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

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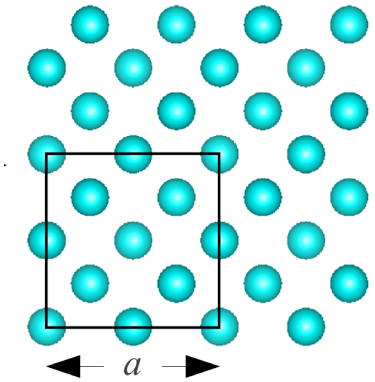
04/04/13

Motivation: experimental accuracy

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



Alloys: isotopic effects, thermoelectric materials

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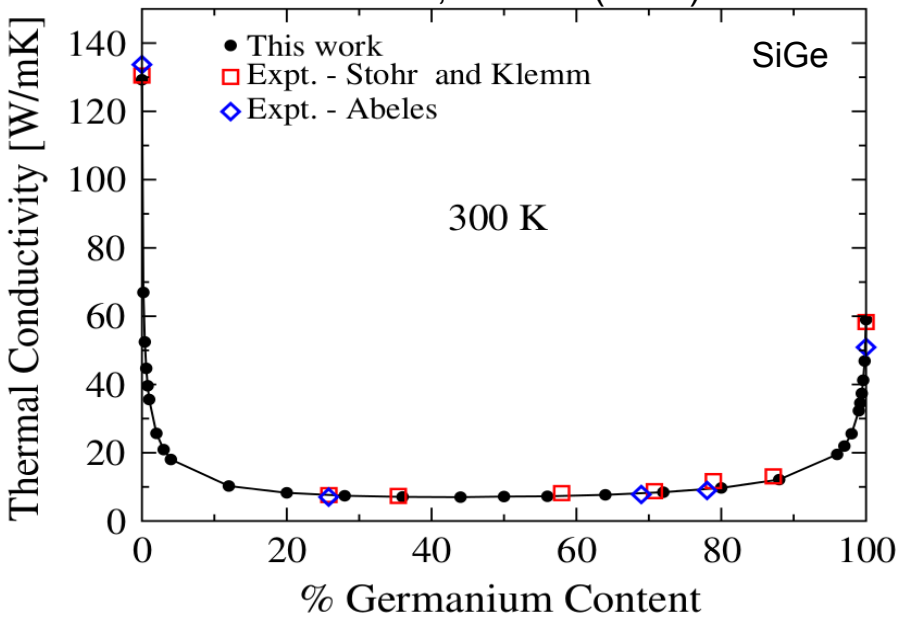

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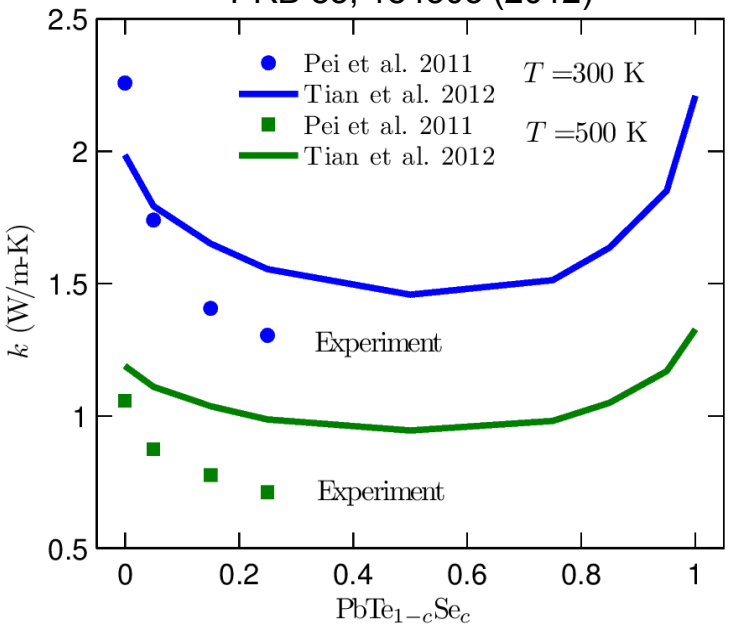
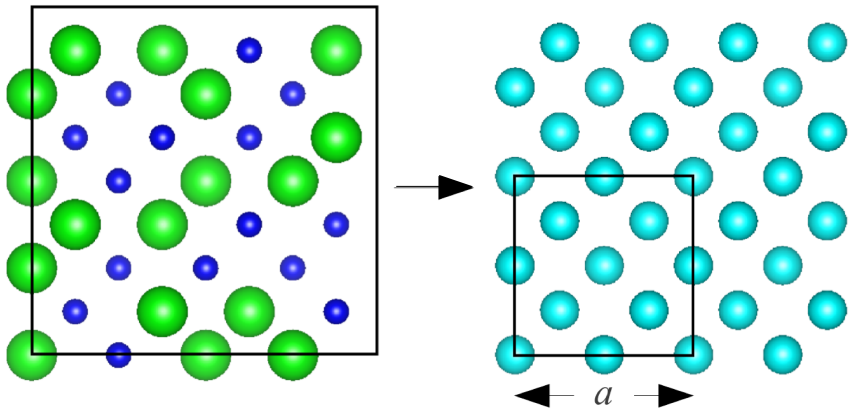


Virtual Crystal Approximation

Gamma

VC

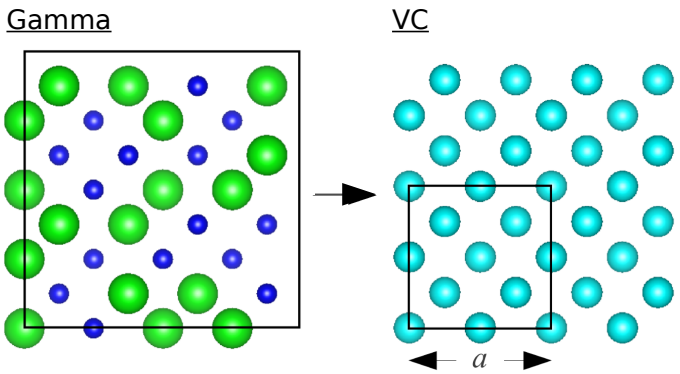


$$\bar{m}^{\mu} = (1-c)m^{i} + cm^{j}$$

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

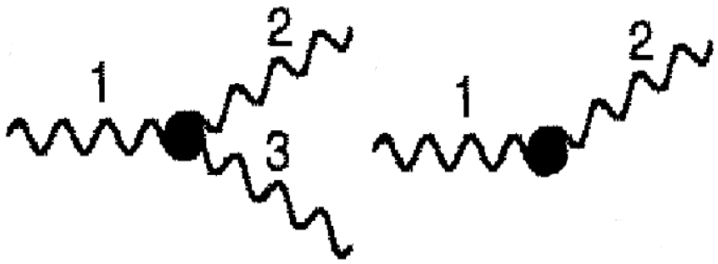
$$D_{ph,\mathbf{n}}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) = v^2_{g,\mathbf{n}}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) \tau\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)$$

VC-ALD Diffusivities



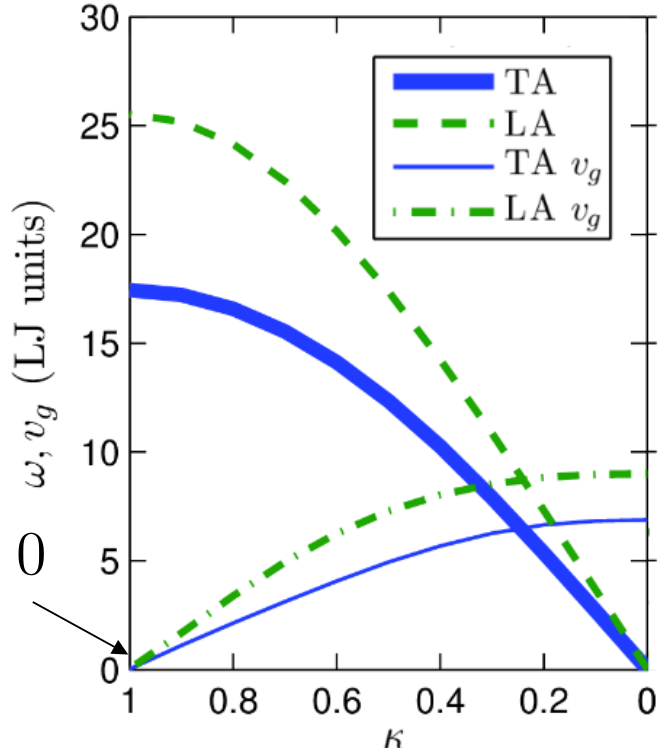
$$D_{ph,\mathbf{n}}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) = v^2_{g,\mathbf{n}}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)\tau\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)$$

