

2011 NCN Summer School

Part II: Molecular Dynamics simulations of materials

Alejandro Strachan

School of Materials Engineering and Birck Nanotechnology Center
Purdue University

strachan@purdue.edu

What is molecular dynamics?

Follow the dynamics (motion) of all the atoms in your material

Numerically solve classical equations of motion (Newton's):

Approximation

$$\vec{F}_i = m_i \vec{a}_i \quad \text{or} \quad \begin{cases} \dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \\ \dot{\vec{p}}_i = \vec{F}_i \end{cases}$$

Forces on atoms come from the interaction with other atoms:

$$\vec{F}_i = -\nabla_{\vec{r}_i} E(\{\vec{r}_j\})$$

Total potential energy (from QM or interatomic potential)

Approximated
(in almost all cases)

Classical mechanics: Hamilton's picture

William Hamilton reformulation of classical mechanics (1800's)

Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = V(\{r_i(t)\}) + \sum_{i=1}^{3N} \frac{p_i(t)^2}{2m_i} \quad \begin{array}{l} i \text{ denotes atom and Cartesian} \\ \text{component (x, y, or z)} \end{array}$$

Equations of motion can be derived from the Hamiltonian:

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial r_i}$$

- These equations can only be solved analytically for very few cases
- MD solves the dynamics of many atoms (billions in supercomputers)

Classical mechanics: conserved quantities

$$H(\{r_i\}, \{p_i\}) = V(\{r_i(t)\}) + \sum_{i=1}^{3N} \frac{p_i(t)^2}{2m_i}$$

Let's calculate the time derivative of the Hamiltonian:

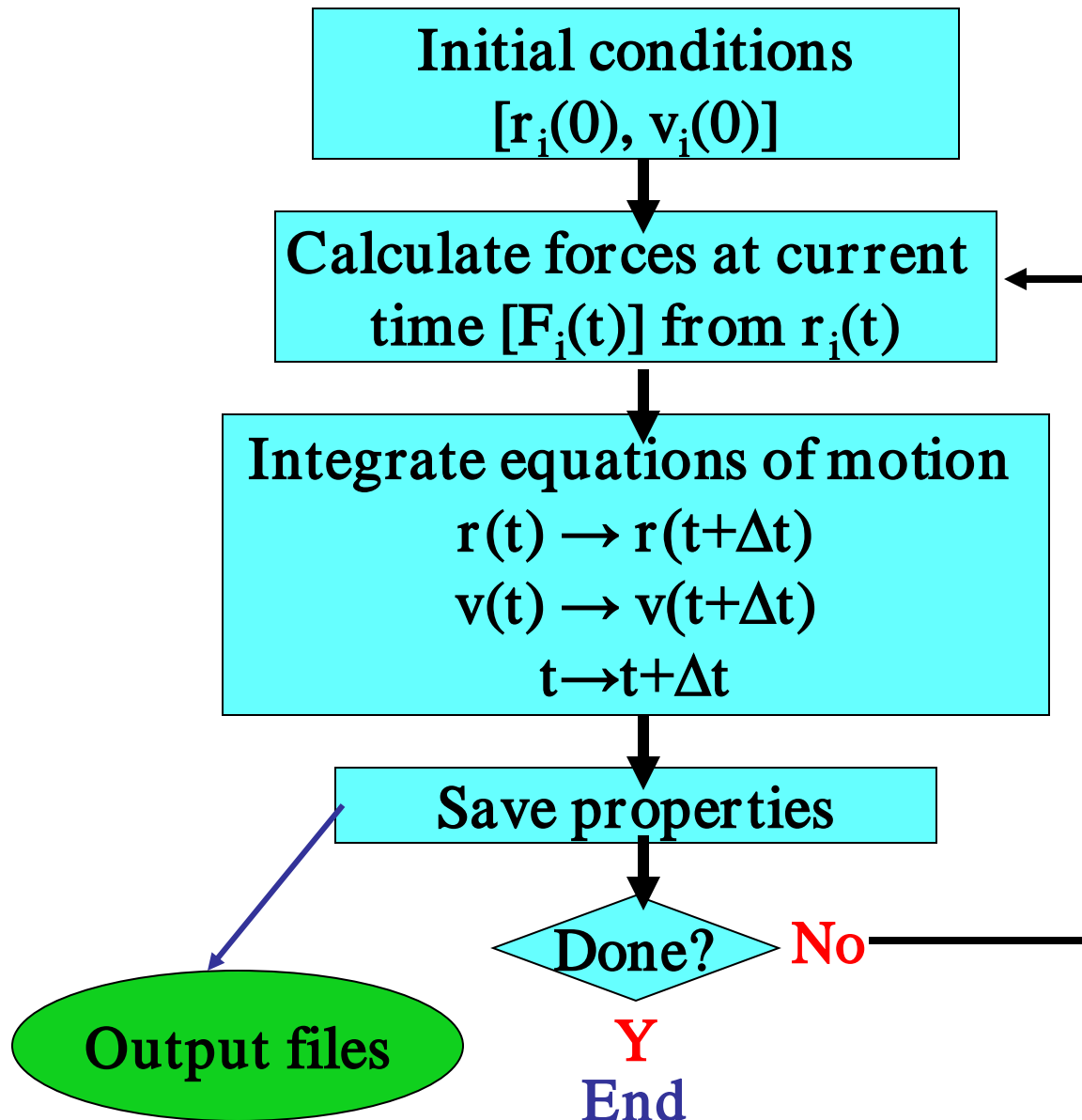
$$\frac{dH}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial r_i} \dot{r}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right)$$

Using the equations of motion we get:

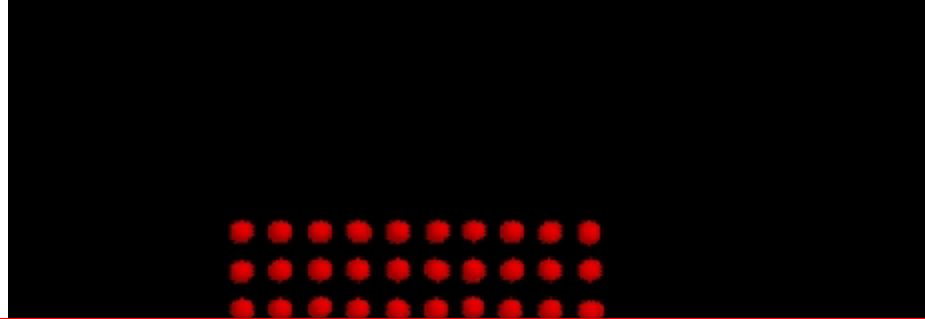
Other constants of motion are:

- Linear momentum:
- Angular momentum:

Structure of a minimalist MD code

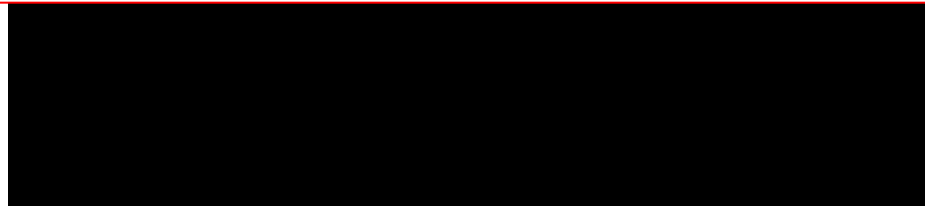


Analysis/interpretation of MD: statistical mechanics



Relate microscopic phenomena and macroscopic properties

- Given a thermodynamic state of a material, what are the probabilities of finding the system in the various possible microscopic states?
- Given a series of microscopic states, what is the corresponding macroscopic state?



