evaluation of the virtual crystal approximation for predicting thermal conductivity

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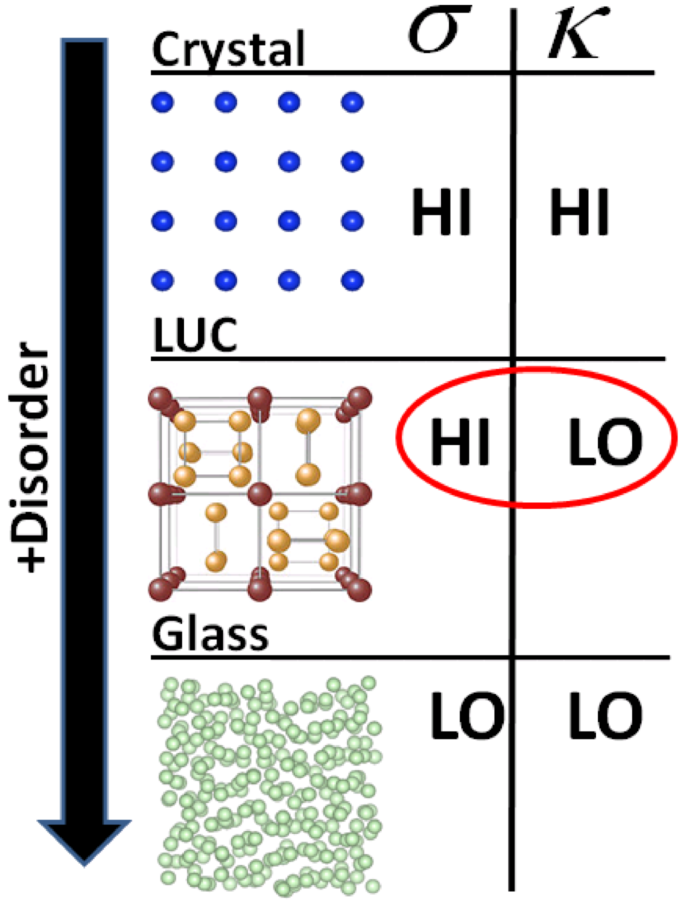
thermoelectric energy conversion materials

- Lower thermal conductivity for improved thermoelectric efficiency:

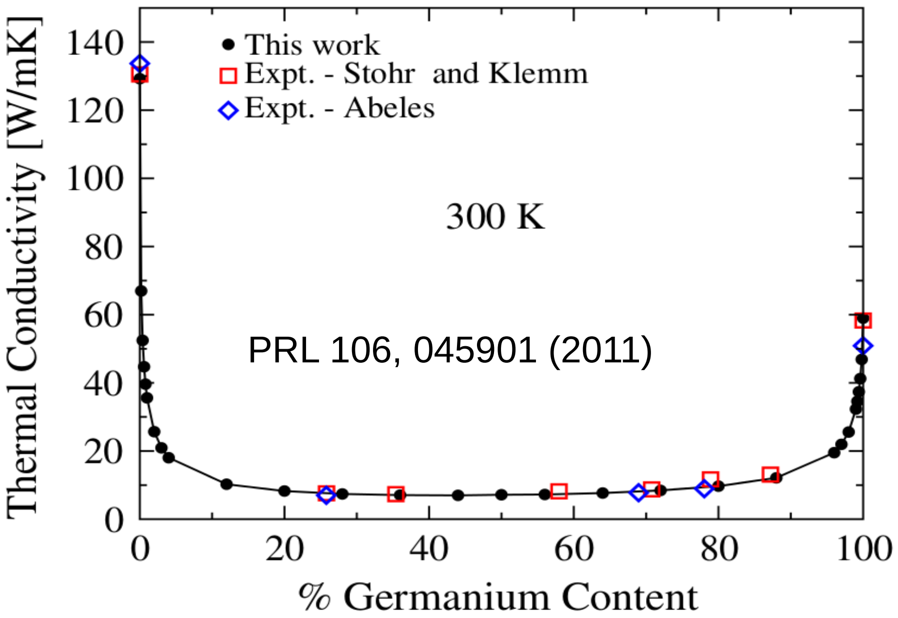
$$ZT = \frac{S^2 \sigma T}{k_{thermal}}$$

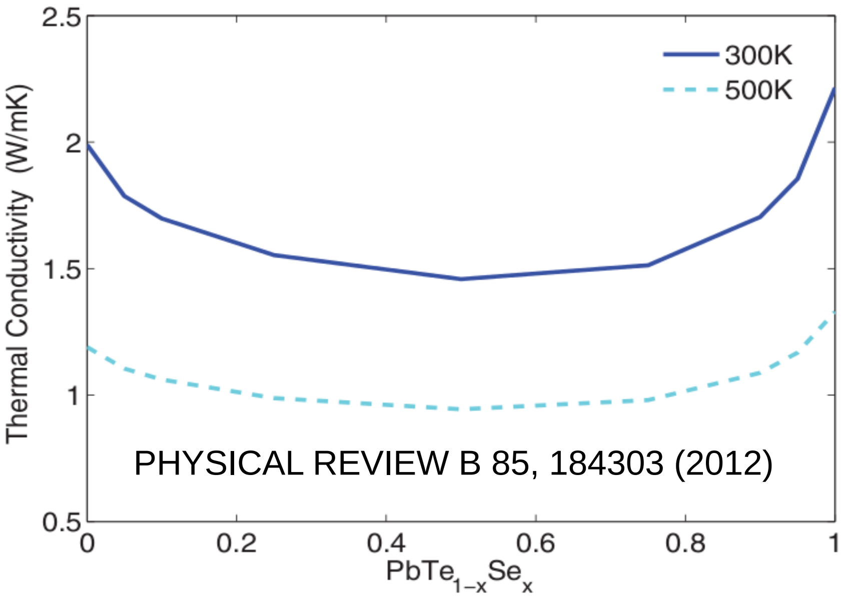
- Skutterudites: “electron-crystal, phonon-glass”

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



modeling thermoelectric materials





- anharmonic lattice dynamics + phonon defect lifetime (**ALD**).

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

- **ALD+VC** can be computationally cheap, even using *ab initio*.

• is this approach valid?