Matthiessen's Rule



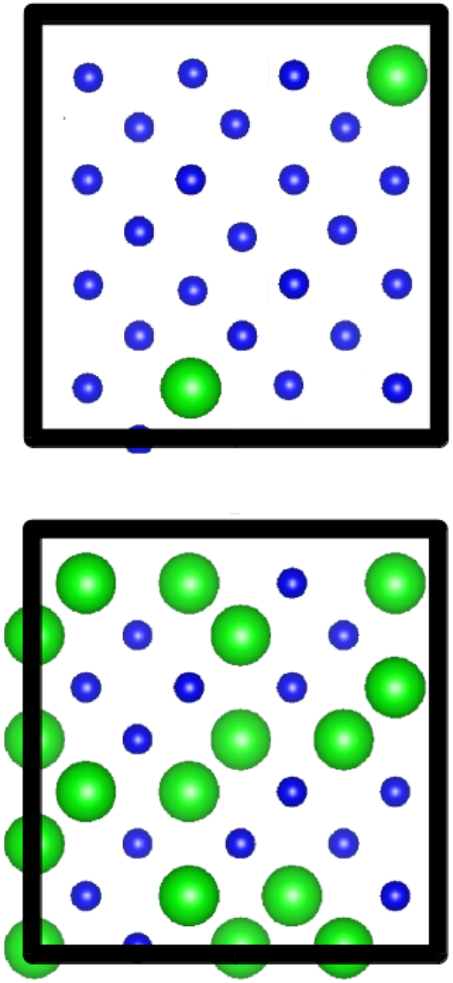
$$\frac{1}{\tau\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)} = \frac{1}{\tau_{p-p}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)} + \frac{1}{\tau_{p-d}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)}$$

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

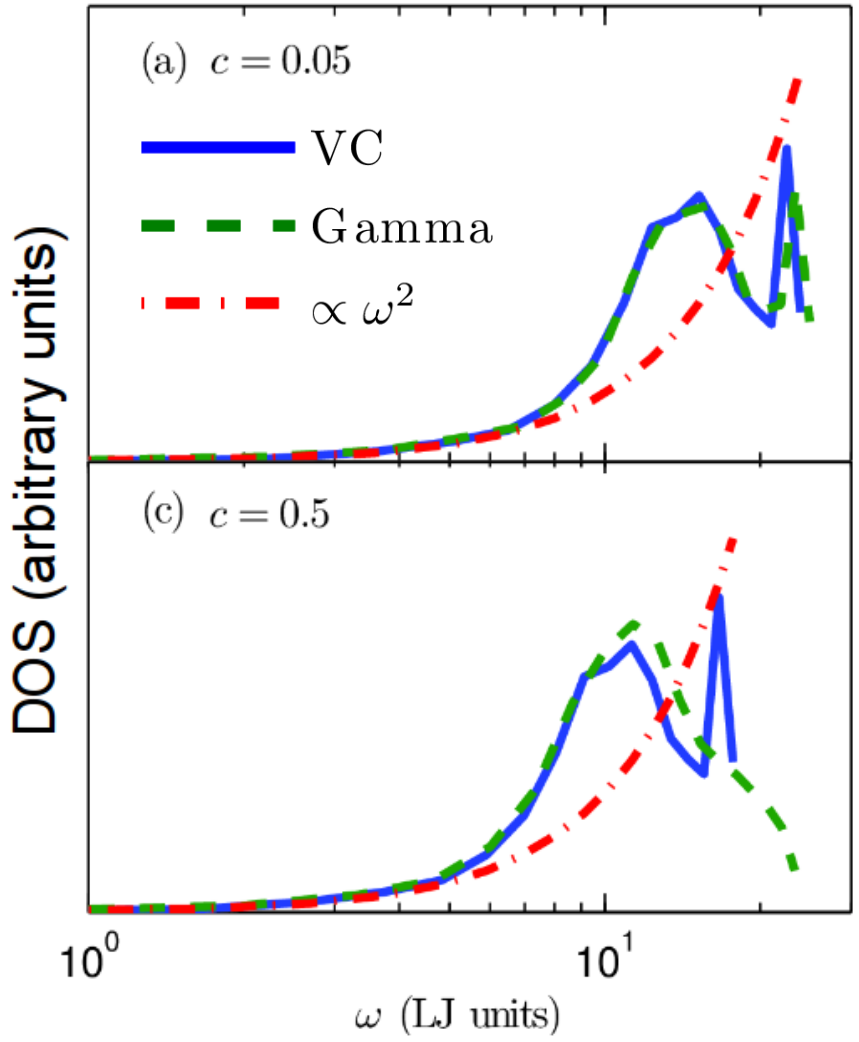


Explicit disorder: VC vs Gamma

Gamma

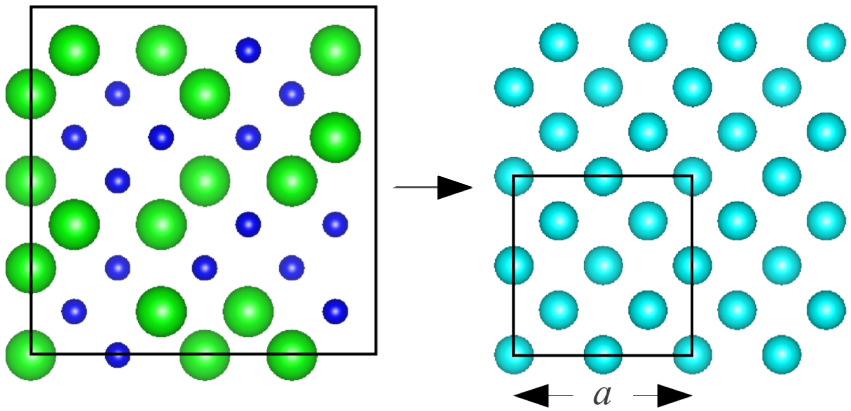


Lennard-Jones Argon Alloys



Explicit disorder: Structure Factor

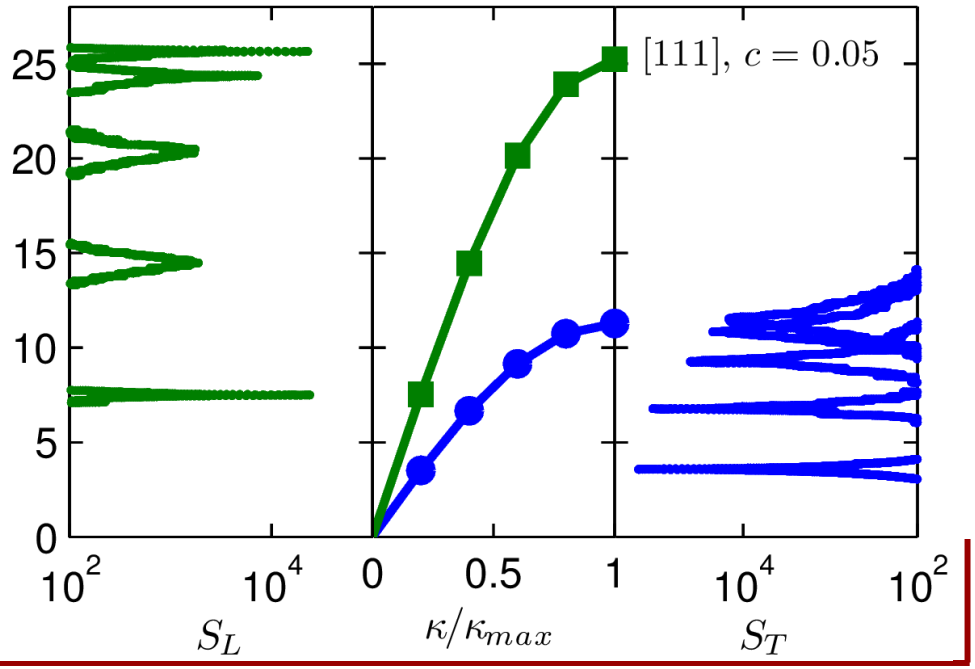
Gamma VC



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

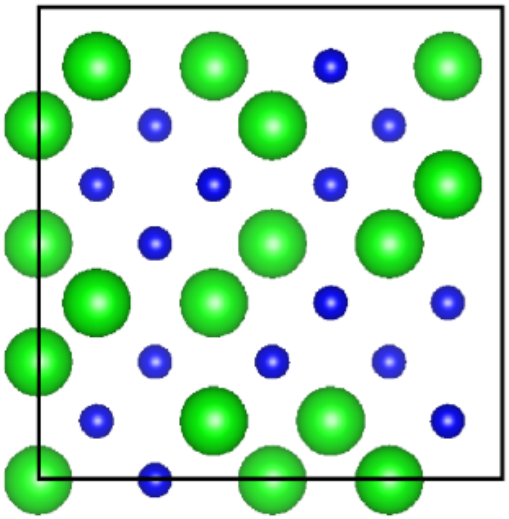
$$v_{g,\mathbf{n}}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) = \frac{\partial\omega\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right)}{\partial\boldsymbol{\kappa}}$$