Goal: describe concepts that enable relating molecular dynamics with macroscopic (thermo) properties

Various important ensembles

Microcanonical (NVE)

Canonical (NVT)

Isobaric/isothermal (NPT)

Probability distributions

$$P(\{r_i\}, \{p_i\}) = \frac{1}{\Omega(E, V, N)}$$

$$P(\{r_i\}, \{p_i\}) = \frac{e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{Z(T, V, N)}$$

$$P(\{r_i\}, \{p_i\}, V) = \frac{e^{-\frac{1}{kT}[H(\{r_i\}, \{p_i\}) - PV]}}{Z_p(T, P, N)}$$

$$\Omega(E, V, N) = \sum \delta(E - H(\{r_i\}, \{p_i\}))$$

$$Z(T, V, N) = \sum_{micro} e^{-\frac{E}{kT}}$$

$$Z_p(T, P, N) = \sum_V \sum_{micro} e^{-\frac{E - PV}{kT}}$$

(atomistic \leftrightarrow macroscopic thermodynamics)

$$F(T, V, N) = -kT \log Z$$

$$G(T, P, N) = -kT \log Z_p$$



Canonical ens.: equipartition of energy

Consider a variable that appears squared in the Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = \lambda p_1^2 + V(\{r_i(t)\}) + \sum_{i=2}^{3N} \frac{p_i(t)^2}{2m_i} = \lambda p_1^2 + H$$

$$\langle \lambda p_1^2 \rangle = \frac{\int d^{3N} p d^{3N} p \lambda p_1^2 e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{\int d^{3N} p d^{3N} p e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}} = \frac{\int d^{3N} p d^{3N-1} p e^{-\frac{H}{kT}} \int dp_1 \lambda p_1^2 e^{-\frac{\lambda p_1^2}{kT}}}{\int d^{3N} p d^{3N-1} p e^{-\frac{H}{kT}} \int dp_1 e^{-\frac{\lambda p_1^2}{kT}}}$$

Change of variable: $\frac{\lambda p_1^2}{kT} = x^2 \quad dp_1 = \frac{kT}{\lambda} dx$

$$\langle \lambda p_1^2 \rangle = \frac{(kT)^2}{\lambda} \frac{\int dx x^2 e^{-x^2}}{\frac{kT}{\lambda} \int dx e^{-x^2}} = \frac{1}{2} kT$$

Equipartition of energy: Any degree of freedom that appears squared in the Hamiltonian contributes $1/2kT$ of energy

Equipartition of energy: MD temperature

$$\langle K \rangle = \frac{3N}{2} kT$$

In most cases c.m. motion is set to zero at time zero (constant of motion → it remains zero)

$$\langle K \rangle = \frac{3N-3}{2} kT$$

Often angular momentum is zeroed (and remains zero)

$$\langle K \rangle = \frac{3N-6}{2} kT$$

Temperature is related to **average** kinetic energy. Instantaneous temperature:

$$K(t) = \frac{N_{eff}}{2} kT(t)$$

Fluctuations

Fluctuations from equilibrium are also related to materials properties

$$\langle \delta A^2 \rangle = \frac{1}{\tau} \int_0^\tau [A(t) - \langle A \rangle]^2 dt = \langle A^2 \rangle - \langle A \rangle^2$$

Specific heat:

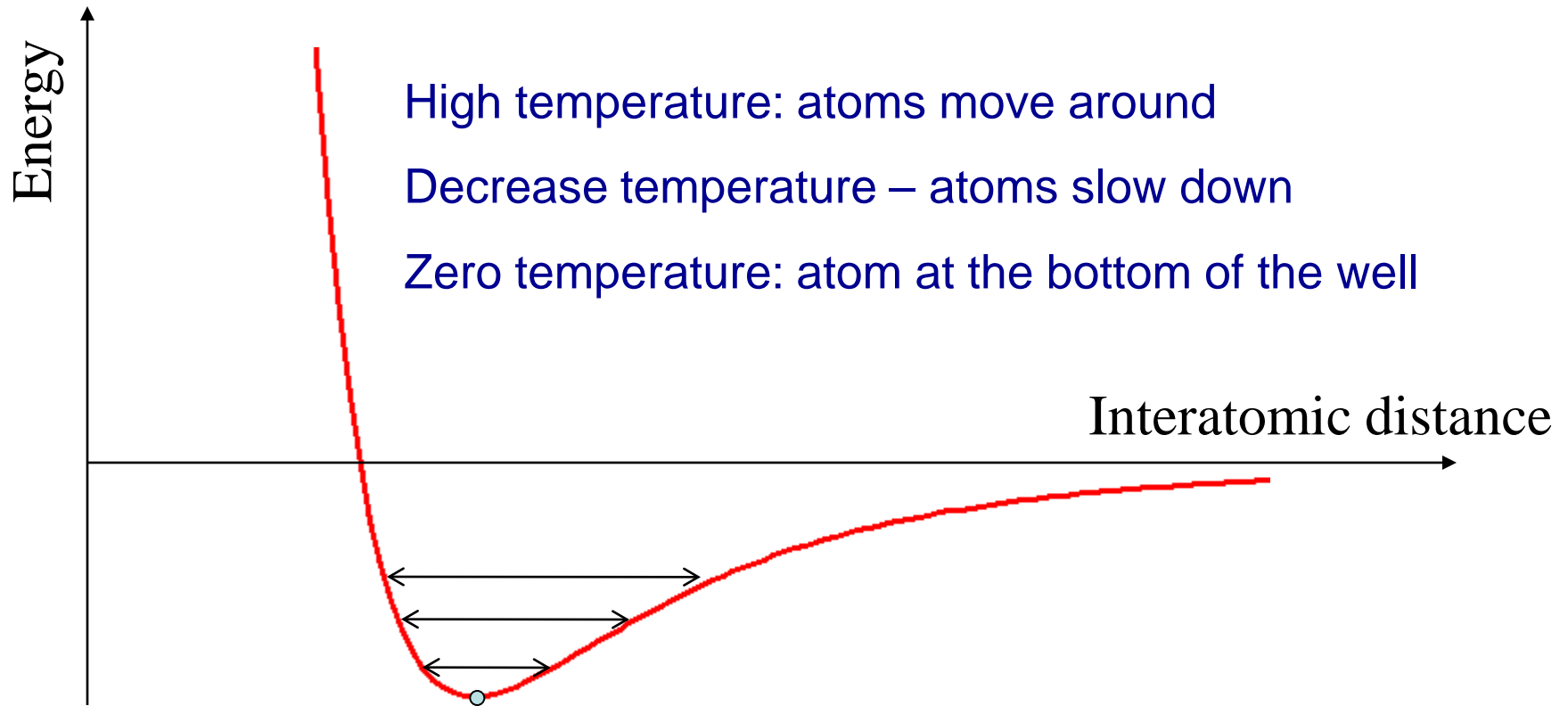
$$C_V = \left. \frac{\partial E}{\partial T} \right|_{NVT} \quad \langle \delta H^2 \rangle_{NVT} = kT^2 C_V$$

Compressibility:

$$\beta_V = \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_{NVT} \quad \langle \delta V^2 \rangle_{NPT} = k \langle V \rangle T \beta_T$$

Quantum effects

When does classical mechanics for atoms stop working?