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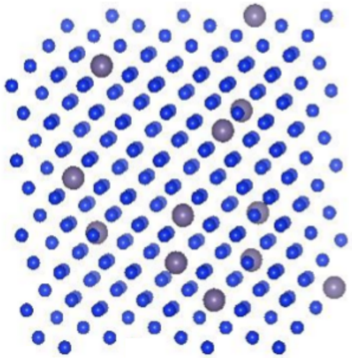
virtual crystal (VC) approx.

c=0.05



$\bar{m} = 1.1$

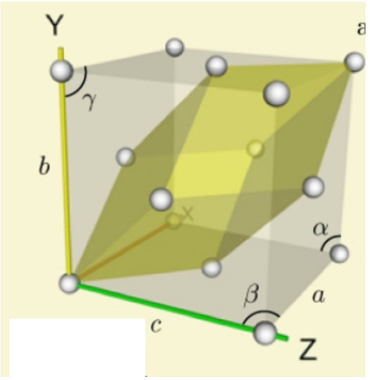
Virtual Crystal (VC)

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

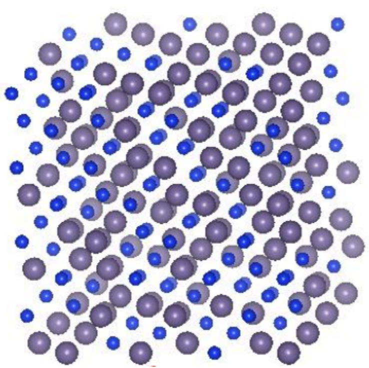
$$m^a = 1 \;\; m^b = 3$$

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

unit cell



c=0.5

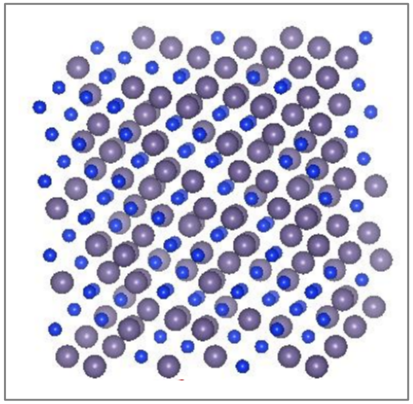


$\bar{m} = 2.0$

Gamma point

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

unit/simulation cell



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thermal conductivity in ordered systems

- conductivity in ordered 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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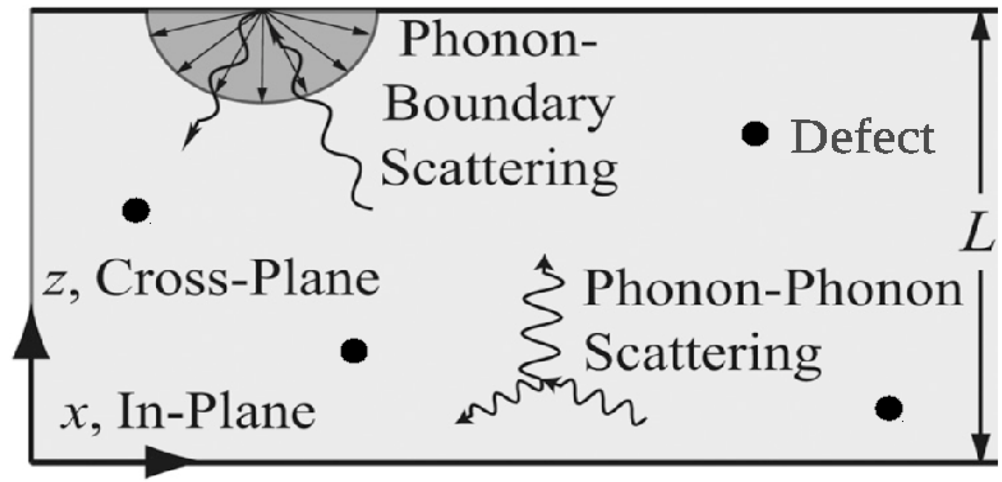
phonon scattering mechanisms

- Matthiessen rule:

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



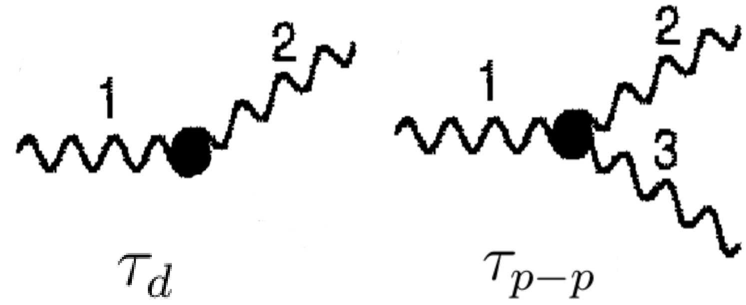
ALD + Debye->

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

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

[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.

NMD vs ALD



ALD:

- LD-based, cheap, includes quantum statistical effects, valid for perturbations.

NMD:

- MD-based, expensive, includes any disorder effects

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

$$\tau\binom{\boldsymbol{\kappa}}{\nu} = \frac{1}{2\Gamma\binom{\boldsymbol{\kappa}}{\nu}}$$

current limiation of plane-wave DFT:

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

ald_calc_num = O(1000)

ald_calc_time = O(17 hours)

nmd_calc_num = O(2^20 ~ 1000000)

nmd_calc_time = O(700 days)

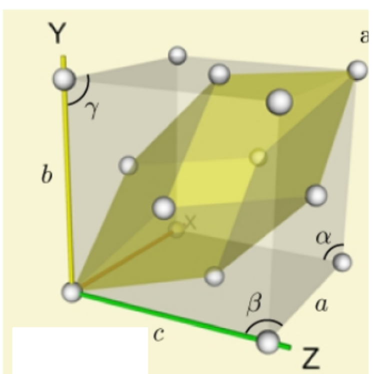
normal mode decomposition (NMD)

$$\Phi\left({\boldsymbol{\kappa} \atop \nu};\omega\right) = \lim_{\tau_0\to\infty}\frac{1}{2\tau_0}\left|\frac{1}{\sqrt{2\pi}}\int_0^{\tau_0}\dot{q}\left({\boldsymbol{\kappa} \atop \nu};t\right)\exp(-i\omega t)\,dt\right|^2$$

- Phonon Normal Mode Coordinate:

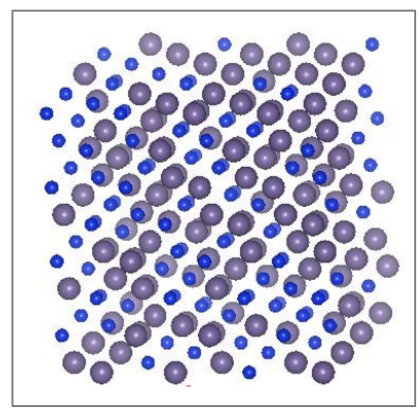
$$\dot{q}\left({\boldsymbol{\kappa} \atop \nu};t\right) = \sum_{\alpha,b,l}^{3,n,N}\sqrt{\frac{m_b}{N}}\,\dot{u}_\alpha\left({l \atop b};t\right)e^*\left({\boldsymbol{\kappa} \atop \nu}\;{b \atop \alpha}\right)\exp\left[i\boldsymbol{\kappa}\cdot\mathbf{r}_0\left({l \atop 0}\right)\right]$$

