Evaluation of the Virtual Crystal Approximation for Predicting Alloy Vibrational Mode Properties and Thermal Conductivity

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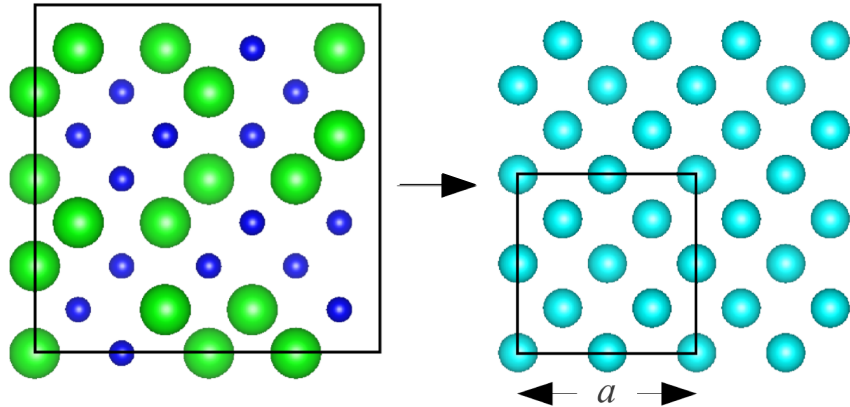Department of Mechanical Engineering
Carnegie Mellon University

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04/04/13

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Virtual Crystal Approximation

Gamma

VC

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

$$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} \frac{k_B}{V} D_{ph,\mathbf{n}}\begin{pmatrix} \boldsymbol{\kappa} \\ \nu \end{pmatrix}$$

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

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VC-ALD Diffusivities: Lifetimes

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

Perturbation theory:

Anharmonic Lattice Dynamics (**ALD**)

Phonon-Defect[1]

Matthiessen's Rule:

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

[1]S. Tamura, Phys. Rev. B 27, 858866 (1983)

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VC-ALD Diffusivities: Group Velocity

$$D_{ph,\mathbf{n}}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right) = v_{g,\mathbf{n}}^2\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right)\tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right)$$

$$\mathbf{V}_{g,\mathbf{n}}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right) = \frac{\partial\omega\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right)}{\partial\boldsymbol{\kappa}}$$

$$D_{ph}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\\nu\end{smallmatrix}\right) \approx 0$$

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

[1]Ann. Rev. of Phys. Chem. 39, 93121 (1988)

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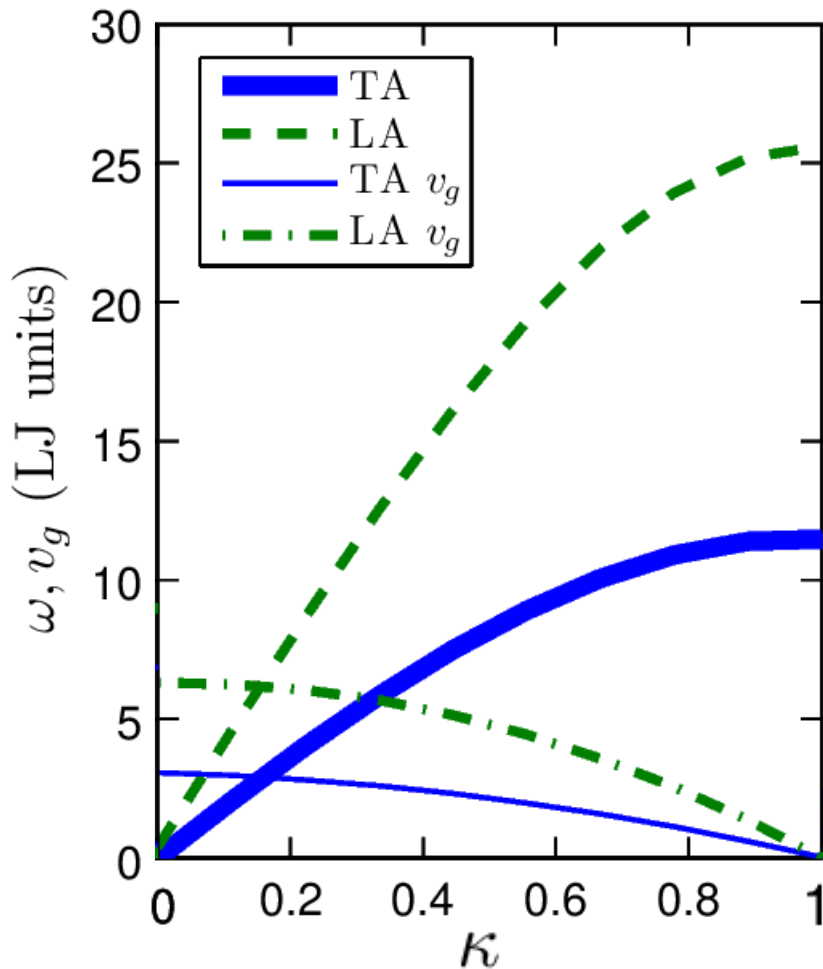
VC-ALD: experimental accuracy

Density Functional Theory (DFT)   +   **(VC-ALD)**
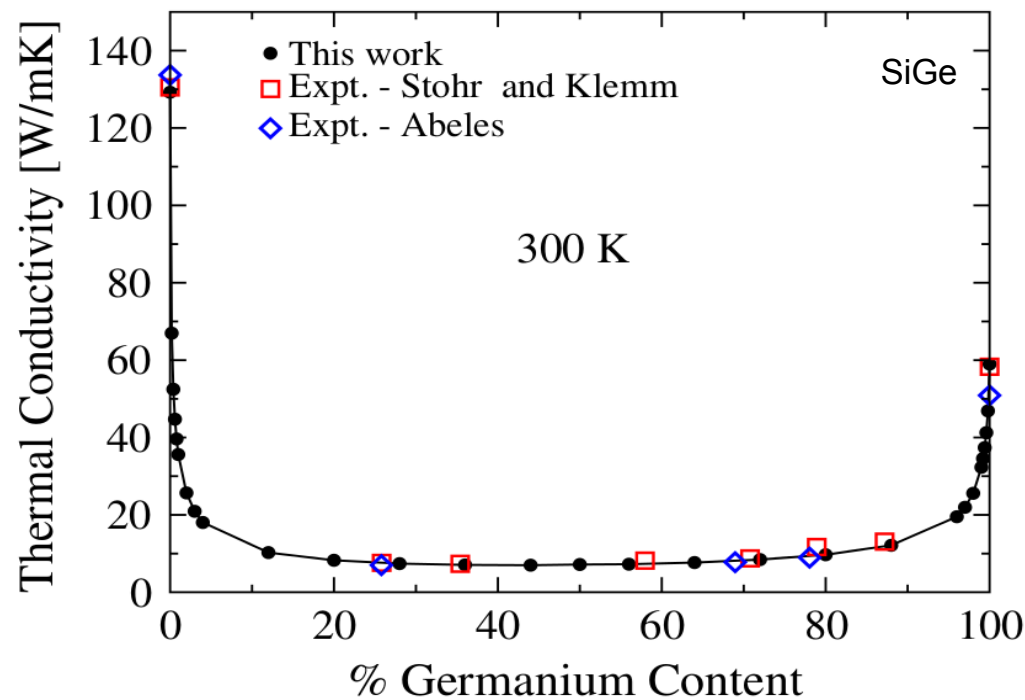
PRL 106, 045901 (2011)
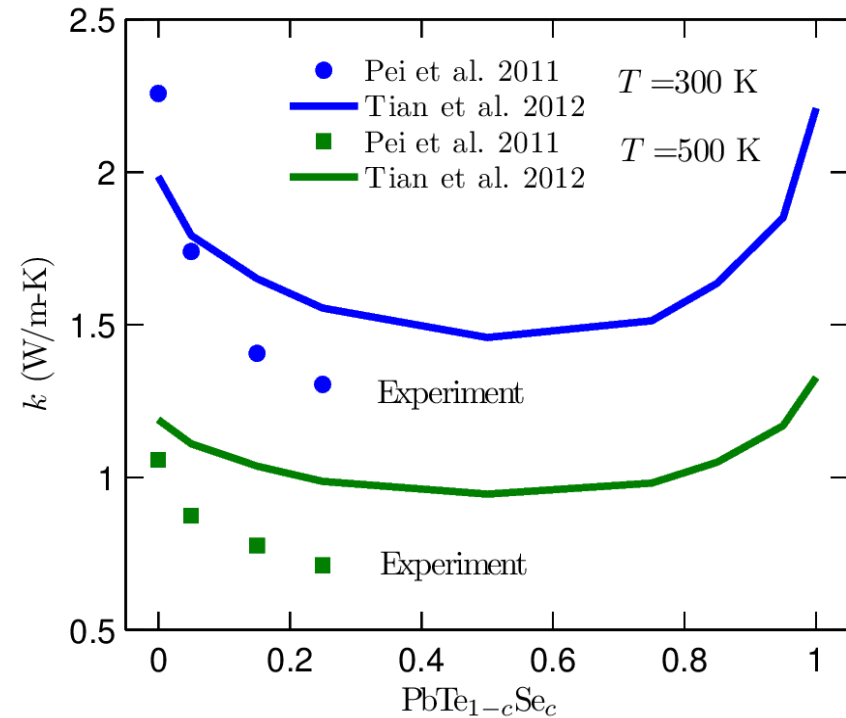
PRB 85, 184303 (2012)
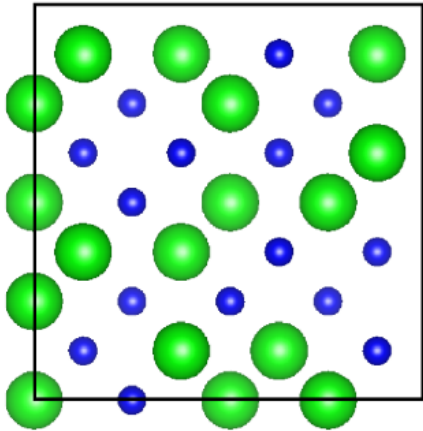
Explicit disorder: VC vs Gamma

