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

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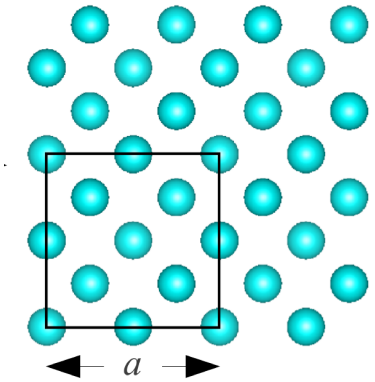
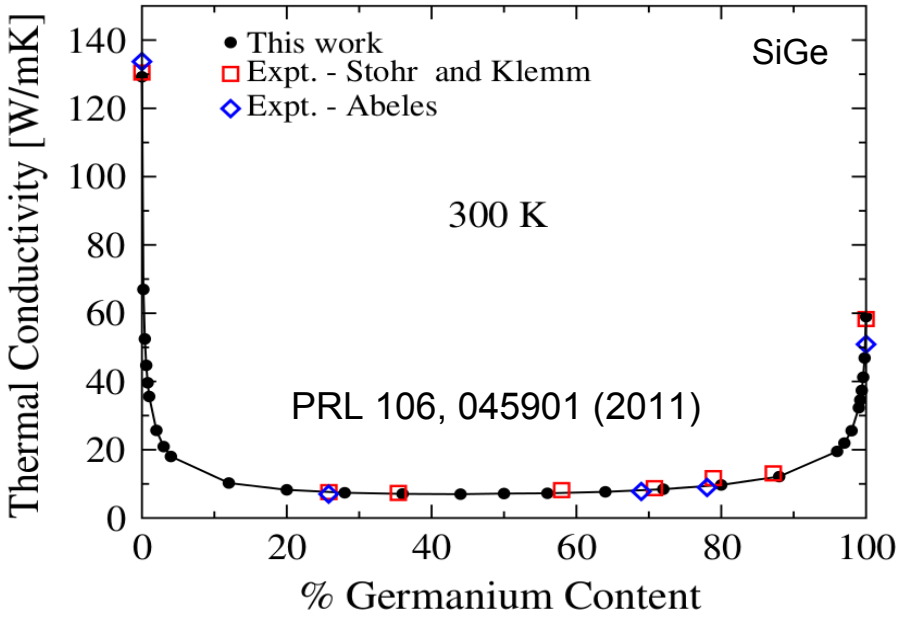
04/04/13

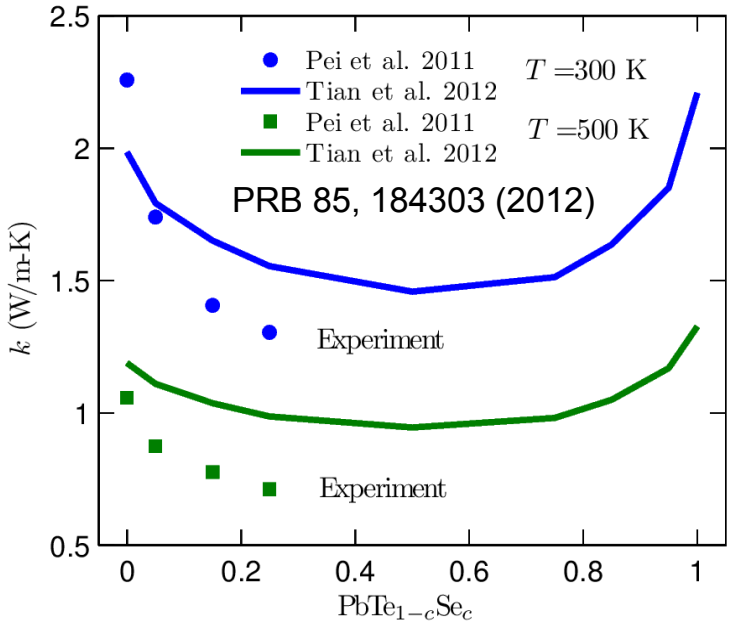
Motivation: experimental accuracy

Density Functional Theory (DFT) + **(VC-ALD)**

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



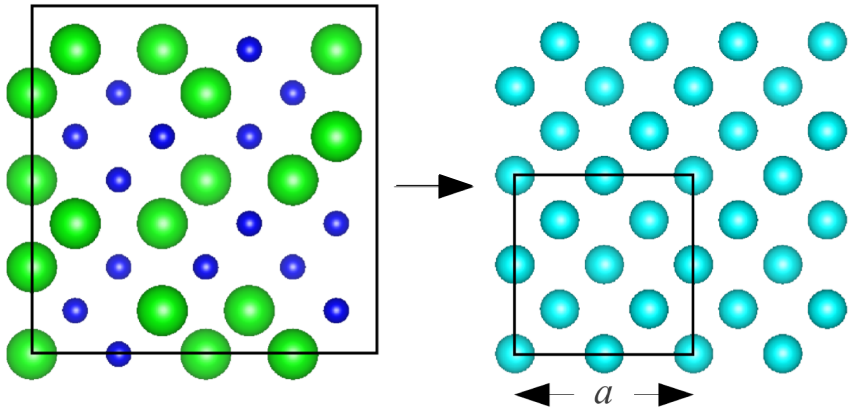




Virtual Crystal Approximation

Gamma

VC



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

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

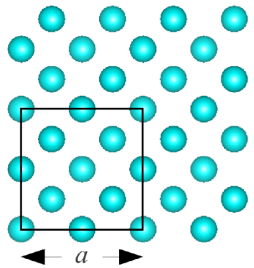
$$D_{ph,\mathbf{n}}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = v^2_{g,\mathbf{n}}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)$$

