evaluation of the virtual crystal approximation

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10/10/2012

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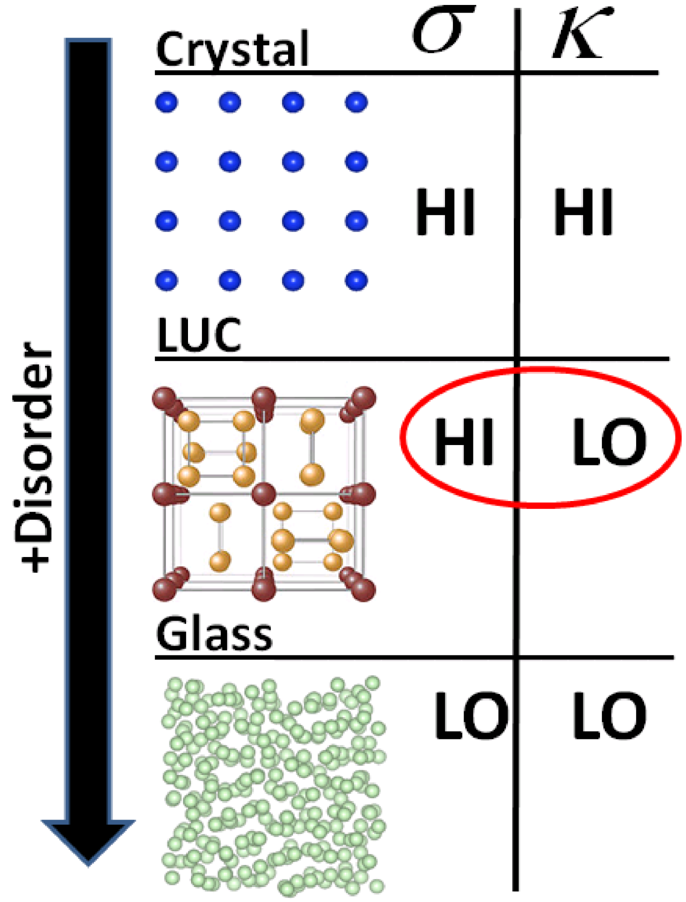
materials for thermoelectric energy conversion

- Lower thermal conductivity for improved thermoelectric efficiency:

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

- Skutterudites: “electron-crystal, phonon-glass”

- What is responsible for low thermal conductivity? Phonon picture, sub-unit cell effects...
- What about simple alloys?



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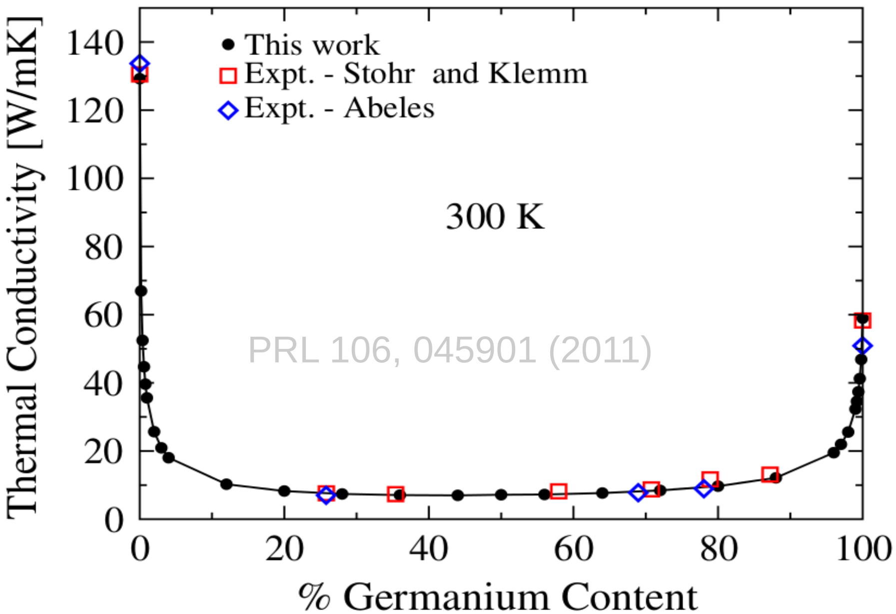
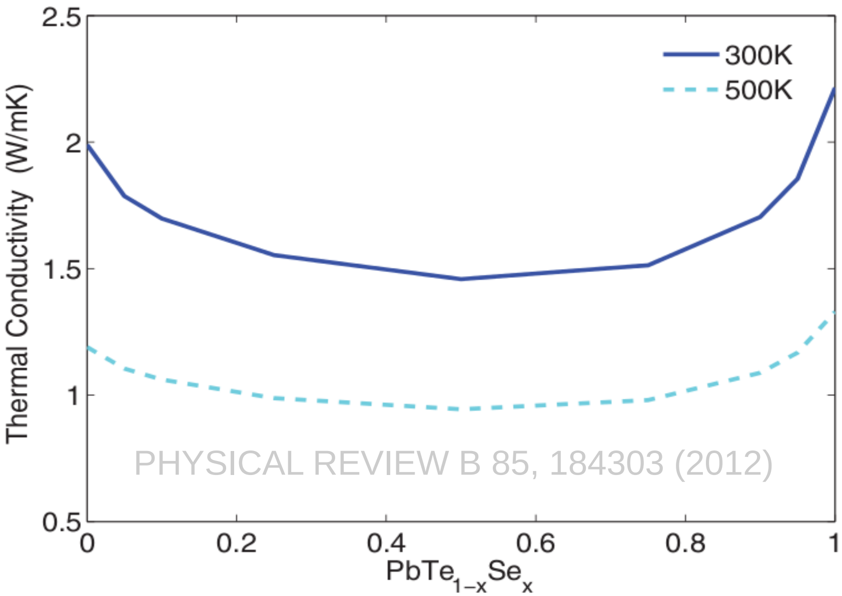
modeling thermoelectric materials





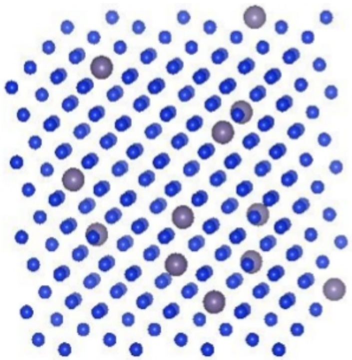
- anharmonic lattice dynamics + phonon defect lifetime (ald+taud).