Gamma

VC

LJ Argon Alloys

(a) $c = 0.05$

VC
Gamma
$\propto \omega^2$

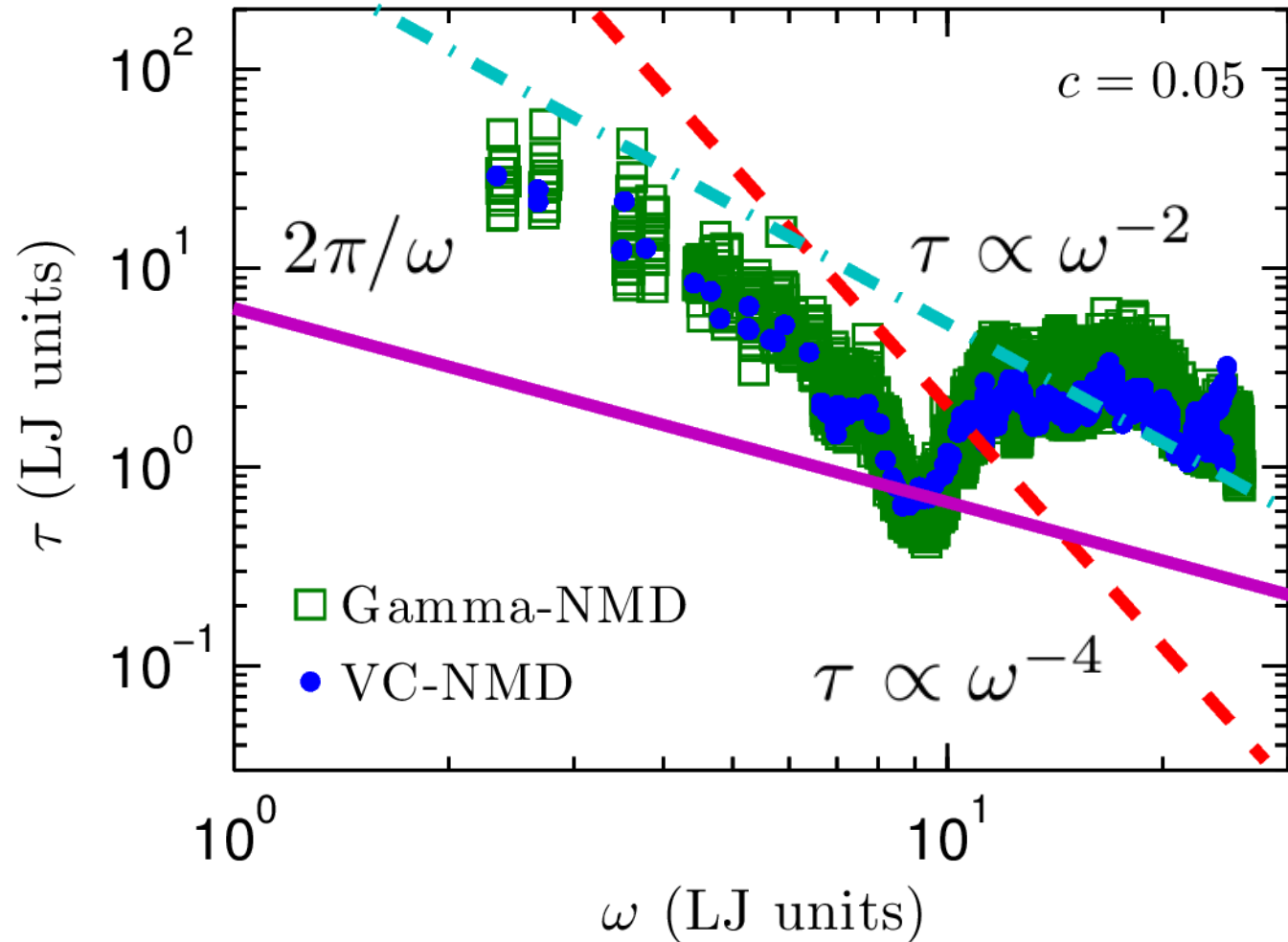(c) $c = 0.5$

DOS (arbitrary units)
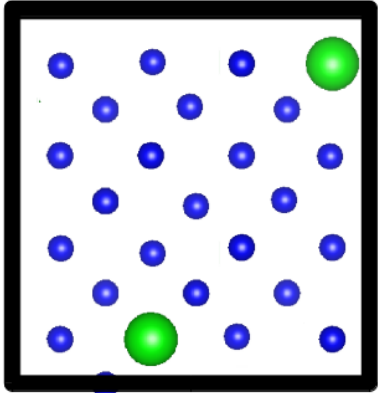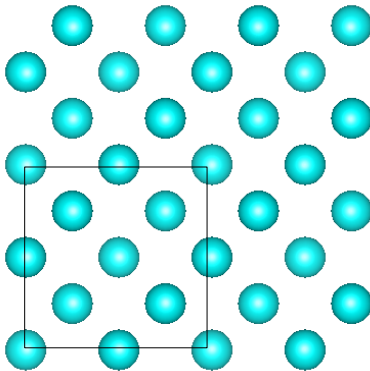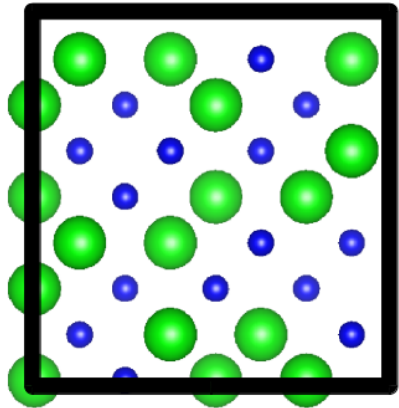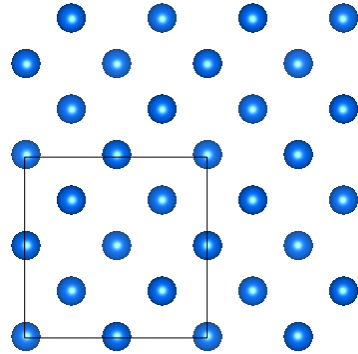
ω (LJ units)
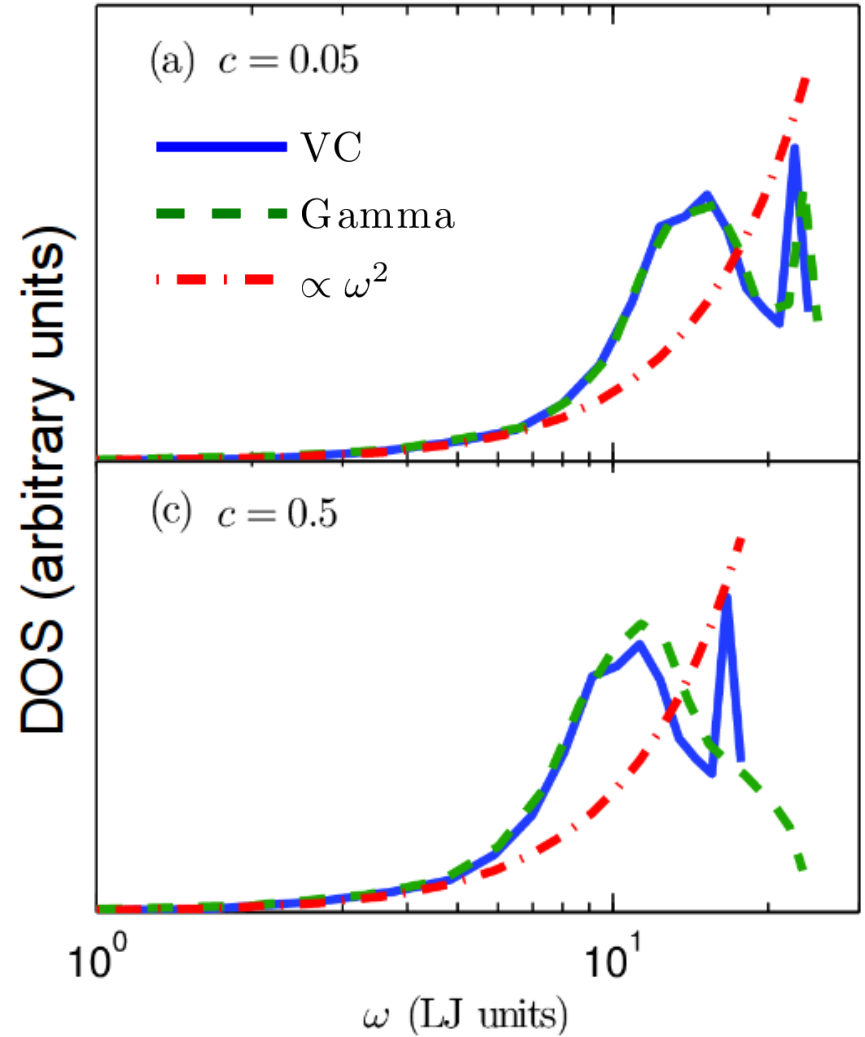
Explicit disorder: NMD
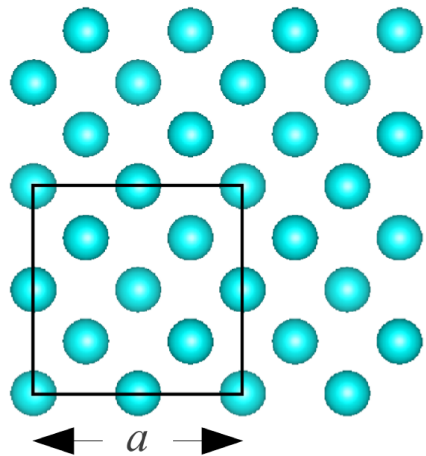
Normal Mode Decomposition (**NMD**): Molecular Dynamics

