

Evaluation of the Virtual Crystal Approximation for Predicting Thermal Conductivity

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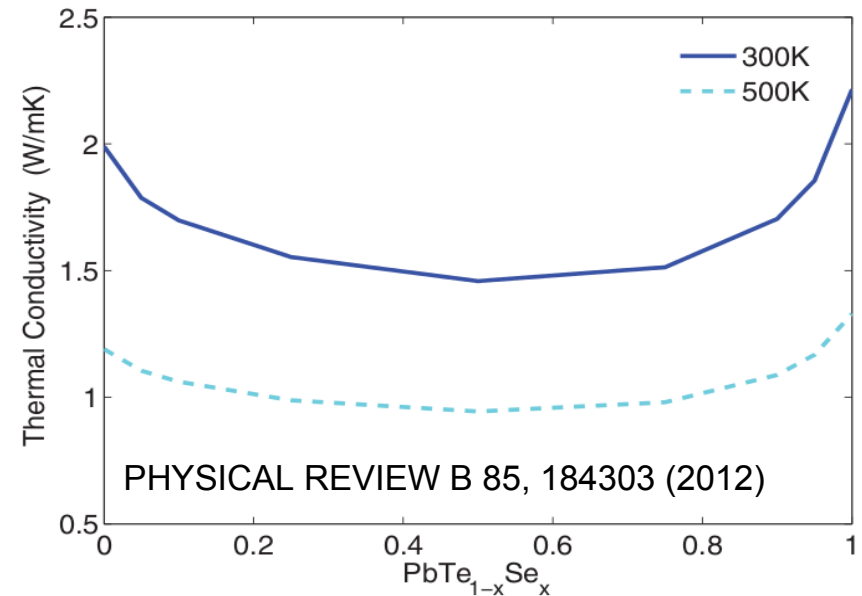
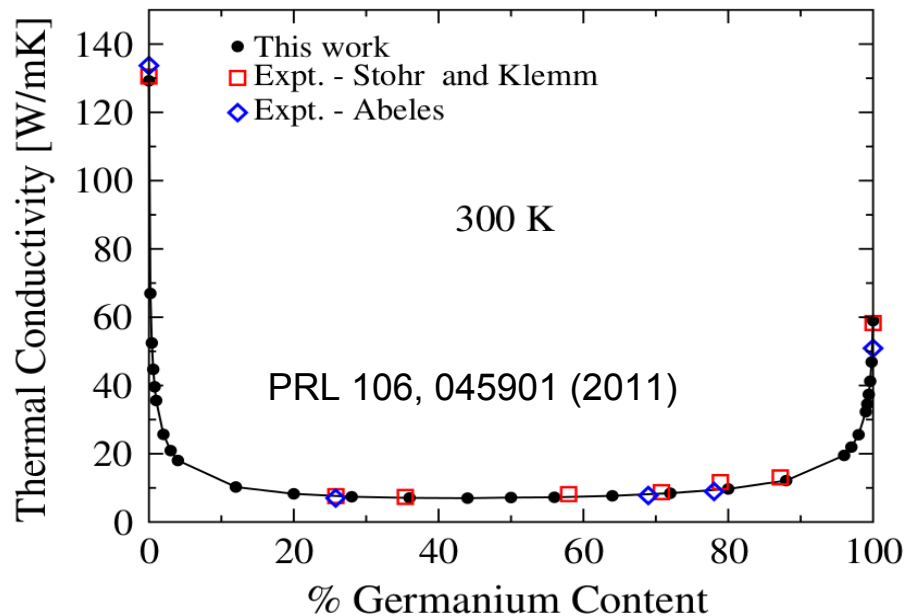
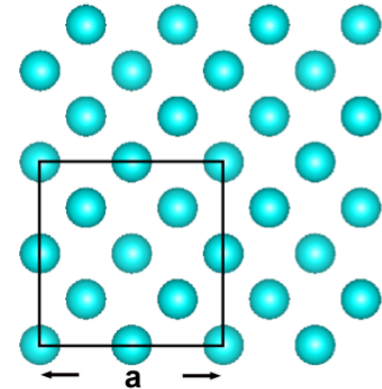
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Motivation: experimental accuracy

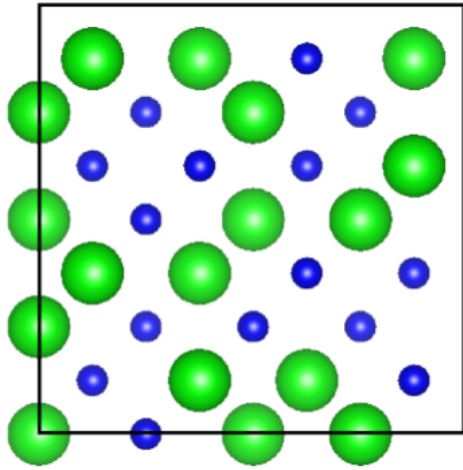
Expensive Density Functional Theory (DFT): force constants

Anharmonic Lattice Dynamics (ALD): based on unit cell

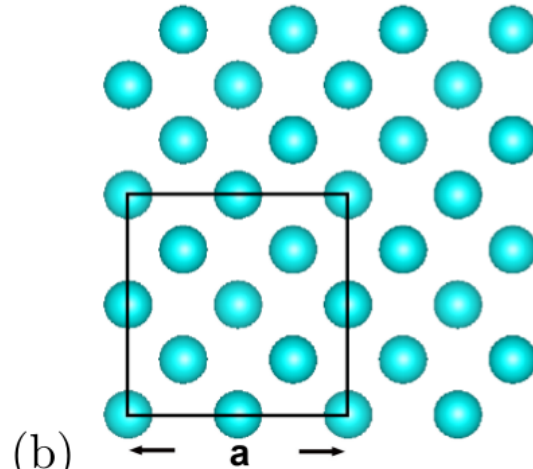
Alloys: isotopic effects, thermoelectric materials