B. Abeles, Phys. Rev. 131, 19061911 (1963)

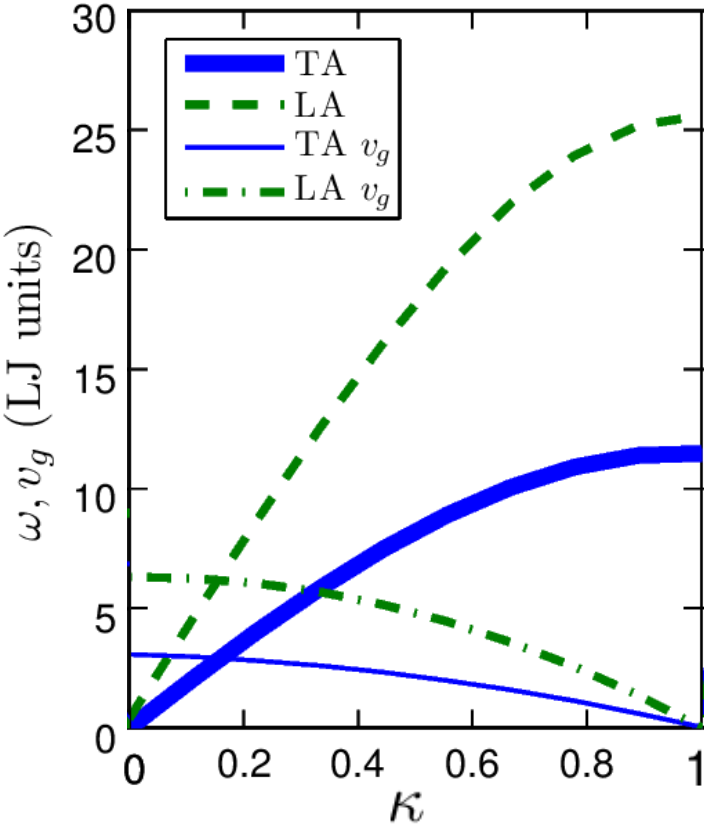
VC-ALD Diffusivities

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

VC Unit Cell



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

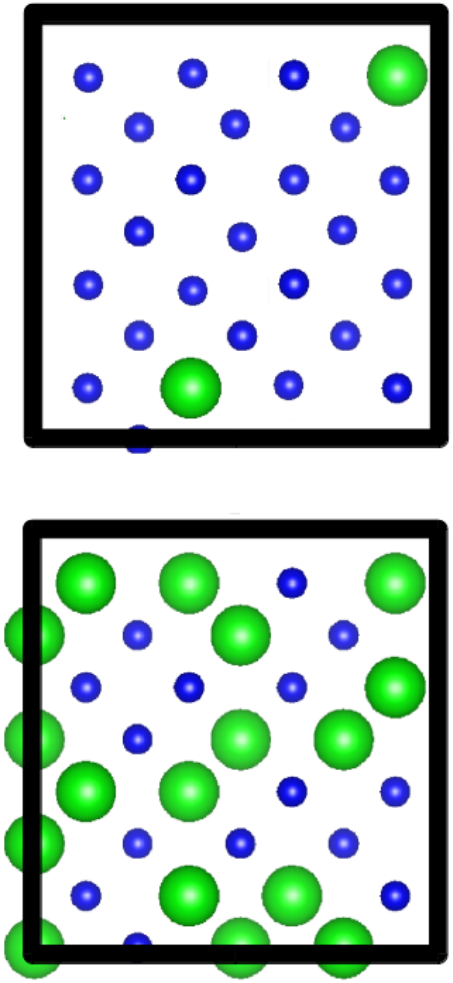


Matthiessen's Rule

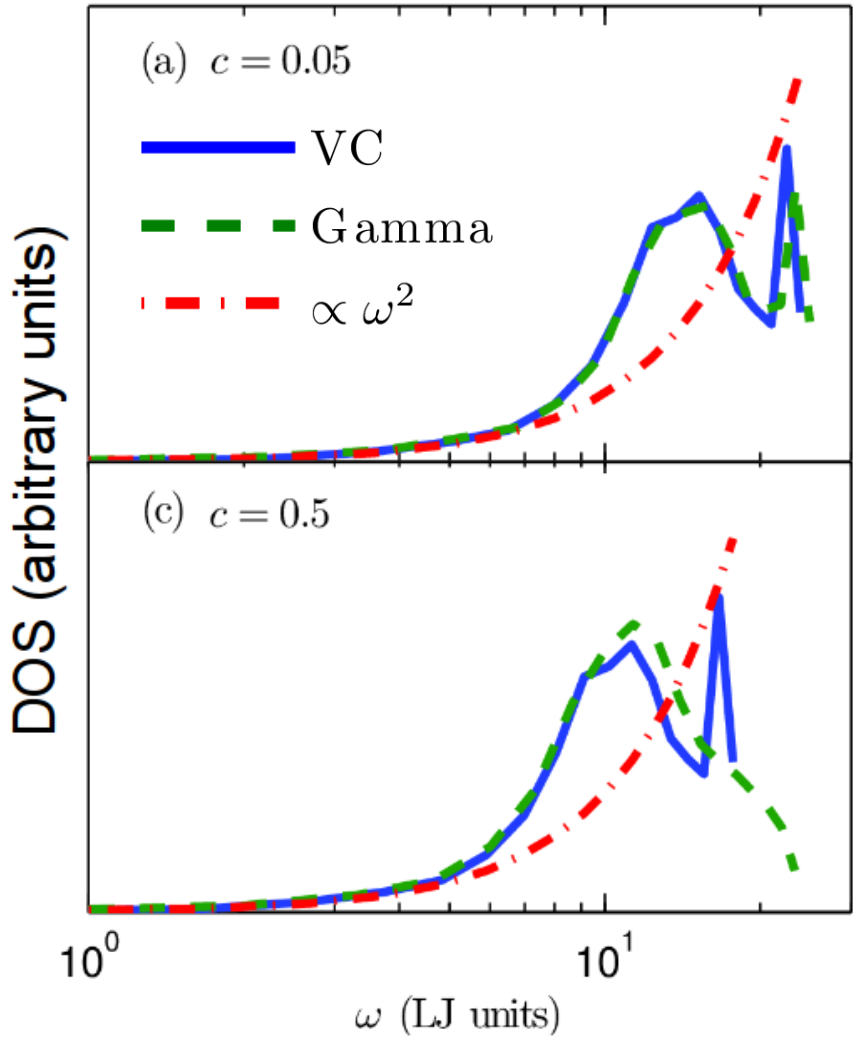
$$\frac{1}{\tau\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)} = \frac{1}{\tau_{p-p}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)} + \frac{1}{\tau_{p-d}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)}$$

