Evaluation of the Virtual Crystal approximation for Predicting Thermal Conductivity

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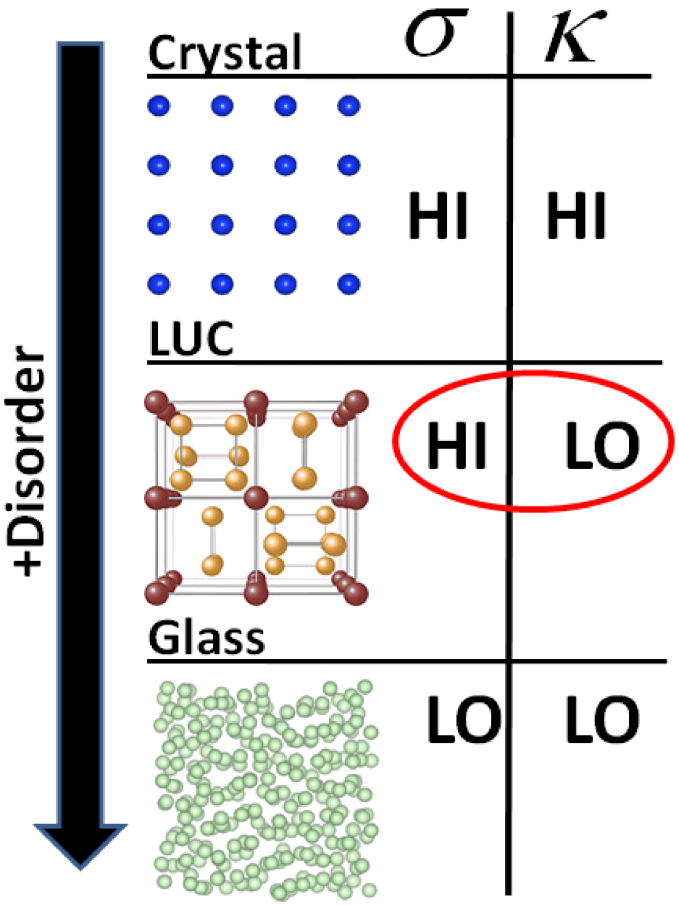
Thermoelectric materials

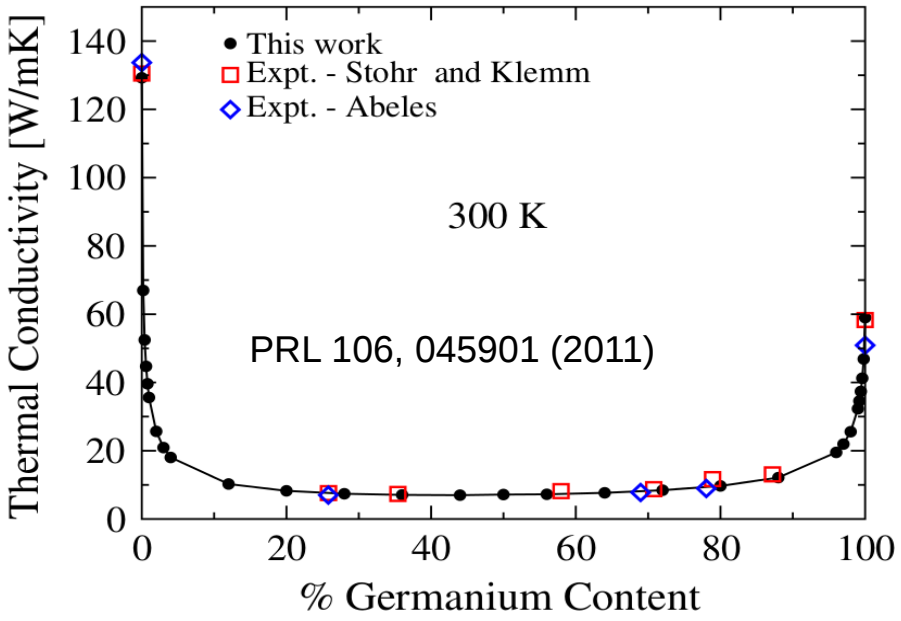
$$ZT = \frac{S^2 \sigma T}{k_{thermal}}$$

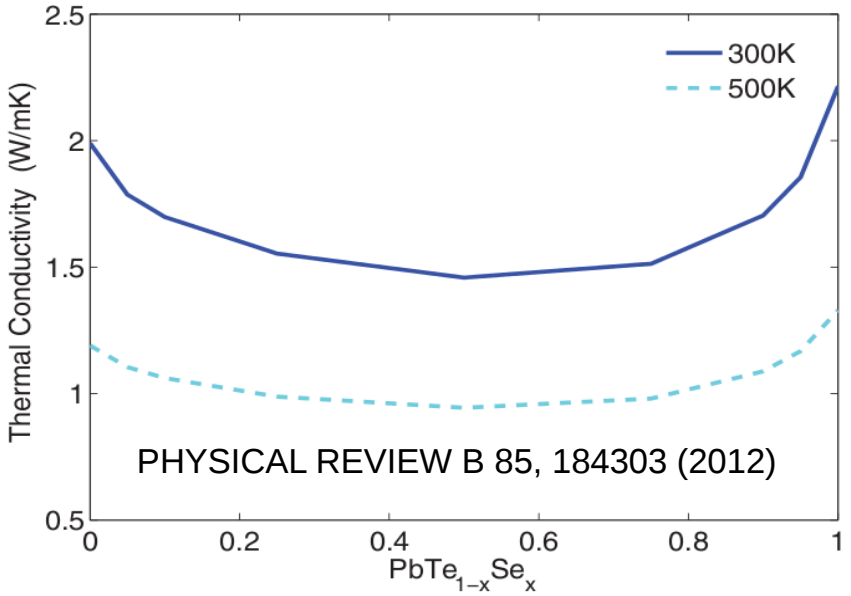
- LUC Skutterudites: “electron-crystal, phonon-glass”

- What about simple alloys?



Modeling thermoelectric materials





- Anharmonic Lattice Dynamics + Virtual Crystal approx. = **ALD+VC**
- **ALD+VC** + *ab initio* = computationally cheap, experimentally accurate.
- Is this approach valid for large disorder?

