# Ordered and Disordered Contributions to Lattice Thermal Conductivity

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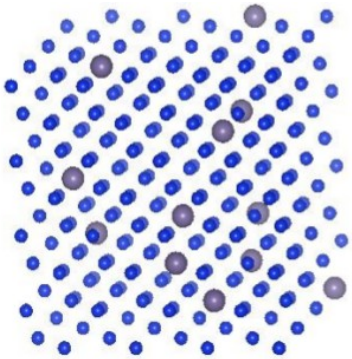
# Thermal Transport in Disordered Materials



- **Phonon** picture valid with perturbations. **Perfect systems and dilute alloys**



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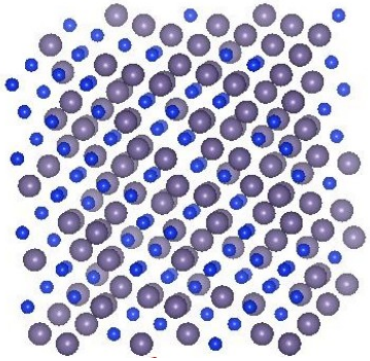
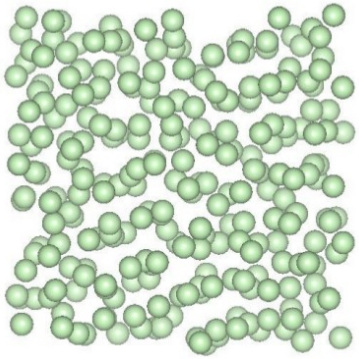
- Phonon picture only valid for very long wavelengths. **Alloy and amorphous**





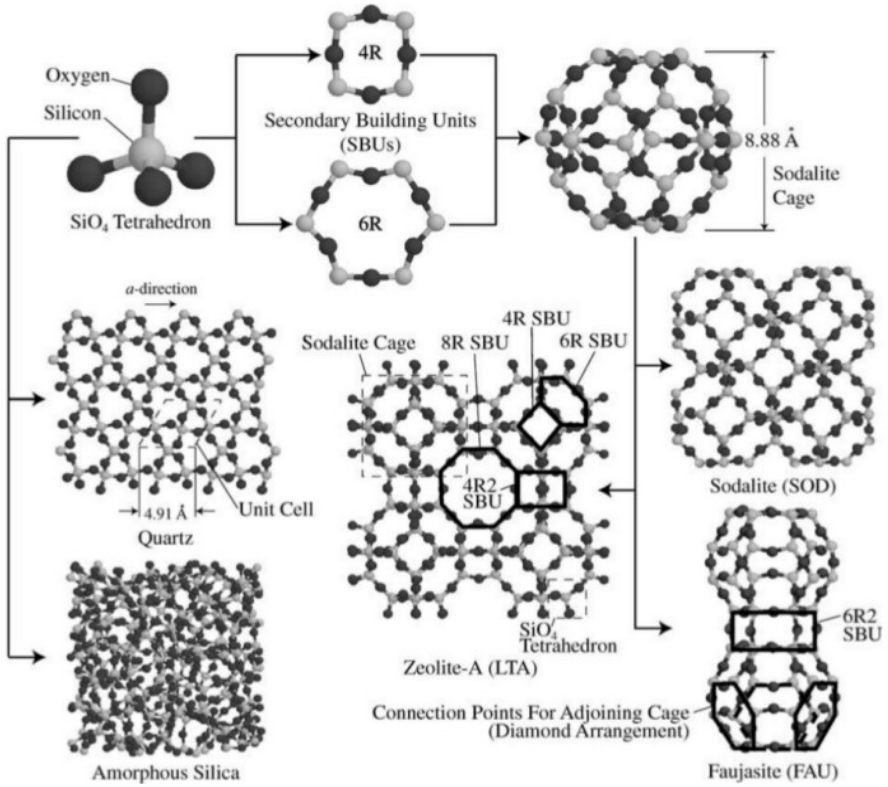
- **Localized** vibrations (diffusons) become important.

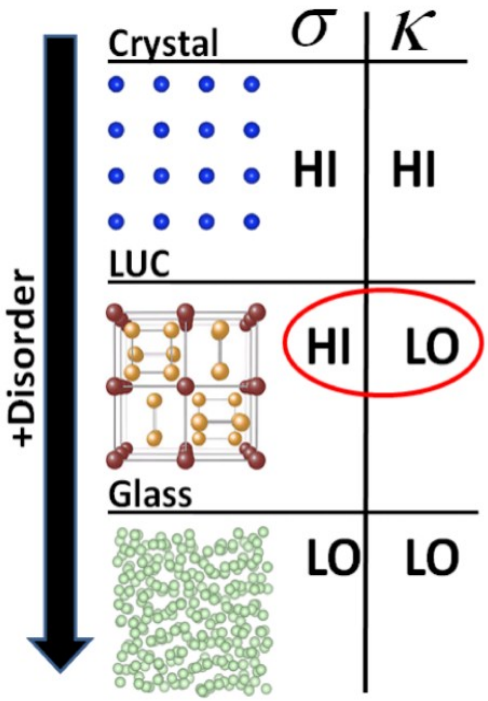
$$k_{vib} = k_{AF} + k_{ph}$$

(disorder) (order)

# Thermal Transport in Disordered Materials: Applications






- Crystal → Large Unit Cell → amorphous

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

# Theoretical Models



$$k_{vib} = k_{AF} + k_{ph}$$

**Phonons (ordered): Interacting Phonon Gas**

$$k_{ph} = \sum_{\boldsymbol{\kappa}} \sum_{\nu} C_{ph}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) v^2_{g,\mathbf{n}}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) \quad \Lambda\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = |\boldsymbol{v}_g| \tau\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right)$$

- phonon-phonon (anharmonicity), defects (dilute), boundaries, (phonon-diffuson?)

