Fundamentals of Phonon Transport Modeling: Formulation, Implementation, and Applications

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ASME IMECE
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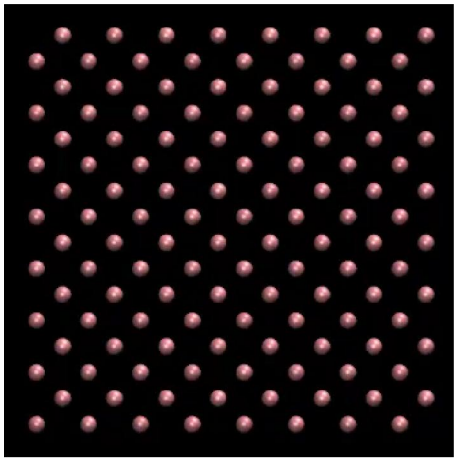
Outline

- Session I (1:30 PM – 3:15 PM)
  1. Introduction (McGaughey)
  2. **MD simulation, Green Kubo, direct method (Ruan)**
  3. Harmonic lattice dynamics, spectral methods (Ruan)

- Session II (3:45 PM – 5:30 PM)
  4. Anharmonic lattice dynamics, first principles (McGaughey)
  5. Phonon-boundary and phonon-defect scattering (McGaughey)
  6. Phonon-electron coupling and non-equilibrium (Ruan)

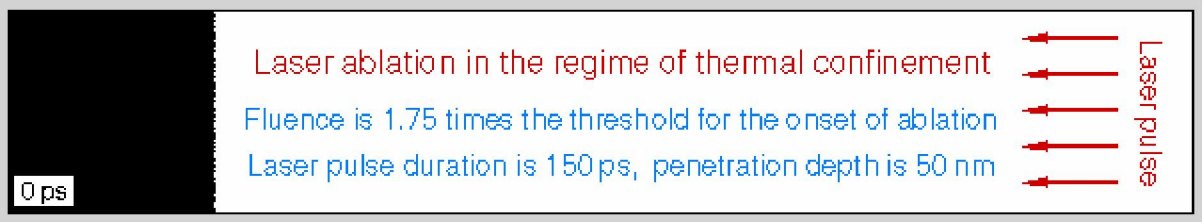
- **2.1 Molecular Dynamics Basics**
- 2.2 The Green-Kubo Method
- 2.3 The Direct Method

Molecular Dynamics Videos



Trajectory of silicon

Motion of protein, Courtesy of Dr. Bert de Groot at Max Planck institute

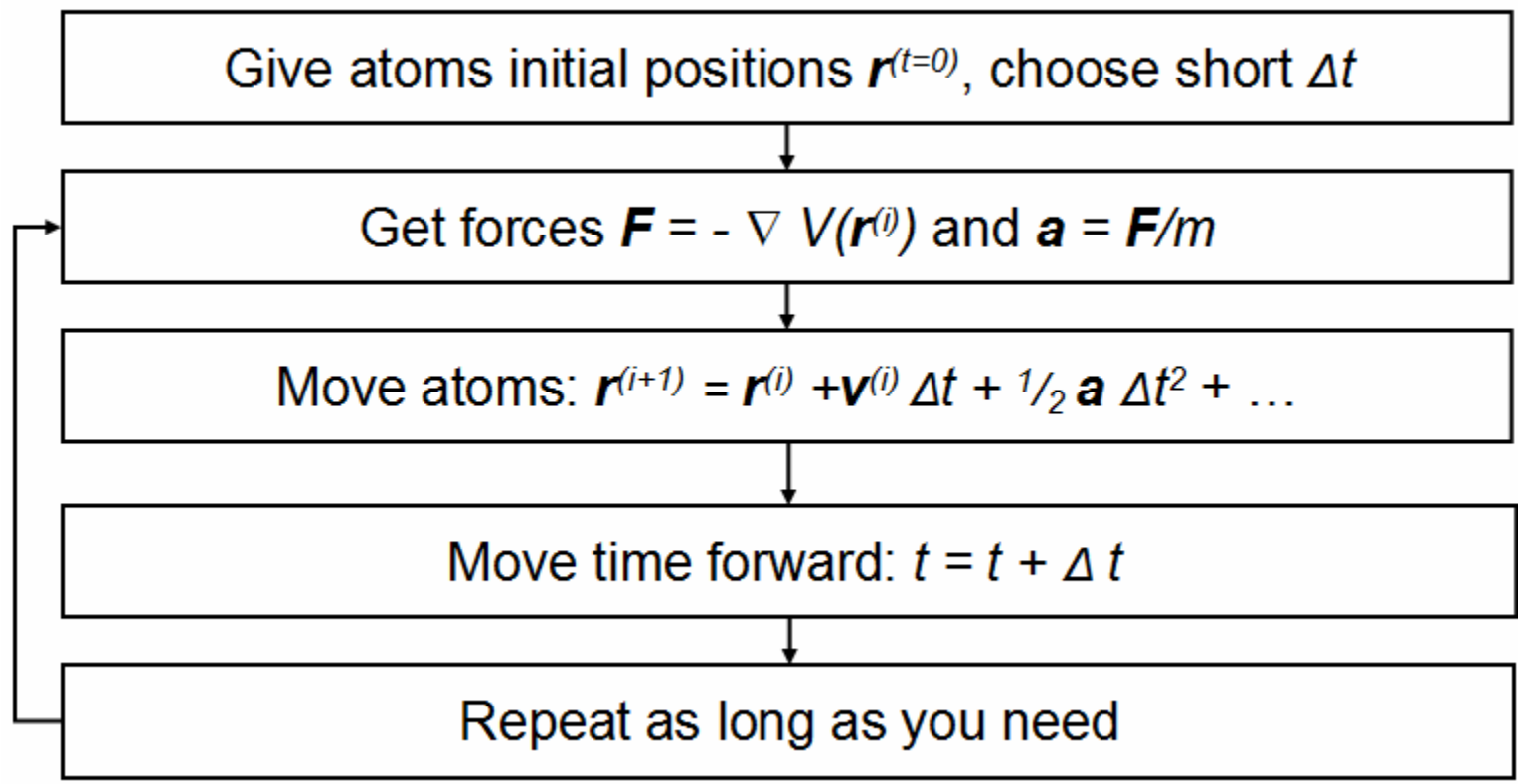


Laser ablation of metals,
Courtesy of Dr. L. V. Zhigilei at University of Virginia.
J. Appl. Phys., 88, 1281-1298 (2000).

Goals of Molecular Dynamics

- MD simulations provide a molecular level picture of structure and dynamics → property/structure relationships
- Experiments often do not provide the molecular level information available from simulations
- Sometimes it is not possible to perform experiments on the problems of interest (extreme pressure, extreme temperature, etc)
- Simulators and experimentalists can have a synergistic relationship, leading to new insights into materials properties.

Basic Algorithm



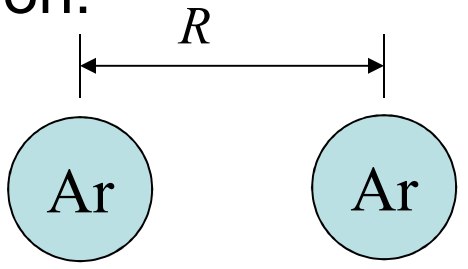
Interatomic Potential

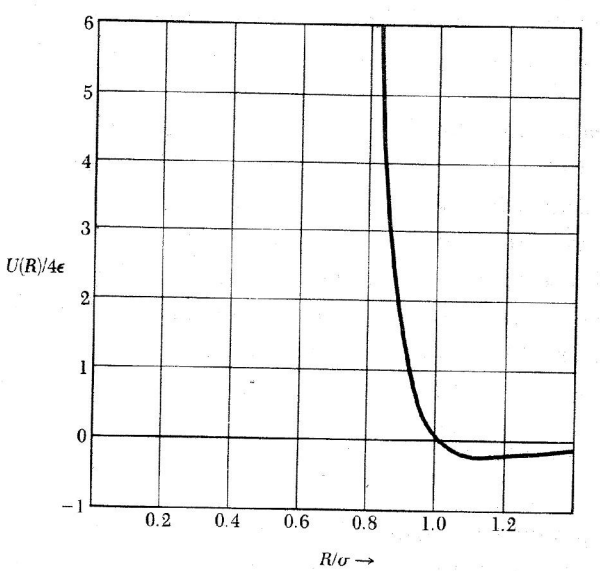
- Lennard-Jones (L-J) potential model for argon:

$$U(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

Repulsive Attractive

where ε and σ are constants
for argon, σ = 3.4 Å, ε = 0.01042 eV





Kittel, Introduction to Solid State Physics.

