

# Role of Disorder in Thermal Transport

Jason Larkin

Nanoscale Transport Phenomena Laboratory  
Carnegie Mellon Department of Mechanical  
Engineering

<http://ntpl.me.cmu.edu/>

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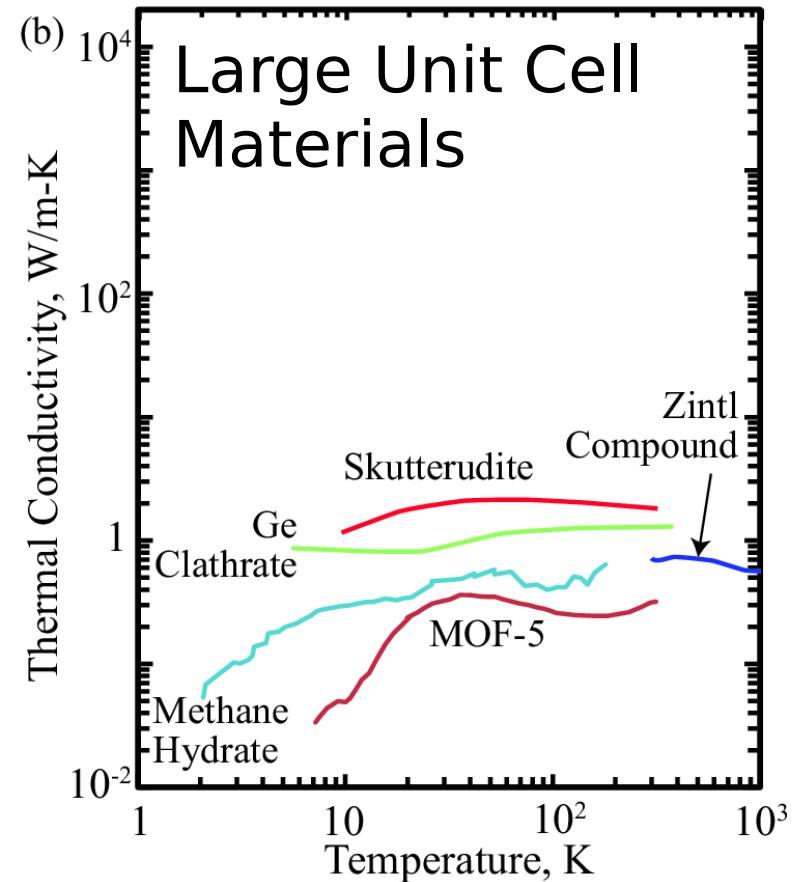
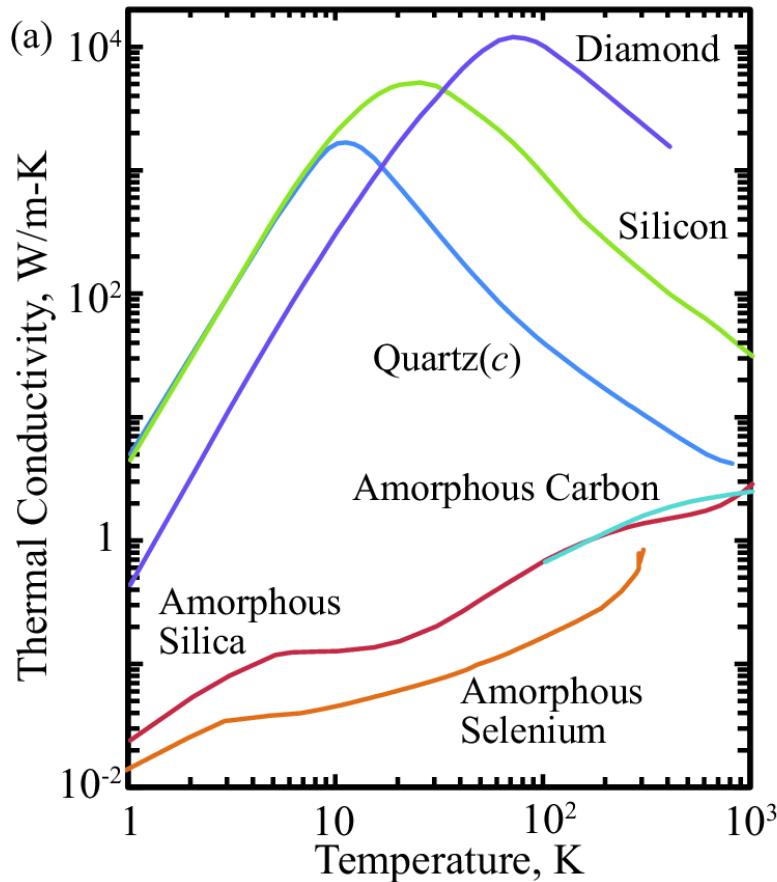


# Outline

- I. Introduction/Motivation
- II. Background
- III. Preliminary Work
- IV. Proposed Work
- V. Schedule

# Range of Thermal Conductivity

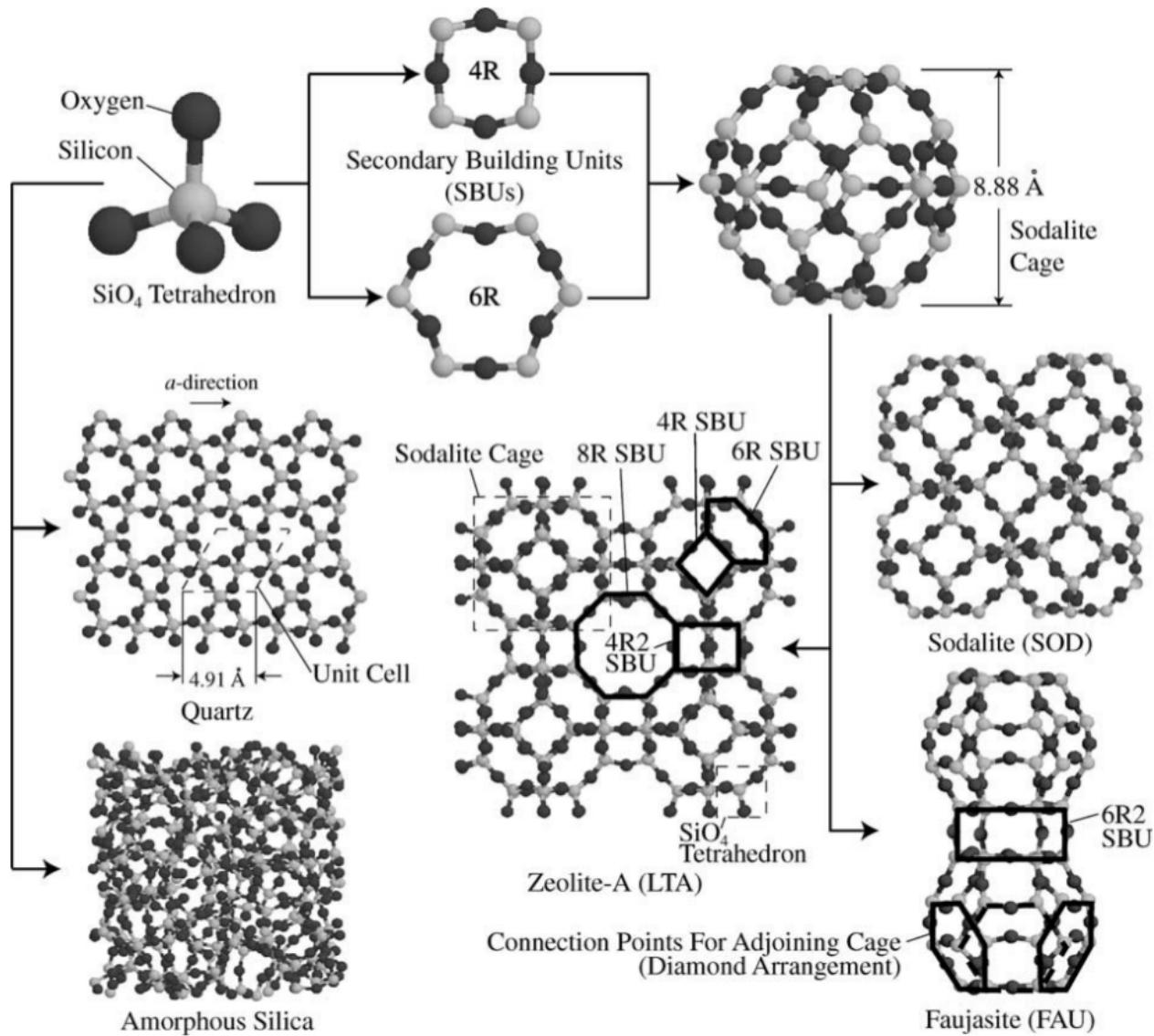
$$k_{\text{thermal}} = k_e + k_{\text{vib}} \approx k_{\text{vib}}$$



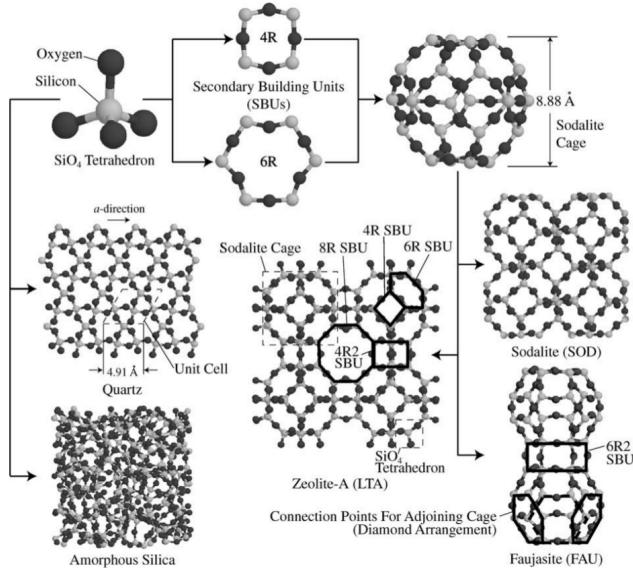
- Conductivity in LUC  $\sim$  amorphous

# Large Unit Cell (LUC) Materials

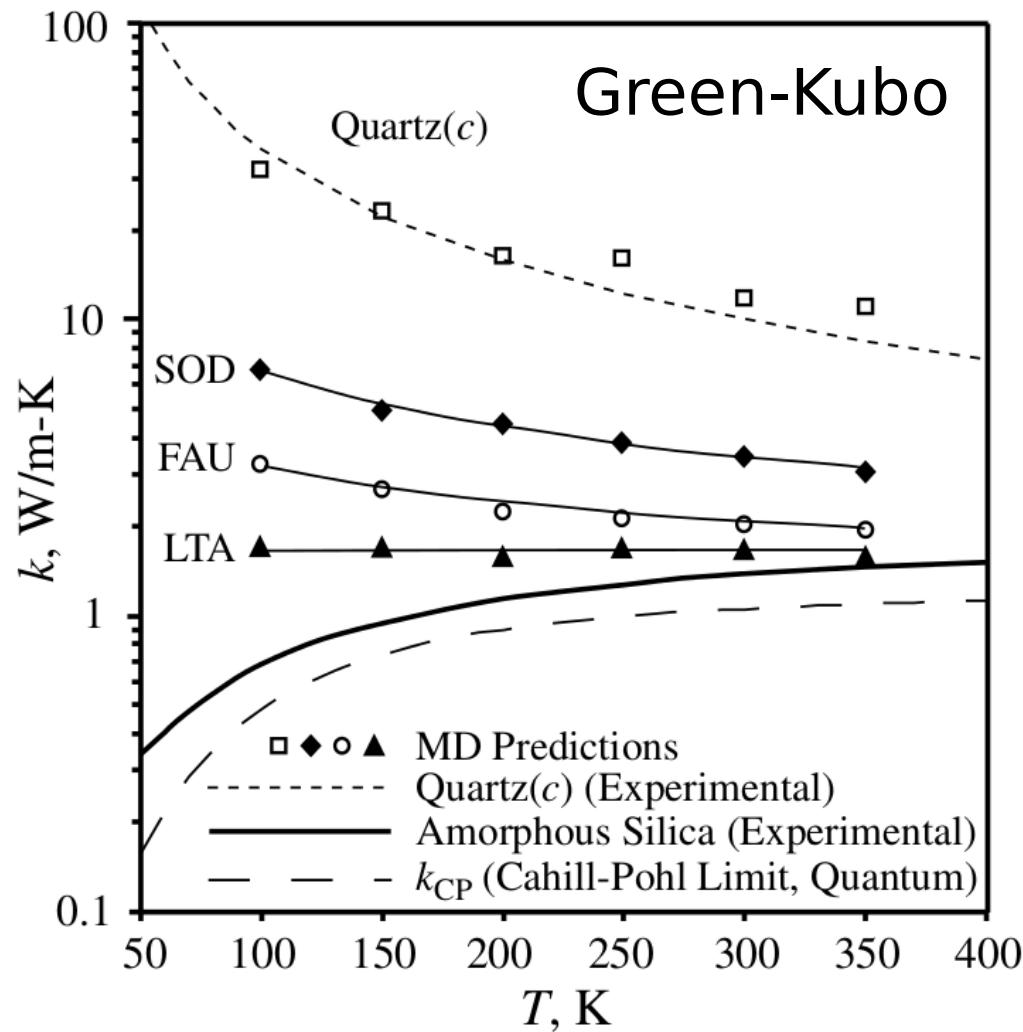
- Effectively disordered.
- Thermal transport from both phonons and diffusons.
- What are sub-unit cell effects?



