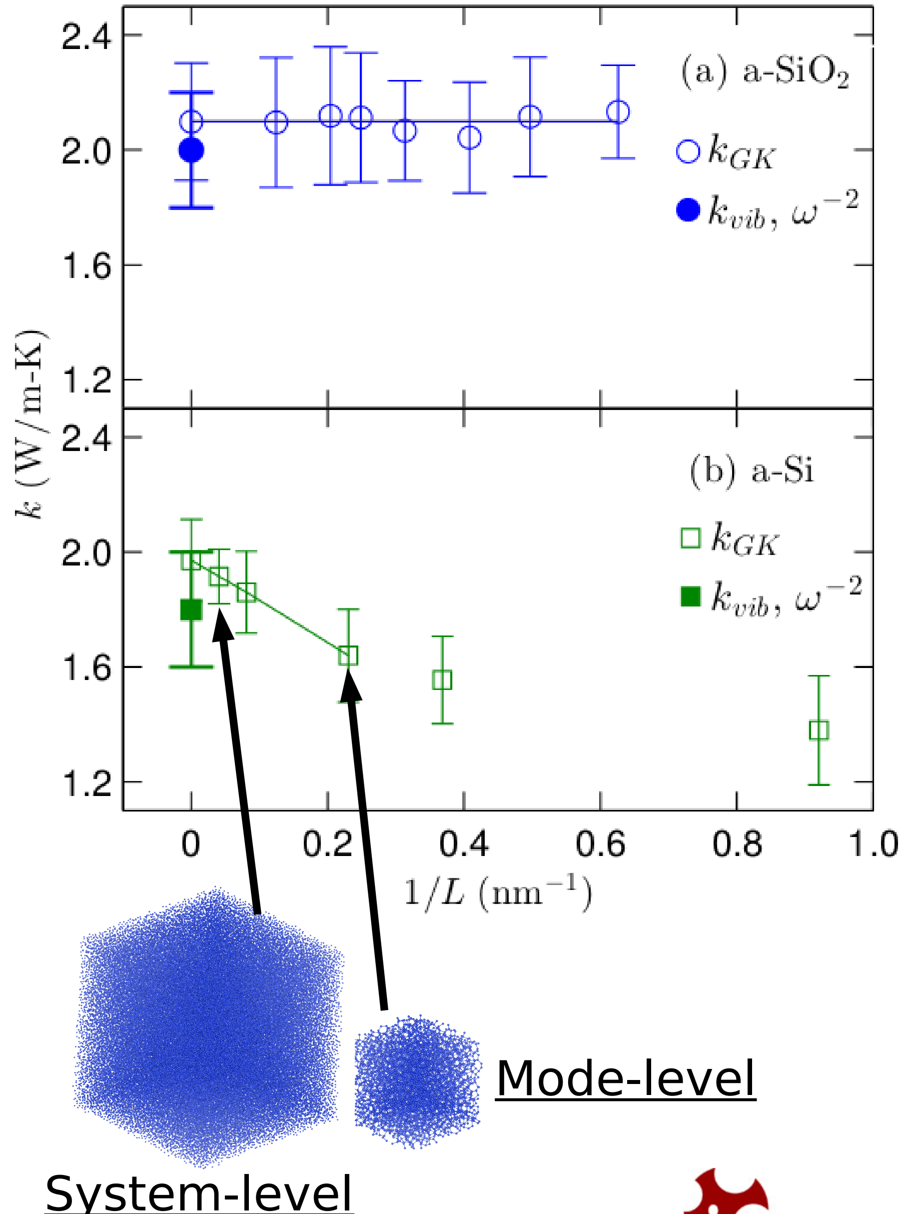
Vibrons: Mode- and System-level

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

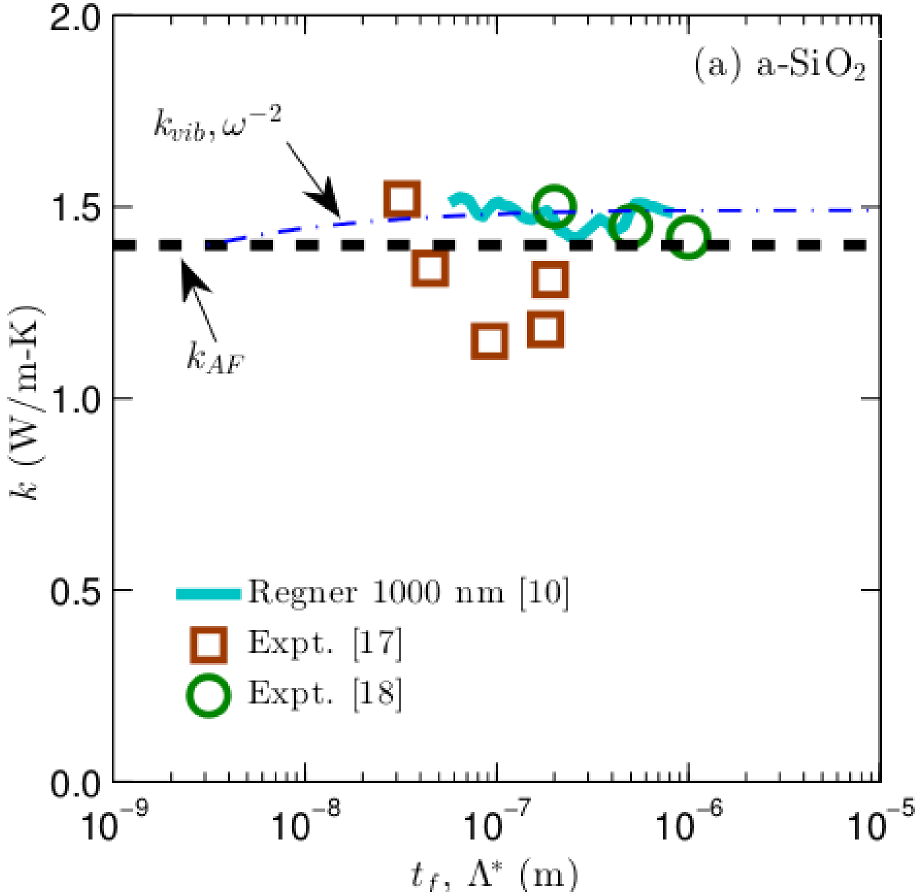
$$\Lambda(\omega) = v_s \tau(\omega)$$

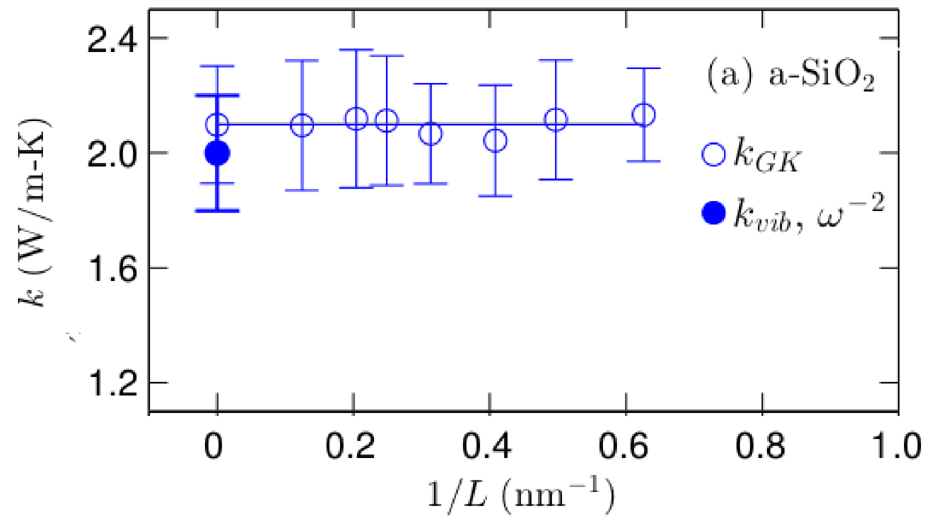