Temperature at which quantum effects kick in depends on frequency

$kT \gg \hbar\omega$ Classical regime

$kT \sim < \hbar\omega$ Quantum regime

Integrating the equations of motion

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = \vec{F}_i$$

Verlet algorithm: Taylor expansion of positions with time

$$r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 + \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

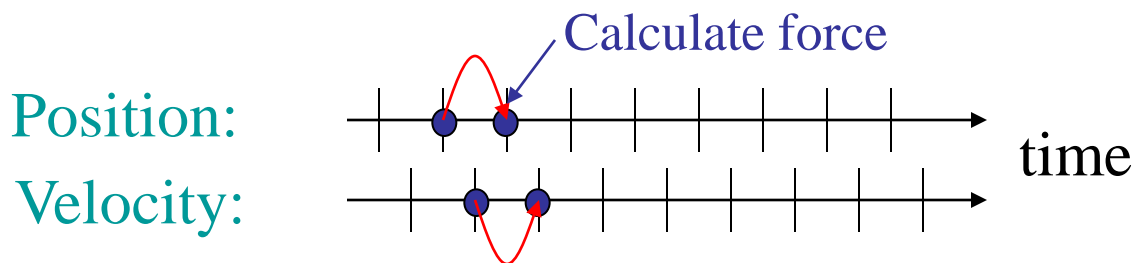
$$r_i(t - \Delta t) = r_i(t) - \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 - \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

Sum two equations:

Verlet algorithm: various equivalent formulations

Velocity Verlet:
$$\begin{cases} p_i\left(t + \frac{1}{2}\Delta t\right) = p_i(t) + \frac{1}{2}F_i(t)\Delta t & \text{Advance } p \text{ half step} \\ r_i(t + \Delta t) = r_i(t) + \frac{p_i\left(t + \frac{1}{2}\Delta t\right)}{m_i}\Delta t & \text{Advance } r \text{ full step} \\ & \text{(with } p \text{ half step ahead)} \\ p_i(t + \Delta t) = p_i\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}F_i(t + \Delta t)\Delta t & \text{Advance } p \text{ half step} \\ & \text{(with } F \text{ at } t + \Delta t) \end{cases}$$

Leap-Frog Verlet:
$$\begin{cases} r_i\left(t + \frac{1}{2}\Delta t\right) = r_i\left(t - \frac{1}{2}\Delta t\right) + v_i(t)\Delta t \\ v_i(t + \Delta t) = v_i(t) + \frac{1}{m_i}F_i\left(t + \frac{1}{2}\Delta t\right) \end{cases}$$



Verlet algorithm: features and advantages

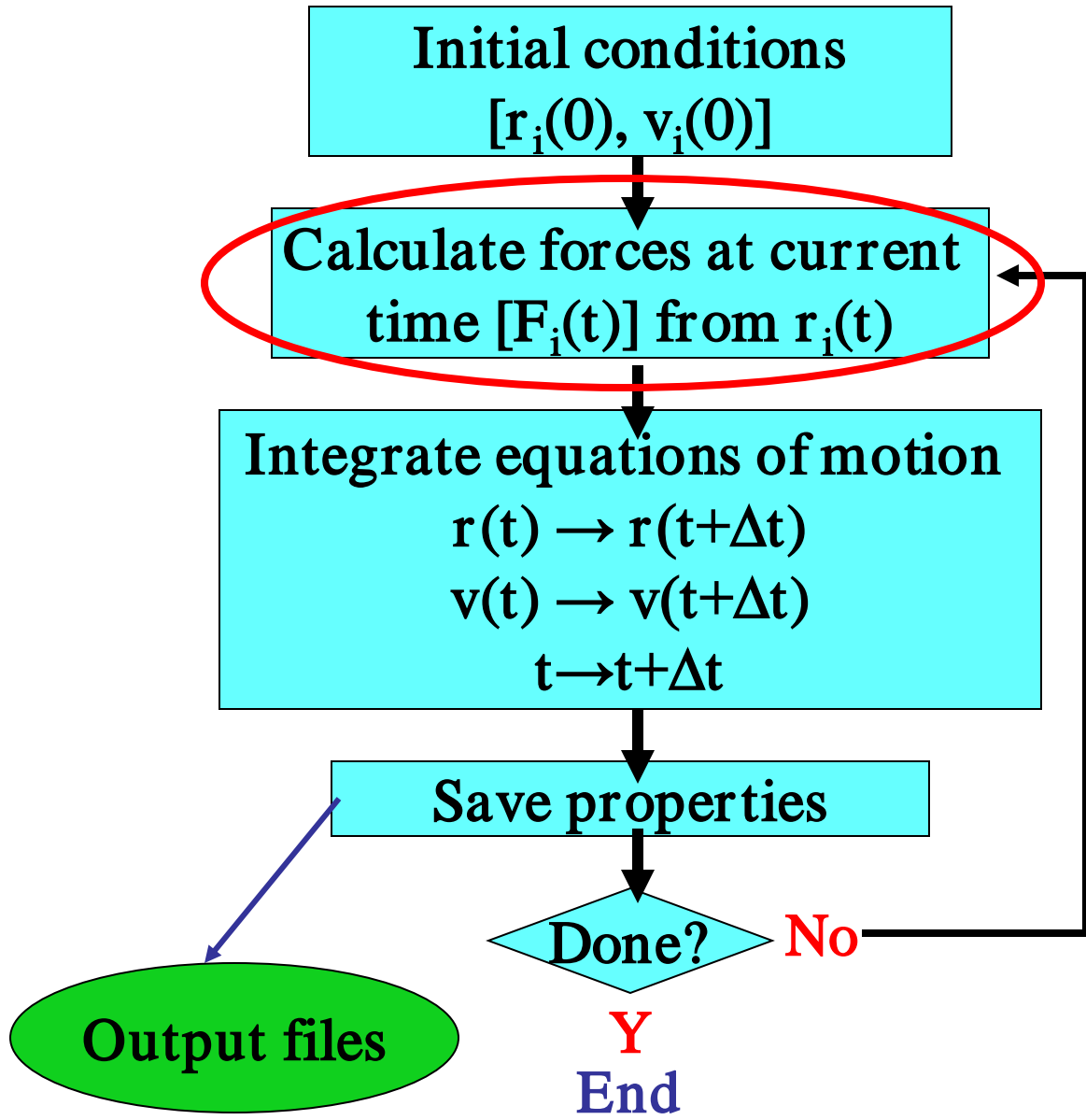
- Exactly time reversible
 - If velocities are reversed at a given time the algorithm traces back its steps
- Symplectic
 - Conserves volume in phase space (as Hamiltonian dynamics does)



- No long-term energy drifts
- The trajectory stays very close to the constant energy hypersurface in phase space

Remember: $S = k \log \Omega(E, V, N)$

How do we calculate atomic forces?



Pair-wise potentials

Simplest, non-trivial, function Sum of pair-wise terms

$$V(\{r_i\}) = \sum_{i < j} \phi(|r_i - r_j|)$$

Lennard-Jones (6-12)

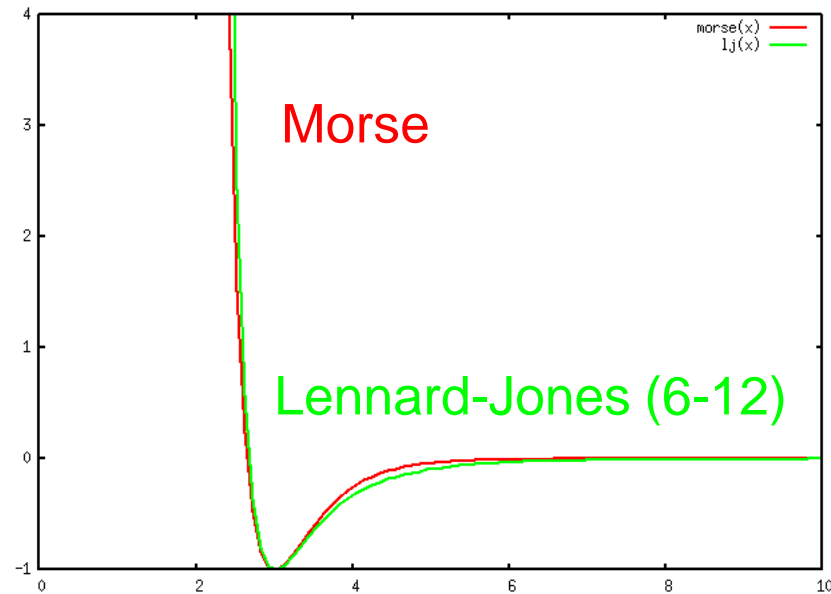
$$\phi_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{Distance \& energy}$$