# Zeolite Range of Conductivity



- Quartz shows crystalline (ordered) behavior.
- Other allotropes more disordered/amorphous.

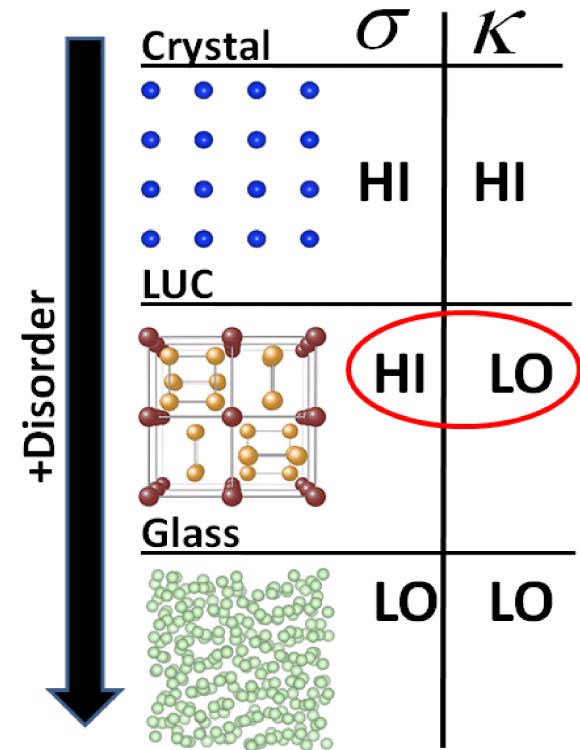


# LUC Materials for Thermoelectric Energy Conversion

- 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...

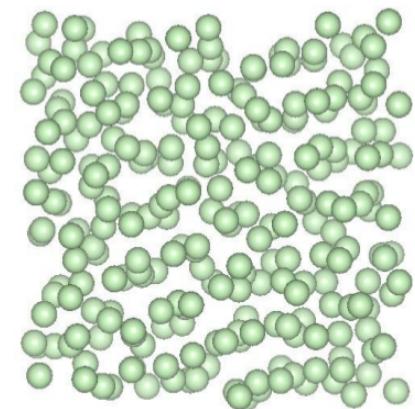
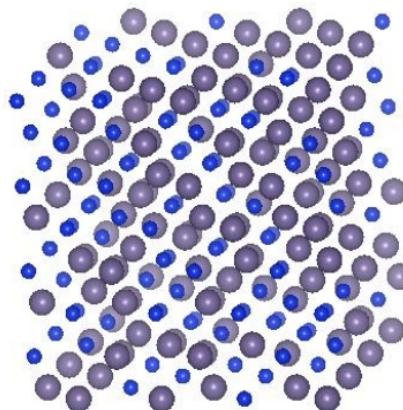
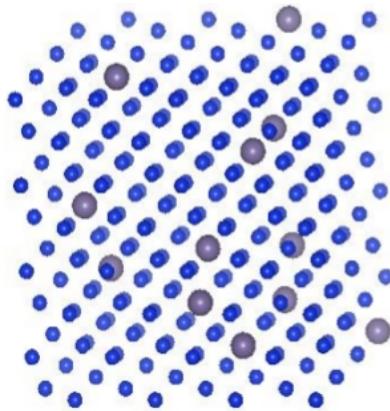


# Objectives

- *Hypothesis: the thermal transport in amorphous and disordered materials can be accounted for using simple, computationally cheap models by considering the contribution from ordered (phonons) and disordered vibrations.*

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

(disorder)      (order)



$$k_{vib} = k_{ph}$$



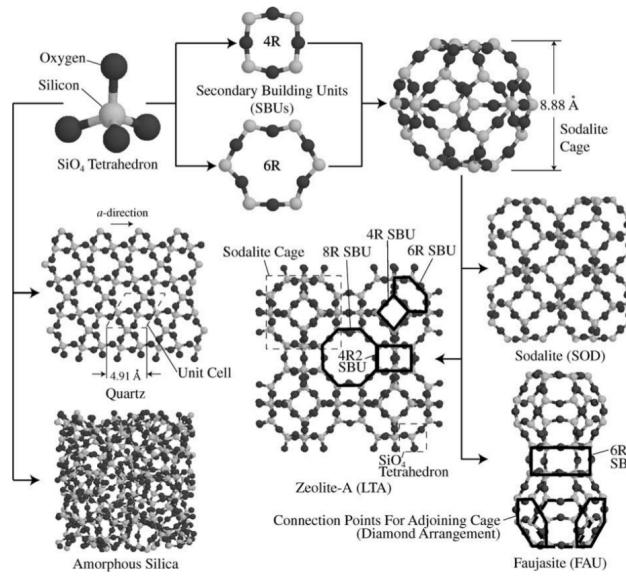
$$k_{vib} = k_{AF} + k_{ph}$$

# Objectives

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

(disorder)      (order)

- *Hypothesis: understanding thermal transport in diverse LUC materials such as Skutterudites and Zeolite allotropes requires analysis of ordered (phonons) and sub-unit cell (disordered) vibrations.*

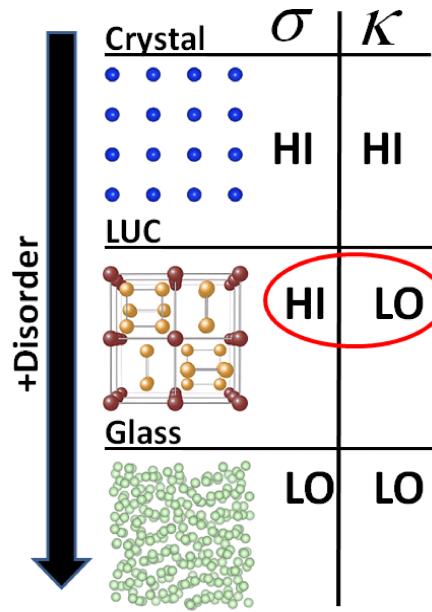


# Objectives

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

(disorder)      (order)

- *Hypothesis: it is likely that the thermoelectric performance of large unit cell Skutterudites has yet to be fully realized until the ordered (phonons) and disordered contributions to minimizing thermal conductivity is understood.*



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**II. Background**

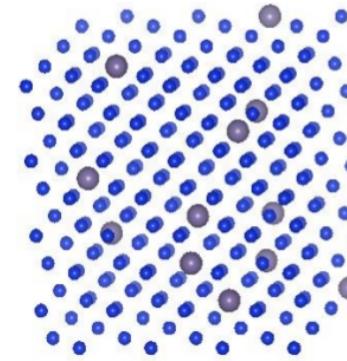
III. Preliminary Work

IV. Proposed Work

V. Schedule

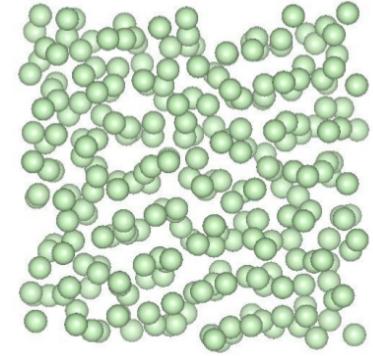
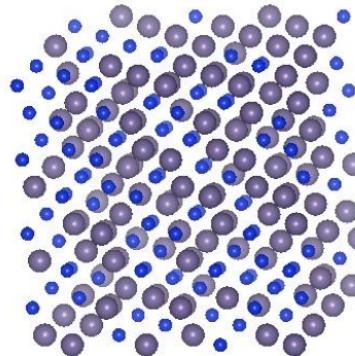
# Thermal Transport in Disordered Materials

- **Phonon** picture valid with perturbations.



- Phonon picture only valid for very long wavelengths.

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



# Thermal Conductivity in Ordered Systems

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

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

- Mode-specific properties:

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

# 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]:

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

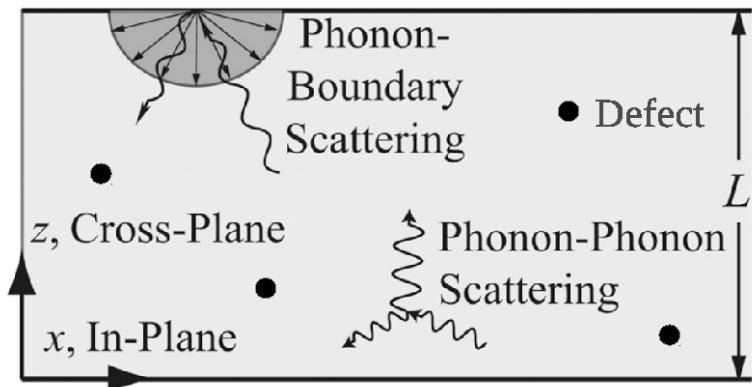
- Boundary scattering [2]:

$$\tau_b = L/v_g$$

- Defect scattering [3]:

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

- These expressions can account for phonon scattering accurately [2,4].



- [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.