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

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

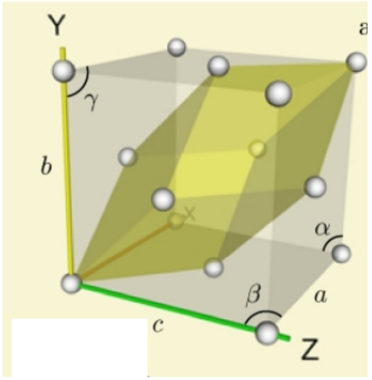
• is this approach valid?

lj alloys using virtual crystal (vc)



virtual crystal (vc)

$$\tau\binom{\boldsymbol{\kappa}}{\nu}$$



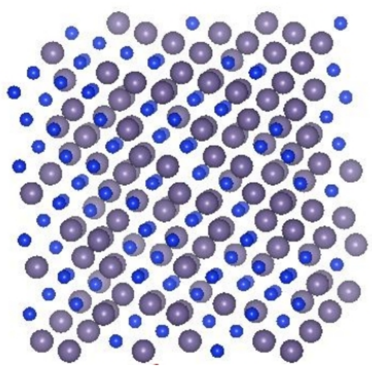
Unit cell

c=0.0 $\bar{m} = 1.0$

$$m^a = 1 \quad m^b = 3$$

$$m^a_{1-c} m^b_c$$

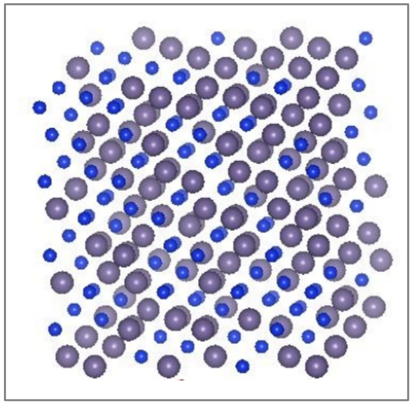
c=0.5 $\bar{m} = 2.0$



gamma point

$$\tau\binom{\boldsymbol{\kappa}=0}{\omega}$$

Unit cell



thermal conductivity in ordered systems

- conductivity in ordered (crystalline) system sum over phonon modes:

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

- relaxation time approximation solution of the BTE.
- mode-specific properties:

Property	Model
$c_{ph}\binom{\boldsymbol{\kappa}}{\nu}$	$c(\omega)_{ph} = \frac{k_B x^2}{V}\frac{exp(x)}{[exp(x)-1]^2}$, $c(\omega)_{ph} = \frac{k_B}{V}$
$v_{g,\mathbf{n}}^{2}\binom{\boldsymbol{\kappa}}{\nu}$	$v_g = \partial\omega/\partial\boldsymbol{\kappa}$
$\Lambda\binom{\boldsymbol{\kappa}}{\nu} = \lvert\boldsymbol{v}_g\rvert\tau\binom{\boldsymbol{\kappa}}{\nu}$	Depends on Scattering Mechanisms

$$x = \frac{\hbar\omega}{k_B T}$$

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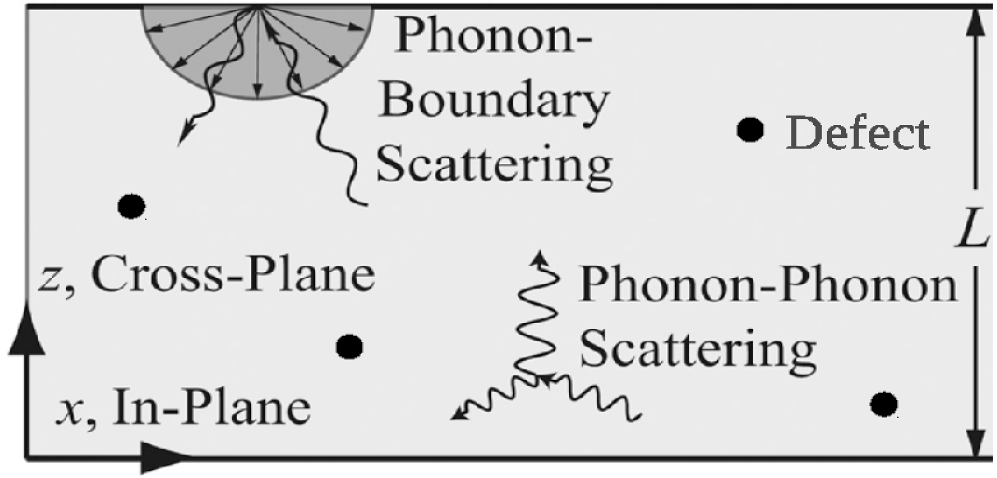
phonon scattering mechanisms

- Matthiessen rule:

$$\frac{1}{\tau} = \frac{1}{\tau_{p-p}} + \frac{1}{\tau_b} + \frac{1}{\tau_d}$$



- assumes scattering processes are independent.
- must be careful about the meaning of mean free path

[1] P. G. Klemens, ed. R. P. Tye, 1969, Vol. 1, Academic Press, London.
[2] Alan J. H. McGaughey and Ankit Jain, Applied Physics Letters, 100(6):061911, 2012.
[3] P. G. Klemens, Proc. Phys. Soc., London, Sect. A, 1955, 68, 1113.
[4] David G. Cahill, Fumiya Watanabe, Angus Rockett, and Cronin B. Vining, Phys. Rev. B, 71:235202, Jun 2005.

phonon scattering mechanisms

- Matthiessen rule: $$\frac{1}{\tau} = \frac{1}{\tau_{p-p}} + \frac{1}{\tau_b} + \frac{1}{\tau_d}$$