Virtual Crystal Approximation



(a)



(b)

$$c^\mu, m^\mu$$

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

disorder strength:

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

Kinetic Theory for Crystal

single-mode relaxation time approximation + Boltzmann Transport Equation + classical harmonic limit:

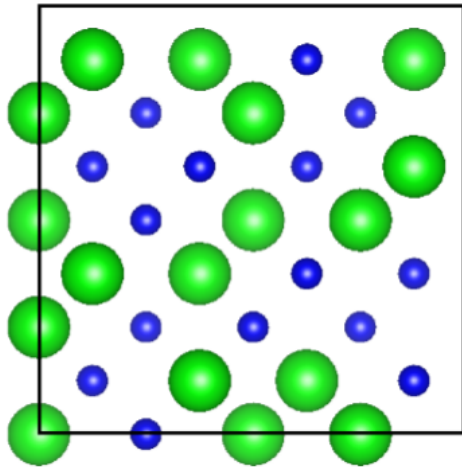
$$k_{ph,\mathbf{n}} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} \frac{k_B}{V} D_{ph,\mathbf{n}}\left(\frac{\boldsymbol{\kappa}}{\nu}\right)$$

mode thermal diffusivity:

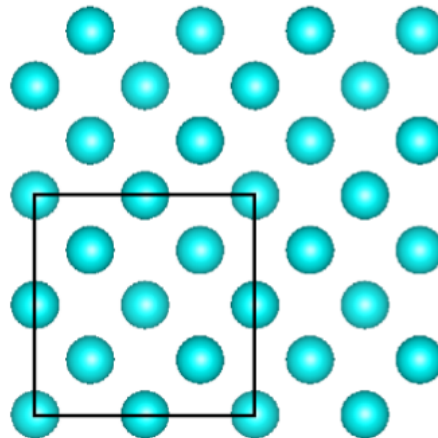
$$D_{ph,\mathbf{n}}\left(\frac{\boldsymbol{\kappa}}{\nu}\right) = v_{g,\mathbf{n}}^2\left(\frac{\boldsymbol{\kappa}}{\nu}\right) \tau\left(\frac{\boldsymbol{\kappa}}{\nu}\right)$$

Macro-theory: $k = \rho C_p \alpha$

VC Approximation with ALD (VC-ALD)



(a)



(b)

$$D_{ph,\mathbf{n}}(\boldsymbol{\kappa}) = v_{g,\mathbf{n}}^2(\boldsymbol{\kappa}) \tau(\boldsymbol{\kappa})$$

ALD

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



Tamura

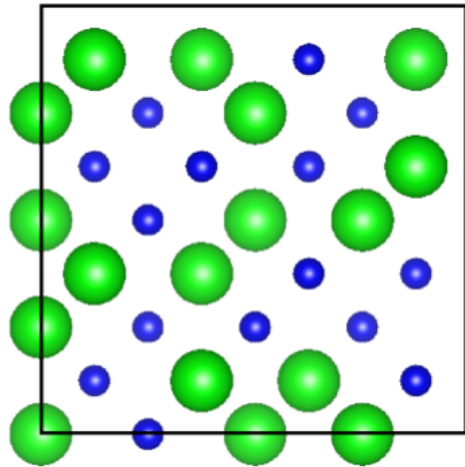
$$\tau_{p-d}(\boldsymbol{\kappa}) \sim 1/\omega^4$$



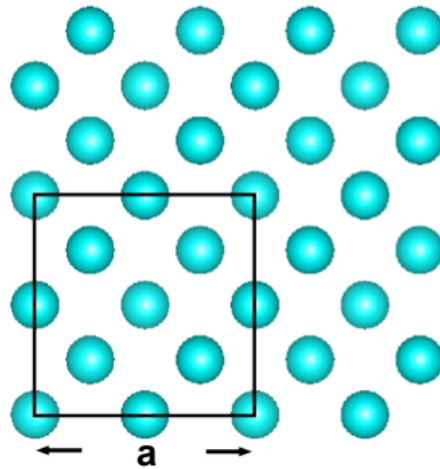
Matthiessen's Rule

$$\frac{1}{\tau(\boldsymbol{\kappa})} = \frac{1}{\tau_{p-p}(\boldsymbol{\kappa})} + \frac{1}{\tau_{p-d}(\boldsymbol{\kappa})}$$

VC Approximation with ALD (VC-ALD)



(a)

