Theory and Simulation of Lattice Thermal Conductivity

Jianjun (JJ) Dong
Department of Physics, Auburn University

2019 NSF Summer School on Computational Materials Physics, Gulfport, MS

Funding: EAR0757847; EAR-1346961

Outline

I. Motivation

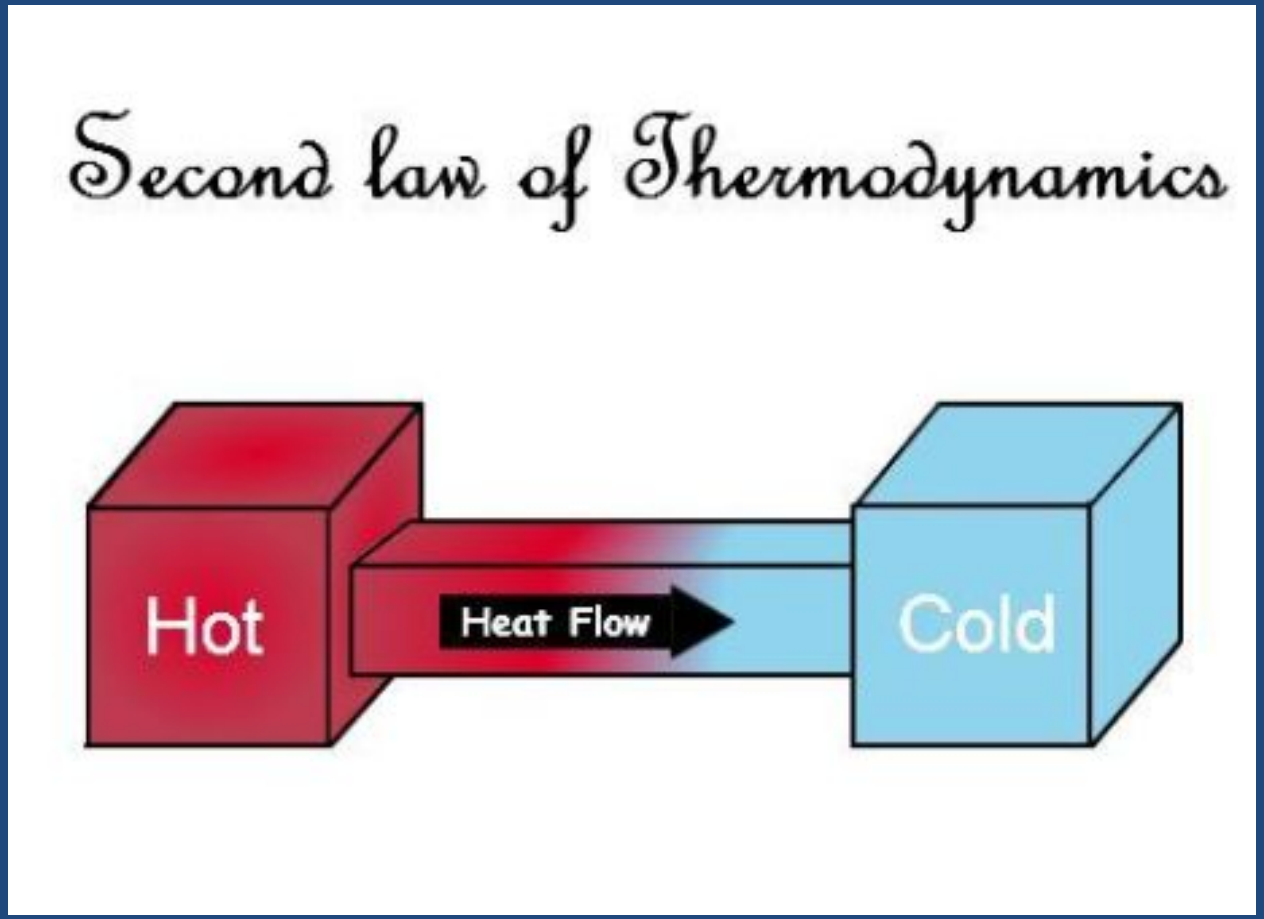
II. Phonon Boltzmann Transport Equation

III. Fokker-Planck Equation for Lattice Dynamics

IV Summary

I. Motivation : *Predicting Lattice Thermal Conductivity from first-principles*

Basic Physics: Heat Transfer is Ubiquitous
a fundamental non-equilibrium physical process

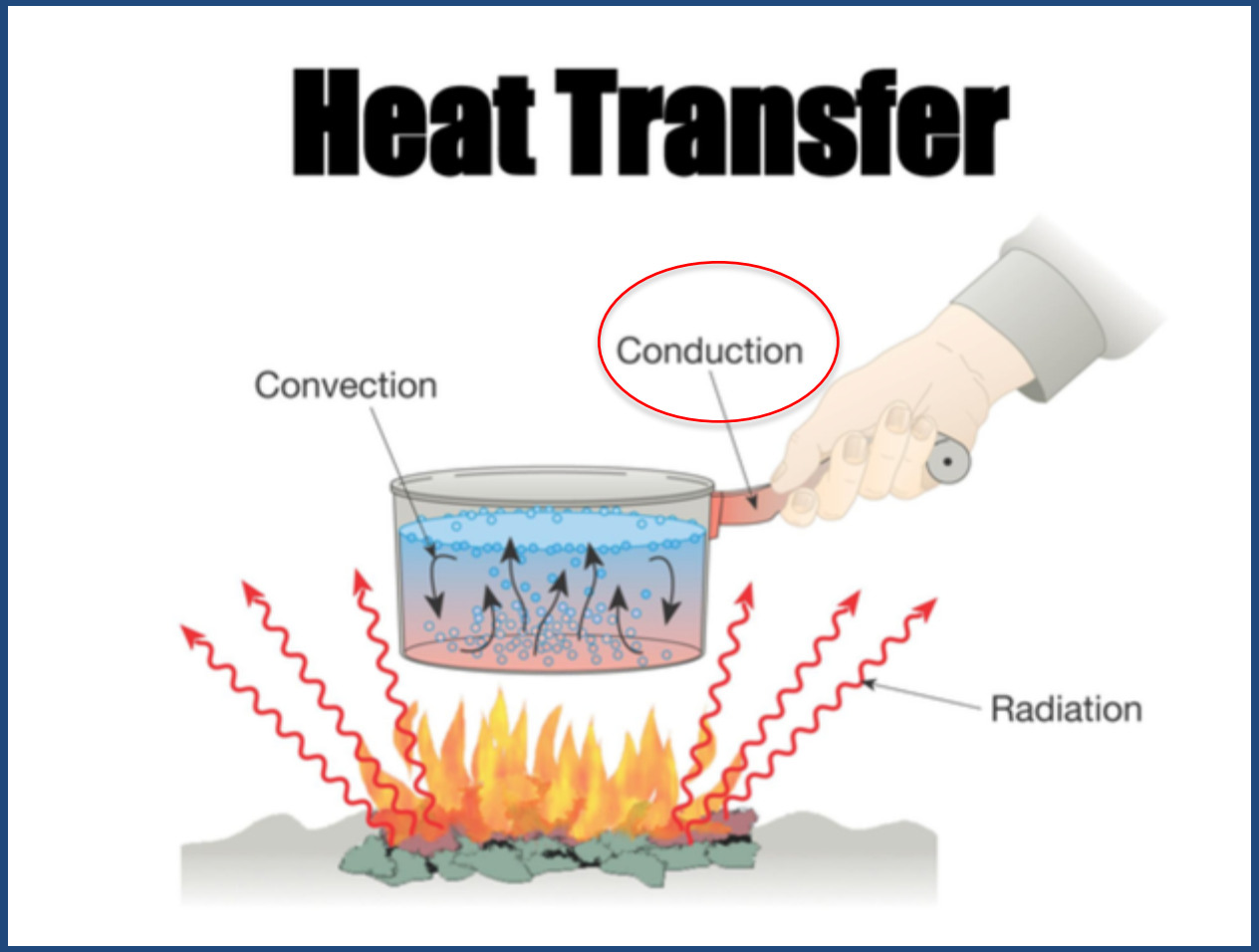


Entropy increase !

But how ?
& how fast ?

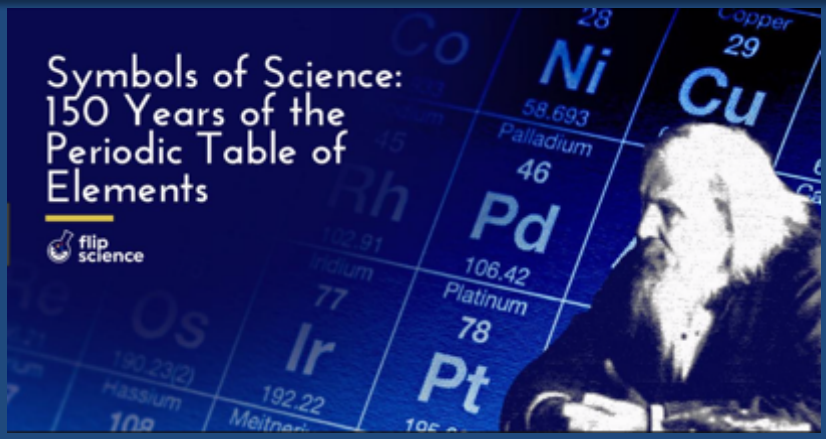
I. Motivation : *Predicting Lattice Thermal Conductivity from first-principles*

Basic Physics: Heat Transfer Mechanisms
Radiation, Convection & Conduction

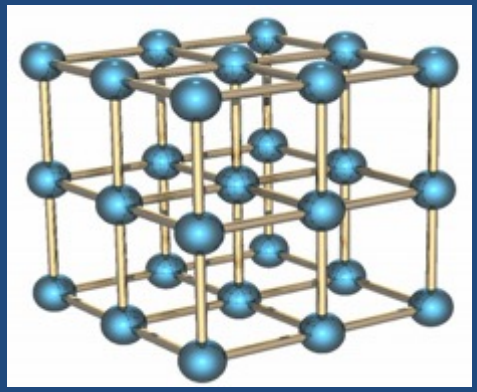


Conduction: Solid media & Heat carriers, such as electrons, phonons, etc.