- phonon-phonon scattering [1] (ald):

$$1/\tau_{p-p}\begin{pmatrix}\boldsymbol{\kappa}\\ \nu\end{pmatrix} = \frac{\pi\hbar}{16N}\sum_{\boldsymbol{\kappa}',\nu'}^{N,3n}\sum_{\boldsymbol{\kappa}'',\nu''}^{N,3n}\left|\Phi\begin{pmatrix}\boldsymbol{\kappa} & \boldsymbol{\kappa}' & \boldsymbol{\kappa}''\\ \nu & \nu' & \nu''\end{pmatrix}\right|^2\left\{\left[f\begin{pmatrix}\boldsymbol{\kappa}'\\ \nu'\end{pmatrix}+f\begin{pmatrix}\boldsymbol{\kappa}''\\ \nu''\end{pmatrix}+1\right]\left[\delta\left(\omega\begin{pmatrix}\boldsymbol{\kappa}\\ \nu\end{pmatrix}-\omega\begin{pmatrix}\boldsymbol{\kappa}'\\ \nu'\end{pmatrix}-\omega\begin{pmatrix}\boldsymbol{\kappa}''\\ \nu''\end{pmatrix}\right)\right]+\left[f\begin{pmatrix}\boldsymbol{\kappa}'\\ \nu'\end{pmatrix}-f\begin{pmatrix}\boldsymbol{\kappa}''\\ \nu''\end{pmatrix}\right]\right.$$
$$\left.\times\left[\delta\left(\omega\begin{pmatrix}\boldsymbol{\kappa}\\ \nu\end{pmatrix}+\omega\begin{pmatrix}\boldsymbol{\kappa}'\\ \nu'\end{pmatrix}-\omega\begin{pmatrix}\boldsymbol{\kappa}''\\ \nu''\end{pmatrix}\right)-\delta\left(\omega\begin{pmatrix}\boldsymbol{\kappa}\\ \nu\end{pmatrix}-\omega\begin{pmatrix}\boldsymbol{\kappa}'\\ \nu'\end{pmatrix}+\omega\begin{pmatrix}\boldsymbol{\kappa}''\\ \nu''\end{pmatrix}\right)\right]\right\}. \qquad (1$$

- f(freq_hld,eigvec_hld,fc_3)
  freq_hld, eigvec_hld = easy
  fc_3 = hard

Debye-> $$\tau_{p-p} = \frac{(6\pi^2)^{1/3}\bar{m}v_g v_p^2}{2V^{1/3}\omega^2\gamma^2 T}$$

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phonon scattering mechanisms

- Defect scattering [3]:

$$\frac{1}{\tau_d\binom{\boldsymbol{\kappa}}{\nu}} = \frac{\pi}{2N}\omega_{\mathbf{q}s}^2 \sum_{\mathbf{q}'s'} \delta(\omega_{\mathbf{q}s} - \omega_{\mathbf{q}'s'}) \sum_b g(b) |e^*_{\mathbf{q}'s'}(b) \cdot e_{\mathbf{q}s}(b)|^2$$

$$g(b) = \sum_i c_i(b)(1 - m_i(b)/\bar{m}(b))^2$$

- f(freq_hld,eigvec_hld)
  freq_hld, eigvec_hld = easy

Debye-> $$\frac{1}{\tau_d} = \frac{V\omega^4}{4\pi v_p^2 v_g} \sum_i c_i(1 - m_i/\bar{m})^2$$

Debye-> $$\tau_{p-p} = \frac{(6\pi^2)^{1/3}\bar{m}v_g v_p^2}{2V^{1/3}\omega^2\gamma^2 T}$$

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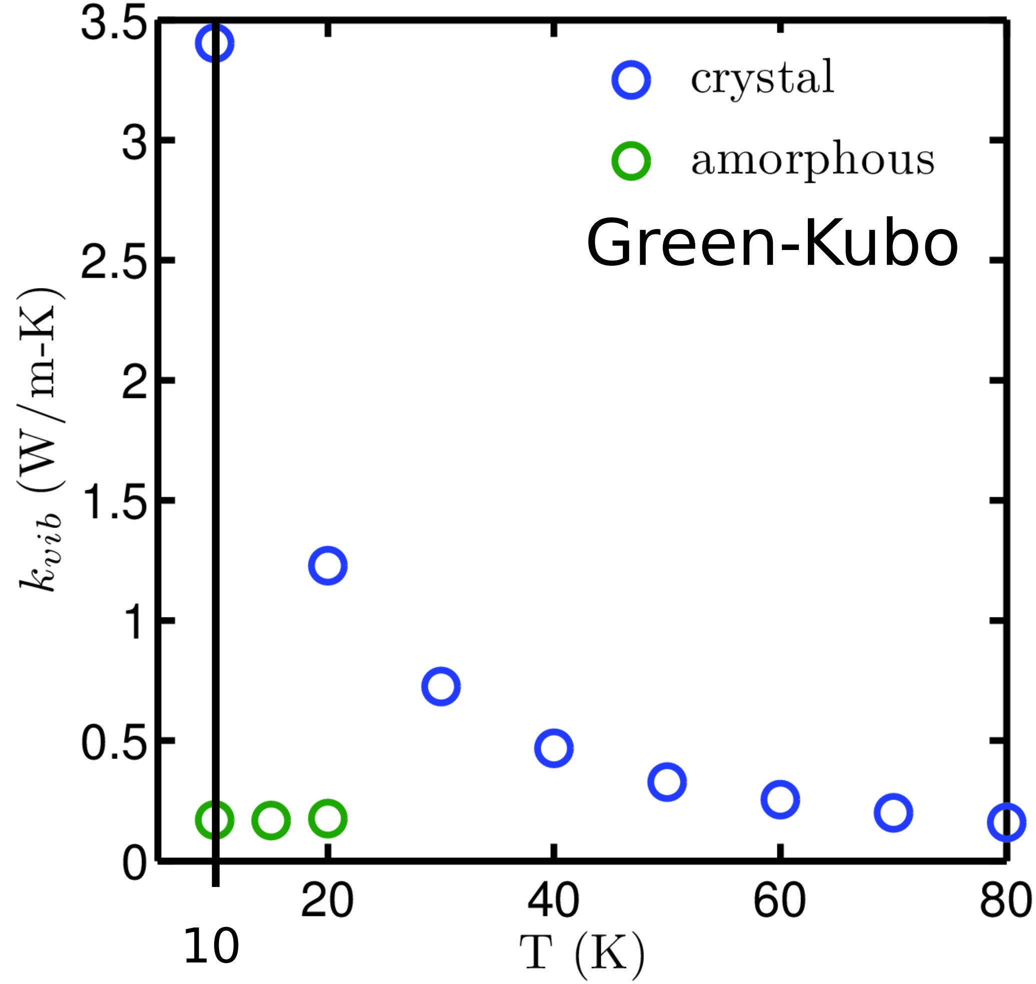
conductivity from md and gk