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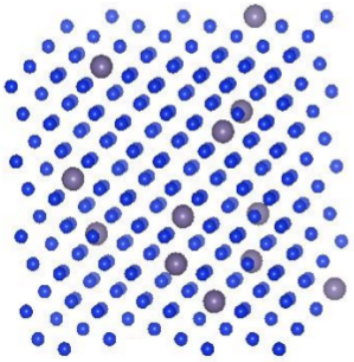
Virtual Crystal (VC) approx.

c=0.05



$\bar{m} = 1.1$

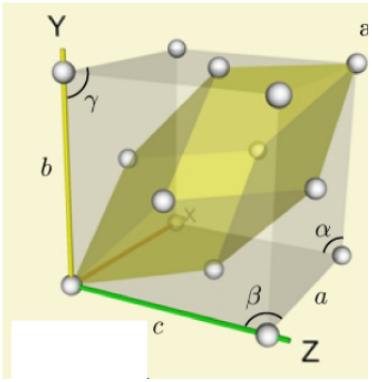
Virtual Crystal (VC)

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

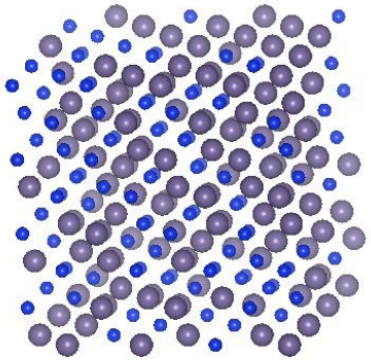
$$m^a = 1 \quad m^b = 3$$

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

unit cell



c=0.5

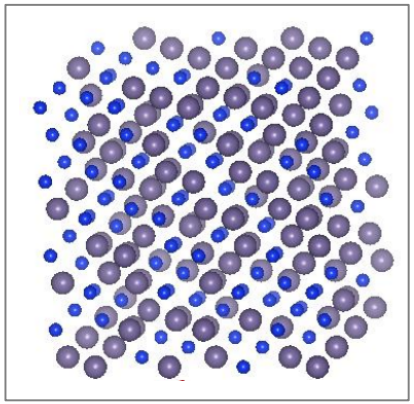


$\bar{m} = 2.0$

Gamma point

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

unit/simulation cell

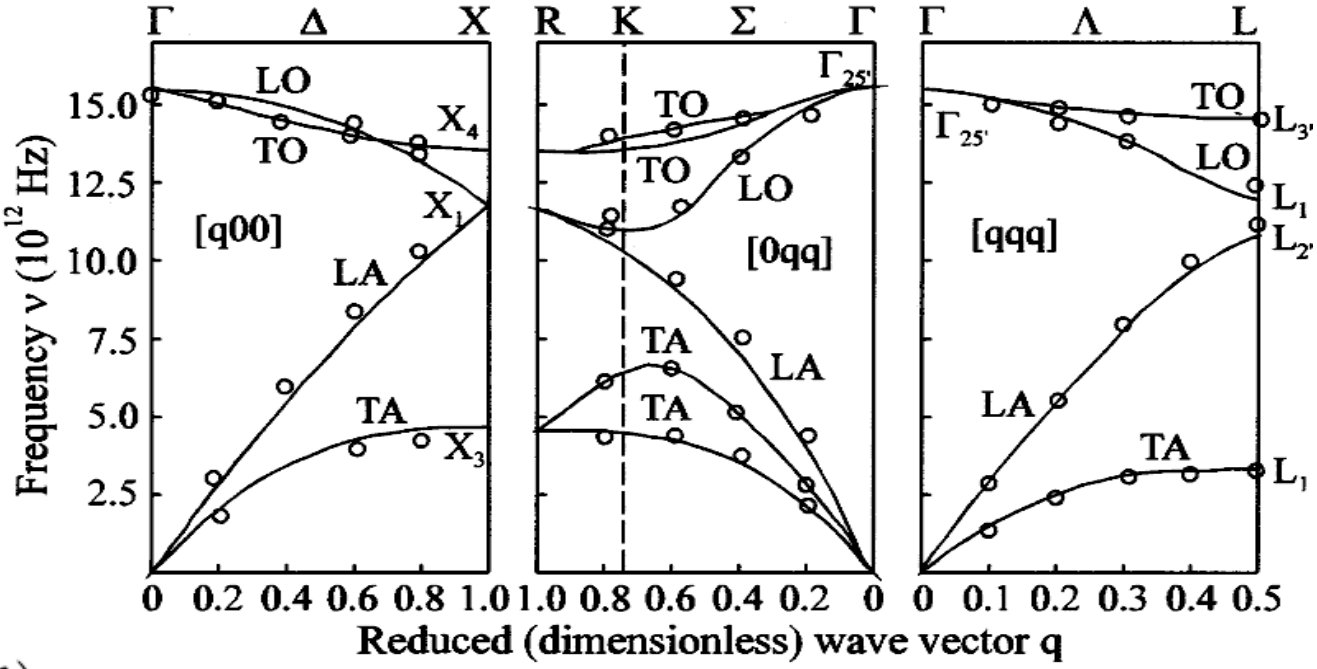


Thermal conductivity of a VC

- conductivity in ordered system sum over phonon modes:

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

$$v_g = \partial\omega/\partial\boldsymbol{\kappa}$$



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

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Phonon Lifetimes: ALD vs NMD

ALD:

ALD+Debye

ald_calc_time = O(17 hours)

$$\tau_d \sim 1/\omega^4 \qquad \tau_{p-p} \sim 1/\omega^2$$

Matthiessen's Rule

$$\frac{1}{\tau\binom{\kappa}{\nu}} = \frac{1}{\tau_{p-p}\binom{\kappa}{\nu}} + \frac{1}{\tau_d\binom{\kappa}{\nu}}$$

NMD:

normal mode decomposition

- Molecular Dynamics-based, computationally expensive.

$$\frac{1}{\tau\binom{\kappa}{\nu}} = \frac{1}{\tau_{p-p}\binom{\kappa}{\nu}} + \frac{1}{\tau_d\binom{\kappa}{\nu}} + \dots$$

nmd_calc_time = O(700 days)