Atom Scale

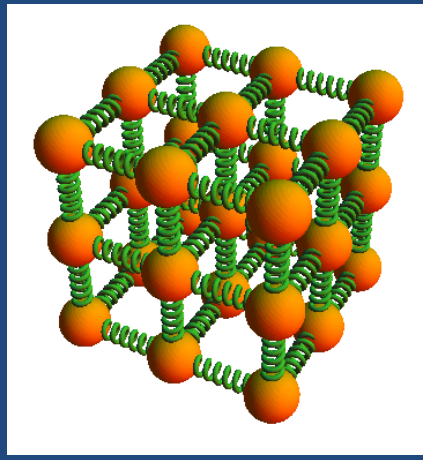


Compositions

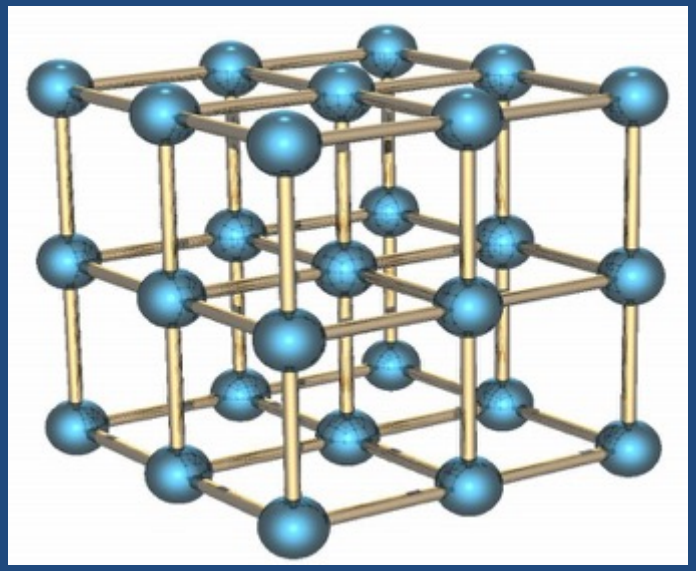


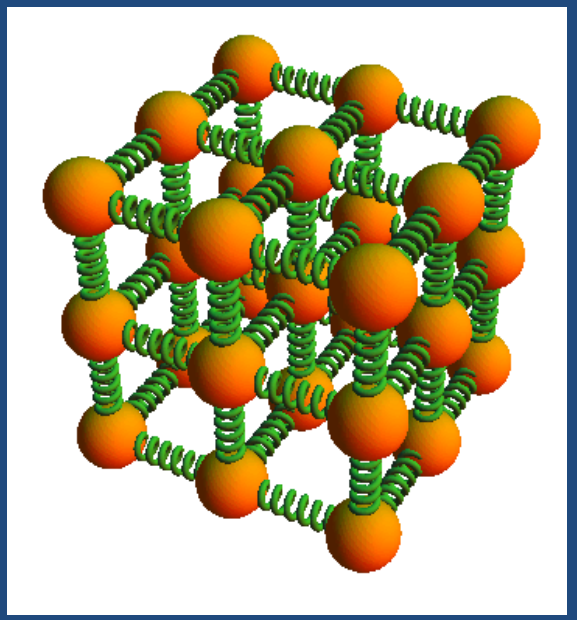
Structures

Dynamics



I. Motivation : *Understanding Thermal Fluctuations of Atomic Lattices*



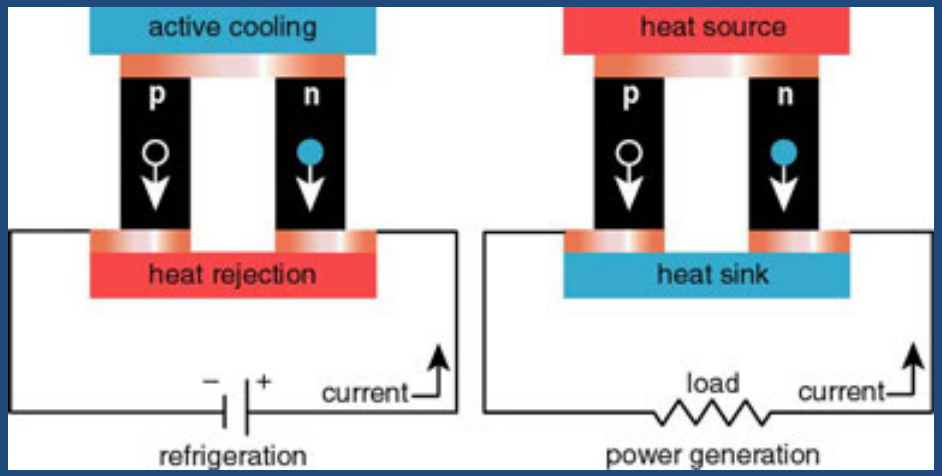


Static *vs* Dynamic

Interaction → Fluctuation → Dissipation

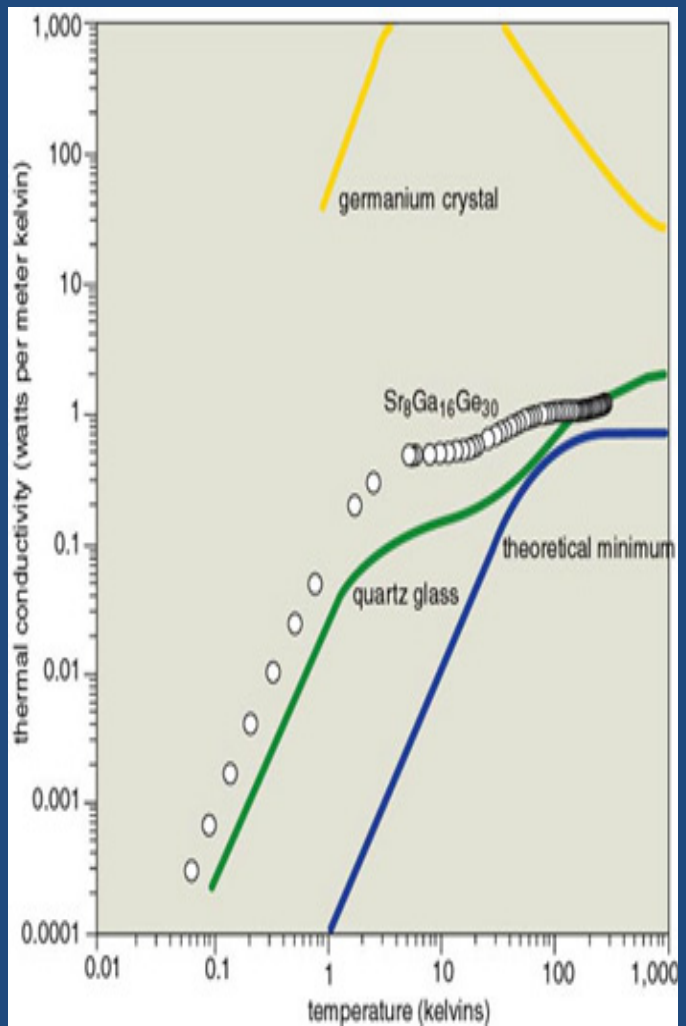
I. Motivation : *Predicting Lattice Thermal Conductivity from first-principles*

Applied Physics: Materials-by-design, e.g. thermometric materials



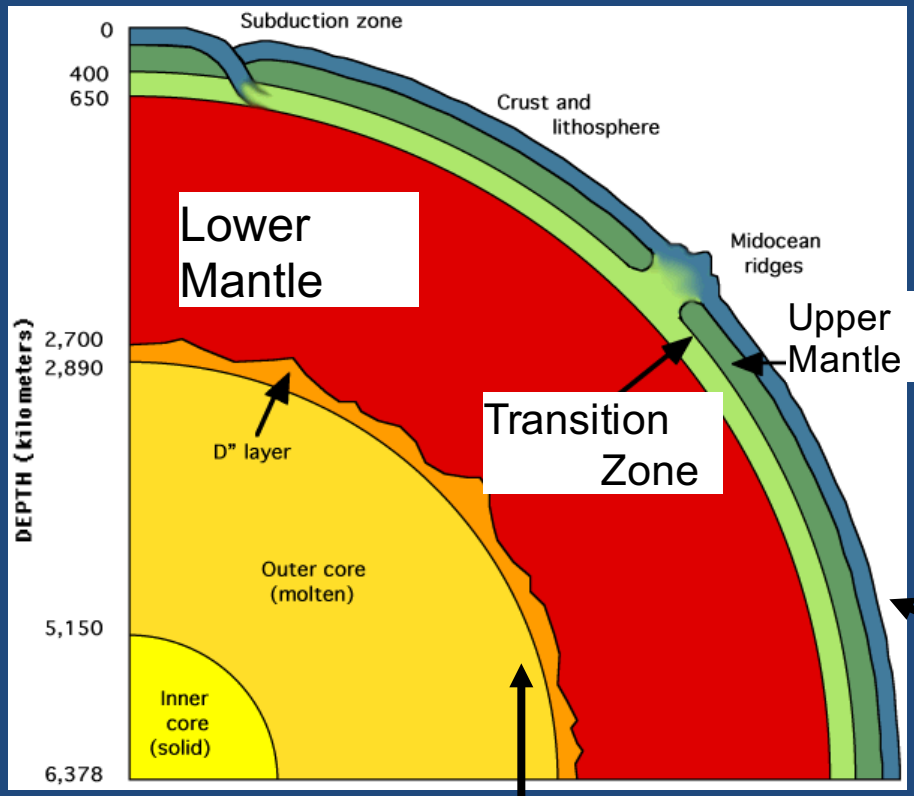
$$ZT = \frac{S^2 T \sigma}{\kappa}$$

High ZT (>3)



I. Motivation : *Predicting Lattice Thermal Conductivity from first-principles*

Thermal processes in deep Earth & outer planets



What is the present T profile?
Surface flux ?
Convection style?