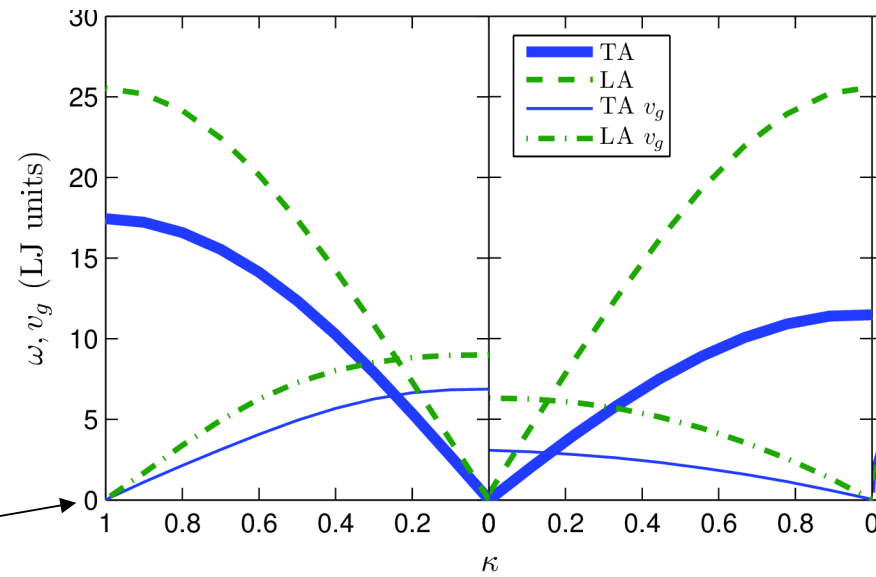


(b)

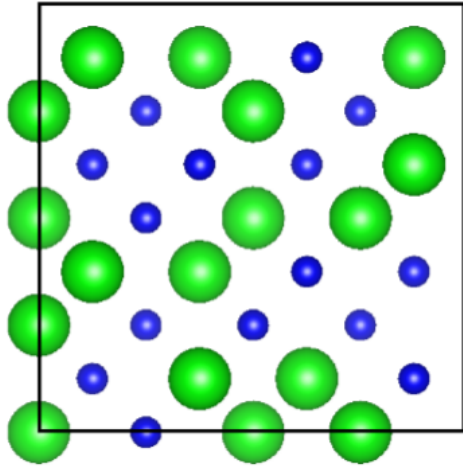
$$D_{ph,\mathbf{n}}(\boldsymbol{\kappa}) = v_{g,\mathbf{n}}^2(\boldsymbol{\kappa}) \tau(\boldsymbol{\kappa})$$

$$\frac{\partial \omega(\boldsymbol{\kappa}_{\nu})}{\partial \boldsymbol{\kappa}} v_{g,\mathbf{n}}(\boldsymbol{\kappa}_{\nu}) = \partial \omega(\boldsymbol{\kappa}_{\nu}) / \partial \boldsymbol{\kappa}$$

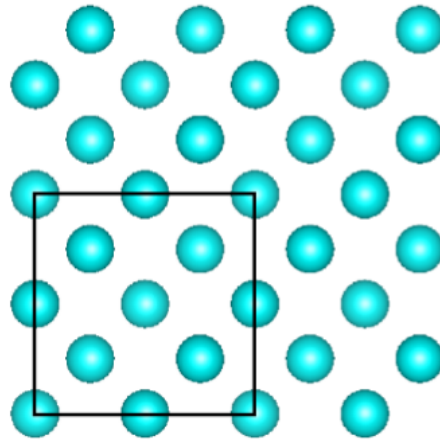
$$D_{ph}(\boldsymbol{\kappa}_{\nu}) \approx 0$$



Explicit disorder: Empirical Potentials



(a)



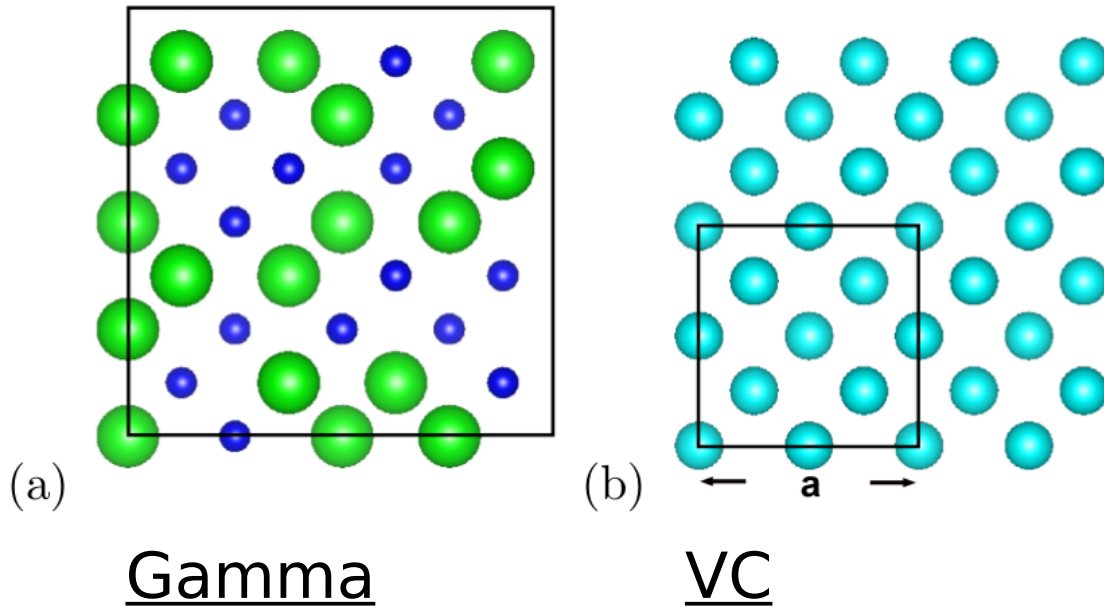
(b)

Virtual Crystal frequencies:

Lennard-Jones argon

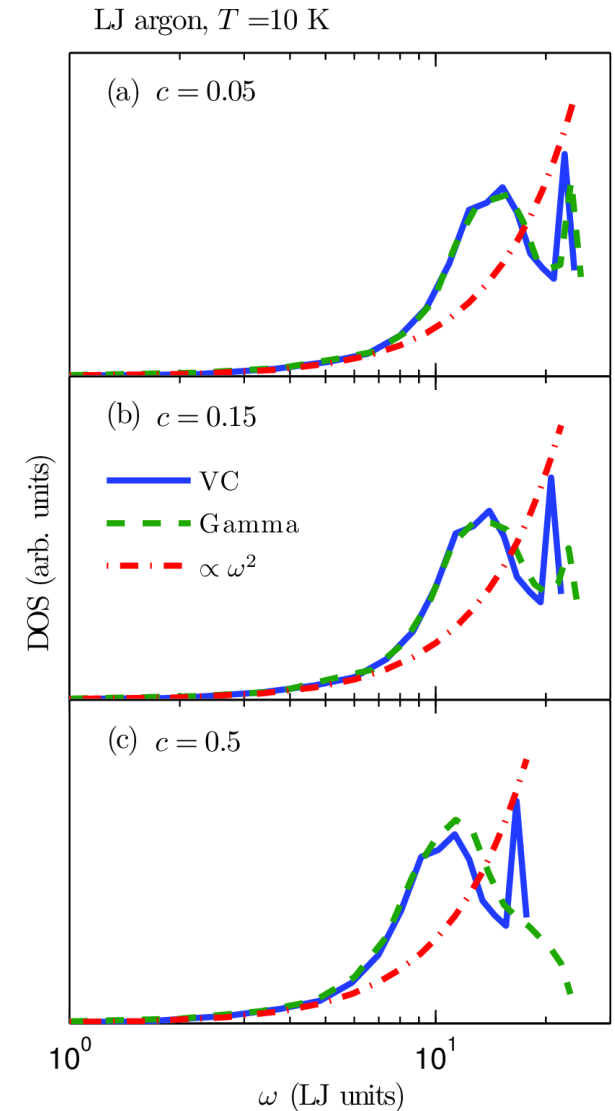
Stillinger-Weber silicon

Explicit disorder: VC vs Gamma

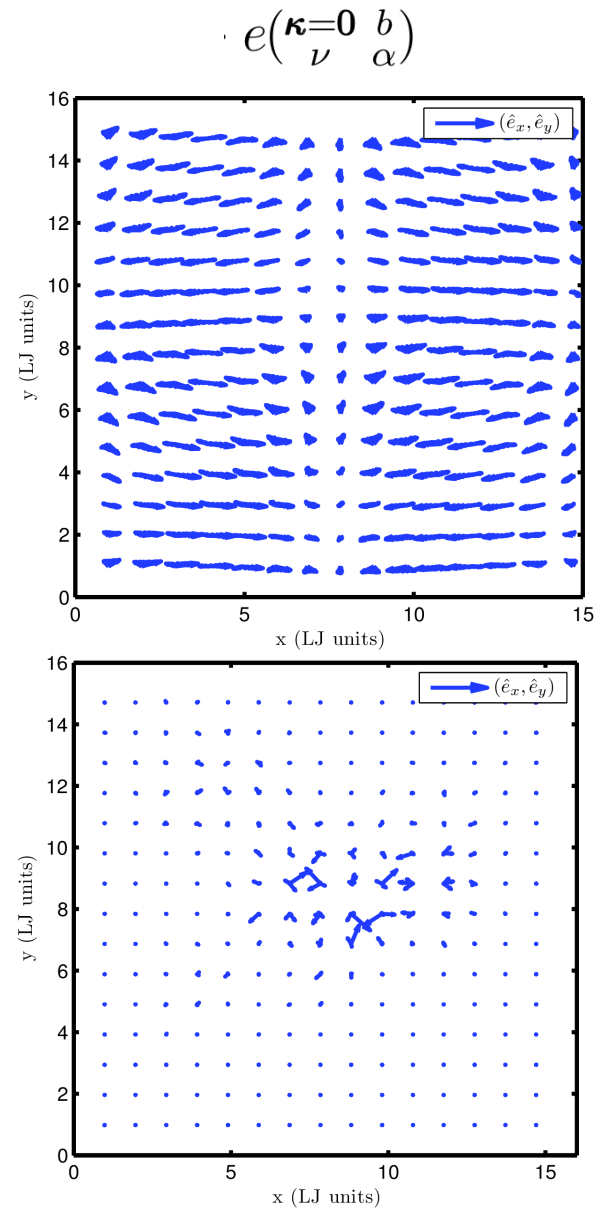
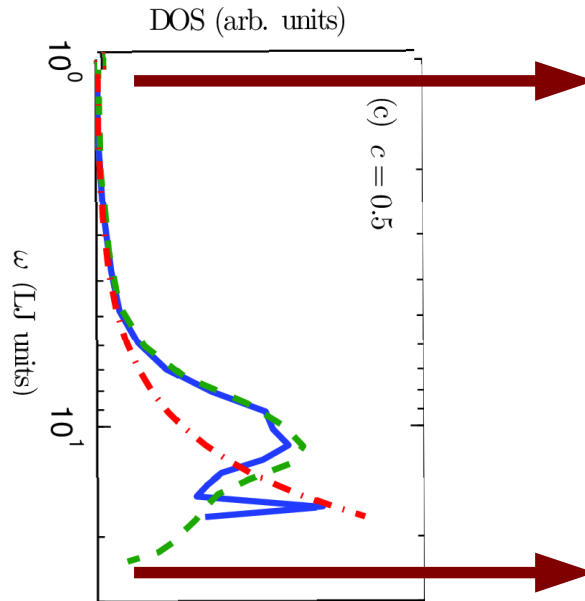
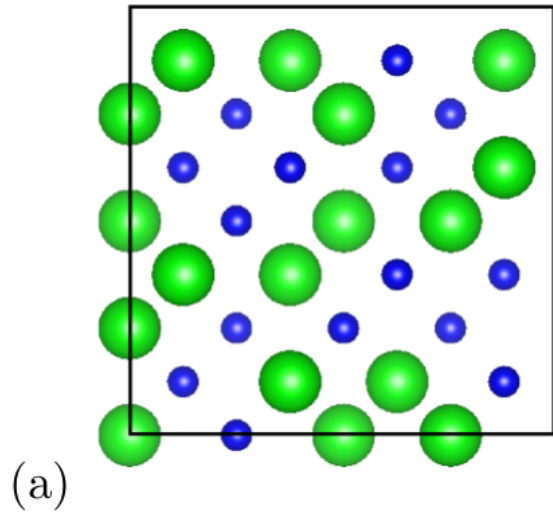