Explicit disorder: VC vs Gamma

Gamma



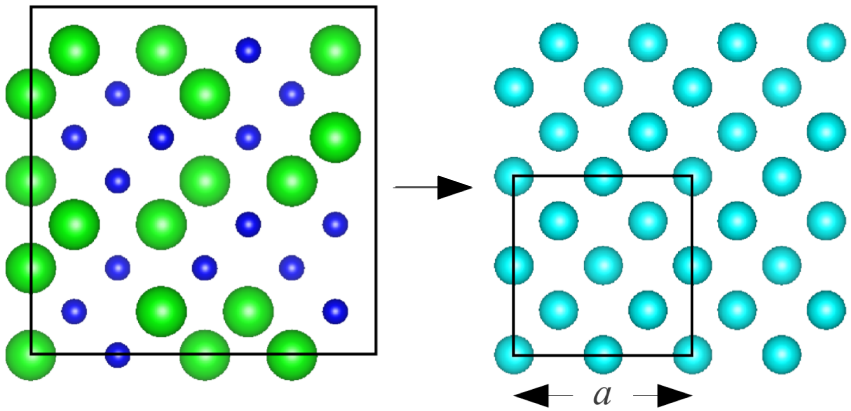
Lennard-Jones Argon Alloys



Explicit disorder: Structure Factor

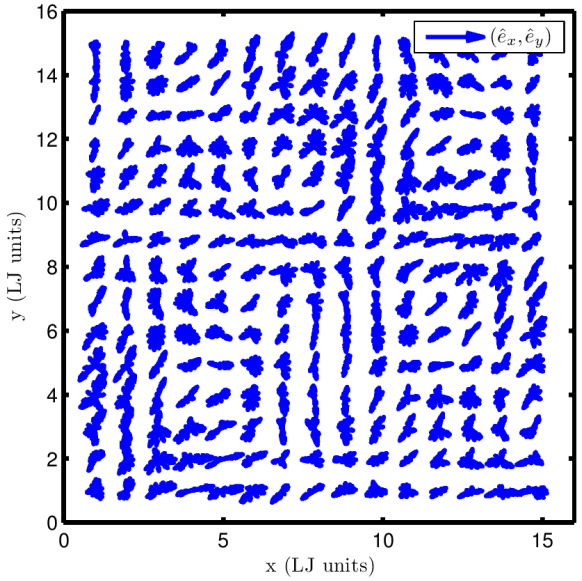
Gamma

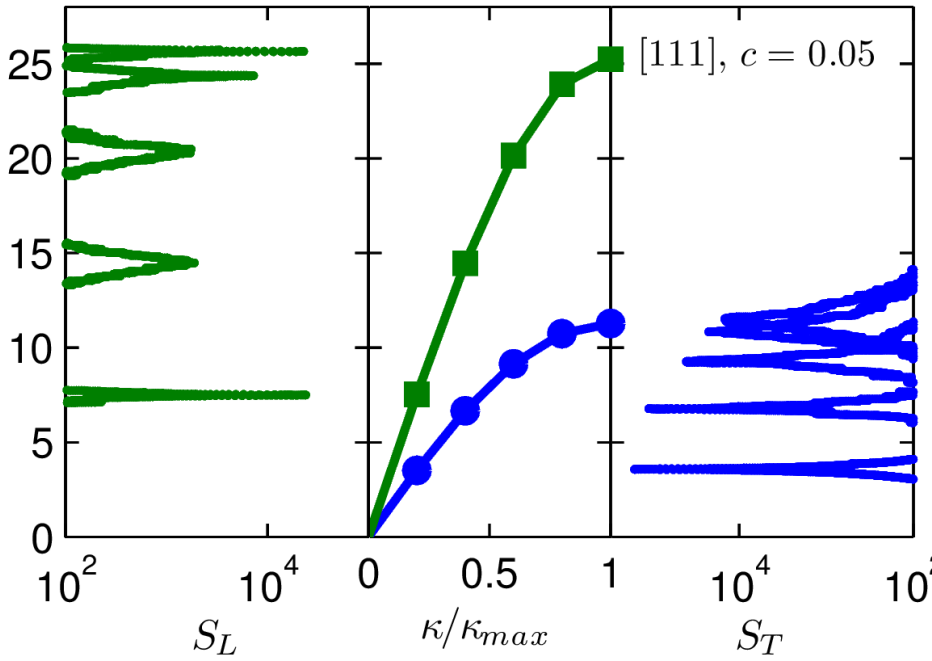
VC



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

Gamma VC Gamma

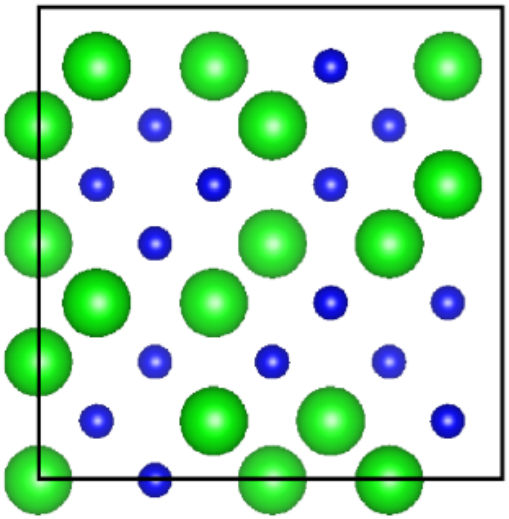




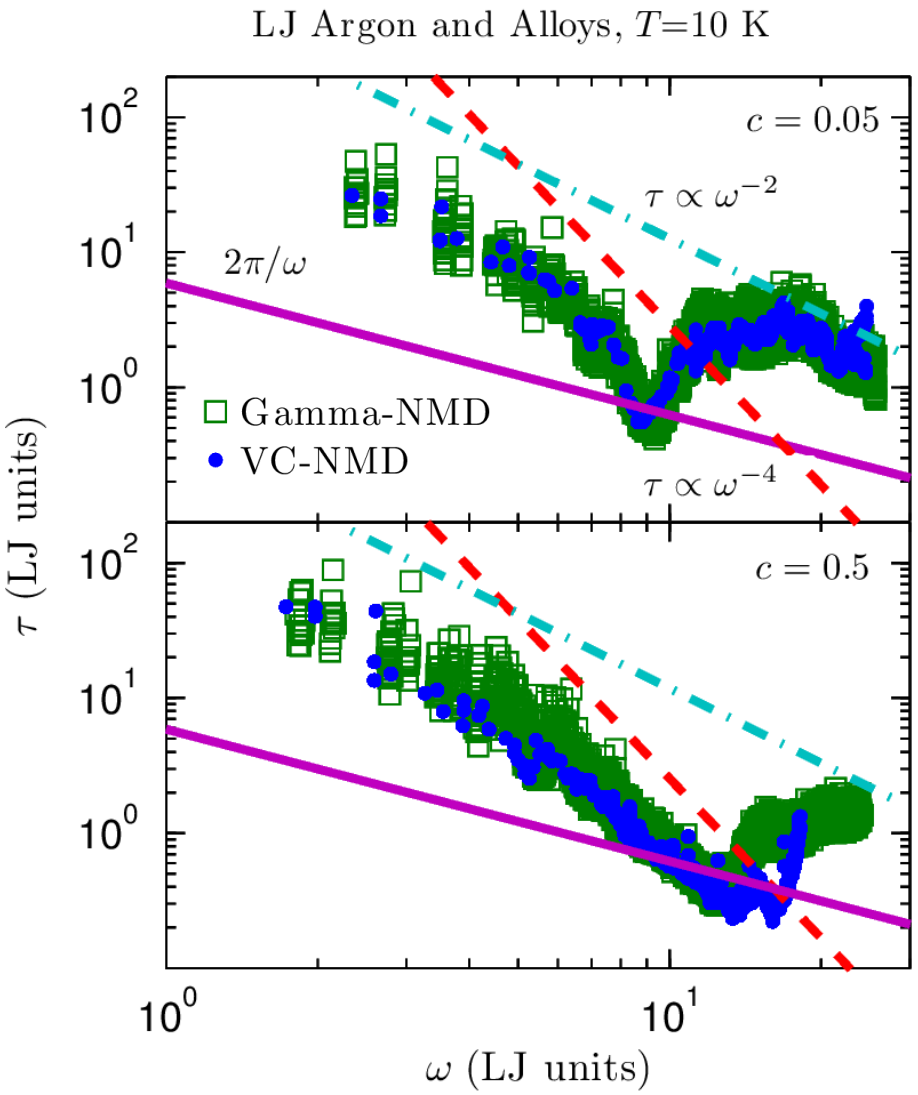
Phys. Rev. B 59, 35513559 (1999)

Normal Mode Decomposition (NMD)

Molecular Dynamics Gamma



$$\tau(\kappa_\nu) = \int_0^{t^*} \frac{< E(\kappa_\nu; t)\, E(\kappa_\nu; 0) >}{< E(\kappa_\nu; 0)\, E(\kappa_\nu; 0) >} dt$$