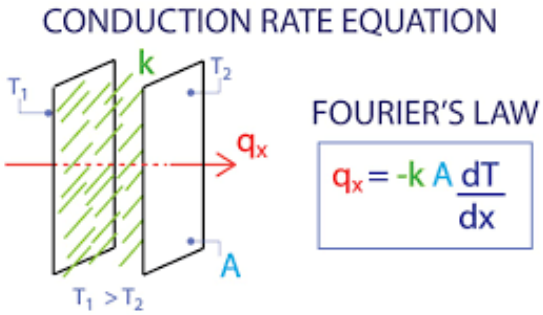
How about Thermal history?

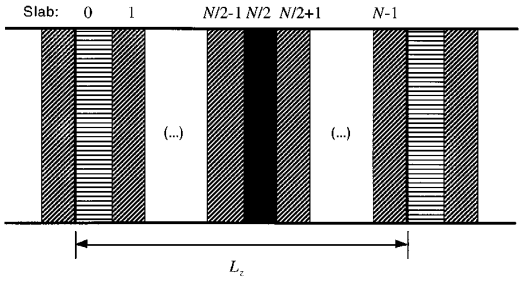
25 C, fixed by solar flux

Pure Fe melts at 3000 C at the top of the core
from experiments of Boehler and others

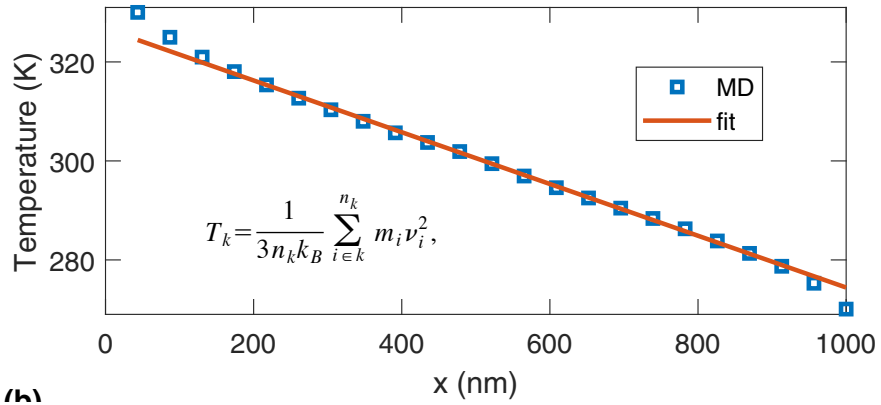
Why Not Non-equilibrium MD Simulations ?

Non-Equilibrium Steady States
(a) Direct MD simulations in real-space: Newton's 2nd Law
(b) Kinetic energy transfer: no additional heat current definition needed

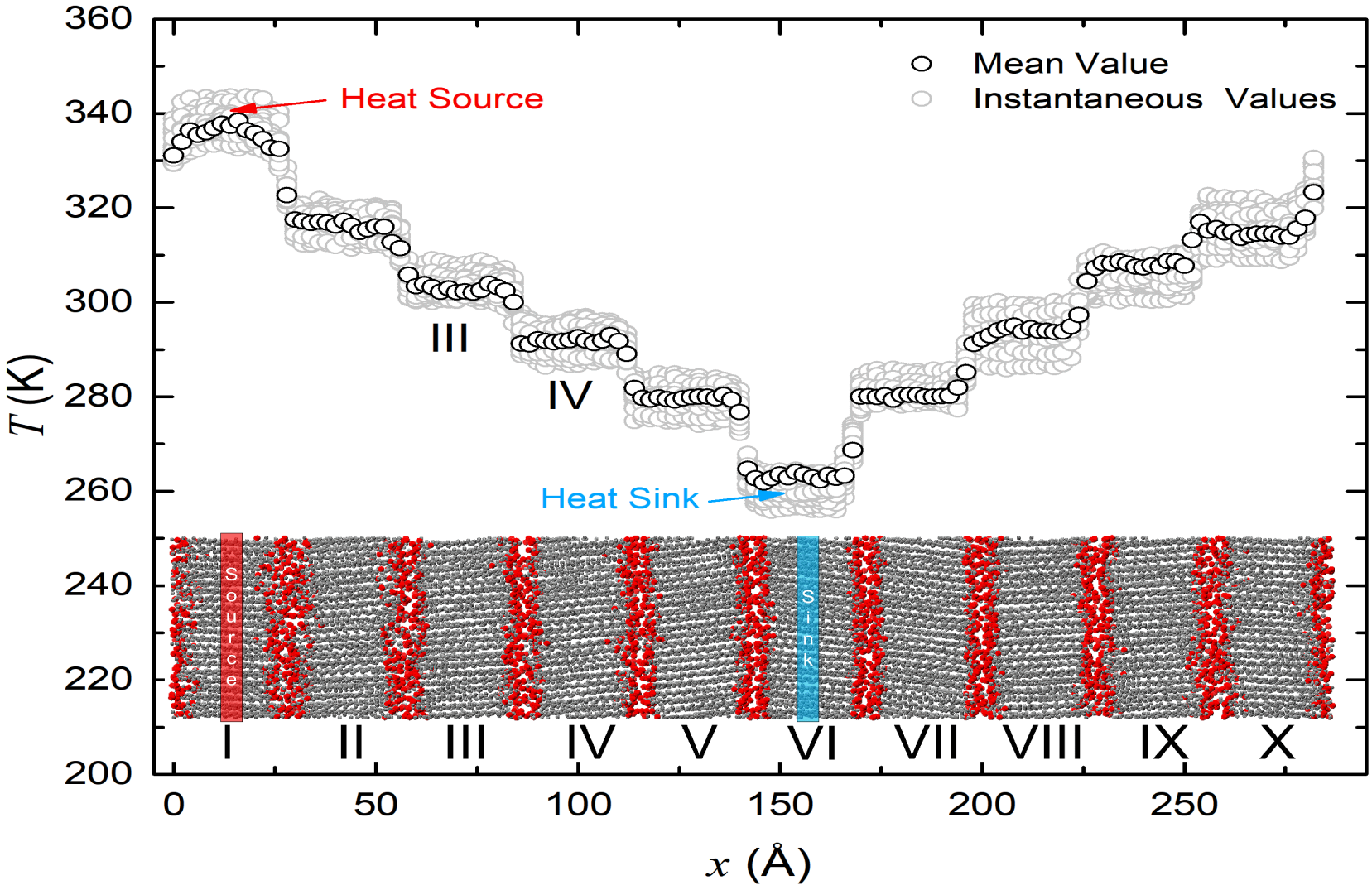




$q_{net} \neq 0$



How to engineer thermal Interfacial conductance?



Zeng, Dong, and Khodadadi, submitted.

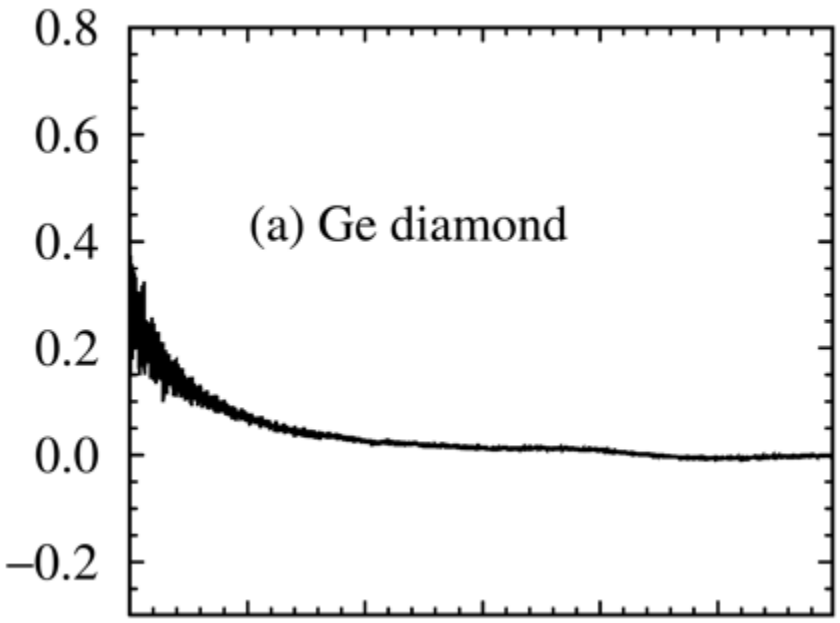
II. Phonon Boltzmann Transport Equation (BTE)

Why Not Green-Kubo (GK) Method?

$$\kappa_{lattice} = \frac{\Omega}{3k_B T^2} \int_0^{\infty} \left(\sum_{i=x,y,z} < J_i(0) J_i(t) > dt \right.$$

$$\vec{J}(t) = \frac{1}{\Omega} [\sum_i \vec{v}_i (E_i - \bar{E}_i) + \sum_{i,j} \vec{r}_{ij} (\vec{v}_j . \nabla_j (V_i))$$