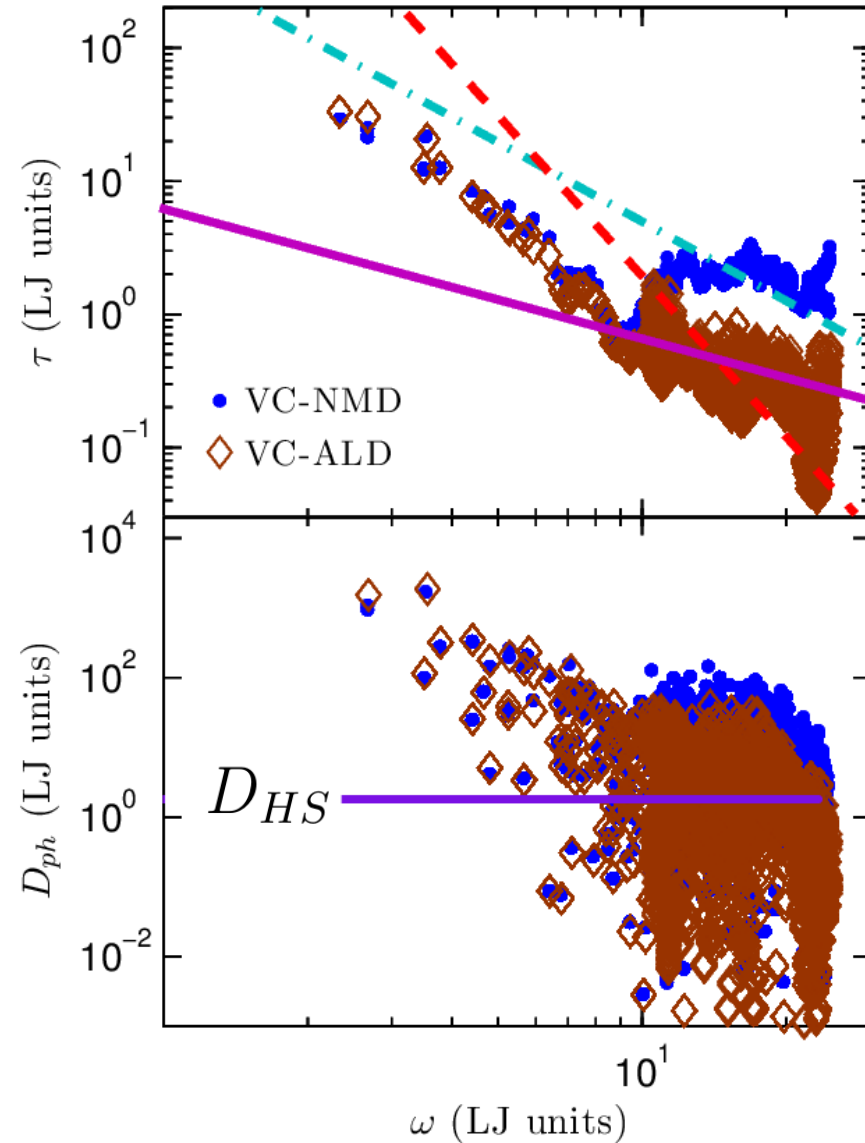**Disordered Supercell**

LJ Argon Alloys, $T = 10$ K

$c = 0.05$

$2\pi/\omega$

$\tau \propto \omega^{-2}$

$\tau \propto \omega^{-4}$

τ (LJ units)

ω (LJ units)

□ Gamma-NMD
● VC-NMD

VC-NMD vs VC-ALD

LJ Argon Alloys, $T = 10$ K

$c = 0.05$

◇ VC-ALD
● VC-NMD

τ (LJ units)

ω (LJ units)

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VC Diffusivities

LJ Argon Alloys, $T = 10$ K

$$D_{ph}\begin{pmatrix} \boldsymbol{\kappa} \\ \nu \end{pmatrix} \approx 0$$
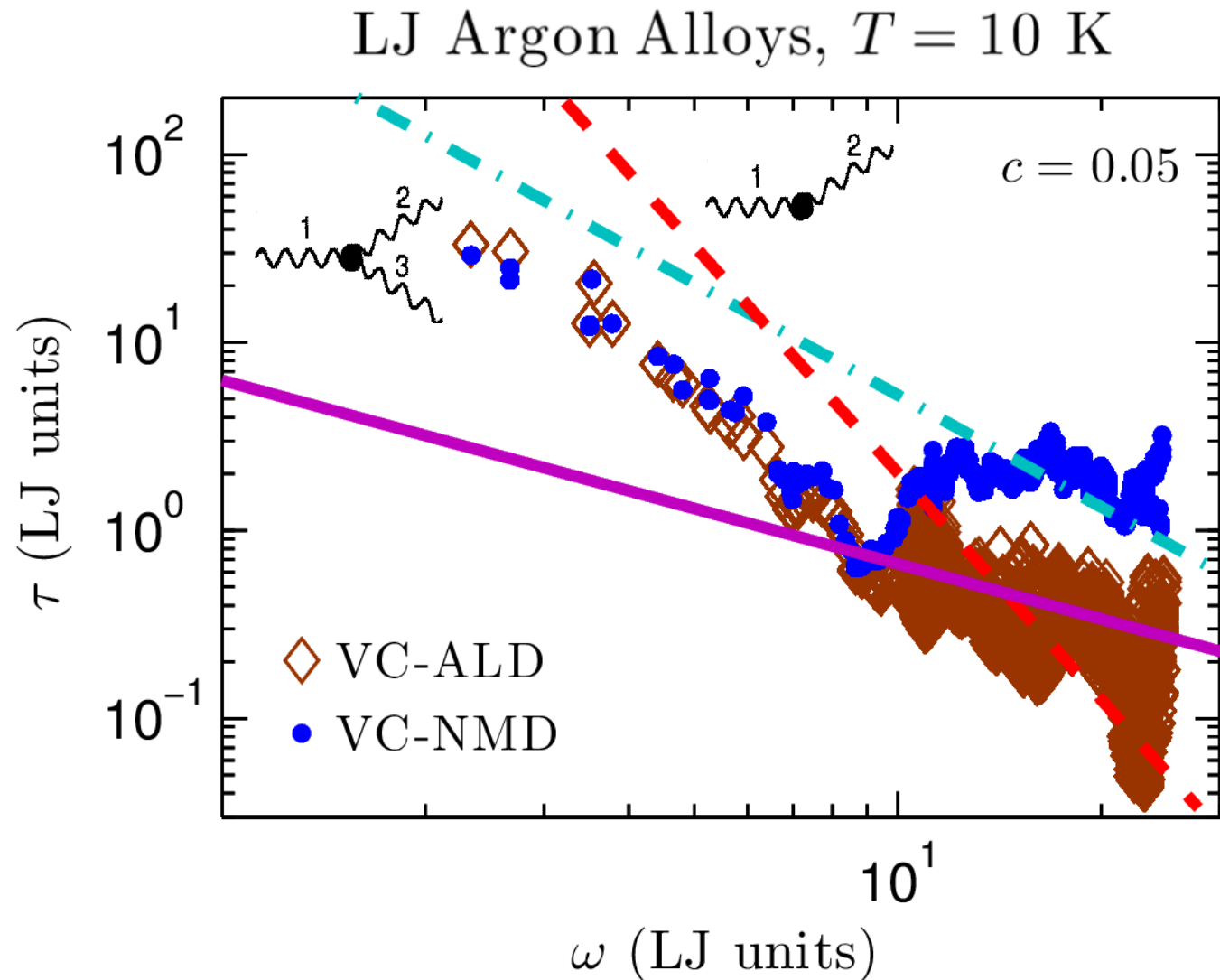
$$D_{HS} = \frac{1}{3} v_s a$$

AF Diffusivities

Allen-Feldman (**AF**) Theory:

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

LJ Argon

Legend: ○ AF $c=0.5$, ● AF amorphous

D_{HS}

Axes: D_{AF} (LJ units) vs ω (LJ units)
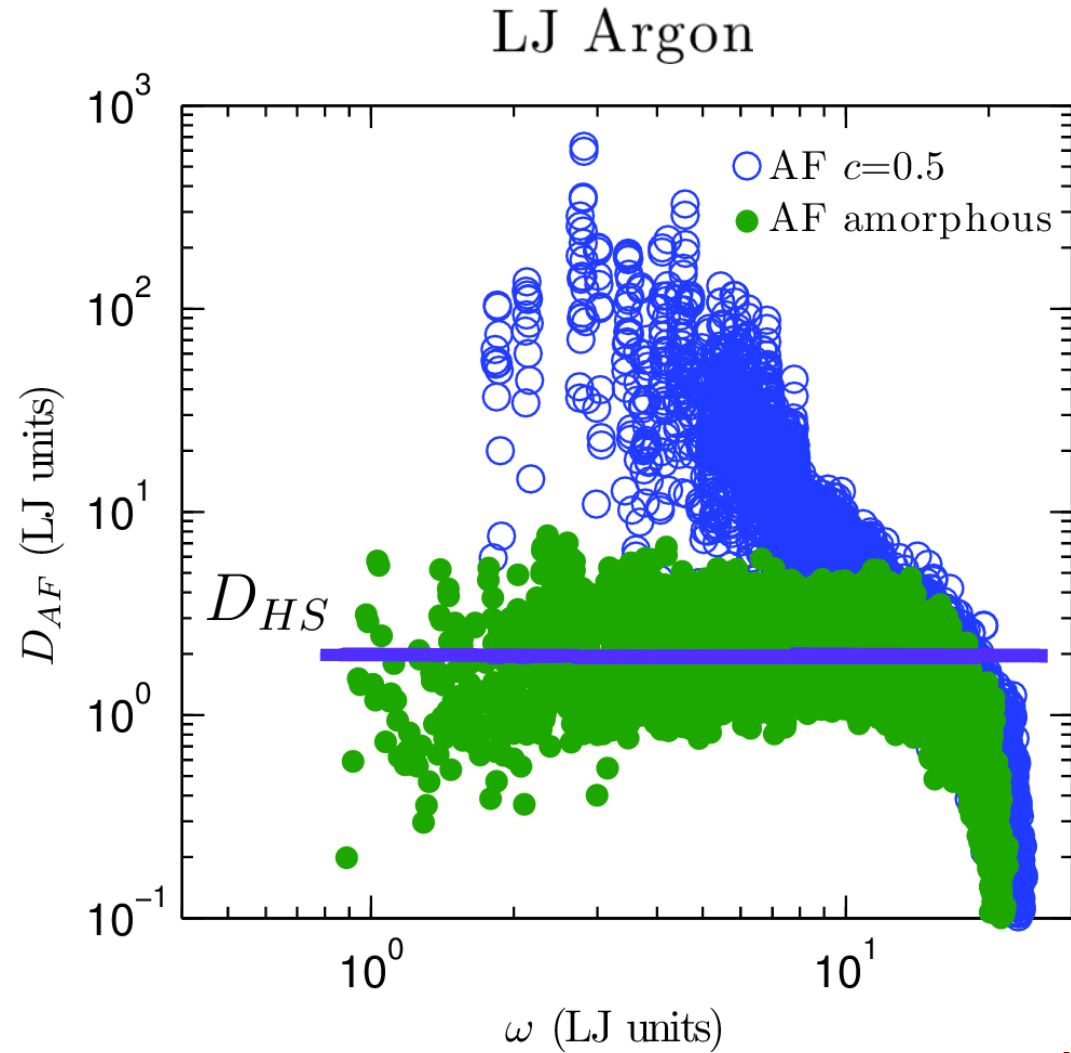
AF Diffusivities