$$D_{pr}(\omega) = \frac{1}{3} v_s \Lambda(\omega)$$



Thermal Conductivity Accumulation

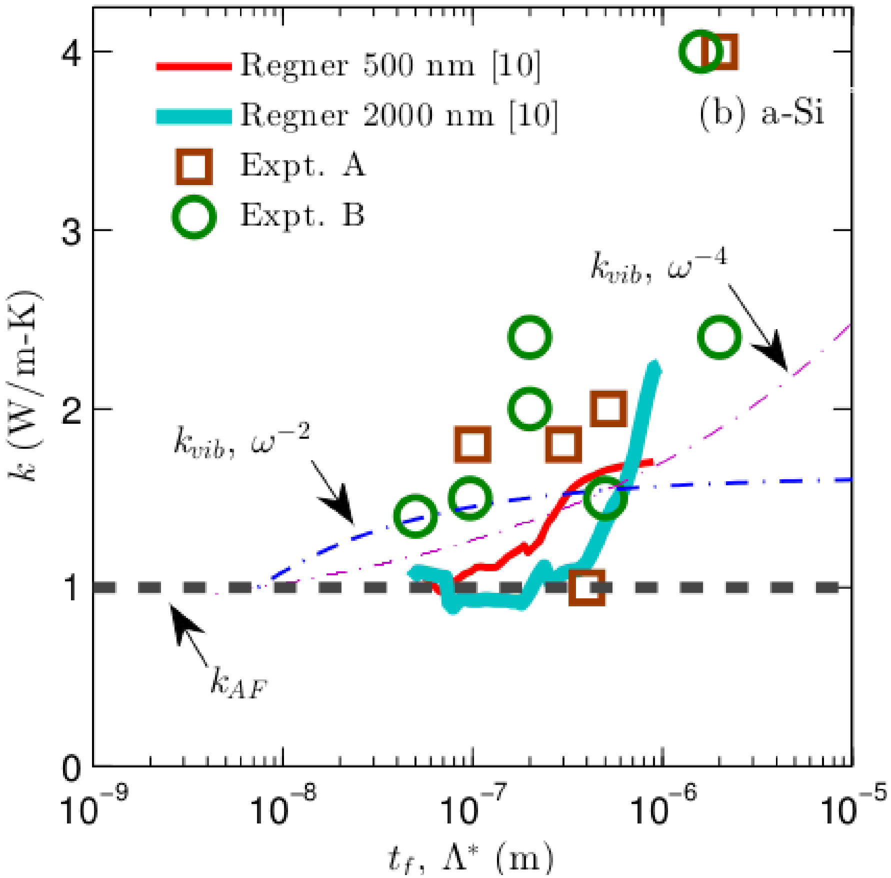
$$k(\Lambda^*) = k_{AF} + \int_{\Lambda_{cut}}^{\Lambda^*} k(\Lambda) d\Lambda$$