Virtual Crystal frequencies:

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



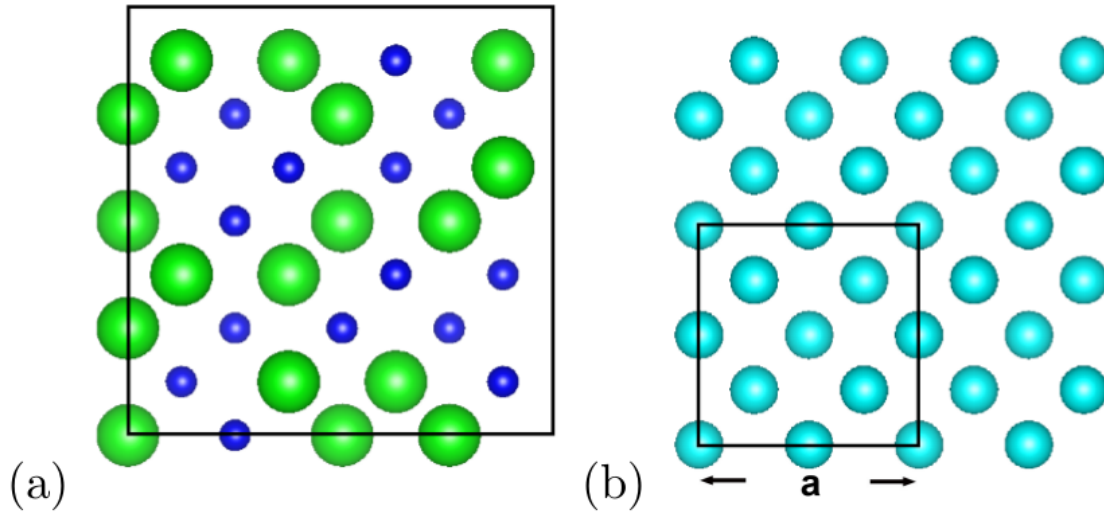
Gamma modes



longitudinal (and transverse) polarizations:

$$E^L(\kappa_{VC}) = \left| \sum_b \hat{\kappa}_{VC} \cdot e(\kappa=0 \begin{smallmatrix} b \\ \alpha \end{smallmatrix}) \exp[i\kappa_{VC} \cdot \mathbf{r}_0(l=0)_b] \right|^2$$

Gamma modes Structure Factor

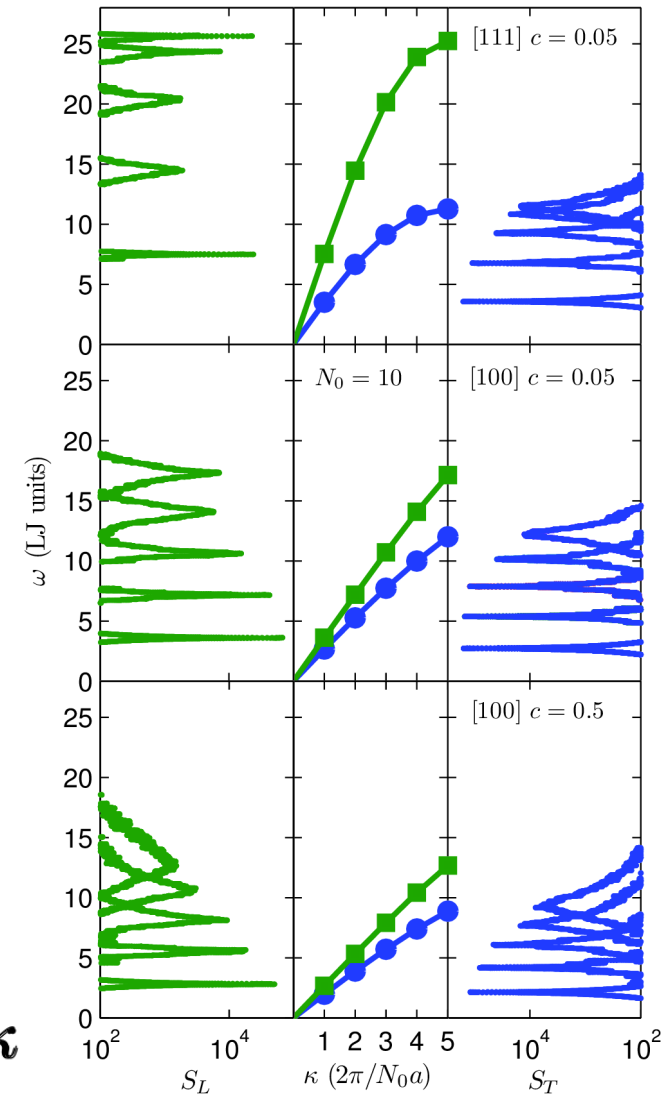


longitudinal (and transverse) polarizations:

VC group velocity:

$$D_{ph,n}(\kappa) = v_{g,n}^2(\kappa) \tau(\kappa)$$

$$v_{g,n}(\kappa) = \partial \omega(\kappa) / \partial \kappa$$



Normal Mode Decomposition (NMD)

$$D_{ph,n}(\boldsymbol{\kappa}) = v_{g,n}^2(\boldsymbol{\kappa}) \tau(\boldsymbol{\kappa})$$

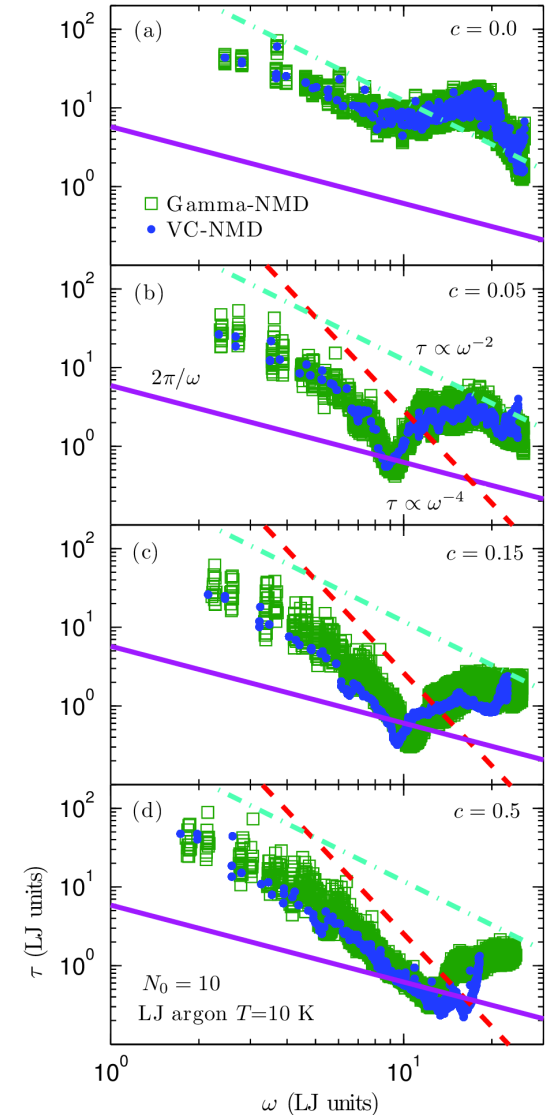
$$\tau(\boldsymbol{\kappa}) = \int_0^{t^*} \frac{\langle E(\boldsymbol{\kappa}; t) E(\boldsymbol{\kappa}; 0) \rangle}{\langle E(\boldsymbol{\kappa}; 0) E(\boldsymbol{\kappa}; 0) \rangle} dt$$

Normal mode coordinate:

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

Normal mode energy:

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



Allen-Feldman (AF), high-scatter limit

Phonons:

$$k_{ph,n} = \sum_{\kappa} \sum_{\nu} \frac{k_B}{V} D_{ph,n}(\kappa_{\nu})$$

Diffusons:

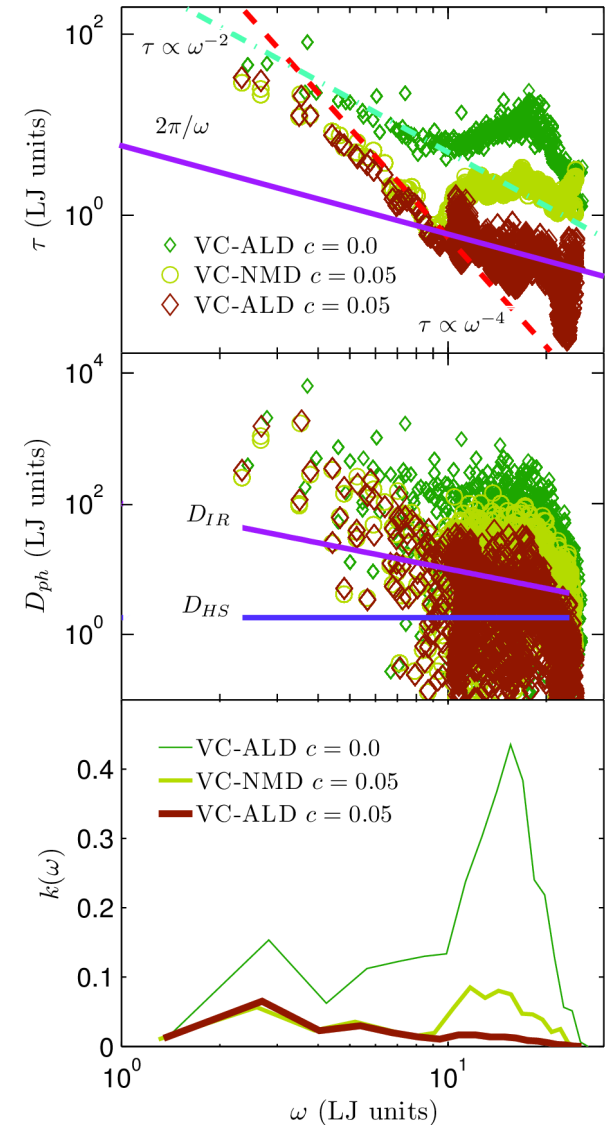
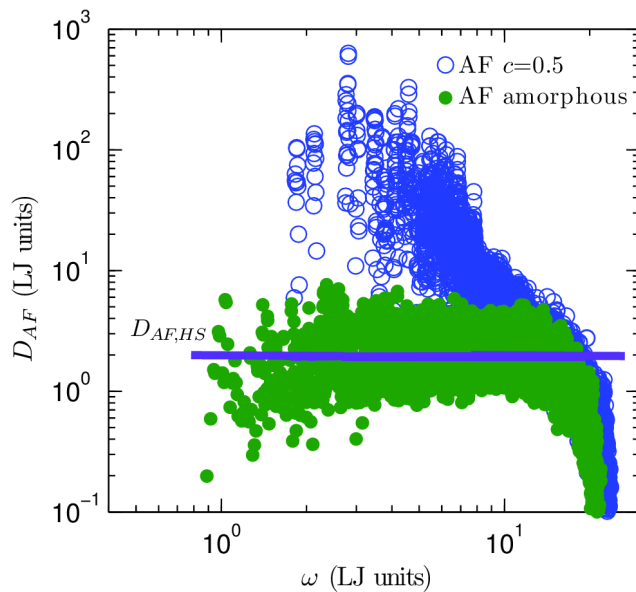
$$k_{AF} = \sum_{diffusons} \frac{k_B}{V} D_{AF,i}(\omega_i)$$

High-scatter limit:

$$k_{HS} = \frac{k_B}{V_b} b v_s a \quad D_{HS} = \frac{1}{3} v_s a \quad D_{IR} = \frac{2\pi}{3} \frac{v_s^2}{\omega}$$