LJ Argon Alloys, $T = 10$ K

LJ Argon

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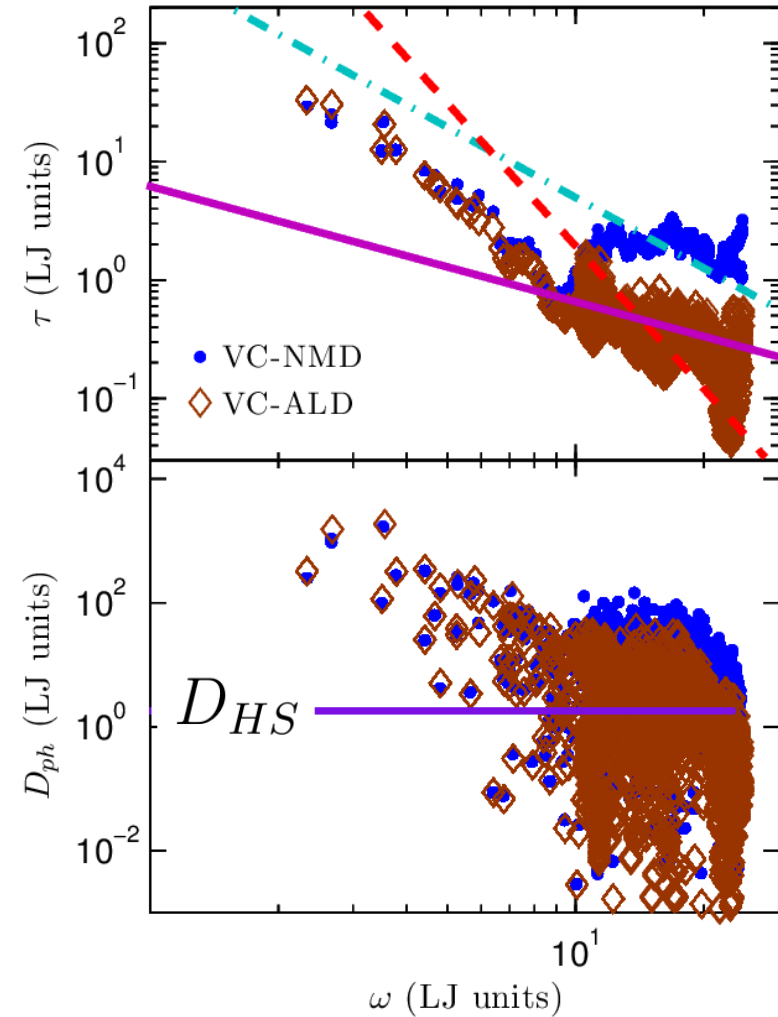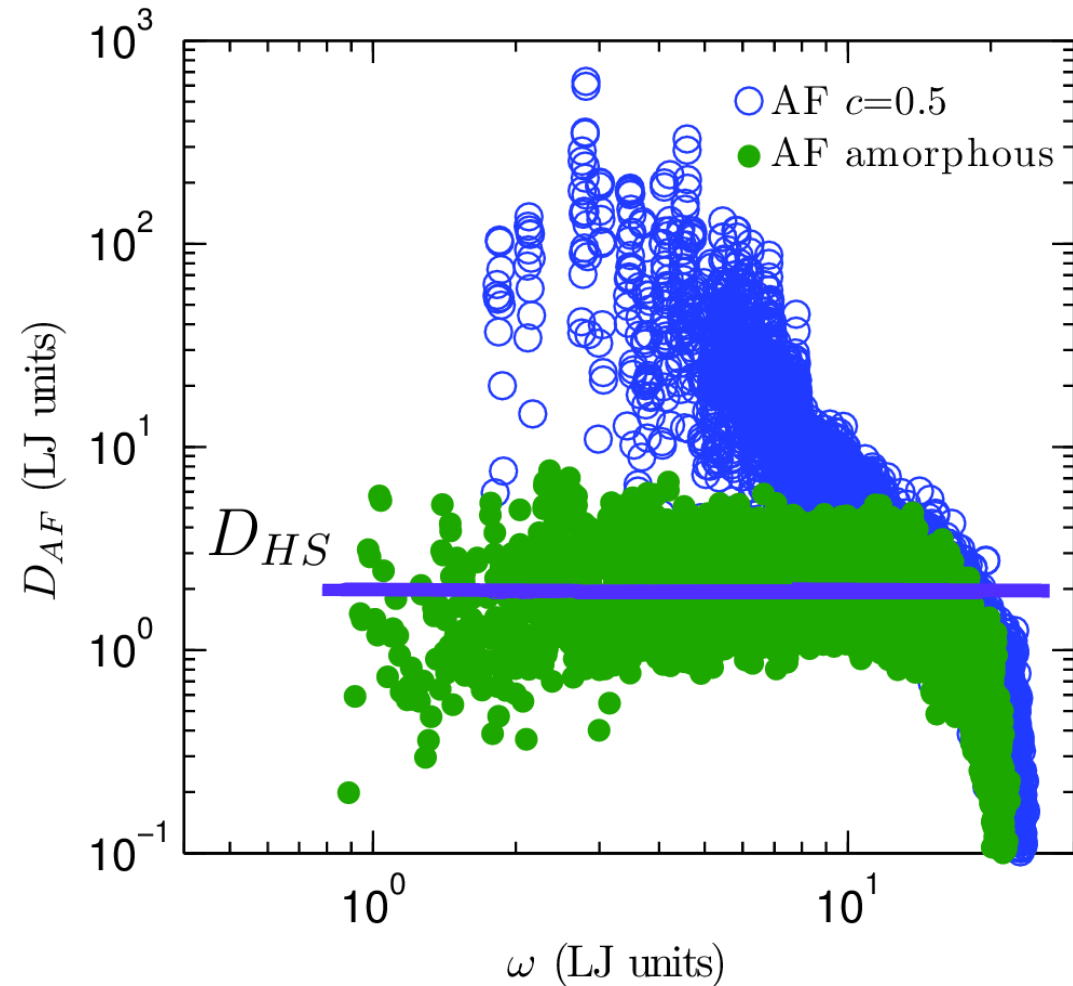
Thermal conductivity

MD-based Green-Kubo (**GK**)

High-scatter adjustment*:

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

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

LJ Argon and Alloys, $T = 10$ K

$T = 10$ K

GK
VC-NMD
VC-ALD

k (W/m-K)

10^0

10^{-1}

0   0.1   0.2   0.3   0.4   0.5
c

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Thermal conductivity

MD-based Green-Kubo (**GK**)

High-scatter adjustment*:

$$D_{ph}\begin{pmatrix}\boldsymbol{\kappa}\\\nu\end{pmatrix} < D_{HS}$$

$$D_{ph}\begin{pmatrix}\boldsymbol{\kappa}\\\nu\end{pmatrix} = D_{HS}$$

LJ Argon and Alloys, $T = 10$ K

$T = 10$ K

- GK
- VC-NMD*
- VC-ALD*

k (W/m-K)