# Diffusion 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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# Thermal Conductivity from MD Simulation

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

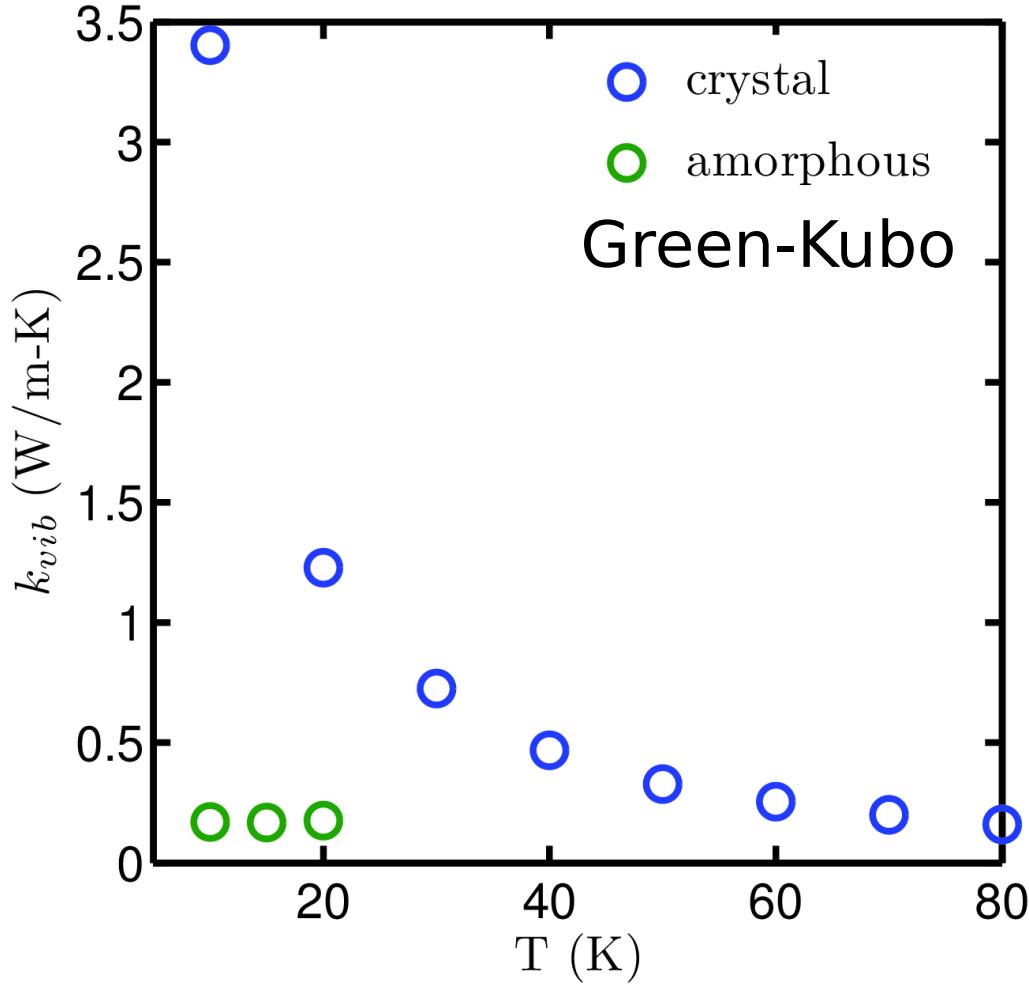
- No vibrational properties are predicted:

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


- Predictions show Green-Kubo can capture all effects.

- MD simulations are classical, no quantum effects.

- Model Lennard-Jones system:



# Predicting Phonon Properties

- Phonon Normal Mode Coordinate:

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

**Molecular Dynamics**  
(anharmonic)

**Lattice Dynamics**  
(harmonic)

$$\lim_{\tau_0 \rightarrow \infty} \frac{1}{2\tau_0} \left| \frac{1}{\sqrt{2\pi}} \int_0^{\tau_0} \dot{q}(\boldsymbol{\nu}; t) \exp(-i\omega t) dt \right|^2 \longrightarrow \Phi(\boldsymbol{\kappa}, \omega) = \sum_{\nu}^{3n} C_0(\boldsymbol{\nu}) \frac{\Gamma(\boldsymbol{\nu}) / \pi}{[\omega_0(\boldsymbol{\nu}) - \omega]^2 + \Gamma^2(\boldsymbol{\nu})}$$

- **Normal Mode Decomposition: Lattice Dynamics + Molecular Dynamics**
- Predicts the Phonon frequency and **lifetime**:

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

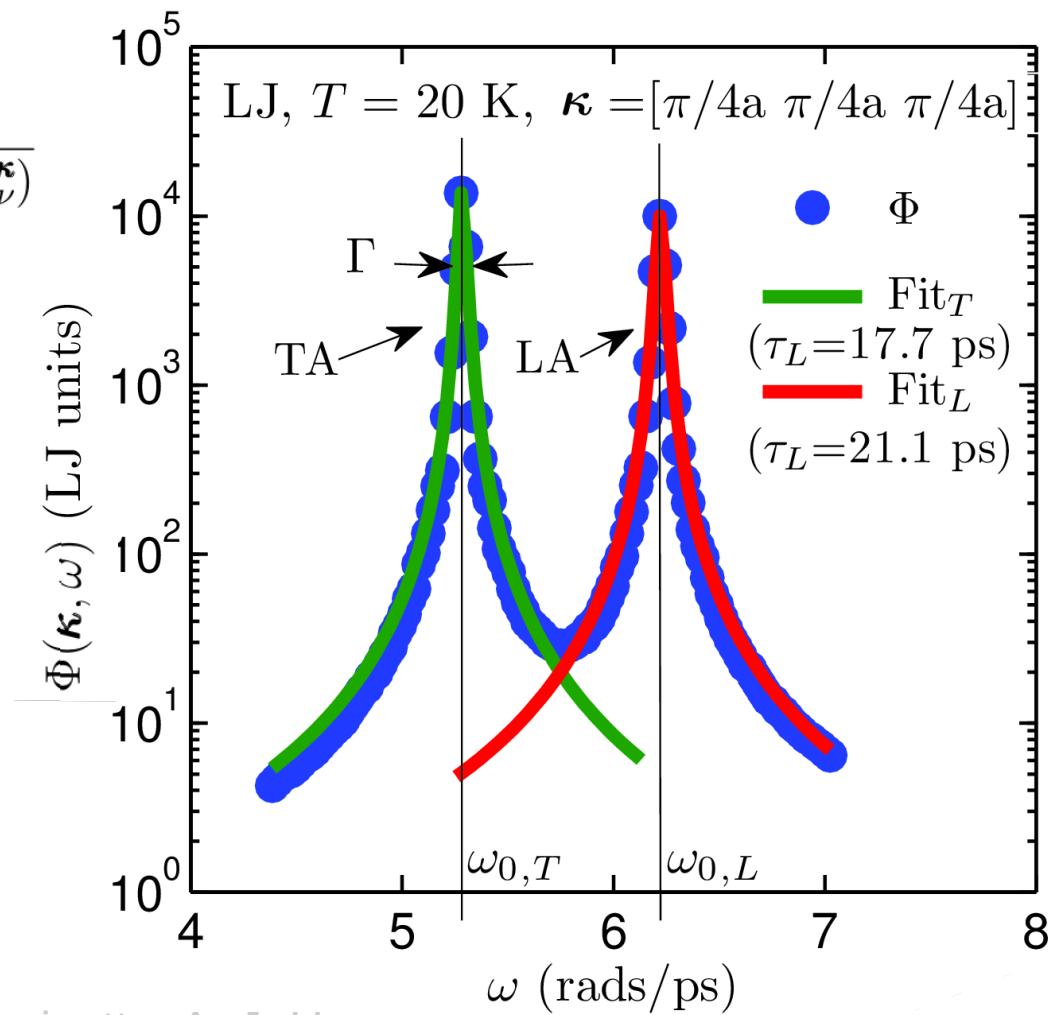
# Predicting Phonon Properties

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

- Predicts the Phonon frequency and lifetime:

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

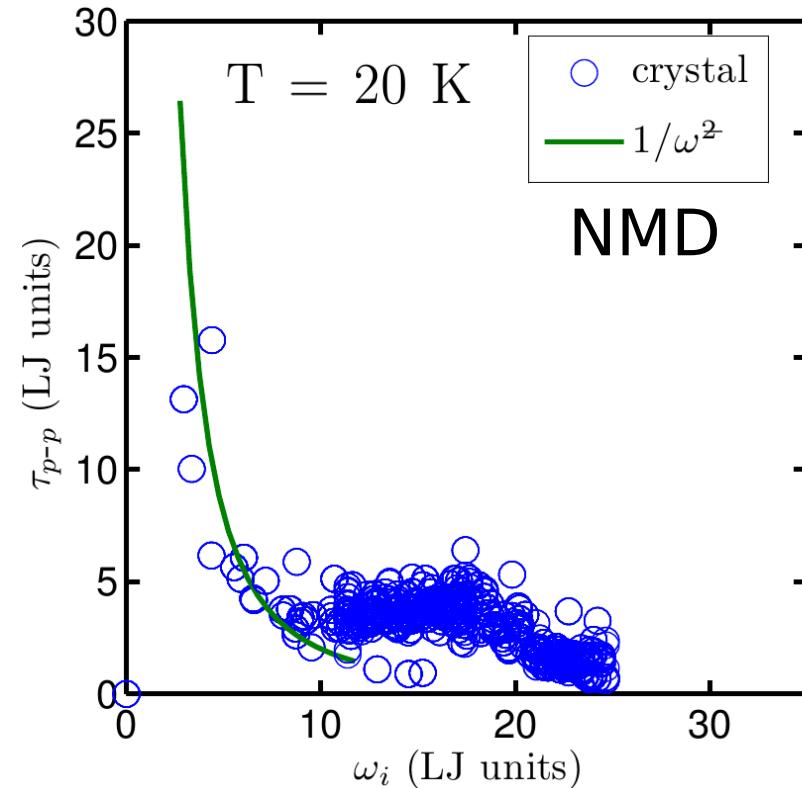
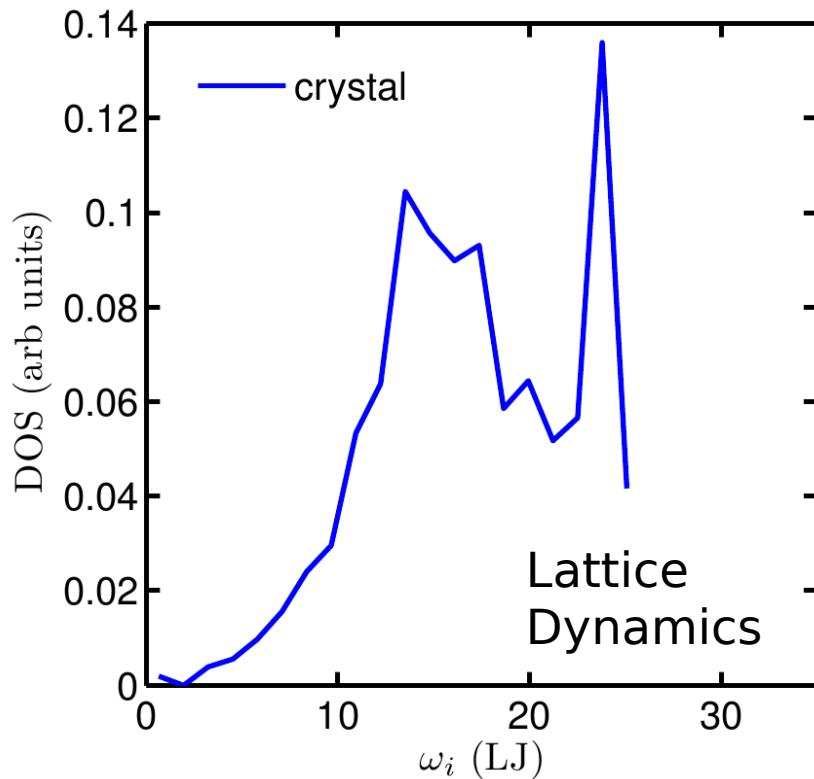
- Have used **NMD** on a variety of systems [1].



[1] J. M. Larkin, J. E. Turney, A. D. Massicotte, A. J. H. McGaughey, C. H. Amon, Comparison and evaluation of spectral energy methods for predicting phonon properties, in submission, 2012.