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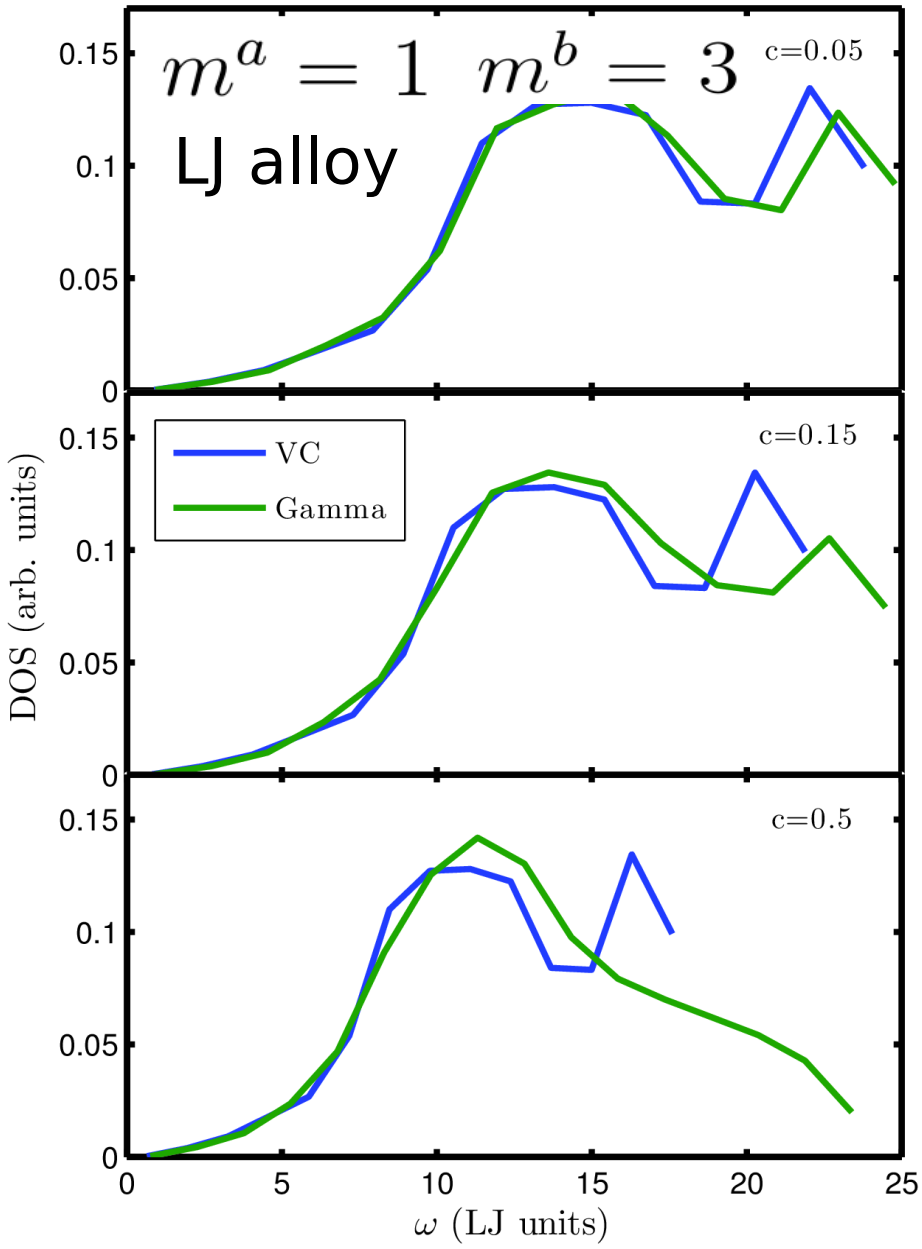
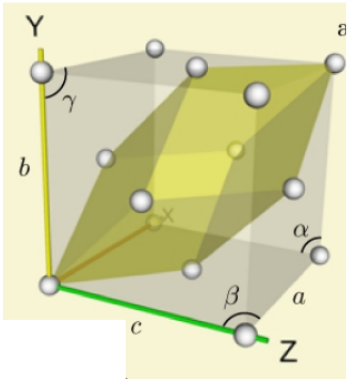
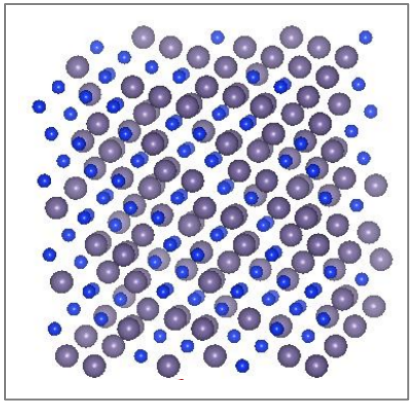
VC vs Gamma DOS