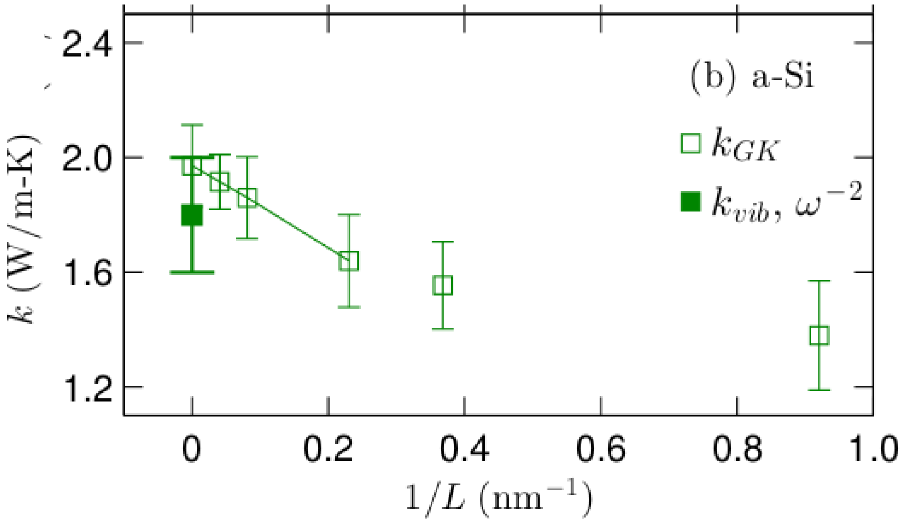




Thermal Conductivity Accumulation

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





Outline

(1) Motivation

(2) Mode-level vs. System-level

(3) Alloys

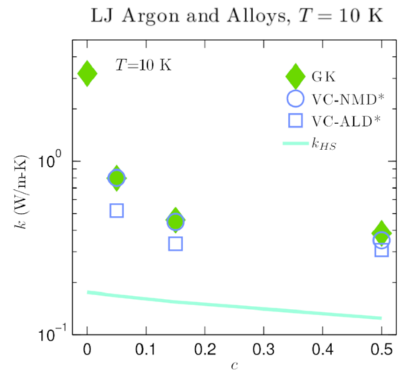
(4) Amorphous

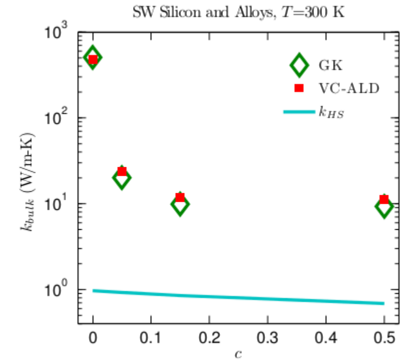
(5) Overview/Future Work

Mechanical Engineering

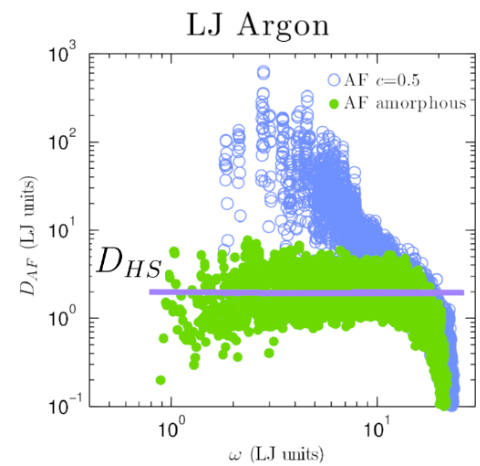
Overview

Limits of Perturbation Methods:

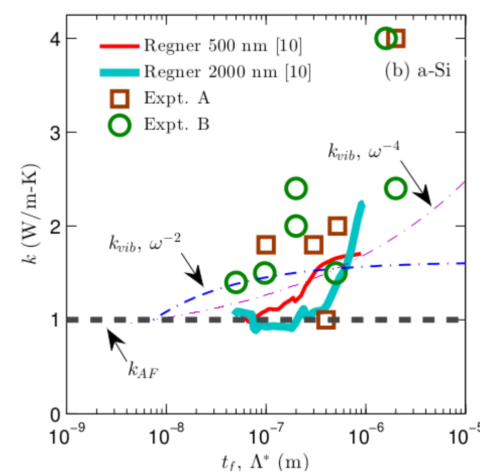




Alloys can behave like Amorphous:



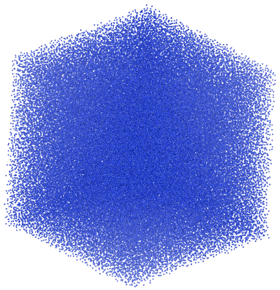
Amorphous can behave like Crystal:

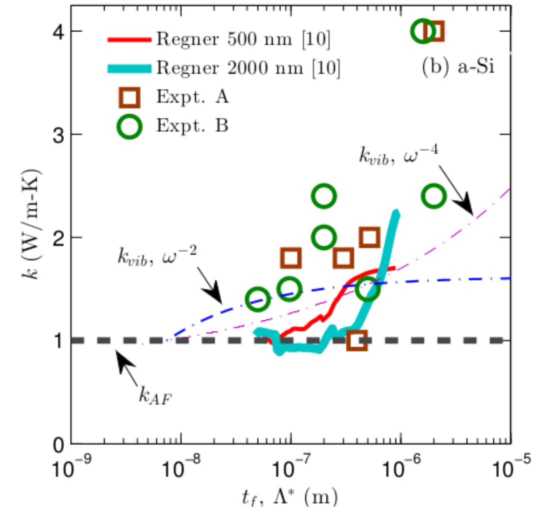


Future Work

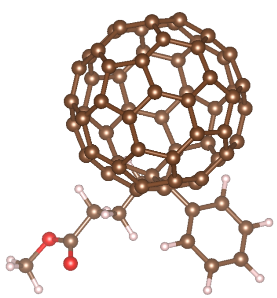
Very Large MD-based Predictions:

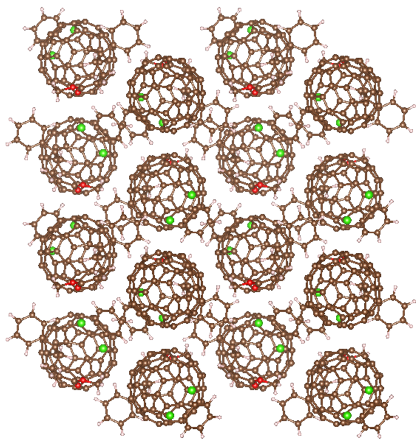
System- and Mode-level

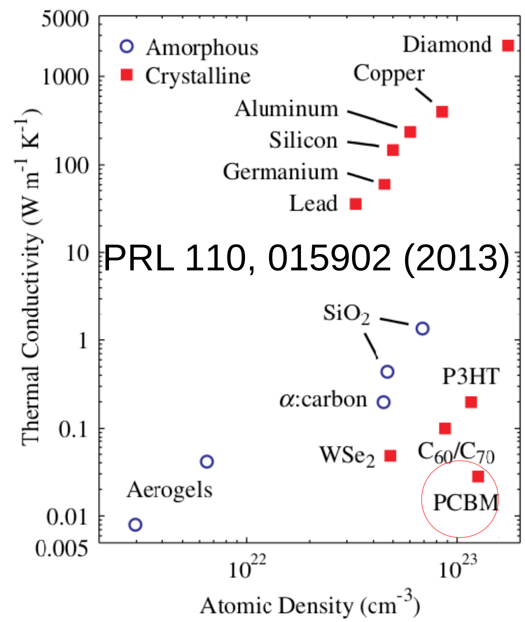




Large Unit Cell Materials (PCBM):







