Evaluation of the Virtual Crystal Approximation for Predicting Thermal Conductivity

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04/04/13

Slides

- Macro-theory: k = \rho C_p \alpha
- Carrier theory (classical harmonic limit):

k_{x} = (kb/V)\sum D_{x} : most general (phonons, diffusons, locons, propagons)

k_{x} = (kb/V)\sum v_{g,x}^2\tau : phonons

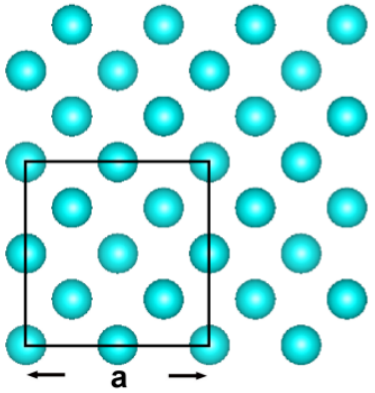
k_{x} = (kb/V)\sum v_{g,x} \Lambda : phonons (\Lambda = |v_g|\tau)

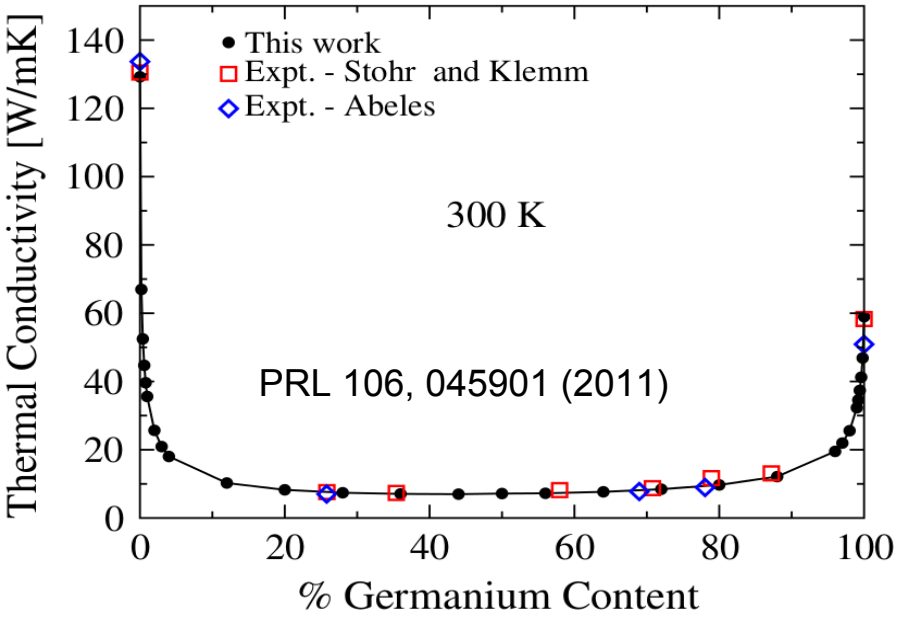
- \Lambda in SW alloys, compare to a, compare to k(\Lambda).
- \Lambda in LJ alloys, compare to a, k(\Lambda).
- LJ alloys k(\omega), fast convergence (k(N_0))
- LJ amorphous, all important modes in a sample 4x (2 nm!), no contributions from phonons
- implications for disordered systems, how to beat high scatter limit

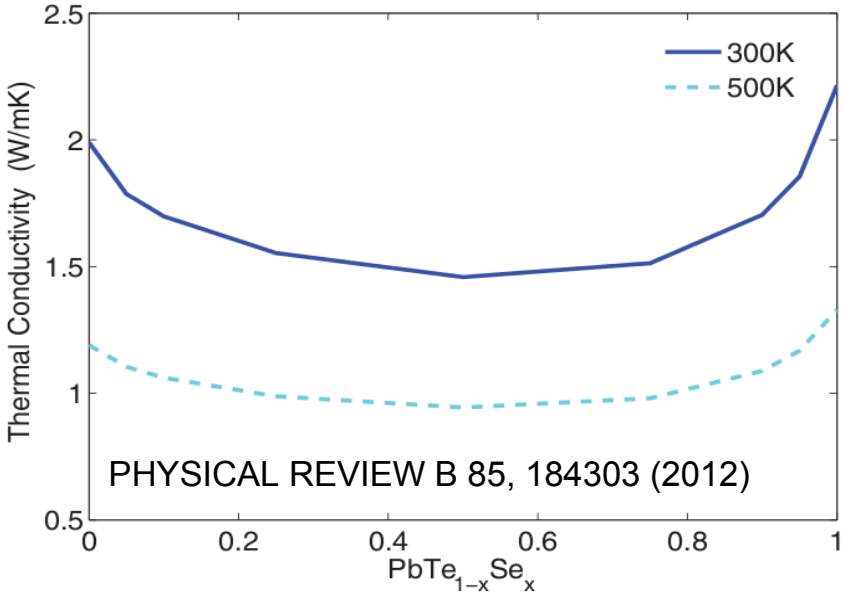
-

Motivation: DFT predictions

- Compuationally expensive DFT, calculations based on unit cell
- Alloys: isotopic effects, thermoelectric materials