Gamma VC Gamma



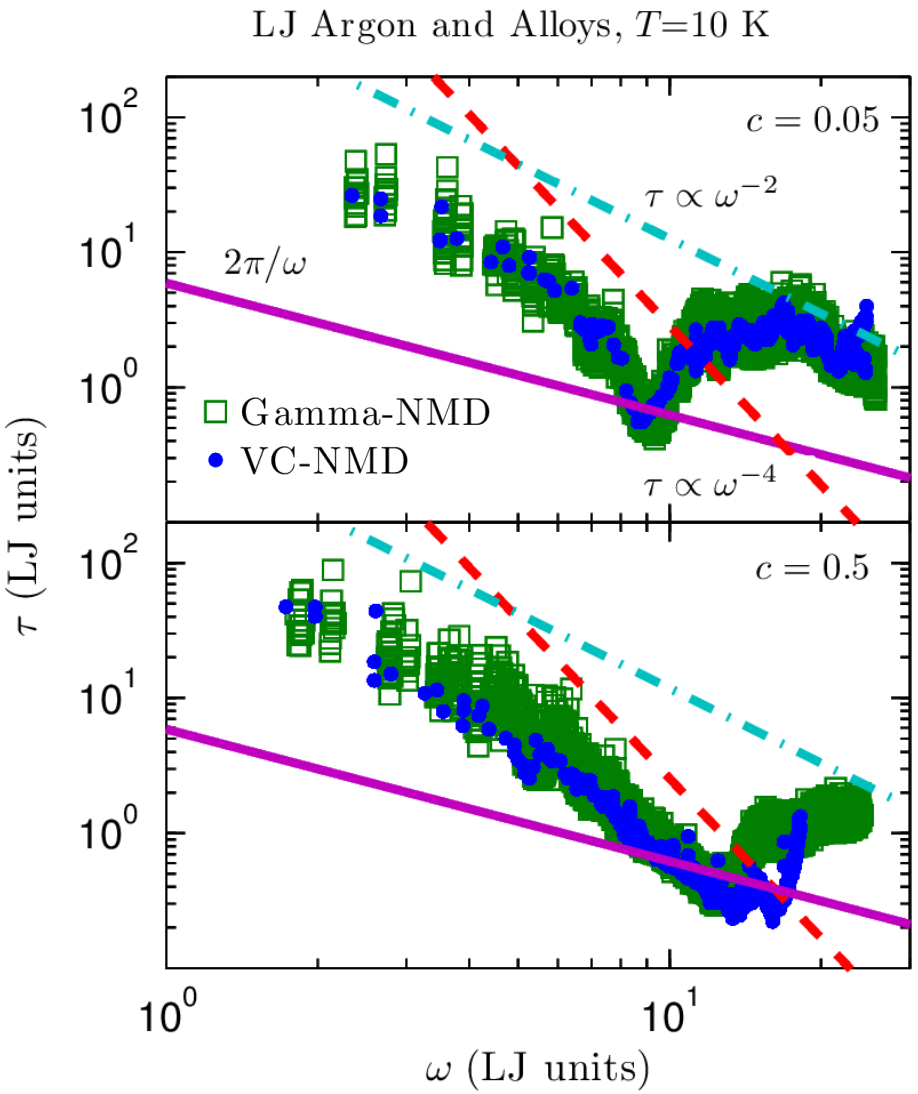
Normal Mode Decomposition (NMD)