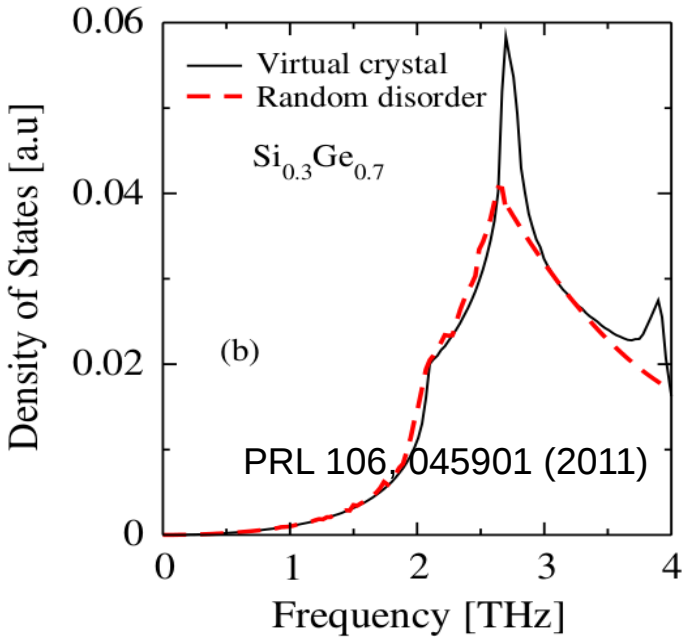


VC

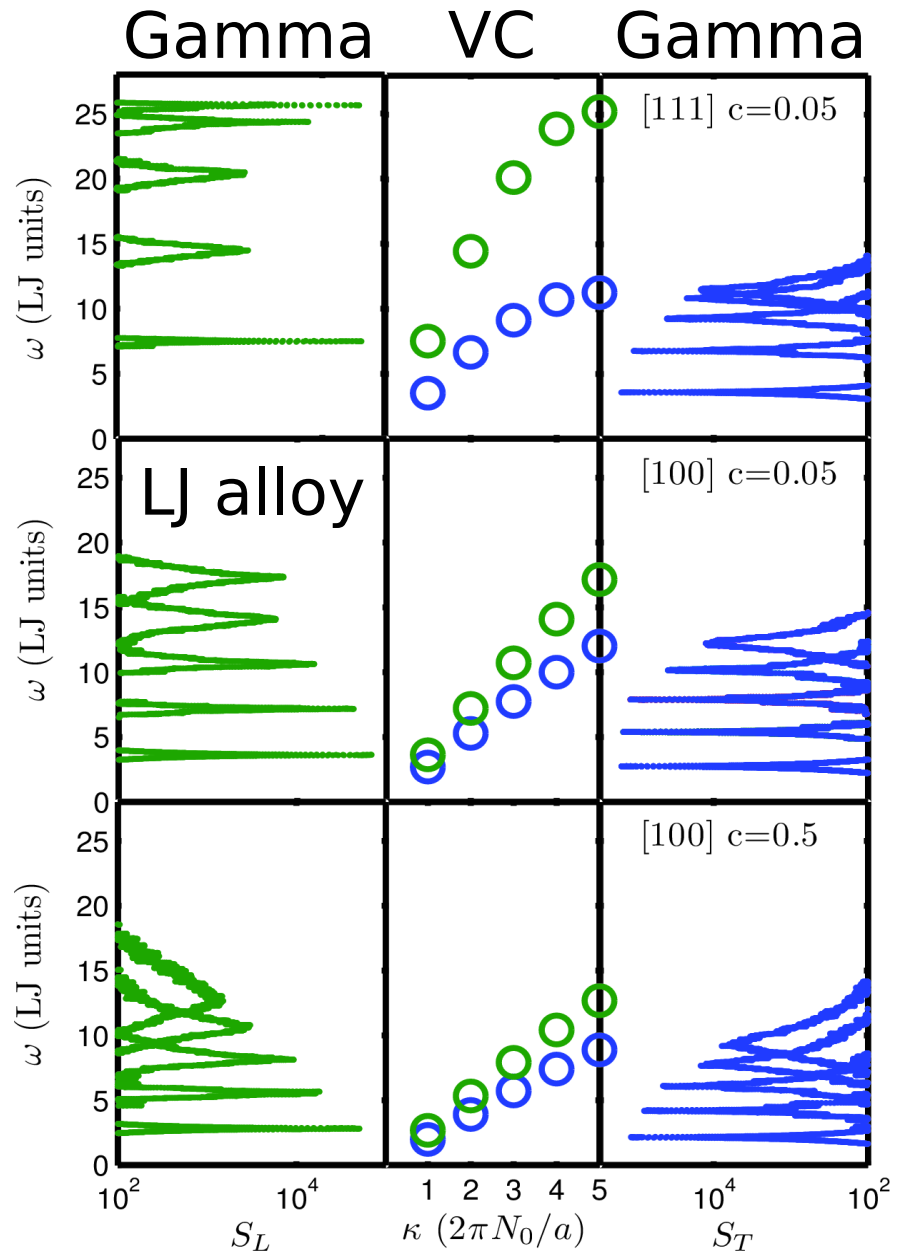


Gamma





Gamma modes plane-wave character



Tran:

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

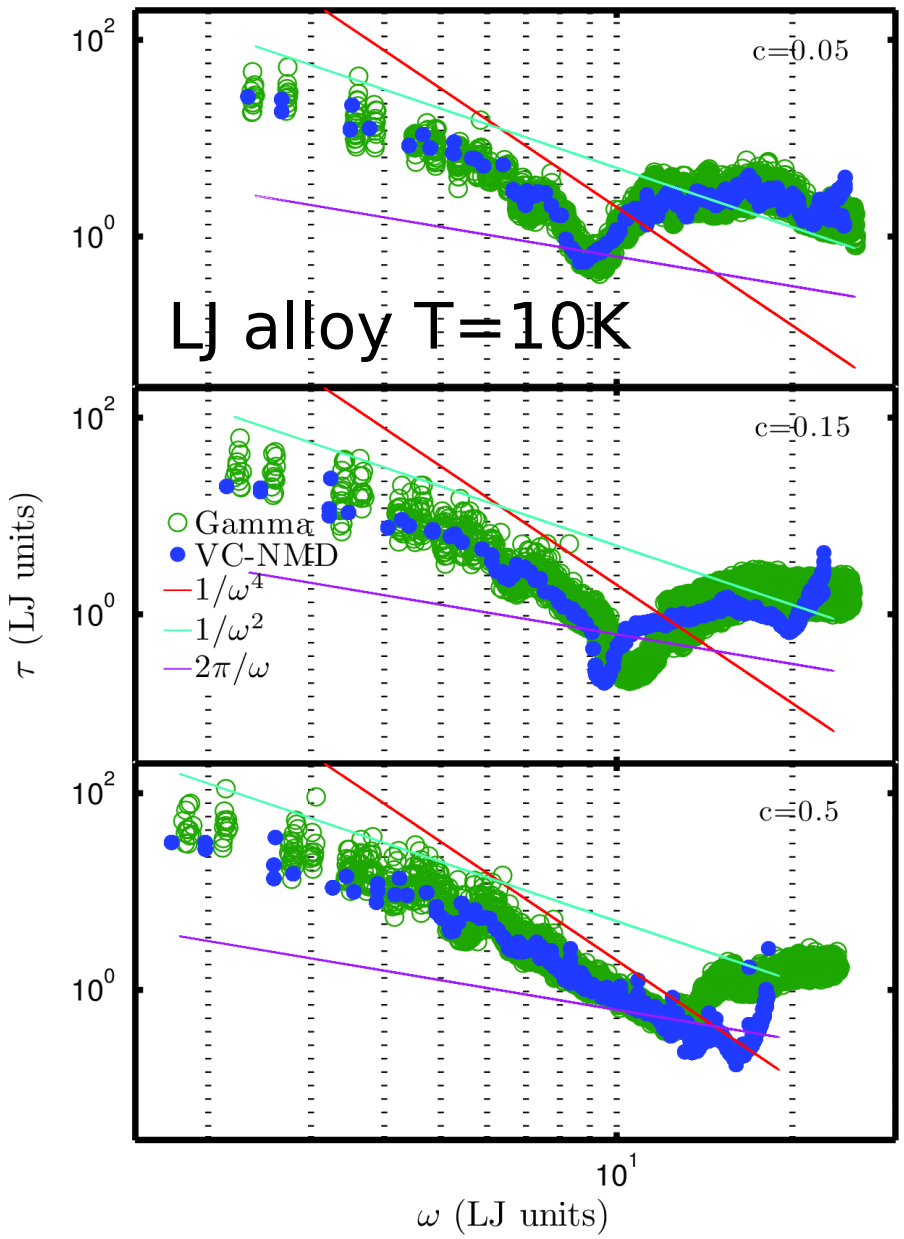
Long:

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

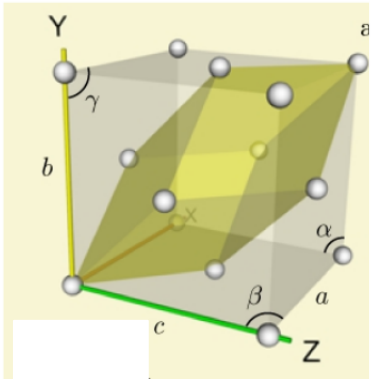
$$S^{L,T}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \omega\end{smallmatrix}\right) = \sum_{\nu} E^{L,T}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \delta\left(\omega - \omega\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)\right)$$

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

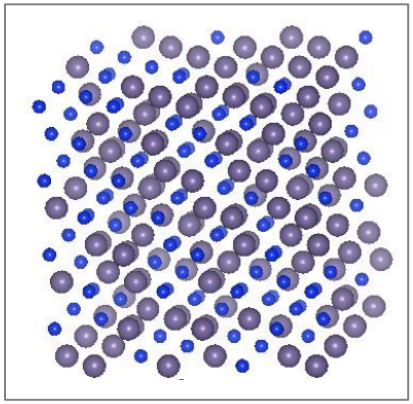
VC-NMD vs Gamma lifetimes



VC



Gamma

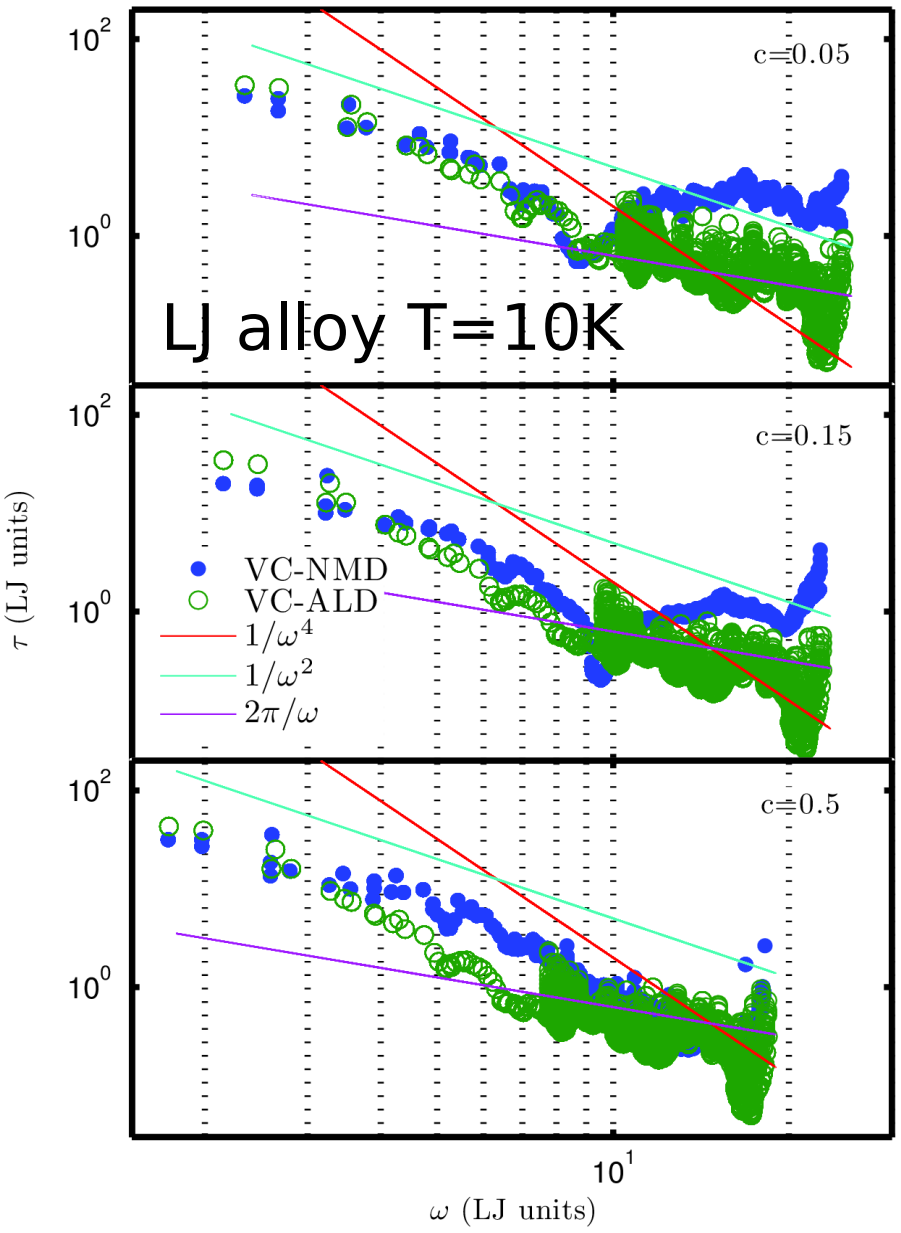


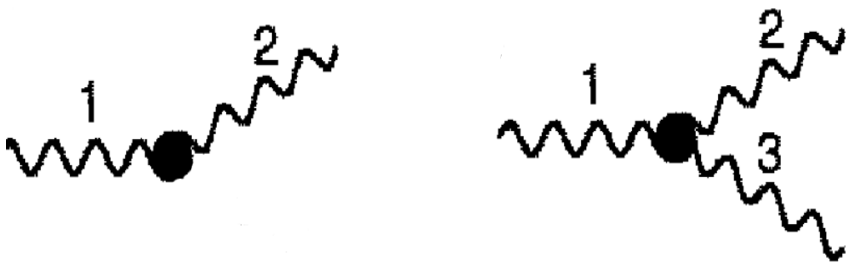