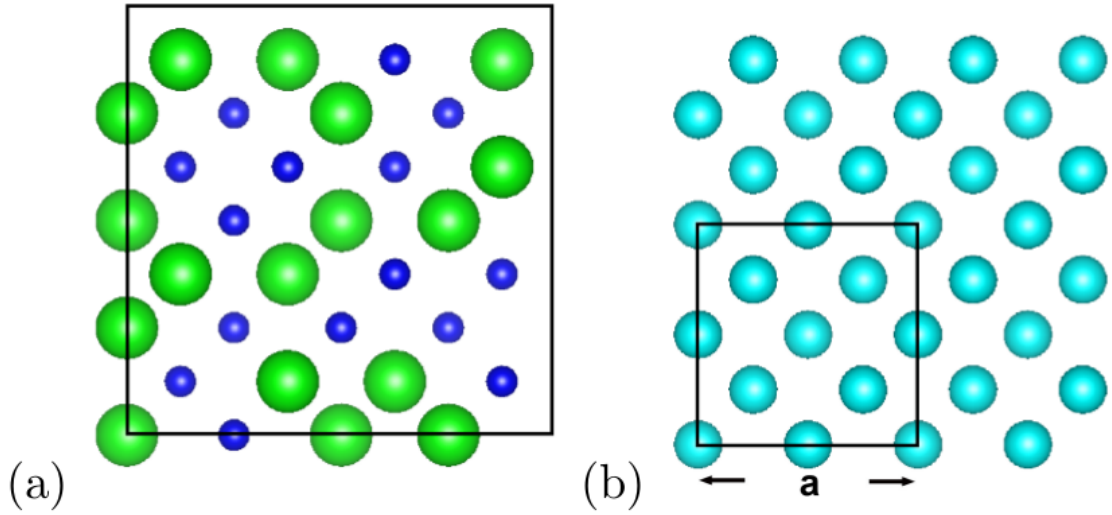


Virtual Crystal Approximation

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

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

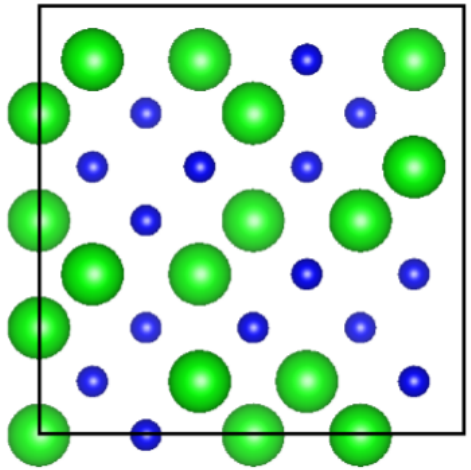
Virtual Crystal Approximation



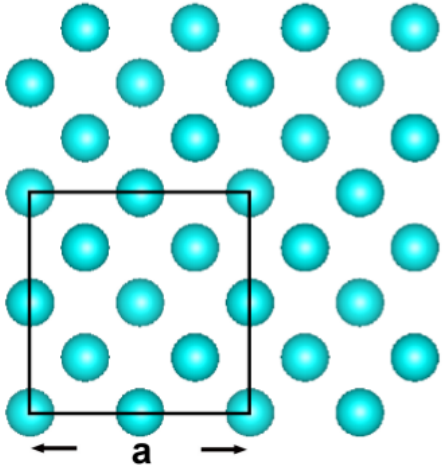
c^μ, m^μ $\qquad$ $\bar{m}^\mu$

$$g_n = \sum_\mu c^\mu (1 - m^\mu / \bar{m}^\mu)^n$$

Virtual Crystal Approximation



(a)



(b)

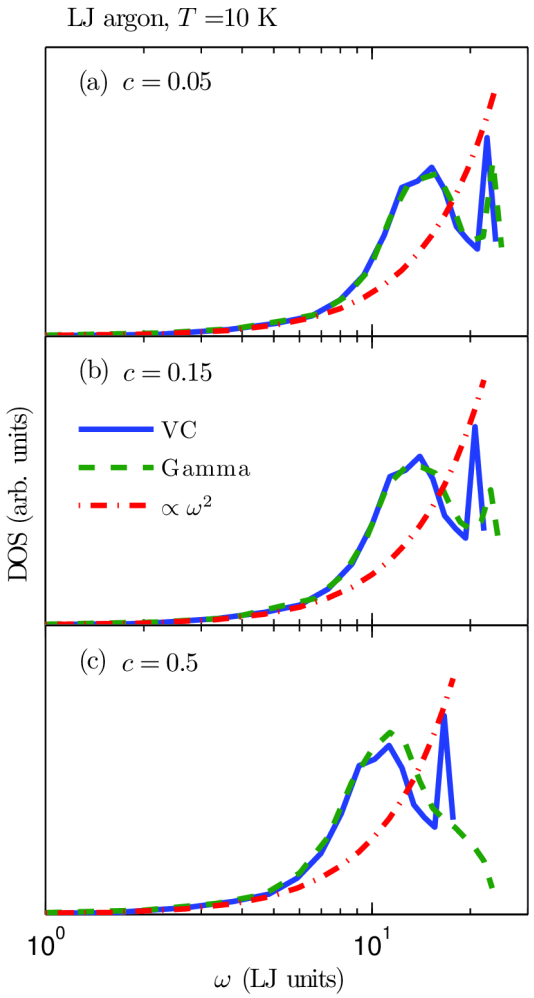
$\tau_{p-d}\left(\begin{smallmatrix}\kappa\\ \nu\end{smallmatrix}\right) \sim 1/\omega^4$

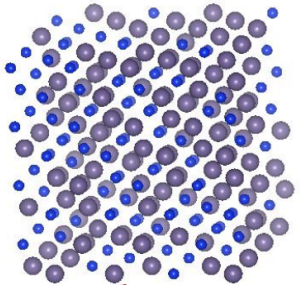
$\tau_{p-p} \sim 1/\omega^2$

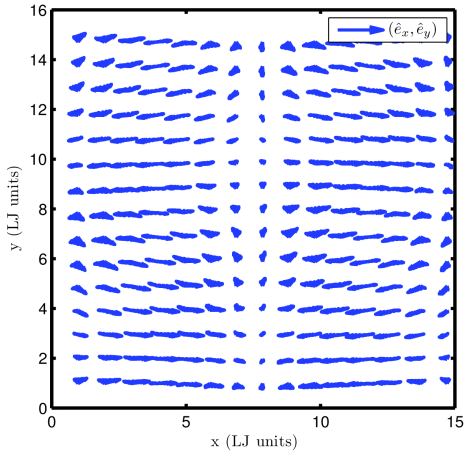
Matthiessen's Rule

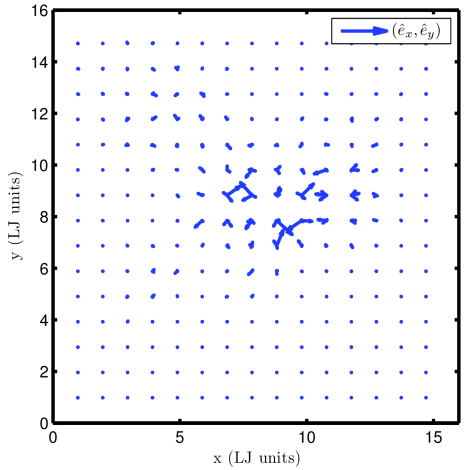
$$\frac{1}{\tau\left(\begin{smallmatrix}\kappa\\ \nu\end{smallmatrix}\right)} = \frac{1}{\tau_{p-p}\left(\begin{smallmatrix}\kappa\\ \nu\end{smallmatrix}\right)} + \frac{1}{\tau_{p-d}\left(\begin{smallmatrix}\kappa\\ \nu\end{smallmatrix}\right)}$$

$$1/[(1-c)m^i + cm^j]^{1/2}$$


LJ argon, T =10 K
(a) $c = 0.05$
(b) $c = 0.15$
(c) $c = 0.5$
VC
Gamma
$\propto \omega^2$
DOS (arb. units)
10^0
10^1
ω (LJ units)



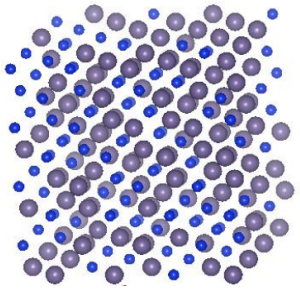


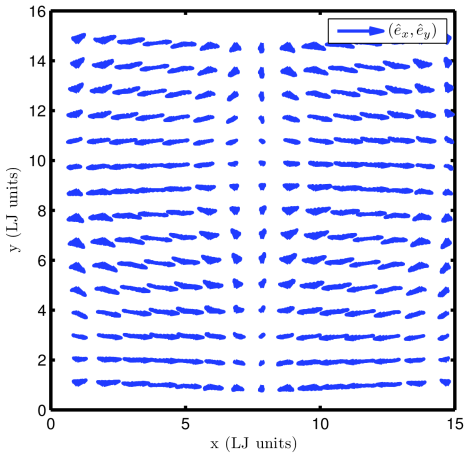


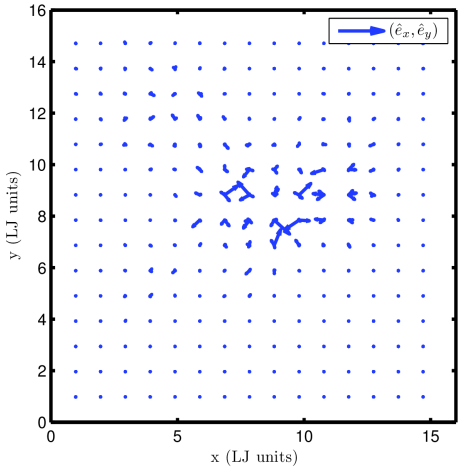
$$S^{L,T}\left(\boldsymbol{\kappa}_{\omega}^{VC}\right) = \sum_{\nu} E^{L,T}\left(\boldsymbol{\kappa}_{\nu}^{VC}\right) \delta\left(\omega - \omega\left(\boldsymbol{\kappa}_{\nu}^{=\mathbf{0}}\right)\right)$$