Exponential-6

$$\phi_{\text{exp-6}}(r) = \varepsilon \left[e^{-\gamma r} - Ar^{-6} \right]$$

Morse

$$\phi_{\text{Morse}}(r) = \varepsilon \left[\exp\left(\gamma \left(1 - \frac{r}{r_0} \right) \right) - 2 \exp\left(\frac{\gamma}{2} \left(1 - \frac{r}{r_0} \right) \right) \right]$$



Distance, energy, & curvature

Two-body potentials: limitations

- Only closed-packed structures (fcc, hcp)
- Vacancy formation \sim cohesive energy
- Metals: $\epsilon_{\text{vac}} \sim 1/3 E_{\text{coh}}$

	E_{coh} (eV)	E_{vac} (eV)	$E_{\text{vac}}/E_{\text{coh}}$
Al	3.39	0.75	0.22
Ni	3.516	1.6	0.46
Cu	3.615	1.2	0.33
Ag	4.086	1.15	0.28
Pt	3.924	1.4	0.36
Au	4.079	0.95	0.23

- Two-body potentials and elastic constants: $c_{12} = c_{44}$
 - Metals: $c_{12} > c_{44}$
 - Pair potentials can only describe simple non-bond interactions
 - Closed-shell atoms (Ne, Ar, Kr, etc.)
 - Atoms that are fully coordinated (e.g. inter-molecular)
 - Pauli repulsion at short distances
 - London dispersion at longer distances
- } van der Waals

Capturing many-body effects in metals

Embedded atom model (EAM)

Mike Baskes and collaborators 1980's + other groups

$$V = \sum_{i < j} \phi(r_{ij}) + \sum_i F(\rho_i)$$

Embedding energy ←

local electronic density at the location of atom i

$\rho_i = \sum_{j \neq i} f(r_{ij})$

Accurate description of:

- Environment dependence of bonding in metals (vacancy and surfaces)
- Elastic constants and plastic deformation
- Phase transformations (melting & solid-solid)
- Alloys

Not very accurate for:

- Cases where bonding is highly directional

Directional bonding in semiconductors

Diamond,
zincblende and
wurtzite structures

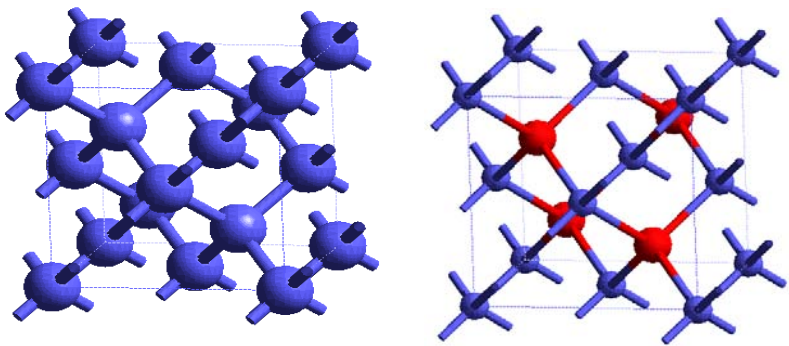
PHYSICAL REVIEW B

VOLUME 31, NUMBER 8

15 APRIL 1985

Computer simulation of local order in condensed phases of silicon

Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)

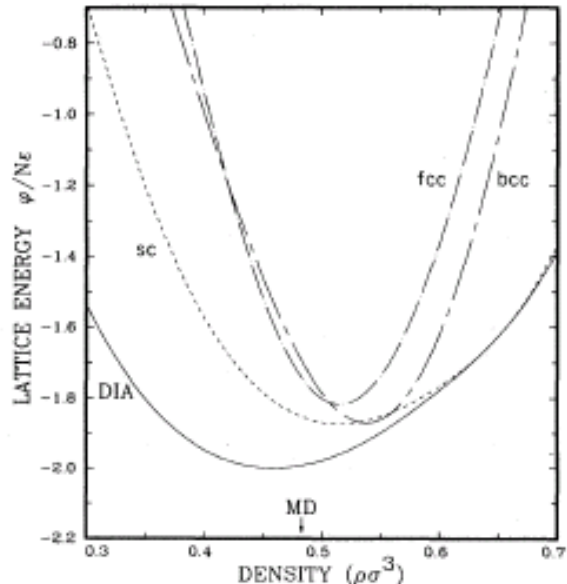


$$V(\{r_i\}) = \sum_{i < j} f_2(r_{ij}) + \sum_{i < j < k} f_3(r_i, r_j, r_k)$$

$$f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases}$$

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}),$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \times (\cos\theta_{jik} + \frac{1}{3})^2;$$



Interatomic potentials for molecular materials

$$V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\})$$

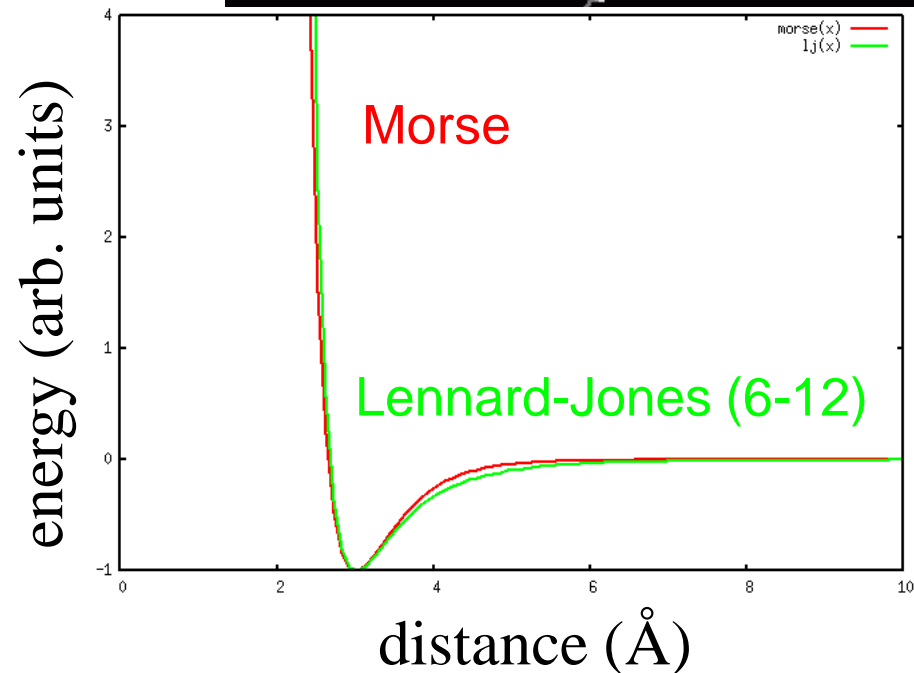
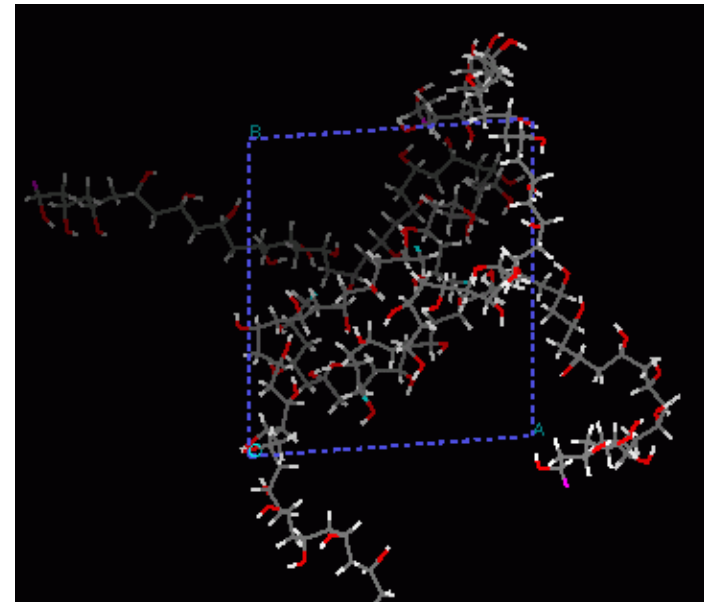


vdW interactions between bonded atoms:

Most molecular potentials use exclusions

No vdW for:

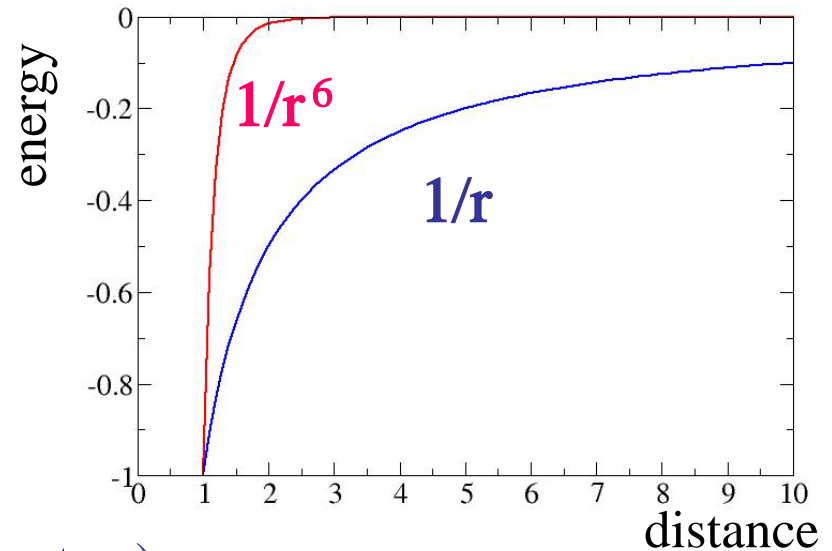
- Bonded atoms
- 1-3 (atoms separated by two covalent bonds)
- 1-4 (atoms separated by three covalent bonds)



Electrostatics & periodic boundary conditions

Coulomb interaction decays
very slowly

$$V_{elec} = C_{unit} \sum_{i < j} \frac{q_i q_j}{r_{ij}}$$



With periodic boundary conditions (infinite system):

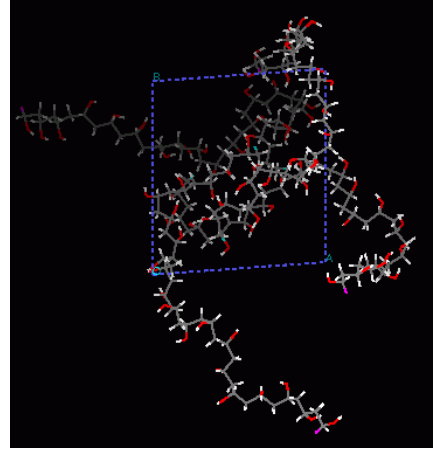
- The Coulomb sum is conditionally convergent:
 - Result depends on the order of the summands
 - Result depends on charge arrangement on the surface
- Need to use special sum techniques and boundary conditions
 - Ewald method [part of the sum in real space and part in reciprocal Fourier space]
 - Particle-mesh Ewald and other techniques

de Leeuw et al. *Proc. Roy. Soc. Lond. A* **373**, 27 (1980)

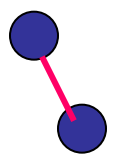
de Leeuw et al. *Proc. Roy. Soc. Lond. A* **373**, 57 (1980)

Molecular materials

$$V(\{r_i\}) = V_{cov}(\{r_i\}) + V_{electr}(\{r_i\}) + V_{vdW}(\{r_i\})$$

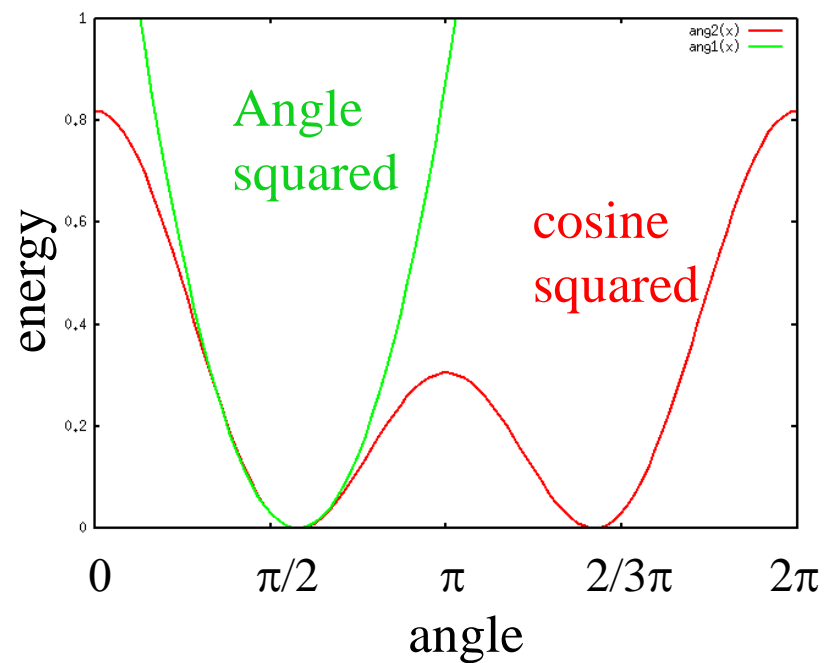


Interaction between atoms separated by chemical bonds

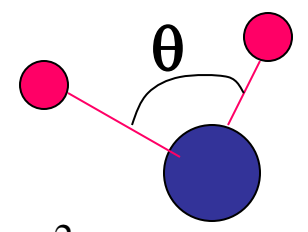


Bond stretch:

$$\phi_{bond}(r) = \begin{cases} \frac{1}{2} k_{ij} (r - r_{ij}^0)^2 \\ \text{Morse, } L - J \end{cases}$$

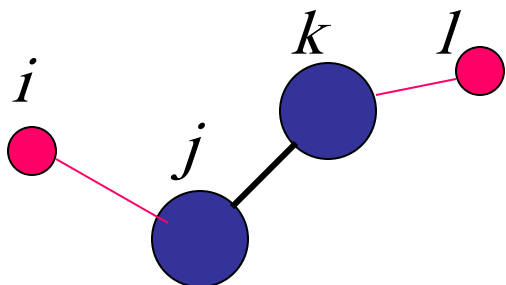


Angle bending:



$$\phi_{angle}(\theta) = \begin{cases} \frac{1}{2} k_{ijk} (\theta - \theta_{ijk}^0)^2 \\ \frac{1}{2} \frac{k_{ijk}}{\sin^2 \theta_{ijk}^0} [\cos \theta - \cos \theta_{ijk}^0]^2 \end{cases}$$

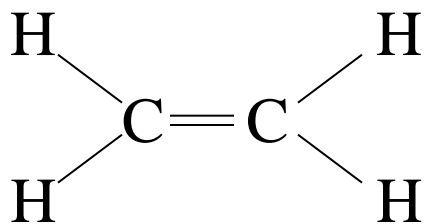
Covalent interactions



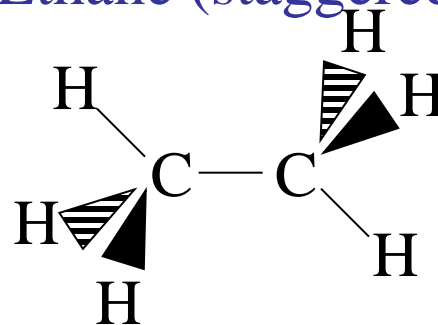
Torsion bending (dihedral angles)

$$\phi_{\text{torsions}}(\varphi) = k_{ijkl} \left[1 - \cos(n_{jk} (\varphi - \varphi_{jk}^0)) \right]$$