VC



vs

Gamma



$$\tau\left({\boldsymbol{\kappa} \atop \nu}\right)$$

$$\tau\left({\boldsymbol{\kappa} = 0 \atop \omega}\right)$$

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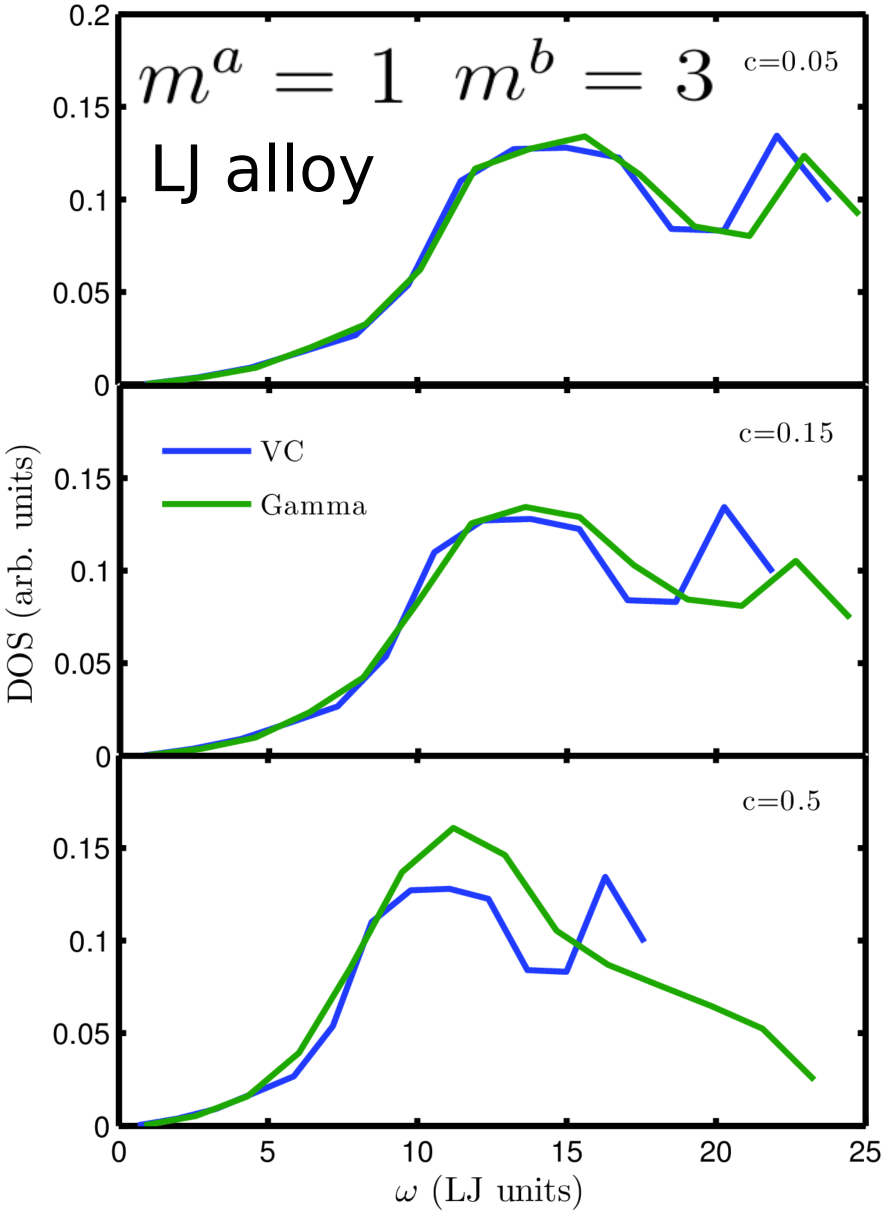
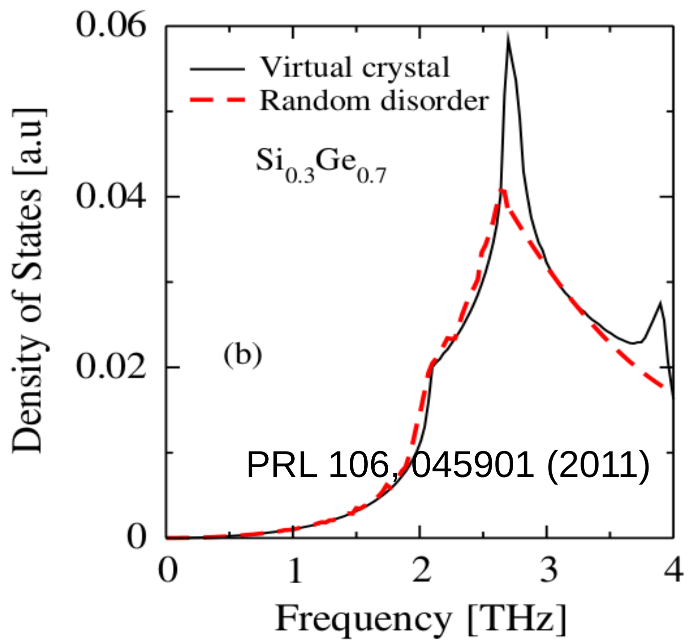
VC vs Gamma DOS