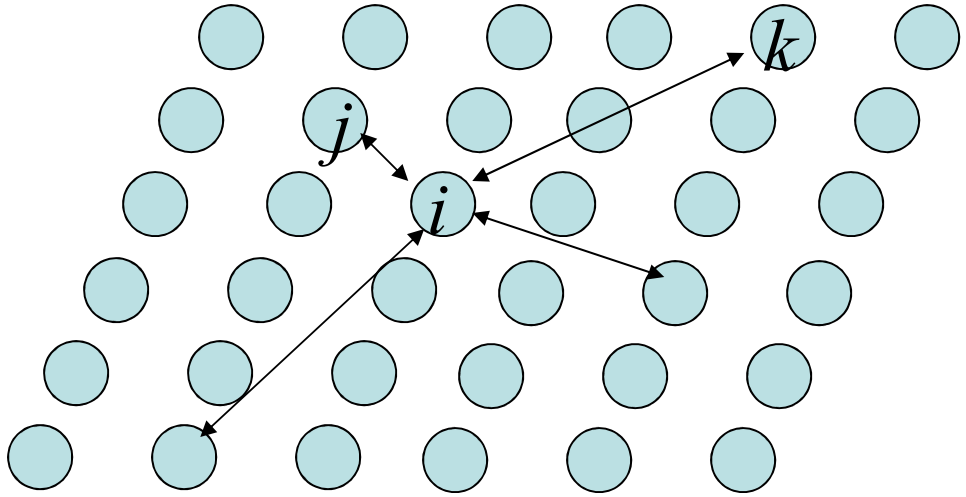
- $U(R) < 0 \quad \text{when} \quad R > \sigma$
- $U(R) > 0 \quad \text{when} \quad R < \sigma$
- $U(R)_{\min} = -\varepsilon \quad \text{at} \quad R = 1.12\sigma$

- Bond energy: ε ~ 0.01 eV (weak): low melting point

Newtonian Mechanics

- Each particle is a point of mass. The potential energy between particle *i* and *j* is

$$U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$$



- The force acted on *i* by *j* is

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_i} U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$$

- The total force acted on particle *i* is

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U_i(\mathbf{r}_i), \text{ where } U_i(\mathbf{r}_i) = \sum_j U_{ij}(\mathbf{r}_i, \mathbf{r}_j)$$

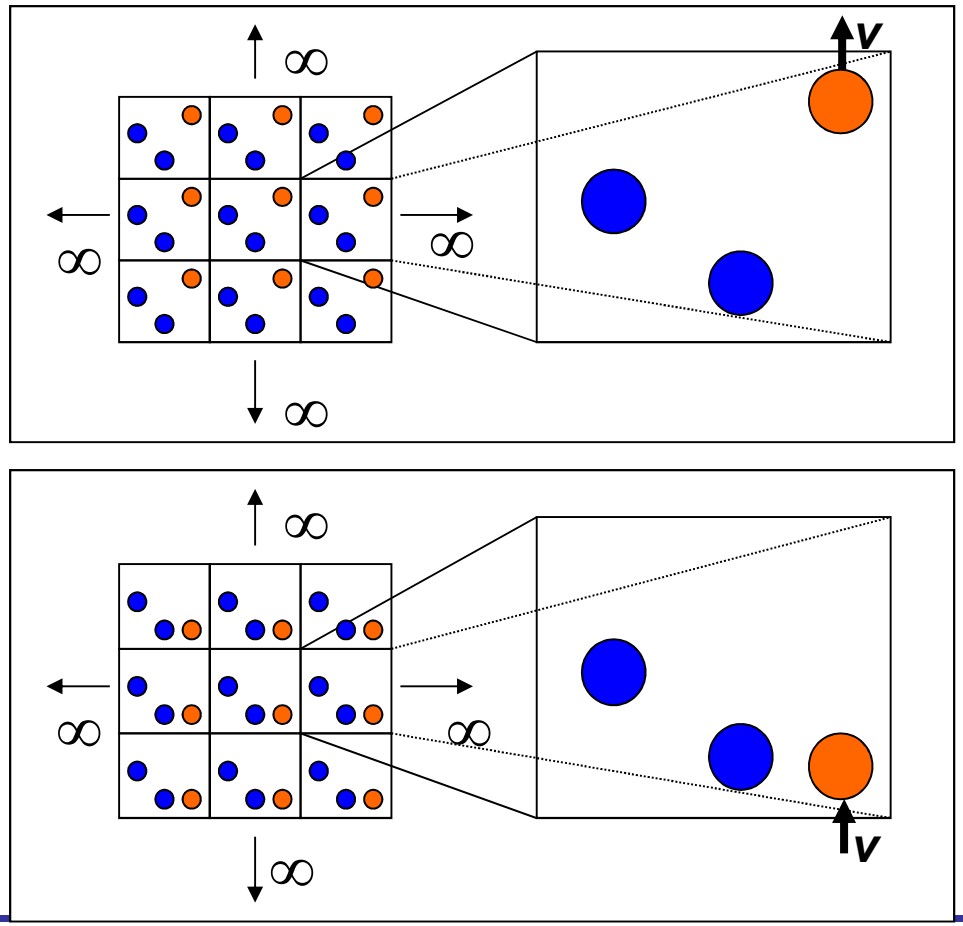
- Equation of motion:

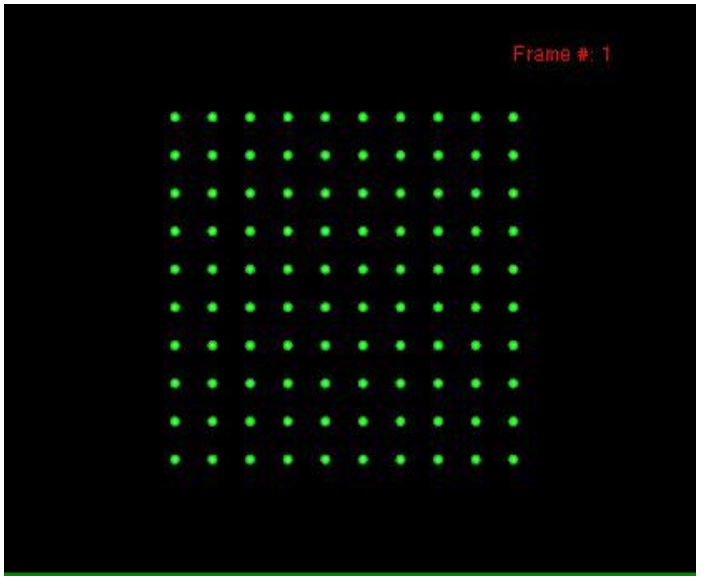
$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i}; \qquad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i$$

  - Need initial and boundary conditions to solve.

Periodic Boundary Conditions

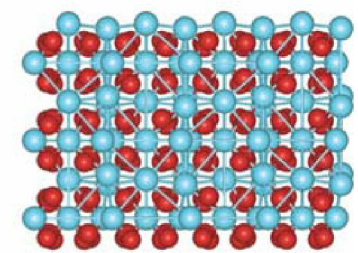
- It is usually not practical to simulate the full size of the real system which consists Avogardo's number of particles. A finite simulation cell is often used with applying periodic boundary conditions.