- Model Lennard-Jones system:

- **Molecular Dynamics** (MD) simulation and **Green-Kubo** method.

- No vibrational properties are predicted:

$$k_{vib} = \sum_{\text{modes}}$$



- Predictions show Green-Kubo can capture all effects.

- MD simulations are classical, no quantum effects.

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normal mode decomposition (nmd)

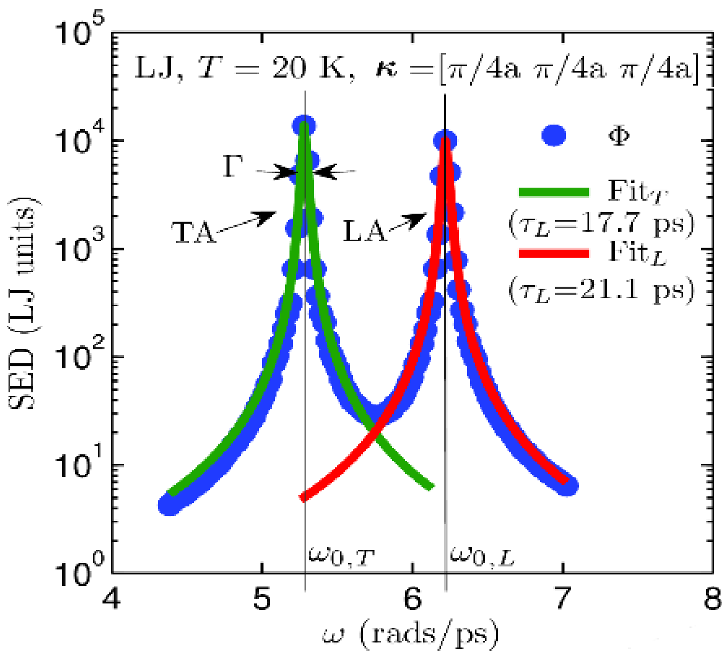
- Phonon Normal Mode Coordinate:

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

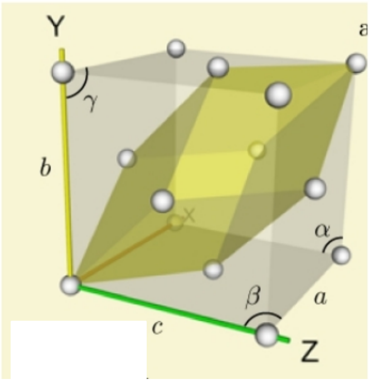
Molecular Dynamics
(anharmonic)

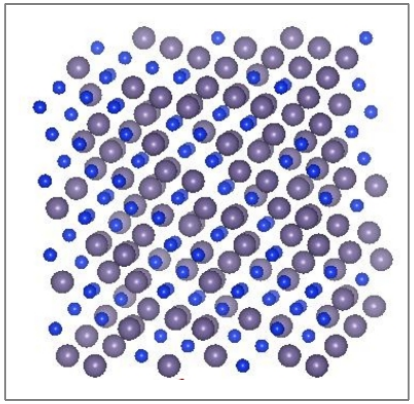
Lattice Dynamics
(harmonic)

$$\Phi(\boldsymbol{\kappa},\omega) = \sum_{\nu}^{3n} C_0\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \frac{\Gamma\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)/\pi}{\left[\omega_0\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) - \omega\right]^2 + \Gamma^2\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)} \qquad \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = \frac{1}{2\Gamma\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)}$$



vc vs gamma





Unit cell?