c
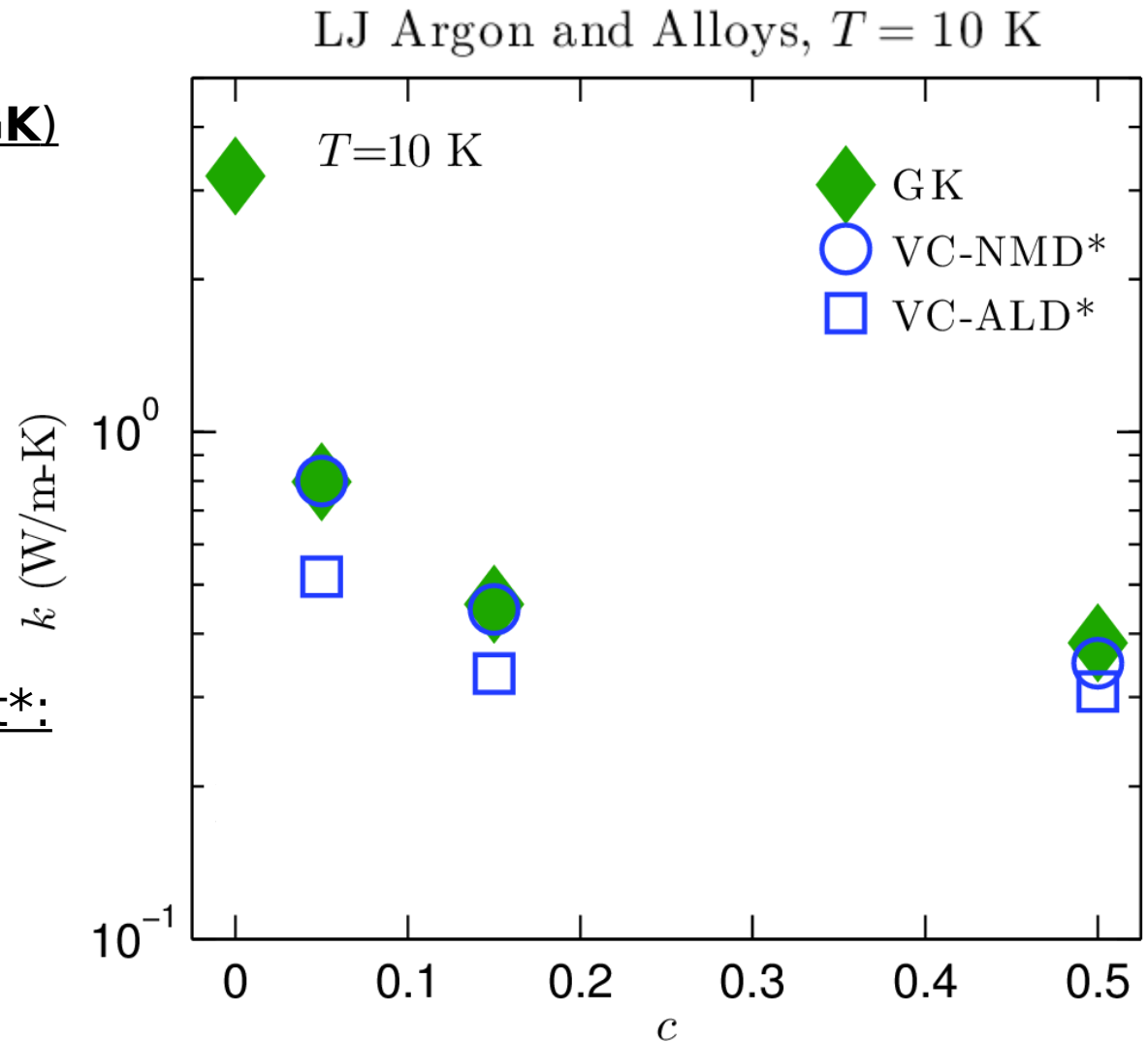
Thermal conductivity spectrum

LJ Argon and Alloys, $T = 10$ K
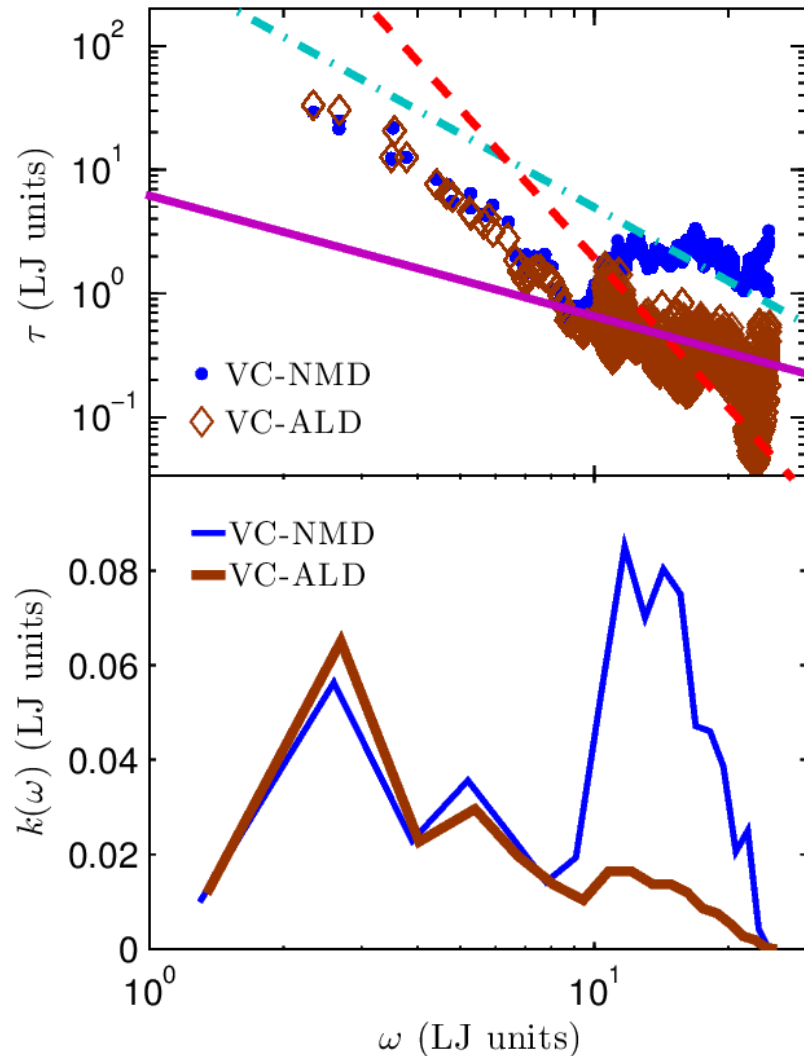
LJ Argon and Alloys, $T = 10$ K
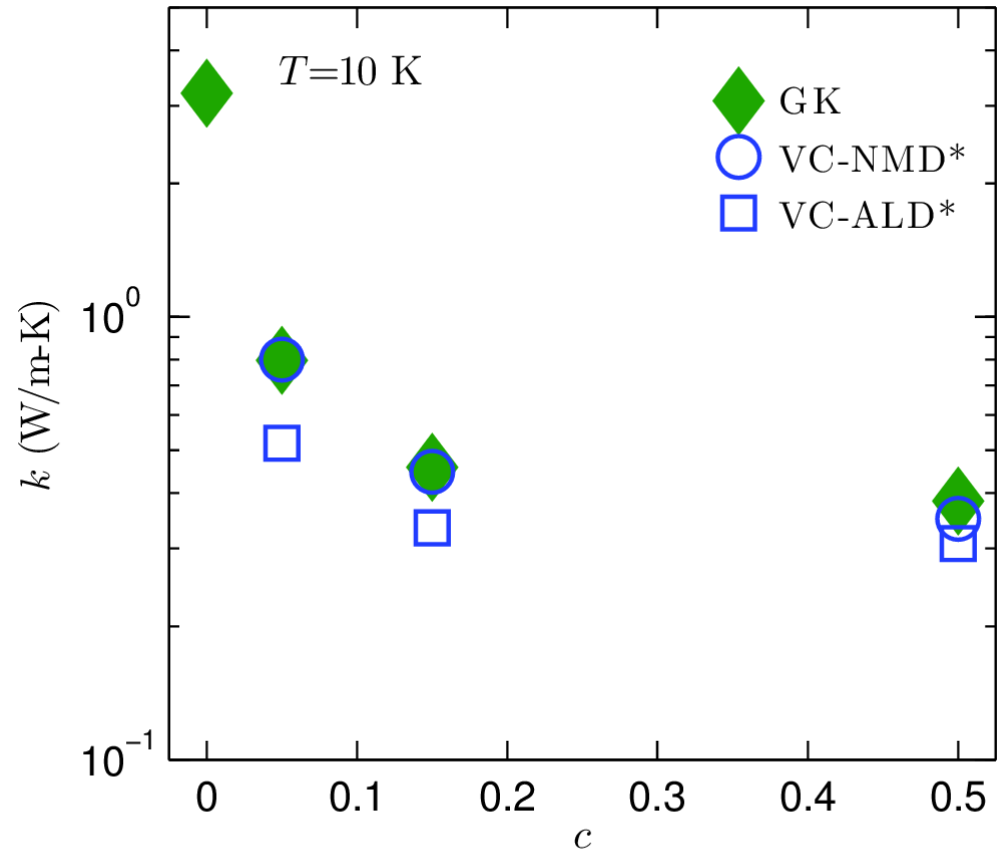
Summary

VC approximation underpredicts mode group velocities at high frequency.

$$D_{ph}\binom{\boldsymbol{\kappa}}{\nu} \approx 0 \qquad D_{HS} = \frac{1}{3}v_s a$$

VC-ALD underpredicts lifetimes at high-frequency.

Breakdown of VC-ALD method is likely for materials near HS limit.