**Diffusons (disordered): Allen-Feldman Theory**

$$k_{AF} = \sum_{i} C(\omega_i) D_{AF}(\omega_i) \qquad \Lambda = \ ?$$

- diffuson-diffuson, (boundaries, diffuson-phonon?)

$$C(\omega_i) = k_B / \mathrm{V} \quad C_{ph}\left(\begin{smallmatrix}\boldsymbol{\kappa}\\ \nu\end{smallmatrix}\right) = k_B / \mathrm{V}$$

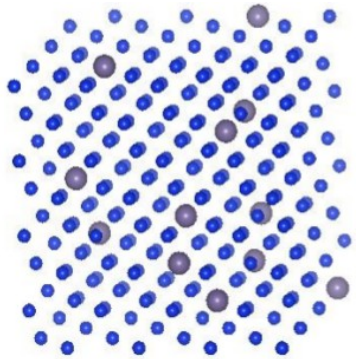
# Modeling Tools

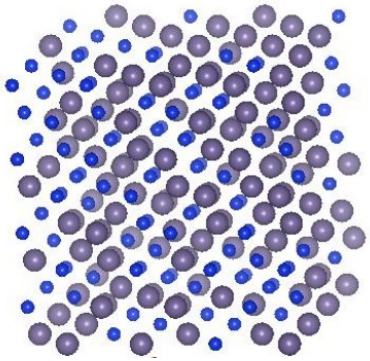


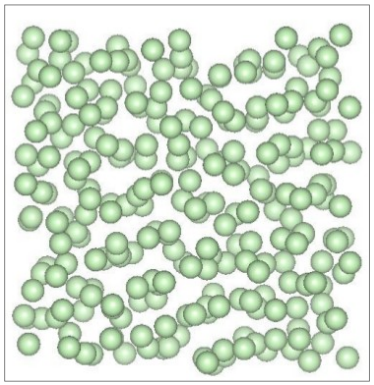
| | Predicted quantities | Computational cost | Code availability |
|---|---|---|---|
| Green-Kubo (**GK**) w/ Molecular Dynamics (MD) | Thermal conductivity | Classical | Several |
| Harmonic Lattice Dynamics (HLD) | Vibrational frequencies, eigenvectors, group velocities, diffuson properties (Allen-Feldman (AF)) | Classical/Ab-Initio | Several |
| Normal Mode Decomposition (**NMD**) w/ HLD and MD | Thermal conductivity, Vibrational frequencies, lifetimes | Classical | None |

# Systems Modeled: LJ Alloys and Amorphous







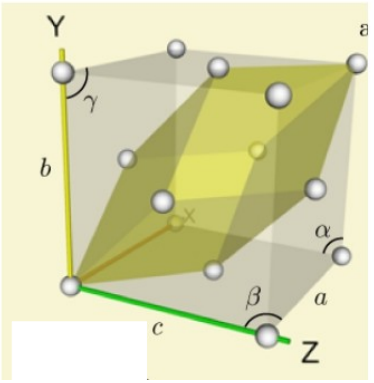


**Virtual Crystal (VC)** approximation



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

Unit cell




$$m^a_{1-c} m^b_c \quad m^a = 1 \quad m^b = 3 \quad \text{T=10K}$$

$$m_r = m^a / m^b = 3 \quad \text{c=0.5, } m_{avg} = 2.0$$

System sizes: up to 4000 atoms, 6 nm



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

Unit cell

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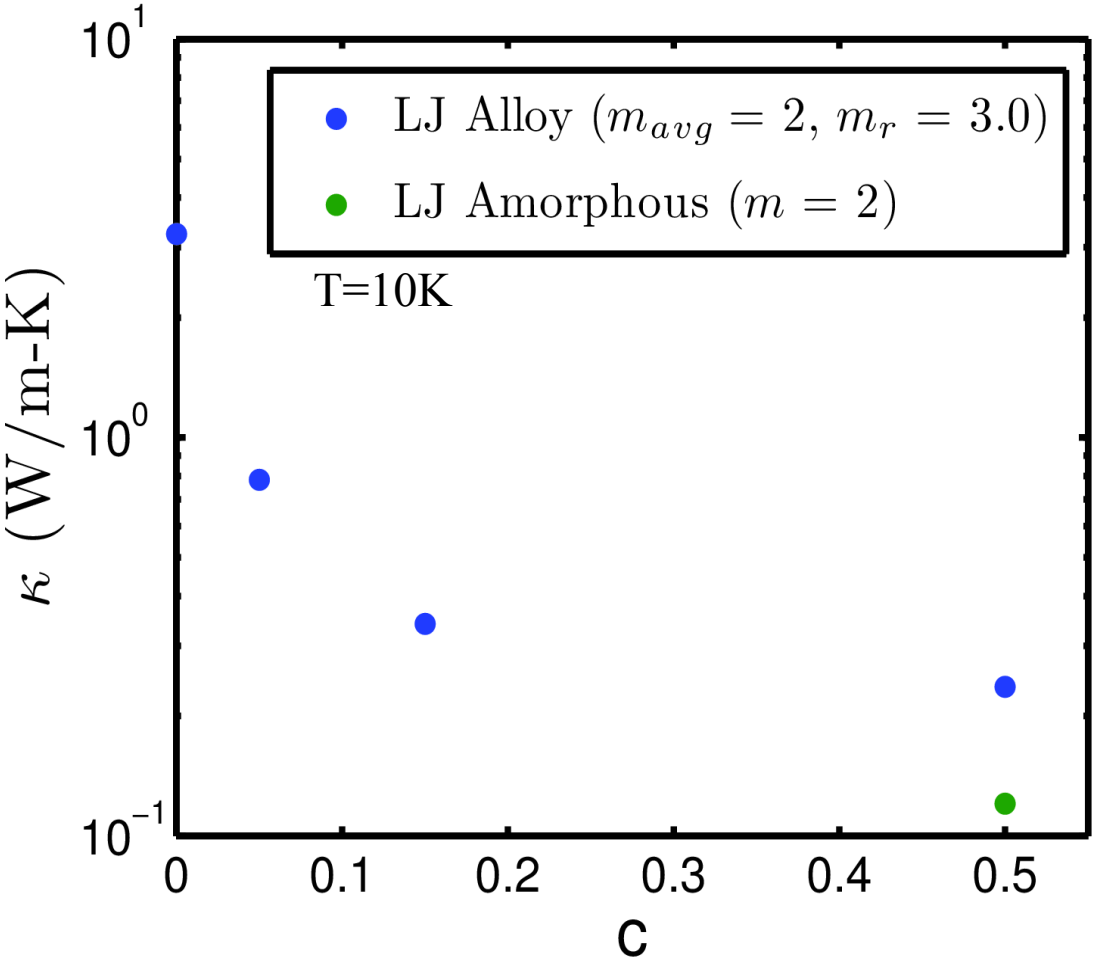
# Thermal Conductivity: System-Level



**Green-Kubo**

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle \, dt$$




- Heat current J has all effects of MD (anharmonicity, defects, etc.)
- Heat current J has KE and PE parts.
- J is difficult to define using *ab-initio* calculations.