Ethylene (planar)



Ethane (staggered)



sp^2 hybridization

- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
 - Rotating around C-C bond breaks the π bond

sp^3 hybridization

- Equilibrium at 60° , 180° , & 300°
- Maxima at: 0° , 120° , & 240°
- Low torsional barrier
 - Dominated by vdW between H

Atom types in molecular force fields

- Element alone is not enough to determine the interactions
 - E.g.: sp^3 carbon and sp^2 carbon behave differently
- In traditional molecular force fields the user specifies *force field types* to establish the character of the atom
 - Force field types & connectivities need to be determined prior to MD simulation
 - FF types and connectivities are kept fixed during run

Widely used force fields for molecular simulations:

AMBER: Cornell, Cieplak, Bayly, Gould, Merz, Ferguson, Spellmeyer, Fox, Caldwell, and Kollman. *J. Am. Chem. Soc.*, **117**, 5179 (1995).

DREIDING: Mayo, Olafson, and Goddard, III, *J. Chem. Phys.* **94**, 8897 (1990).

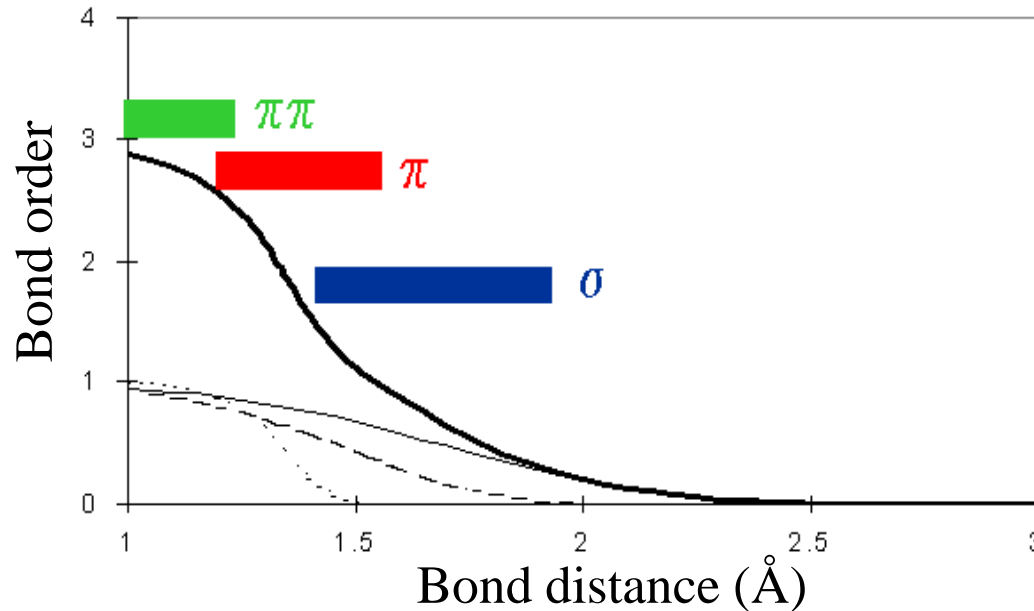
CHARMM: Brooks, Bruccoleri, Olafson, States, Swaminathan, and Karplus. *J. Comput. Chem.*, **4**, 187 (1983).

COMPASS:

Reactive force fields

No predetermined connectivities

Bond distance \rightarrow bond order \rightarrow bond energy



- Bond stretch, angle, & torsion terms depend on bond orders involved
 - E.g. distinguish between sp^2 and sp^3 carbon
- As a bond order goes to zero all terms involving also tend to zero
 - Bond orders are pre-factors for all covalent terms
- Over-coordination penalty
 - Limit the number of bonds an atom can make

Reactive force fields: key developments

- **Reactive Empirical Bond Order (REBO):**

- Robertson, Brenner, White, *J. Phys. Chem.*, **99**, 15721 (1995)

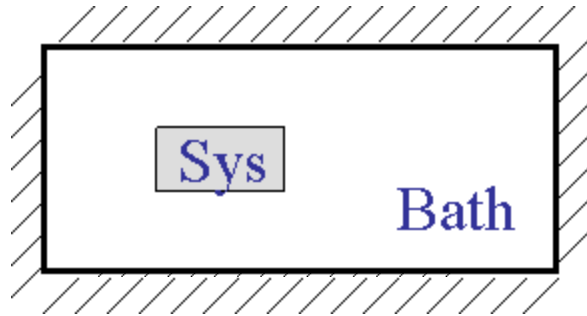
- **AI-REBO:**

- Brenner, Shenderova, Harrison, Stuart, Ni, Sinnott, *J. Phys. Condensed Matter*, **14**, 783 (2002)

- **ReaxFF:**

- Van Duin, Dasgupta, Lorant, Goddard III, *J. Phys. Chem. A*, **105**, 9396 (2001)

MD at constant temperature



Canonical (NVT)
ensemble averages



Time averages

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$
$$\dot{\vec{p}}_i = \vec{F}_i$$

+?

What do we expect from an NVT MD simulation?

- Average kinetic energy should correspond to desired temperature
- Dynamics of system to be consistent with the canonical distribution

Isothermal MD: Andersen approach

Coupling of system with heat bath:

Stochastic collisions between randomly selected particles with the bath that result in a new velocity consistent with the desired temperature

1. Integrate equations of motion for time Δt
2. Number of atoms that underwent collisions during Δt is: $\nu \Delta t$ – select them randomly
3. Assign new velocities to selected atoms from a Maxwell-Boltzmann distribution at temperature T

Coupling constant



PROS:

Leads to canonical distribution

CONS:

Collisions affect atomic dynamics
(e.g. diffusion coefficient)

Isothermal MD: Berendsen approach

Can we modify the equations of motion to obtain desired temperature?

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t) - \gamma p(t)$$

$$\gamma(t) = \nu \frac{T(t) - T_0}{T(t)}$$

Berendsen thermostat

- Direct feedback to control temperature
- γ is a heat flow variable (can be negative or positive)
- γ defined in terms of instantaneous temperature (T) and thermostat temperature (T_0)
- MD temperature converges to desired thermostat temperature

PROS:

Thermalizes system to desired temperature efficiently

CONS:

Does not lead to the canonical distribution

Isothermal MD: Nosé-Hoover approach

Berendsen thermostat

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t) - \gamma(t) \vec{p}_i(t)$$

$$\dot{\gamma}(t) = \nu \frac{T(t) - T_0}{T(t)}$$

Nosé-Hoover thermostat

$$\dot{\vec{r}}_i(t) = \frac{\vec{p}_i(t)}{m_i}$$

$$\dot{\vec{p}}_i(t) = \vec{F}_i(t) - \nu \gamma(t) \vec{p}_i(t)$$

$$\dot{\gamma}(t) = \nu \frac{T(t) - T}{T}$$

- Heat flow variable has its own equation of motion: integral feedback
- Enables kinetic energy fluctuations

PROS:

- Leads to canonical distribution
- Time reversible

Andersen, J. Chem. Phys. 72, 2384 (1980)

Nosé, Mol. Phys. 52, 255 (1984)

Hoover, Phys. Rev A, 31 1695 (1985)

Holian, Voter, and Ravelo, Phys. Rev. E. 52, 2338 (1995).