Molecular Dynamics Gamma



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

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

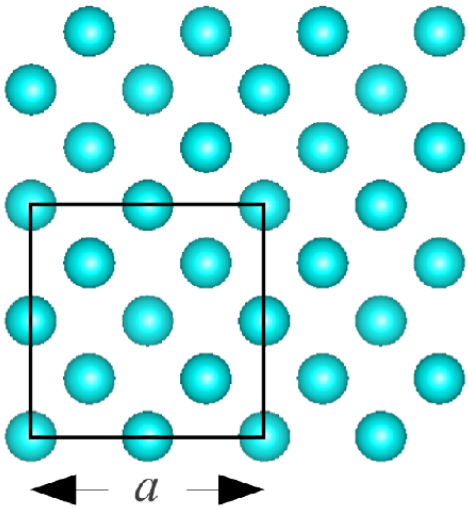


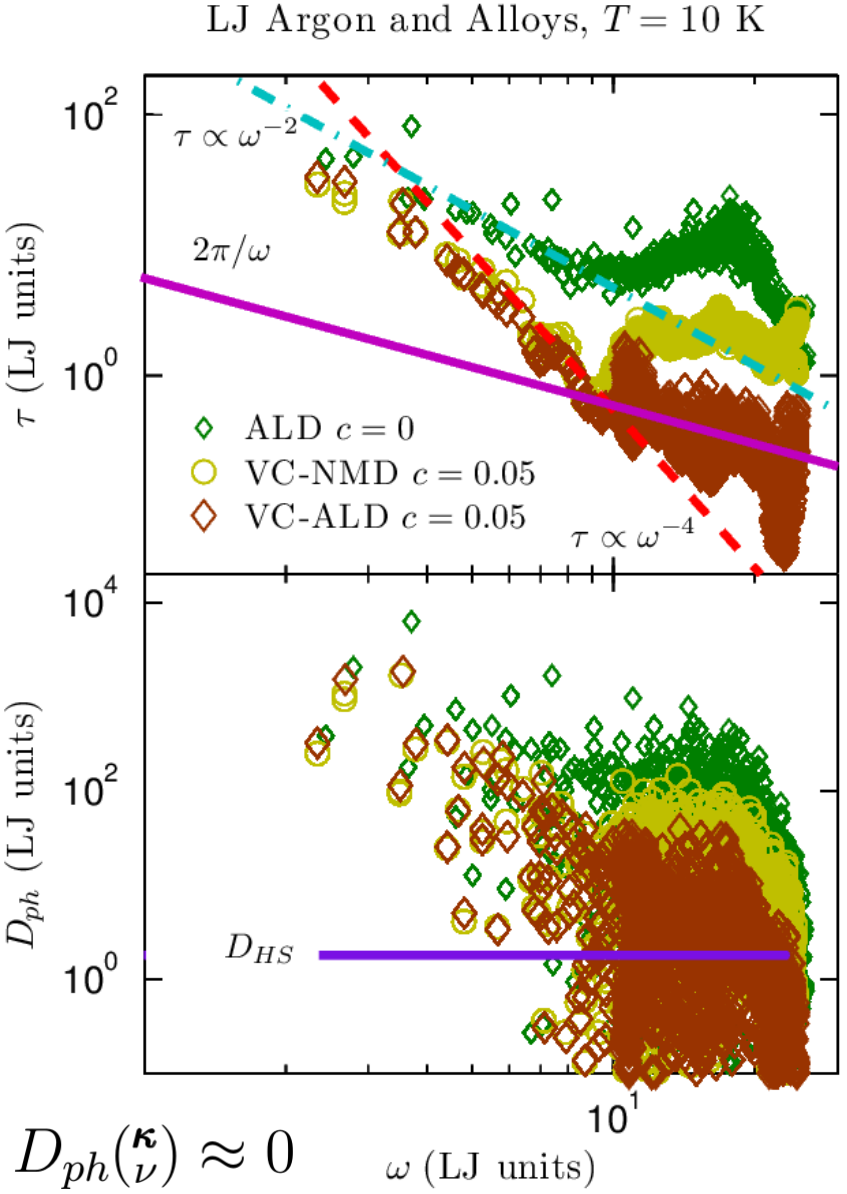
VC Diffusivities

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

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

VC Unit Cell

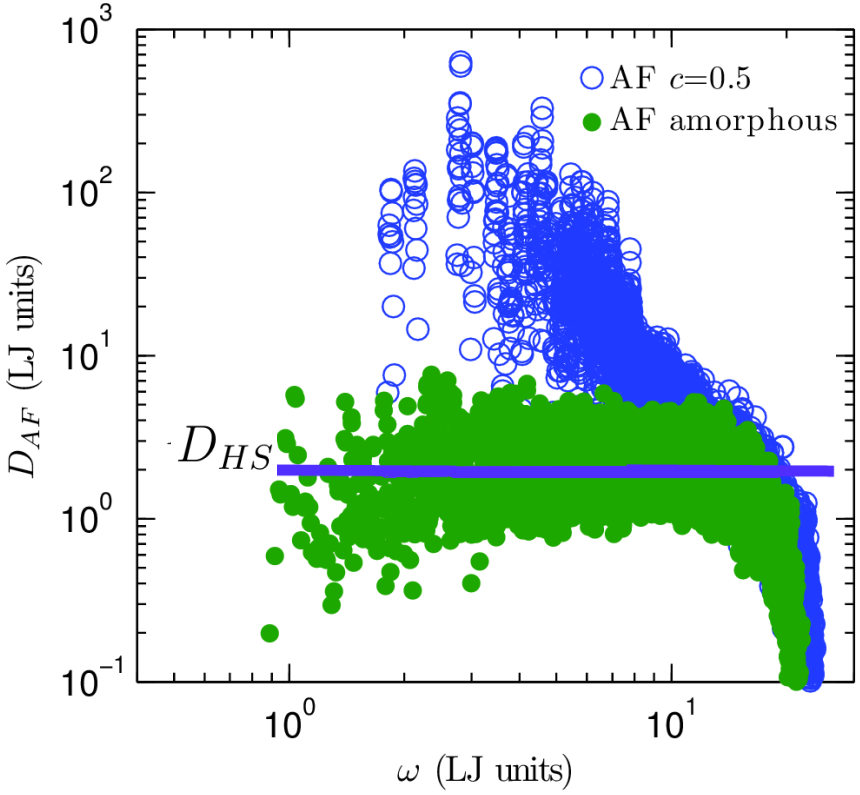


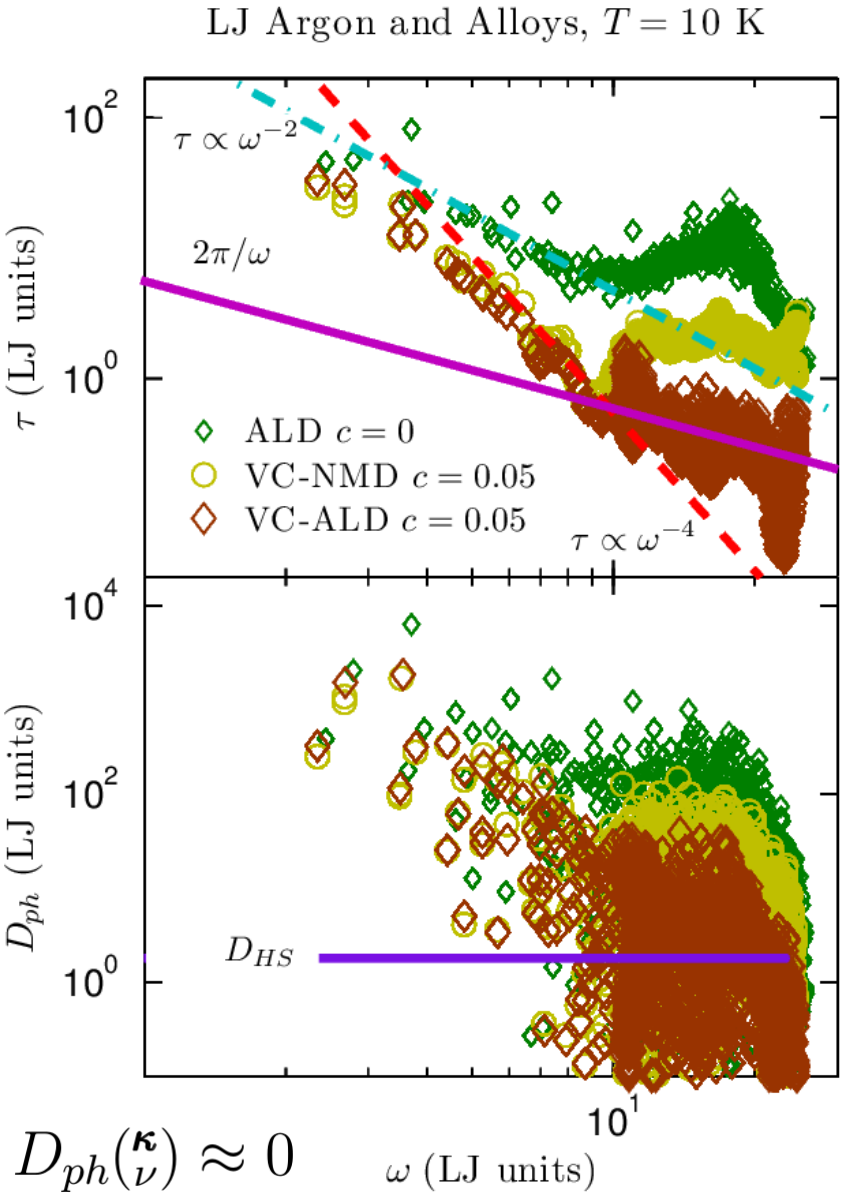


$$D_{ph}\left(\begin{matrix}\boldsymbol{\kappa}\\ \nu\end{matrix}\right) \approx 0$$

AF Diffusivities

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





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

Thermal conductivity

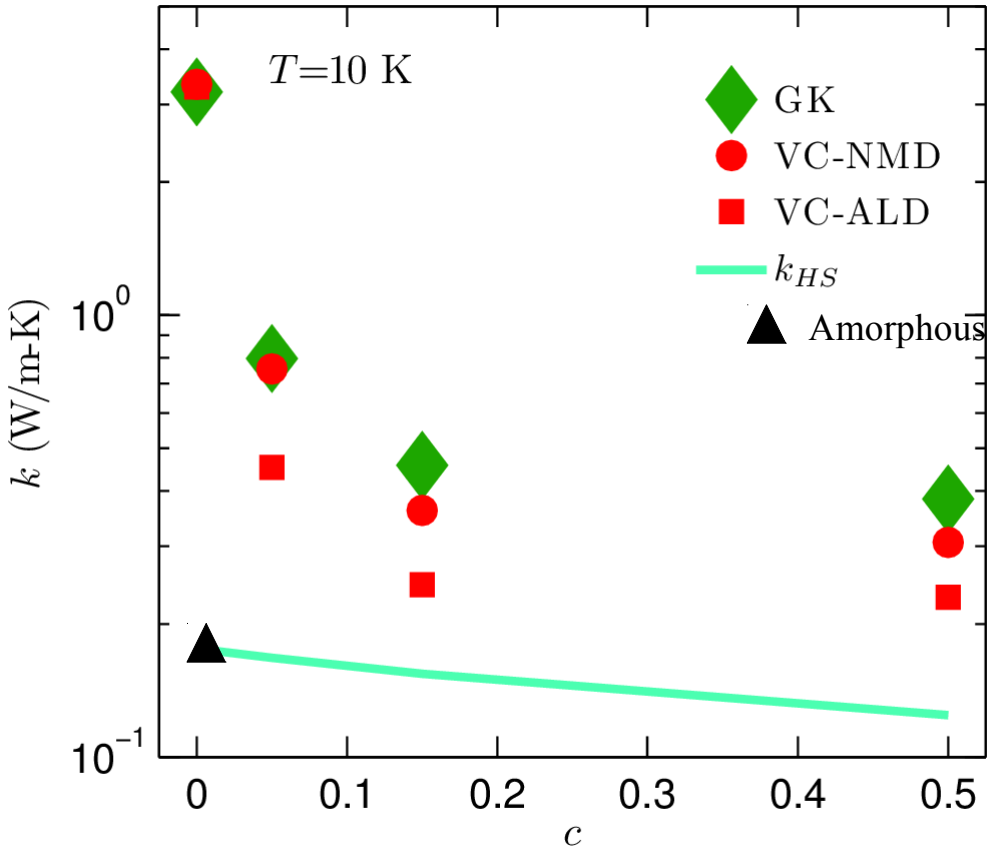
Green-Kubo (GK): top-down method, no assumptions

High-scatter adjustment*:

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

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

$$k_{HS} = \frac{k_B}{V_b} b v_s a$$



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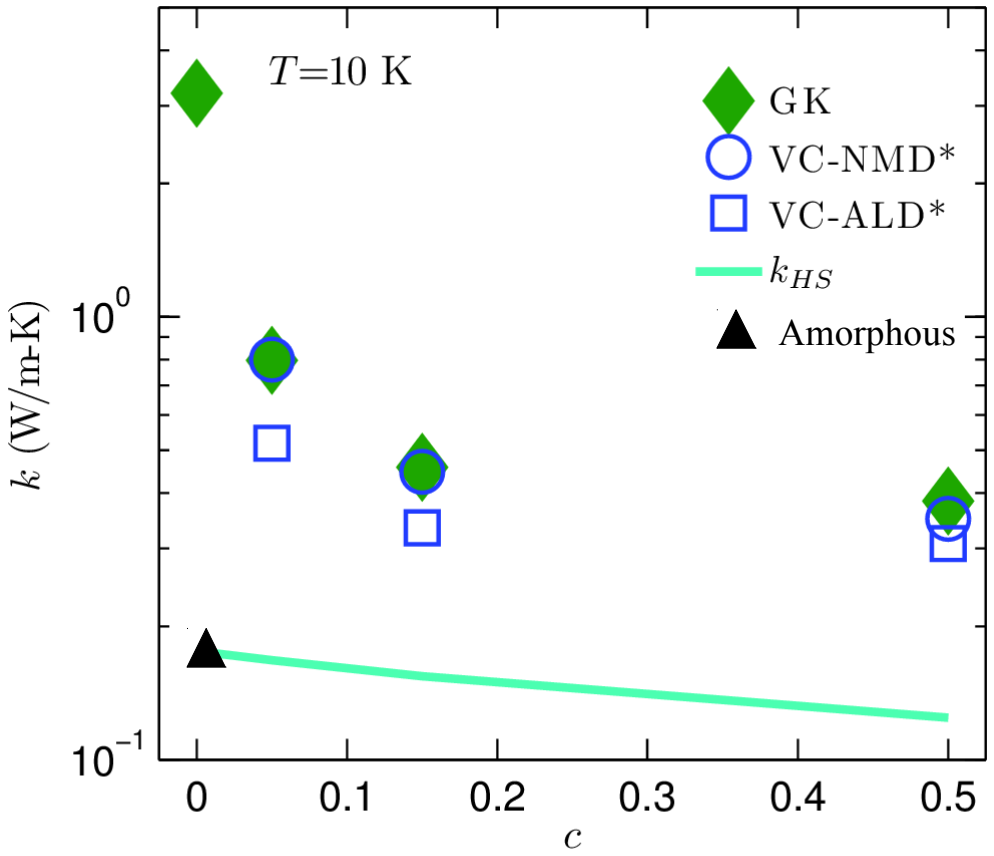
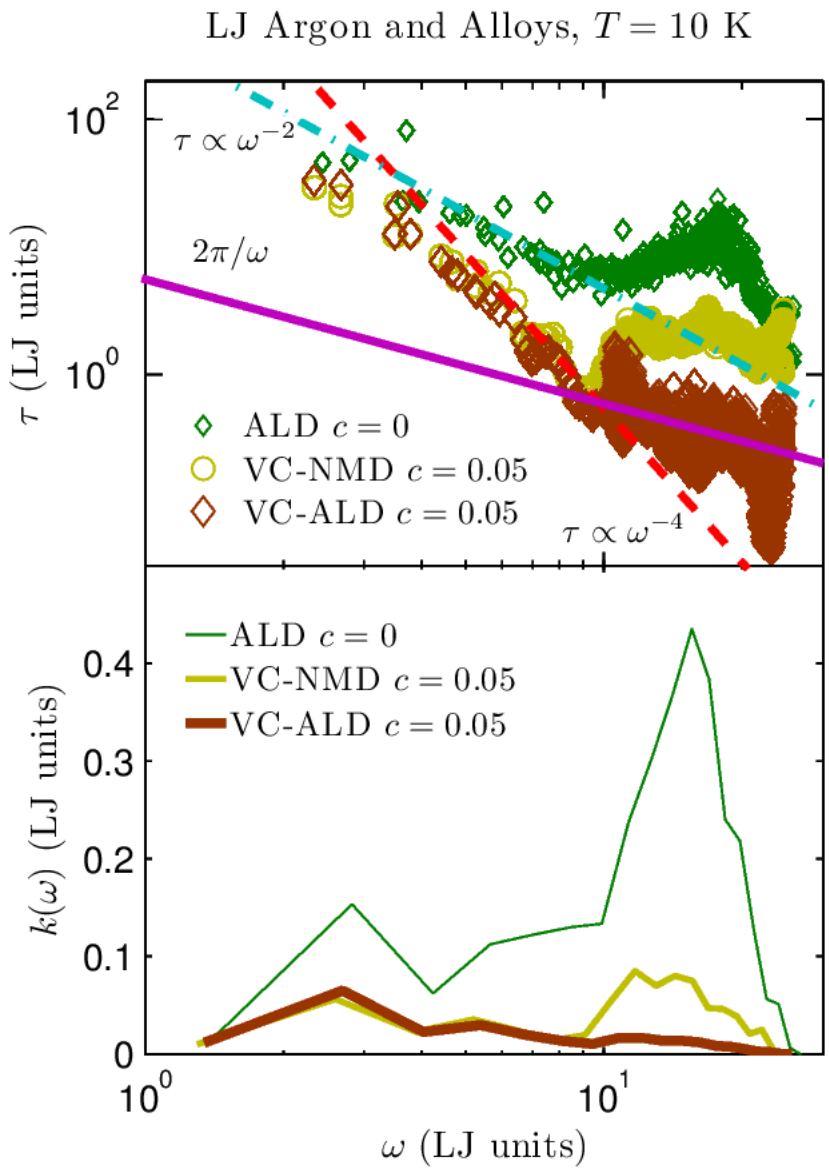
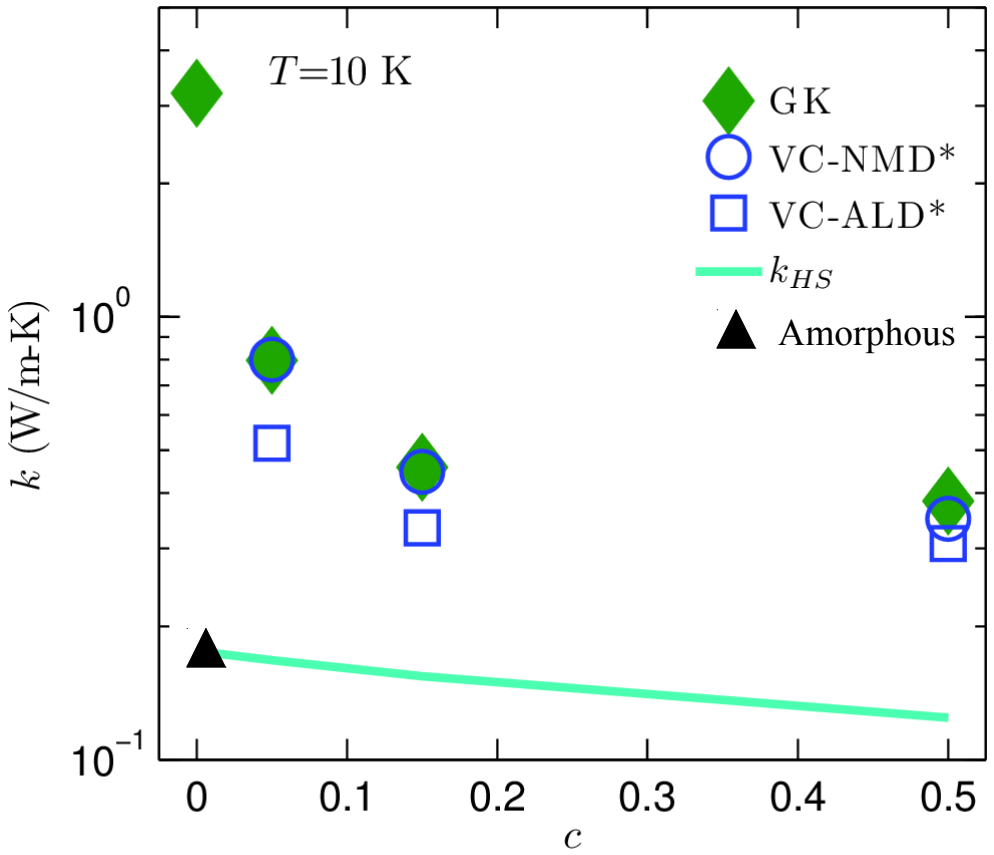