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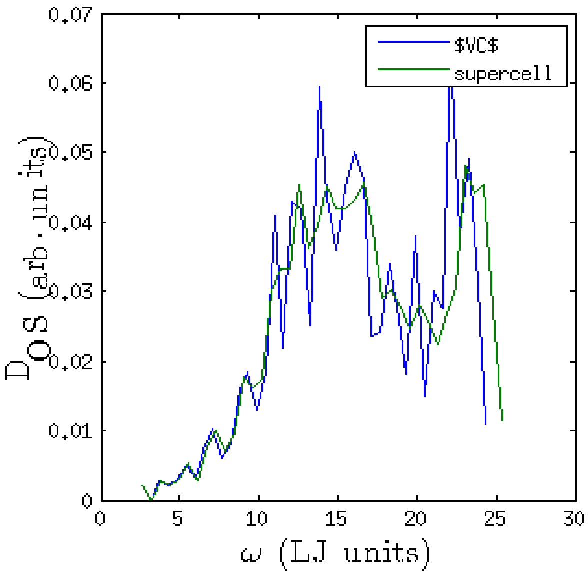
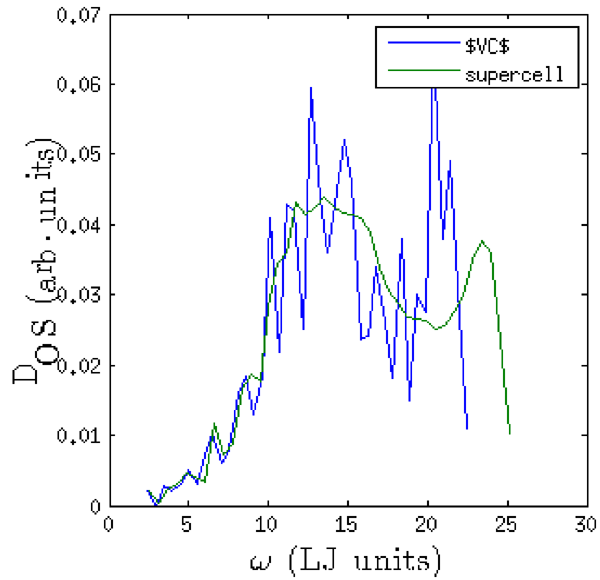
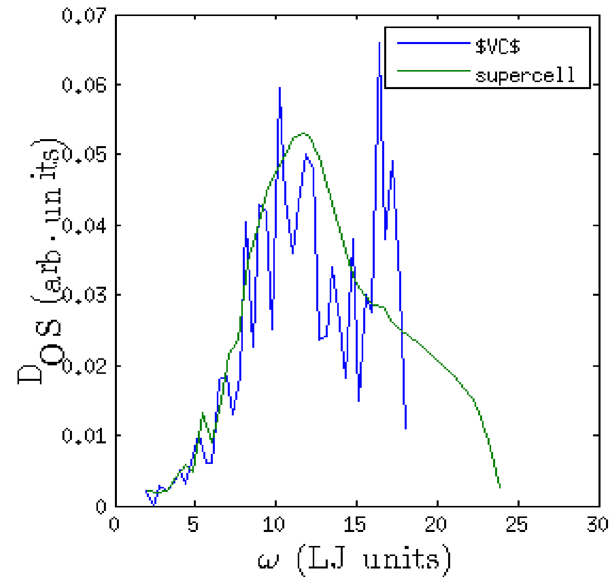
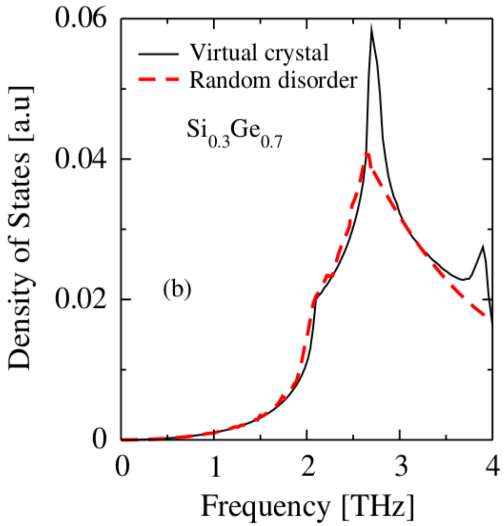
vc vs gamma dos







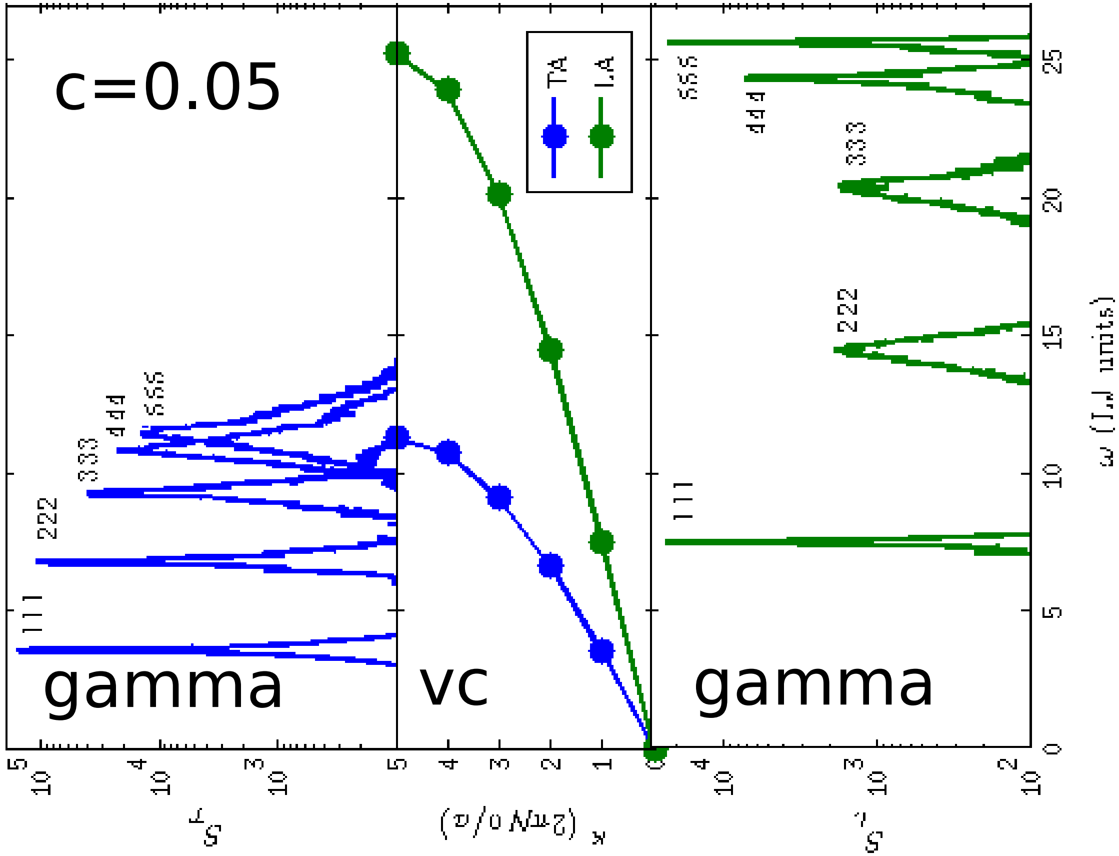


PRL 106, 045901 (2011)

- vc and gamma agree well at low frequencies.
- at high freq, gamma modes are smeared.

gamma modes plane-wave character

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



- vc and gamma agree well at low frequencies.
- at high freq, gamma modes are smeared.

$$S^{L,T}\binom{\boldsymbol{\kappa}}{\omega} = \sum_{\nu} E^{L,T}\binom{\boldsymbol{\kappa}}{\nu}\,\delta(\omega - \omega\binom{\boldsymbol{\kappa}}{\nu})$$