# Predicted Phonon Properties

- Model Lennard-Jones system:



Green-Kubo (W/m-K)	NMD (W/m-K)
$1.3 \pm 0.15$	$1.2 \pm 0.07$

Lattice Dynamics + Molecular Dynamics

# Thermal Conductivity Integral

$$k_{vib,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} c_{ph}(\kappa) v_g^2(\kappa) \tau(\kappa)$$

- Would like to write as an integral with simple property scalings :

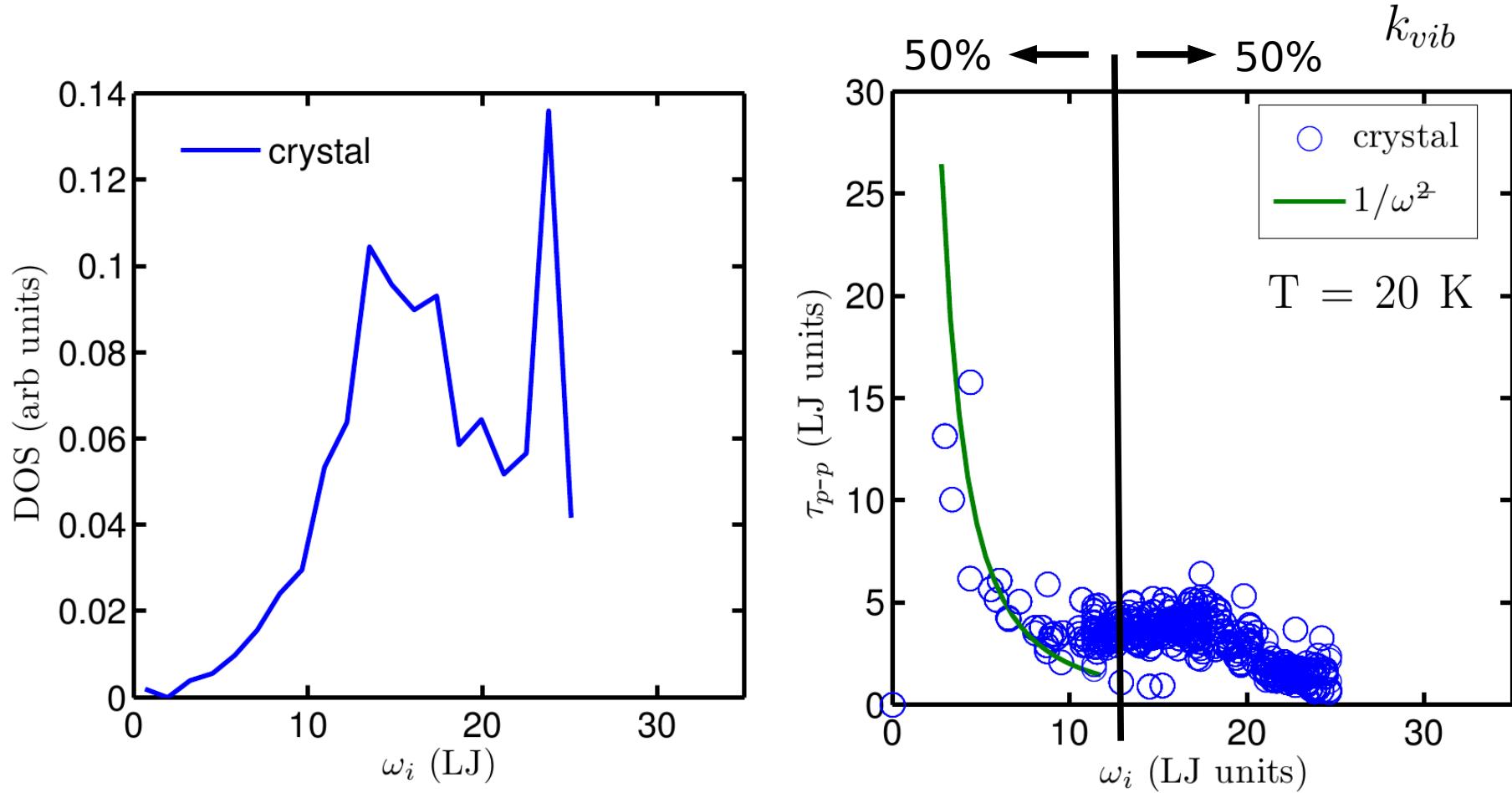
$$k_{vib} = \int_0^{\omega_{max}} c(\omega)_{ph} D(\omega) v_g^2(\omega) \tau(\omega) d\omega$$

- Debye model:  $\omega = v_g \kappa \longrightarrow D(\omega) = A \omega^2$

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

[1] P. G. Klemens, Theory of Thermal Conductivity in Solids, in Thermal Conductivity, ed. R. P. Tye, 1969, Vol. 1, Academic Press, London.

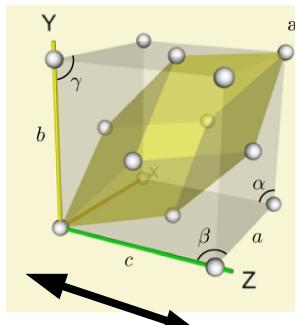
# Predicted Phonon Properties



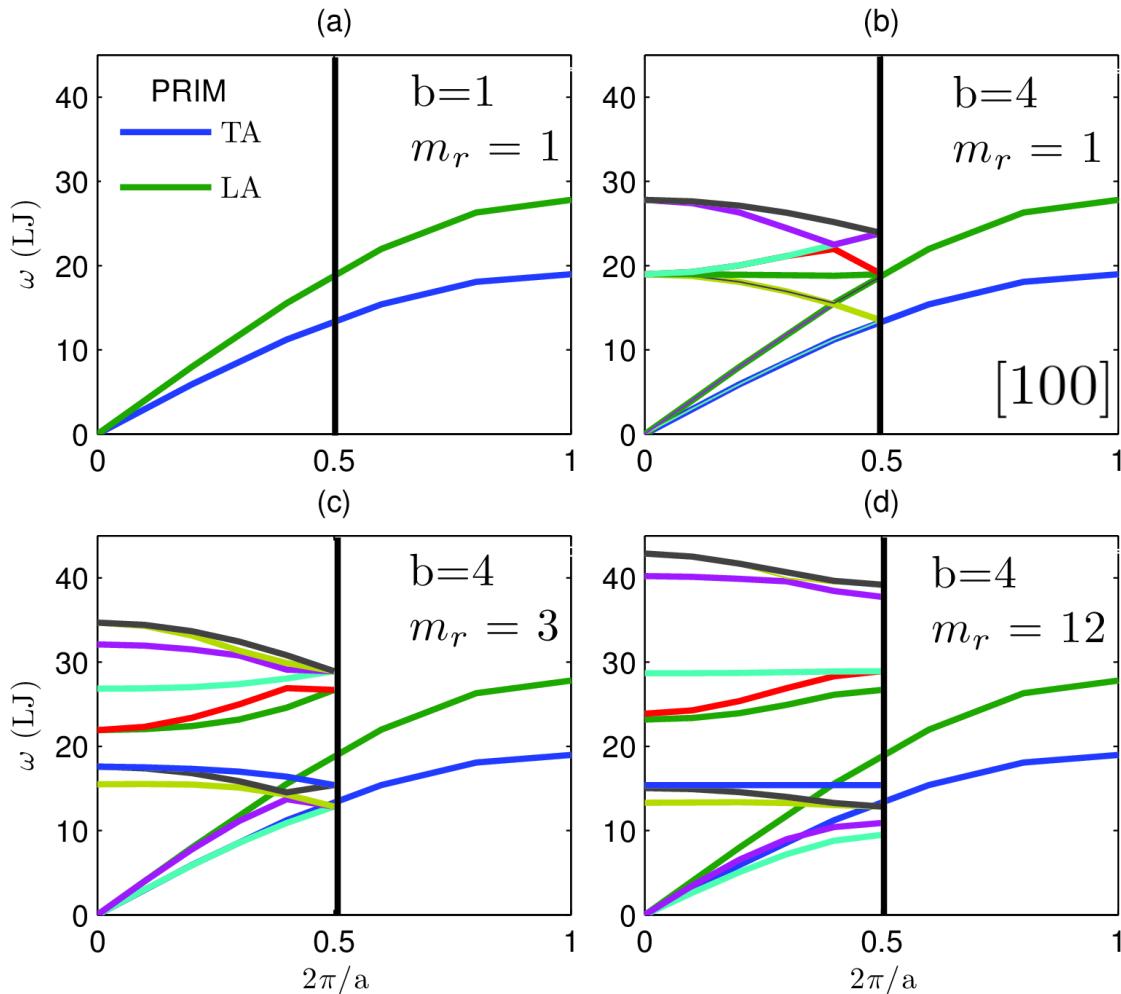
- DOS/lifetimes follows Debye/Umkapp scaling only at low frequencies.
- Significant contributions come from “non-Debye” type modes.

# Dispersion in Multi-Species Systems

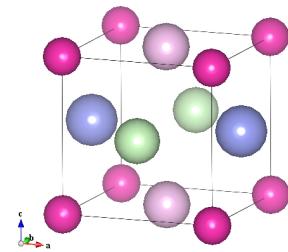
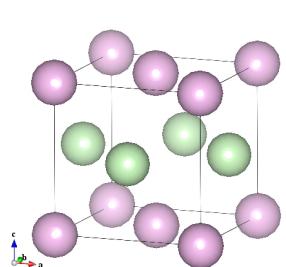
22



**a**



$$v_g = \partial\omega / \partial\kappa$$

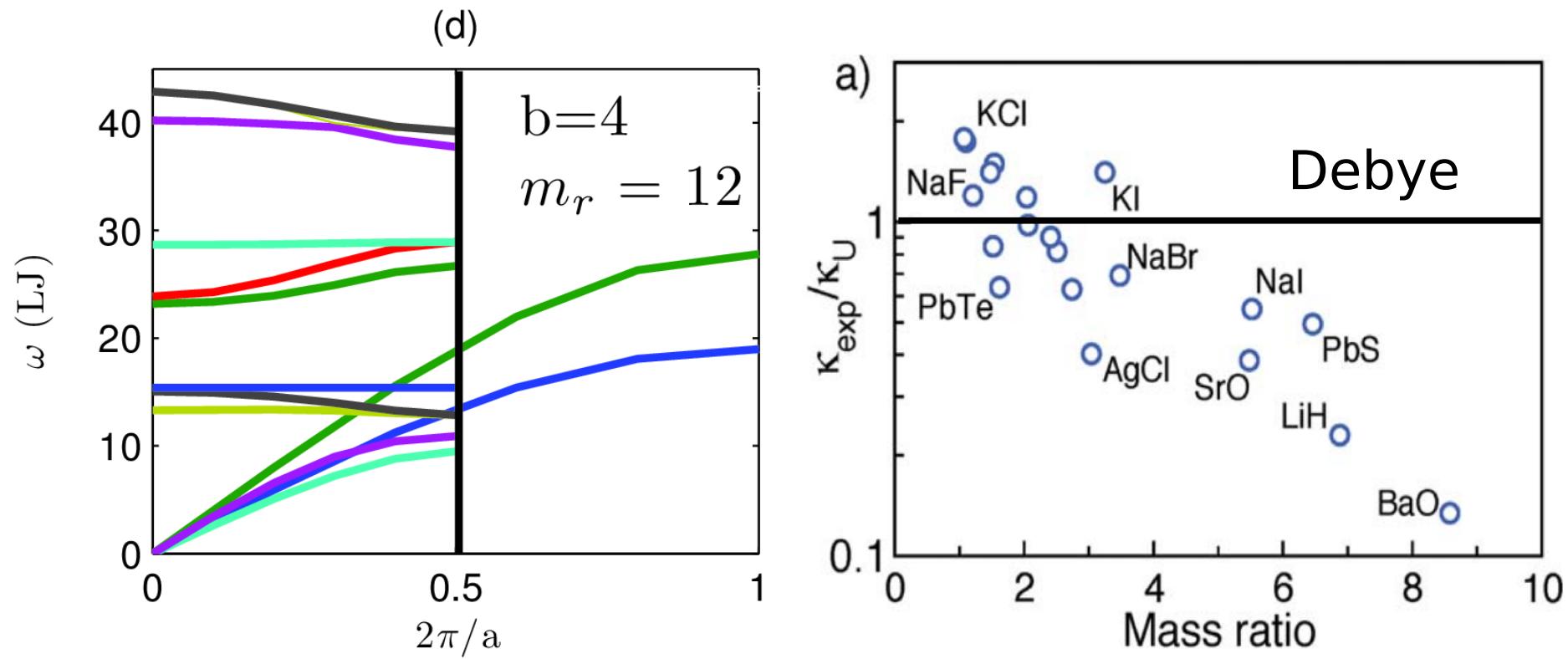


- LJ model dispersion using Lattice Dynamics
- Breakdown of Debye Model  $\omega = v_g \kappa$