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



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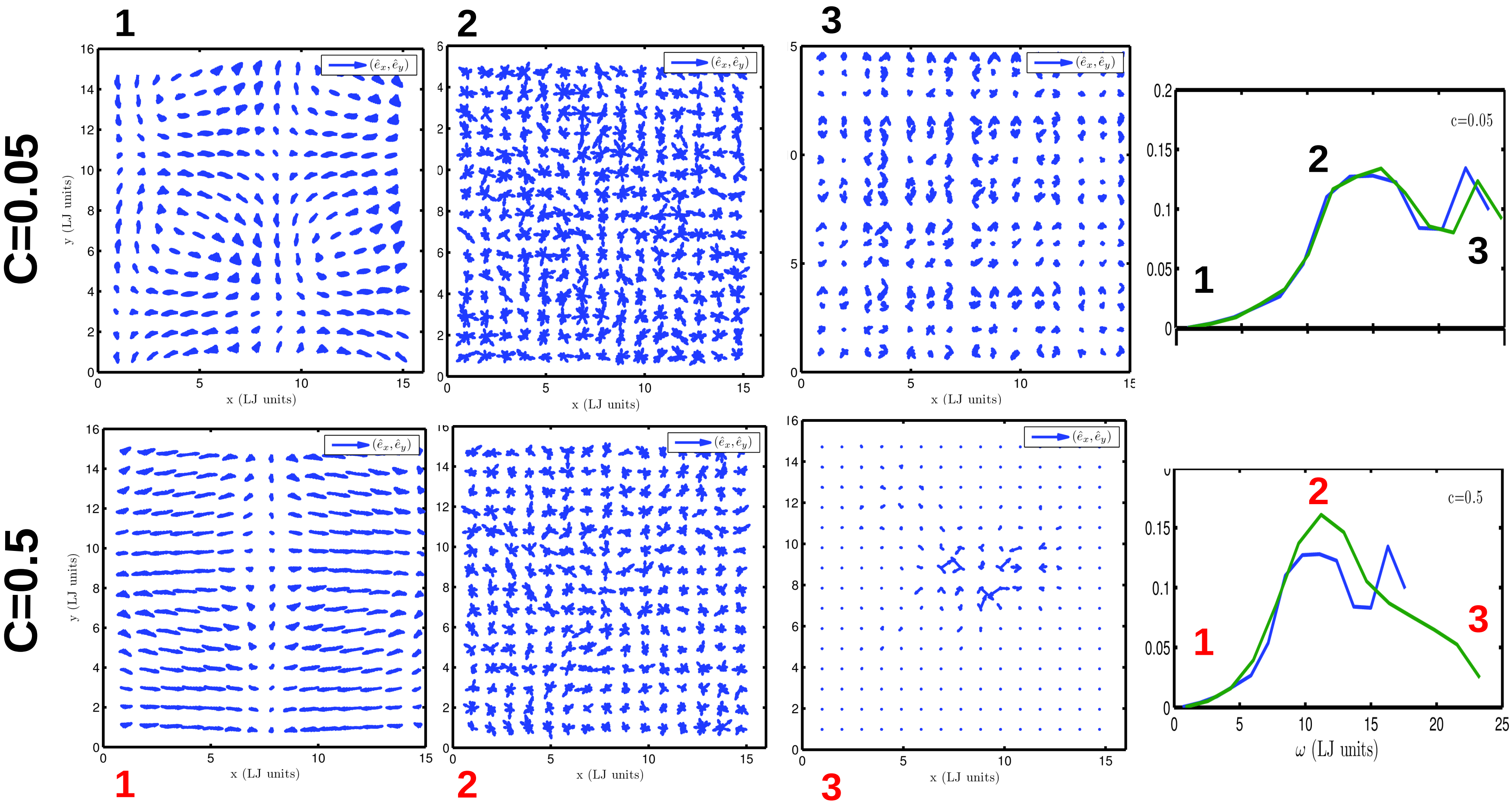
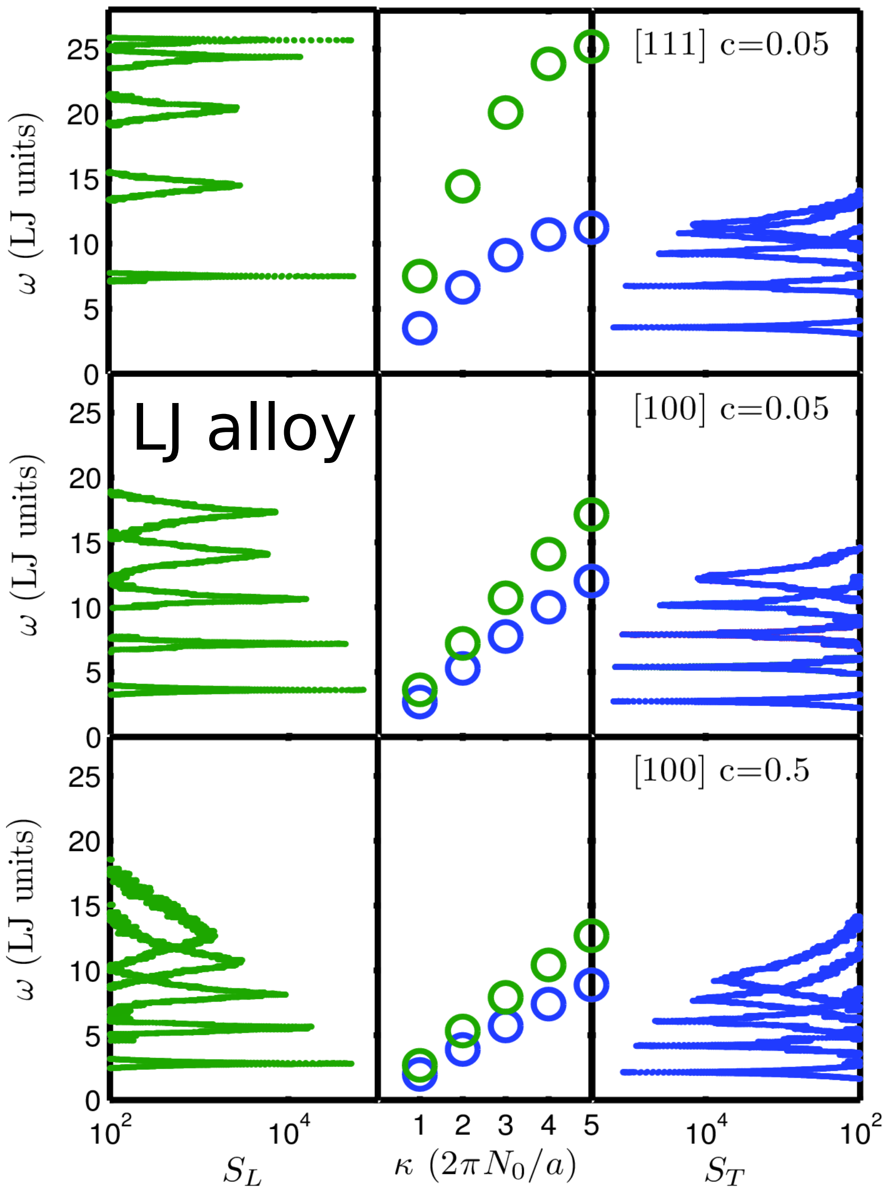
Gamma mode shapes



Gamma modes plane-wave character



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

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

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

- gamma modes show anisotropic dispersion

- gamma modes show VC mass and disorder effects

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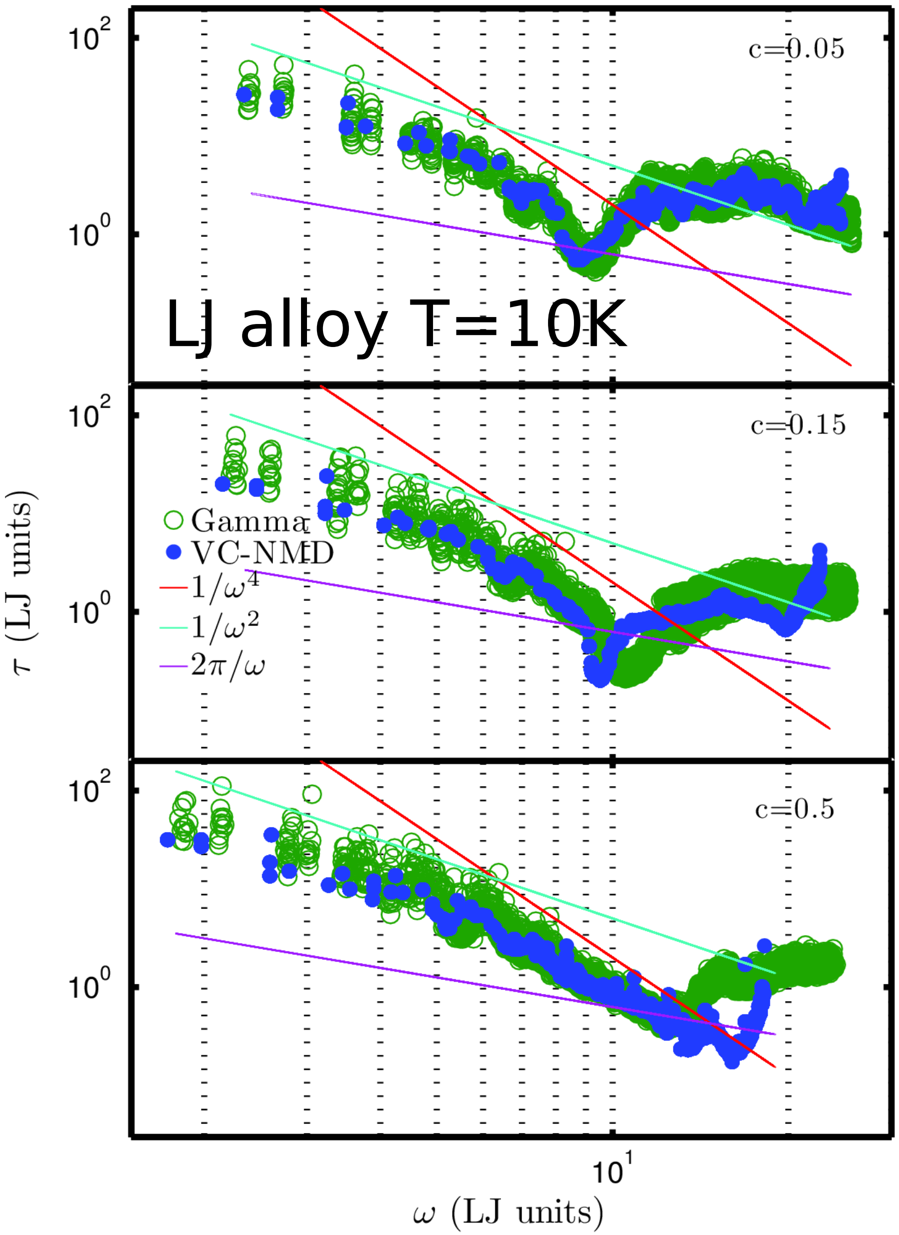
VC-NMD vs Gamma lifetimes