# Normal Mode Decomposition (NMD)



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

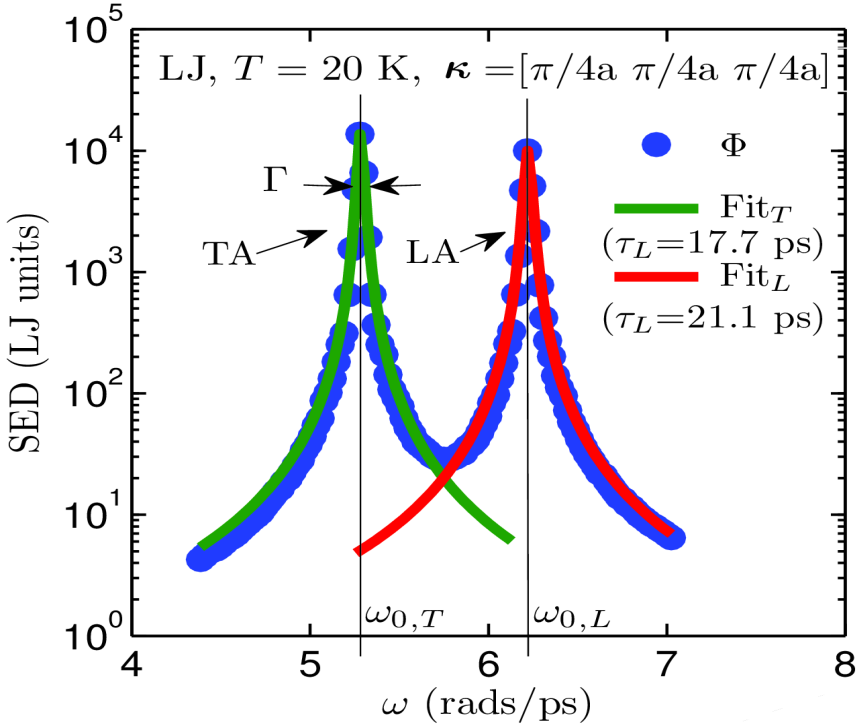
## NMD: Frequency-Domain

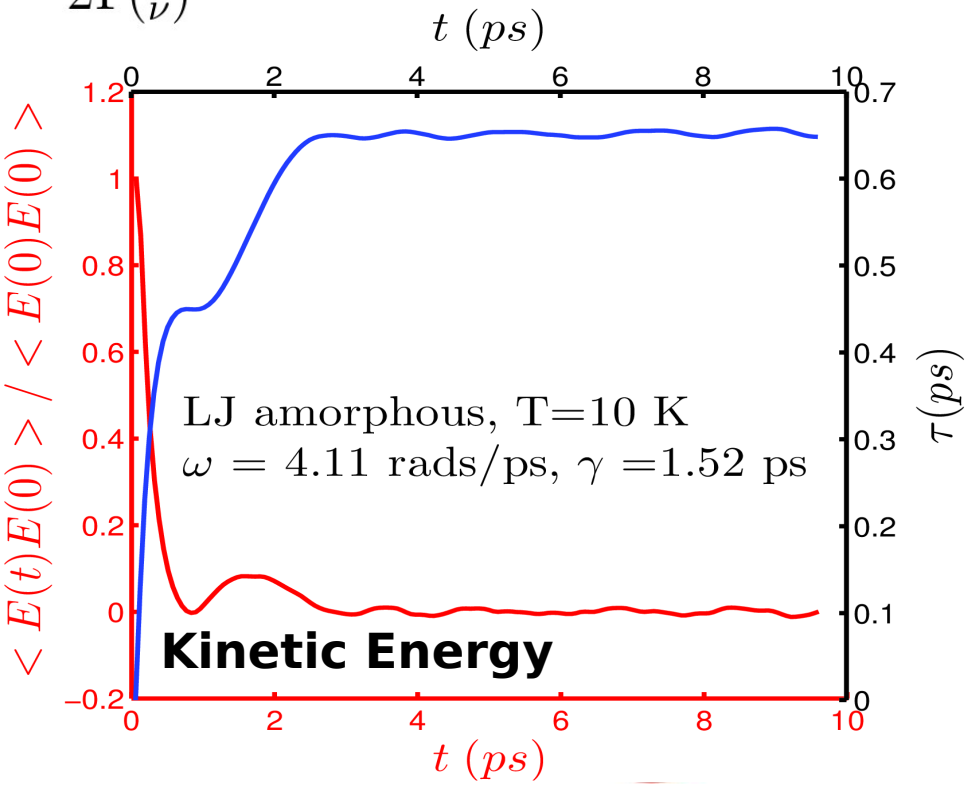
$$\Phi(\boldsymbol{\kappa},\omega) = \sum_{\nu}^{3n} C_0(\kappa;\nu)\, \frac{\Gamma(\kappa;\nu)/\pi}{[\omega_0(\kappa;\nu)-\omega]^2 + \Gamma^2(\kappa;\nu)}$$

## NMD: Time-Domain

$$\exp\left[-t/\tau\begin{pmatrix}\boldsymbol{\kappa}\\ \nu\end{pmatrix}\right] = \frac{\langle E_{\boldsymbol{\kappa},\nu}(t)E_{\boldsymbol{\kappa},\nu}(0)\rangle}{\langle E_{\boldsymbol{\kappa},\nu}(0)E_{\boldsymbol{\kappa},\nu}(0)\rangle}$$