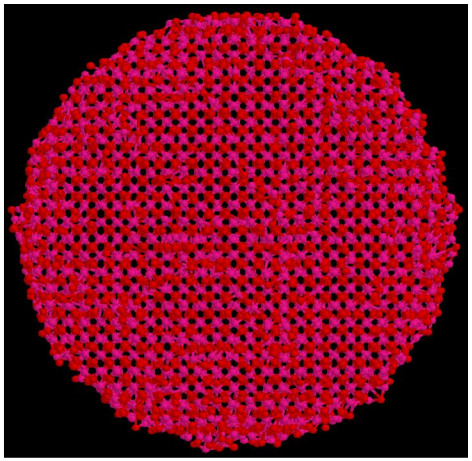


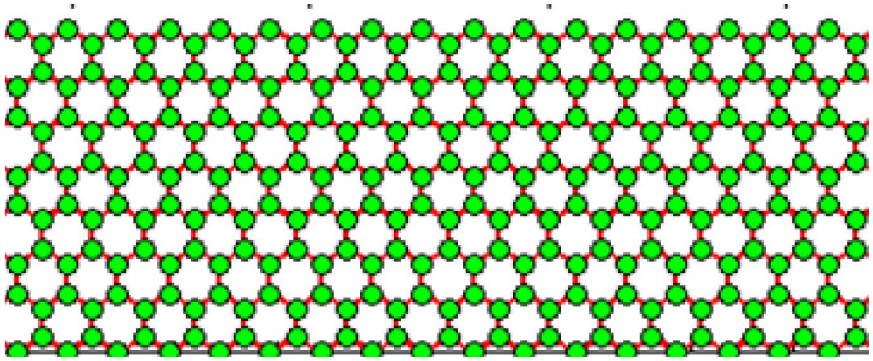


Courtesy of Dr. Sylke Boyd at UMN

Other Boundary Conditions







- Free boundary condition
  - On a free boundary, atoms lose their outer neighbors, and the forces are from their inner neighbors.
  - Surface reconstruction
  - Appropriate for the confined direction of free-standing nanostructures: cross-plane boundary of thin films, radial boundary of nanowires, etc

Integration: Verlet Algorithm

$$\begin{cases} \mathbf{F}_i = -\nabla_{\mathbf{r}_i} U_i(\mathbf{r}_i) \\ \dfrac{d\mathbf{p}_i}{dt} = \mathbf{F}_i \qquad , i = 1, 2, \ldots N \\ \dfrac{d\mathbf{r}_i}{dt} = \dfrac{\mathbf{p}_i}{m_i} \end{cases}$$

- Taylor expansion:

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \frac{\partial \mathbf{r}_i(t)}{\partial t}\Delta t + \frac{1}{2}\frac{\partial^2 \mathbf{r}_i(t)}{\partial t^2}(\Delta t)^2 + O\left[(\Delta t)^3\right]$$

$$= \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)(\Delta t)^2 + O\left[(\Delta t)^3\right]$$

$$= \mathbf{r}_i(t) + \left[\mathbf{v}_i(t) + \frac{1}{2}\mathbf{a}_i(t)\Delta t\right]\Delta t + O\left[(\Delta t)^3\right]$$

$$= \mathbf{r}_i(t) + \frac{\mathbf{p}_i(t+\frac{1}{2}\Delta t)}{m}\Delta t + O\left[(\Delta t)^3\right]$$

$$\mathbf{p}_i(t+\frac{1}{2}\Delta t) = \mathbf{p}_i(t-\frac{1}{2}\Delta t) + \frac{\partial \mathbf{p}_i(t-\frac{1}{2}\Delta t)}{\partial t}\Delta t + \frac{1}{2}\frac{\partial^2 \mathbf{p}_i(t-\frac{1}{2}\Delta t)}{\partial t^2}(\Delta t)^2 + O\left[(\Delta t)^3\right]$$

$$= \mathbf{p}_i(t-\frac{1}{2}\Delta t) + \mathbf{F}_i(t)\Delta t + O\left[(\Delta t)^3\right]$$

Implementation

- Start with initial positions and velocities of atoms
- Force

$$\mathbf{F}_i(t) = -\sum_{j \neq i} \frac{\partial \phi\left[r_{ij}(t)\right]}{\partial r_{ij}(t)} \hat{\mathbf{r}}_{ij}(t)$$

- Update momentum

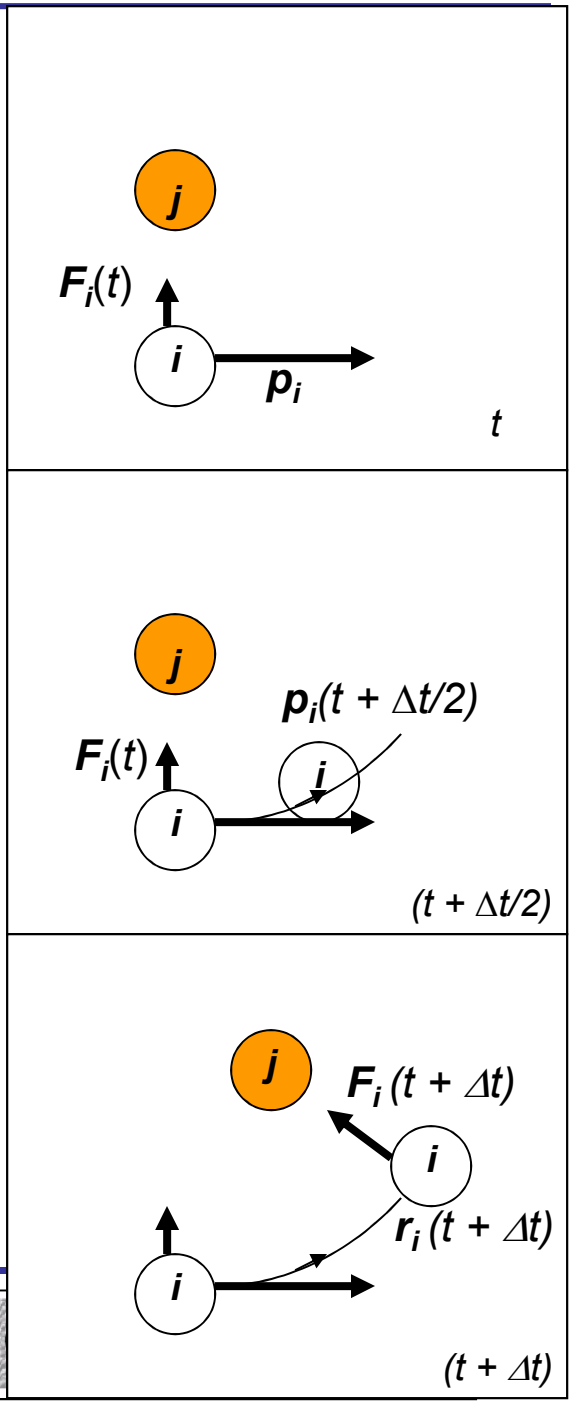
$$\mathbf{p}_i(t + \Delta t/2) = \mathbf{p}_i(t - \Delta t/2) + \mathbf{F}_i \Delta t$$

- Update position

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{\mathbf{p}_i(t + \Delta t/2)}{m_i} \Delta t$$

- Update force

$$\mathbf{F}_i(t + \Delta t) = -\sum_{j \neq i} \frac{\partial \phi\left[r_{ij}(t + \Delta t)\right]}{\partial r_{ij}(t + \Delta t)} \hat{\mathbf{r}}_{ij}(t + \Delta t)$$



Other Important Settings for MD

- Time step
  - One order of magnitude smaller than the period of the highest-frequency vibrational mode - lattice dynamics calculation is useful beforehand!
  - Typically can be in the order of 1-5 fs for common materials.

- Temperature control: scale the velocities

$$\frac{1}{2}\sum_i m_i v_i^2 = \frac{3}{2} N k_B T \;\Rightarrow\; T = \frac{1}{3Nk_B}\sum_i m_i v_i^2$$

  - Thermostats: Noose Hoover, Langevin, etc

- Initial positions: equilibrium lattice structure at *T*
- Initial velocities: small and random velocities, zero net momentum

- 2.1 Molecular Dynamics Basics
- **2.2 The Green-Kubo Method**
- 2.3 The Direct Method

Thermal Conductivity Calculation Methods

- Equilibrium method: no temperature gradient needed
  - Using the fluctuation-dissipation signal of the system
  - Domain size effect is easier to handle

- Non-equilibrium method: non-zero temperature gradient
  - Fourier Law

$$q'' = -k\frac{dT}{dx}$$

  - Approach 1: Apply a constant temperature gradient and calculate the resulted heat current
  - Approach 2: Apply a constant heat flux and calculate the resulted temperature gradient
  - Domain size effect is more significant.