Kubo Ryōgo



GK Formula

(a) Linear-response Fluatuation-Dissipation Theorem

(b) Direct equilibrium MD simulations in real-space: Newton's 2nd Law

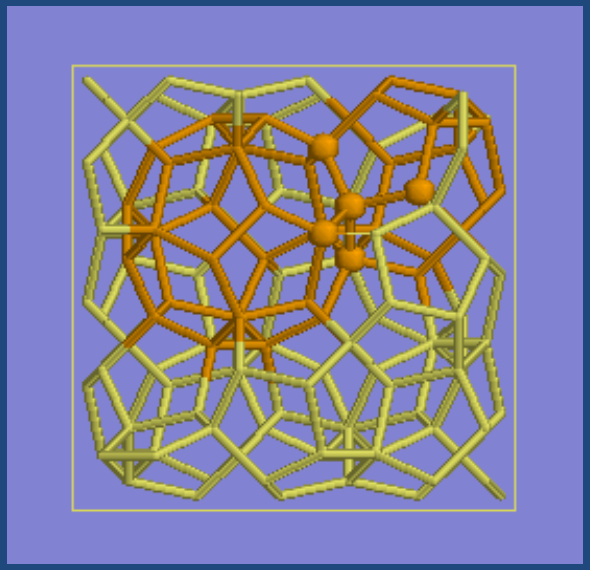
(c) Definition of heat current needed

II. Phonon Boltzmann Transport Equation (BTE)

VOLUME 86, NUMBER 11 PHYSICAL REVIEW LETTERS 12 MARCH 2001

Theoretical Study of the Lattice Thermal Conductivity in Ge Framework Semiconductors

Jianjun Dong,[1,2] Otto F. Sankey,[1] and Charles W. Myles[3]



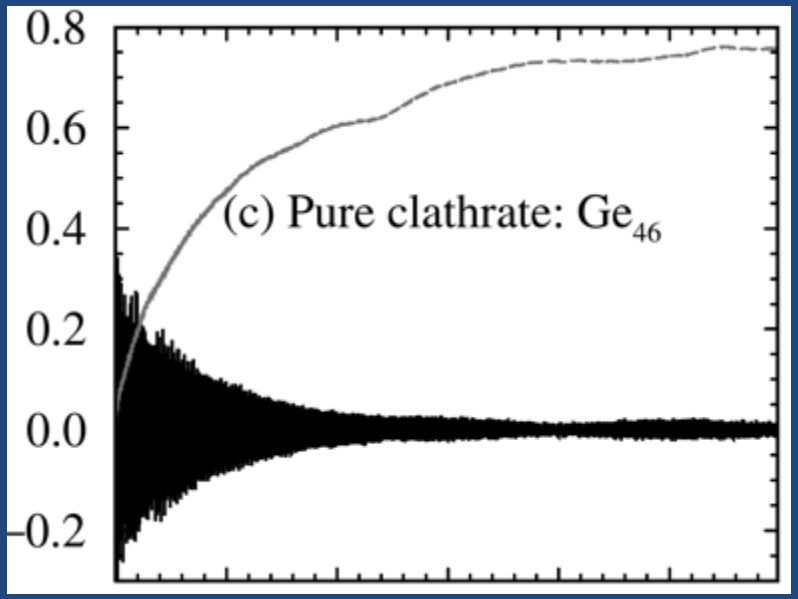


TABLE I. Results of the MD simulations for the four different Ge materials. The final column is experiment, where available. All results are at 300 K.

Material (No. atoms)	τ_I (ps)	$G(0)$ (W/K m ps)	κ—Theory (W/K m)	κ—Expt. (W/K m)
d-Ge (512)	10.82 ± 0.27	10.5	114 ± 3	62. [13,14]
a-Ge (512)	0.013 ± 0.003	48.8	0.63 ± 0.15	0.50 [18]
Ge_{46} (2944)	0.745 ± 0.015	16.4	12.2 ± 0.25	···
Sr_6Ge_{46} (3328)	0.078 ± 0.011	21.0	1.64 ± 0.24	0.89* [3]

*($Sr_8Ga_{16}Ge_{30}$)

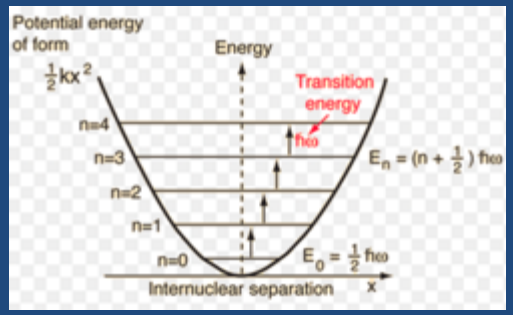
Clathrate framework:
a factor of 10 reduction

Guest rattler: Another a factor of 10 reduction

II. Phonon Boltzmann Transport Equation (BTE)

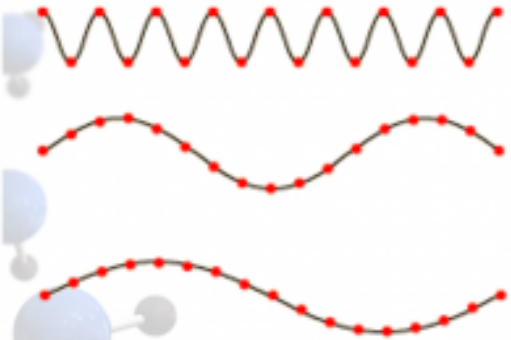
Quasi-particle Phonon + Kinetic Transport Theory

Sir Rudolf Ernst Peierls
06/05/1907 – 09/19/1995

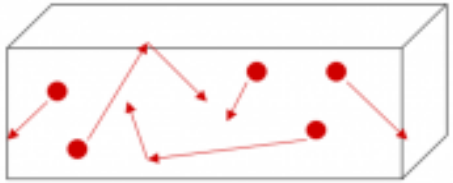


Phonon Gas Model

What is a phonon?



What is the phonon gas model (PGM)?

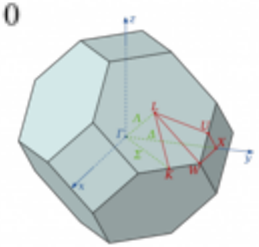


$$\kappa = \frac{1}{3}\sum_{p}\int_{0}^{\nu_{\max}} C \cdot \mathrm{v} \cdot \Lambda \cdot d\nu$$

$$\text{Energy} = \hbar\omega$$

$$\text{Wavelength} = \lambda \rightarrow \mathbf{k} = 2\pi/\lambda$$

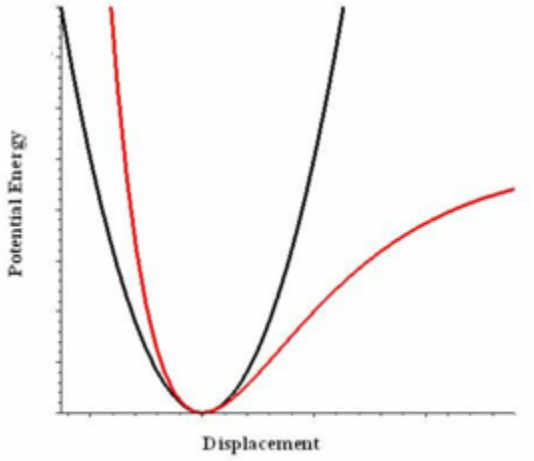
$$\text{Speed} = \mathbf{v}_p = \omega/\mathbf{k} \quad \mathrm{v}_g = d\omega/d\mathbf{k}$$



Quantum vs Classical: $\frac{\hbar\omega_D}{k_B T}$

II. Phonon Boltzmann Transport Equation (BTE)

Step 1: harmonic potential + normal modes (eigen-frequencies & eigen-vectors)



Simple harmonic oscillation

Ideal case: no friction

Hooke's law: $F = -kx$

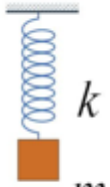
Newton's 2nd law: $F = m\ddot{x}$

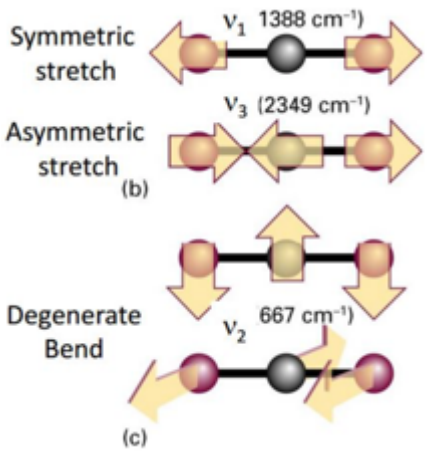
$\Rightarrow -kx = m\ddot{x}$

$m\ddot{x} + kx = 0 \qquad \omega^2 = \frac{k}{m}$

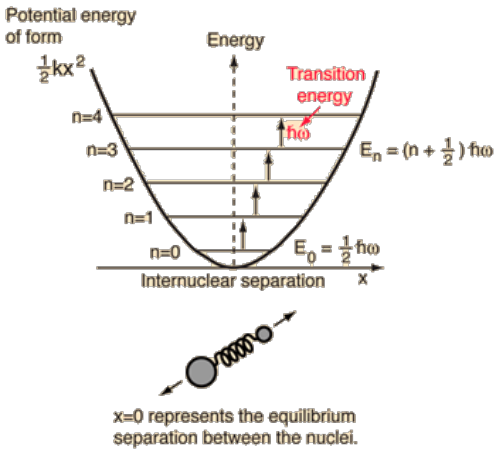
$\ddot{x} + \omega^2 x = 0 \qquad T = \frac{2\pi}{\omega} = 2\pi\sqrt{\frac{m}{k}}$

