Molecular Dynamics for Thermal Transport Simulations in Solid Materials

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Brief Introduction to Molecular Dynamics

Molecular Dynamics (MD) Overview

- Computational technique that models
 - Physical properties of materials
 - Dynamical behavior of materials
- Basis: classical mechanics of interacting particles that comprise the material

• Can treat vapor, liquid, solid phases

• The focus of this talk will be solids



Liquid



Solid (FCC crystal structure)

How Does It Work?

- Compute trajectories of each particle in the system
- Required inputs:

NOTE: atoms, not phonons, are tracked in MD

- Initial positions (crystal structure), initial velocities (temperature)
- System evolution:
 - Interatomic potential function ("spring") gives force
 - Position is determined from force, velocity, and previous position

Displacements in video scaled by 100



Potential Energy of the System

• Most general (multibody) form:

$$\phi = \sum_{i} v_1(r_i) + \sum_{i} \sum_{j>i} v_2(r_i, r_j) + \sum_{i} \sum_{j>i} \sum_{k>j>i} v_3(r_i, r_j, r_k) + \dots$$
external field term pair potential term three-body potential term terms

 Often the potential energy is treated as two-body or three-body in form, with other terms neglected



Where Do the Potential Functions Come From?

- The functional forms of v_2 and v_3 are empirical or semi-empirical
- Fitted to experimental property measurements or first principles simulation data
- Potentials have been developed for many materials
- Multiple potentials may exist for a given material
 - Example: over 30 different potentials for silicon! (Stillinger-Weber, Tersoff, EDIP, MEAM, ...)
 - Different potentials arise from fitting to different properties or applying different functional forms
 - No single potential function replicates all physical properties well



Common Intermolecular Potentials

- Two-Body
 - Lennard-Jones
 - Argon model system
- Three-Body
 - Stillinger-Weber
 - Silicon, germanium, carbon (group IV)



Lennard-Jones Argon Potential

- Often used in MD for preliminary, qualitative studies of material behavior
- Advantages
 - Agreement with experimental data
 - Simple two-body form:

$$\phi(r_{ij}) = 4\varepsilon \left\{ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right\}$$



Physically meaningful parameters



Equations of Motion (Two-Body Potential)

Force
$$f_{ij_n} = -\frac{d\phi(r_{ij_n})}{dr_{ij_n}}$$
 $F_{i_n} = \sum_j f_{ij_n}, \ j \neq i$

velocity Verlet algorithm

Velocity
$$v_{1/2} = v_{i_o} + \frac{1}{2} \frac{F_{i_o}}{m_i} \Delta t$$
 $v_{i_n} = v_{1/2} + \frac{1}{2} \frac{F_{i_n}}{m_i} \Delta t$

Position
$$r_{i_n} = r_{i_o} + v_{i_o}\Delta t + \frac{1}{2}\frac{F_{i_o}}{m_i}(\Delta t)^2$$

Other integration algorithms are also used such as Gear 5th order, Runge-Kutta, etc. Usually explicit integration is performed due to time savings



More Things to Note

- $1 \,\mu\text{m}^{3} \leftrightarrow 10$ billion atoms!
- Limited to short length scales
 - Max. 10s-100s of nm
- Short time steps required for stability of algorithm
 - Max. 100s of ns
 - Time step should be < 0.1*vibrational period of 'spring' (~ 1fs in solids)



Maximum wavelength

- Results are influenced by boundary conditions and size effects
 - Periodic BC: unphysical cutoff of long wavelength phonons
 - Non-periodic BC: physically meaningful confinement



Thermal Property Calculations with Molecular Dynamics

Calculation of Temperature Profile

- Kinetic temperature is calculated via equipartition
 - Equate kinetic energy to $3/2 k_B T$

$$\mathcal{T}(t) = \sum_{i=1}^{N} m_i(t) v_i^2(t) / 3Nk_B$$

• Temperature is time average of kinetic temperature

$$T = \left\langle T(t) \right\rangle$$

• Temperature can be computed in local regions to obtain temperature distribution