Equilibrium (Green-Kubo) Method

M. S. Green, J. Chem. Phys. **22**, 398 (1954).
R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).

- The heat current vector is given by

$$\mathbf{S} = \frac{d}{dt}\sum_i \mathbf{r}_i E_i = \frac{d}{dt}\sum_i \mathbf{r}_i \left(E_{k,i} + E_{p,i}\right)$$

- For a pair potential, such as the LJ potential, the expression can be recast as:

$$\mathbf{S} = \sum_i E_i \mathbf{v}_i + \frac{1}{2}\sum_{i,j}\left(\mathbf{F}_{ij}\cdot\mathbf{v}_i\right)\mathbf{r}_{ij}$$

  - where **v** is the velocity vector of a particle, and $\boldsymbol{r}_{ij}$ and $\boldsymbol{F}_{ij}$ are the inter-particle separation vector and force vector between particles *i* and *j*.

- For multi-body potentials, see: Zheyong Fan et al., PRB 92, 094301 (2015).

Heat Current Autocorrelation Function and k

- In general, for anisotropic systems:

$$k_x = \frac{1}{k_B T^2 V}\int_0^\infty \left\langle S_x(t)\cdot S_x(0)\right\rangle dt$$

$$k_y = \frac{1}{k_B T^2 V}\int_0^\infty \left\langle S_y(t)\cdot S_y(0)\right\rangle dt$$

$$k_z = \frac{1}{k_B T^2 V}\int_0^\infty \left\langle S_z(t)\cdot S_z(0)\right\rangle dt$$

- For isotropic system,

$$k = \frac{k_x + k_y + k_z}{3} = \frac{1}{k_B T^2 V}\int_0^\infty \frac{\left\langle \mathbf{S}(t)\cdot \mathbf{S}(0)\right\rangle}{3} dt$$

$$= \frac{1}{k_B T^2 V}\int_0^\infty \frac{\left\langle S_x(t)\cdot S_x(0) + S_y(t)\cdot S_y(0) + S_z(t)\cdot S_z(0)\right\rangle}{3} dt$$

Ensemble Average

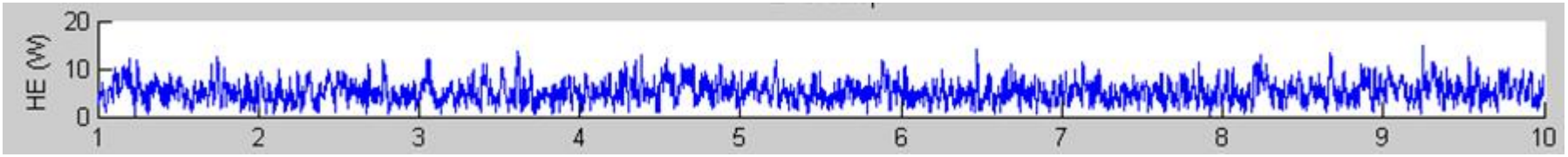
- The heat current autocorrelation function is

$$AC(t) = \frac{\langle \mathbf{S}(t) \cdot \mathbf{S}(0) \rangle}{3}$$

  - Where $\langle \mathbf{S}(t) \cdot \mathbf{S}(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \mathbf{S}(t_0 + t) \cdot \mathbf{S}(t_0) dt_0$

- Implementation:

$$\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \mathbf{S}(t_0 + t) \cdot \mathbf{S}(t_0) dt_0 = \frac{1}{N} \sum_{j=0}^{N-1} \mathbf{S}(j\Delta t + t) \cdot \mathbf{S}(j\Delta t)$$

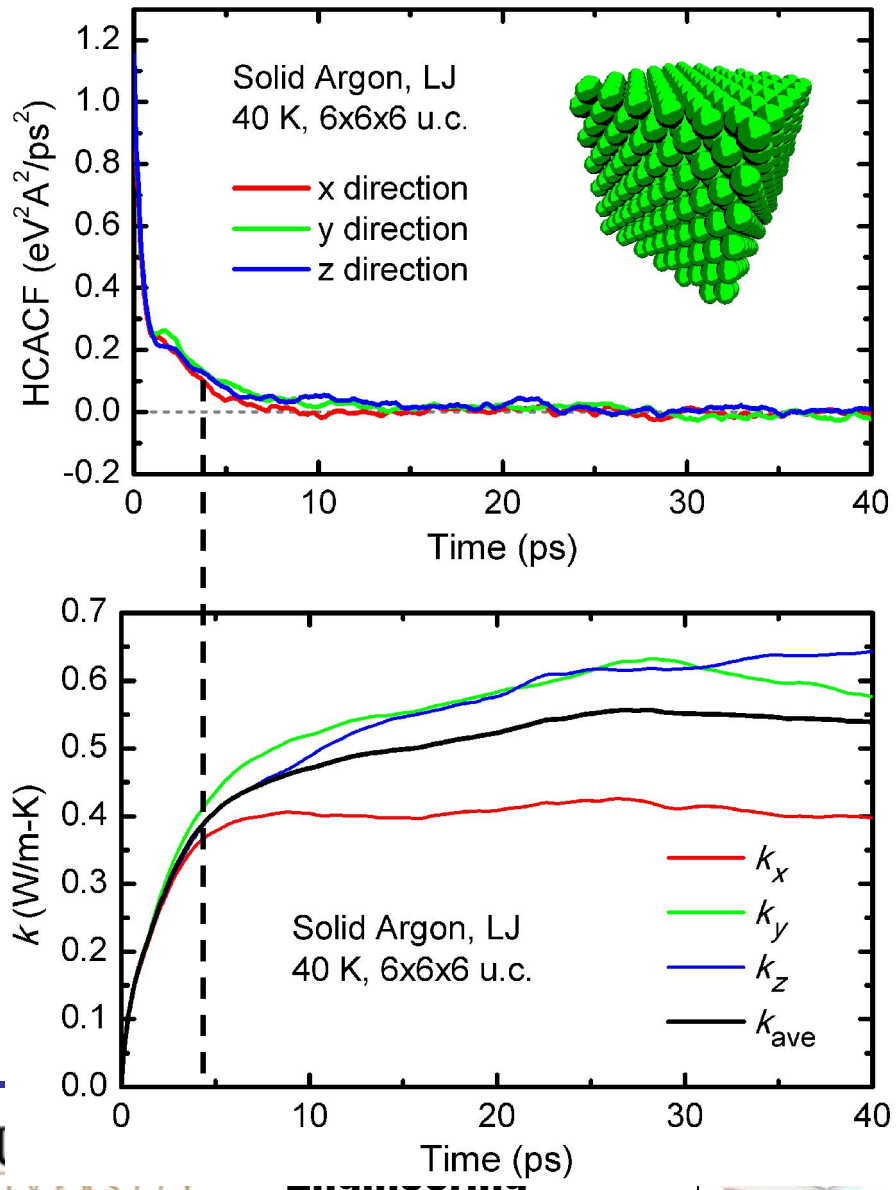


$\mathbf{S}(t) \cdot \mathbf{S}(0)$ (t)