LJ Argon Alloys, $T = 10$ K

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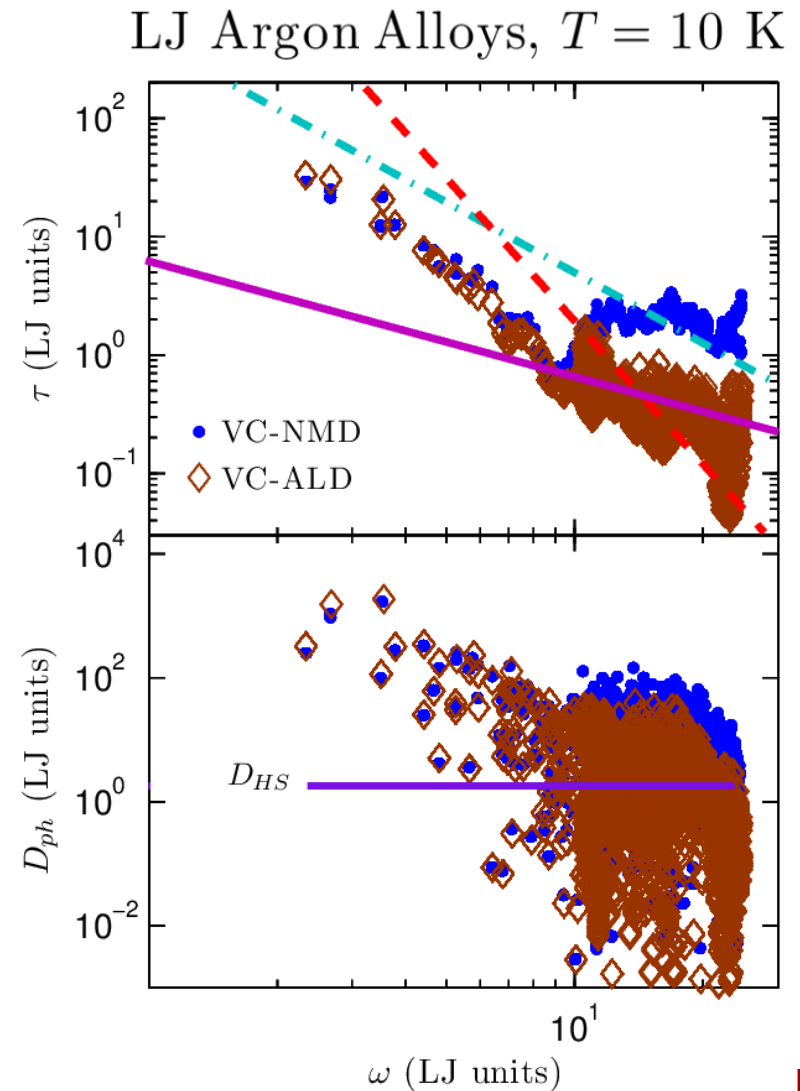
Explicit disorder: Structure Factor
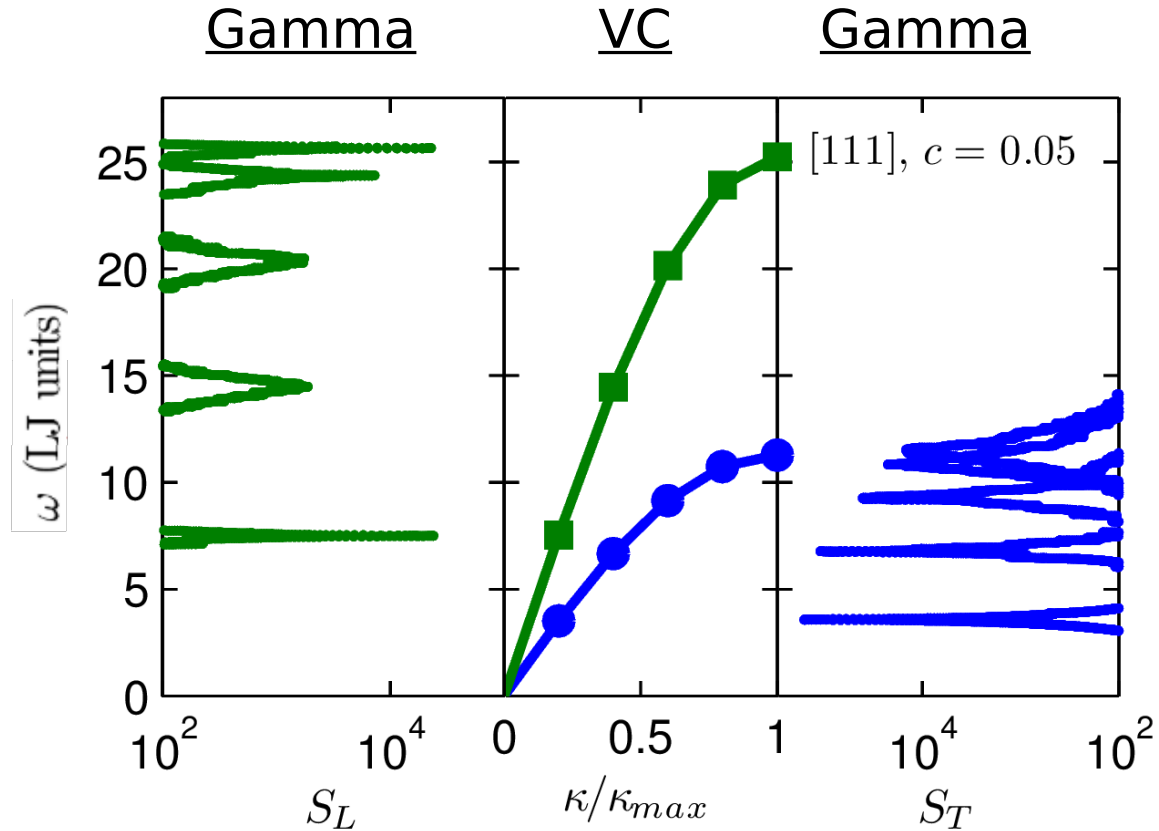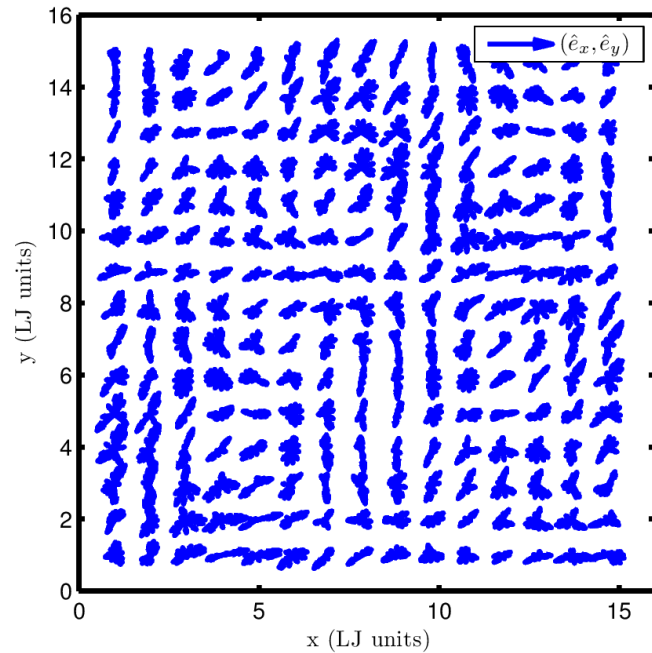
HS/IR Limit

$$D_{IR} = \frac{2\pi}{3}\frac{v_s^2}{\omega}$$
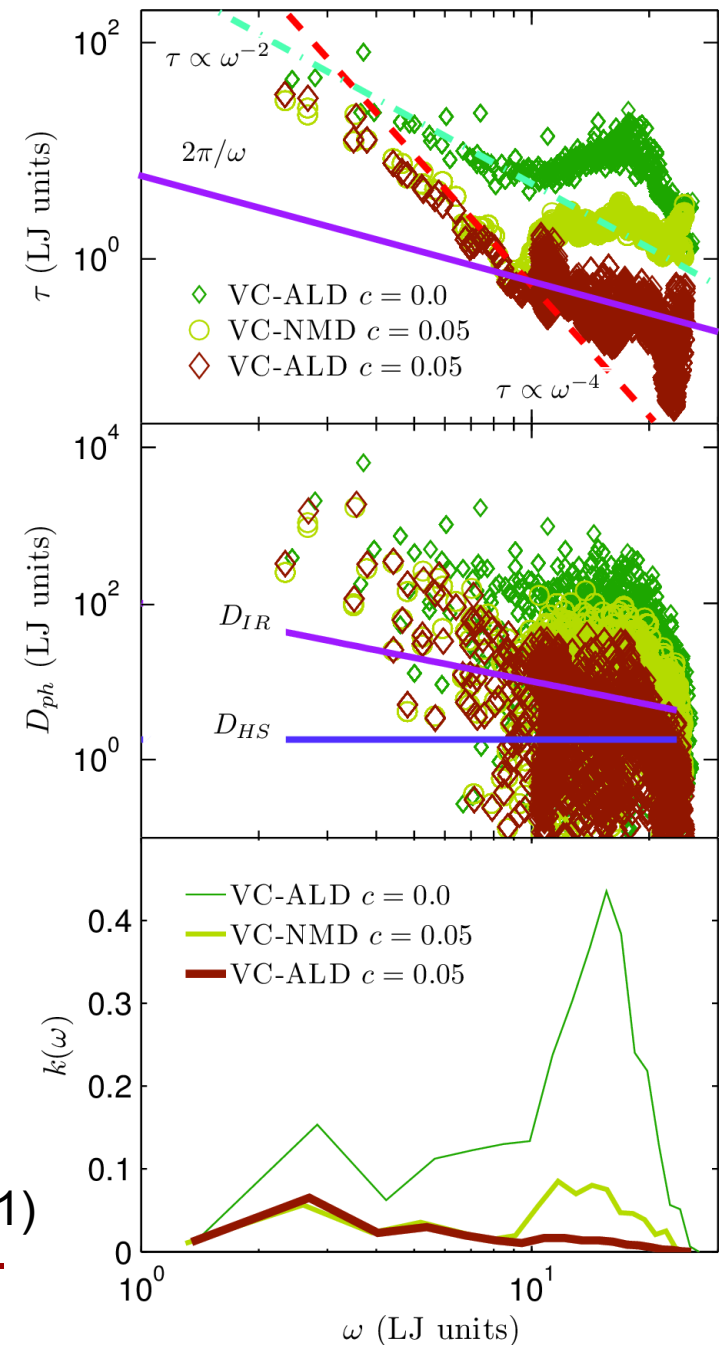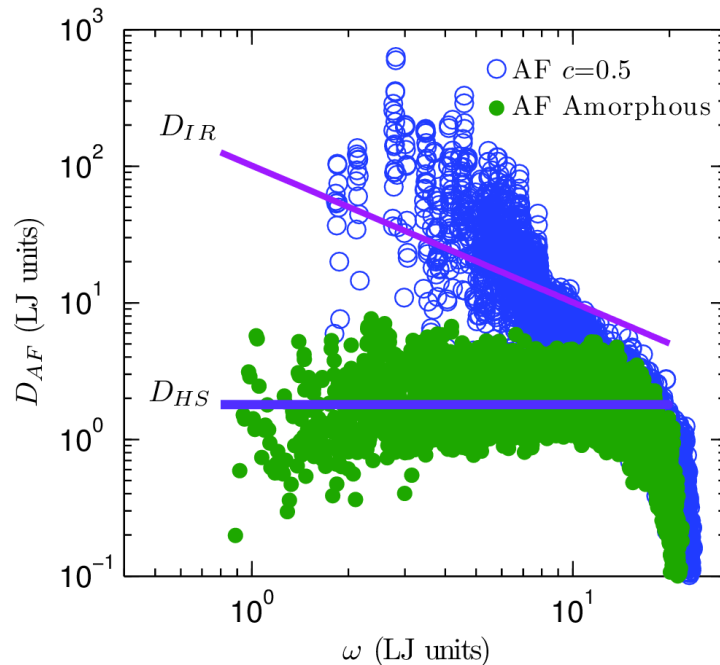
P. Sheng and M. Zhou, Science 253, 539542 (1991)