Thermal conductivity spectrum





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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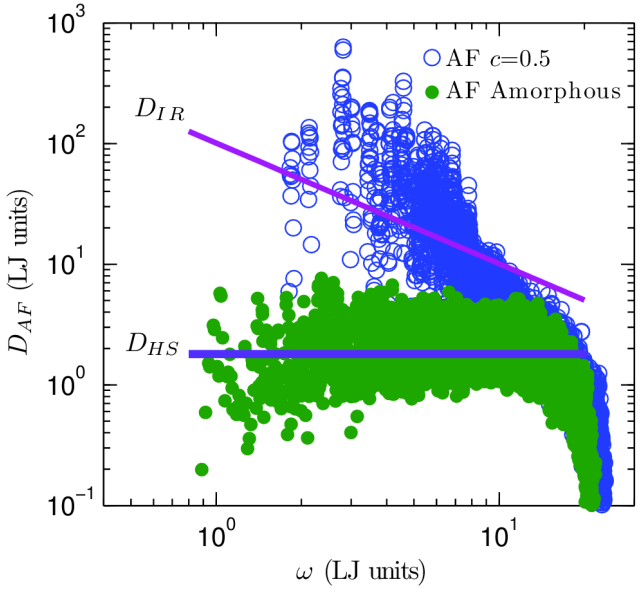
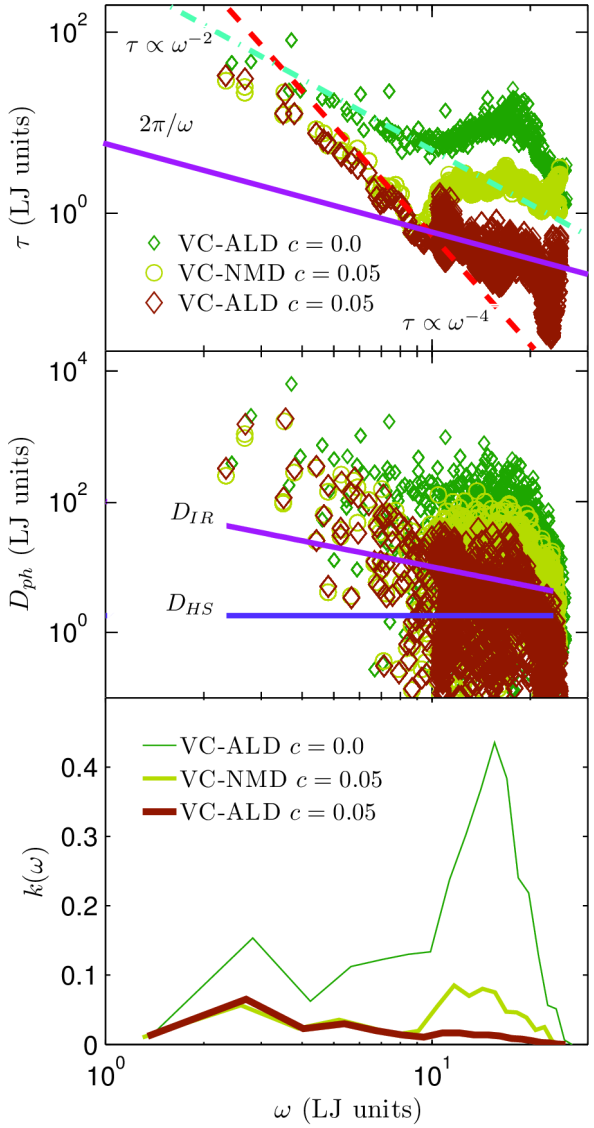
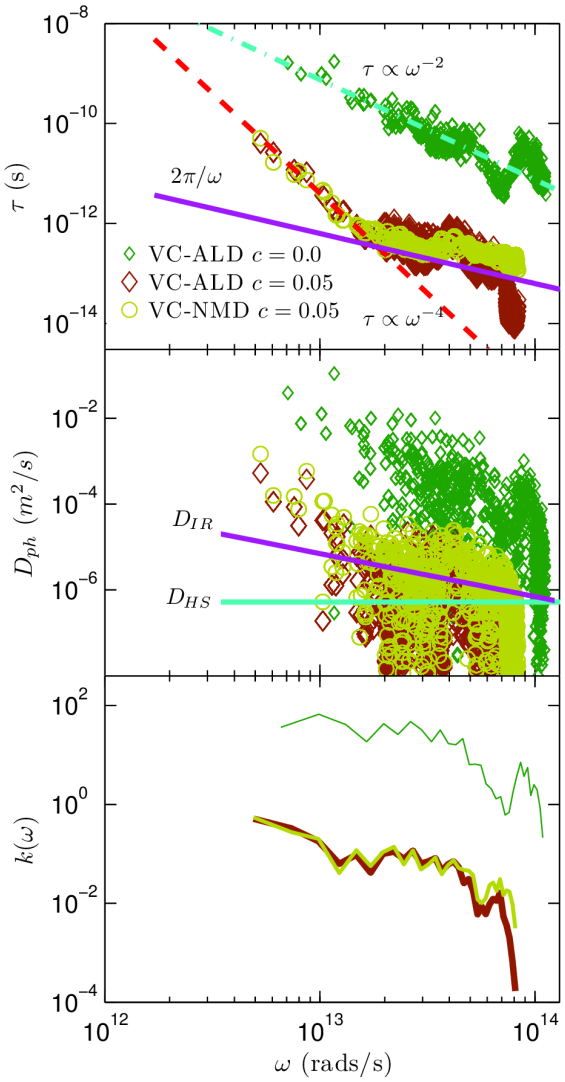
HS/IR Limit

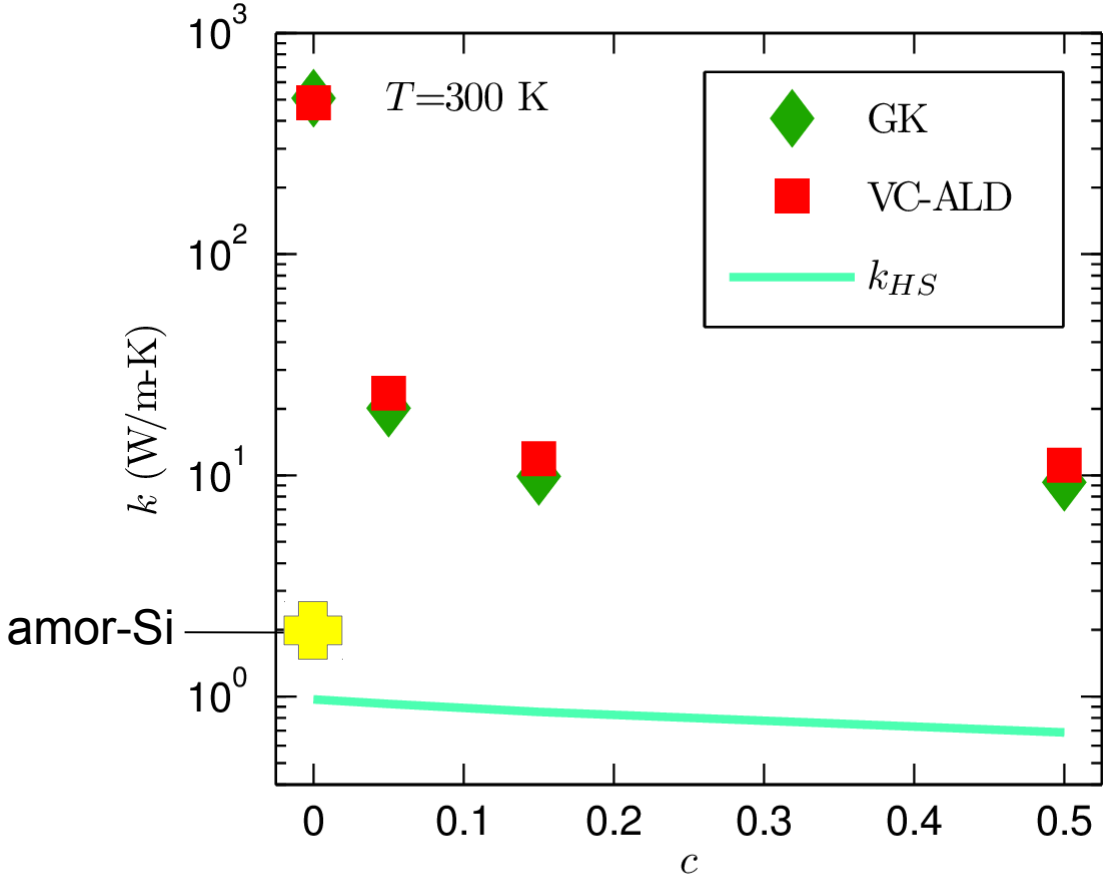
$$D_{IR} = \frac{2\pi}{3}\frac{v_s^2}{\omega}$$