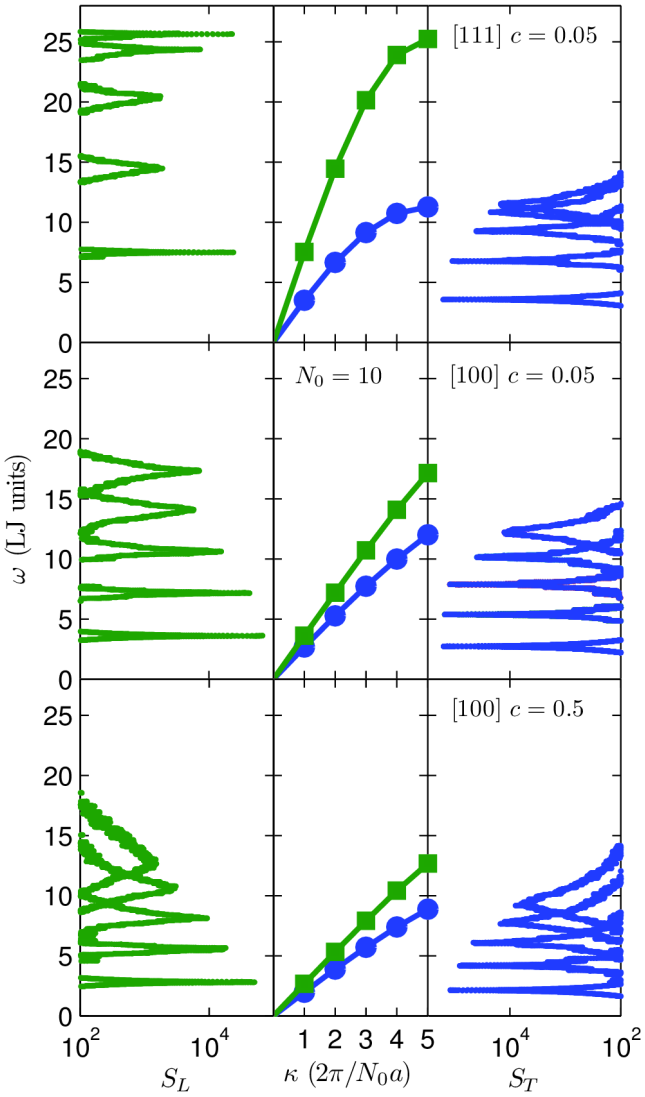
$$E^{L}\left(\boldsymbol{\kappa}_{\nu}^{VC}\right) = \left| \sum_{b} \hat{\boldsymbol{\kappa}}_{VC} \cdot e\left(\boldsymbol{\kappa}_{\nu}^{=\mathbf{0}} \; {}_{\alpha}^{b}\right) \exp\left[i\boldsymbol{\kappa}_{VC} \cdot \boldsymbol{r}_0\left(_{b}^{l=0}\right)\right] \right|^2$$

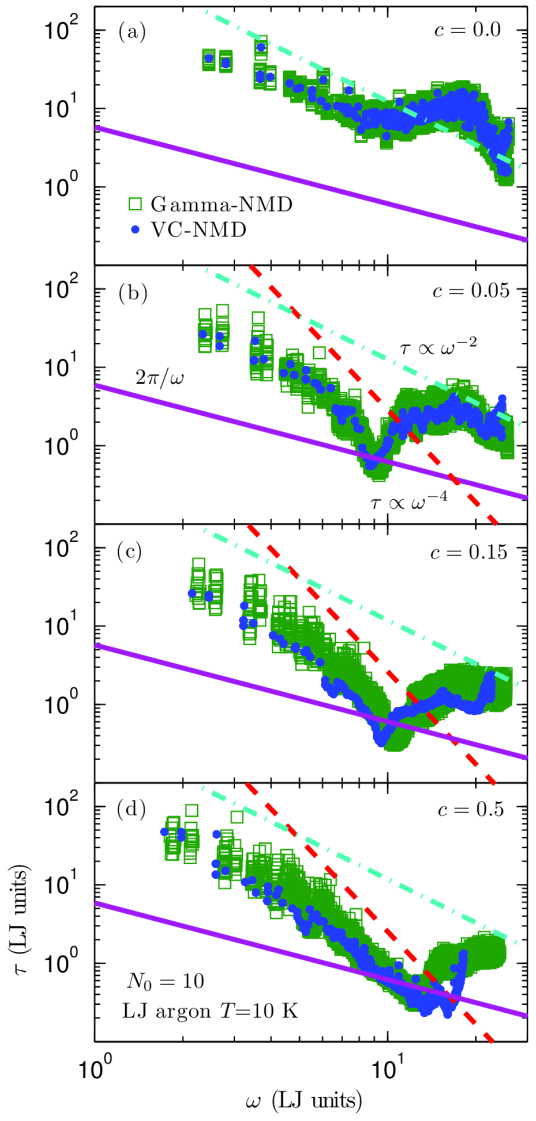
$$E^{T}\left(\boldsymbol{\kappa}_{\nu}^{VC}\right) = \left| \sum_{b} \hat{\boldsymbol{\kappa}}_{VC} \times e\left(\boldsymbol{\kappa}_{\nu}^{=\mathbf{0}} \; {}_{\alpha}^{b}\right) \exp\left[i\boldsymbol{\kappa}_{VC} \cdot \boldsymbol{r}_0\left(_{b}^{l=0}\right)\right] \right|^2$$




$(\hat{e}_x, \hat{e}_y)$
y (LJ units)
x (LJ units)


$(\hat{e}_x, \hat{e}_y)$
y (LJ units)
x (LJ units)


[111] $c = 0.05$
$N_0 = 10$
[100] $c = 0.05$
[100] $c = 0.5$
ω (LJ units)
S_L
κ $(2\pi/N_0 a)$
S_T


(a)
$c = 0.0$
Gamma-NMD
VC-NMD
(b)
$c = 0.05$
$\tau \propto \omega^{-2}$
$2\pi/\omega$
$\tau \propto \omega^{-4}$
(c)
$c = 0.15$
(d)
$c = 0.5$
$N_0 = 10$
LJ argon T=10 K
τ (LJ units)
ω (LJ units)

Virtual Crystal Approximation

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

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

Diamond

GaN

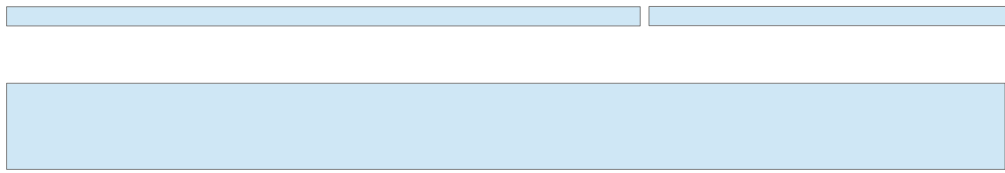
si

Si,HS

Si/Ge

PbTe,PbTe/Se,
(1/4)Tmelt = 300K

LJ,20K,
(1/4)T_melt



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

$$q\binom{\boldsymbol{\kappa}}{\nu};t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} u_\alpha\binom{l}{b};t)\, e^*\binom{\boldsymbol{\kappa}}{\nu}\ \binom{b}{\alpha}) \exp[i\boldsymbol{\kappa}\cdot \mathbf{r}_0\binom{l}{0})$$

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

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

Car

$$\tau = \frac{2\pi}{\omega}$$

$$\frac{1}{\tau_{p-d}\binom{\boldsymbol{\kappa}}{\nu}} = \frac{\pi}{2} g_2 \omega^2\binom{\boldsymbol{\kappa}}{\nu}\, DOS\left(\omega\binom{\boldsymbol{\kappa}}{\nu}\right)$$

modeling thermoelectric materials

- anharmonic lattice dynamics + phonon defect lifetime (ald+taud).