Checking Local Thermodynamic Equilibrium

x,y,z velocity component distributions plotted against Maxwell distribution



Averaging for longer time and over larger numbers of atoms → local kinetic temperature approaches local thermodynamic equilibrium



Thermal Conductivity Calculation Methods

- Equilibrium MD (Green-Kubo method*)
- Direct Nonequilibrium MD
- Homogeneous Nonequilibrium MD (Evans method**)



Equilibrium MD (Green-Kubo method*)

• Compute and store heat current (J)

$$\vec{J} = \sum_{i} \varepsilon_{i} \vec{v}_{i} + \frac{1}{2} \sum_{i} \sum_{j} \left(\vec{F}_{ij} \cdot \vec{v}_{i} \right) \vec{r}_{ij} \qquad \qquad \vec{q}'' = \vec{J} / V$$

Integrate heat current (J) autocorrelation

$$\kappa_{\alpha\beta} = \frac{1}{Vk_B T^2} \int_0^\infty \left\langle J_\alpha(t) J_\beta(0) \right\rangle dt$$





Test Case: (10,10) Single Wall Carbon Nanotube



http://www.photon.t.u-tokyo.ac.jp/~maruyama/agallery/nanotubes/1010vib.gif

REBO potential*

$$E_{pot} = \sum_{i} \sum_{j>i} u_B(r_{ij}) = \sum_{i} \sum_{j>i} \left[V_R(r_{ij}) - \overline{B_{ij}} V_A(r_{ij}) \right]$$

• 1 fs time step



* Brenner, J. Phys.: Condens. Matter 14, pp. 783-802, 2002.

Thermal Conductivity vs. Length and Temperature



- Thermal conductivity increases with nanotube length. Why?
 - More long wavelength modes are supported
- EMD conductivity decreases with increasing temperature--trend does not match experiments! Why?
 - MD is purely classical. Only valid at high temperature



Boundary Condition Effect



Free boundary reduces heat current autocorrelation

Effect of Compressive Strain



1% axial compression \rightarrow ~ 50% κ enhancement at 300K



Effect of Potential





Direct Nonequilibrium MD

- Compute local time averaged temperatures
- Compute temperature gradient and use Fourier law to obtain thermal conductivity

$$\kappa_{\alpha} = -\frac{\vec{q}_{\alpha}''}{\left(dT/dx_{\alpha}\right)}$$







Nonequilibrium MD Temperature Profiles



Homogeneous Nonequilibrium MD*

- Perturb equilibrium equations of motion
 - Add terms containing a perturbation (F_e) to the force calculation
- Compute the heat current as before
- Take the long-time average of heat current and take the limit ${\rm F_e} \to 0$ to obtain macroscopic thermal conductivity

$$k_{\alpha} = \lim_{\overrightarrow{F_e} \to 0} \lim_{t \to \infty} \frac{\langle J_{\alpha}(\overrightarrow{F_e}, t) \rangle}{F_e T V}$$



*Evans, *Phys. Lett.*, 91A, 457-60, 1982.

HNEMD Equilibration Time





Thermal Conductivity Dependence on Perturbation

- Extrapolate to Fe = 0 to get thermal conductivity
- Values depend on curve fit:
 - exp(-x) gives listed values
- Significant questions remain about this method





Density of States is not directly needed for thermal conductivity calculation

$$D(\omega) = \int dt e^{-i\omega t} < \stackrel{\rightarrow}{v(t)} \stackrel{\rightarrow}{\bullet} \stackrel{\rightarrow}{v(0)} >$$



Phonon Density of States



- Low frequency vibrational peaks found for tubes with free boundaries
- Similar low frequency modes for small particles with free surfaces found by Dickey and Paskin (*Phys. Rev. B*, 1, 851-7, 1970)

Thermal Boundary Resistance Calculation Methods

- Two methods:
 - Steady-state
 - Transient
- Case of interest: carbon nanotube thermal coupling