Thermal conductivity: SW silicon alloy
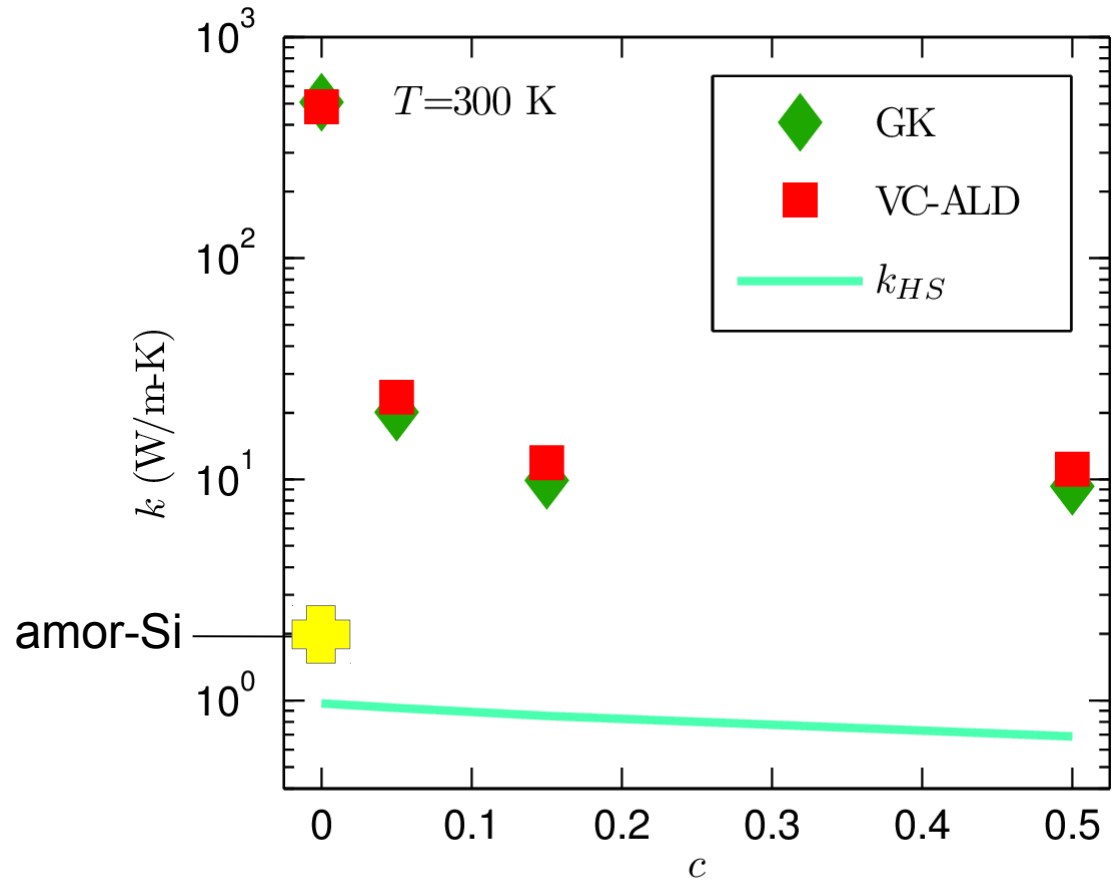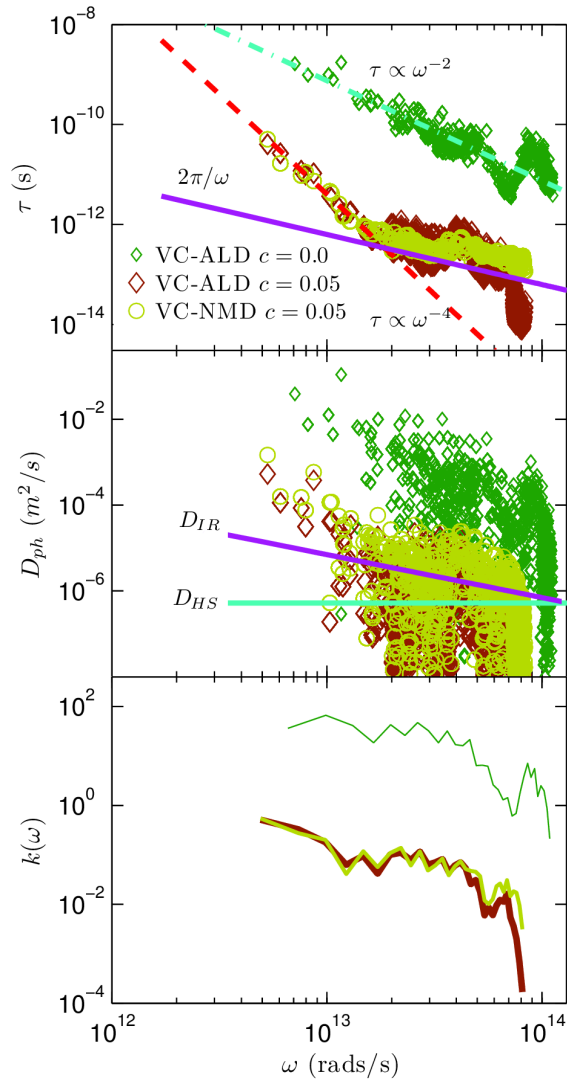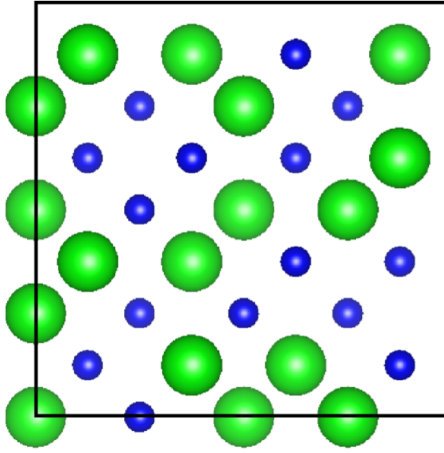
Gamma modes

$$e\begin{pmatrix} \boldsymbol{\kappa}=\mathbf{0} & b \\ \nu & \alpha \end{pmatrix}$$