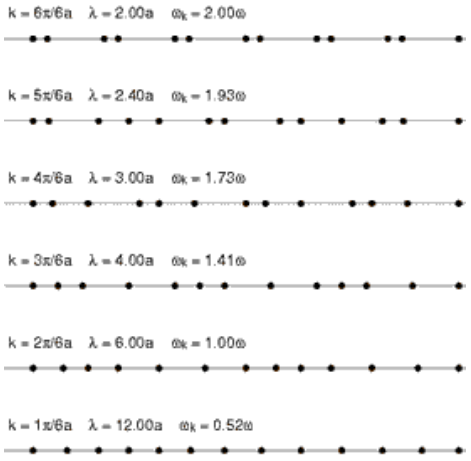
solution: $x = A\cos(\omega t + \phi)$ A: Amplitude, ϕ: phase

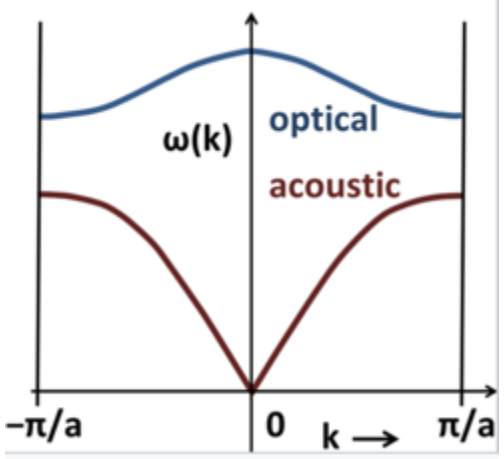




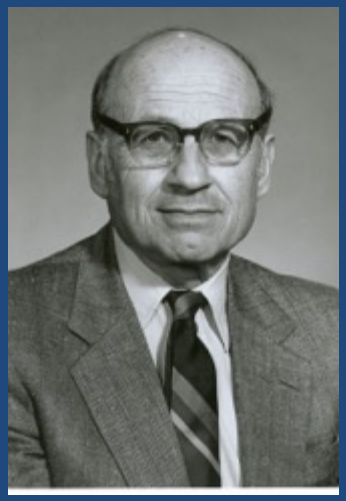
Step 2: K-space dispersion relation + quantum particles (phonons)





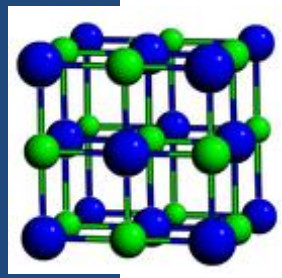


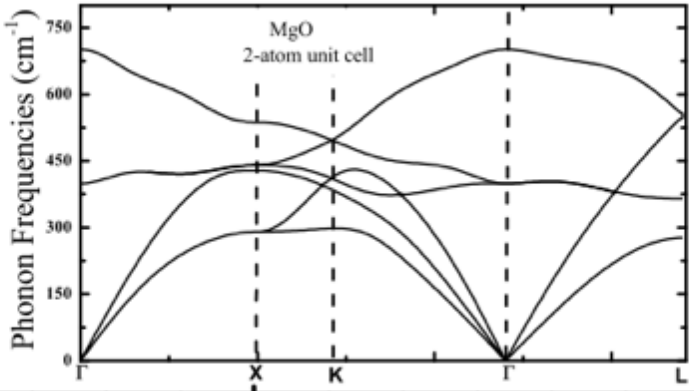
II. Phonon Boltzmann Transport Equation (BTE)

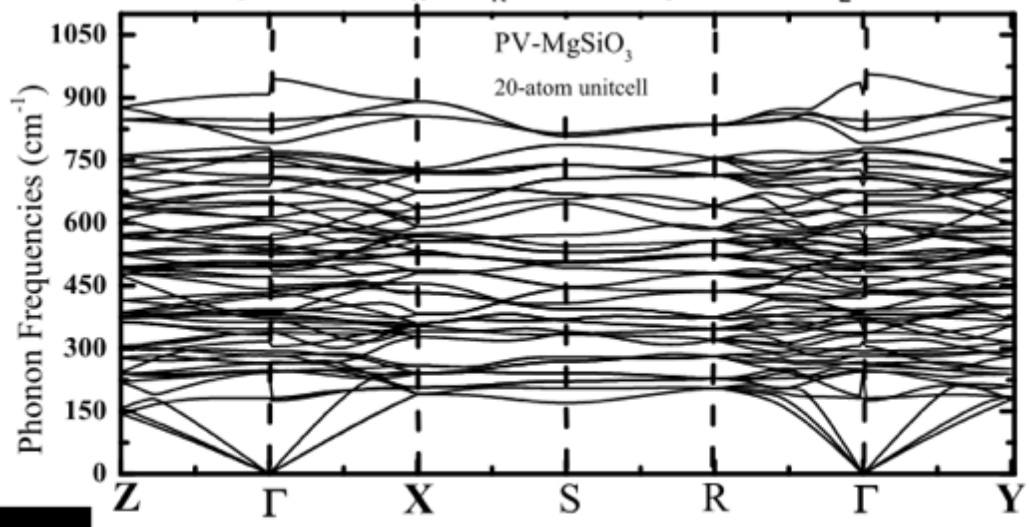


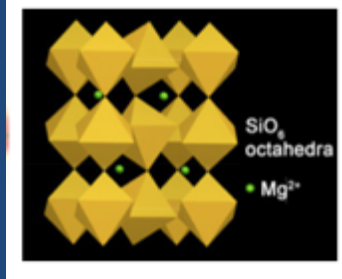
Walter Kohn

- DFT theory first proposed in 1960s
- Nobel Prize in Chemistry awarded in 1998.





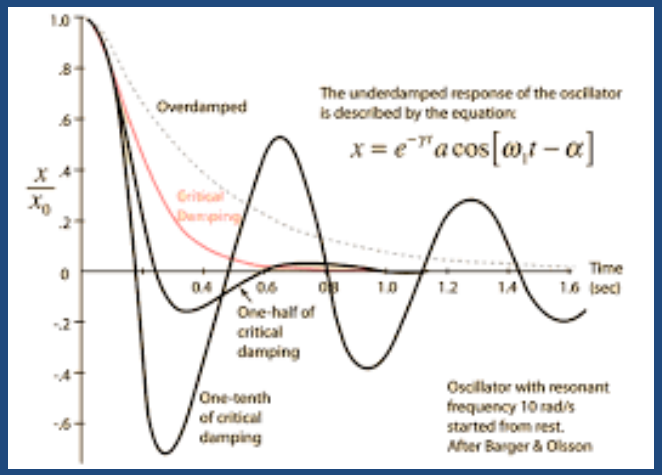


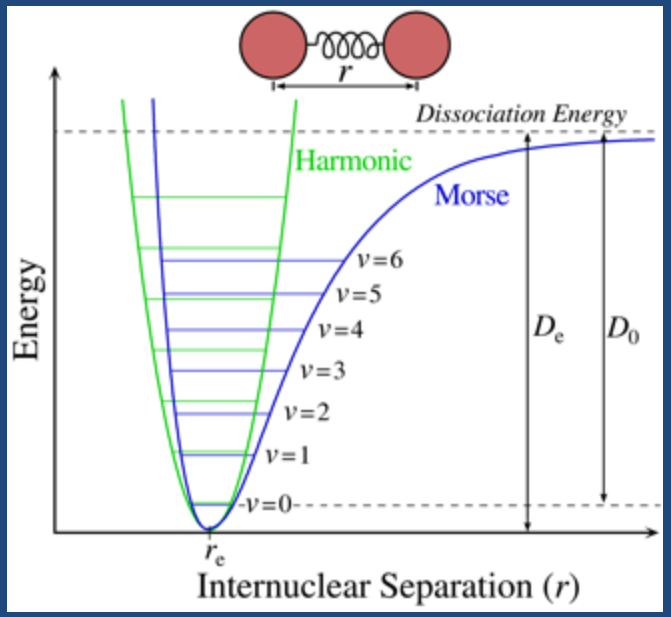


First-principles, no fitting parameters !

II. Phonon Boltzmann Transport Equation (BTE)

Anharmonic effects: damped oscillators, phonon scatterings






Physics of the Earth and Planetary Interiors 174 (2009) 33–38

Contents lists available at ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

ELSEVIER

Pressure dependence of harmonic and anharmonic lattice dynamics in MgO: A first-principles calculation and implications for lattice thermal conductivity

Xiaoli Tang*, Jianjun Dong

Physics Department, Auburn University, Auburn, Alabama 36849-5311, United States

Yes, DFT is capable to accurately describe the 3rd order lattice anharmonicity.