- nmd mapping using vc or gamma modes.
- Lifetimes show same general trends.
- Gamma modes have no symmetry averaging so more scatter.

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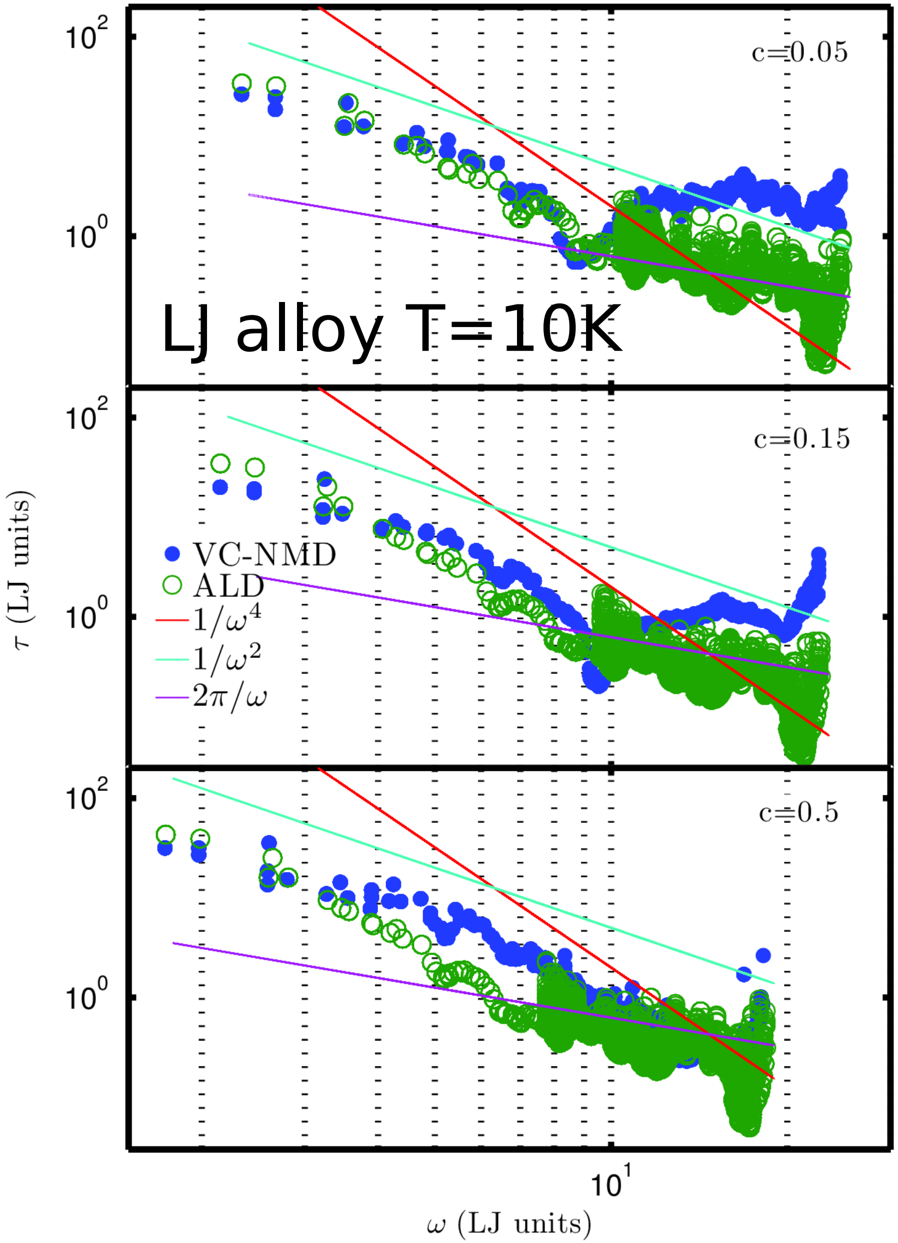
VC-NMD vs ALD lifetimes



- nmd mapping using vc or gamma modes.
- Lifetimes show same general trends.
- Gamma modes have no symmetry averaging so more scatter.