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 pacakge

https://github.com/ntpl/ntpy

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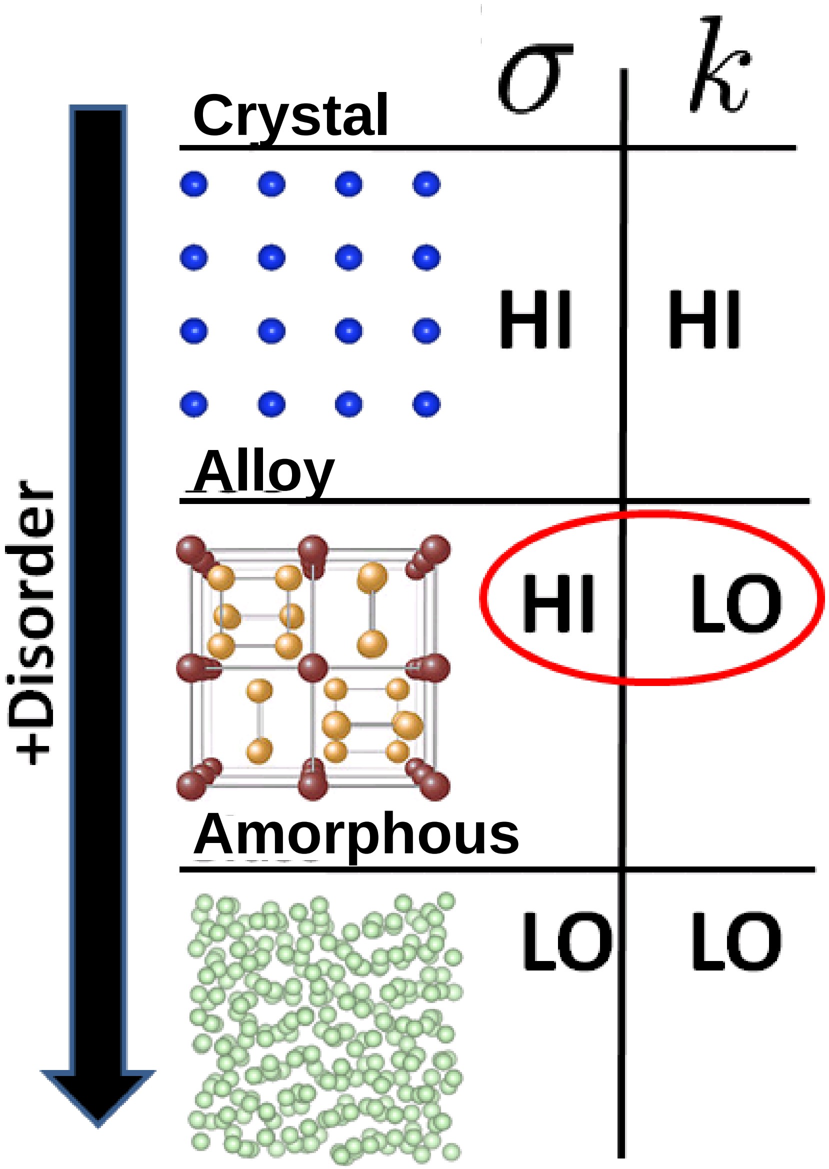
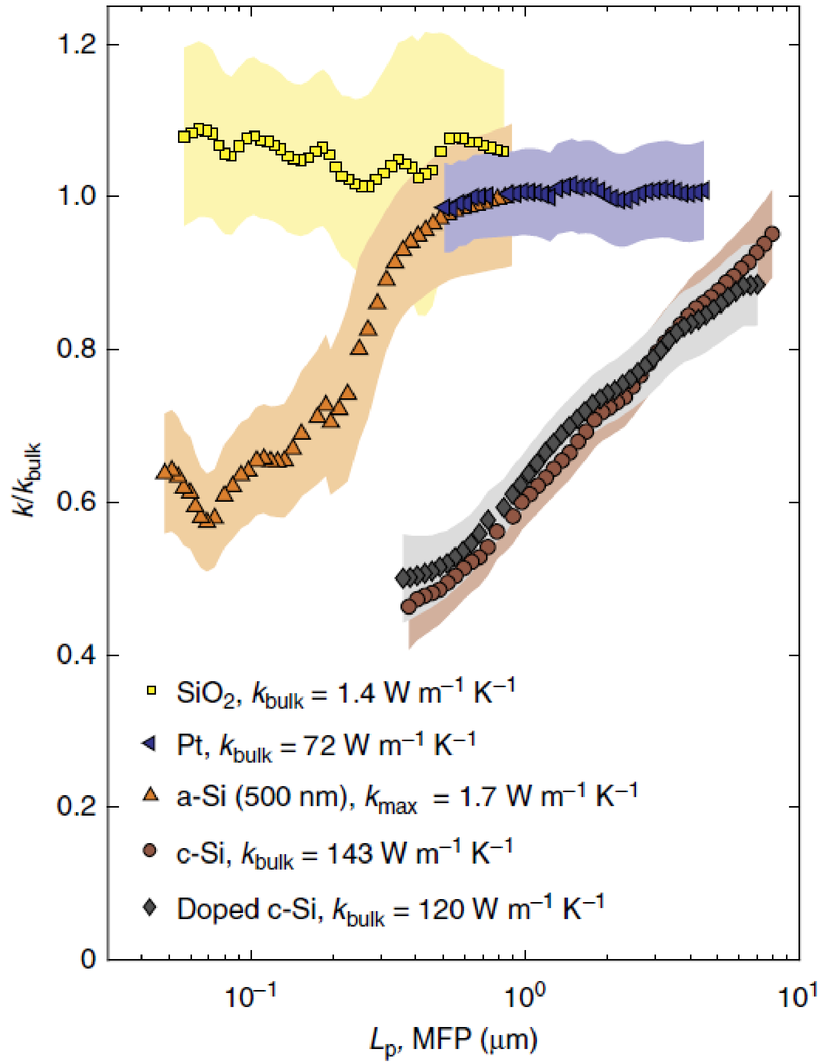
Supplimentary