II. Phonon BTE – first-principles implementation

Phonon gas model
phonon-phonon scattering

$$\kappa = \frac{1}{3}\sum_{i,\vec{q}} c_V(i,\vec{q}) v_g^{\ 2}(i,\vec{q}) \tau(i,\vec{q})$$

First-principles calculations

2nd order force constant matrix

$$\phi_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

3rd order lattice anharmonicity

$$A_{ijk} = \frac{\partial^3 E}{\partial x_i \partial x_j \partial x_k}$$

Independent Phonons:
Phonon-phonon interaction c_V, v_g

Quantum Scattering Theory

$$\frac{1}{\tau} \propto P_i^{\ j} = \frac{2\pi}{\hbar}\left|\langle f|\Delta H|i\rangle\right|^2 \delta(\varepsilon_f - \varepsilon_i)$$

$$\Delta H^{anh} = \frac{1}{6}\sum_{\alpha i}\sum_{\beta jl}\sum_{\gamma kl'} A_{\alpha i 0,\beta jl,\gamma kl'} \Delta x_{\alpha i 0} \Delta x_{\beta jl} \Delta x_{\gamma kl'}$$

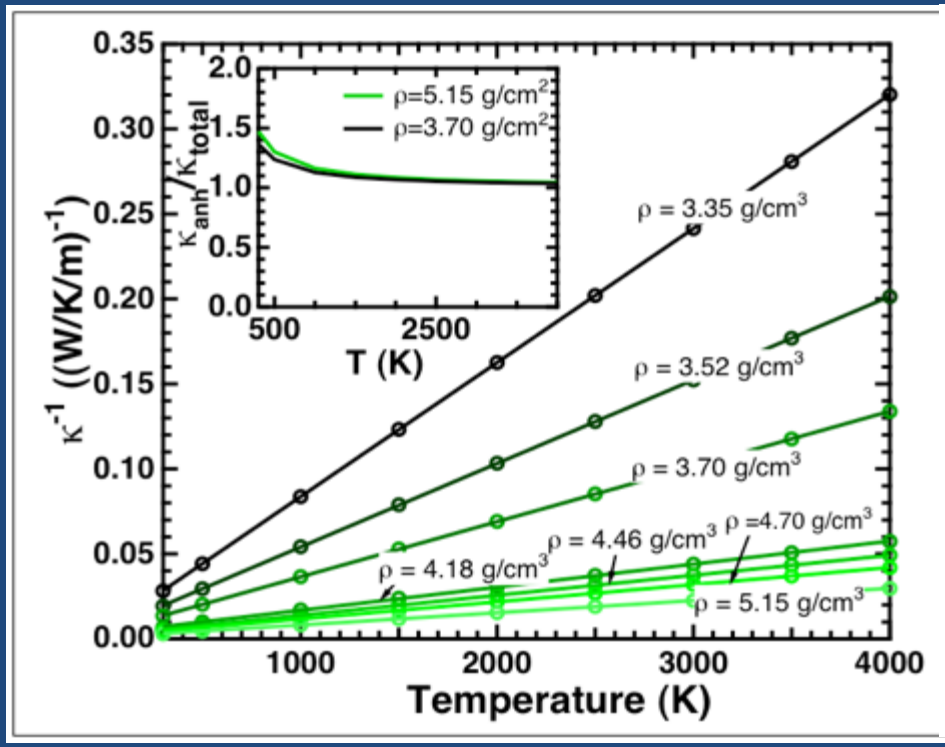
$$\Delta H^{iso} = \frac{1}{2}\sum_{\alpha il}[m(il) - \overline{m}(i)] x_\alpha^{\ 2}(il)$$

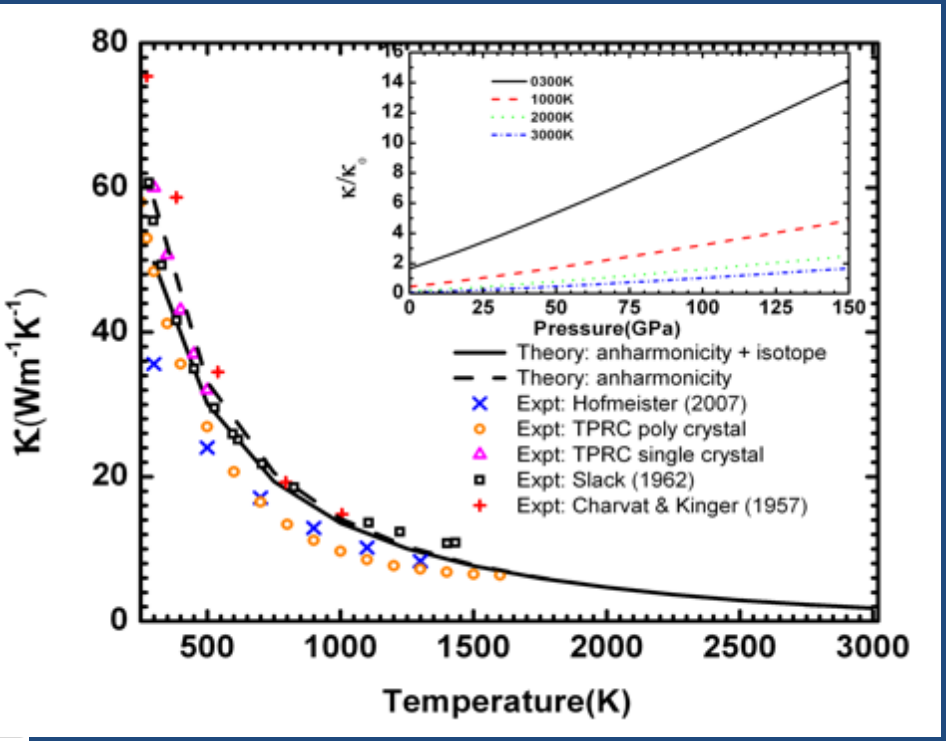
$$1/\tau = 1/\tau_{anh} + 1/\tau_{iso}$$

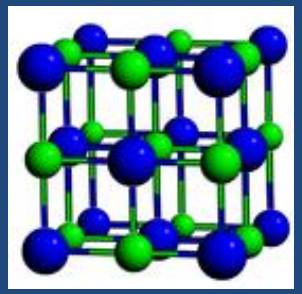
More details: (1) Tang & Dong, PEPI 2009; (2) Tang and Dong, PNAS 2010

II. Phonon BTE – first-principles results of MgO

Fe-free MgO bulk crystals: Tang and Dong, PEPI 2009; Tang and Dong, PNAS 2010







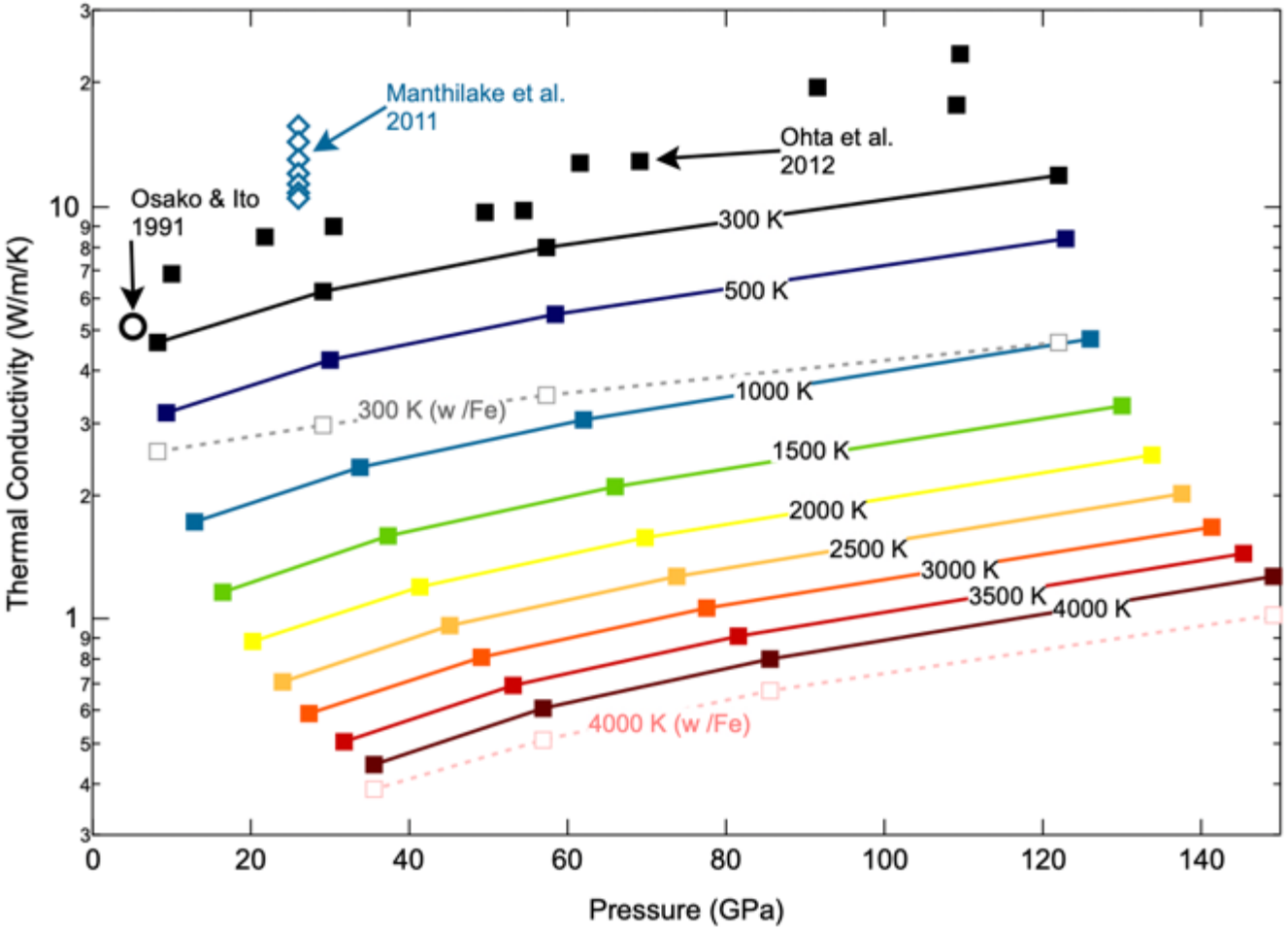
Quick Summary:

(i) Good agreement with experiments

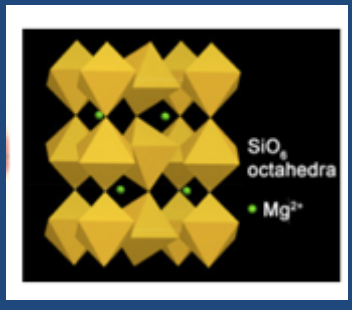
(ii) Useful information on heat conducting properties of individual phonons; e.g. useful to estimate grain boundary scattering

(iii) Well tested numerical convergence.