CONS:

- Approach to equilibrium: can lead to oscillations
- Persistent, non-canonical oscillations can occur if care is not taken

Further reading

- Andersen, J. Chem. Phys. 72, 2384 (1980)
- Parrinello and Rahman, Phys. Rev. Lett., 45, 1196 (1980)
- Parrinello and Rahman, J. Appl. Phys. 52, 7182 (1981)
- Nosé, Mol. Phys. 52, 255 (1984)
- Hoover, Phys. Rev A, 31 1695 (1985)
- Melchionna, Ciccoti and Holian, Mol Phys. 78, 533 (1993)
- Martyna, Tobias, and Klein, J. Chem. Phys. 101 4177 (1994)
- Holian, Voter, and Ravelo, Phys. Rev. E. 52, 2338 (1995).

Demos and examples

Non-equilibrium MD

- **Heat flux** $J = -\kappa \nabla T$

∇T : temperature gradient

κ : thermal conductivity

- **To calculate κ :**

Step 1.

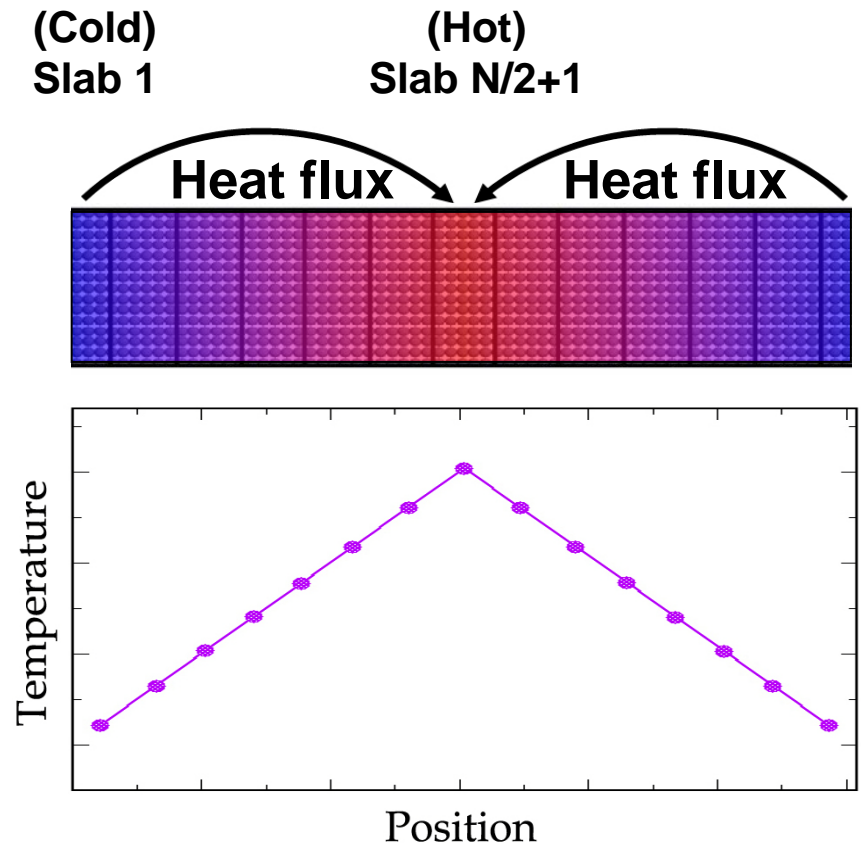
Impose a heat flux

Step 2.

Measure the corresponding temperature gradient

Step 3.

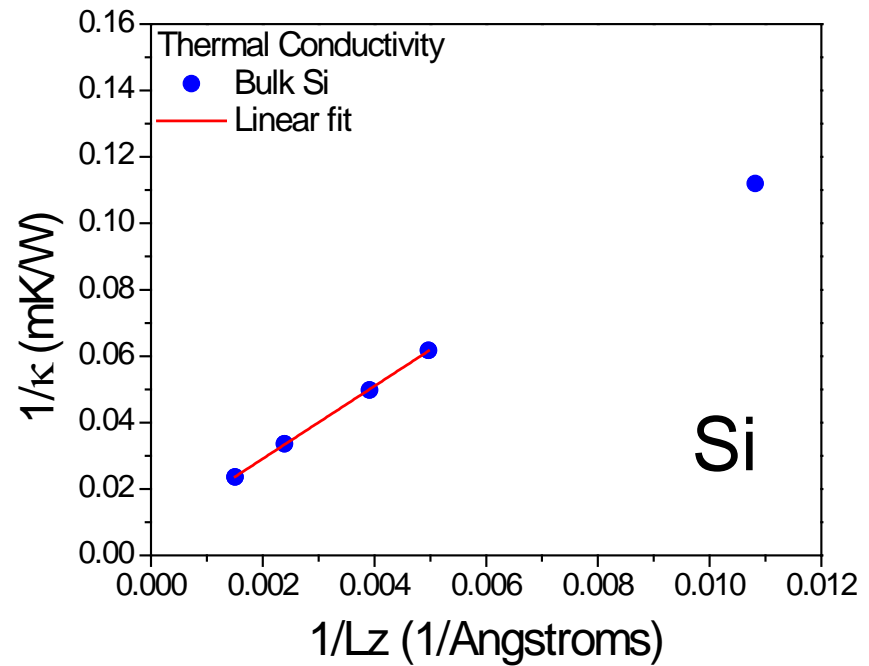
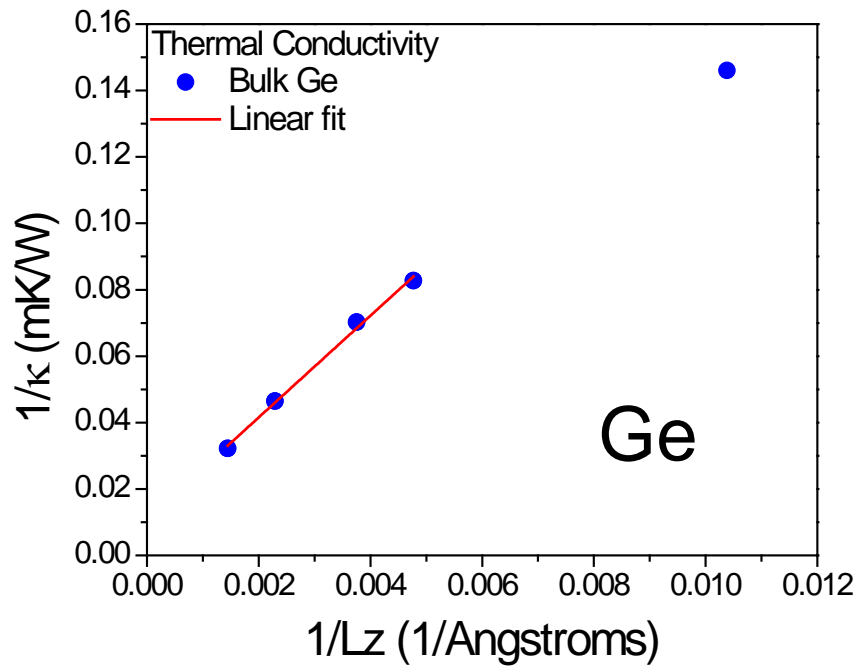
Obtain thermal conductivity, κ



Thermal Conductivities of Bulk Si and Ge

- Kinetic theory:** $\kappa = \frac{1}{3} C v l$ $\xrightarrow{\frac{1}{l} = \sum_i \frac{1}{l_i}}$ $\frac{1}{\kappa \kappa} = \frac{l_\infty}{\text{bulk}} \left(\frac{1}{l_\infty} + \frac{2}{L_z} \right)$

sample thermal conductivity phonon mean-free-path in the bulk
sample size:
distance between cold/hot slabs