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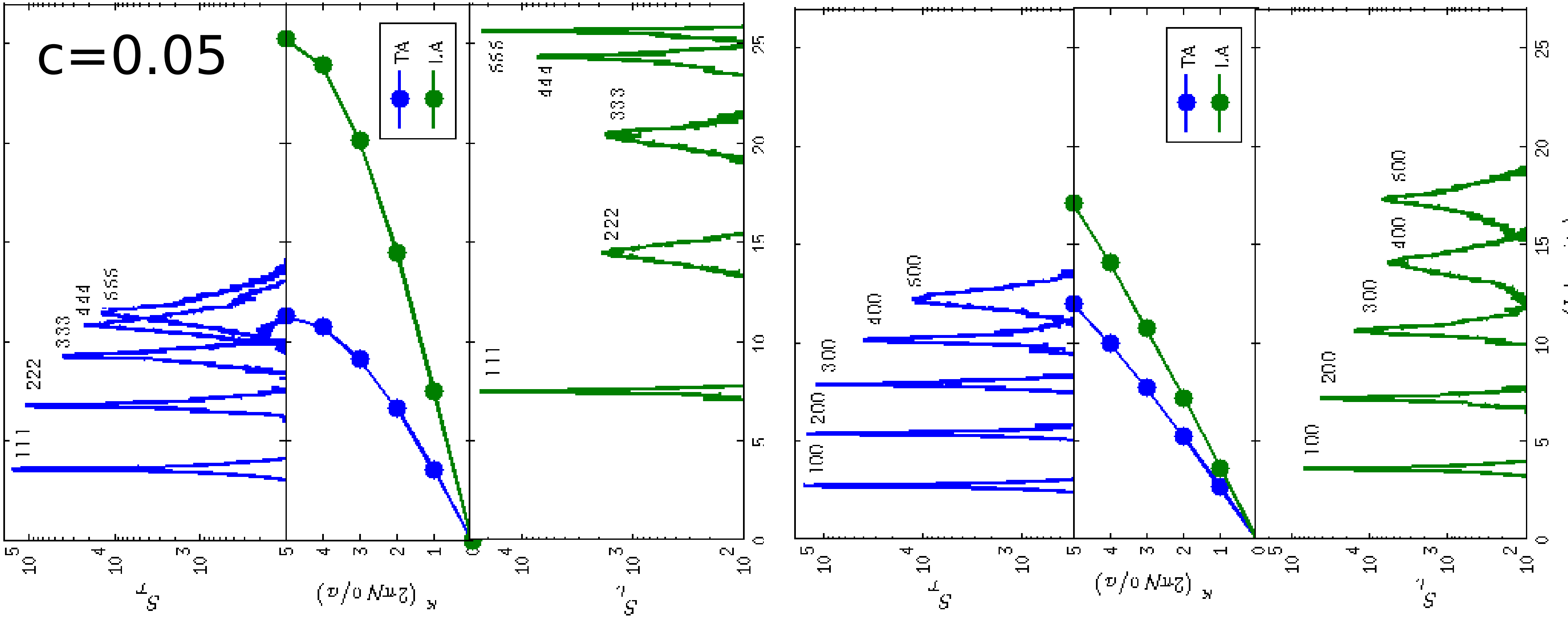
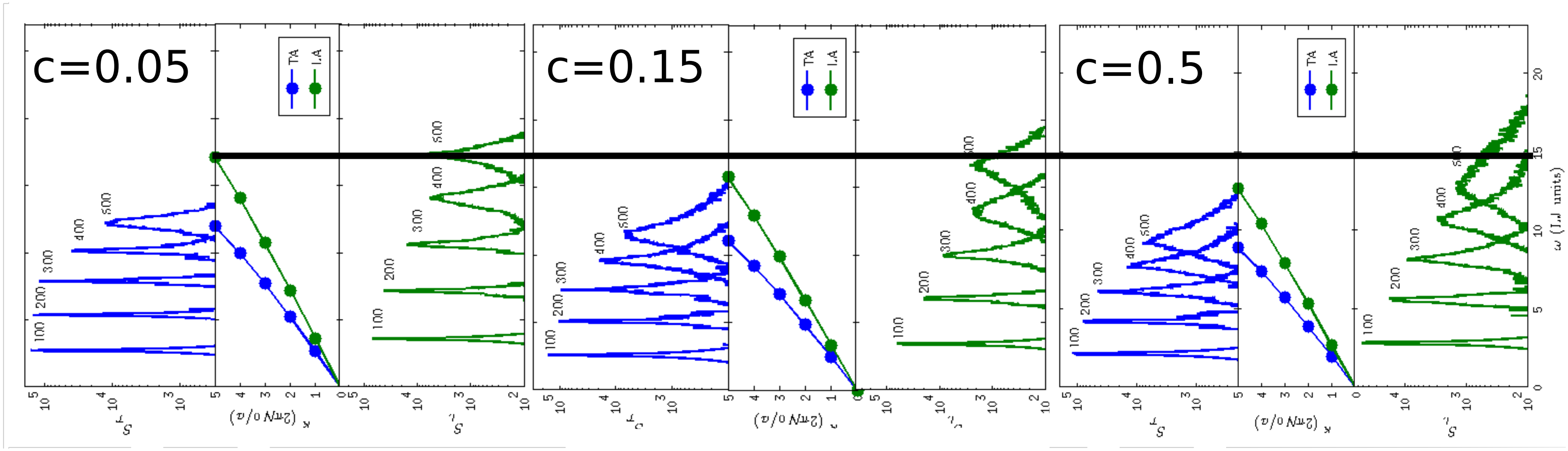
gamma modes plane-wave character



- gamma modes show anisotropic dispersion

gamma modes plane-wave character



$\bar{m} = 1.1$ $\bar{m} = 1.3$ $\bar{m} = 2.0$

- gamma modes show effect of increasing vc mass.
- gives indication that vc group velocity is appropriate even with disorder.