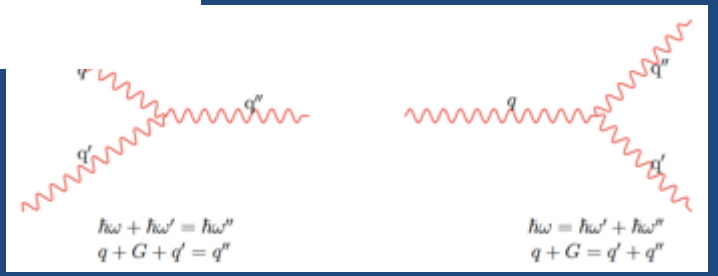
II. Phonon BTE – first-principles results of $MgSiO_3$ perovskite



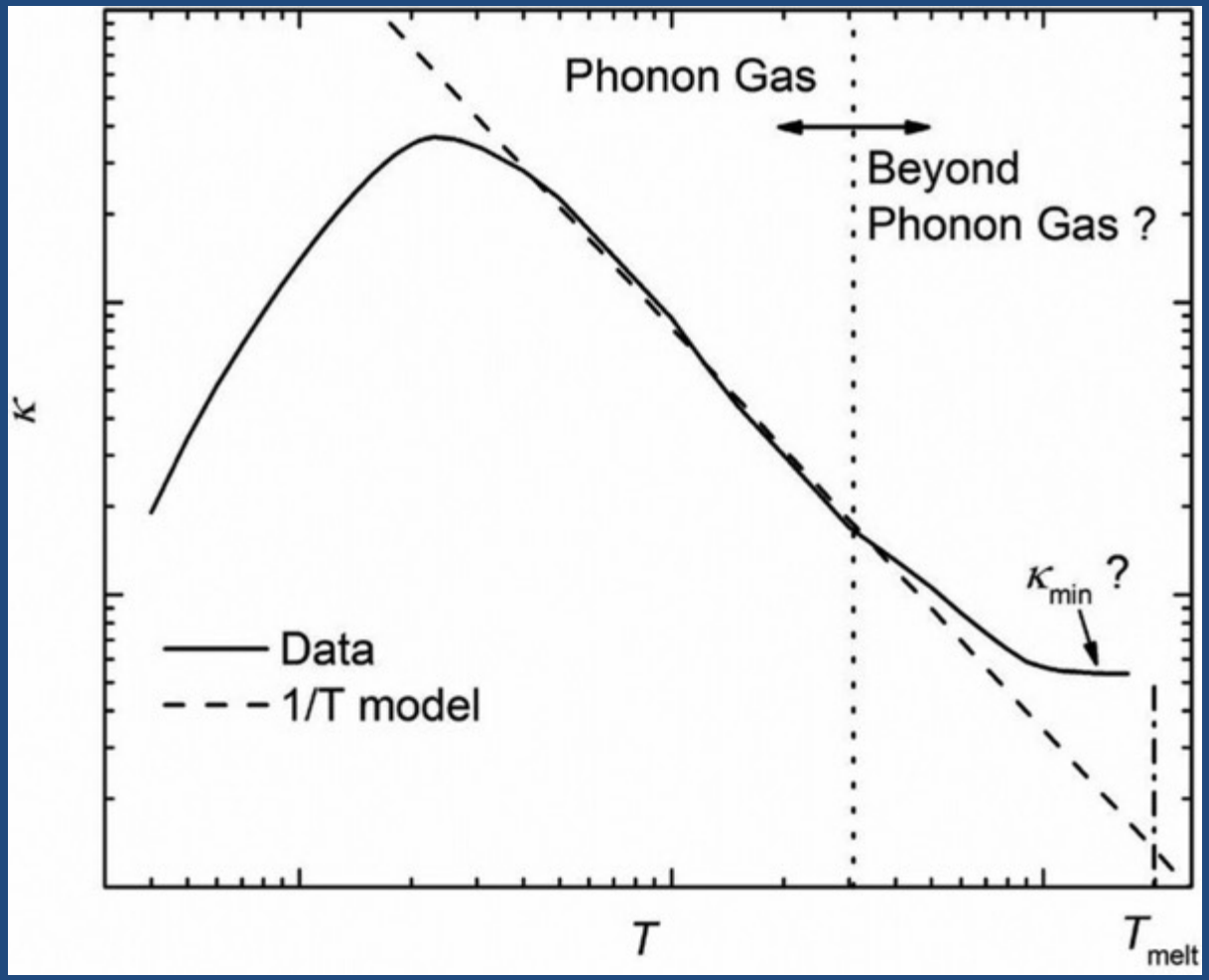
1.5 millions of CPU-hours massive parallelization



Pv-MgSiO3 perovskite: Tang et al GRL 2014



II. Phonon BTE – break-down conditions?



- *High T?*
- *Amorphous?*

What is the quantitative break-down criteria ?

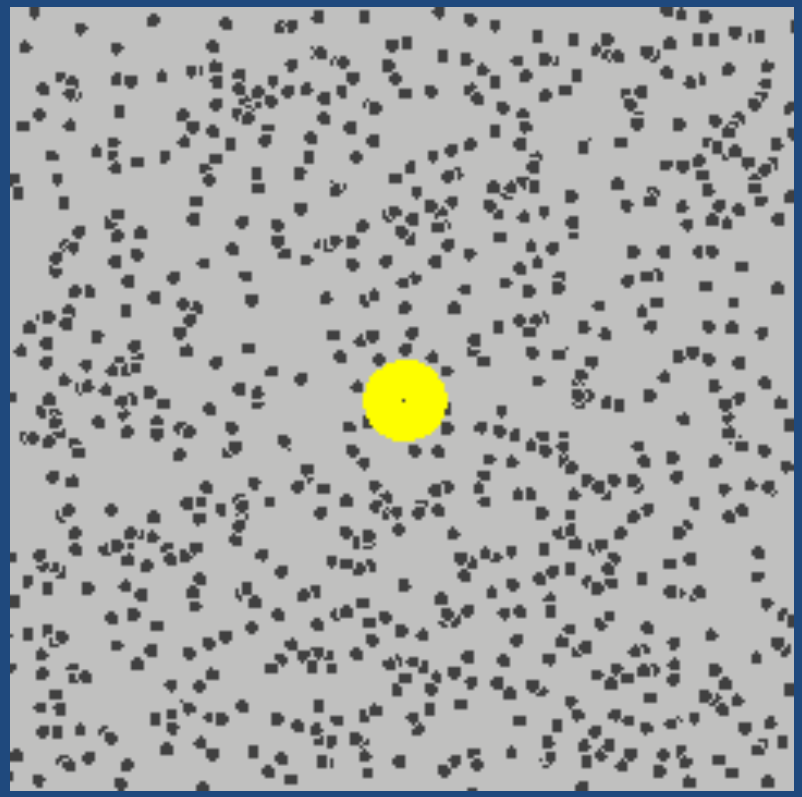
II. Phonon BTE – weakness and limitation

Weakness/Limitation of the Kinetic Transport Theory

- *What is the break-down condition of the phonon gas approximation?*
- *How to include higher order lattice anharmonicity as T increases?*
- *Why does the RTA fail at lower T where the magnitude anharmonicity is small?*
- *How to study disordered lattices with no clearly defined phonon group velocity?*
- *How to improve numeric efficiency for complex crystals with large amounts of phonon branches?*

III. Fokker-Planck Equation for Lattice Vibration - stochastic dynamics

Brownian motion



Langevin Equation

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = v(t)$$

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = -\frac{\gamma}{m}v(t) + \frac{1}{m}\xi(t)$$

dissipation fluctuation

Einstein Relation

Interaction → Fluctuation → Dissipation

III. Fokker-Planck Equation for Lattice Vibration

PHYSICAL REVIEW B **99**, 014306 (2019)

Fokker-Planck equation for lattice vibration: Stochastic dynamics and thermal conductivity

Yi Zeng
Department of Mechanical Engineering, Auburn University, Auburn, Alabama 36849-5341, USA

Jianjun Dong*
Department of Physics, Auburn University, Auburn, Alabama 36849-5311, USA

(Received 20 November 2018; revised manuscript received 7 January 2019; published 22 January 2019)

We propose a Fokker-Planck equation (FPE) theory to describe stochastic fluctuation and relaxation processes of lattice vibration at a wide range of conditions, including those beyond the phonon gas limit. Using the time-dependent, multiple state-variable probability function of a vibration FPE, we first derive time-correlation functions of lattice heat currents in terms of correlation functions among multiple vibrational modes, and subsequently predict the lattice thermal conductivity based on the Green-Kubo formalism. When the quasiparticle kinetic transport theories are valid, this vibration FPE not only predicts a lattice thermal conductivity that is identical to the one predicted by the phonon Boltzmann transport equation, but also provides additional microscopic details on the multiple-mode correlation functions. More importantly, when the kinetic theories become insufficient due to the breakdown of the phonon gas approximation, this FPE theory remains valid to study the correlation functions among vibrational modes in highly anharmonic lattices with significant mode-mode interactions and/or in disordered lattices with strongly localized modes. At the limit of weak mode-mode interactions, we can adopt quantum perturbation theories to derive the drift/diffusion coefficients based on the lattice anharmonicity data derived from first-principles methods. As temperature elevates to the classical regime, we can perform molecular dynamics simulations to directly compute the drift/diffusion coefficients. Because these coefficients are defined as ensemble averages at the limit of $\delta t \rightarrow 0$, we can implement massive parallel simulation algorithms to take full advantage of the paralleled high-performance computing platforms. A better understanding of the temperature-dependent drift/diffusion coefficients up to melting temperatures will provide new insights on microscopic mechanisms that govern the heat conduction through anharmonic and/or disordered lattices beyond the phonon gas model.