Mechanical Engineering

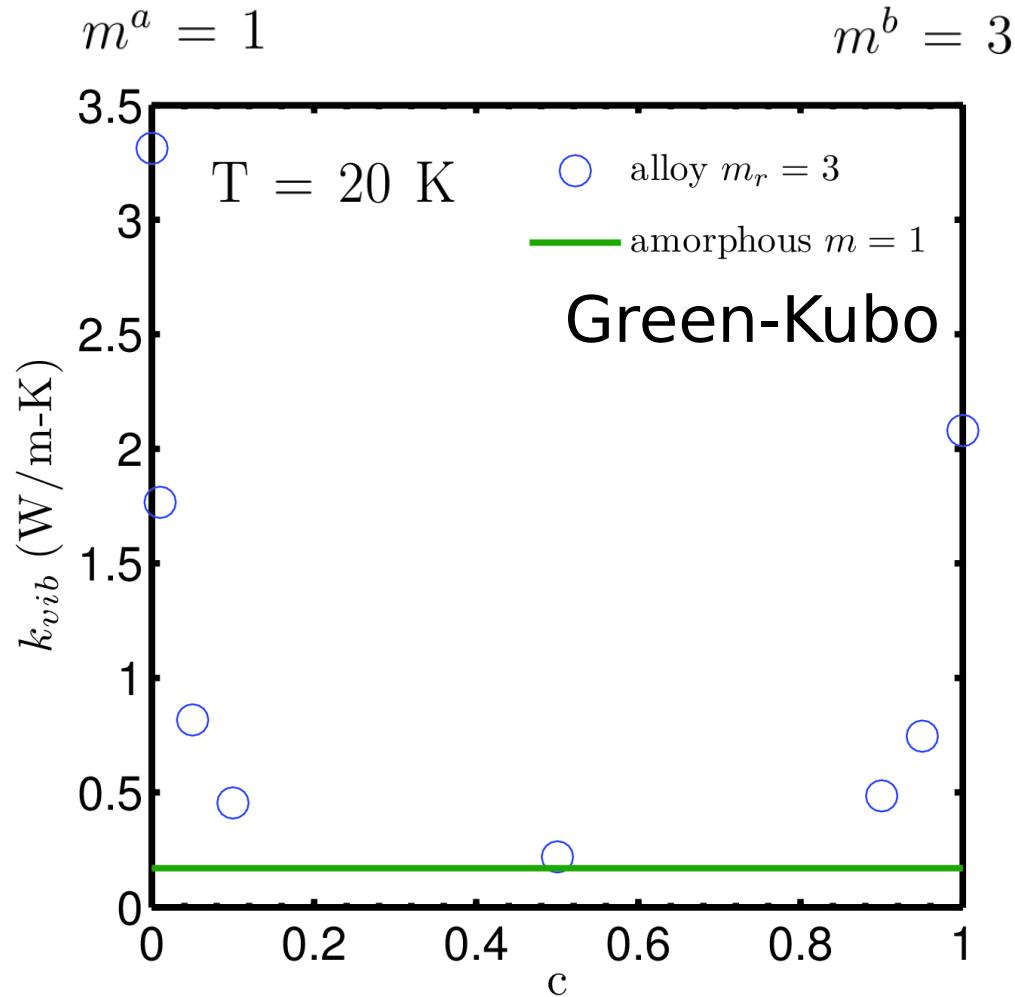
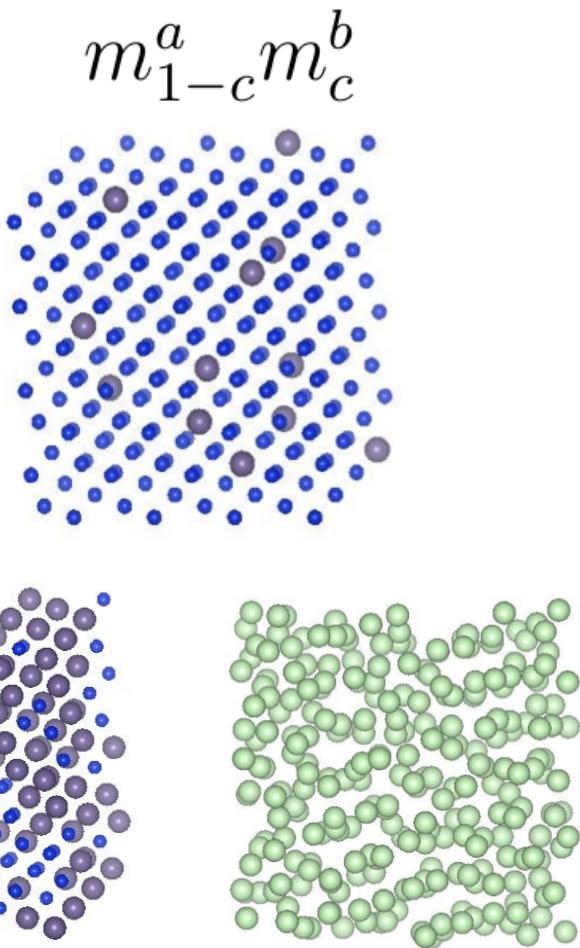
# Effect of Dispersion on Thermal Conductivity



- Breakdown of Debye Model for dispersion [1]:  $v_g = \partial\omega/\partial\kappa$

[1] Eric S. Toberer, Alex Zévalkink, and G. Jeffrey Snyder. Phonon engineering through crystal chemistry. *J. Mater. Chem.*, 21, 2011.

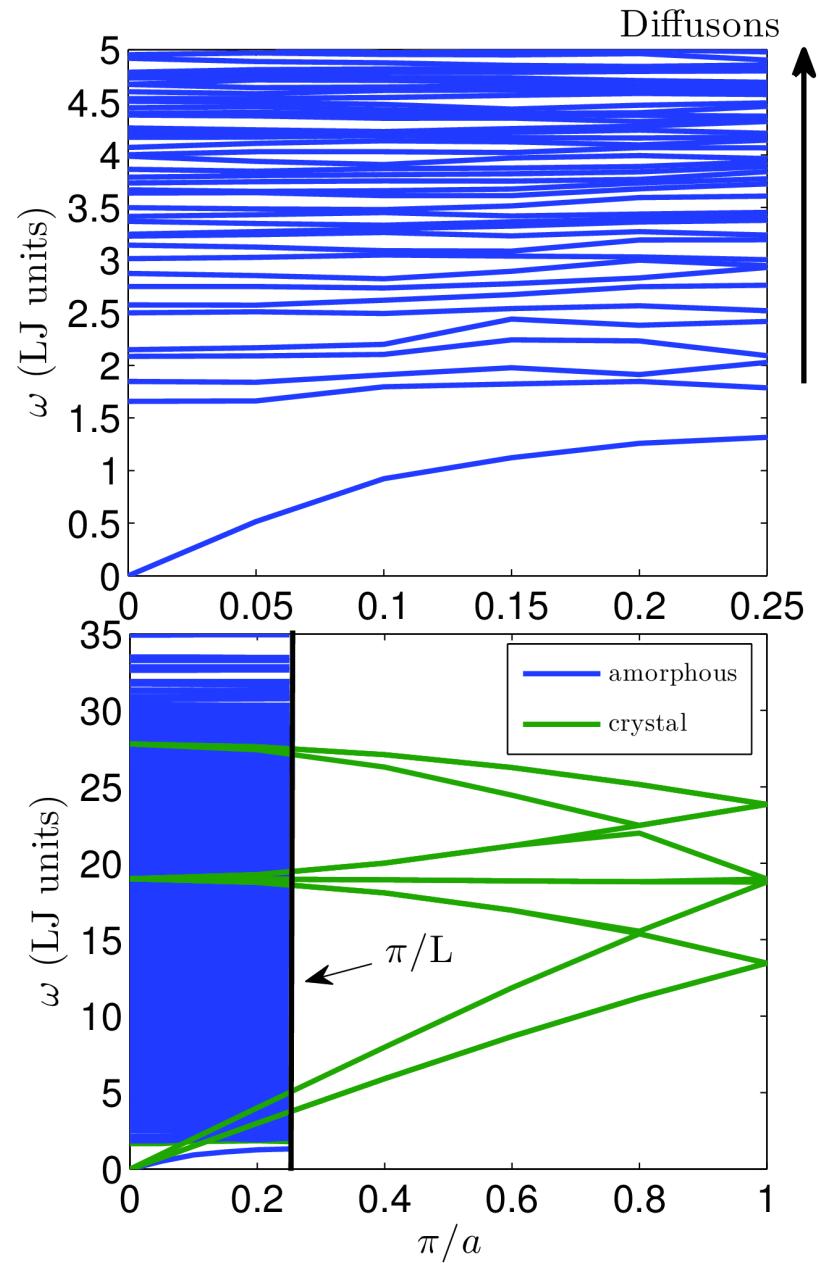
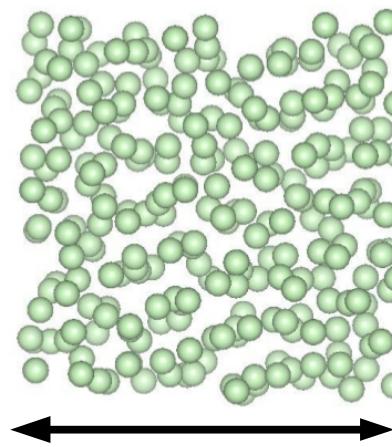
# Thermal Conductivity of LJ Alloys



- Breakdown of phonon picture

# Dispersion in Amorphous System

- Use MD to melt-quench LJ crystal to produce amorphous structure.
- Treat 256 atom amorphous LJ as a LUC



# Diffusion 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.

# Thermal Diffusivity

- Classical harmonic limit:

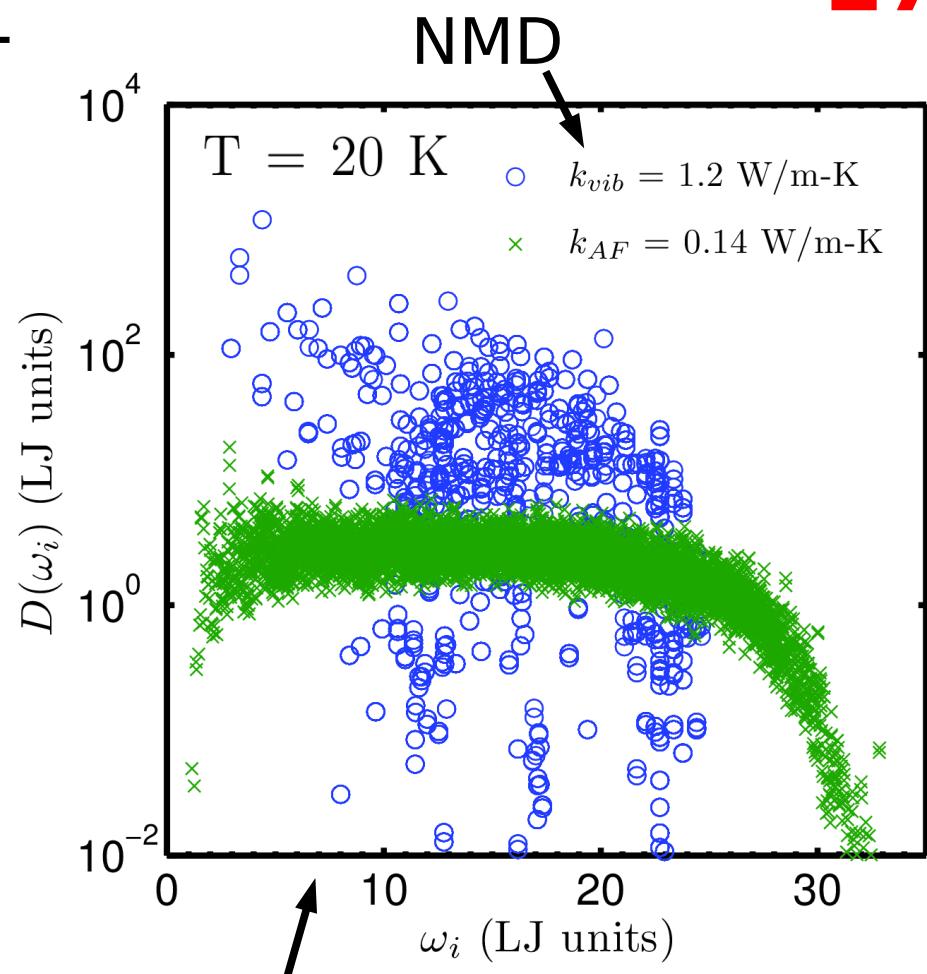
$$C(\omega_i) = k_B \quad c_{ph}(\kappa) = k_B$$

$$k_{vib,\mathbf{n}} = \sum_{\kappa} \sum_{\nu} k_B D_{ph}(\kappa)$$

- Phonon mode diffusivity:

$$D_{ph}(\kappa) = v(\kappa)^2 \tau(\kappa)$$

$$D_{AF}(\omega_i) = \frac{\pi V^2}{3 \hbar^2 \omega_i^2} \sum_j^{ \neq i} |S_{ij}|^2 \delta(\omega_i - \omega_j)$$



$$D_{ph}(\kappa) \approx 0$$



# Phonons in Amorphous System

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

- Green-Kubo prediction (includes all modes):

$$k_{vib} = 0.17 \pm 0.1 \text{ W/m-K}$$

- AF prediction (diffusons):