PRL 106, 045901 (2011)

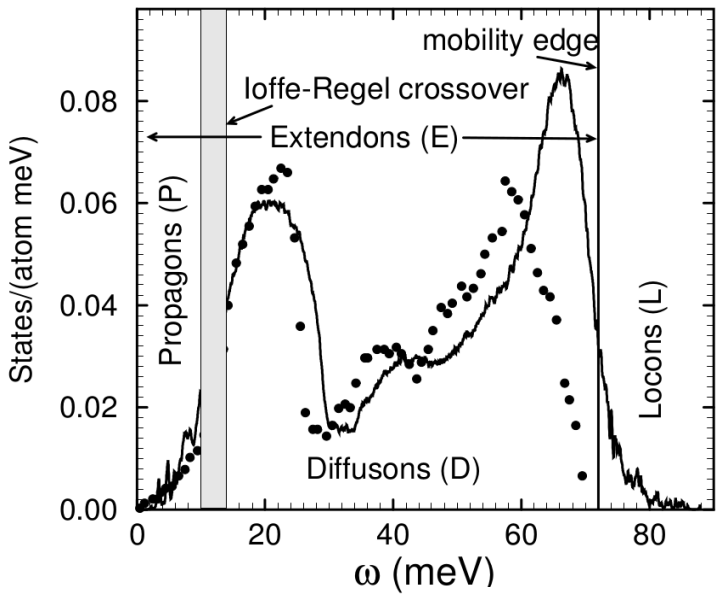
- this approach referred to as **virtual crystal (vc)** approximation.

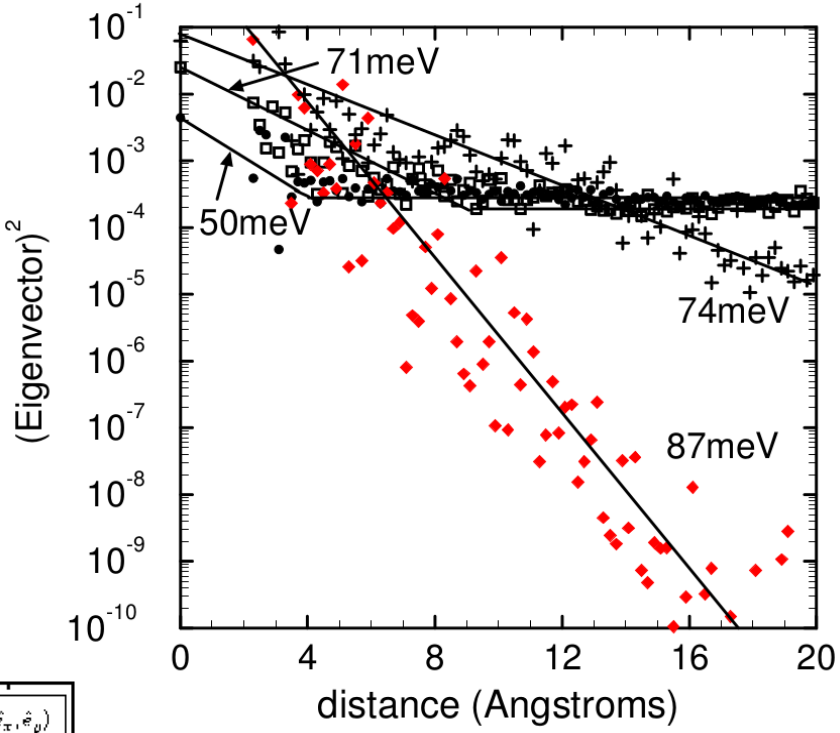
- ald+taud vc can be computationally cheap, even using ab initio.

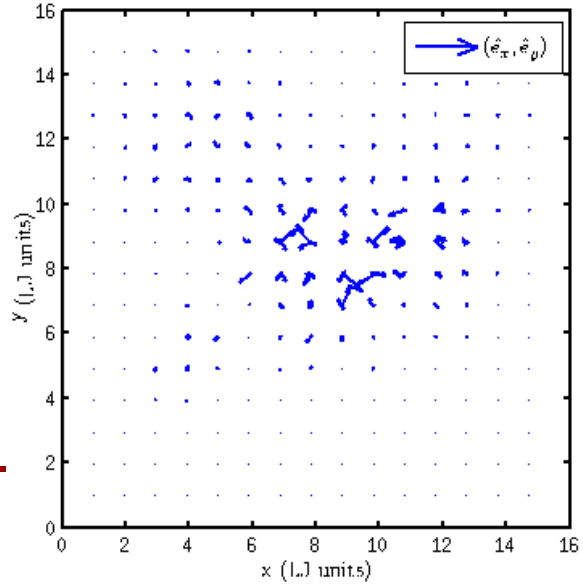
is this approach valid?

PHYSICAL REVIEW B 85, 184303 (2012)

propagons, diffusons, locons







Thermal Transport: Ordered and Disordered

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

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

$$D_{ph}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = \boldsymbol{v}^2_g\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)$$

$$\Lambda\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = |\boldsymbol{v}_g| \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)$$

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

In a disordered material, it is not possible (in general) to specify v_g and \tau independently

$$k_{AF} = \sum_{modes} \frac{k_B}{V} D_{AF}\left(\omega\left(\begin{smallmatrix}\boldsymbol{\kappa}=\mathbf{0}\\ \nu\end{smallmatrix}\right)\right)$$

Phys. Rev. B 59, 3551–3559 (1999)

http://prb.aps.org/abstract/PRB/v59/i5/p3551_1

Thermal Transport: Ordered and Disordered

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

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

$$D_{ph}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = \boldsymbol{v}^2_g\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)$$