$\mathbf{S}(\Delta t + t) \cdot \mathbf{S}(\Delta t)$

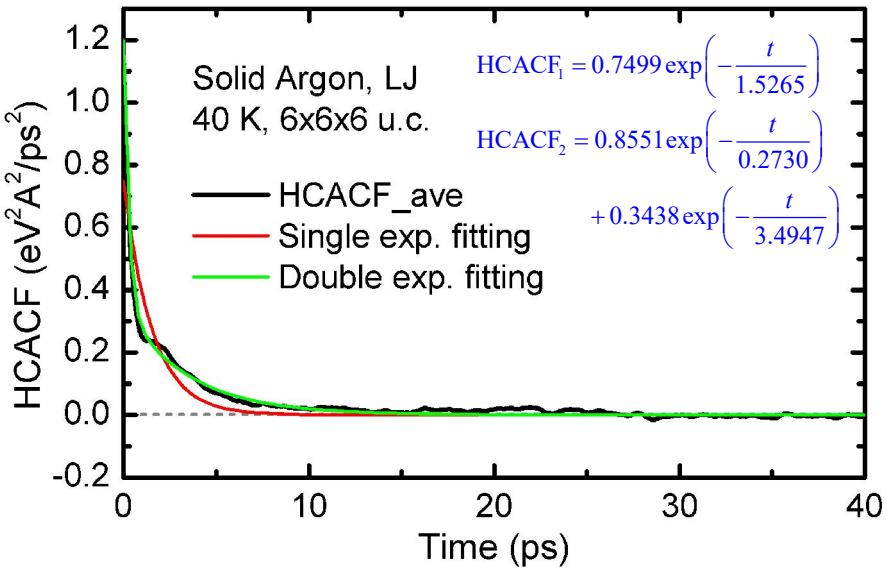
$\mathbf{S}(2\Delta t + t) \cdot \mathbf{S}(2\Delta t)$

EMD on Solid Argon



- Settings:
  - Lennard-Jones potential
  - T = 40 K
  - Domain size: 6x6x6 unit cells
  - Time step: 4 fs
  - *NPT*: 0.4 ns; *NVE*: 4 ns
  - Max. correlation time: 40 ps
- Thermal conductivity:
  - k_x = 0.398 W/m-K
  - k_y = 0.575 W/m-K
  - k_z = 0.642 W/m-K
  - k_{ave} = 0.538 W/m-K
  - (k_{exp} = 0.56 W/m-K) (Touloukian *et al.*, 1970)
- Repeat multiple times to reduce statistical errors

Exponential fitting of the HCACF



- Single exponential fitting:

$$k = \frac{1}{k_B V T^2}\int_0^\infty AC(t)dt$$

$$= \frac{1}{k_B V T^2}\int_0^\infty AC(t=0)\exp\left(-\frac{t}{\tau}\right)dt$$

$$= \frac{1}{k_B V T^2} AC(t=0)\tau$$

$$= 0.385 \text{ W/m-K}$$

- Double exponential fitting:

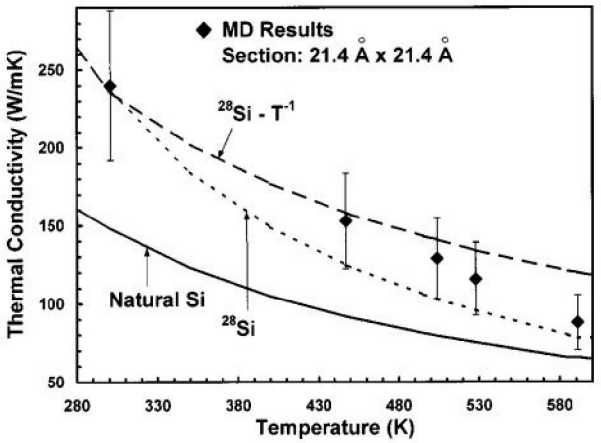
$$k = \frac{1}{k_B V T^2}\left(AC_1\tau_1 + AC_2\tau_2\right)$$

$$= 0.482 \text{ W/m-K}$$

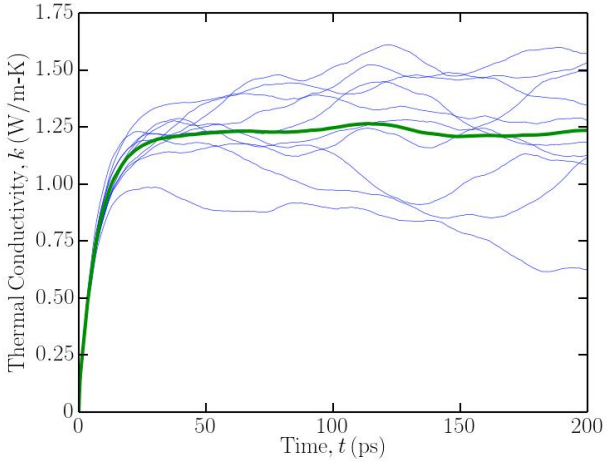
- Here τ's are the vibrational coherence times, or the effective phonon relaxation times.

Applications of GK-MD in calculating *k*

SW Si



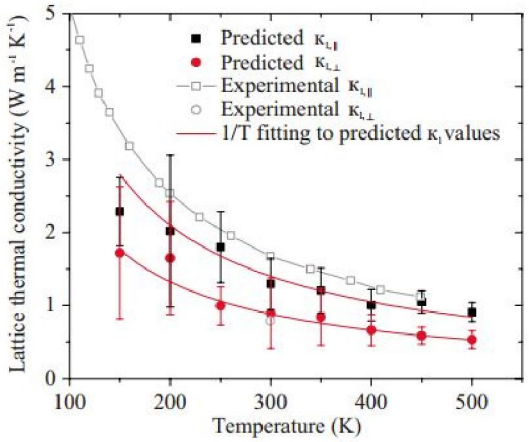
S. G. Volz and G. Chen,
Phys. Rev. B **61**, 2651 (2000).



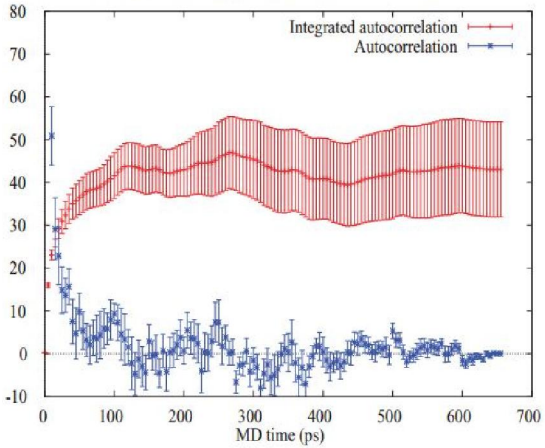
LJ Ar

McGaughey and Kaviany, IJHMT
47, 1783 (2004)