$$\tau(\kappa;\nu) = \frac{1}{2\Gamma(\kappa;\nu)}$$

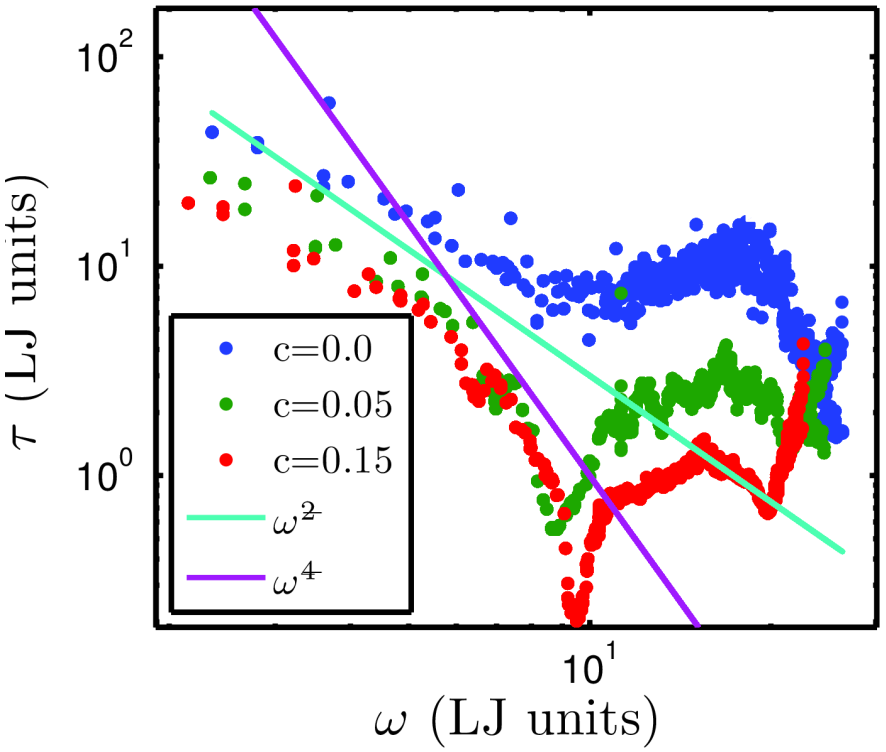


# Normal Mode Decomposition (NMD)

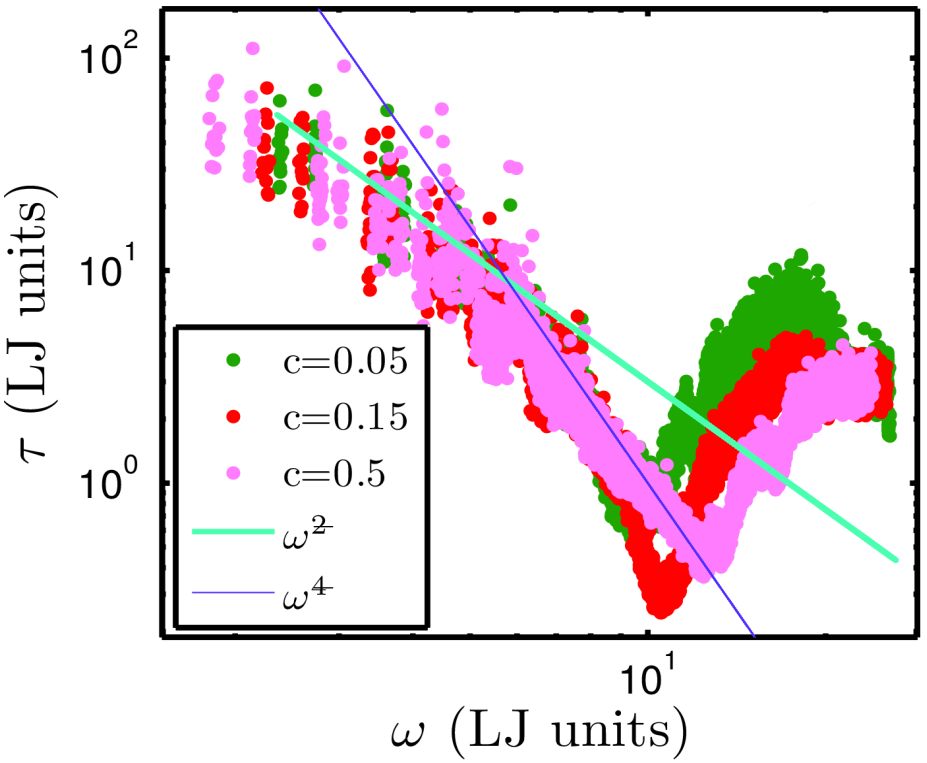


## Virtual Crystal




$$\tau\begin{pmatrix}\kappa\\ \nu\end{pmatrix}$$

## Gamma point




$$\tau\begin{pmatrix}\kappa = 0\\ \omega\end{pmatrix}$$

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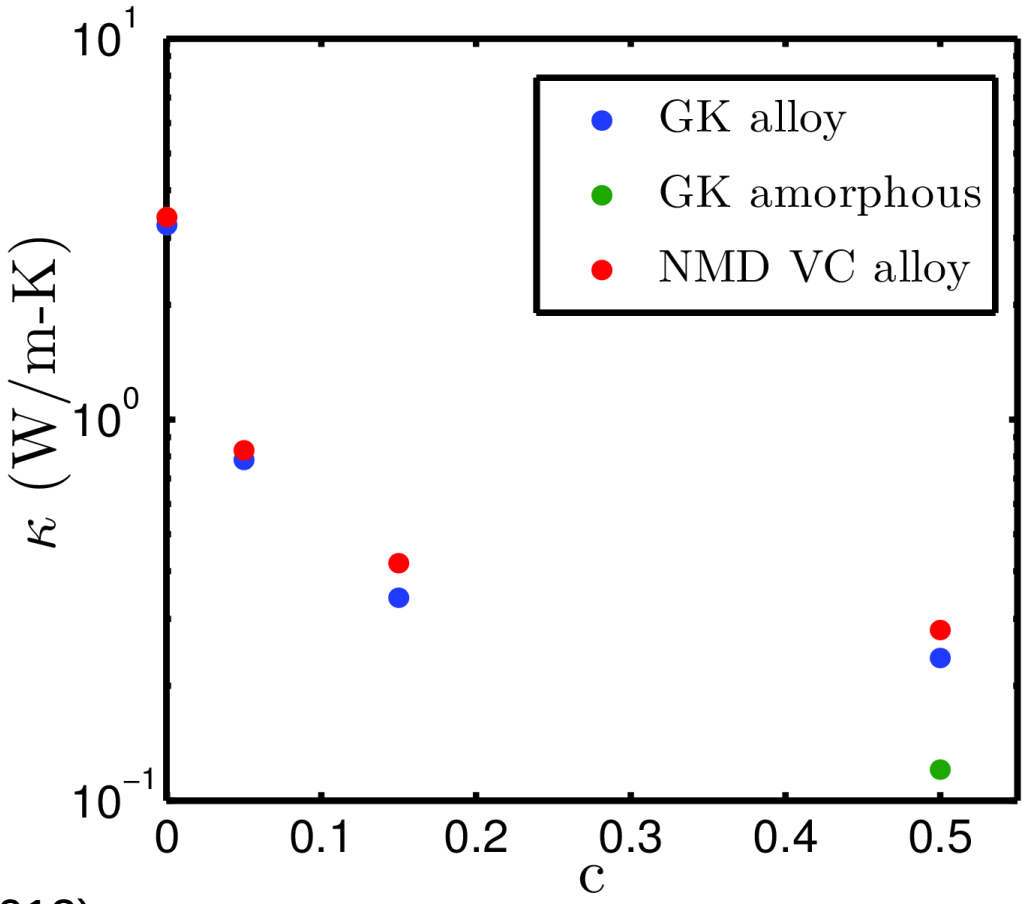
# Thermal Conductivity: System- and Carrier-Level