Thermal conductivity: SW silicon alloy

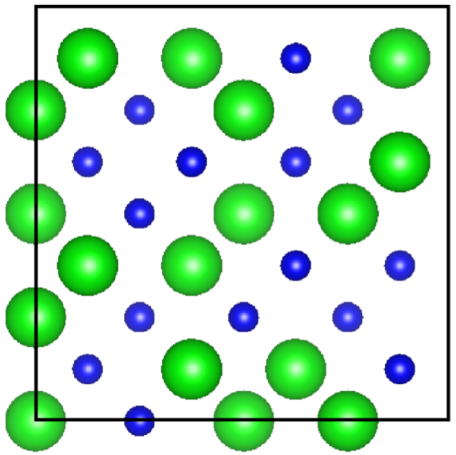


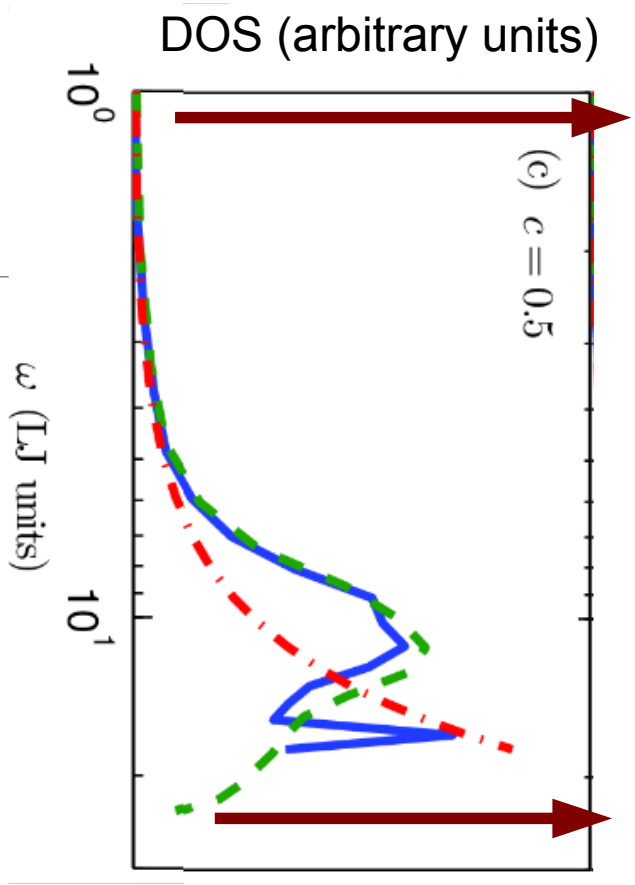


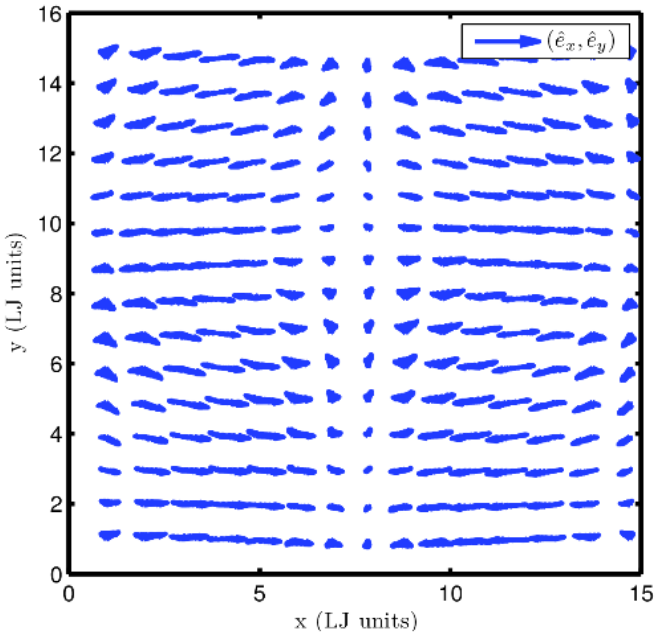
Gamma modes

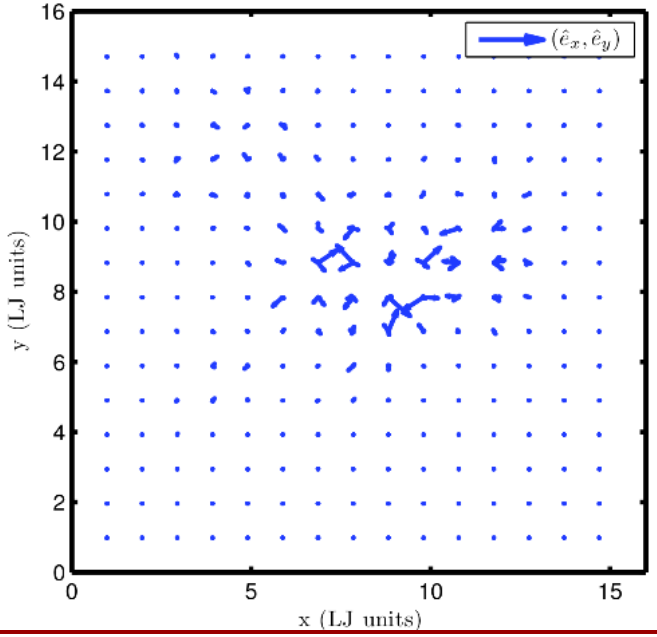
$e\left(\begin{smallmatrix}\kappa=0 & b\\ \nu & \alpha\end{smallmatrix}\right)$