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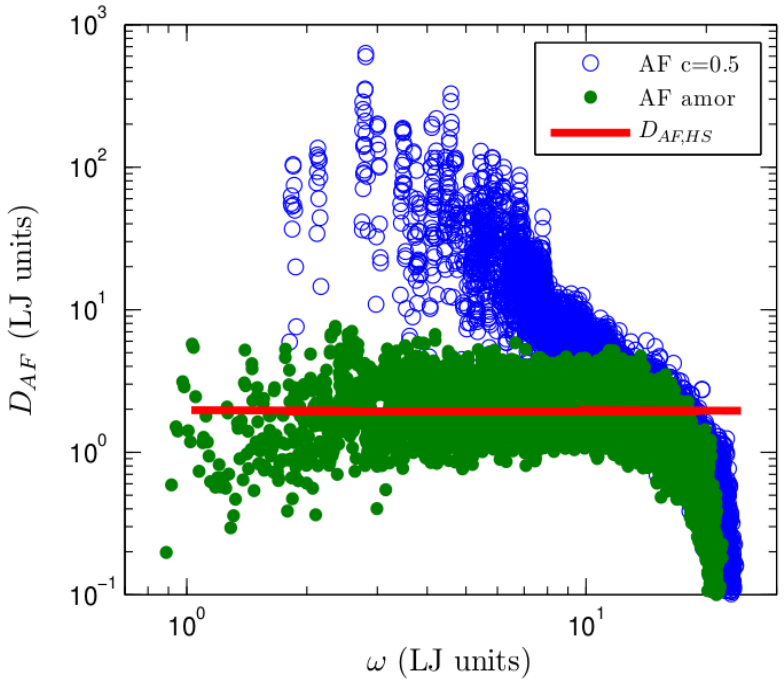
Phys. Rev. B 59, 3551–3559 (1999)