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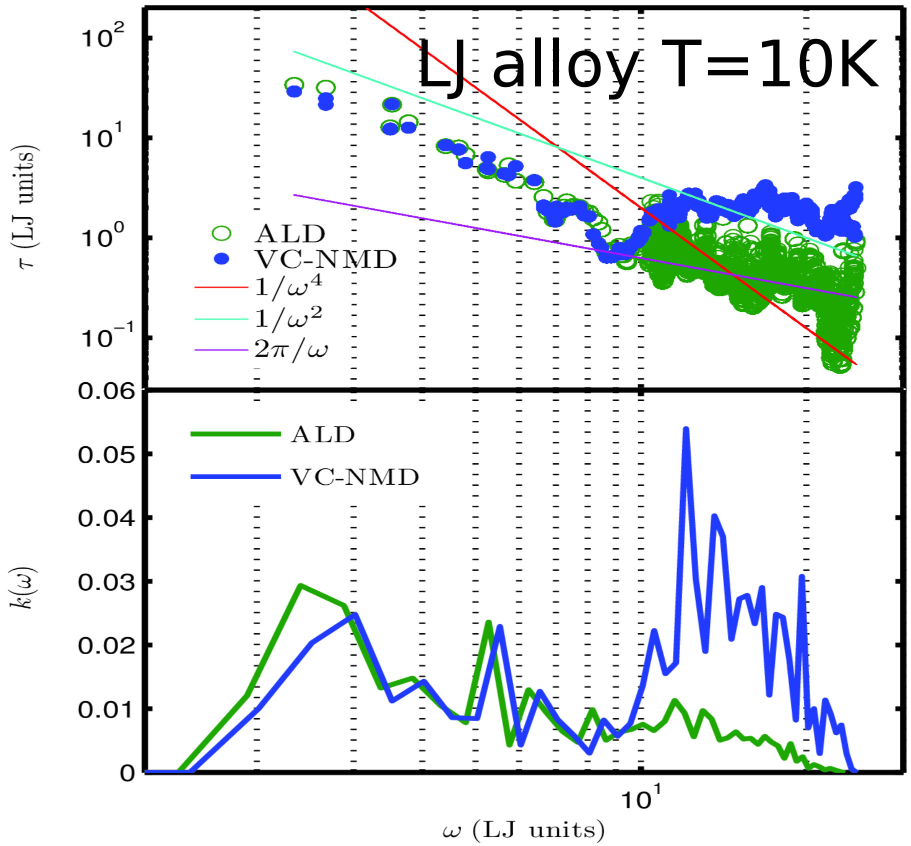
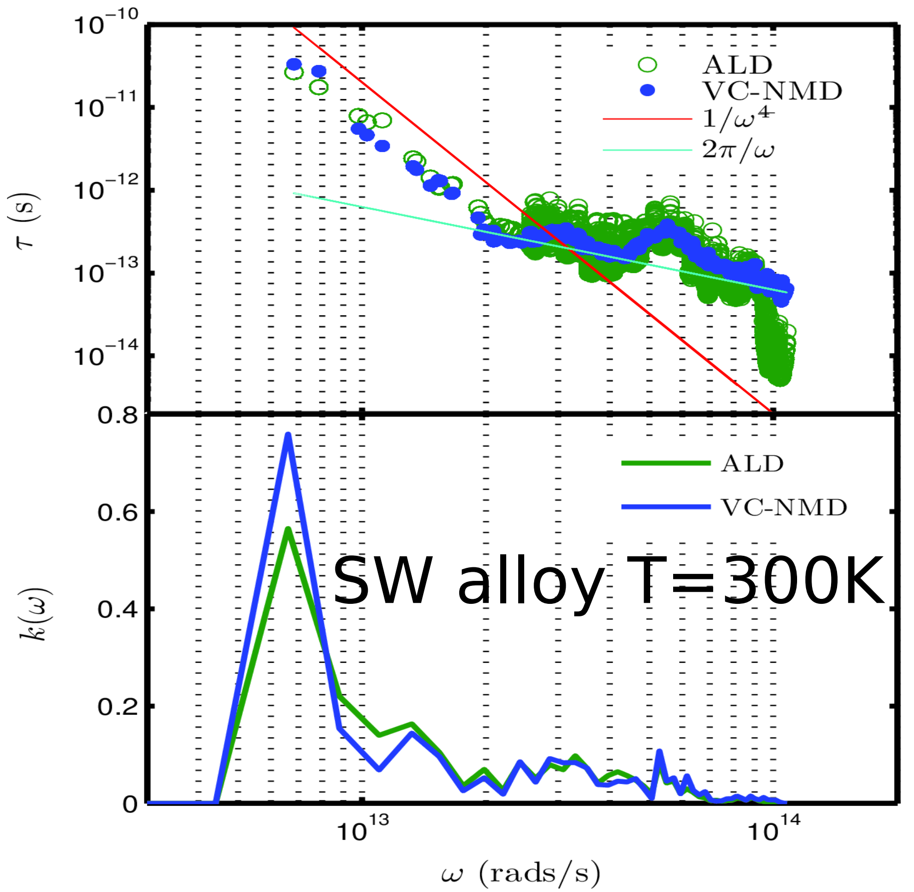
VC-NMD vs ALD conductivity spectra



LJ:

- ALD underpredicts lifetimes at high freq vs. VC-NMD.



SW:

- ALD agrees with VC-NMD.

conductivity from MD and GK

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

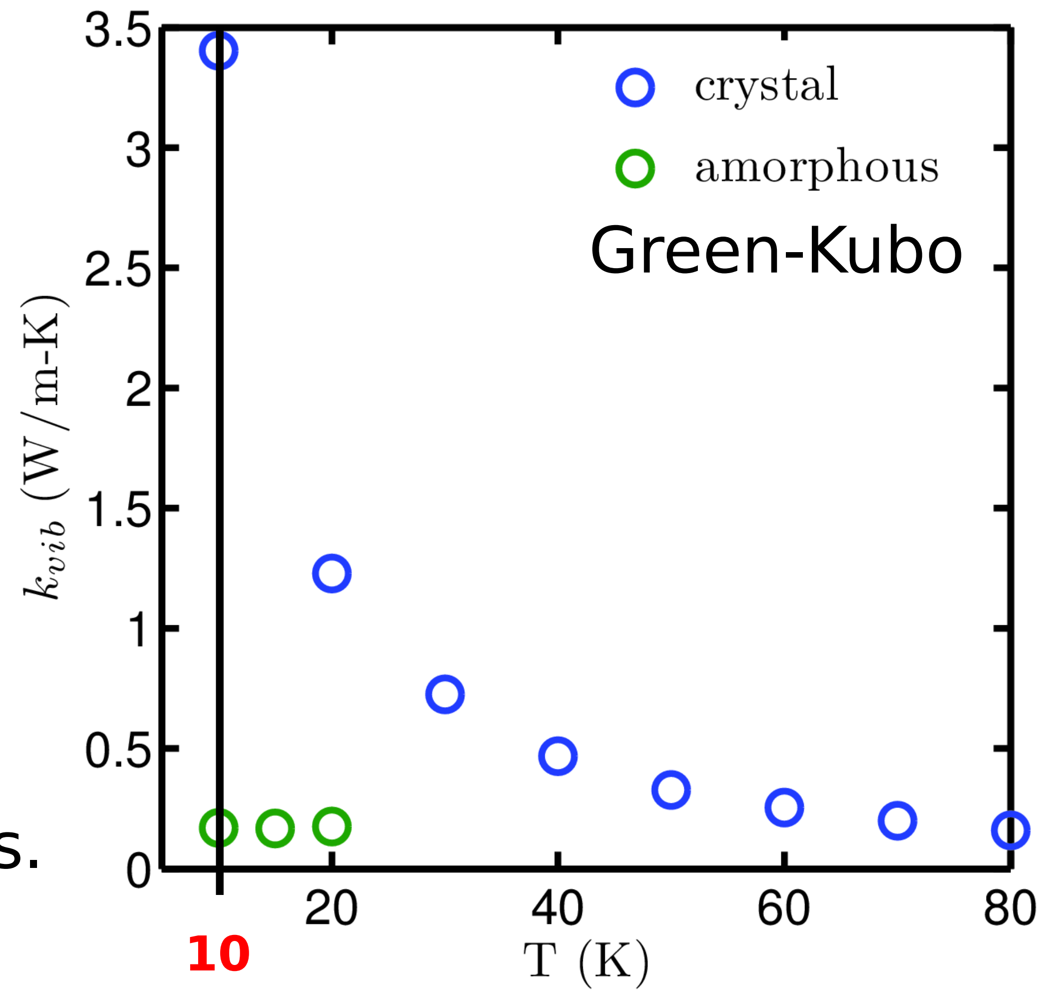
- No vibrational properties are predicted:

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

- Predictions show Green-Kubo can disorder effects.