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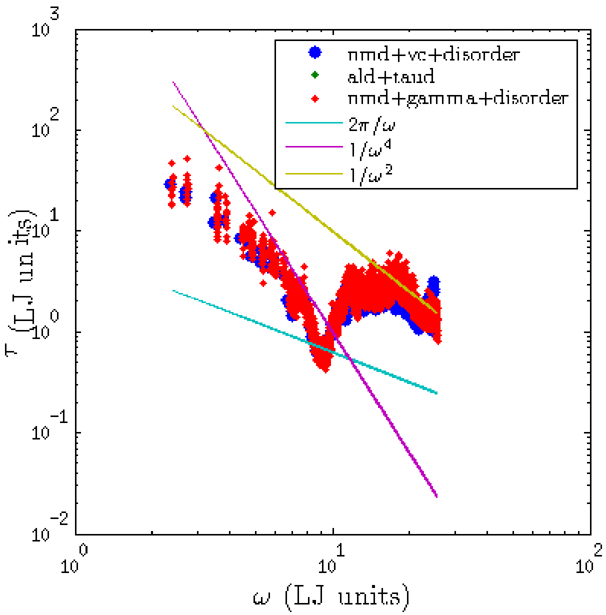
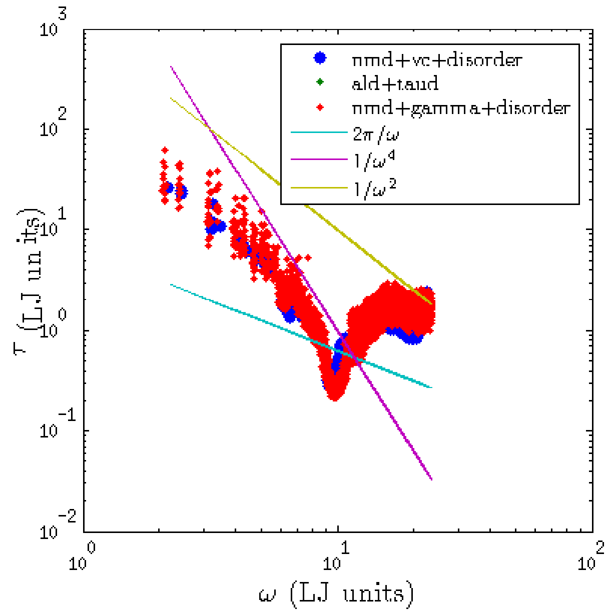
nmd vc vs gamma lifetimes

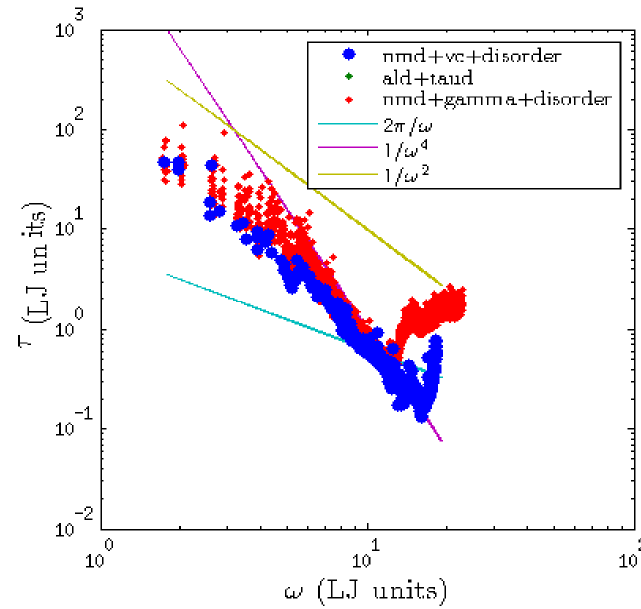
c=0.05



c=0.15



c=0.5



- nmd mapping using vc or gamma modes shows very similar results.
- lifetimes look good, as do group velocities...