http://prb.aps.org/abstract/PRB/v59/i5/p3551_1

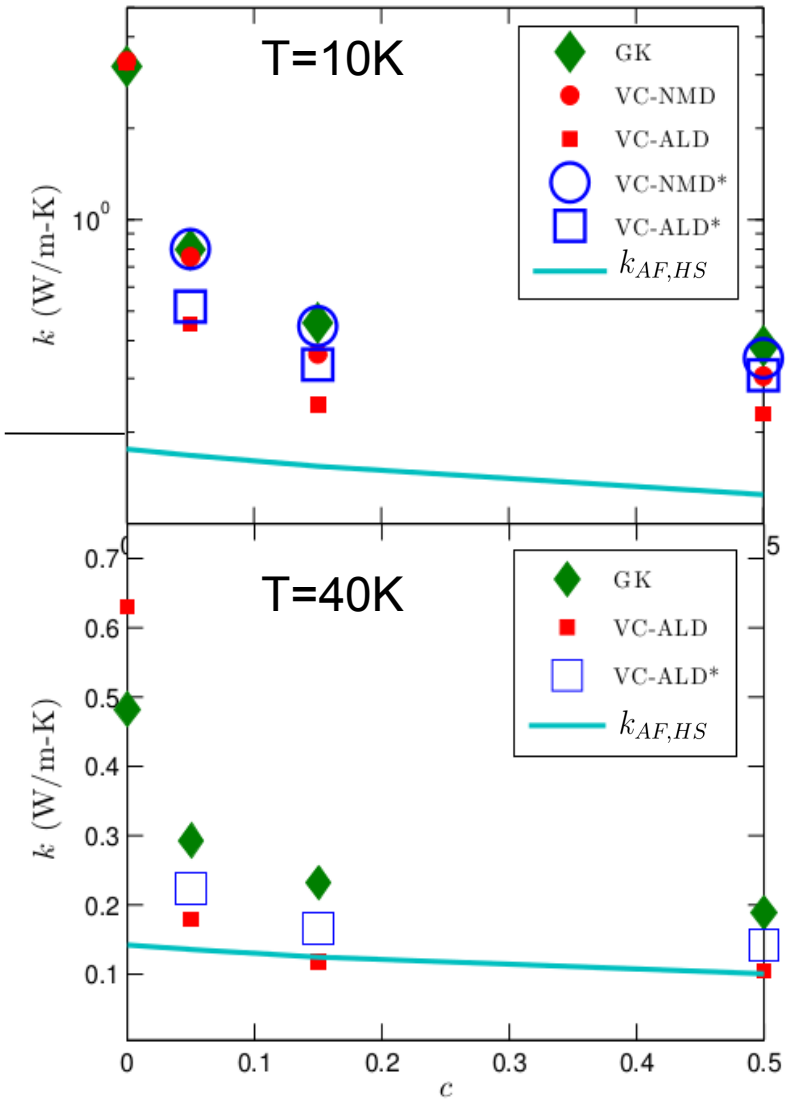
High-Scatter Limit: LJ Ar

$$k_{AF} = \sum_{modes} \frac{k_B}{V} D_{AF}(\omega(\kappa=0, \nu))$$

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

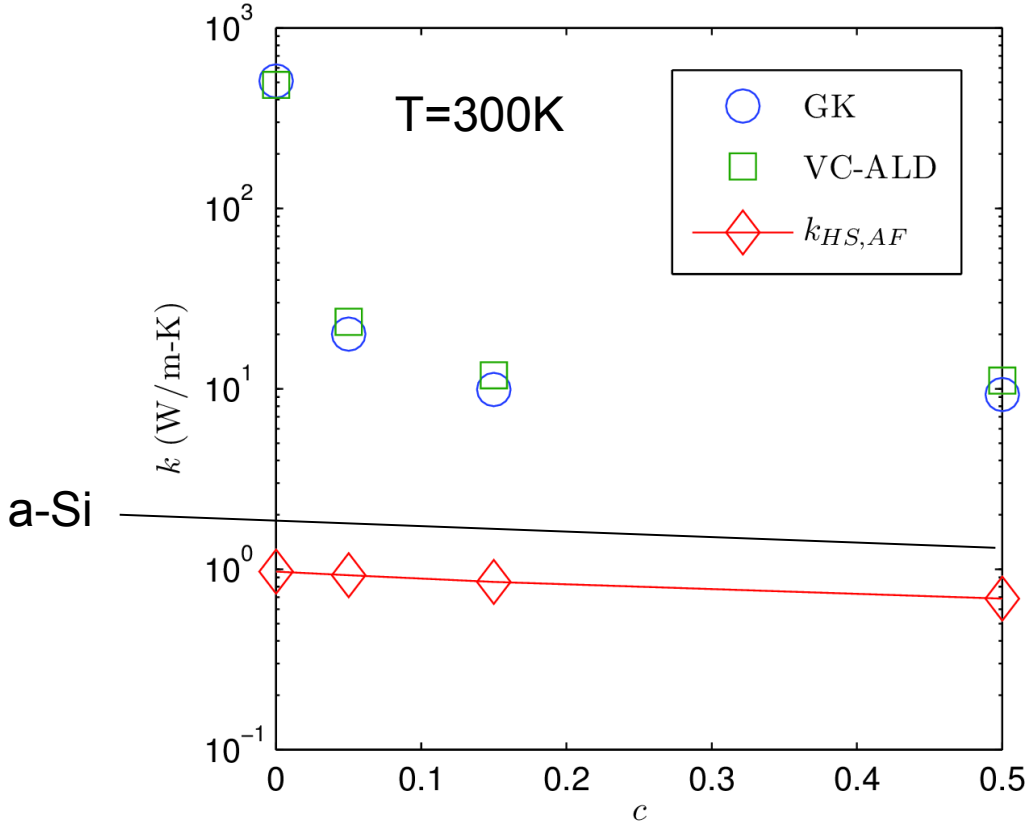


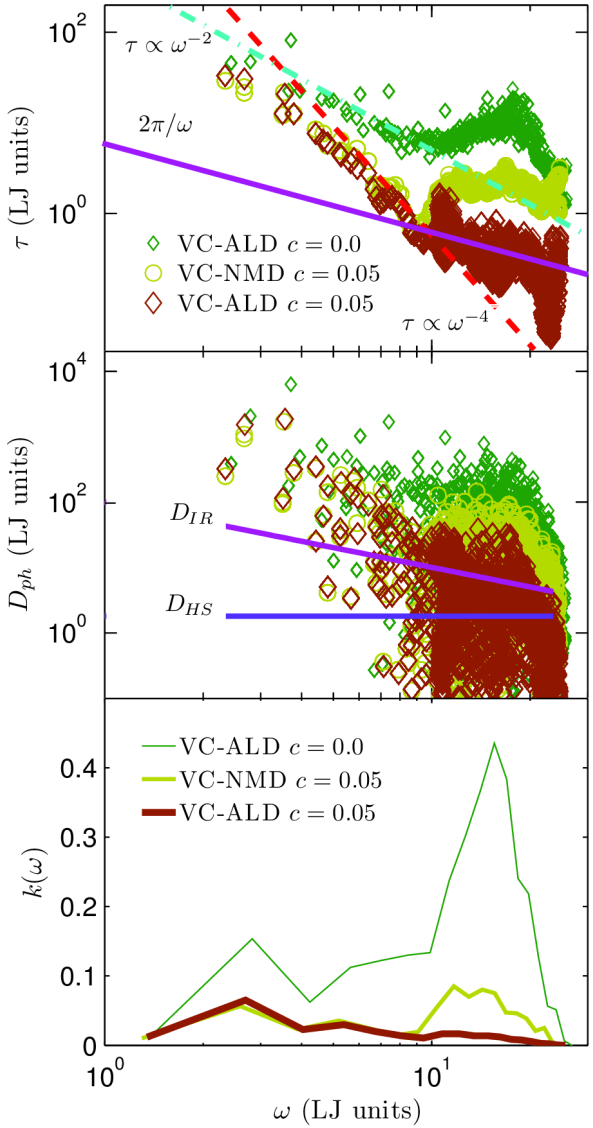
a-Ar

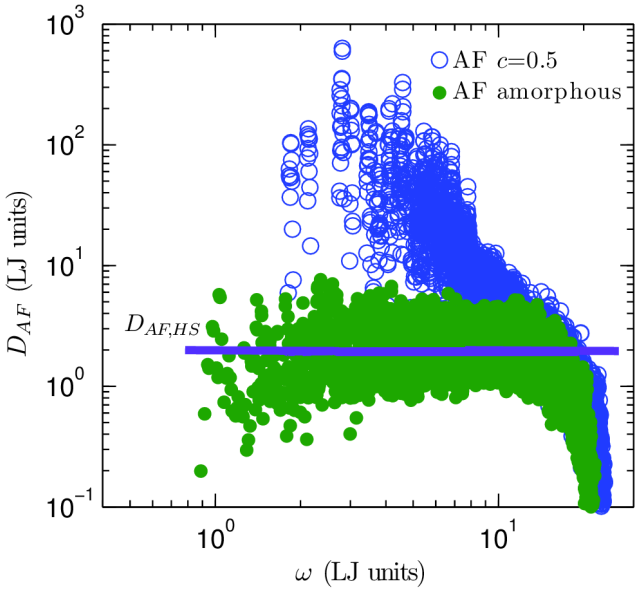


High-Scatter Limit: SW Si

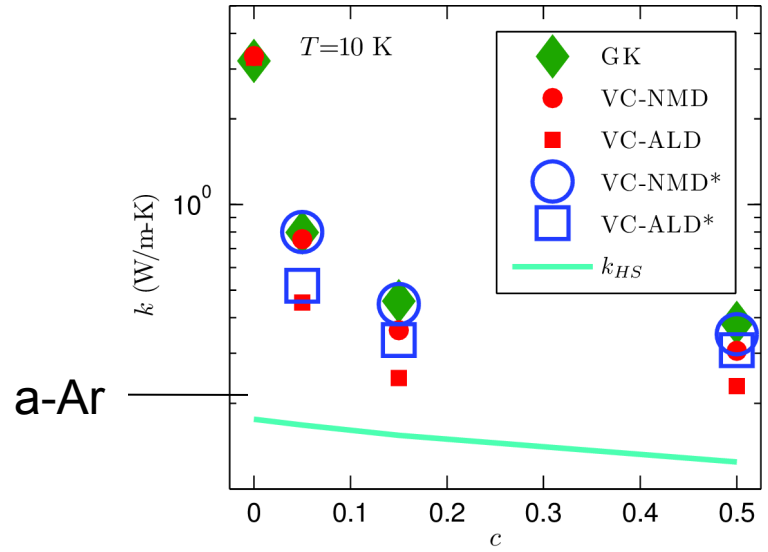
$$k_{AF,HS} = \frac{k_B}{V_b} b v_s a$$



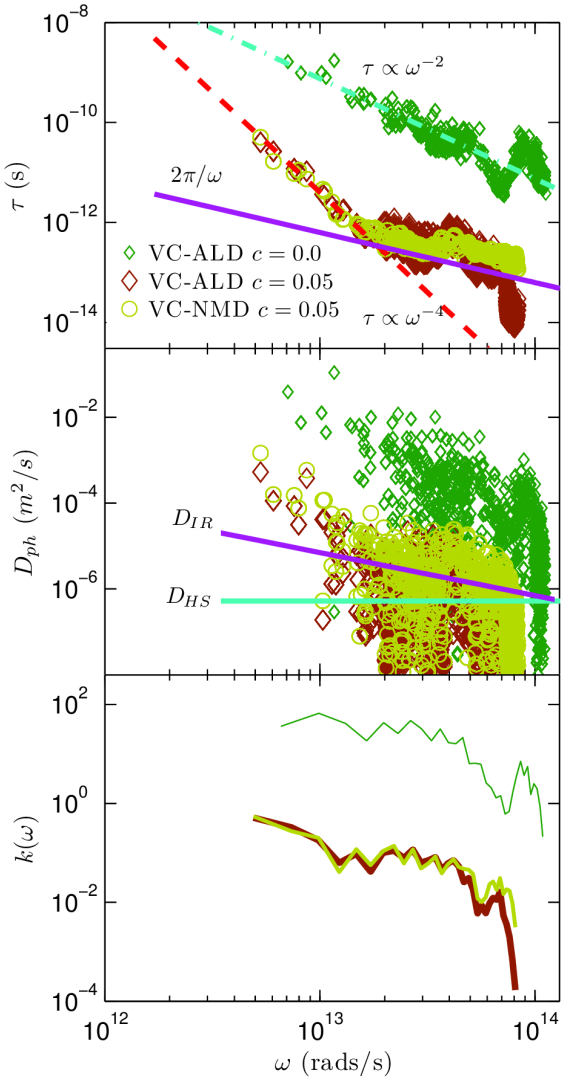

$\tau \propto \omega^{-2}$
$2\pi/\omega$
VC-ALD $c = 0.0$
VC-NMD $c = 0.05$
VC-ALD $c = 0.05$
$\tau \propto \omega^{-4}$
τ (LJ units)
D_{IR}
D_{HS}
D_{ph} (LJ units)
VC-ALD $c = 0.0$
VC-NMD $c = 0.05$
VC-ALD $c = 0.05$
$k(\omega)$
ω (LJ units)


AF c=0.5
AF amorphous
$D_{AF,HS}$
D_{AF} (LJ units)
ω (LJ units)