Virtual Crystal approximation and phonon scaling relations work well!

Anharmonic Lattice Dynamics + Defect scaling =



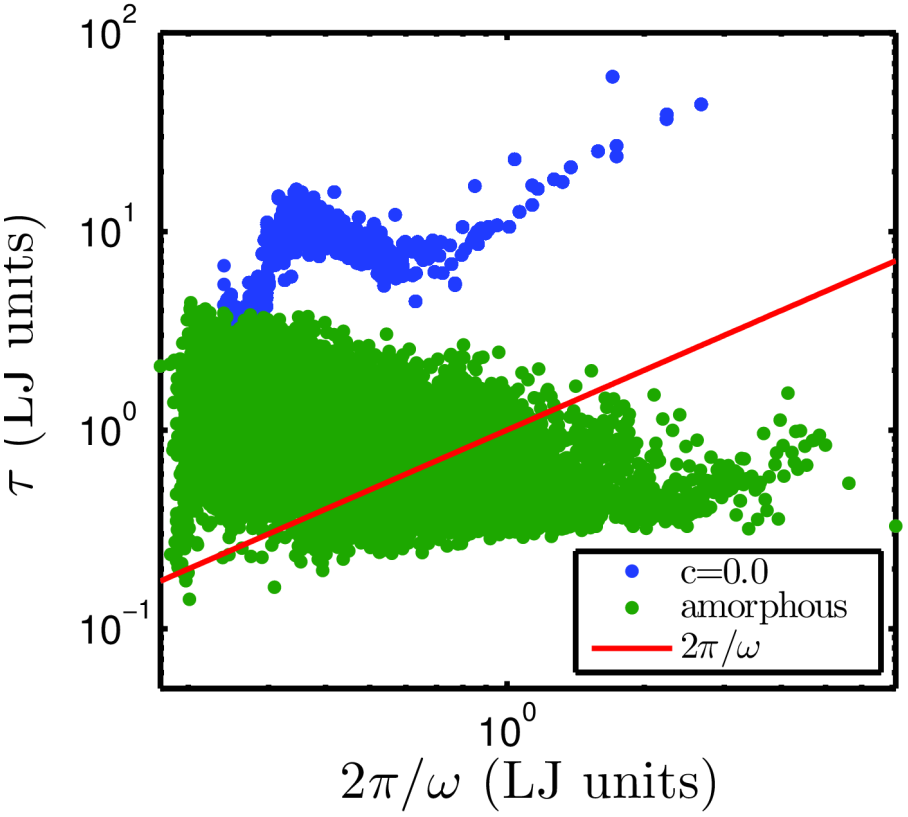

PHYSICAL REVIEW B 85, 184303 (2012)

PRL 106, 045901 (2011)

# Ordered and Disordered Vibrations

Ioffe-Regel Limit:

$$\tau(\omega) = 2\pi/\omega$$




Cahill-Pohl Model:

$$\tau(\omega) = 2\pi/\omega \qquad v_s \longrightarrow k_{vib}$$

Solid State Communications 70 (1989) 927-930.

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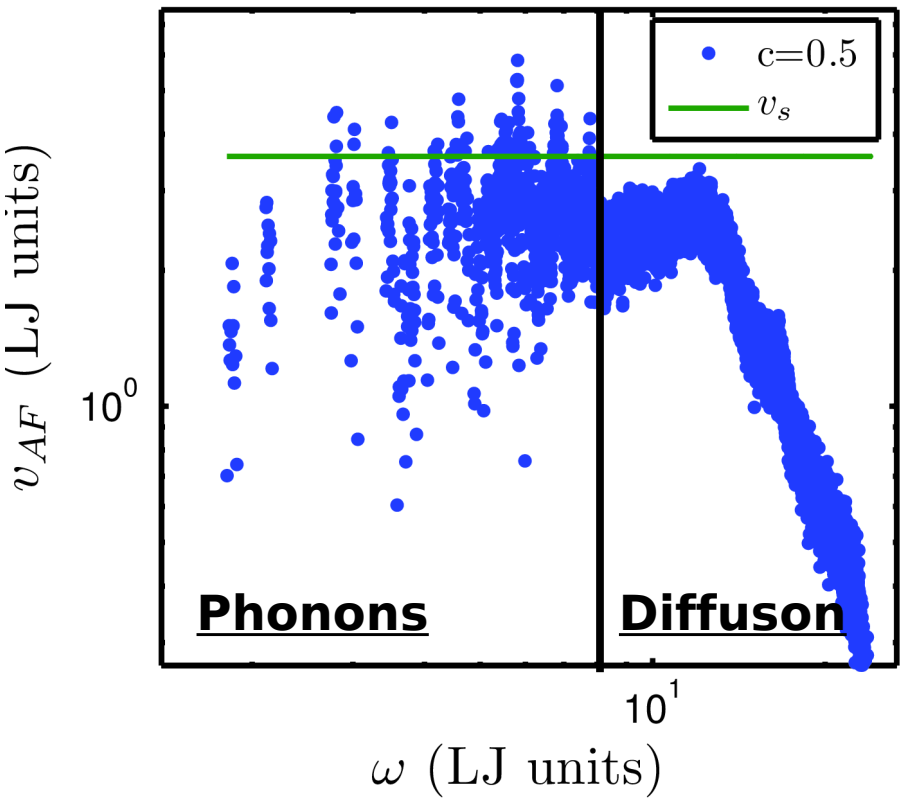
# Ordered and Disordered Vibrations