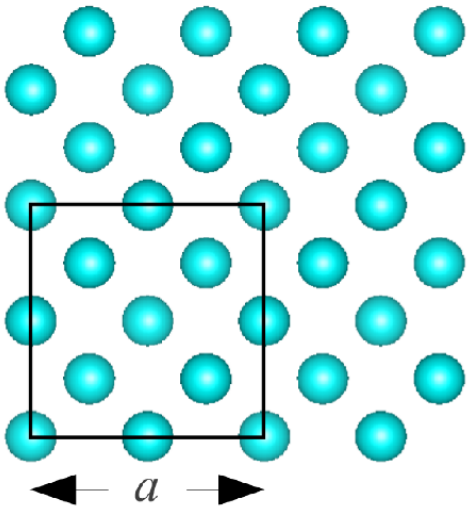


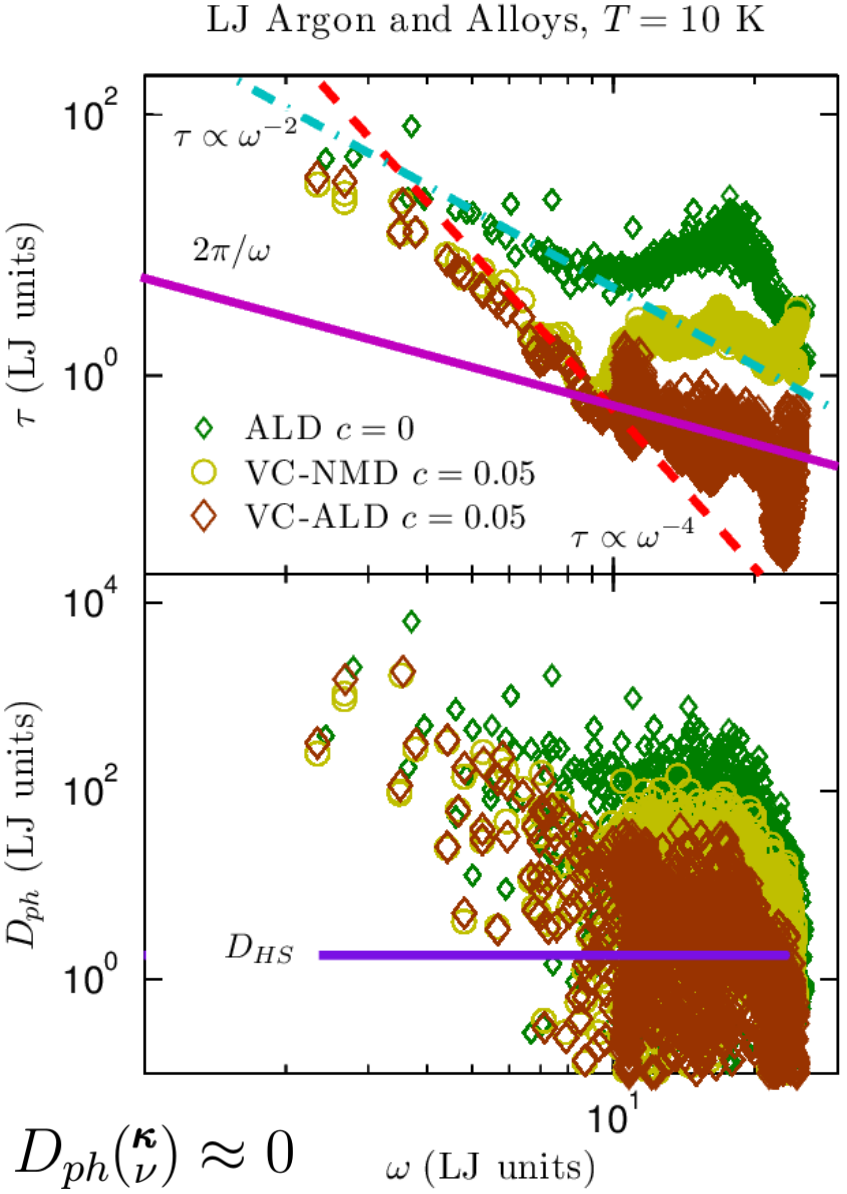
VC Diffusivities

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

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

VC Unit Cell

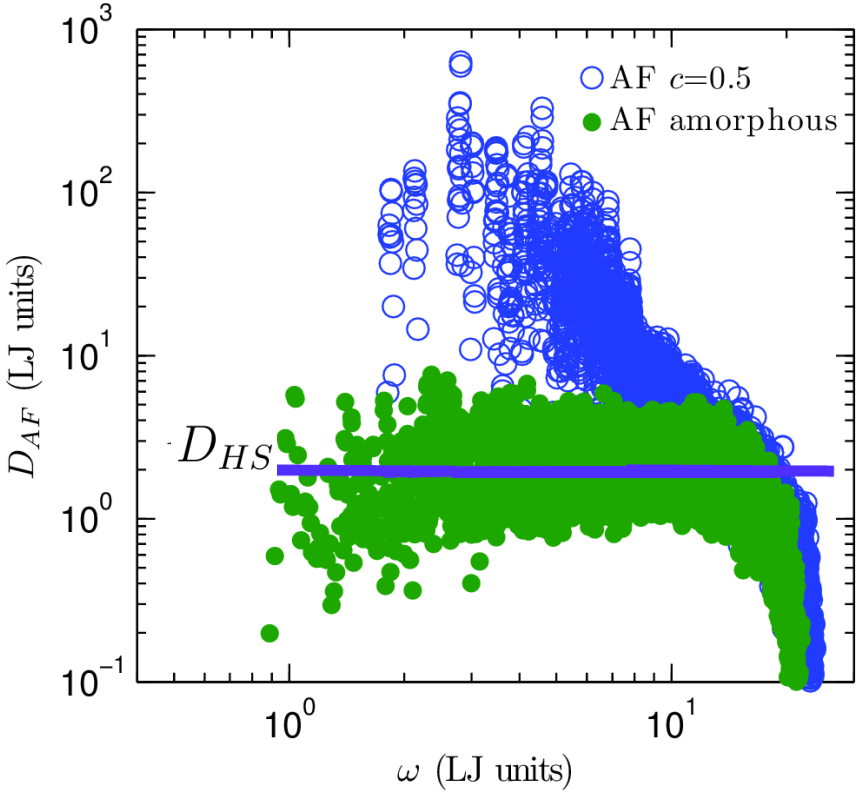


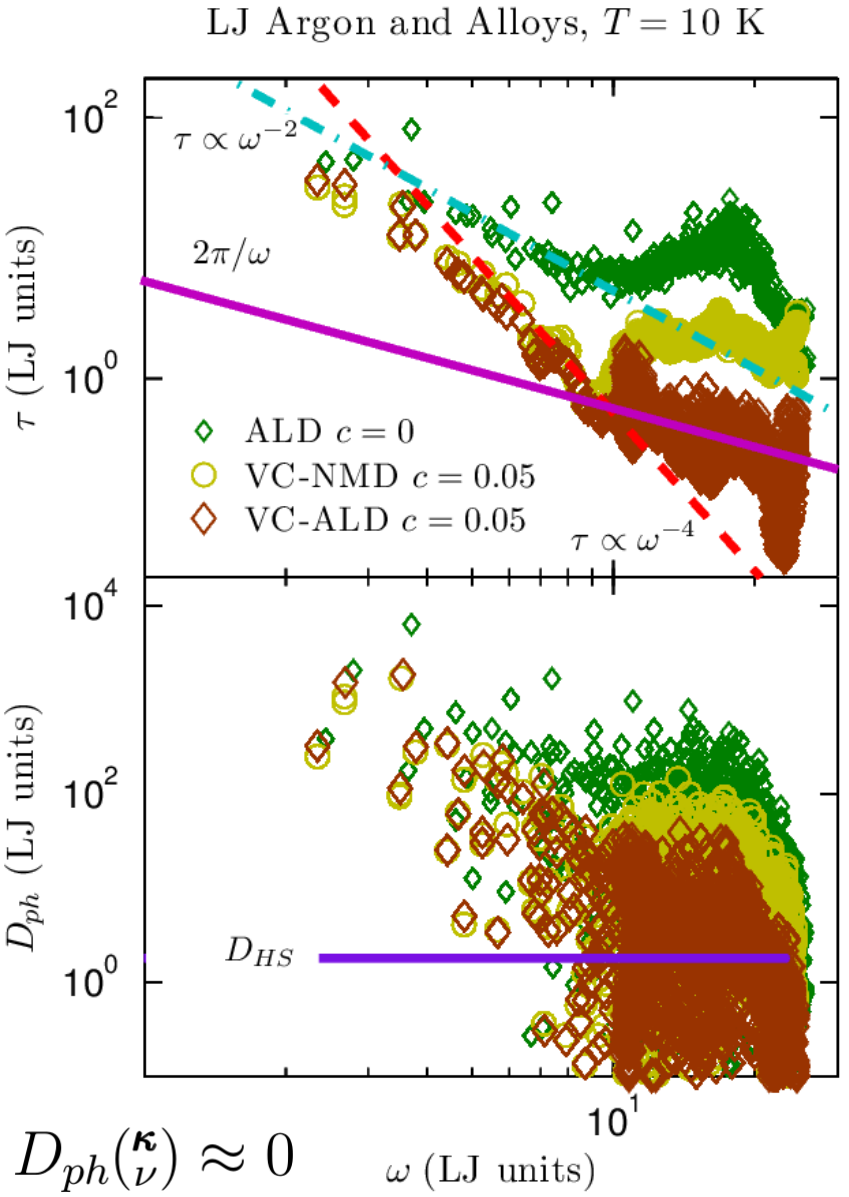


$$D_{ph}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) \approx 0$$

AF Diffusivities

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





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

Physical Review B 48, 1258112588 (1993)

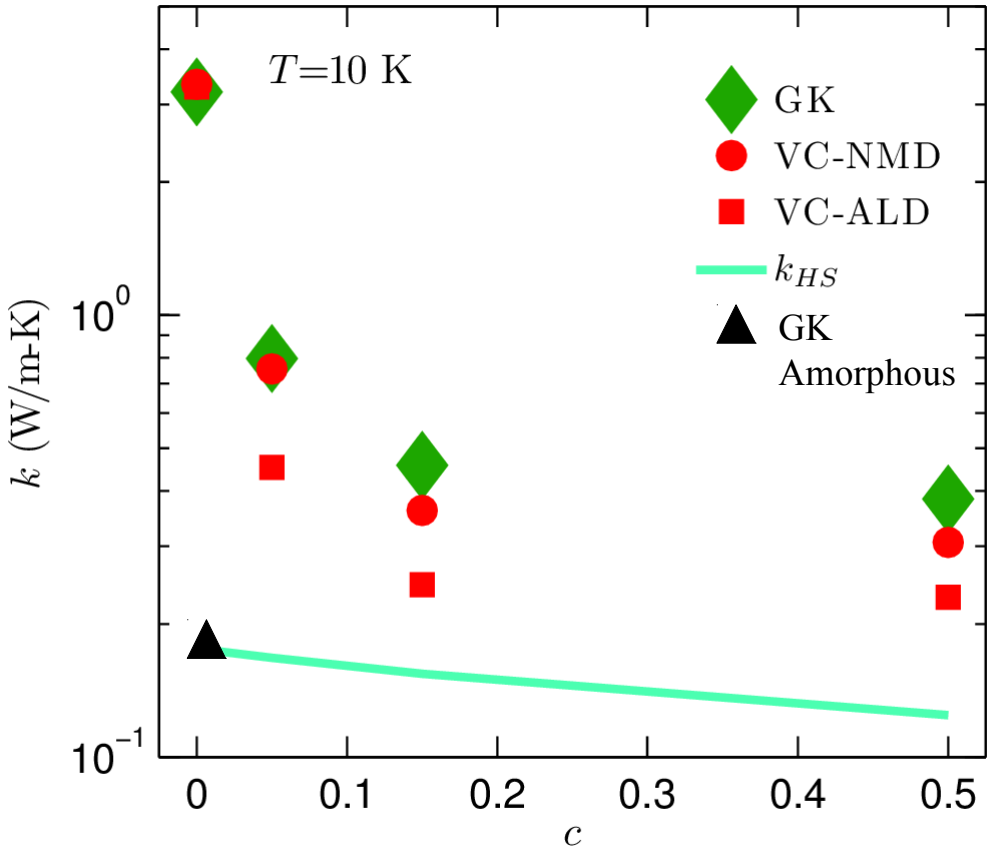
Thermal conductivity

Green-Kubo (GK): MD-based, no assumptions

High-scatter adjustment*:

$$D_{ph}\left(\begin{matrix}\kappa\\ \nu\end{matrix}\right) < D_{HS}$$

$$D_{ph}\left(\begin{matrix}\kappa\\ \nu\end{matrix}\right) = D_{HS}$$



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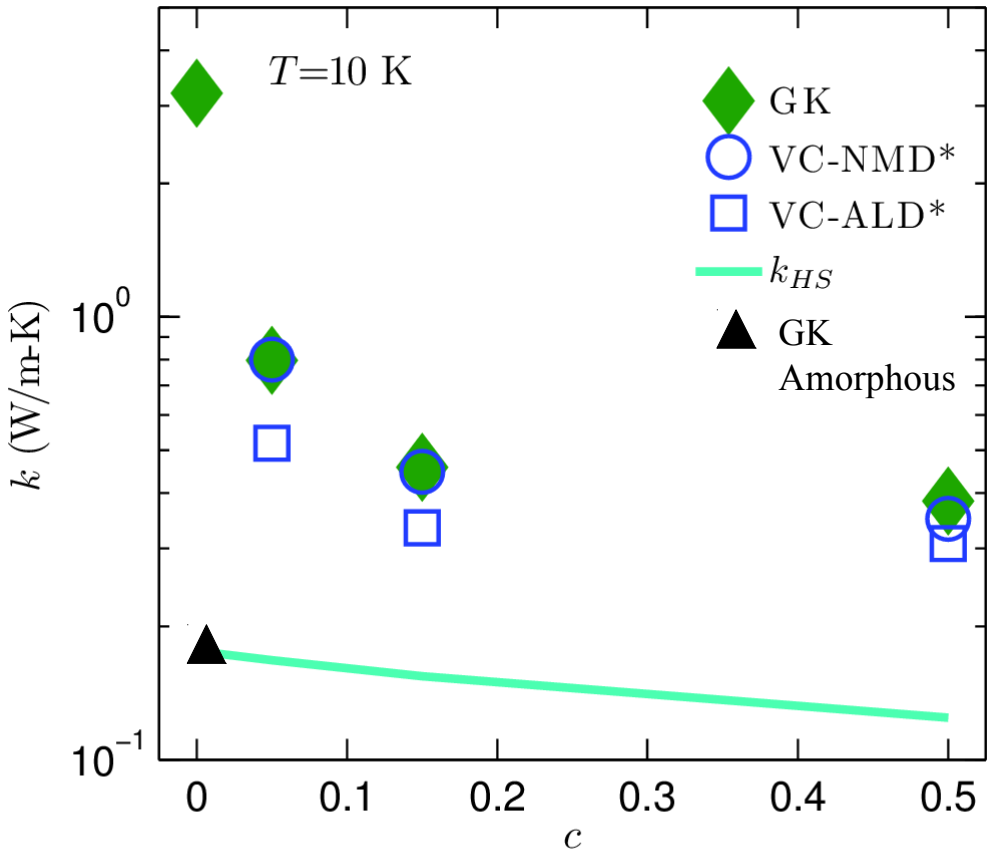
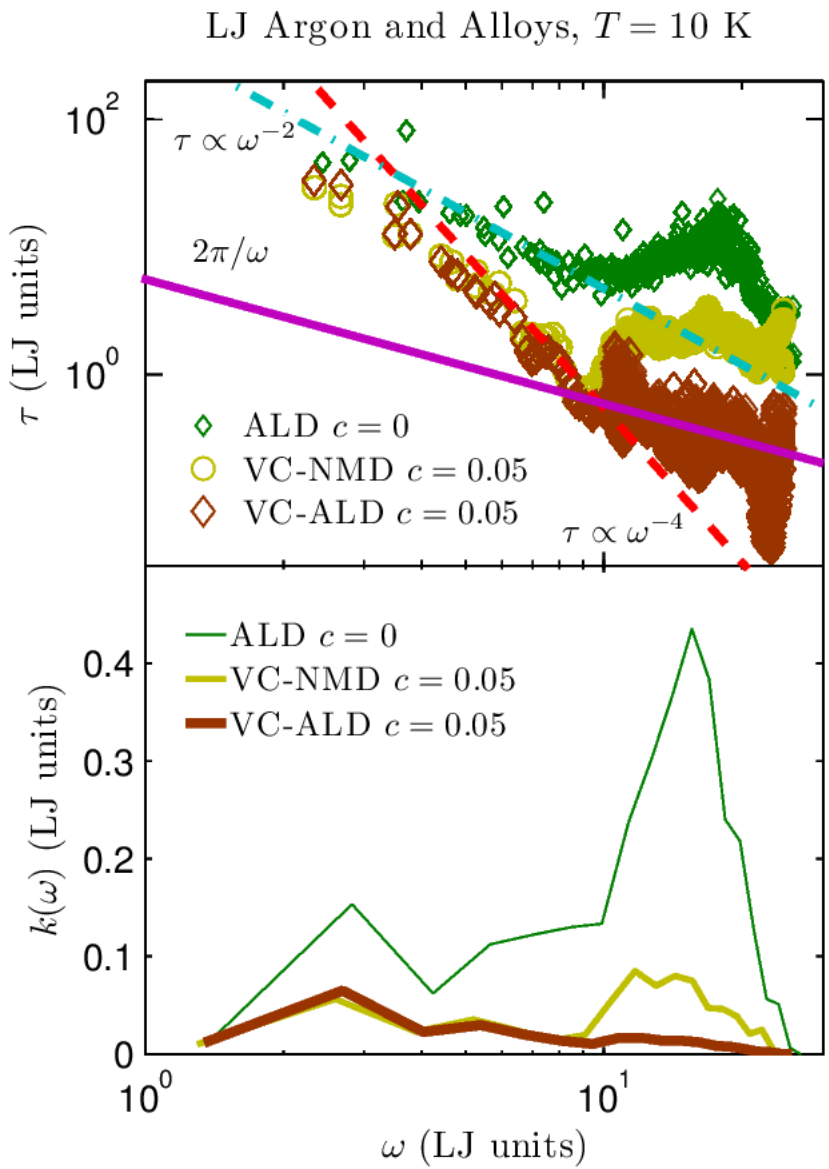
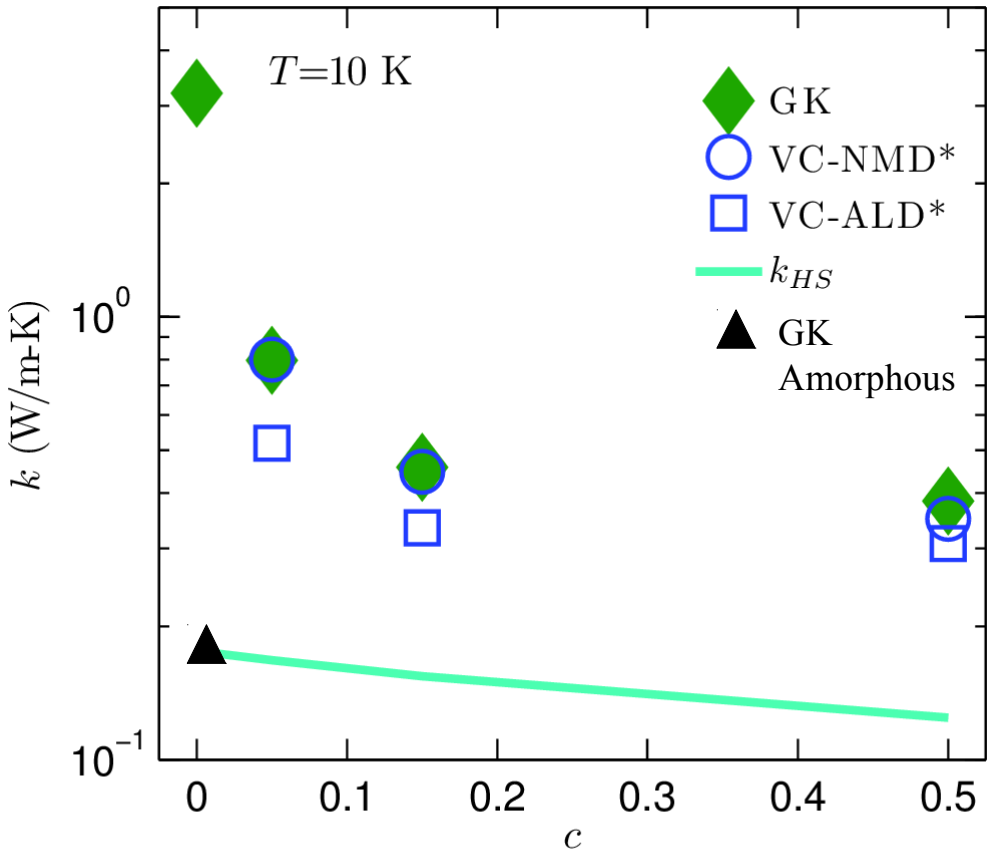


Thermal conductivity spectrum





Summary

VC approximation underpredicts mode group velocities at high frequency, which lead to underprediction of mode diffusivity.

VC-ALD underpredicts lifetimes at high-frequency.

LJ Argon has important contribution from high-frequency modes to thermal conductivity.

Breakdown of VC-ALD method is likely for materials with thermal conductivity near the high-scatter limit, or for modes below the high-scatter limit.