Motivation: Mode-level Properties





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

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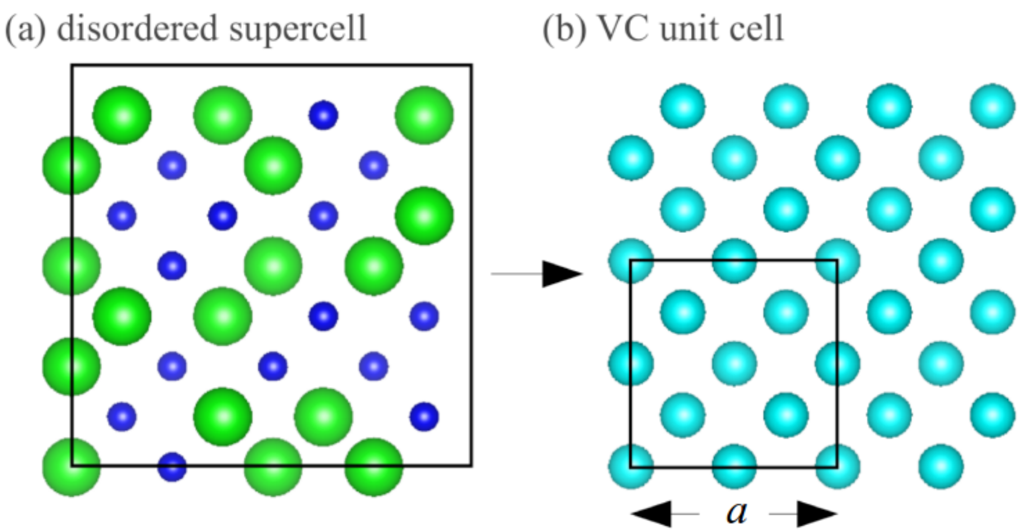
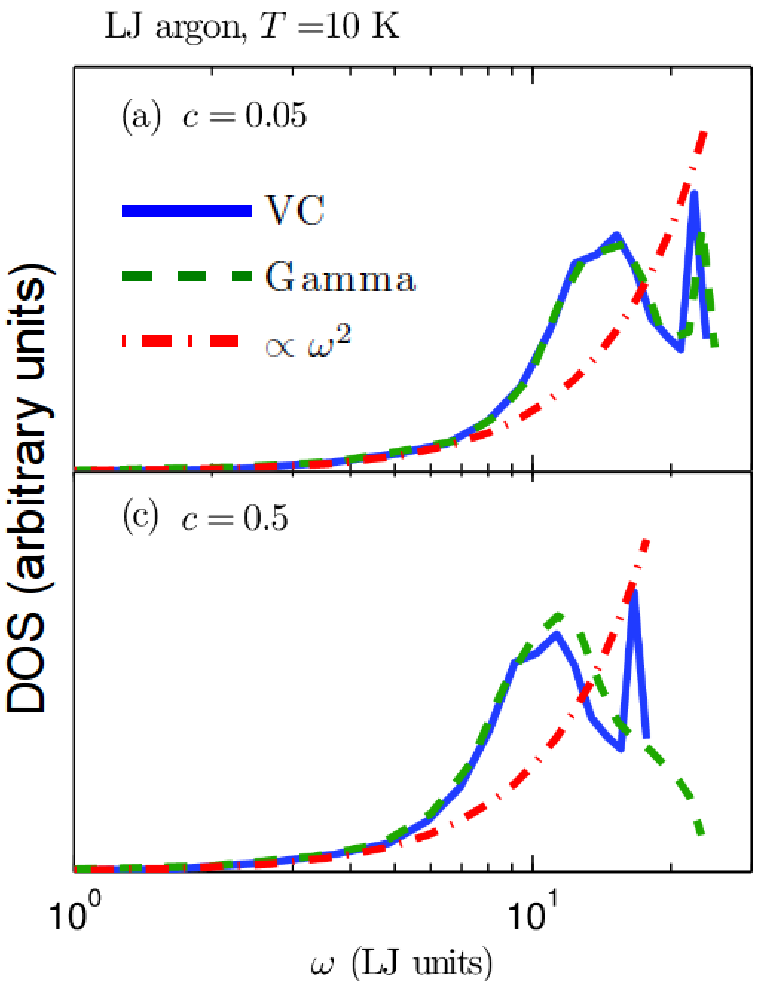
Explicit disorder: VC vs Gamma