Dynamic Structure Factor:
Low-frequency modes can identify a **wavelength**, not possible in general:

PHIL. MAG. B 79, 1715-1731 (1999)

PHIL. MAG. B 79, 1747-1754 (1999)

$$\Lambda = \ ?$$




$$v_{AF}^2(\omega) = D_{AF}(\omega)/\tau(\omega)$$

$v_s$ = sound speed

**Phonon:** $\Lambda = v_s \tau(\omega)$

**Diffuson:** $\Lambda = (D_{AF}(\omega)\tau(\omega))^{1/2}$

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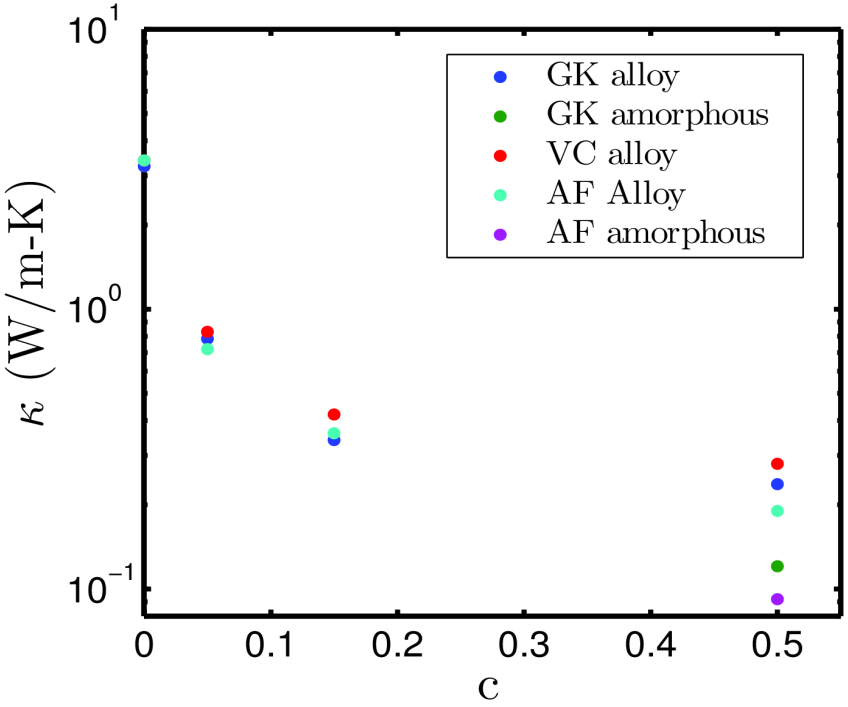
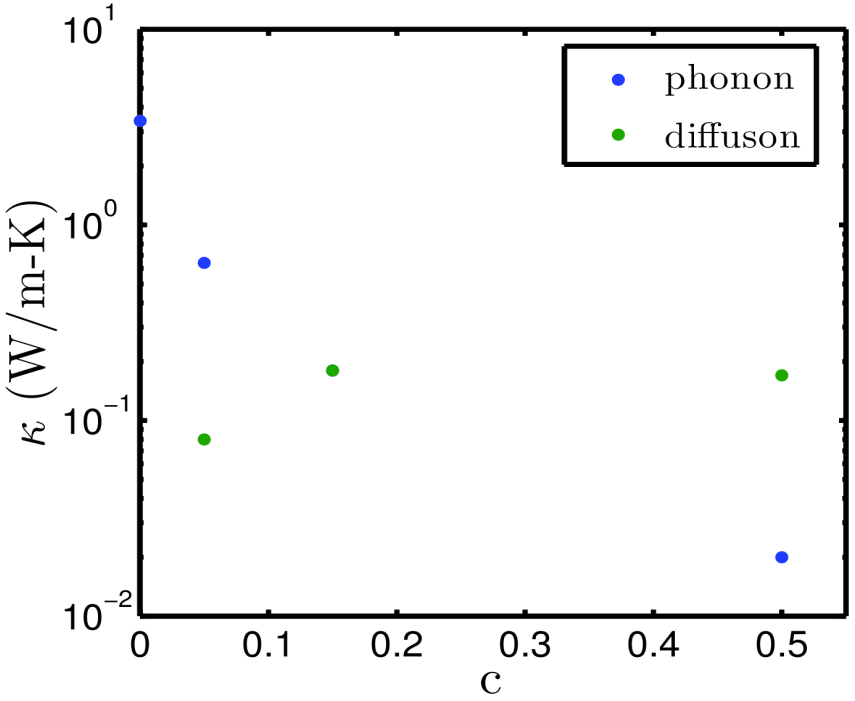
# Predicted Thermal Conductivity