DOI: 10.1103/PhysRevB.99.014306

A theory of stochastic dynamics

Modeling thermal fluctuation & relaxation processes in lattice vibration with a focus on time-correlation functions among modes

Not a transport theory

Combining with the GK formalism to model bulk thermal conductivity based on the predicted mode time-correlation functions, i.e. GK+FPE

III. Fokker-Planck Equation for Lattice Vibration

$$\frac{\partial P}{\partial t} = -\sum_{\alpha=1}^{N} \frac{\partial}{\partial n_\alpha}[A_\alpha(\Gamma)\cdot P] + \frac{1}{2}\sum_{\alpha\beta} \frac{\partial^2}{\partial n_\alpha \partial n_\beta}[B_{\alpha\beta}(\Gamma)\cdot P]$$

- Stochastic Processes
- Transition from one micro-state to another
- P is the time-evolving probability distribution function
- Not only expectation values, but also fluctuation around the expectation values

$$A_\alpha(\Gamma) \equiv \lim_{\delta t\to 0}\frac{1}{\delta t}\int_0^{\delta t} d\Gamma' \delta n_\alpha(\Gamma,\Gamma')P(\Gamma',\delta t|\Gamma),$$

drifting

$$B_{\alpha\beta}(\Gamma) \equiv \lim_{\delta t\to 0}\frac{1}{\delta t}\int_0^{\delta t} d\Gamma' \delta n_\alpha(\Gamma,\Gamma')\delta n_\beta(\Gamma,\Gamma')P(\Gamma',\delta t|\Gamma).$$

diffusion

III. Fokker-Planck Equation for Lattice Vibration

Vibration FPE predicts:

- Expectation values
- Fluctuation --> correlation functions

$$C_{XY}(t) = \langle \delta X(\Gamma_0) \cdot \overline{\delta Y}(t|\Gamma_0) \rangle_{\text{eq}}$$

$$= \int d\Gamma_0 P_{\text{eq}}(\Gamma_0)(X(\Gamma_0) - X_{\text{eq}}) \int d\Gamma P(\Gamma, t|\Gamma_0)(Y(\Gamma) - Y_{\text{eq}})$$

Fluctuation-Dissipation Theorem/GK formula

$$\kappa_{lattice} = \frac{\Omega}{3k_B T^2} \int_0^\infty \left(\sum_{i=x,y,z} < J_i(0) J_i(t) > dt \right.$$

$$\vec{J}(t) = \frac{1}{\Omega} [\sum_i \vec{v}_i (E_i - \overline{E}_i) + \sum_{i,j} \vec{r}_{ij} (\vec{v}_j . \nabla_j (V_i))$$

Ornstein-Uhlenbeck (OU) condition

$$P(\tilde{\Gamma}, t|\tilde{\Gamma}^0) = \prod_{\lambda=1}^{N} \frac{1}{\sqrt{2\pi\,\Delta_\lambda(t)}} e^{-\frac{[x_\lambda - \overline{x_\lambda}(t)]^2}{2\Delta_\lambda(t)}}$$

- Phonon BTE $\kappa_{IJ} = \frac{1}{\Omega N_{\text{Cell}}} \sum_{\alpha\beta} (\boldsymbol{L})^{-1}_{\alpha\beta} \cdot \frac{\sqrt{n_{\alpha,\text{eq}}(n_{\alpha,\text{eq}}+1)}\sqrt{n_{\beta,\text{eq}}(n_{\beta,\text{eq}}+1)}\hbar\omega_\alpha\hbar\omega_\beta}{k_B T^2} v_{\alpha I} \cdot v_{\beta J}$

$$= \frac{1}{\Omega N_{\text{Cell}}} \sum_{\alpha\beta} (c_\alpha c_\beta)^{1/2} \cdot v_{\alpha I} \cdot v_{\beta J} \cdot (\boldsymbol{L})^{-1}_{\alpha\beta},$$

- Fokker-Planck Equation

$$\kappa_{IJ} = \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha}\Lambda_{J\beta}(\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \sum_{\lambda=1}^{N} \int_0^\infty dt e^{-\gamma_\lambda t} u_{\lambda,\alpha} u_{\lambda,\beta}$$

$$= \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha}\Lambda_{J\beta}(\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} \sum_{\lambda=1}^{N} (\gamma_\lambda)^{-1} u_{\lambda,\alpha} u_{\lambda,\beta}$$

$$= \frac{1}{k_B T^2 \Omega N_{\text{Cell}}} \sum_{\alpha\beta} \Lambda_{I\alpha}\Lambda_{J\beta}(\Delta_{\alpha,\text{eq}} \cdot \Delta_{\beta,\text{eq}})^{1/2} (\boldsymbol{\mathcal{D}})^{-1}_{\alpha\beta}.$$

III. Fokker-Planck Equation for Lattice Vibration – OU condition

$$A_\alpha(\Gamma) = -\sum_\beta \mathcal{D}_{\alpha\beta}\left(\frac{\Delta_{\alpha,\mathrm{eq}}}{\Delta_{\beta,\mathrm{eq}}}\right)^{1/2}(n_\beta - n_{\beta,\mathrm{eq}})$$

$$B_{\alpha\beta}(\Gamma) = 2(\Delta_{\alpha,\mathrm{eq}} \cdot \Delta_{\beta,\mathrm{eq}})^{1/2}\mathcal{D}_{\alpha\beta}$$

Single Phonon Mode Relaxation Time Approximation (RTA)

$$\mathcal{D} \approx \begin{bmatrix} \gamma_1 & 0 & 0 & \dots & 0 \\ 0 & \gamma_2 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \gamma_N \end{bmatrix} \Longleftrightarrow \mathcal{D}^{-1} \approx \begin{bmatrix} \tau_1 & 0 & 0 & \dots & 0 \\ 0 & \tau_2 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & \tau_N \end{bmatrix}$$

Phonon Mode-Mode Correlation Functions

$$c_{\alpha\beta}(t) = \sum_{\lambda=1}^{N} e^{-\gamma_\lambda t} u_{\lambda,\alpha} u_{\lambda,\beta}$$

with $c_{\alpha\beta}(t=0) = \sum_{\lambda=1}^{N} u_{\lambda,\alpha} u_{\lambda,\beta} = \delta_{\alpha\beta}$.

$$c_{\alpha\beta}(t) = \int_0^\infty d\gamma\, \chi_{\alpha\beta}(\gamma) e^{-\gamma t}$$

Two-phonon time-correlation functions:: self v.s. cross

III. Fokker-Planck Equation for Lattice Vibration – OU condition

$$\langle \delta n_\alpha(0)\delta n_\beta(0)\delta n_\mu(0)\delta n_\nu(t)\rangle_{\mathrm{eq}} = (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha}u_{\lambda',\beta}u_{\lambda'',\mu}u_{\lambda''',\nu}) \cdot \langle x_\lambda(0)\cdot x_{\lambda'}(0)\cdot x_{\lambda''}(0)\cdot x_{\lambda'''}(t)\rangle_{\mathrm{eq}}$$

$$= (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot [\delta_{\alpha\mu}c_{\beta\nu}(t) + \delta_{\beta\mu}c_{\alpha\nu}(t) + \delta_{\alpha\beta}c_{\mu\nu}(t)], \quad (32)$$

$$\langle \delta n_\alpha(0)\delta n_\beta(t)\delta n_\mu(t)\delta n_\nu(t)\rangle_{\mathrm{eq}} = (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha}u_{\lambda',\beta}u_{\lambda'',\mu}u_{\lambda''',\nu}) \cdot \langle x_\lambda(0)\cdot x_{\lambda'}(t)\cdot x_{\lambda''}(t)\cdot x_{\lambda'''}(t)\rangle_{\mathrm{eq}}$$

$$= (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot [\delta_{\mu\nu}c_{\alpha\beta}(t) + \delta_{\beta\nu}c_{\alpha\mu}(t) + \delta_{\beta\mu}c_{\alpha\nu}(t)], \quad (33)$$

$$\langle \delta n_\alpha(0)\delta n_\beta(0)\delta n_\mu(t)\delta n_\nu(t)\rangle_{\mathrm{eq}} = (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot \sum_{\lambda\lambda'\lambda''\lambda'''} (u_{\lambda,\alpha}u_{\lambda',\beta}u_{\lambda'',\mu}u_{\lambda''',\nu}) \cdot \langle x_\lambda(0)\cdot x_{\lambda'}(0)\cdot x_{\lambda''}(t)\cdot x_{\lambda'''}(t)\rangle_{\mathrm{eq}}$$

$$= (\Delta_{\alpha,\mathrm{eq}}\Delta_{\beta,\mathrm{eq}}\Delta_{\mu,\mathrm{eq}}\Delta_{\nu,\mathrm{eq}})^{\frac{1}{2}} \cdot [\delta_{\alpha\beta}\delta_{\mu\nu} + c_{\alpha\mu}(t)\cdot c_{\beta\nu}(t) + c_{\alpha\nu}(t)\cdot c_{\beta\mu}(t)], \quad (34)$$

Multi-phonon time-correlation functions

III. Fokker-Planck Equation for Lattice Vibration – non OU condition

- *A middle ground solution between BTE theory and full GK theory*
- *A unified theory for both weak-and strong mode interactions*
- *A much more numerically more feasible MD algorithm at high T*
- *Complementary to on-going efforts of first-principle heat current calculations*

IV. Summary

- Phonon Boltzmann Transport Equation Theory
  - State-of-the-art
  - Implemented with first-principles DFT method
  - Based on the phonon gas model (PGM) assumption
  - Valid only for crystals, i.e. group velocity defined

- Vibration Fokker-Planck Equation Theory
  - A new paradigm
  - Consistent with the BTE results within PGM
  - Applicable beyond PGM
  - Practical with first-principles implementation
  - Connecting with new experimental measurements?