NMD, VC-ALD, AF thermal diffusivity

$$D_{ph}(\mathbf{\kappa}_{\nu}) < D_{HS}$$



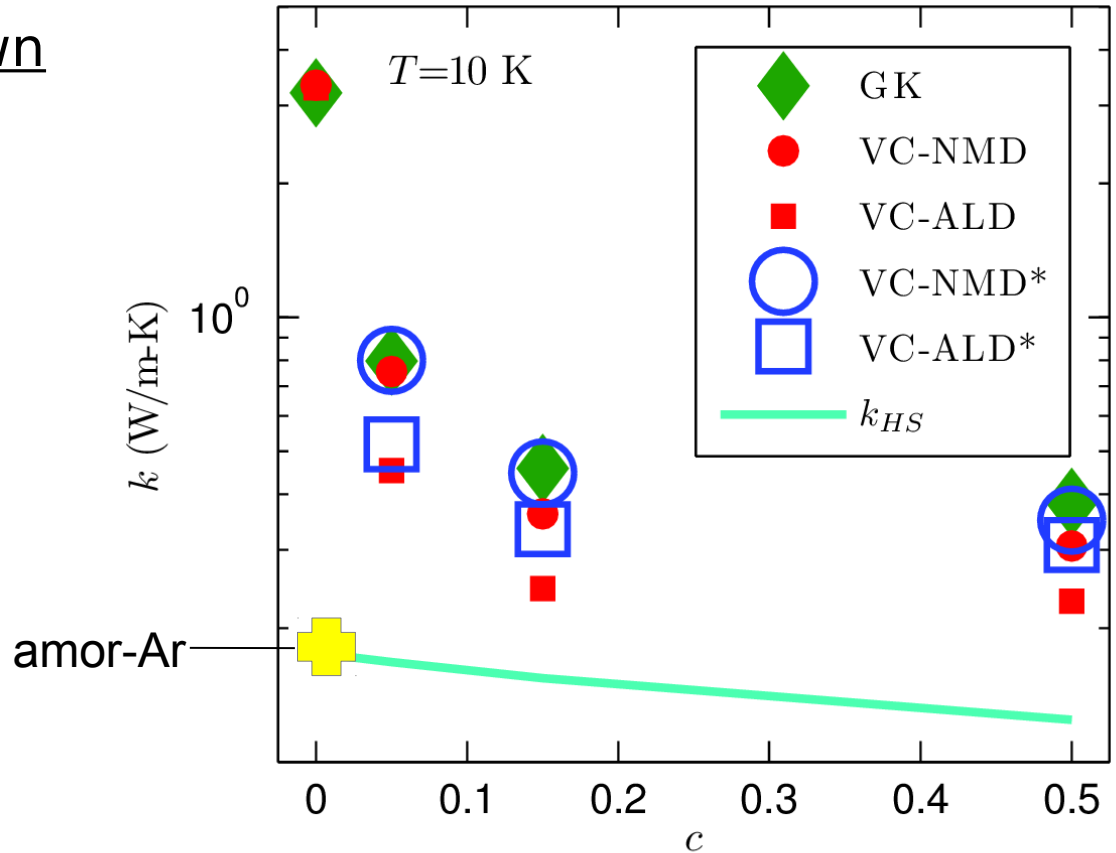
Thermal conductivity: LJ argon alloy

Green-Kubo (GK): top-down method

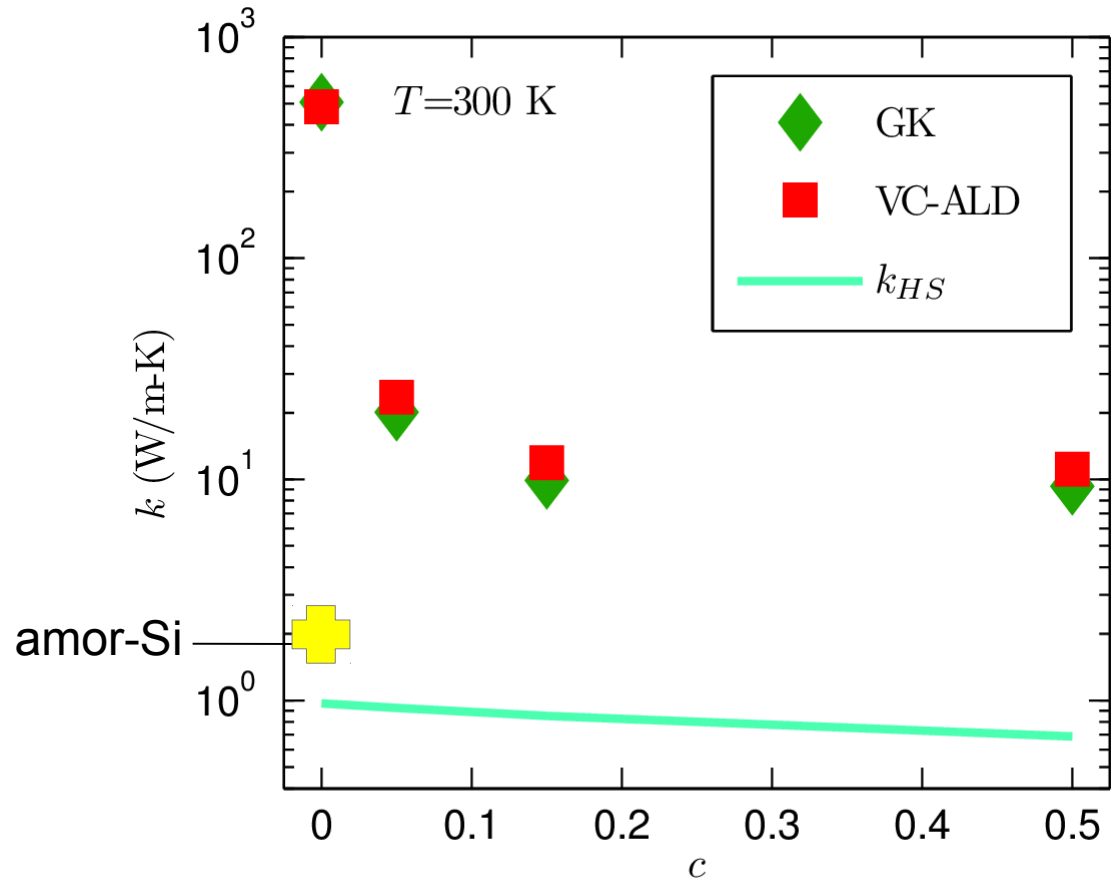
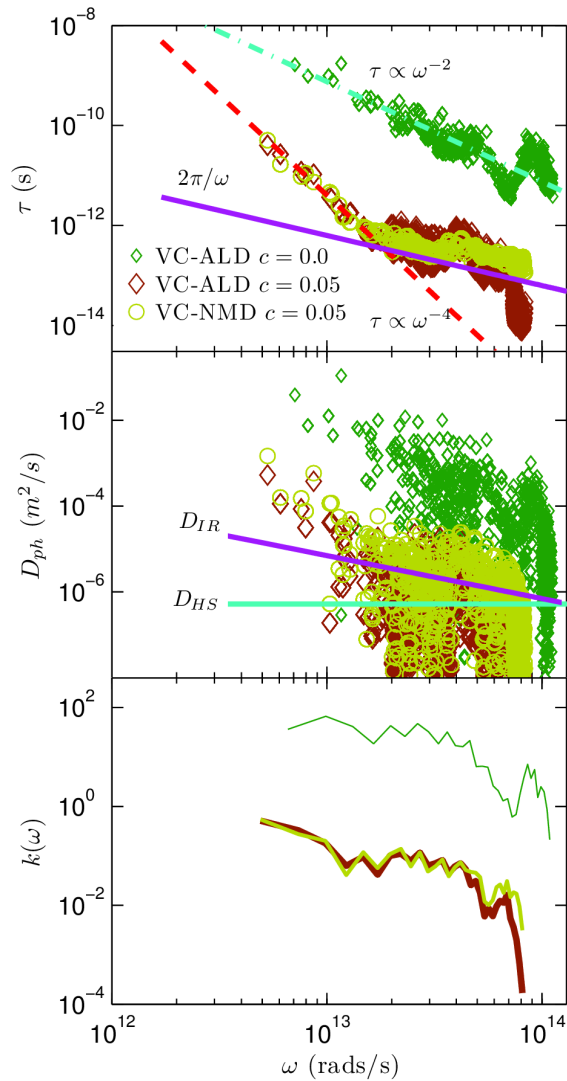
High-scatter adjustment*:

$$D_{ph}(\kappa) < D_{HS}$$

$$D_{ph}(\kappa) = D_{HS}$$



Thermal conductivity: SW silicon alloy



Summary