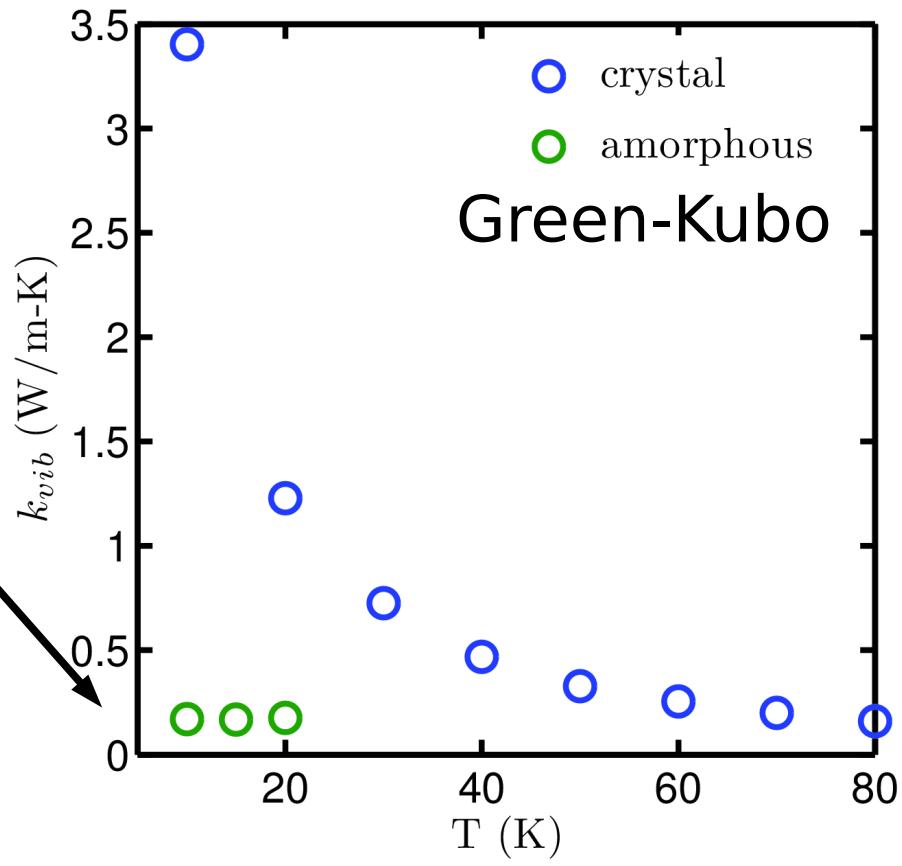
$$k_{AF} = 0.14 \pm 0.01 \text{ W/m-K}$$

- Phonon contribution?:

$$k_{ph} = 0.03 \text{ W/m-K}$$

- Atomistic prediction for amorphous silicon [1]:

$$k_{ph} = 0.5k_{vib}$$



[1] Yuping He, et al.. Heat transport in amorphous silicon: Interplay between morphology and disorder. Applied Physics Letters, 98:144101, 2011.

# Toolbox

Method	Type of Analysis	Information	Classical	<i>Ab-initio</i>
Green-Kubo	Anharmonic	Top-down: Phonons + Diffusons	✓	✗
Normal Mode Decomposition	Anharmonic	Bottom-up: Phonons + (Diffusons?)	✓	✗
Lattice Dynamics (AF)	Harmonic	Bottom-up: Diffusons	✓	✓

Importance of anharmonicity:

- Can we capture thermal transport properties using (quasi)-harmonic analysis?

*Ab-initio* calculations:

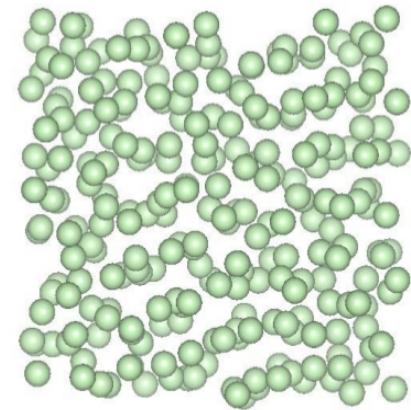
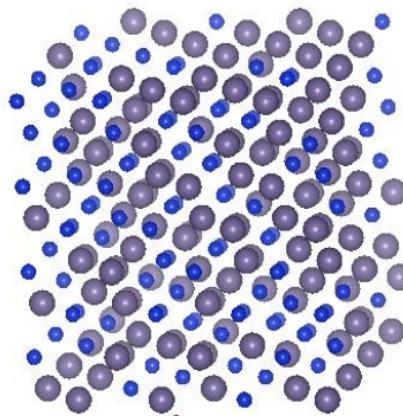
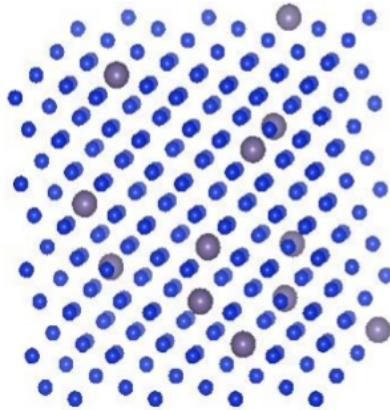
- Physically accurate
- Computationally expensive

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# Ordered and Disordered Contributions to Thermal Transport

LJ models of crystal, alloy, and amorphous phases using MD, Green-Kubo, NMD, and AF



$$k_{vib} = k_{ph}$$



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

# Role of Anharmonicity

From LJ study:

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

Debye-type model?



Lattice Dynamics (harmonic)

What is role of anharmonicity?

- Use Lattice Dynamics (harmonic) and MD-NMD (anharmonic) to investigate.
- Results will inform *ab-initio* calculations for amorphous silicon.
- Would like a simple model for phonon contribution, all parameters calculated using Lattice Dynamics (harmonic):

$$k_{ph} = \int_0^{\omega_{max}} c(\omega)_{ph} D(\omega) v_g^2(\omega) \tau(\omega) d\omega$$

$$\gamma(\omega_i) = -\frac{V}{\omega_i} \frac{\partial \omega_i}{\partial V}$$

$$D(\omega) = A\omega^2$$

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



# Validity of Theoretical Models

Cahill-Pohl model [1]: physically meaningful?

All modes in a glass are “phonons” with sound speed group velocity:

$$v_g = v_s \propto \sqrt{B_{glass}/\rho}$$

“Phonon” mode mean free paths equal to half the “wavelength”:

$$\Lambda_{glass} = \lambda/2$$

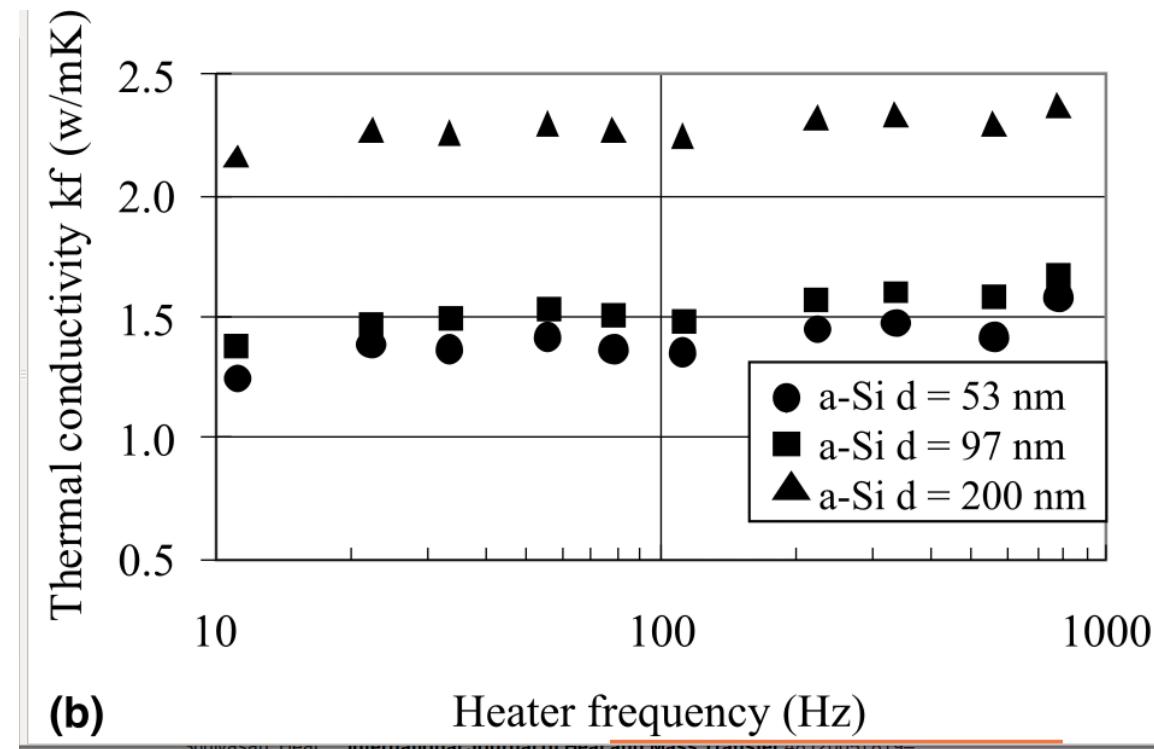
[1] David G. Cahill, et al.. Lower limit to the thermal conductivity of disordered crystals. Phys. Rev. B, 46:6131–6140, Sep 1992.

# Thermal Transport in Amorphous Silicon using *Ab Initio* Calculations

- Classical atomistic prediction for amorphous silicon [2]:

$$k_{ph} = 0.5k_{vib}$$

- Design *ab-initio* calculations based on LJ results.
- Will inform calculations for LUC.



S Moon, International Journal of Heat and Mass Transfer, 45(12):2439–2447, 2002.

[2] Yuping He, et al.. Heat transport in amorphous silicon: Interplay between morphology and disorder. Applied Physics Letters, 98:144101, 2011.