$$k_{vib} = k_{AF} + k_{ph}$$



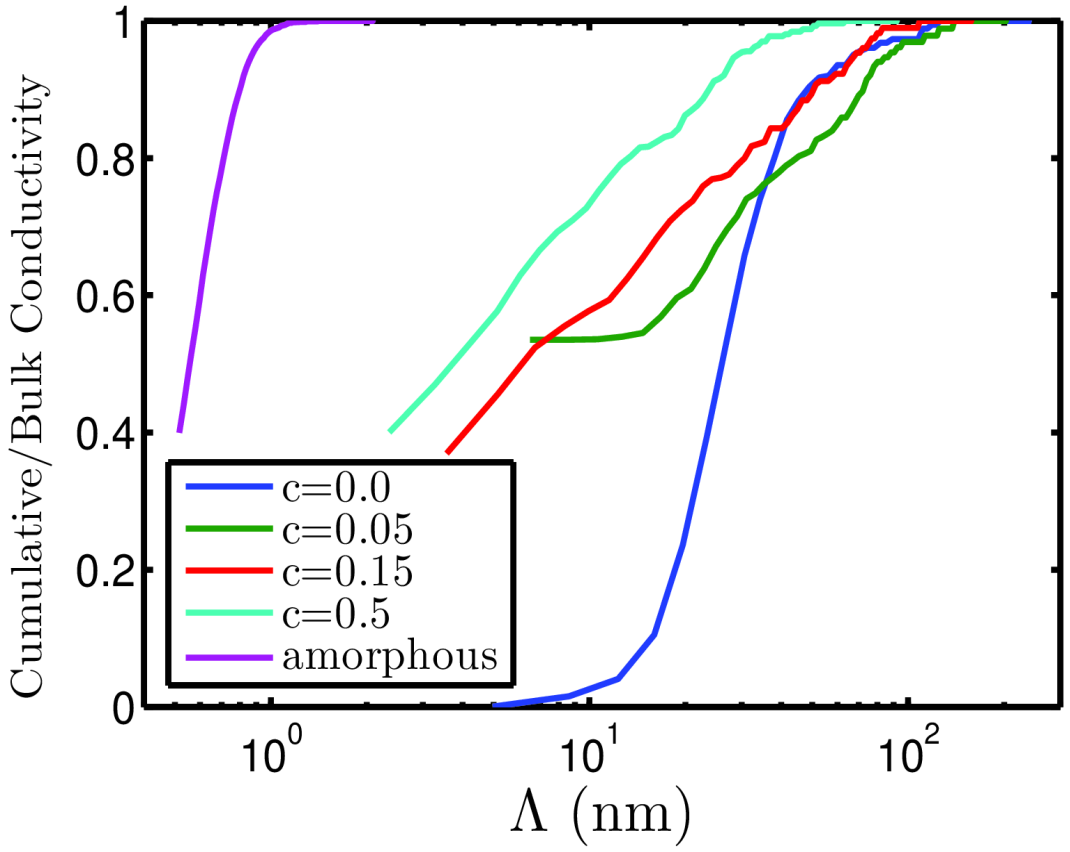



# Cumulative Thermal Conductivity

- Boundary Scattering: Cumulative Thermal Conductivity

- Large c alloys and amorphous vibrations have decreased MFP

- Boundary scattering less effective for length scales >10 nm



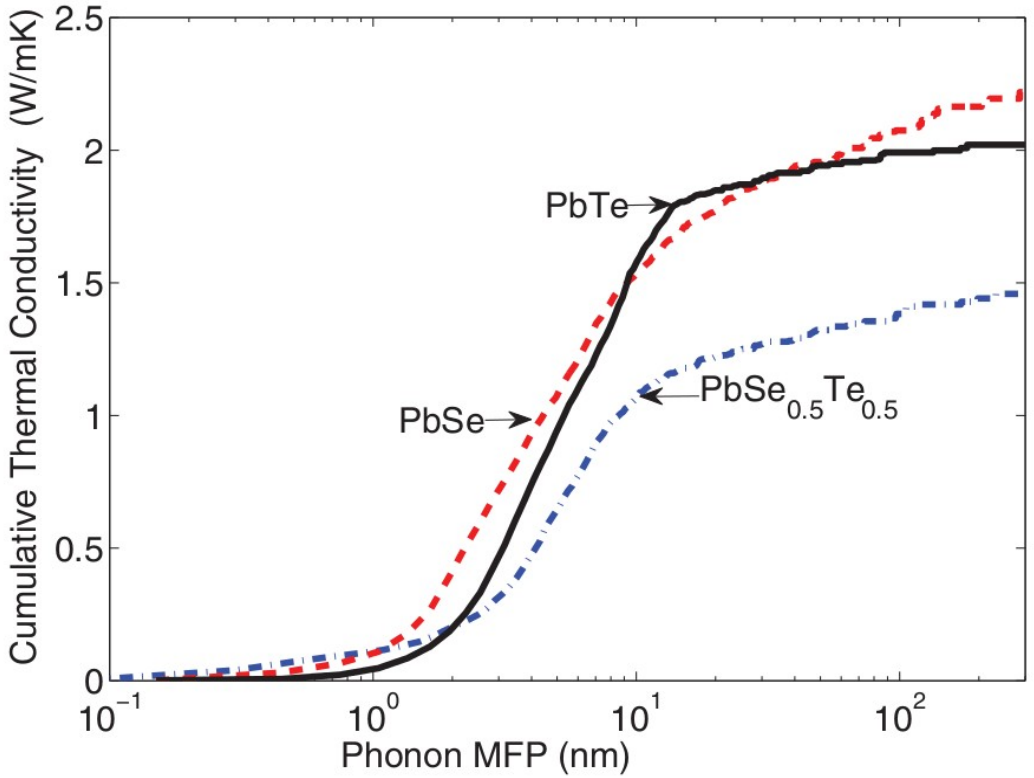
# Bulk Thermoelectrics



- Bulk thermoelectric systems are “soft” (small group velocities, small lifetimes)

- MFPs are typically < 100 nm, boundary scattering not effective

- Alloying can still be effective




PHYSICAL REVIEW B 85, 184303 (2012)

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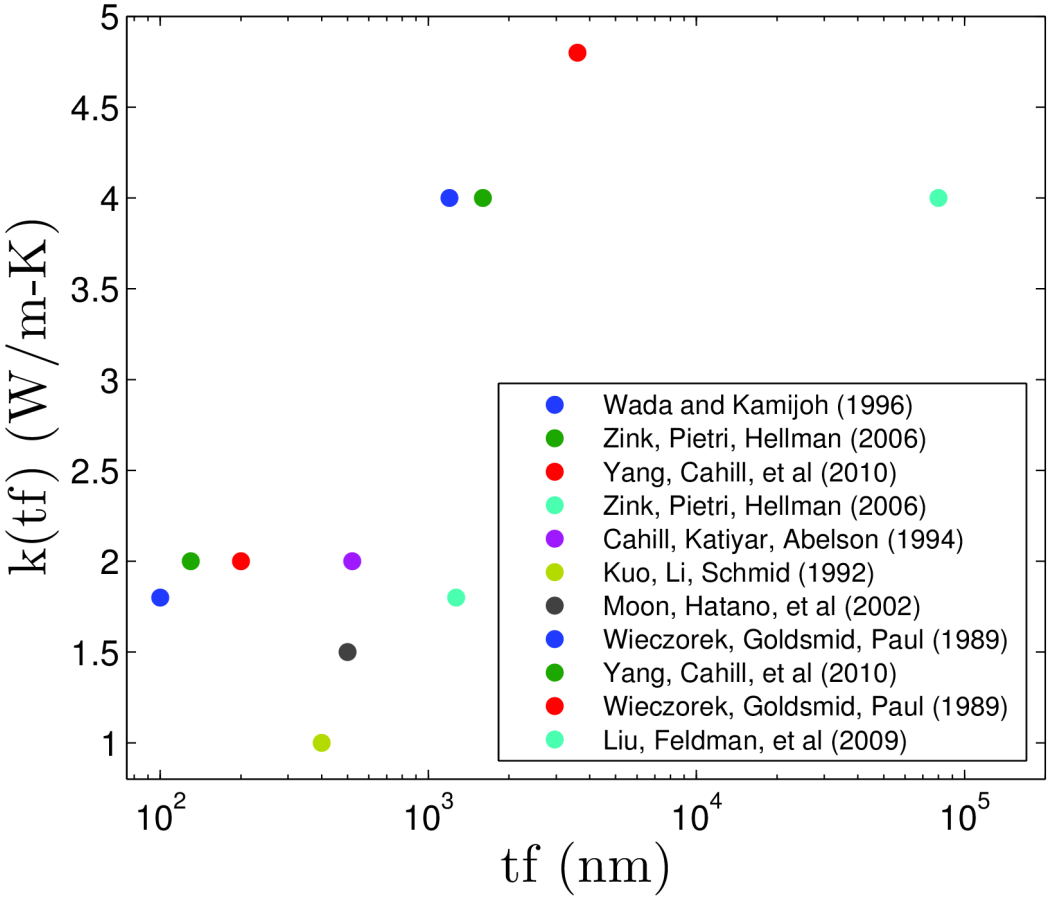
# Amorphous Silicon