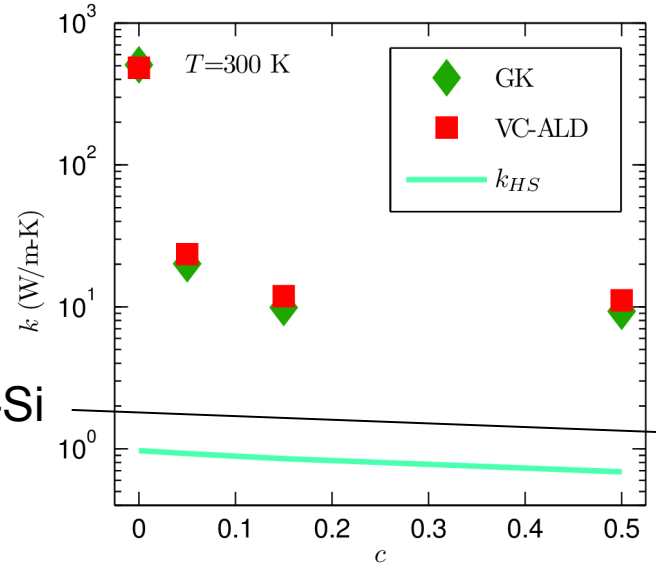
$$\frac{k(N_0)}{k_0} = 1 - \frac{c_0}{N_0}$$

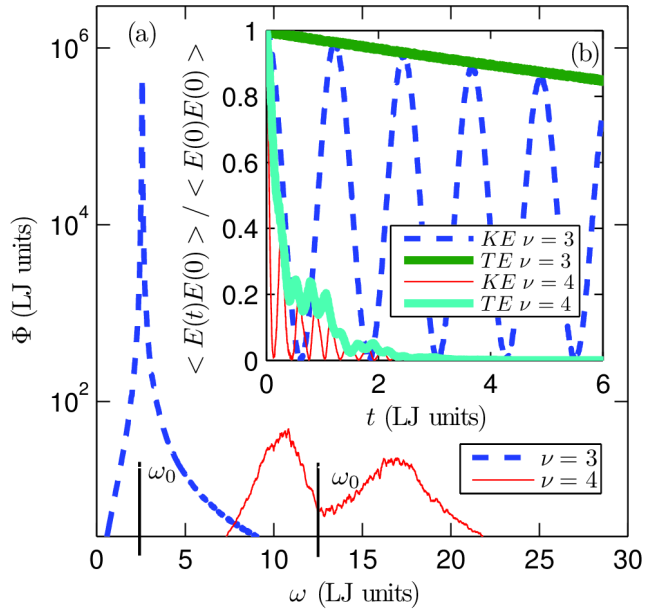


a-Ar


$\tau \propto \omega^{-2}$
$2\pi/\omega$
VC-ALD $c = 0.0$
VC-ALD $c = 0.05$
VC-NMD $c = 0.05$
$\tau \propto \omega^{-4}$
τ (s)
D_{IR}
D_{HS}
D_{ph} (m^2/s)
$k(\omega)$
ω (rads/s)

a-Si

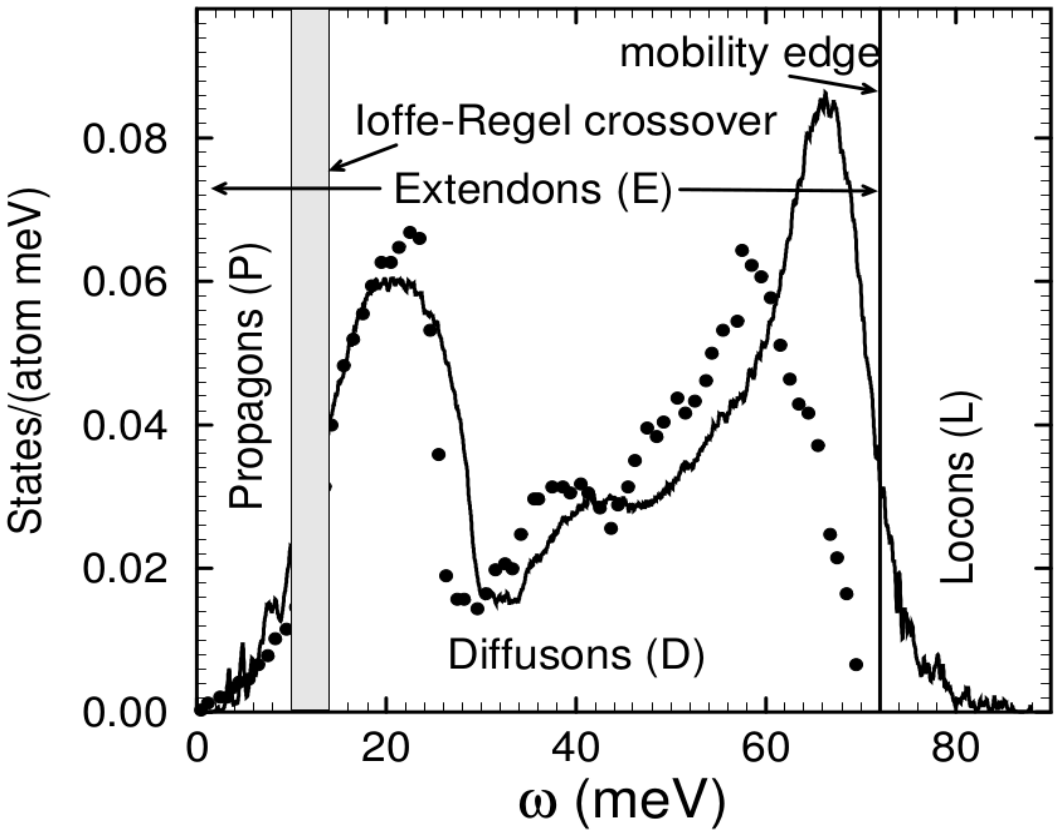

T=300 K
GK
VC-ALD
k_{HS}
k (W/m-K)
c


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

Propagons, Diffusons, Locons

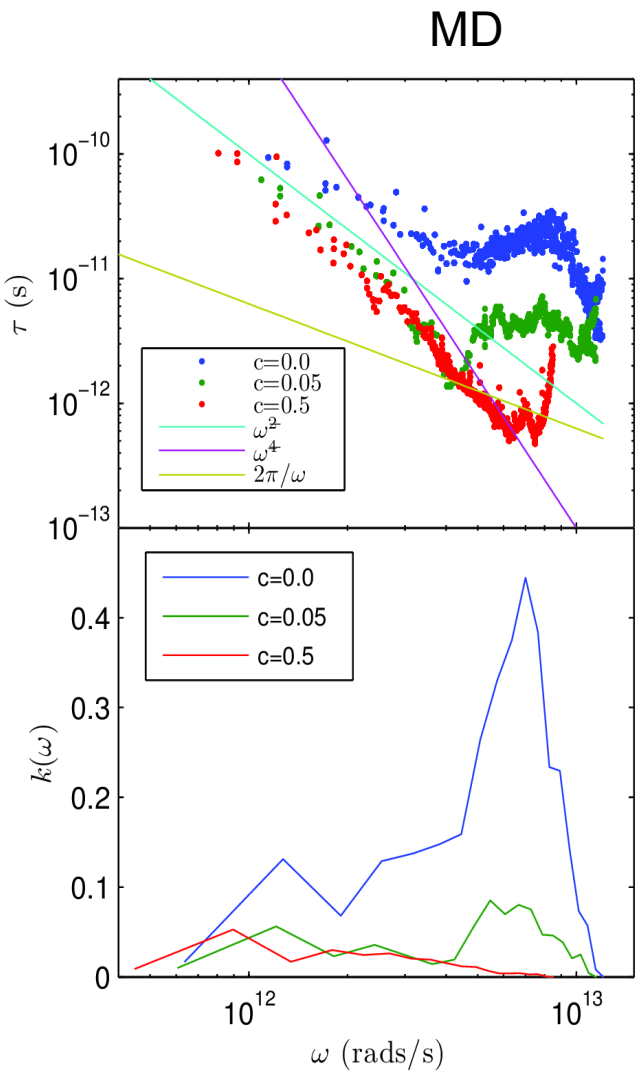
Numerical studies of amorphous silicon show that the lowest 4% of vibrational modes are plane-wave like ("propagons") and the highest 3% of modes are localized ("locons"). The rest are neither plane-wave like nor localized. We call them "diffusons."