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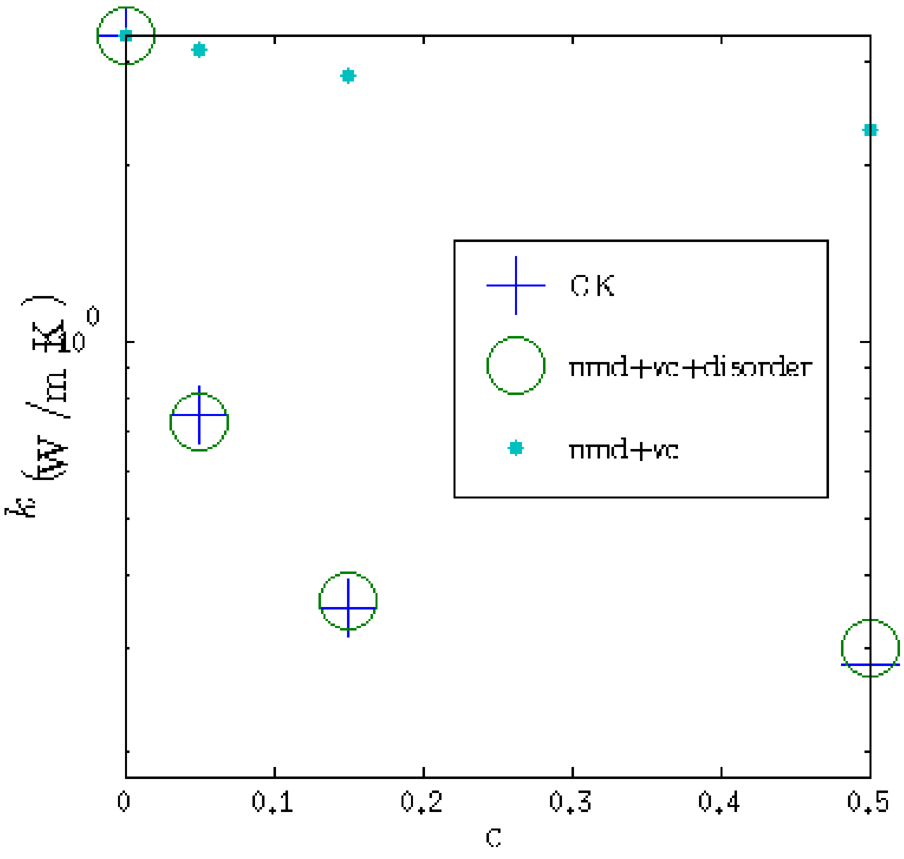
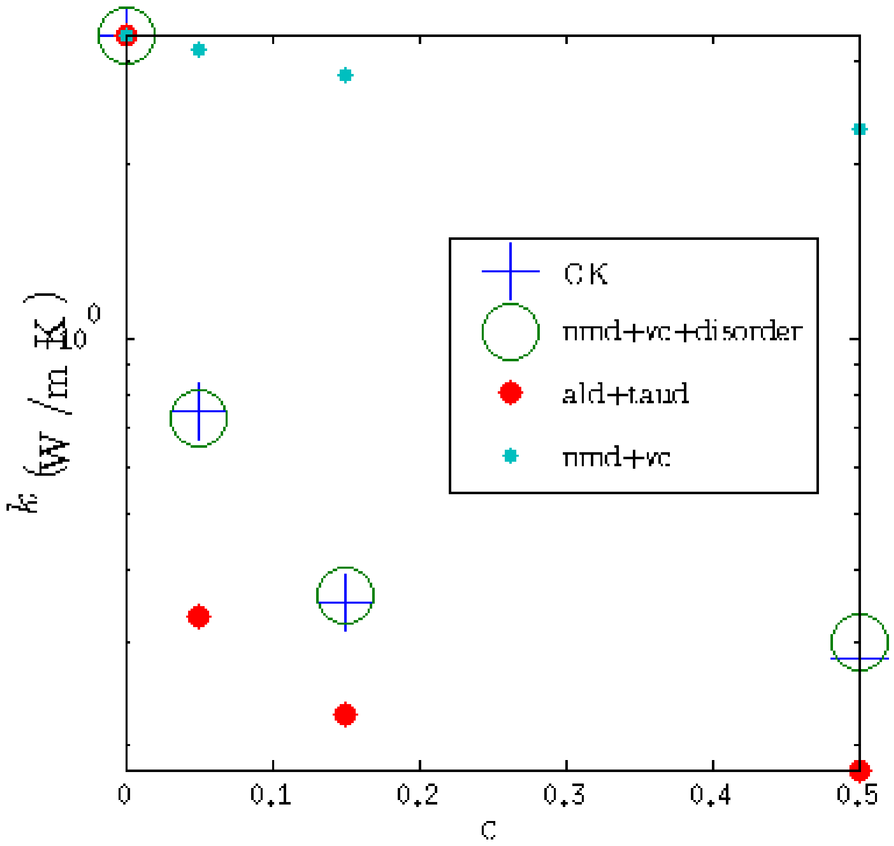
nmd + vc + disorder conductivity

- nmd mapping using vc predicts conductivity in good agreement with GK.
- Results indicate the importance of vc group velocities.
- Results indicate the importance of phonon lifetime reduction due to scattering.



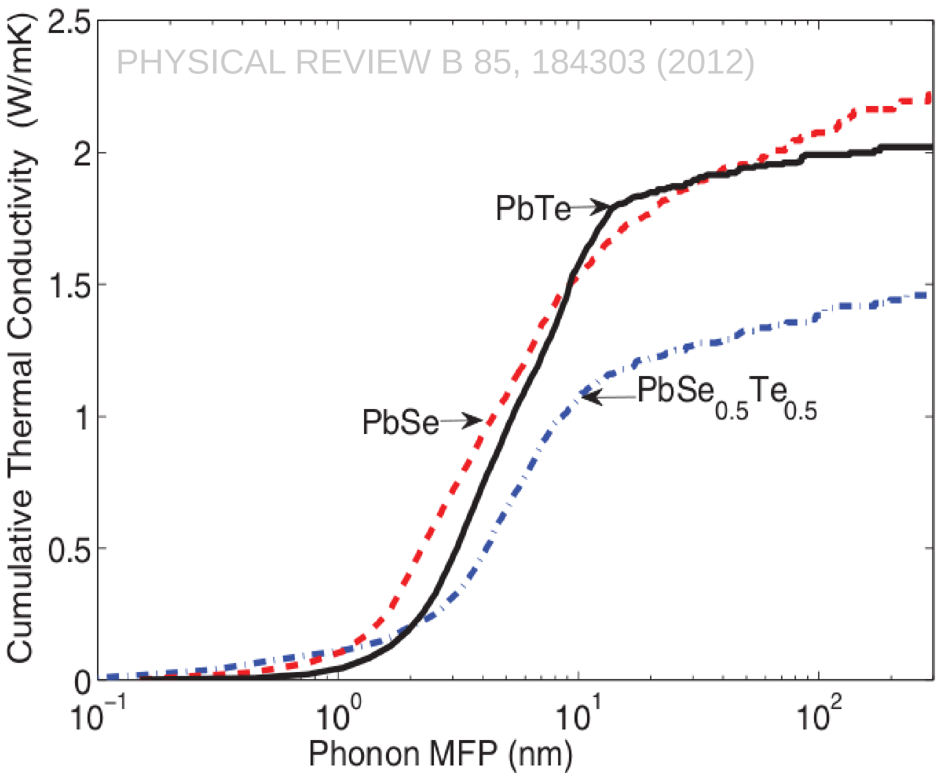
nmd + vc + disorder vs ald+taud conductivity

- ald+taud under-predicts conductivity for lj.
- Need to check si/ge



importance of ald+taud

- ald+taud is cheap, even using ab initio.
- It is important to understand any limitations
- ald+taud is a valuable tool for predicting thermal conductivity of thermoelectric materials



current limiation of DFT plane wave:

calc_time_1 = 1 min (O(100 atoms), Si perfect supercell)

ald_calc_num = O(1000)

ald_calc_time = O(17 hours)

md_calc_num = O(2^20 ~ 1000000)

calc_time_2 = 1000 min

calcultion time_necessary = O(700 days)

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Questions

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.

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