	Slope	Intercept	Bulk κ (W/m*K)	Phonon mfp (nm)
Ge (NVT)	15.32171	0.0109	76	140
	0.65891	0.00219	-114	
Ge (Experiment)			58	

	Slope	Intercept	Bulk κ (W/m*K)	Phonon mfp (nm)
Si (NVT)	10.93991	0.00722	132	151
	0.09789	3.39084E-4	-145	
Si (Experiment)			130	200-300

Structure of Nanolaminates and Nanowires



Si

- Sample Size: $10 \times 10 \times 158$ unit cells (126400 atoms)

- Lattice Parameter: $a_{\text{Si}} = a_{\text{Ge}} = b_{\text{Si}} = b_{\text{Ge}} = 0.554 \text{ nm}$,

- $c_{\text{Si}} = c_{\text{Ge}} = 0.55055 \text{ nm}$



Ge

longitudinal view



Periodicity: 0.275275nm



Periodicity: 0.5055nm



Periodicity: 1.1011nm



Periodicity: 2.2022nm

Heat Baths



Periodicity: 4.4044nm



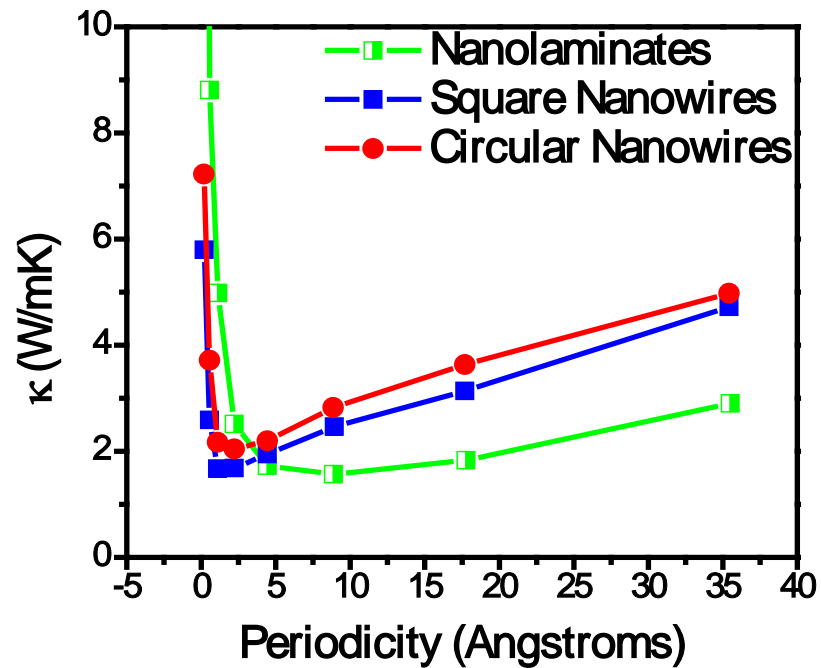
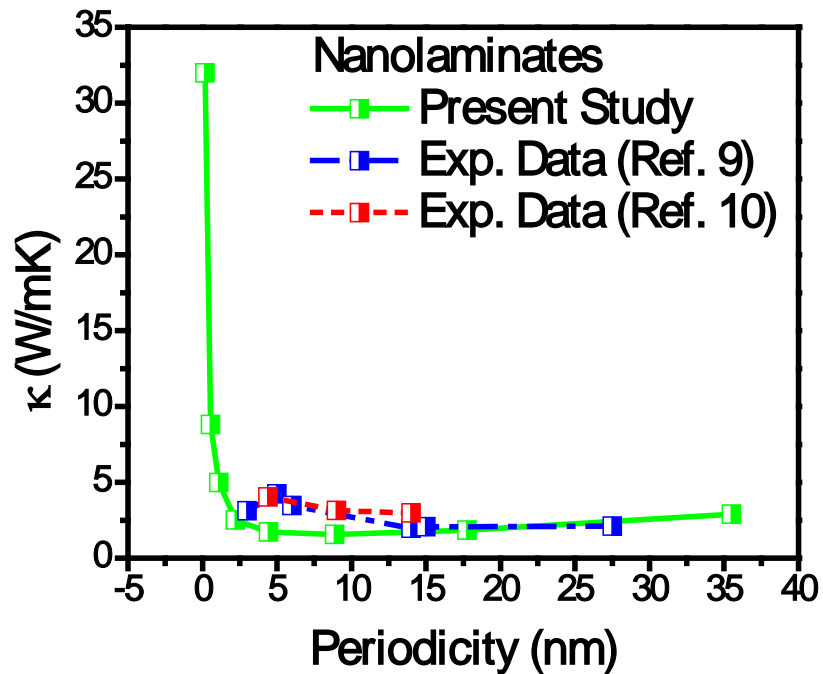
Periodicity: 8.8088nm

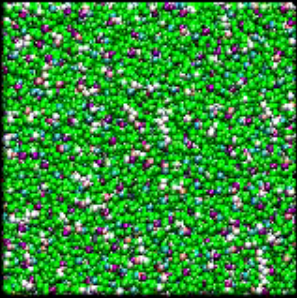


Periodicity: 17.6176nm



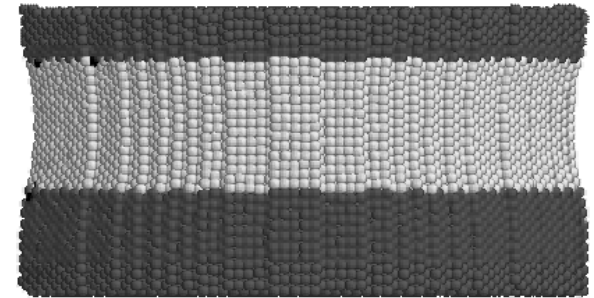
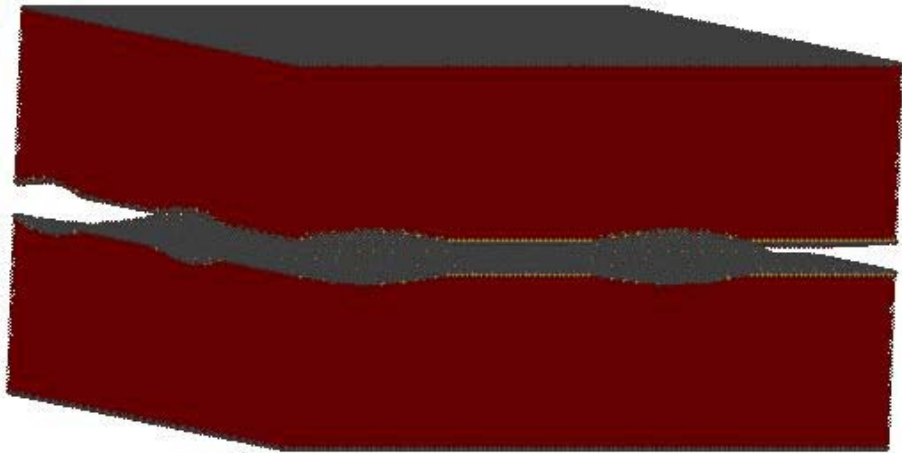
Periodicity: 35.252nm





Ultimate properties of polymers

Nanoscale contact mechanics



Coherency limit in nanostructures

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Molecular dynamics simulations of materials

by [Alejandro Strachan](#)

Article Edit History

What is MD?

Molecular dynamics involves the numerical solution of the classical equations of motion ($F=ma$) for every single atom in material. The result is a very detailed description of the temporal evolution of the material: we obtain the position, velocity and force of every atom as a function of time. The total force acting on an atom comes from its interaction with other atoms and external fields and an accurate model to describe atomic interactions is critical in any MD simulation. If you are interested in MD read on; you will find more information, additional resources, simulation codes, and online tool that enables running live MD simulations using simply your web-browser.