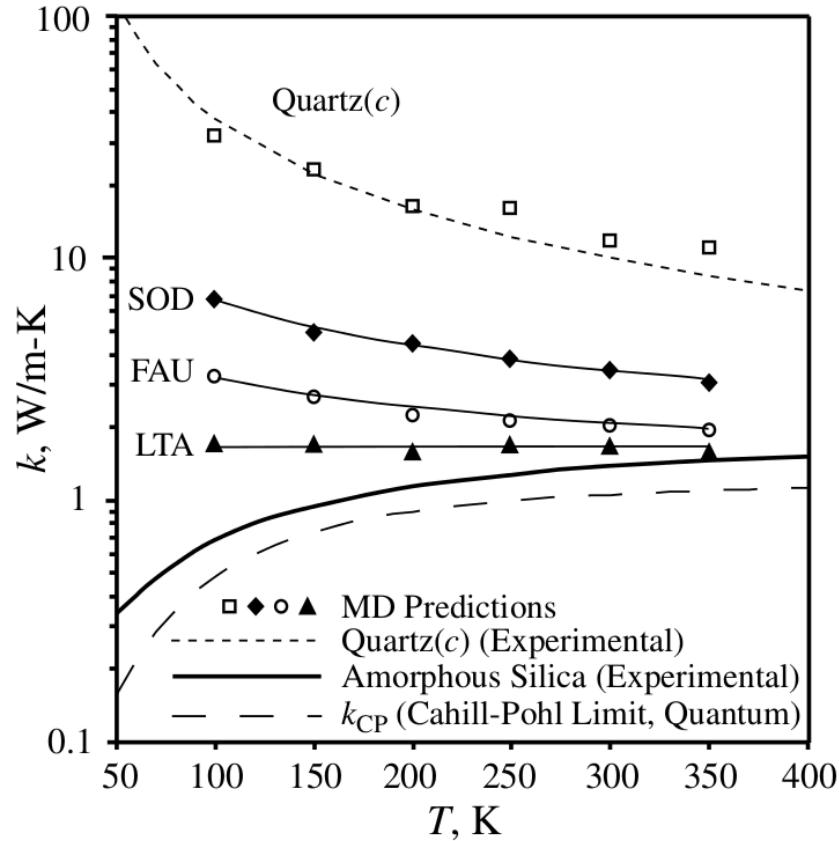
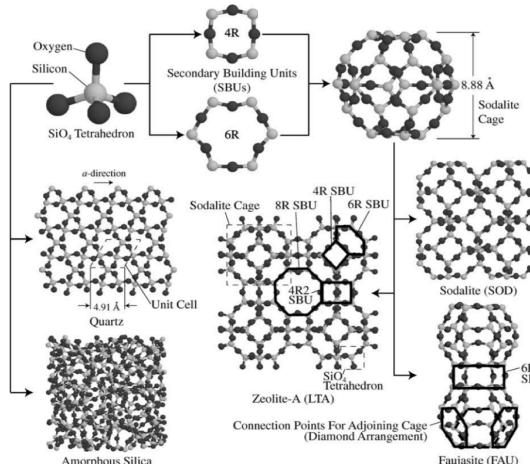
# Large Unit Cell (LUC) Materials

- Use silica structures as model LUC materials
- Top-down (Green-Kubo) predictions exist [1]
- Phonon and diffuson contributions:

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

What are sub-unit cell effects?

- Coordination
- Adsorbed molecules



[1] A. J. H. McGaughey and M. Kaviany, International Journal of Heat and Mass Transfer, 47:1799–1816, 2004.

# LUC Materials for Thermoelectrics

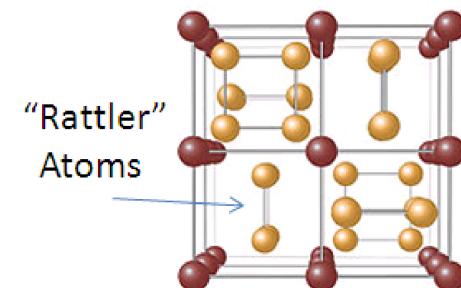
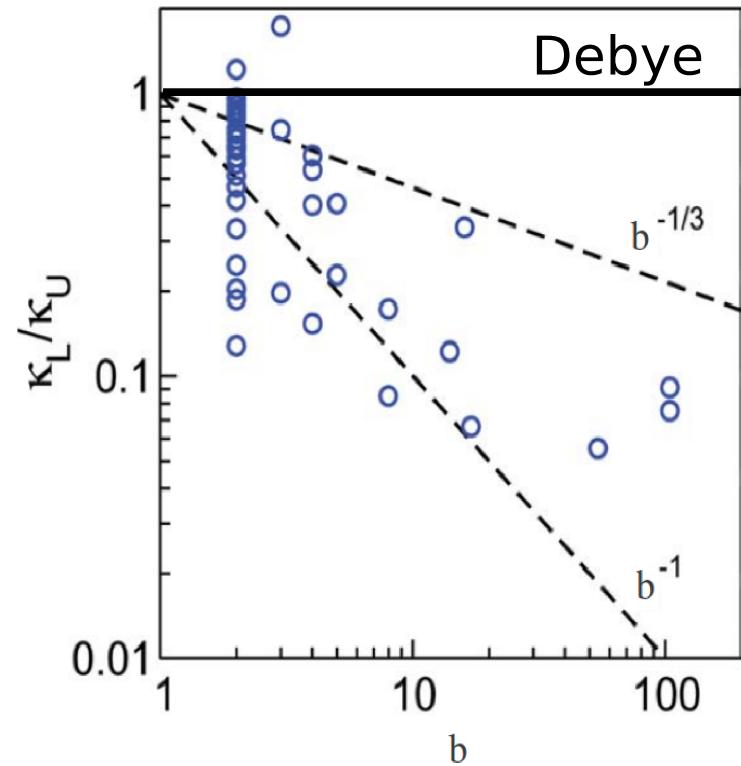
Debye models not sufficient:

- Two scalings with  $b$  indicate phonon picture qualitatively right [1]

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

What are sub-unit cell effects?

- “Rattler” atoms effect on phonon dispersion, scattering?



[1] Eric S. Toberer, Alex Zévalkink, and G. Jeffrey Snyder. Phonon engineering through crystal chemistry. *J. Mater. Chem.*, 21, 2011.

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# Schedule

The schedule for my proposed research is:

Task	Fall 2011	Winter 2012	Spring 2012
Characterization of Disordered LJ Models	—	—	
Investigate (an)Harmonic Contributions			—

Task	Summer 2012	Fall 2012	Winter 2013
Investigate Transport in Amorphous Si using Ab-Initio Calculations	—	—	
Investigate Transport in LUC using Classical Models			—

Task	Spring 2013	Summer 2013
Investigate Transport in LUC using Ab-Initio Calculations	—	
Deliver thesis		—

# Questions

# Open Questions

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

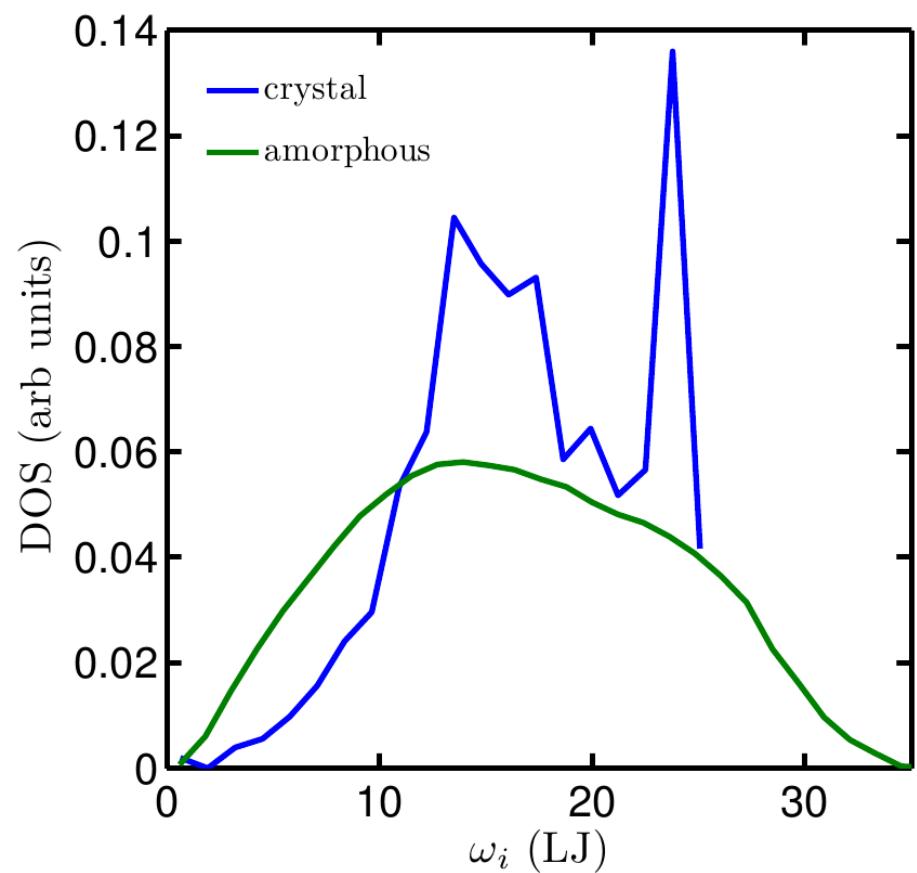
How do phonons and diffusons interact?

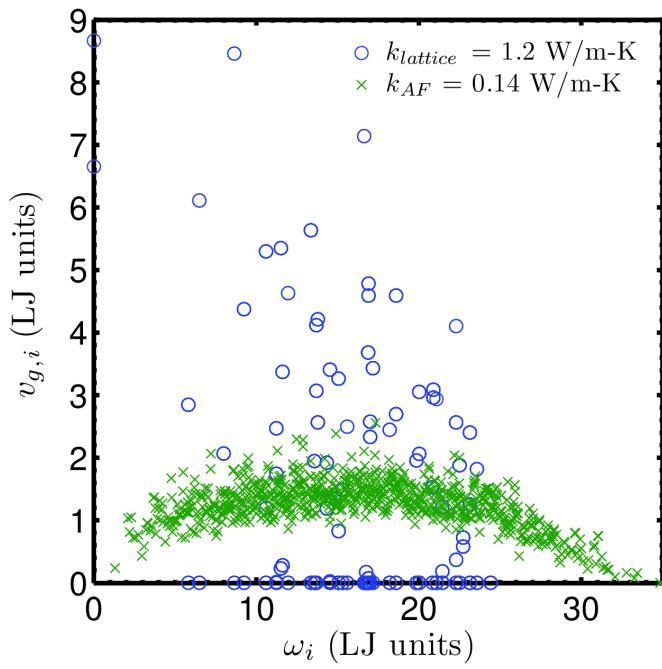
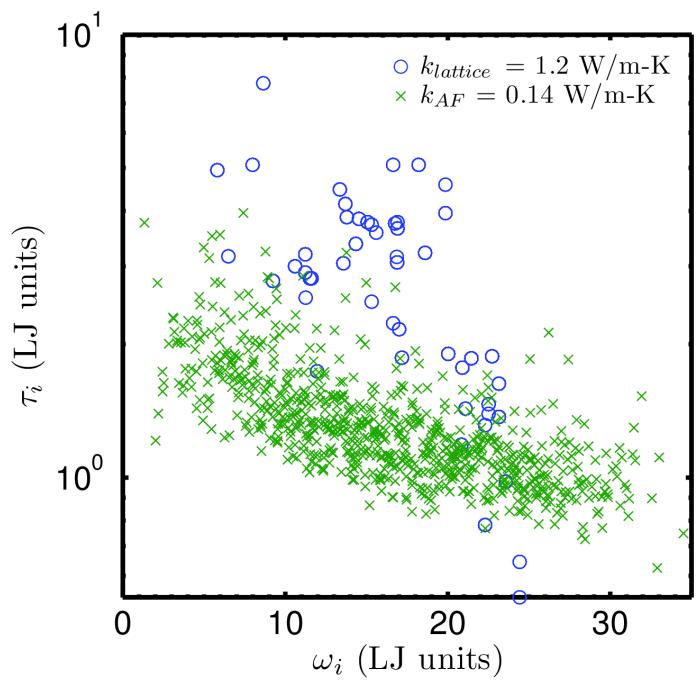
$$\omega(\kappa_\nu) + \omega(\kappa'_{\nu'}) = \omega(\kappa''_{\nu''})$$