(a) disordered supercell
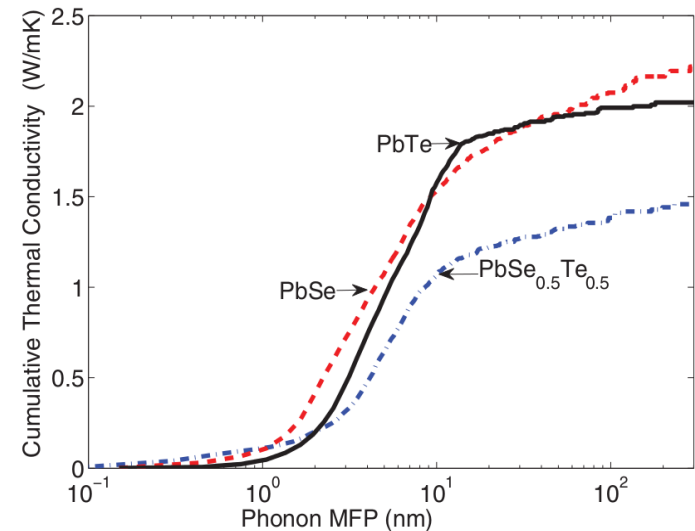
DOS (arbitrary units)
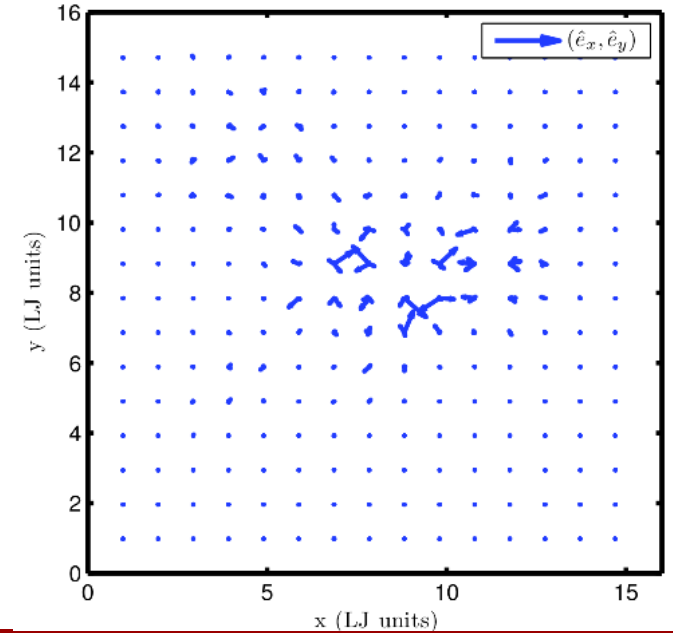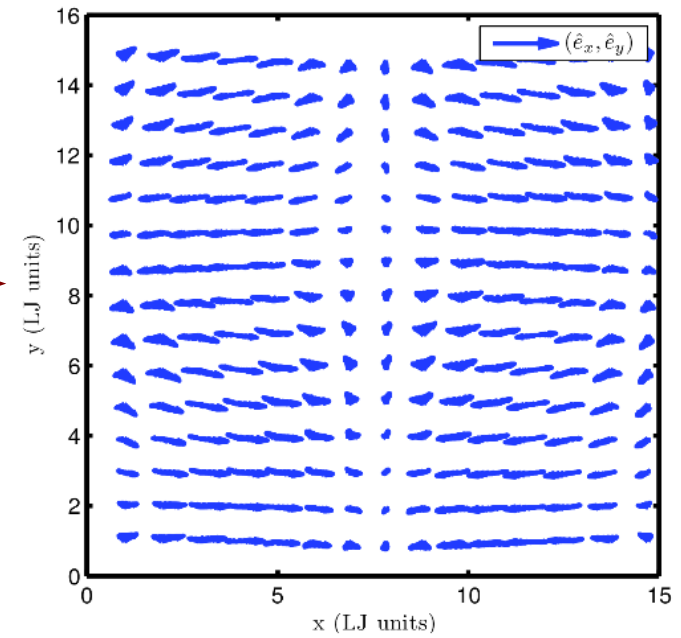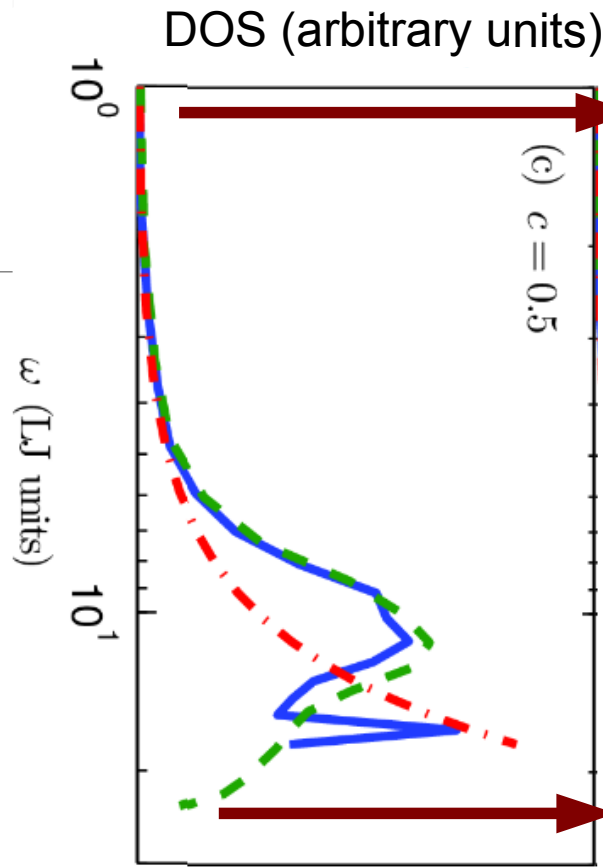
NMD using VC modes
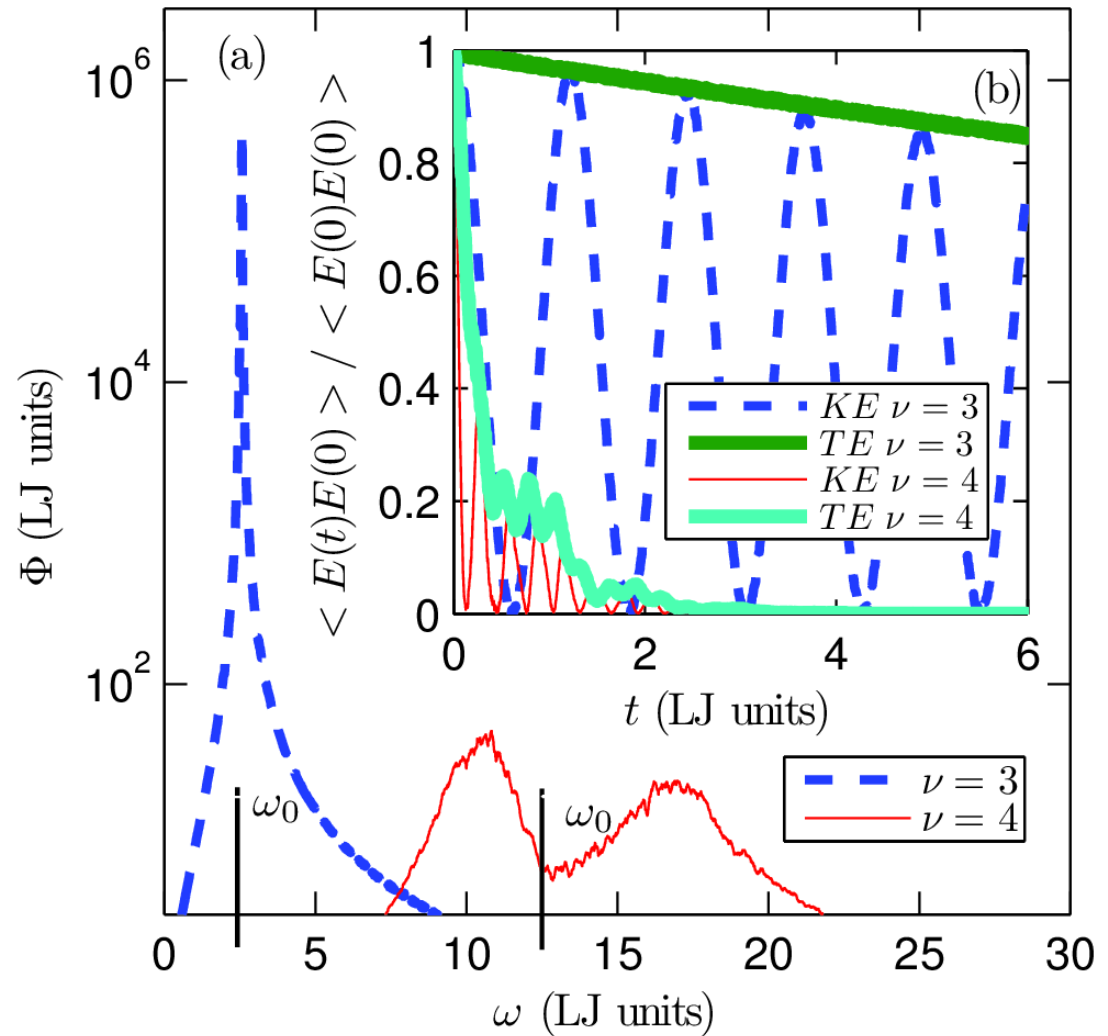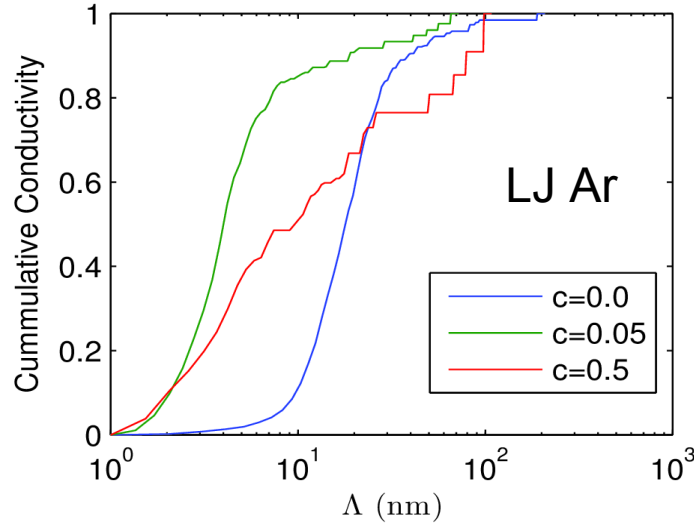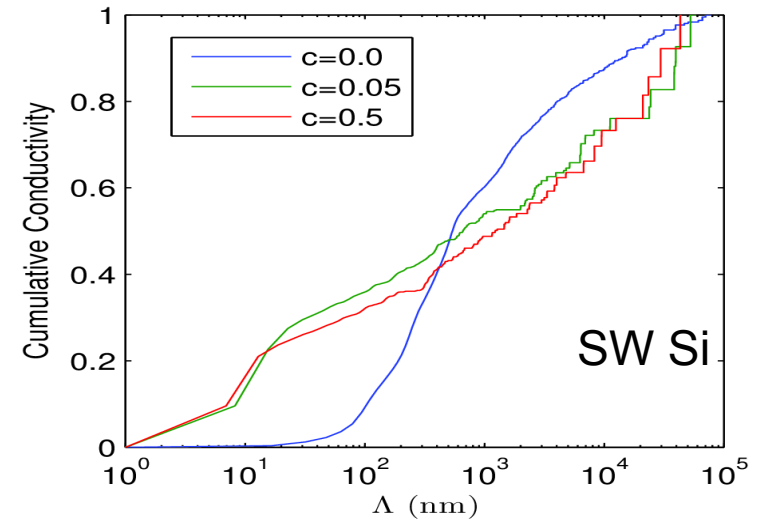
Phonon Spectrum: LJ Ar vs SW Si
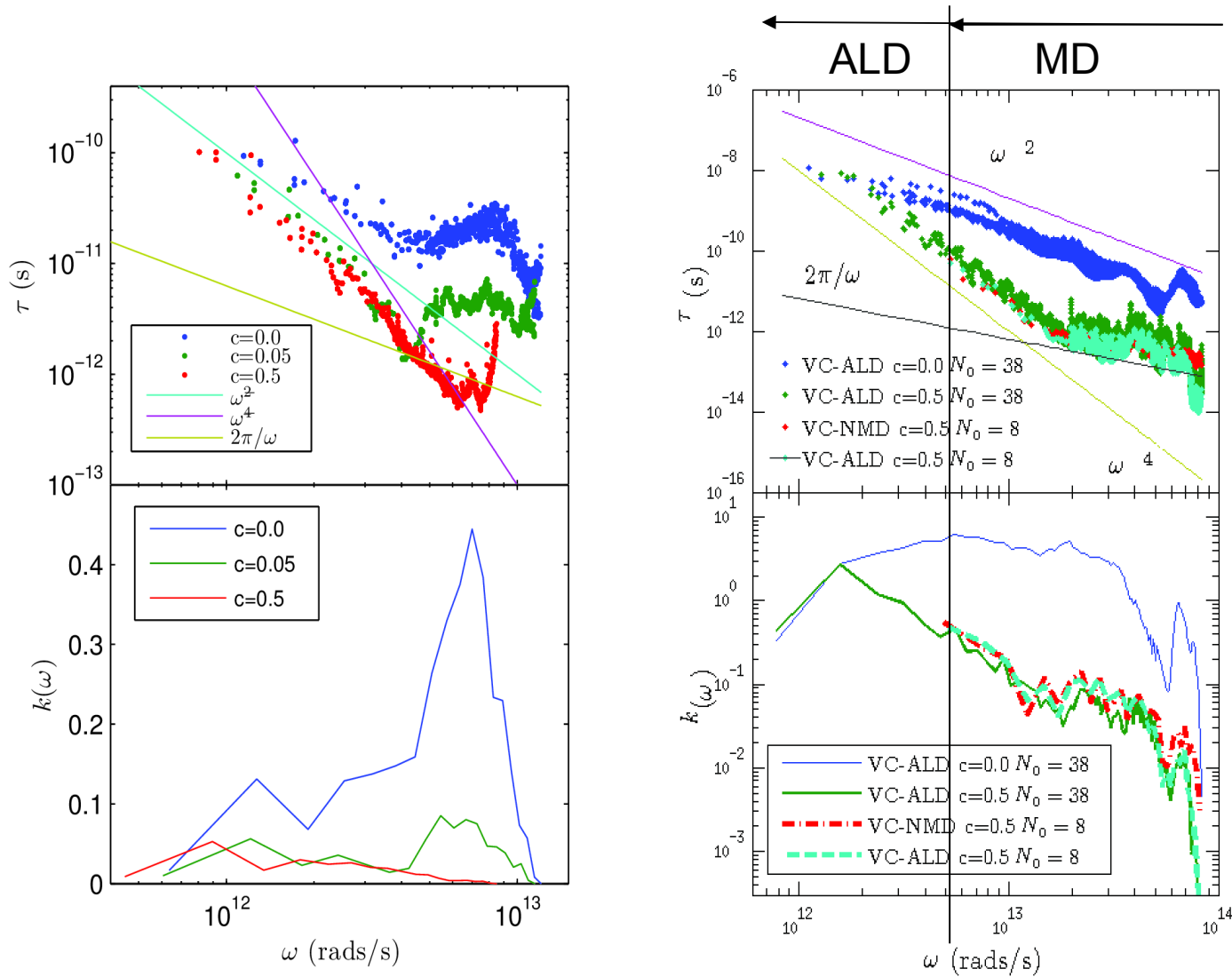
Conductivity Accumulation

SW Si

LJ Ar

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