ALD+Debye

$$\tau_d \sim 1/\omega^4 \qquad \tau_{p-p} \sim 1/\omega^2$$

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

VC-NMD vs VC-ALD lifetimes





ALD+Debye

$$\tau_d \sim 1/\omega^4 \quad \tau_{p-p} \sim 1/\omega^2$$

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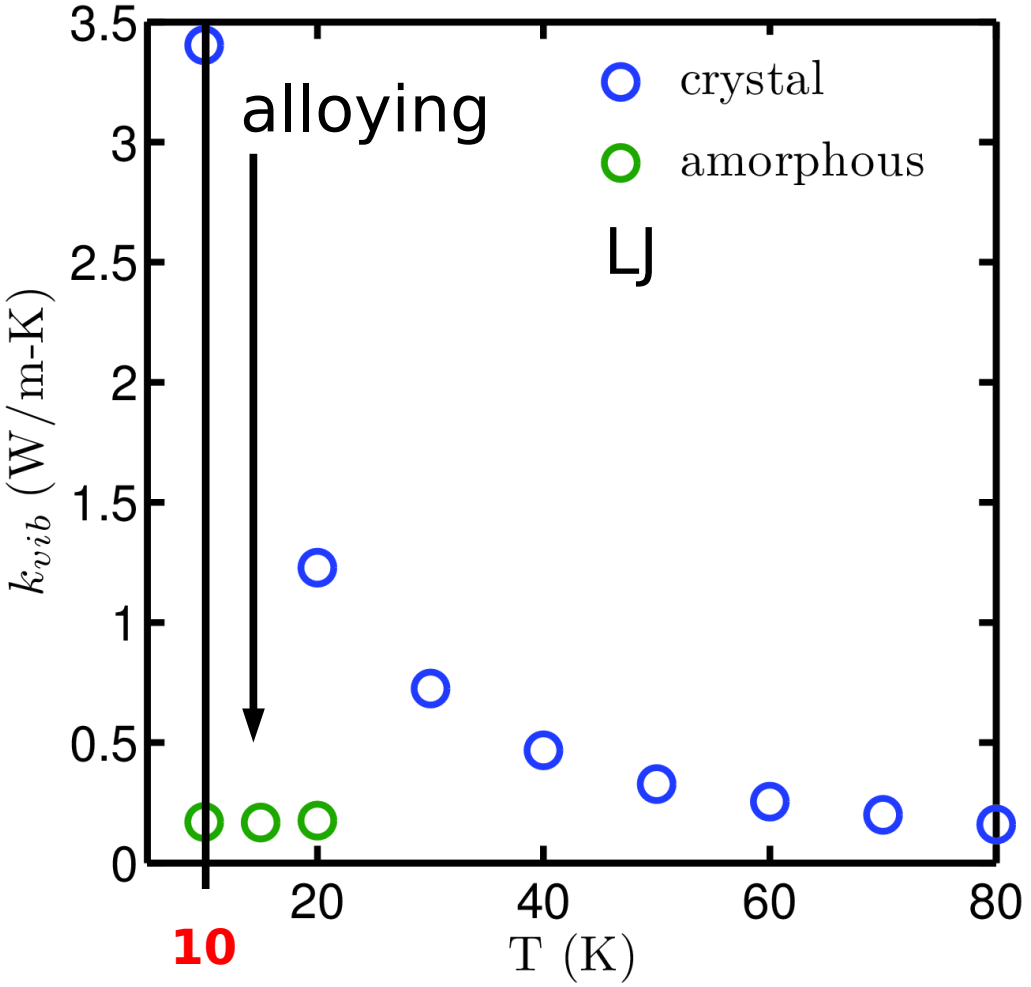
Conductivity from MD and GK

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

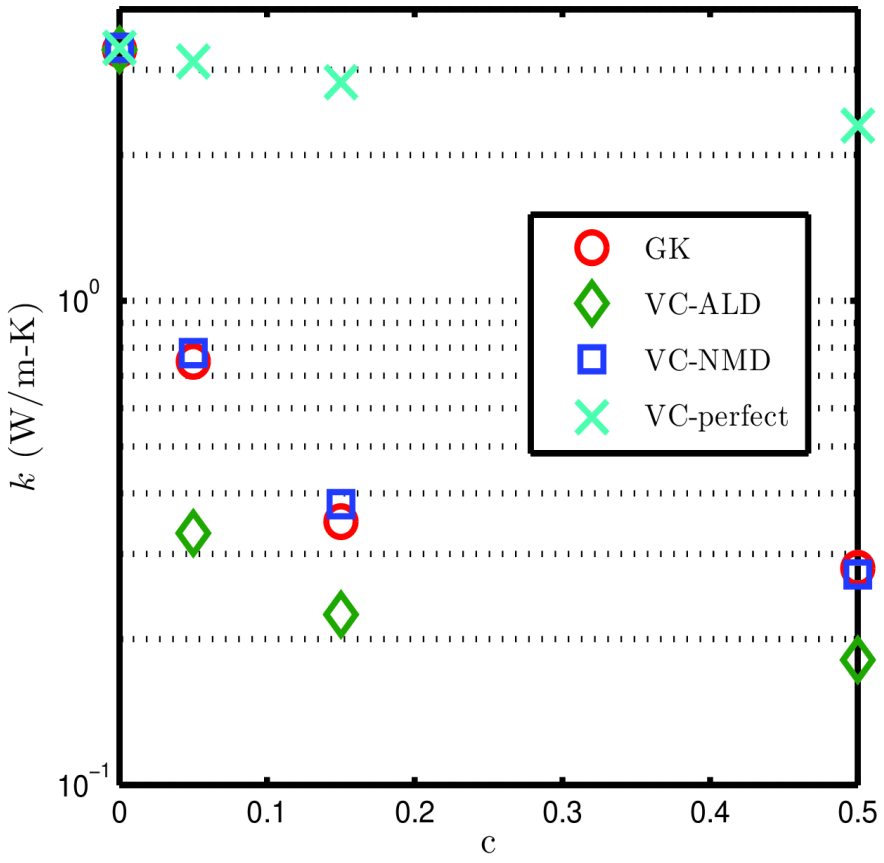
$$k_{vib} = \sum_{\text{modes}}$$

- MD simulations are classical, no quantum effects.