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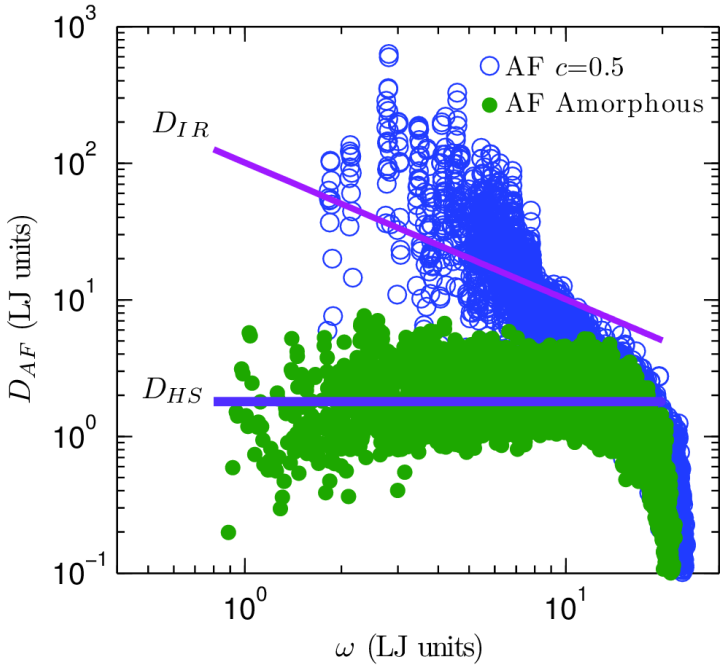
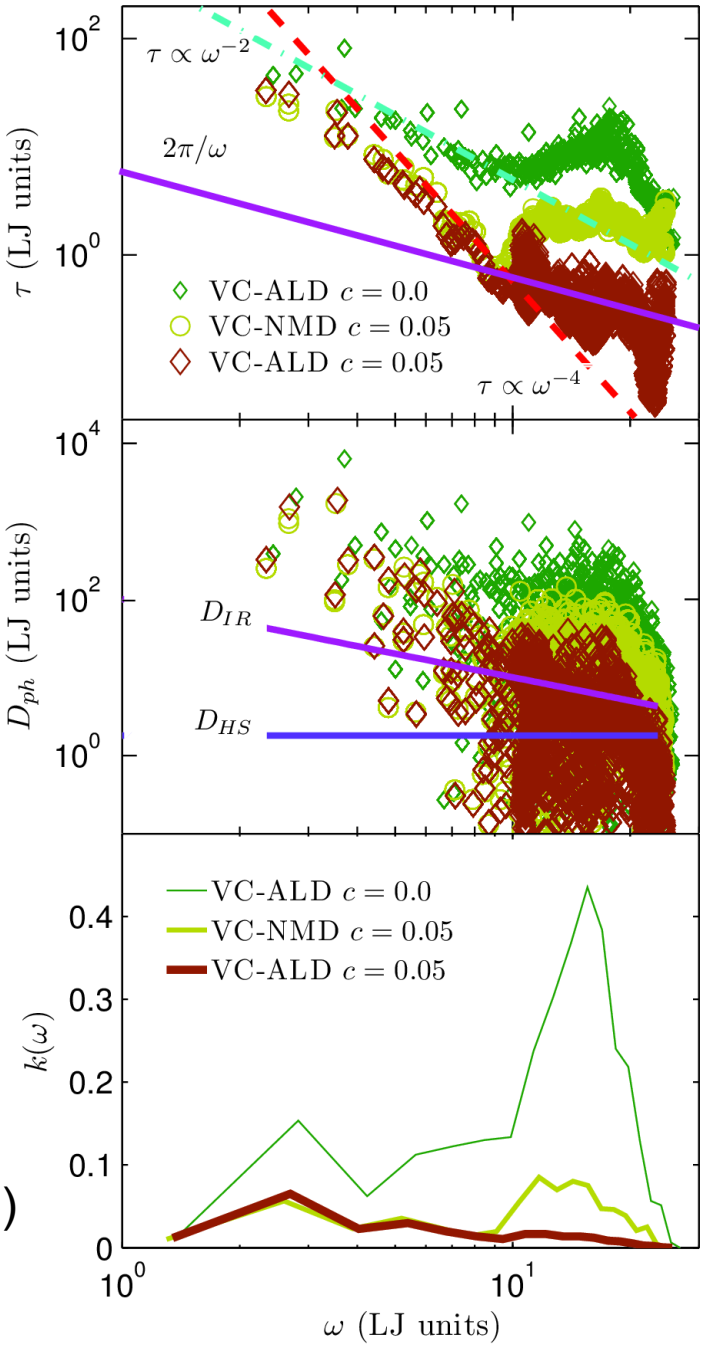
HS/IR Limit

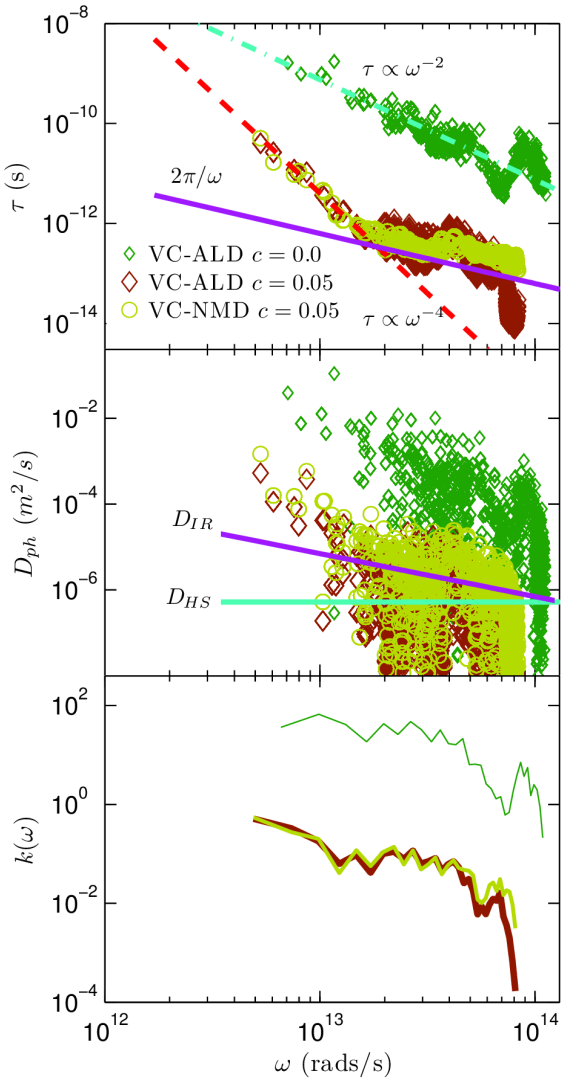
$$D_{IR} = \frac{2\pi}{3}\frac{v_s^2}{\omega}$$