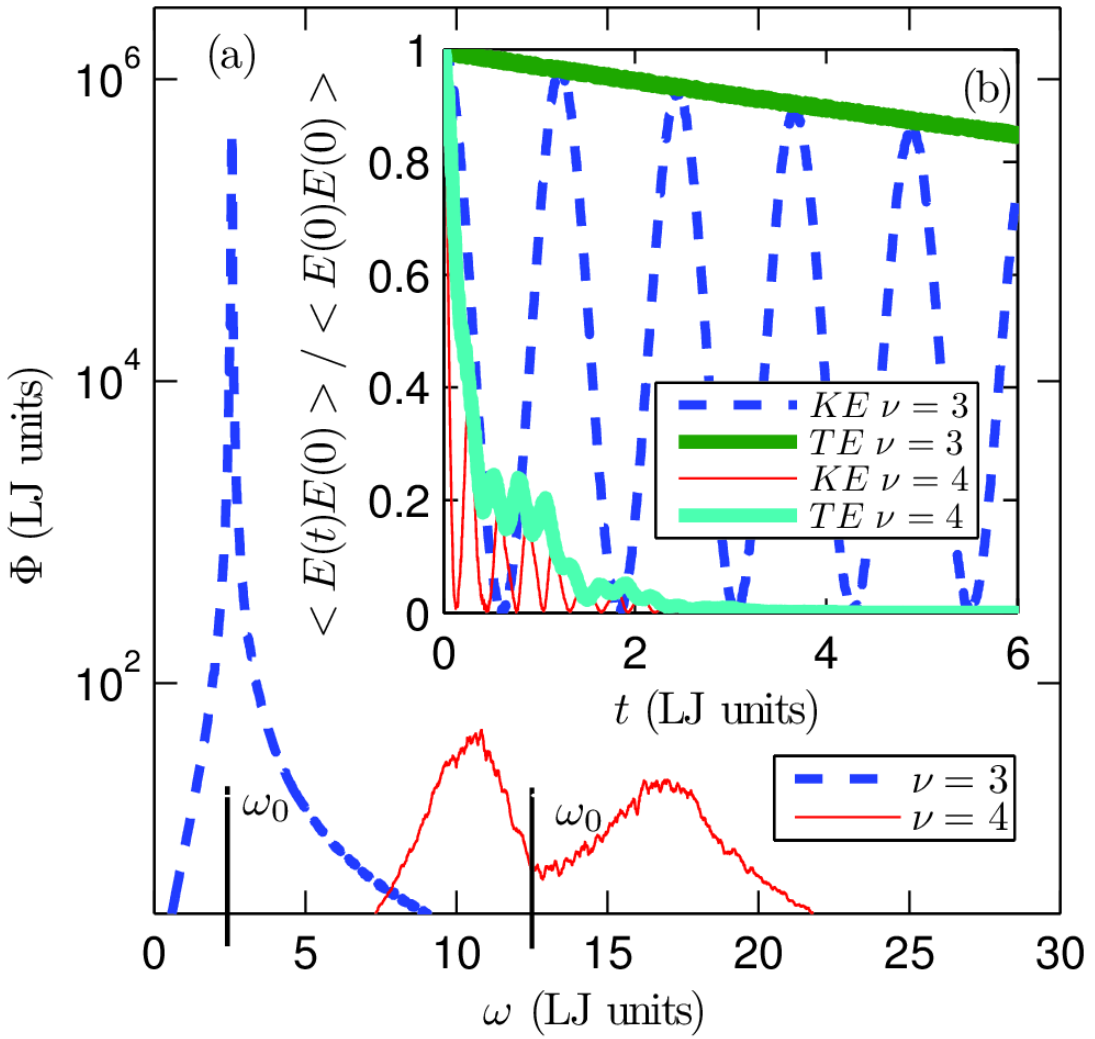
(a) disordered supercell



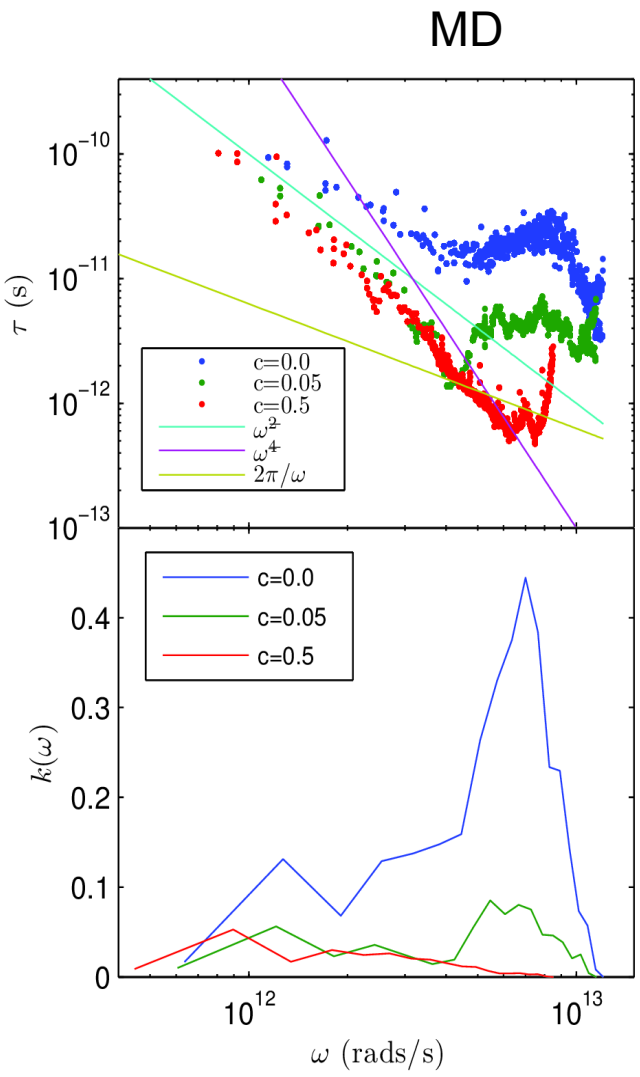


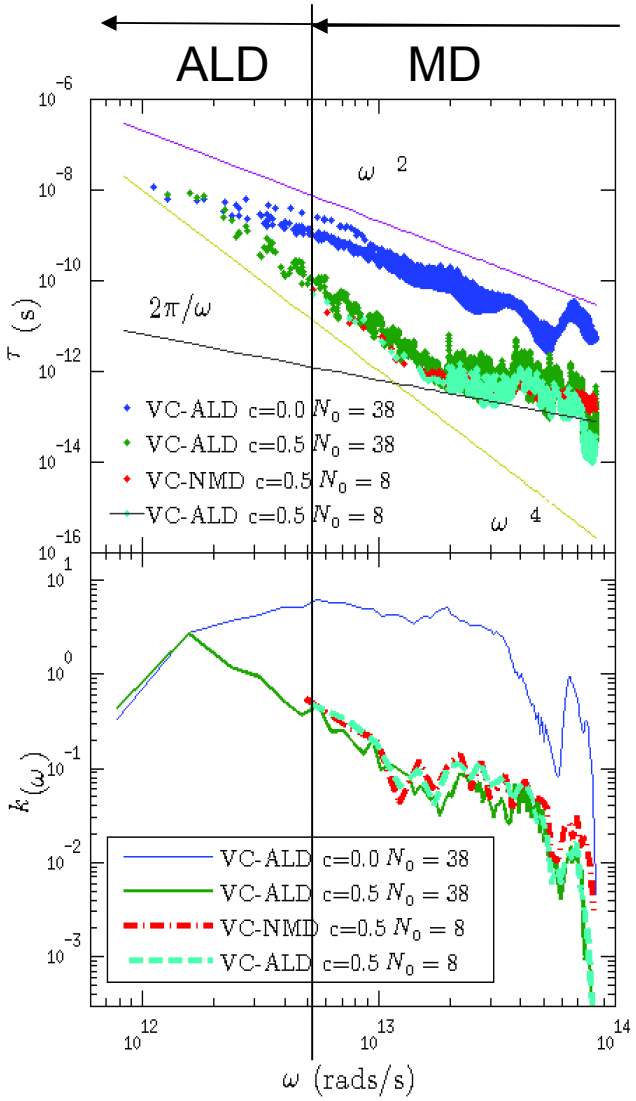





(a)
(b)
10^6
10^4
10^2
Φ (LJ units)
ω_0
ω_0
0
5
10
15
20
25
30
ω (LJ units)
$\nu = 3$
$\nu = 4$
1
0.8
0.6
0.4
0.2
0
$< E(t)E(0) > / < E(0)E(0) >$
0
2
4
6
t (LJ units)
$KE\ \nu = 3$
$TE\ \nu = 3$
$KE\ \nu = 4$
$TE\ \nu = 4$

Phonon Spectrum: LJ Ar vs SW Si





MD-based:

1E4 modes

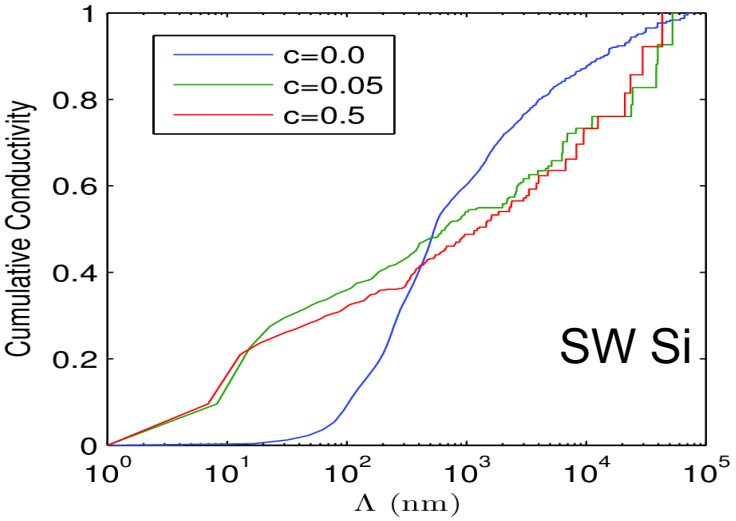
(7 days)*(100 cpu)

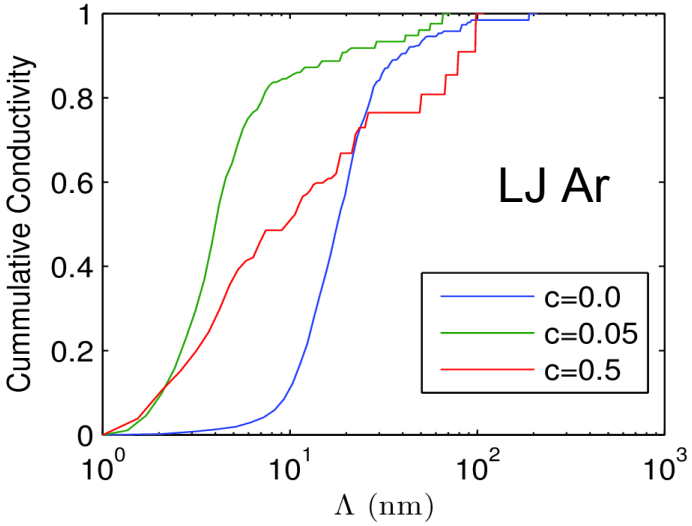
ALD:

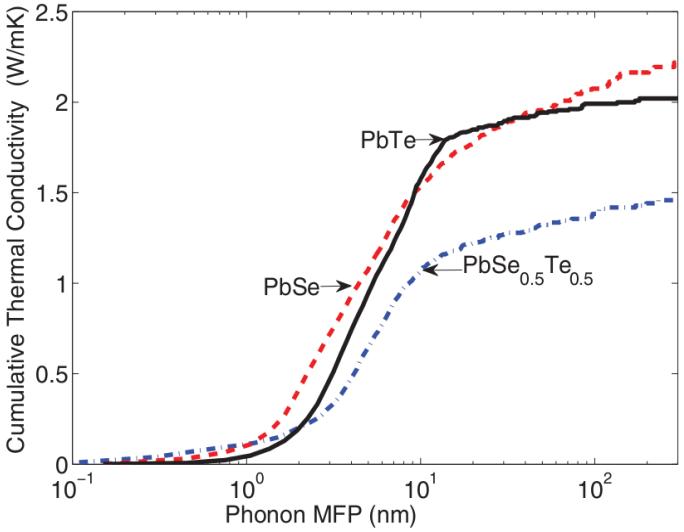
1E6 modes

(7 days)*(12 cpu)

Conductivity Accumulation







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