Modeling Approach

- Simulate two overlapping parallel (10,10) SWNT in a temperature gradient using molecular dynamics
 - Bonded interactions: REBO*
 - Nonbonded interactions: Lennard-Jones



Find thermal resistance at nanotube junction



Steady State Method



q

- Initial temperature 300 K
- Resistance increases w/spacing
- Calculations prohibitive for long tubes

Transient Method

Fitting of MD to transient finite difference solution enables treatment of long tubes



Interfacial Thermal Resistance between Two Tubes

- Four order of magnitude resistance change with intertube spacing
- Comparable to other resistance studies (4 A spacing):
 - Resistance between SWNT and 6 neighbors*: 6.46x10⁻⁸ m²-K/W
 - Water in SWNT*: 13x10⁻⁸ m²-K/W
 - SWNT-SDS in D20 (experiment)**: 8.3x10⁻⁸ m²-K/W





*Maruyama et al., Proc. 1st Intl. Symp. on Micro and Nano Technology, 2004 ³ **Huxtable et al, Nature Materials, 2, 731-4, 2003

Phonon Scattering Phase Function Calculation

Nanoparticles in Alloy

PRL 96, 045901 (2006)

PHYSICAL REVIEW LETTERS

week ending 3 FEBRUARY 2006

Thermal Conductivity Reduction and Thermoelectric Figure of Merit Increase by Embedding Nanoparticles in Crystalline Semiconductors

Woochul Kim,¹ Joshua Zide,² Arthur Gossard,² Dmitri Klenov,² Susanne Stemmer,² Ali Shakouri,³ and Arun Majumdar^{1,4,*}



1-4 nm ErAs nanoparticles + $In_{0.53}Ga_{0.47}As$ alloy = factor of 2 reduction below alloy limit



Question:

How do phonons interact with individual nanoparticles?



Scattering Phase Functions

- Used in acoustics, elasticity, radiation
- Depend on polarization, wavelength, direction, particle shape





Phonon Scattering Phase Functions

- Goal: study dependence of scattering phase function on wavelength, particle configuration
- Use <u>molecular dynamics simulation</u> to calculate scattering phase function





MD realization of nanoparticle



Wave 'Sensing' using 'Detectors'

- Select monitoring points on a spherical surface surrounding the scatterer.
- As the wave moves through, record local atomic velocity and stress fields at these points, then calculate scattered wave heat flux q(r,t) at each point.



half model shown (y <0) 44 x 16 x16 cells



time integral of $q_{scattered}(r,t) \rightarrow phase$ function Φ time and surface integrals of $q_{scattered}(r,t) \rightarrow cross$ section Σ_s

Particle Size Parameter

- ka: size parameter
 - k: wavevector magnitude
 - a: radius (size) of particle
- ka << 1: Rayleigh scattering (small particle/long wavelength)
- ka >> 1: geometric scattering (large particle/small wavelength)

Length measured in units of Lennard-Jones parameter σ



Effect of Scatterer Shape

'Sphere' versus Cube Scatterer shapes are affected by lattice granularity.



Cube-shaped inclusion shows stronger backscatter.





ka=3, k=1/ σ , a = 3σ

Effect of Scatterer Orientation



Incident on apex: Little backscatter. Strong forward (0°) and +/- 45° scattering

Incident on base: Very strong backscatter (-180°) and +/- 135° scattering. Noticeable forward scattering.



Effect of k, with ka Fixed

- Diagonals (colors) represent constant values of ka
- Previous theoretical calculations: all scattering phase functions with the same ka are identical
- Present results disagree
- An additional parameter is needed to quantify scattering phase function



Longitudinal incident wave, spherical scatterer ka = 1.5 (yellow), 2.1 (purple), 3 (blue), 4.2 (orange), 6 (green)



Effect of Roughness



As roughness (kA_{cell}) increases, scattering phase functions transition between specular and diffuse scattering limits



Summary

- Molecular dynamics simulation can provide a rich array of thermal transport information
 - Temperature
 - Thermal conductivity
 - Density of states
 - Thermal boundary resistance
 - Phonon scattering phase functions
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