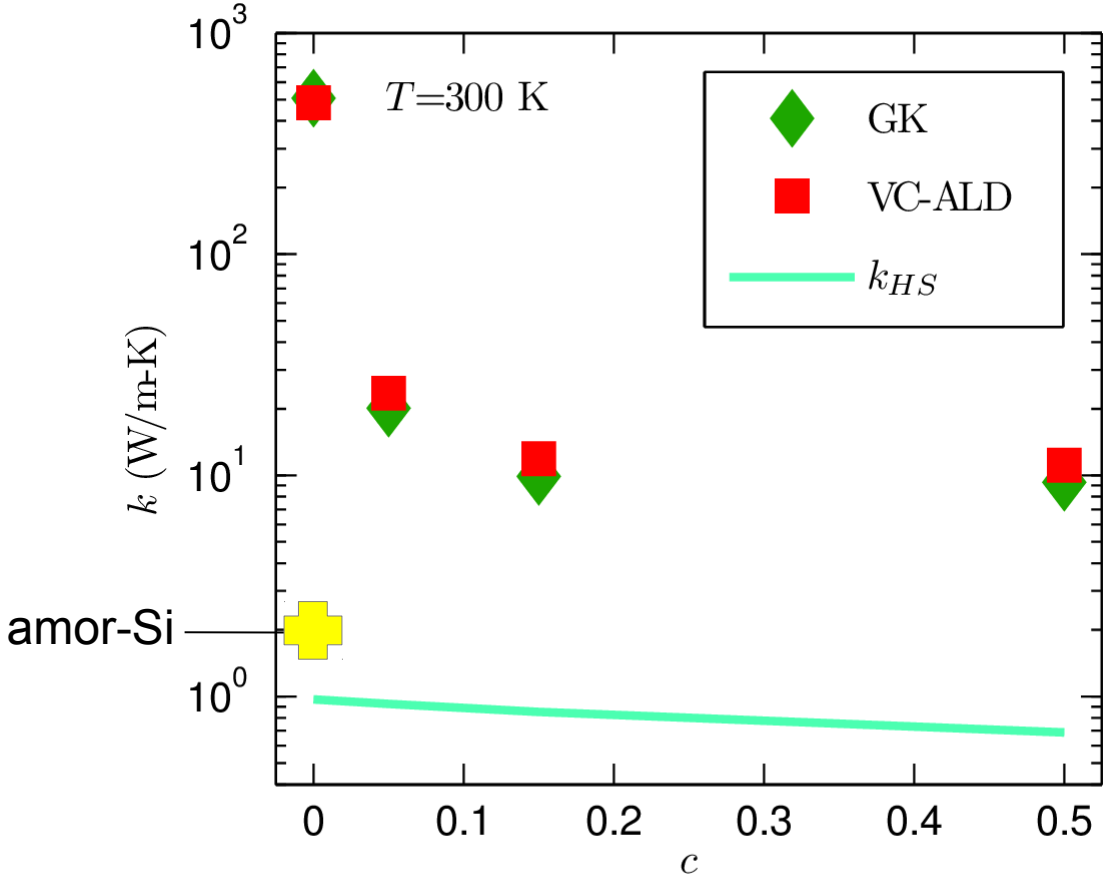




P. Sheng and M. Zhou, Science 253, 539542 (1991)

Thermal conductivity: SW silicon alloy

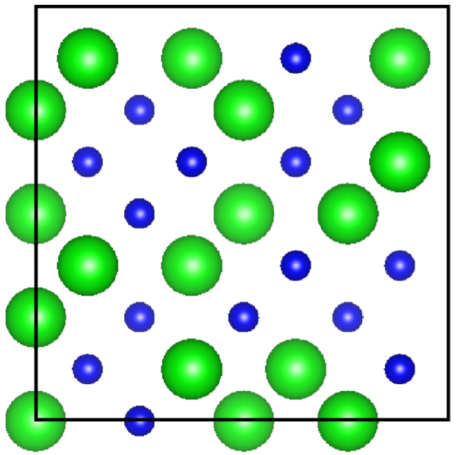


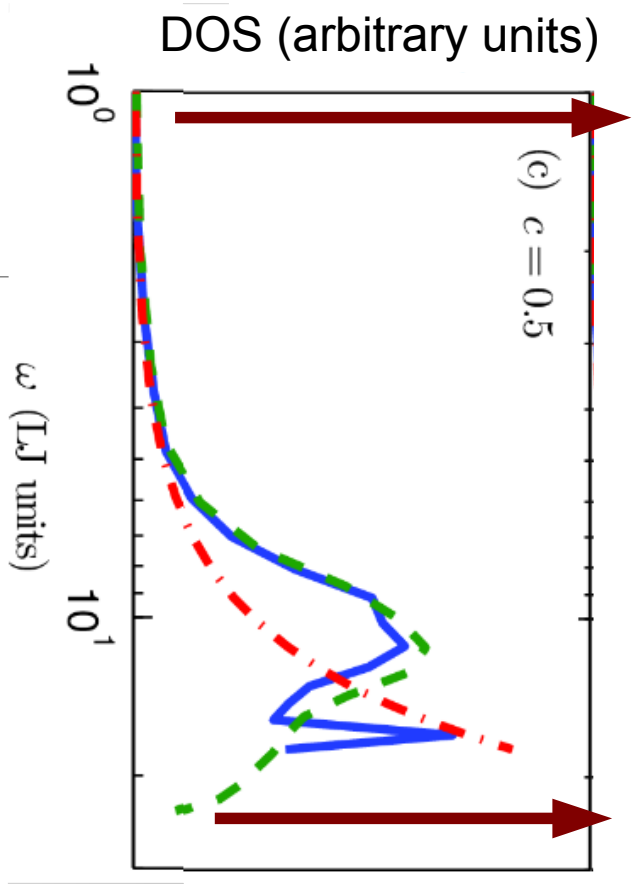


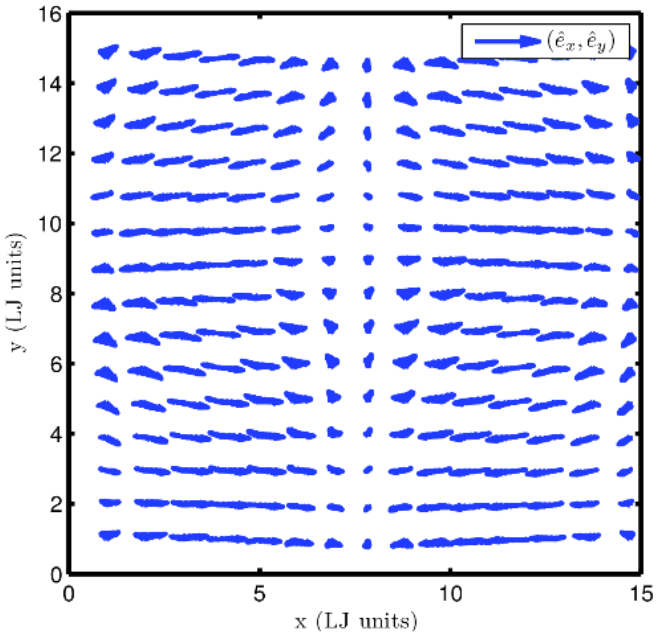
Gamma modes

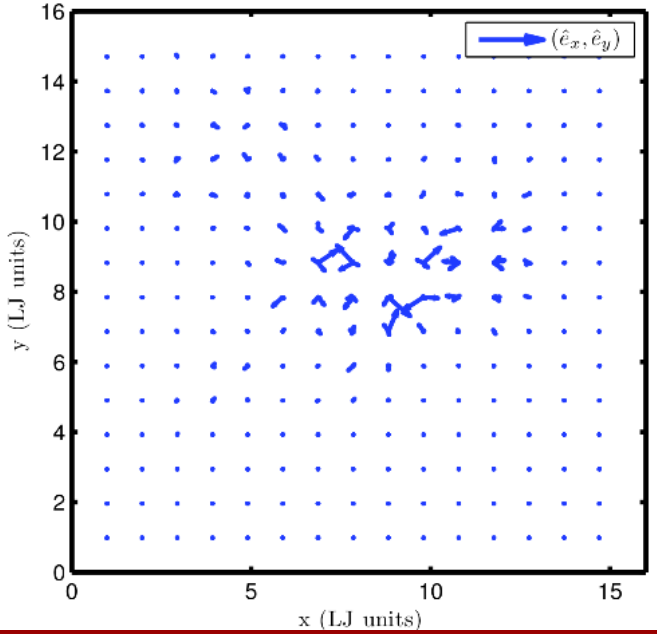
$e\left(\begin{smallmatrix}\kappa=0 & b\\ \nu & \alpha\end{smallmatrix}\right)$