- MD simulations are classical, no quantum effects.

- Model Lennard-Jones system:



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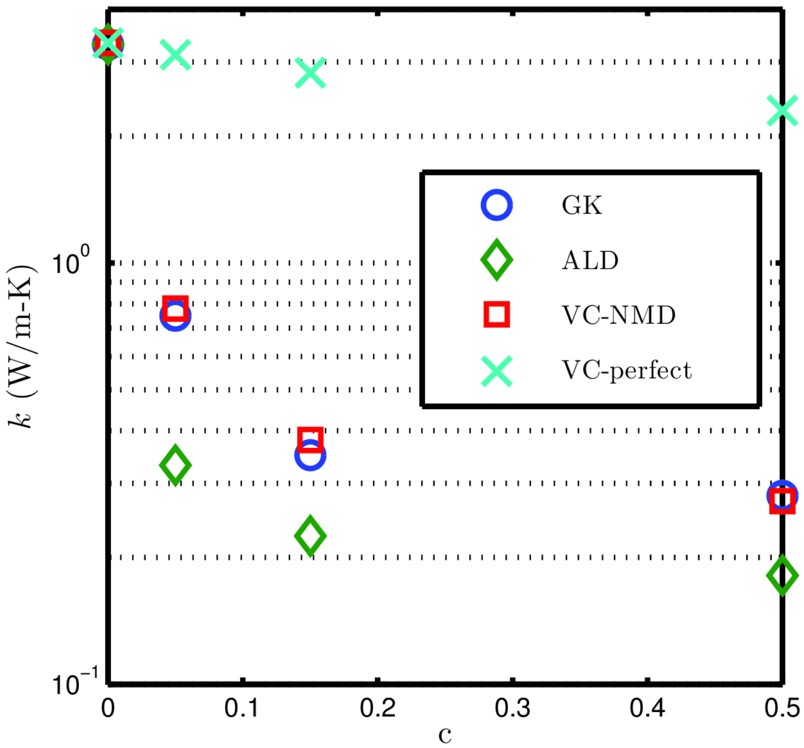
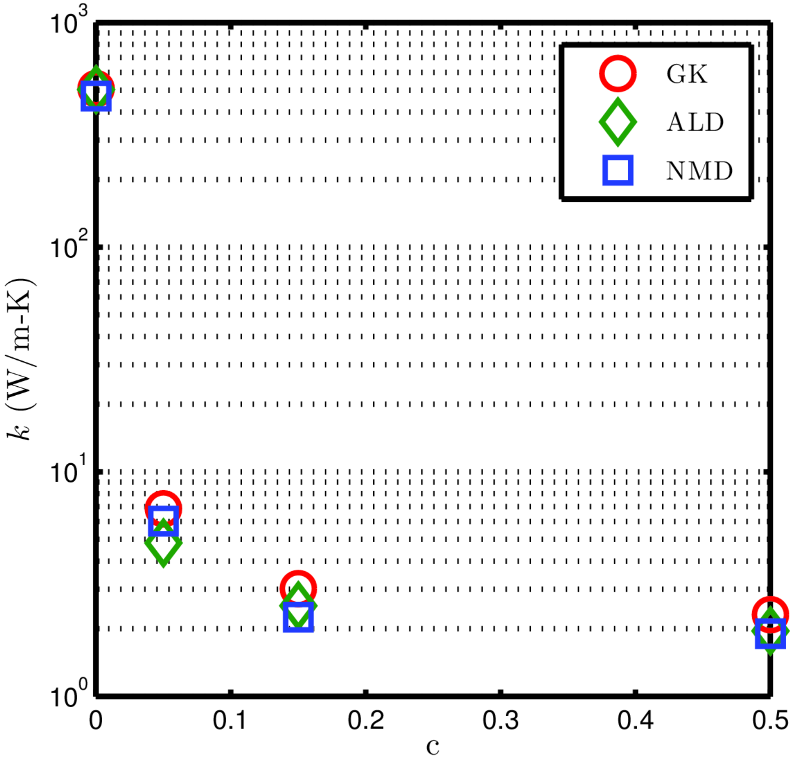
VC-NMD vs ALD vs GK conductivity



LJ:

- ALD underpredicts conductivity significantly.

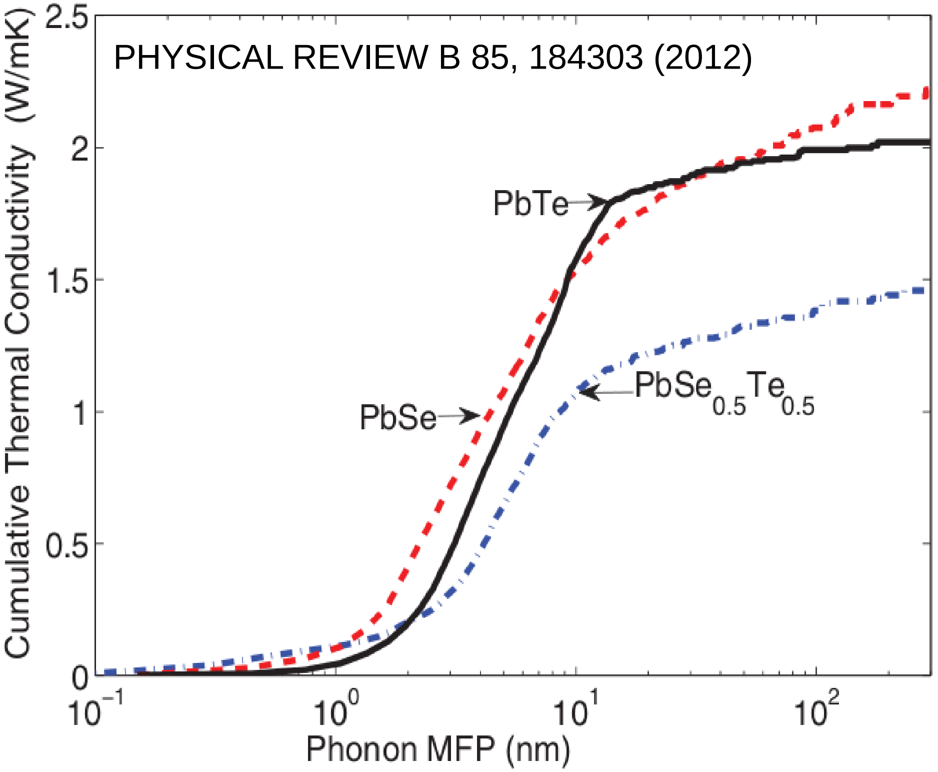


SW:

- VC-NMD, ALD, GK conductivity agree well.