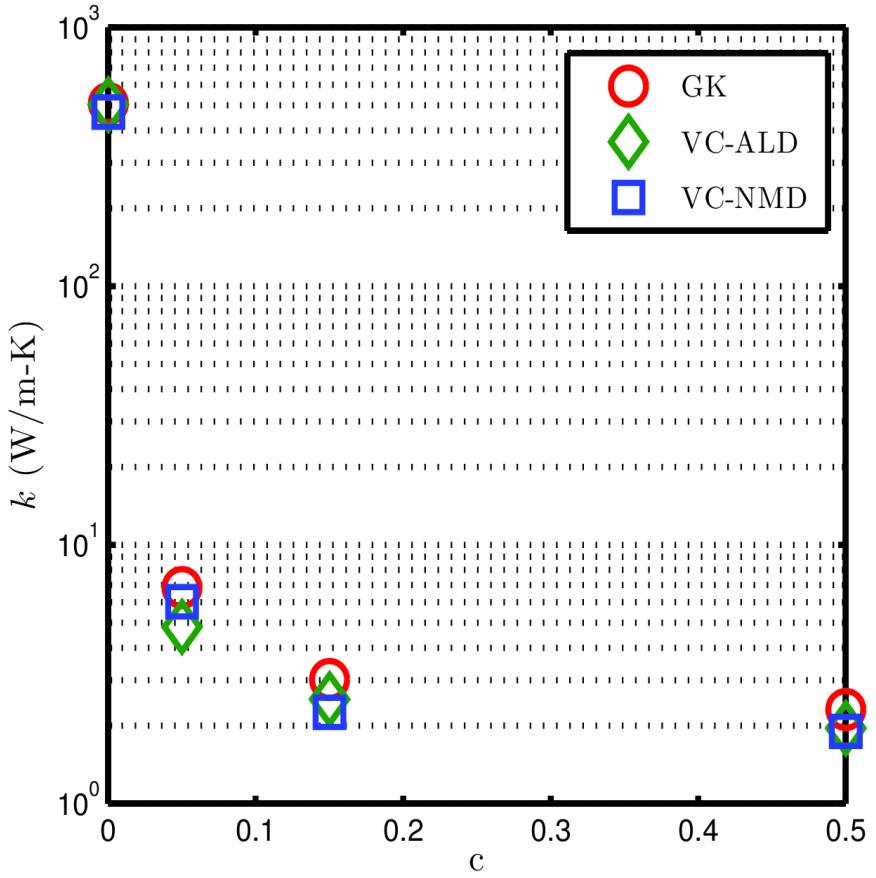


VC-NMD vs VC-ALD vs GK conductivity

LJ Ar:

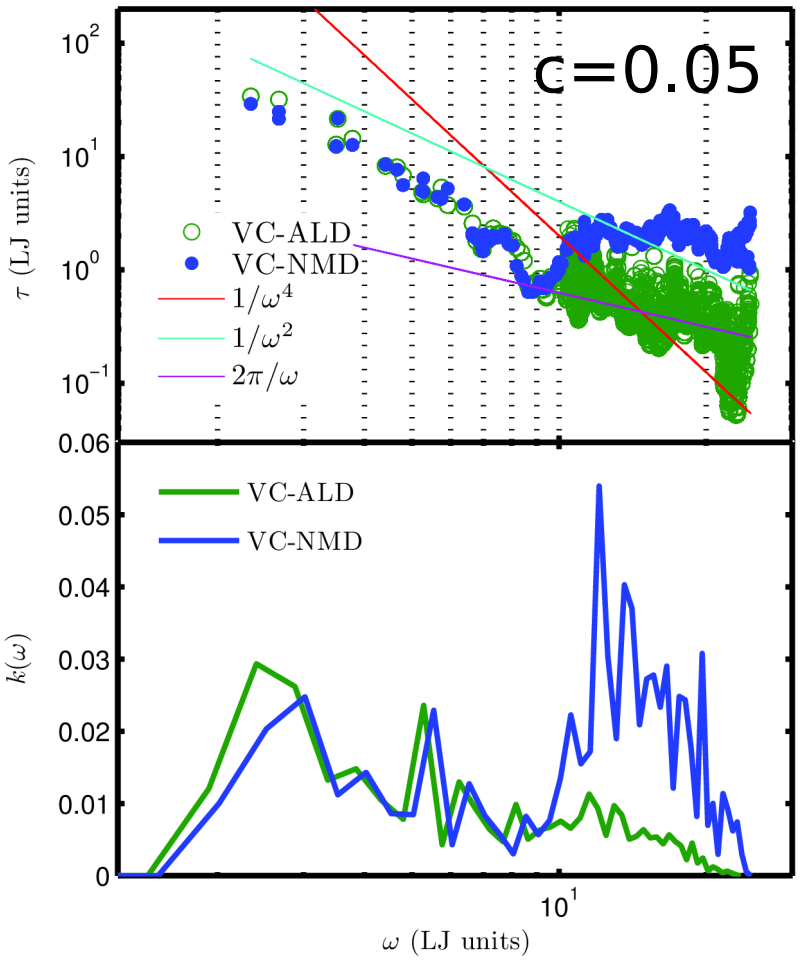


SW Si:

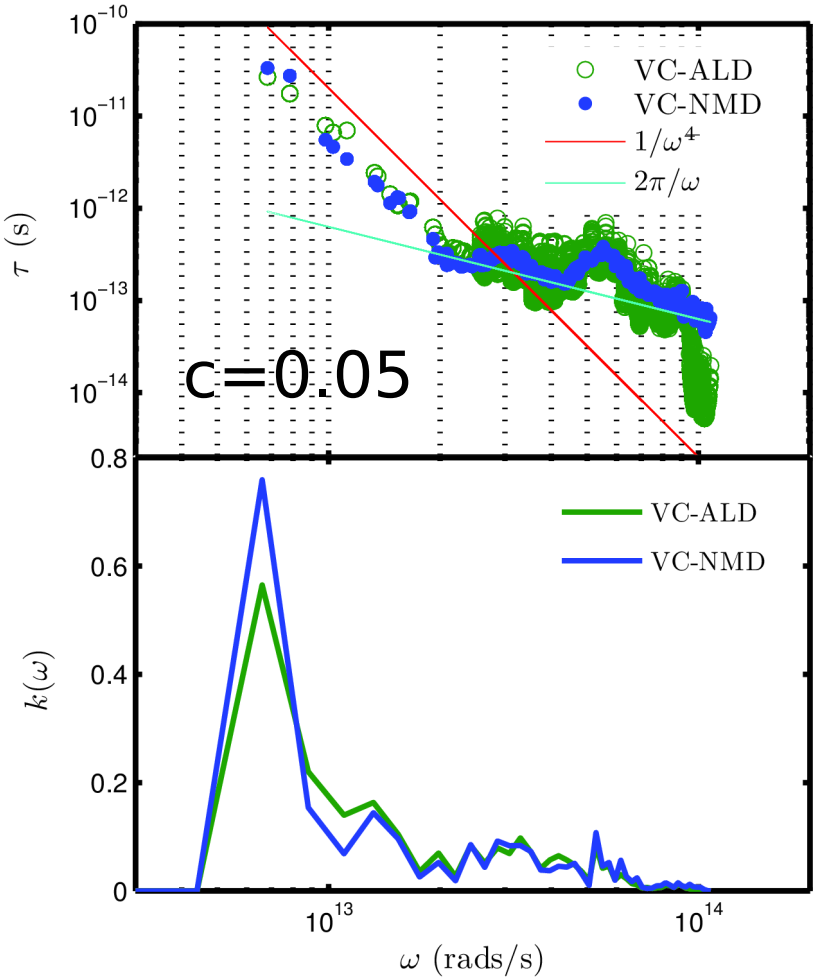


VC-NMD vs VC-ALD conductivity spectra

LJ alloy T=10K



SW alloy T=300K



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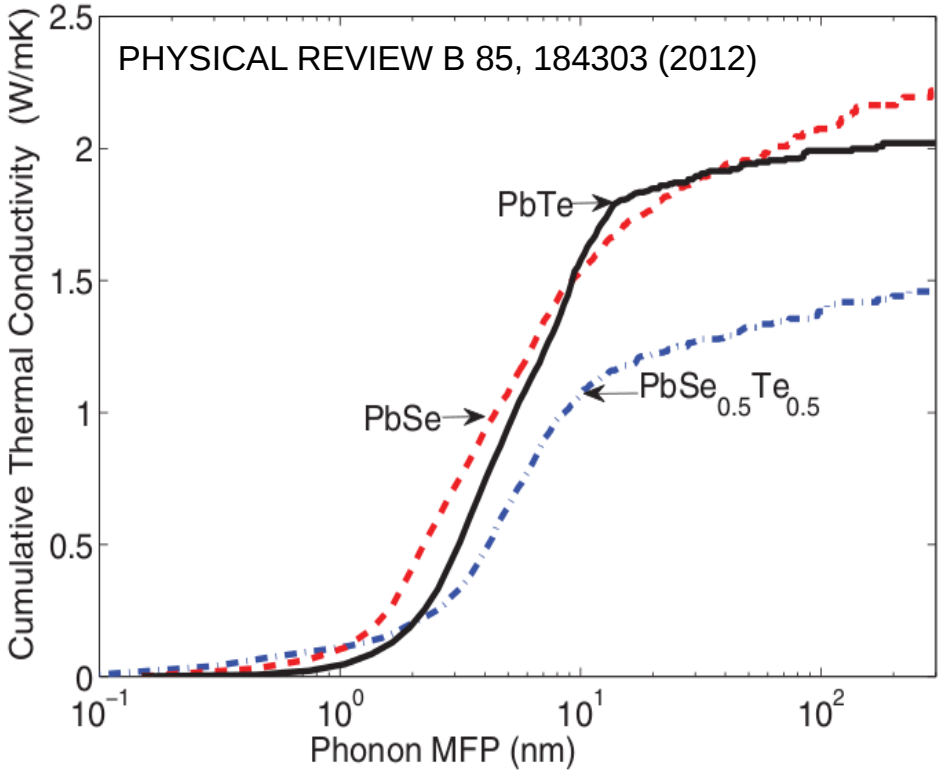
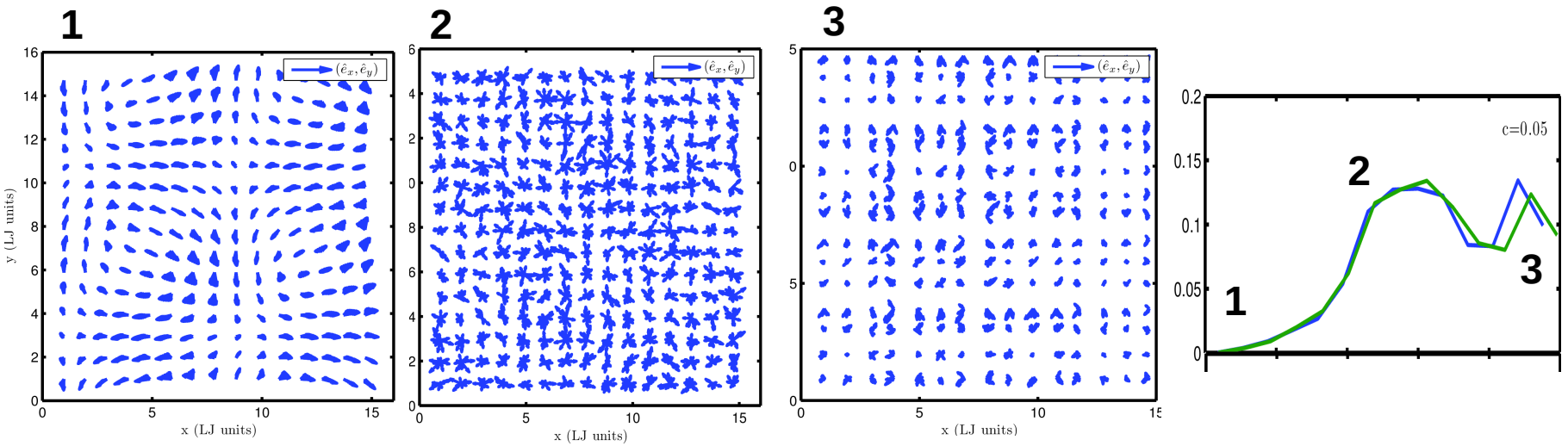
Summary

- VC-ALD is cheap, even using *ab initio* (DFT).
- VC-ALD can explore thermoelectric material design space.
- It is important to understand any limitations (underpredicts for LJ).



Gamma mode shapes

C=0.05



C=0.5