Gamma



Computationally-inexpensive empirical potential:
Lennard-Jones argon

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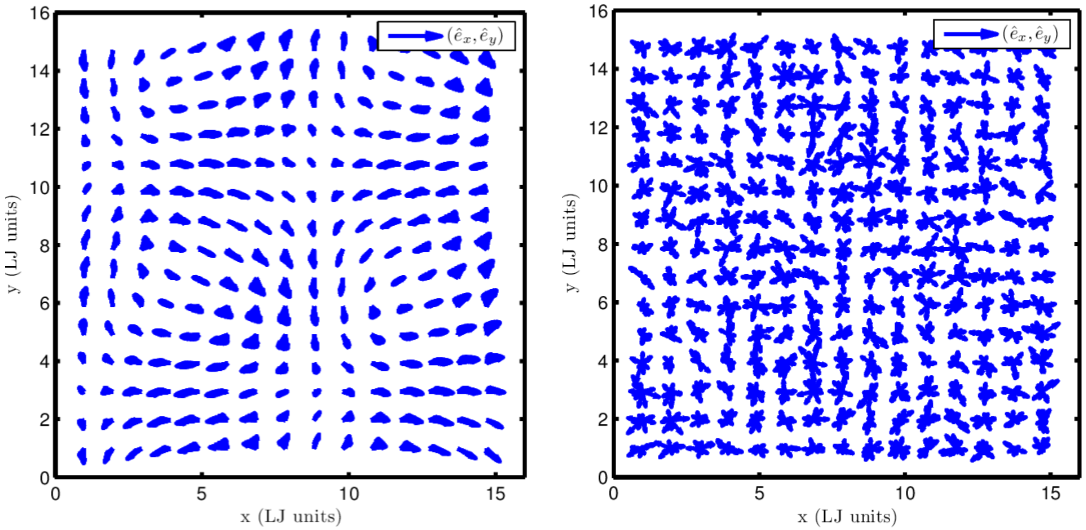
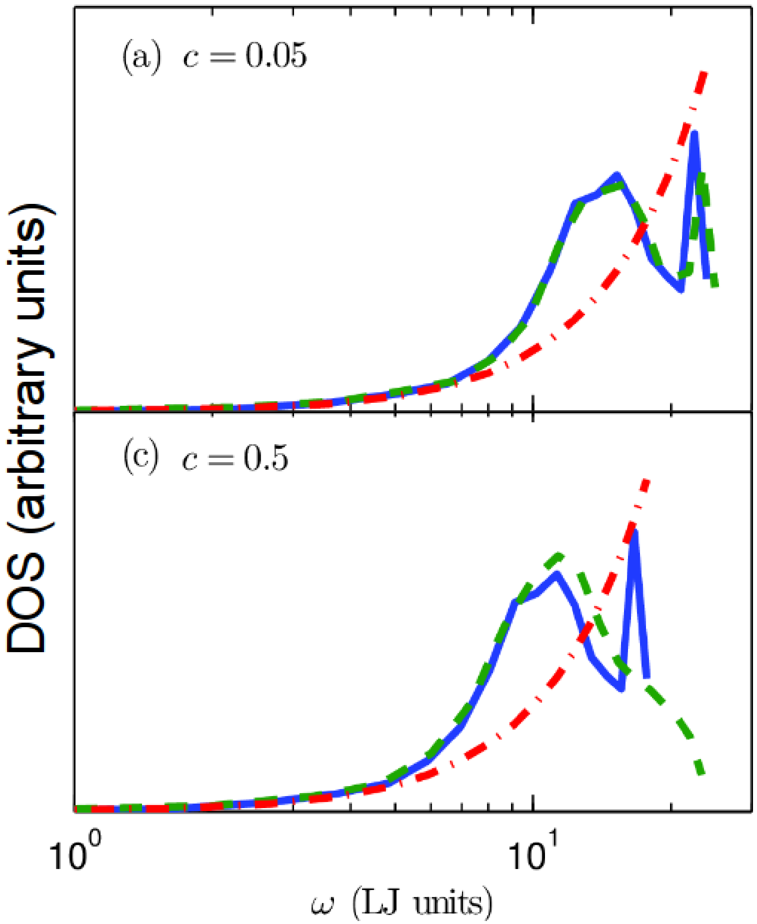
Structure Factor: Effective Dispersion