Morse Bi_2Te_3



B. Qiu and X. Ruan,
Phys. Rev. B **80**, 165203 (2009).

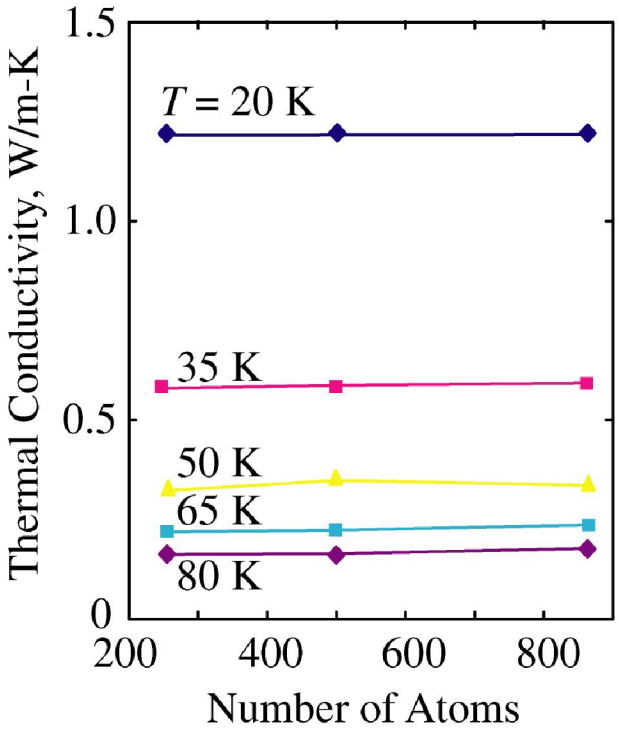


SW Si

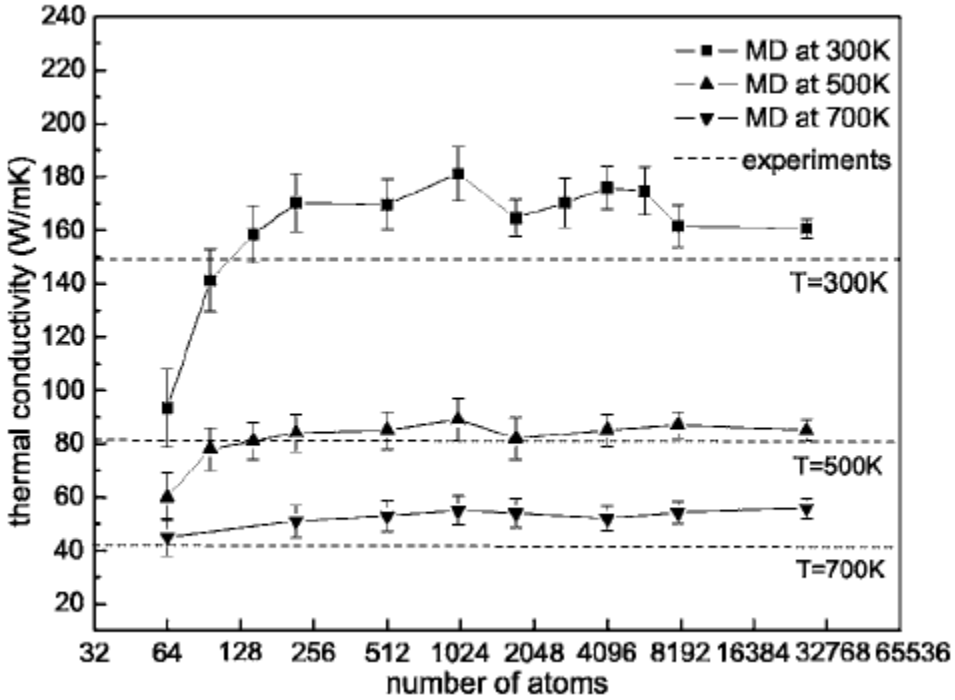
K. Esfarjani, G. Chen, and H. T. Stokes,
Phys. Rev. B **84**, 085204 (2011).

Simulation Domain Size Effect

- The equilibrium (Green-Kubo) method do not usually show significant size effect – periodic boundary conditions helps.



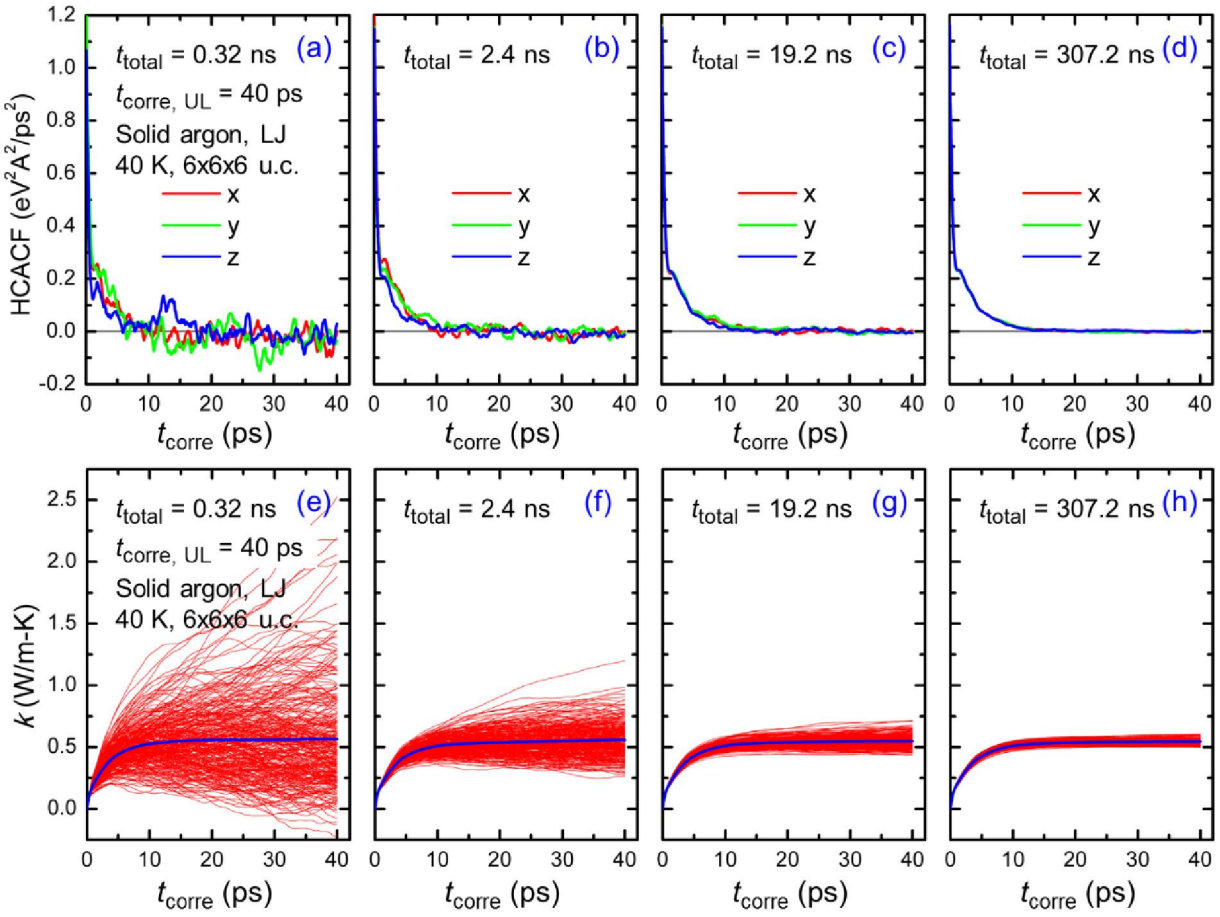
LJ Argon
McGaughey and Kaviany, *PRB* **71**, 184305 (2004)



Silicon

L. Sun and J.Y. Murthy, Appl. Phys. Lett. 89, 171719 (2006).

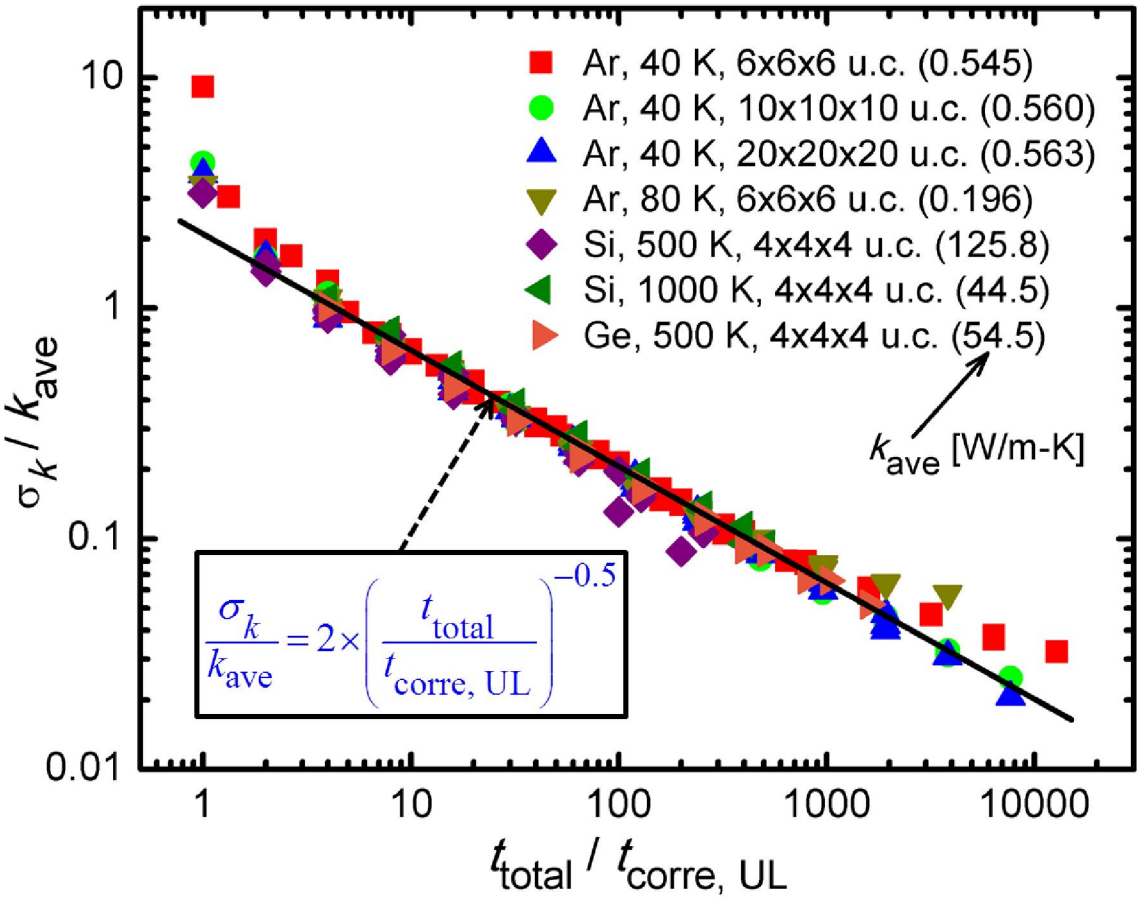
Uncertainty: HCACF and *k* Distributions of Ar



Z.Y. Wang and X.L. Ruan, "Uncertainty quantification of thermal conductivities from equilibrium molecular dynamics simulations", paper IMECE2016-68083. Also submitted to journal publication.