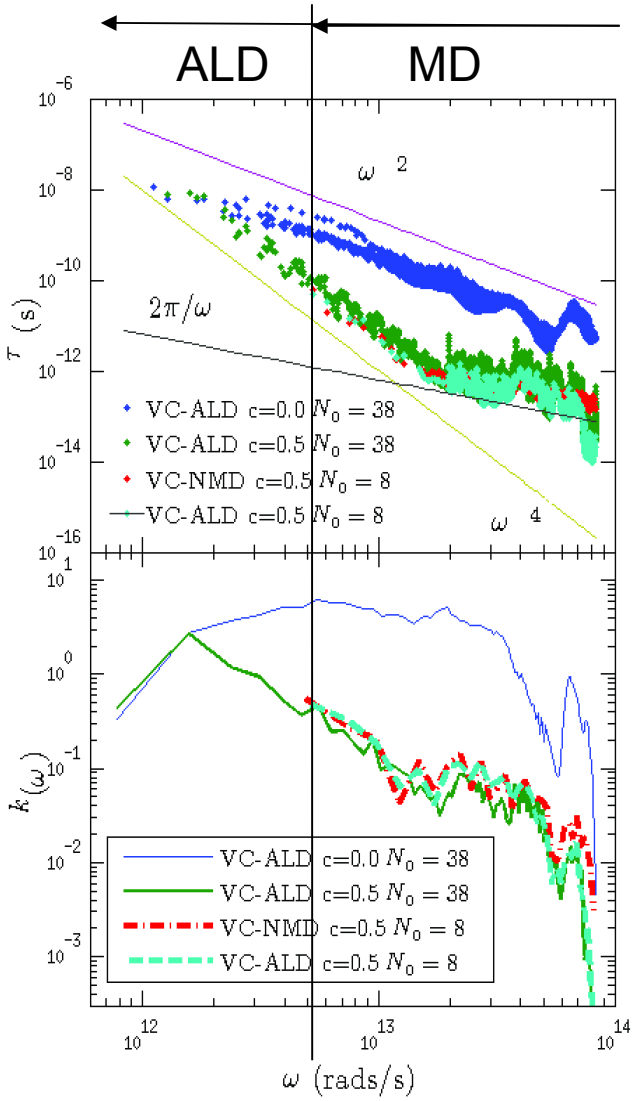
\cite{diffusons_allen_1999}



vibrons { extendons { propagons, diffusons; locons }

Phonon Spectrum: LJ Ar vs SW Si





MD-based:

1E4 modes

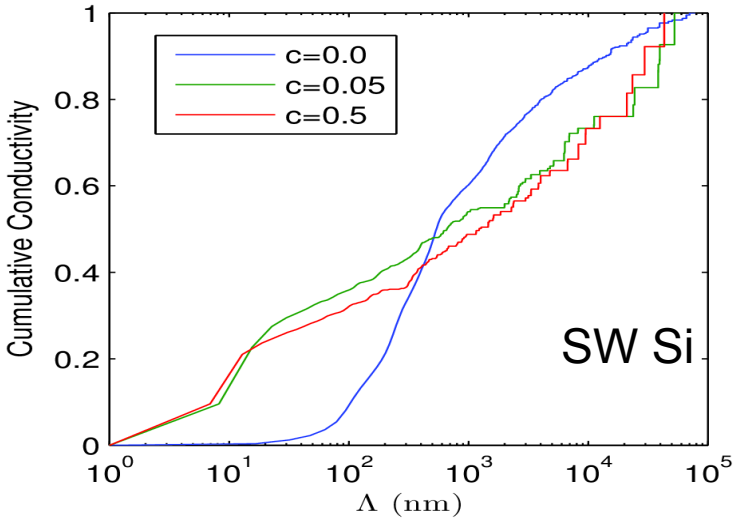
(7 days)*(100 cpu)

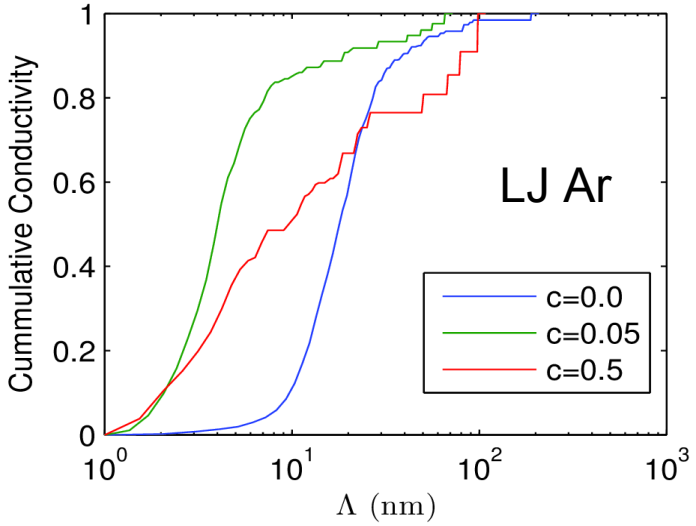
ALD:

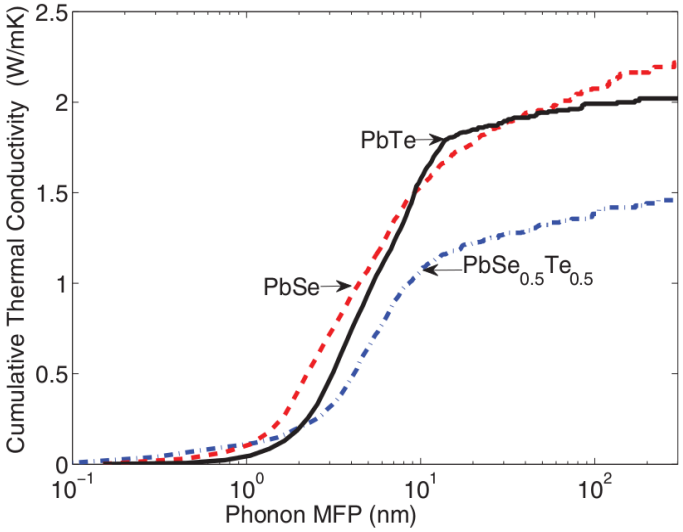
1E6 modes

(7 days)*(12 cpu)

Conductivity Accumulation







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Diffuson Theory

- Allen Feldman theory of diffusons [1]:

$$k_{AF} = \sum_i C(\omega_i) D_{AF}(\omega_i)$$

$$D_{AF}(\omega_i) = \frac{\pi V^2}{3\hbar^2 \omega_i^2} \sum_j^{\neq i} |S_{ij}|^2 \delta(\omega_i - \omega_j)$$

- Conservation of energy:

$$\delta(\omega_i - \omega_j)$$

- Heat current operator:

$$|S_{ij}|^2$$

- Ingredients: **harmonic** Lattice Dynamics

[1] Philip B. Allen and Joseph L. Feldman. Thermal conductivity of disordered harmonic solids. Physical Review B, 48(17):12581–12588, Nov 1993.