Summary

- ALD+VC is cheap, even using *ab initio* (DFT).
- It is important to understand any limitations
- ALD+VC is a valuable tool for predicting thermal conductivity of thermoelectric materials



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Summary

normal mode decomposition (nmd)

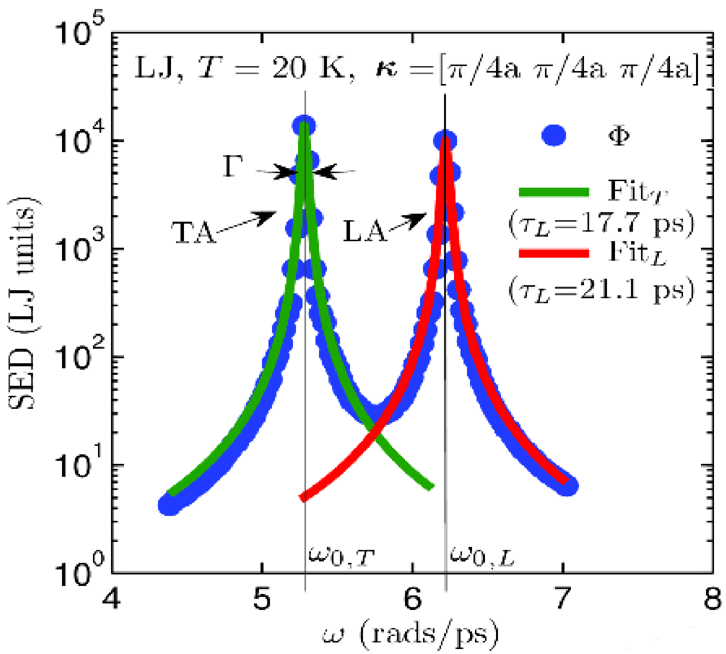
- Phonon Normal Mode Coordinate:

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

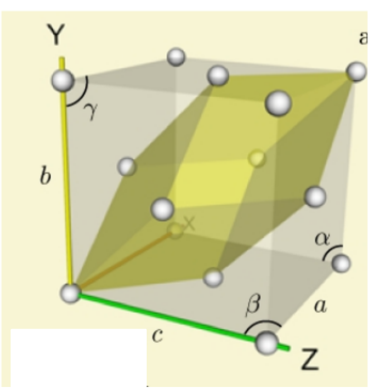
MD (anharmonic)

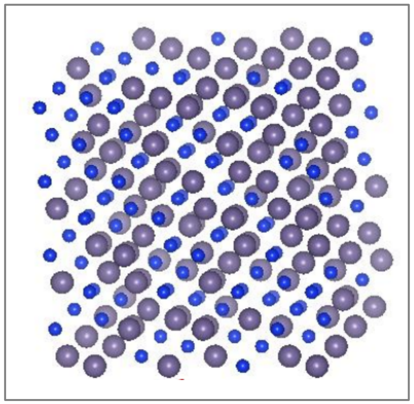
Lattice Dynamics (harmonic)

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



vc vs gamma





Unit cell?

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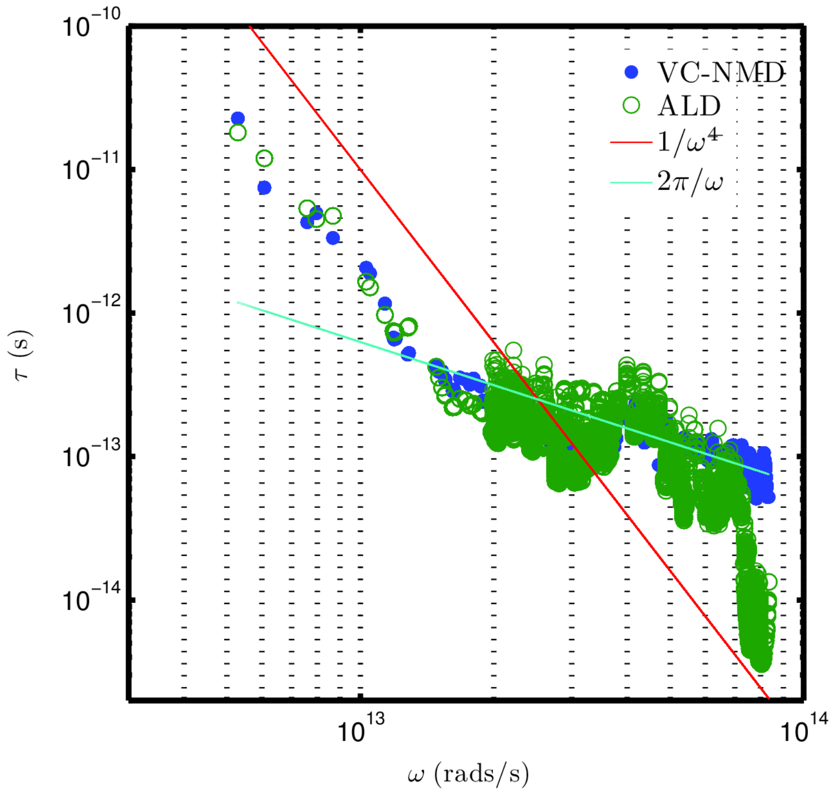
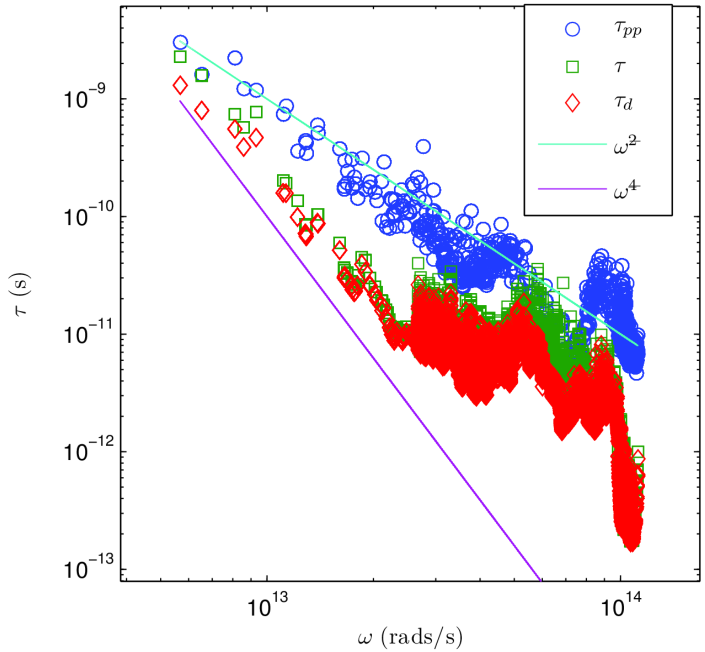
nmd vc vs ald lifetimes

SW:

- ALD+taud agrees with VC-NMD.





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phonon scattering mechanisms

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

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

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

- 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]:

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

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

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

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

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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