- $t_{corre, UL}$ >> $\tau_{p, eff}$ for a good integration. Here 40 ps is sufficient.
- As t_{total} increases, the HCACF and k profiles start to converge.

A Universal Relation of the Uncertainty



Z.Y. Wang and X.L. Ruan, "Uncertainty quantification of thermal conductivities from equilibrium molecular dynamics simulations", paper IMECE2016-68083. Also submitted to journal publication.

- A universal relation of the relative uncertainty
- A long t_{total} and short $t_{corre,UL}$ will decrease σ_k/k_{ave}. However, a physical constrain is that $t_{corre,\,UL} >> \tau_{p,\,eff}$

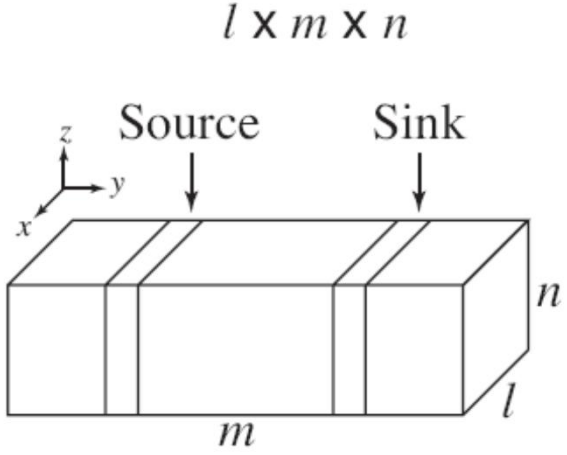
- 2.1 Molecular Dynamics Basics
- 2.2 The Green-Kubo Method
- **2.3 The Direct Method**

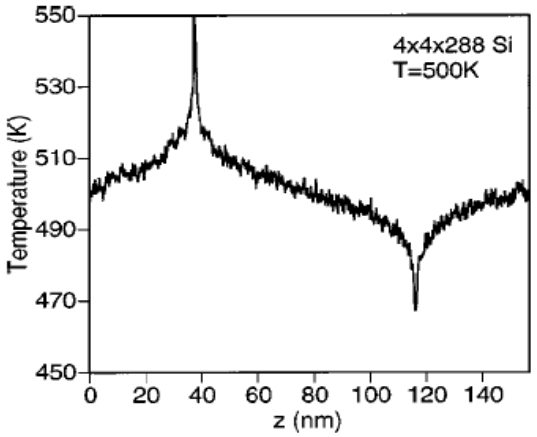
Direct Method

- Approach 1: The temperatures of heat source and sink are controlled using thermostats. The heat flux is calculated using

$$q'' = \frac{1}{A}\frac{\sum_{j=1}^{n}\Delta E_j}{j\cdot\Delta t}, \text{ where } \Delta E_j = \frac{1}{2}\sum_{i=1}^{N} m_i\left(v_{i,new}^2 - v_{i,old}^2\right)$$

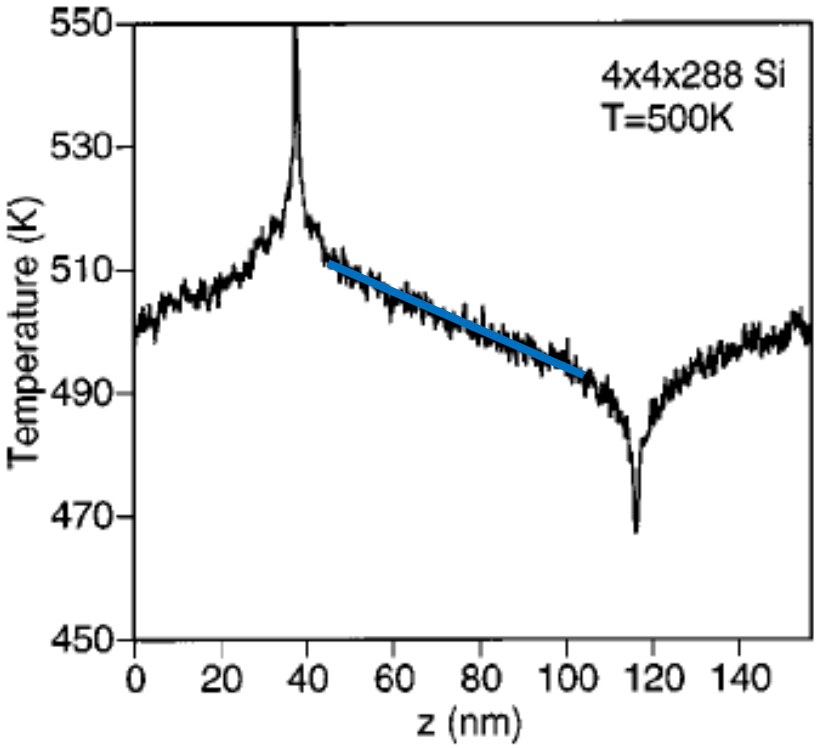
- Approach 2: The heat flux is controlled using velocity scaling, and the resulted temperature gradient is calculated from MD.



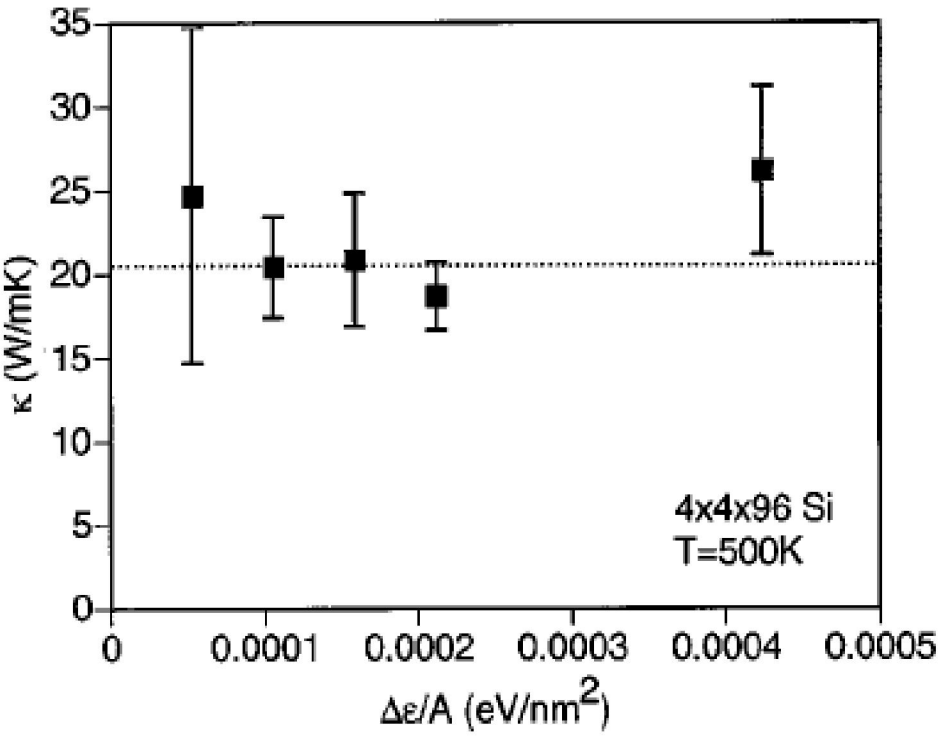


Schelling, Phillpot, and Keblinski, *PRB* 65, 144306 (2002).