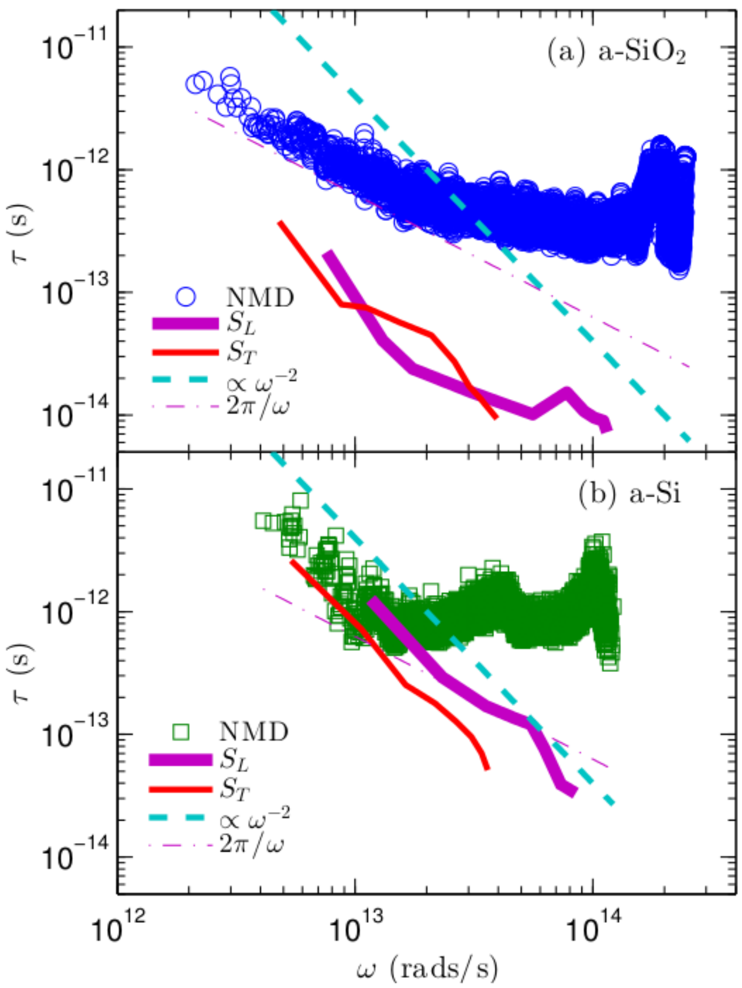
$$e^{*}\binom{\boldsymbol{\kappa}' \quad b}{\nu \quad \alpha}$$

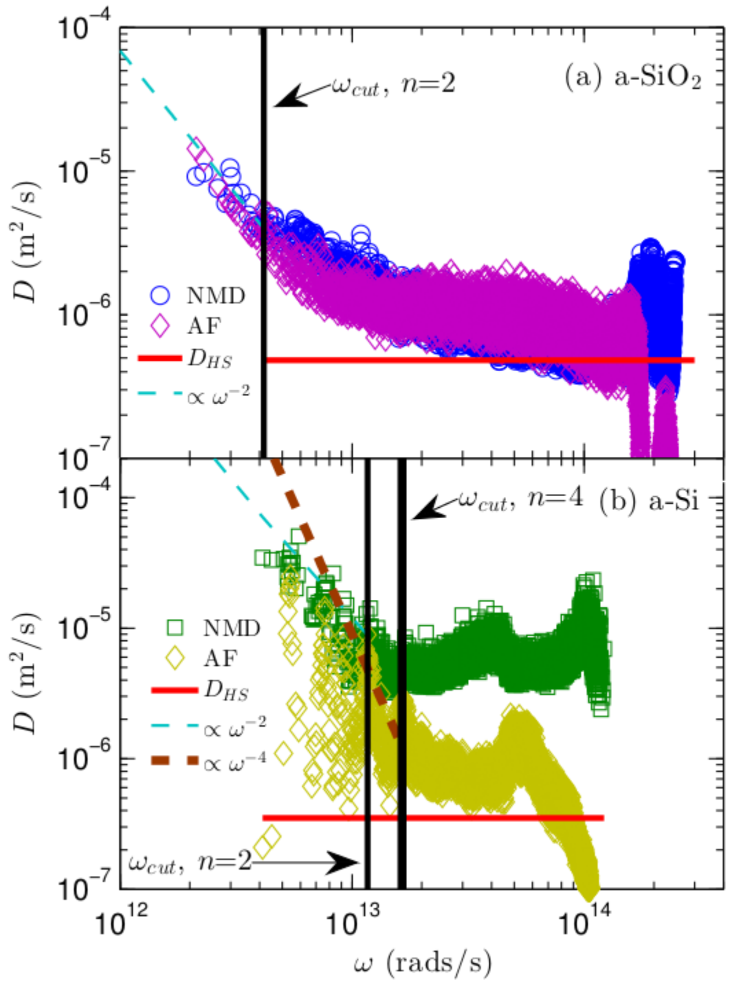


$$E^{T}\binom{\boldsymbol{\kappa}_{VC}}{\nu} = \left| \sum_{b} \hat{\boldsymbol{\kappa}}_{VC} \times e\binom{\boldsymbol{\kappa}=\mathbf{0} \quad b}{\nu \quad \alpha} \exp[i\boldsymbol{\kappa}_{VC} \cdot \boldsymbol{r}_0\binom{l=0}{b}] \right|^2$$

$$E^{L}\binom{\boldsymbol{\kappa}_{VC}}{\nu} = \left| \sum_{b} \hat{\boldsymbol{\kappa}}_{VC} \cdot e\binom{\boldsymbol{\kappa}=\mathbf{0} \quad b}{\nu \quad \alpha} \exp[i\boldsymbol{\kappa}_{VC} \cdot \boldsymbol{r}_0\binom{l=0}{b}] \right|^2$$

Vibrons: Lifetimes and Diffusivities





Mechanical Engineering