(a) disordered supercell

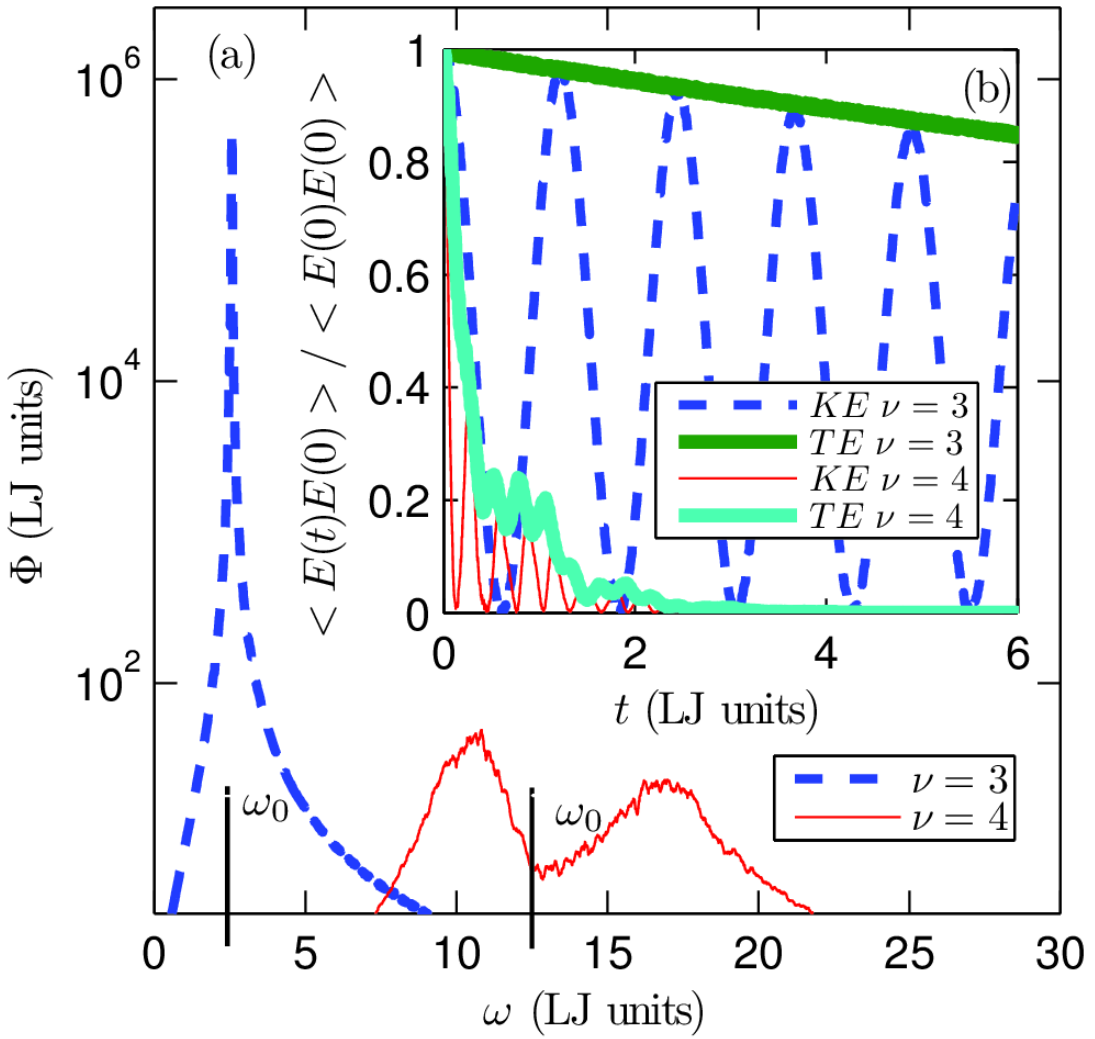




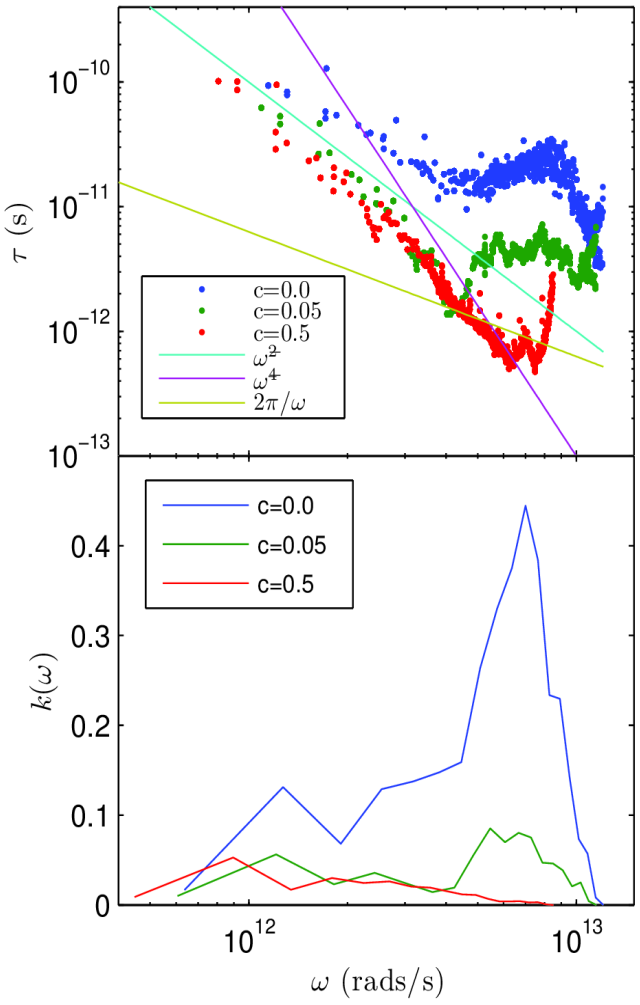


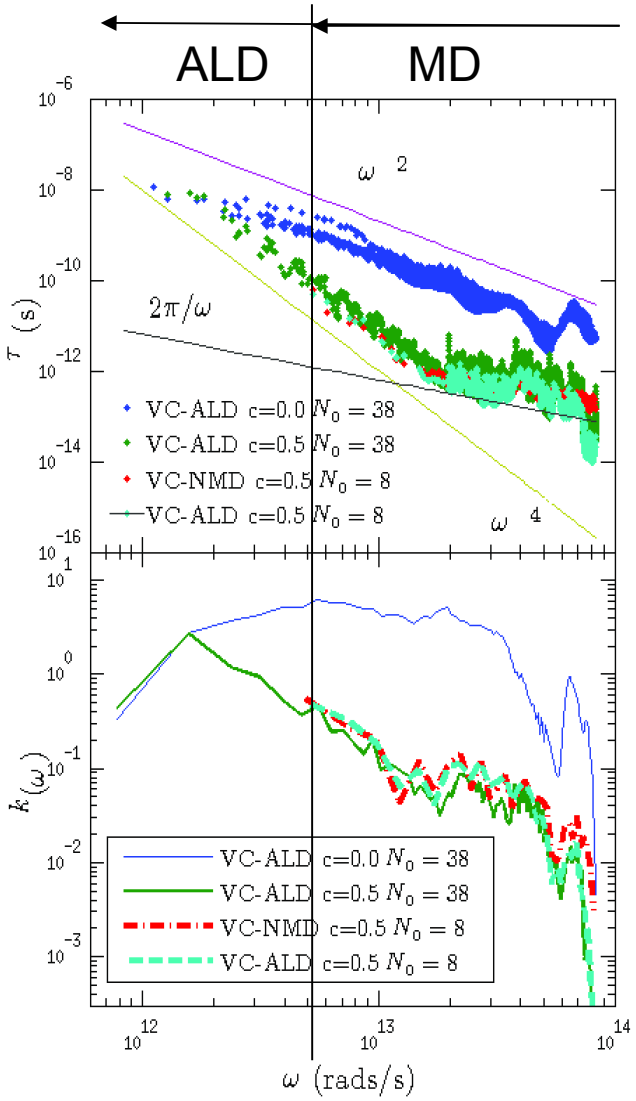


NMD using VC modes

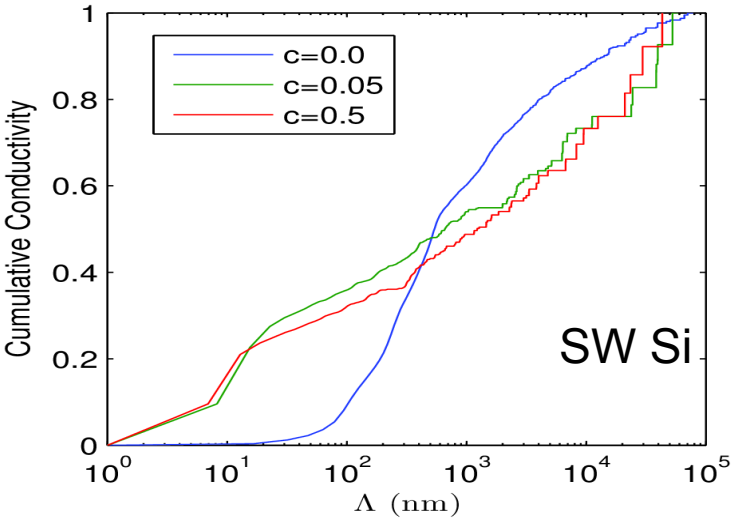


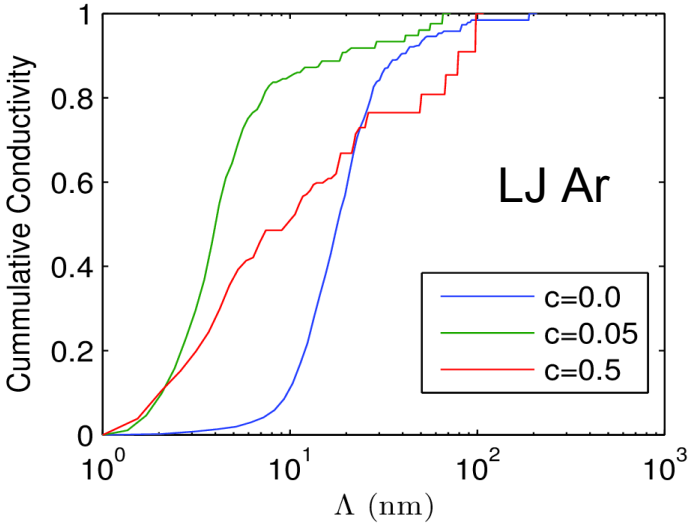
Phonon Spectrum: LJ Ar vs SW Si

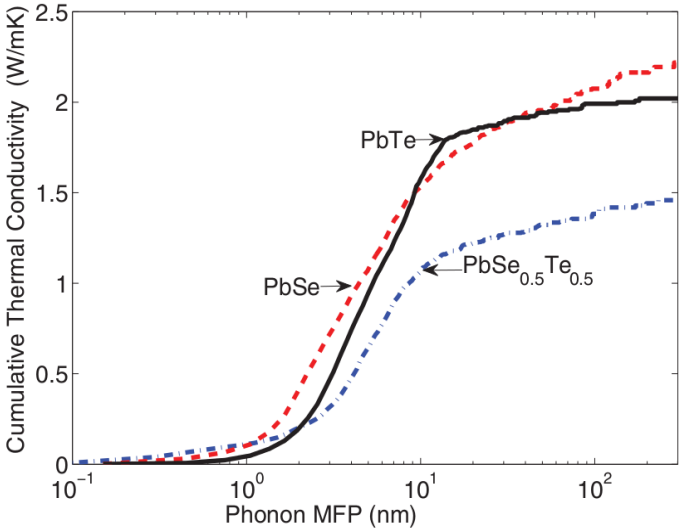




Conductivity Accumulation







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