A Few Things to Check



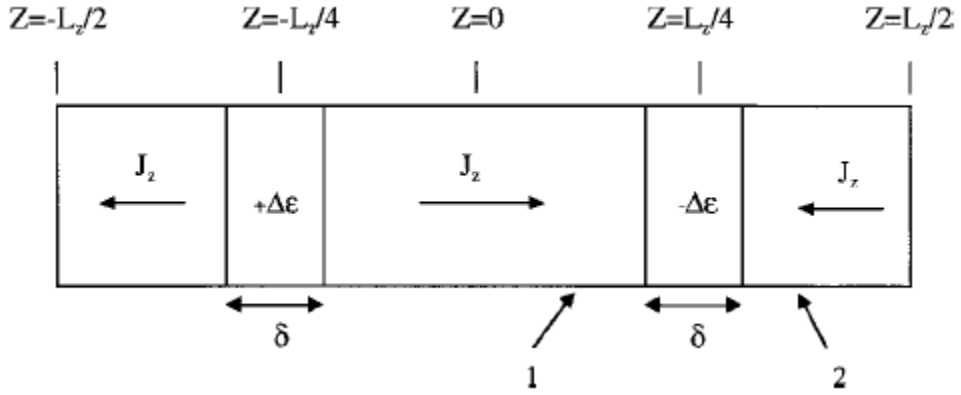
Linear temperature fitting



effects of $\Delta\varepsilon$

P.K. Schelling, S.R. Phillpot, and P. Keblinski, Physical Review B 65, 144306 (2002).

Domain Size Effect of NEMD



- Domain size effects arise when the length of the simulation domain is not significantly longer than the phonon mean-free path.

- Casimir limit: because the atomic dynamics in the hot and cold slabs is altered by the simulation algorithm, the mean-free-path is limited by the size of the system.

P.K. Schelling, S.R. Phillpot, and P. Keblinski, Physical Review B 65, 144306 (2002).

Extrapolation Technique

- The effective mean free path λ_{MD} of the MD system is

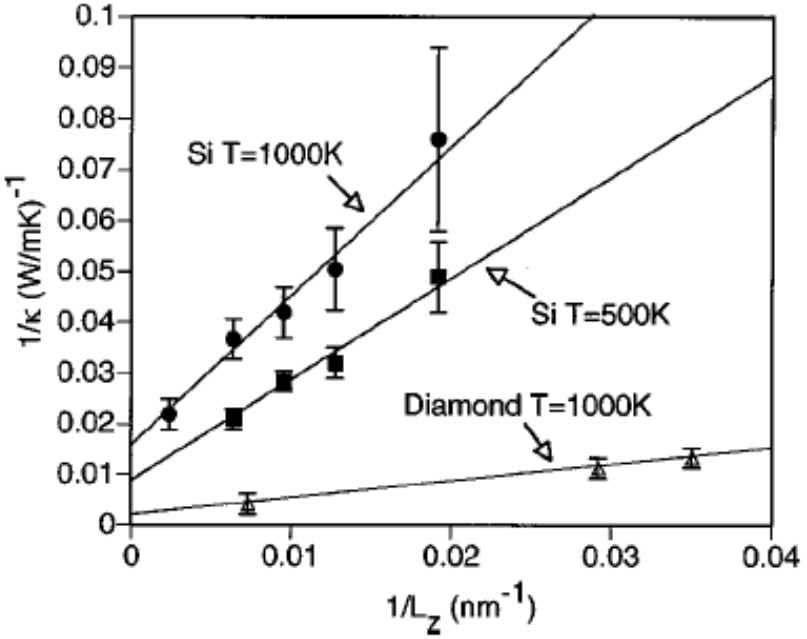
$$\frac{1}{\lambda_{MD}} = \frac{1}{\lambda_\infty} + \frac{1}{L/4} = \frac{1}{\lambda_\infty} + \frac{4}{L}$$

  - λ_∞: intrinsic phonon mean free path of the bulk material
  - L: simulation cell length

- The thermal conductivity

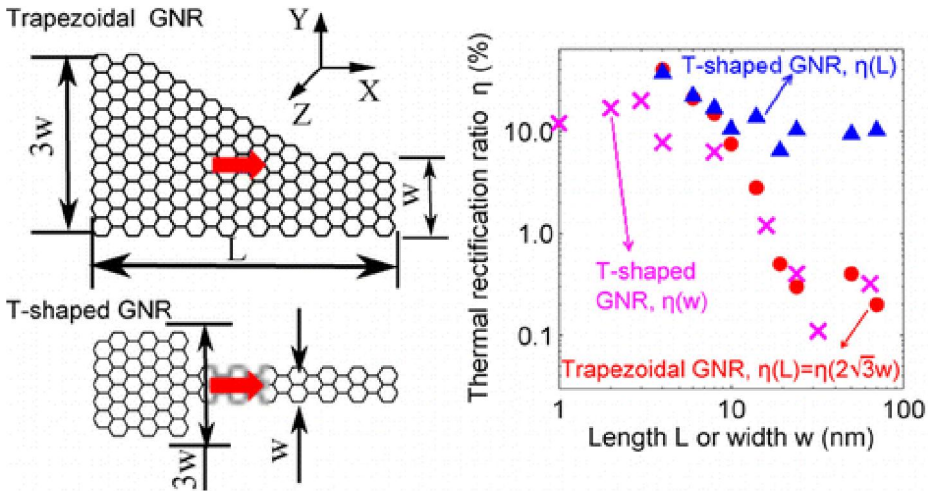
$$\frac{1}{k_{MD}} \propto \frac{1}{\lambda_{MD}} = \frac{1}{\lambda_\infty} + \frac{4}{L}$$

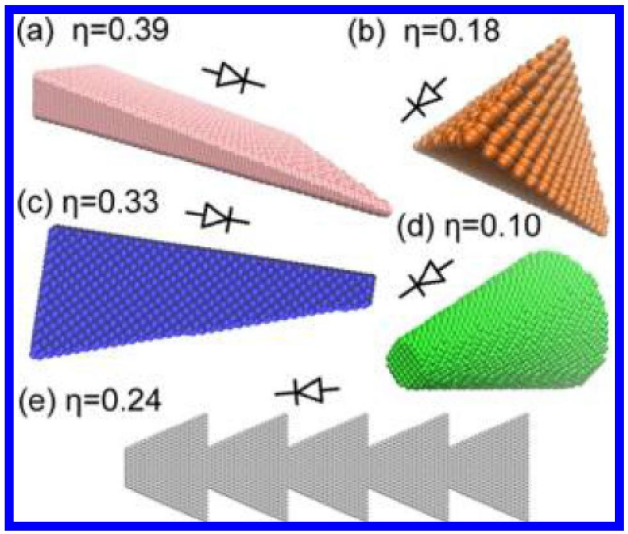
- Plot 1/k v.s. 1/L, the interception gives k for the bulk material.



P.K. Schelling, S.R. Phillpot, and P. Keblinski, Physical Review B 65, 144306 (2002).

Thermal Rectification in Asymmetric Structures





- For TR to occur in single materials:
  - Asymmetric in geometry
  - **Lateral size smaller than the phonon mean free path**

Wang, Vallabhaneni, Hu, Qiu, Chen, and Ruan, *Nano Lett.* **14**, 592 (2014).

Remarks

- Advantages of MD:
  - Real space behavior – intuitive
  - Easy to perform (LAMMPS)
  - Can handle complicated structures: defects, boundary, interface, roughness, etc

- Disadvantages of MD:
  - Classical nature (take caution when simulating below the Debye T)
  - Interatomic potentials are only available for a small fraction of materials, high quality potentials are even rarer.

- Opportunities:
  - Simulate larger-size systems: coarse grain MD?
  - Develop high quality potentials for new materials
  - Ab initio MD, tight-binding MD

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