- a-Si thermal conductivity displays clear film thickness dependance

- Indicates a phonon-like boundary scattering dependance

- Ordered/Disordered analysis could measure the MFP spectrum in a-Si




APPLIED PHYSICS LETTERS 98, 144101 (2011)

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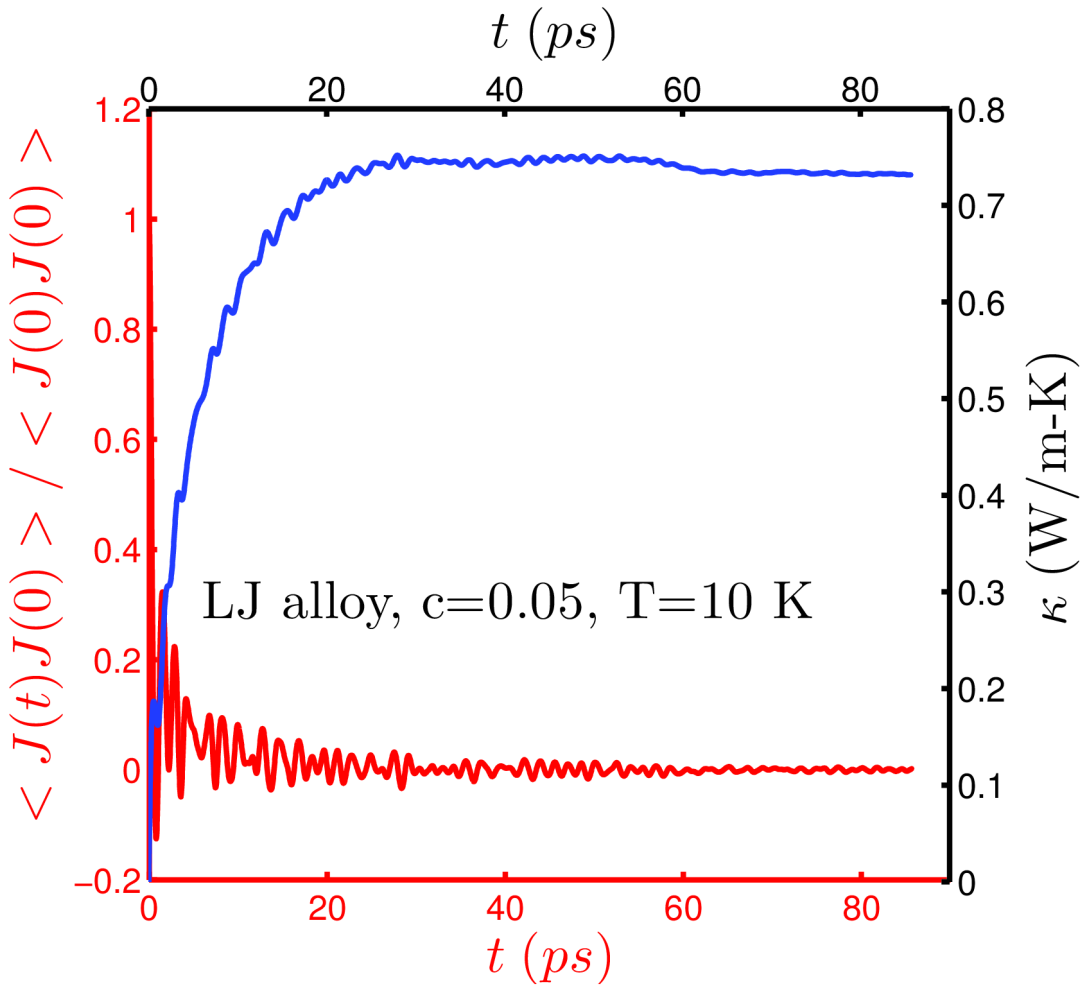
# Questions

# Green-Kubo



$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle \, dt$$




- Heat current J has all effects of MD (anharmonicity, defects, etc.)
- Heat current J has KE and PE parts.
- J is difficult to define using *ab-initio* calculations.

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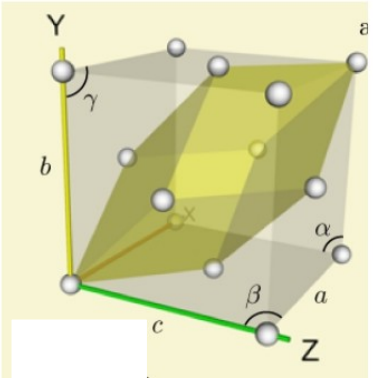
# Normal Mode Decomposition (NMD)



**Perfect system**: vibrations are phonons with an allowed wavevector $\tau\begin{pmatrix}\kappa\\ \nu\end{pmatrix}$




**Perturbed system**: vibrations are phonons with an allowed wavevector (dilute alloy). **Virtual Crystal (VC)** approximation.

**Disordered system**: vibrations are phonons/diffusons. Vibrations analyzed at Gamma point.

$$\tau\begin{pmatrix}\kappa = 0\\ \omega\end{pmatrix}$$