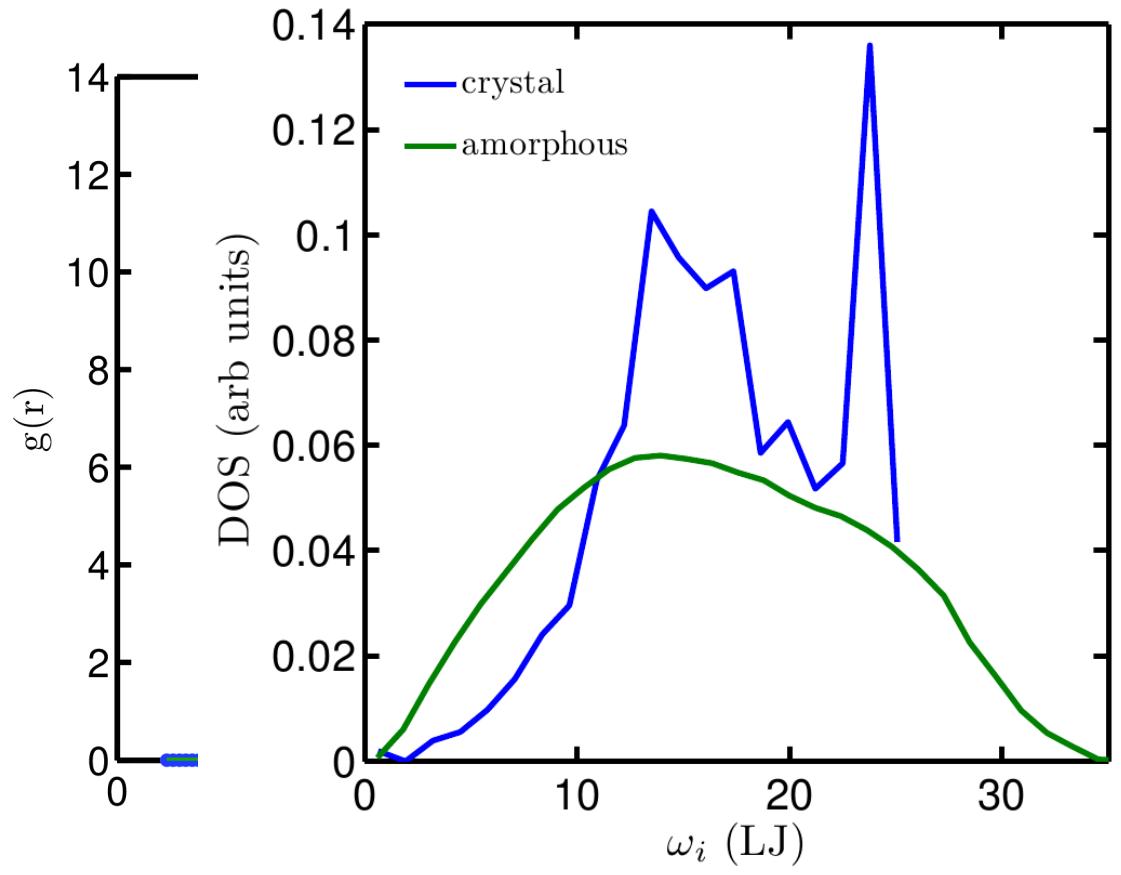
Conservation of energy

$$\kappa + \kappa'' = \kappa'' + G$$

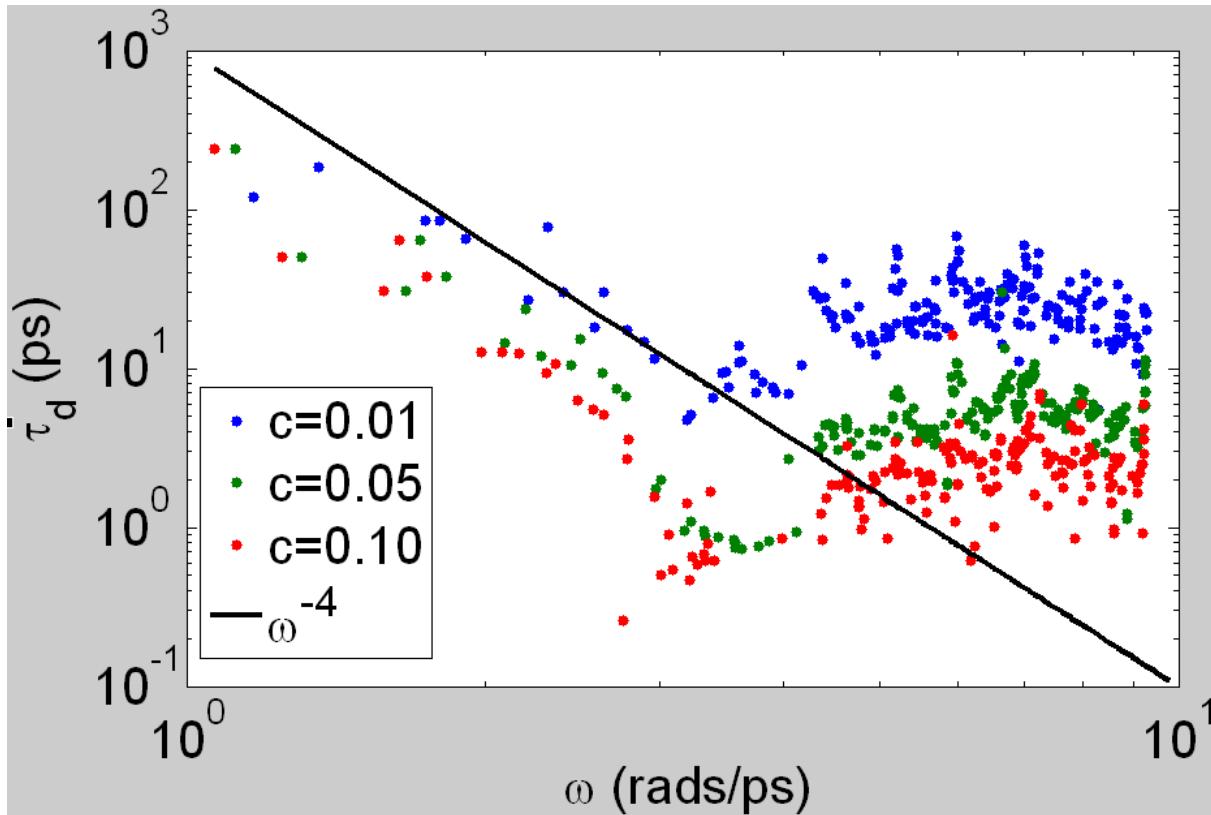
Conservation of crystal momentum







# Defect Scattering



- Matthiesen Rule:
- Rayleigh scattering:



```
jason@jason-Pangolin-Performance:~/lammps/LJ/4x
jason@jason-Pangolin-Performance:~/lammps/LJ/4x$ lmp_serial < in.LJAr.SED
LAMMPS (2 Nov 2010)
Reading data file ...
orthogonal box = (0 0 0) to (6.2235 6.2235 6.2235)
1 by 1 by 1 processor grid
256 atoms
256 atoms in group Ar1
Setting up run ...
Memory usage per processor = 1.38005 Mbytes
Step Temp Press TotEng Volume
   0   0.16534735  -0.62918712  -7.2115662
1000  0.17104453  0.79480522  -6.9665383
2000  0.1571641   0.91642864  -6.9638586
3000  0.1676963   0.90621555  -6.9515928
4000  0.16944953  0.80540567  -6.9649896
5000  0.17355547  0.68163125  -6.9805654
6000  0.16163061  0.86116178  -6.9655506
7000  0.16542596  0.75116271  -6.9796995
8000  0.16551304  0.75899938  -6.9796496
9000  0.16012006  0.88635951  -6.9649338
10000 0.16584685  0.82626678  -6.9671833
11000 0.16222234  0.82895305  -6.9696633
12000 0.16767795  0.81002516  -6.9687163
13000 0.16534735  0.80747768  -6.9716398
14000 0.16827664  0.78303168  -6.9714696
15000 0.16584199  0.80638547  -6.9719307
16000 0.16908827  0.7771169   -6.9716068
17000 0.16091132  0.74450775  -6.988783
18000 0.16832609  0.77748273  -6.9731959
19000 0.16459738  0.88500598  -6.9591849
20000 0.17076714  0.74014943  -6.9746534
21000 0.16702837  0.85102961  -6.9607162
22000 0.16297074  0.87611303  -6.9618026
23000 0.16774514  0.73397515  -6.9803283
24000 0.16879312  0.80262569  -6.9671436
25000 0.1684090  0.80166785  -6.968331
26000 0.16268766  0.83529544  -6.969743
27000 0.16598709  0.80737991  -6.9699574
28000 0.16428114  0.82715399  -6.9687746
29000 0.1602667  0.77797406  -6.9819076
30000 0.16548086  0.83544039  -6.9654546
31000 0.16100867  0.88073728  -6.963762
32000 0.16719105  0.74744094  -6.9793429
33000 0.16745523  0.81621263  -6.9659967
34000 0.1660937  0.83596931  -6.9646266
35000 0.16472322  0.75746417  -6.9811821
36000 0.17083916  0.80447465  -6.964496
37000 0.15629911  0.82958102  -6.9799388
38000 0.15835579  0.8067132   -6.9811655
39000 0.16158849  0.86970252  -6.9660097
40000 0.16335385  0.77172461  -6.9788122
41000 0.16923234  0.84749744  -6.961333
42000 0.17220296  0.81956776  -6.9612127
43000 0.16737025  0.83628668  -6.9649884
44000 0.16238087  0.77985144  -6.9795274
```

241.0483  
241.0483

NMD\_temp.m (~/lammps/LJ/4x) - gedit

```
NMD=load('./NMD.mat');

%---ISEED-----
iseed = ISEED;
%-----

%---IKSLICE-----
ikslice = IKSLICE;
%-----


SED.SED(1:NMD.NUM_KPTS,1:(NMD.NUM_TSTEPS/2),1:NMD.NUM_MODES) = 0.0;

for ifft = 1:NMD.NUM_FFTS
%VELOCITIES
str_read=strcat(NMD.str.main,'/dump_',int2str(iseed),'_',int2str(ifft),'.vel');
fid=fopen(str_read);
dummy = textscan(fid,'%f%f%f','Delimiter',' ','commentStyle', '-');
fclose(fid);

%Store velocity data of all atoms: subtract off the last time step
velx = zeros(NMD.NUM_ATOMS,NMD.NUM_TSTEPS);
vely = zeros(NMD.NUM_ATOMS,NMD.NUM_TSTEPS);
velz = zeros(NMD.NUM_ATOMS,NMD.NUM_TSTEPS);

%
tic
%
for iatom = 1:NMD.NUM_ATOMS
    velx(iatom,1:NMD.NUM_TSTEPS) = ...
        dummy{1}(iatom:NMD.NUM_ATOMS:(length(dummy{1}(:))-NMD.NUM_ATOMS));
    vely(iatom,1:NMD.NUM_TSTEPS) = ...
        dummy{2}(iatom:NMD.NUM_ATOMS:(length(dummy{1}(:))-NMD.NUM_ATOMS));
    velz(iatom,1:NMD.NUM_TSTEPS) = ...
        dummy{3}(iatom:NMD.NUM_ATOMS:(length(dummy{1}(:))-NMD.NUM_ATOMS));
end
%
toc
%
```

Objective-C ▾ Tab Width: 8 ▾ Ln 20, Col 17 INS

4x

Bookmarks

Computer

Name Size Type Date Modified

prepare			
Home			
lammmps			
LJ			
4x			
NMD	9 items	Folder	Wed 21 Dec 2010
old\_matlab	4 items	Folder	Sun 12 Feb 2011
dump\_1.vel	15.6 MB	plain text document	Sun 12 Feb 2011
	99.6 kB	plain text document	Tue 20 Dec 2010
	69 bytes	plain text document	Tue 20 Dec 2010
	3.2 kB	MATLAB script/function	Mon 05 Mar 2011
	6.6 kB	plain text document	Mon 05 Mar 2011
	1.2 kB	plain text document	Tue 20 Dec 2010
	2.7 kB	plain text document	Mon 05 Mar 2011
	4.1 kB	plain text document	Mon 05 Mar 2011
	2.6 kB	unknown	Sun 12 Feb 2011
	915 bytes	Objective-C source code	Sun 12 Feb 2011
	5.3 kB	MATLAB script/function	Sun 12 Feb 2011
	331 bytes	shell script	Sun 12 Feb 2011
	11 bytes	shell script	Sun 12 Feb 2011
	5.4 kB	Objective-C source code	Sun 12 Feb 2011
	617 bytes	shell script	Sun 12 Feb 2011
	15.8 kB	plain text document	Tue 20 Dec 2010
	6.3 kB	plain text document	Fri 16 Dec 2010
