Simulating Matter with Molecular Dynamics
(Straightforward, Obvious, Ridiculously Effective)

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Course: **Computational Physics II**
What Can You Do with Molecular Dynamic?

Problem

Will a collection of argon molecules form a liquid and then an ordered solid as the temperature is lowered?

- Recall introductory chemistry, “ideal” gas
- Derived $PV = nRT$ via billiard ball collisions off only walls
- Now nonideal: molecule-molecule interactions
- Argon: inert gas (closed e shell) $\simeq$ hard spheres
Molecular Dynamics (MD) Theory

MD Overview

- MD: simulate phys & chem properties: solids, liquids, amorphous, bio
- MD: $F = ma$ for bulk properties
- QM = correct description, but ...
- Bulk: not small-$r$ behaviors
- QM (DFT): derive $V_{\text{eff}}(r)$
- “HS physics problem from hell”
- Can’t run $10^{23}–10^{25}$ particles
- Can $\sim 10^6$: proteins; $\sim 10^8$: materials
Relation MD to Monte Carlo (MC) Thermodynamics

2 Powerful Simulation Techniques

- Both: large $N$ particles
- Both: initial arbitrary, equilibrate
- MD: microcanonical ensemble: $E, V, N$ fixed
- MC: canonical ensemble: heat bath, fixed $T, N$
- MD: has dynamics ($F = ma$); MC: not, random
- MD: $x_i, v_i$ change continuously, calc thermo variables
Applying Newton’s Laws ($E$ Determines Visibility)

Atom-Atom Interactions

- 1st Prin:
  - $18 \text{ e} - 18 \text{ e, } Z^+ \ V_c$
- $\sim 1000 \text{ e-e, e-Z}$
- Ignore internal
- Conservative ($E_o$), central $V(r)$
- $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$

\[
m \frac{d^2 \mathbf{r}_i}{dt^2} = F_i(\mathbf{r}_0, \ldots, \mathbf{r}_{N-1}) \quad (1)
\]
\[
F_i = - \nabla_{r_i} U(\mathbf{r}_0, \mathbf{r}_1, \ldots) \quad (2)
\]
\[
U = \sum_{i<j} u(r_{ij}) \quad (3)
\]
\[
m \frac{d^2 \mathbf{r}_i}{dt^2} = - \sum_{i<j=0}^{N-1} \frac{du}{dr_{ij}} \quad (4)
\]
Phenomenological Lennard-Jones Potential

\[ u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

\[ f(r) = -\frac{du}{dr} = 48\epsilon \frac{r}{r^2} \left[ \left( \frac{\sigma}{r} \right)^{12} - \frac{1}{2} \left( \frac{\sigma}{r} \right)^6 \right] \]

- Attractive \( r^{-6} \)
- Large \( r \) van der Waals
- Weak induced dipole–dipole
- \( \epsilon \leftrightarrow \text{strength} \)
- \( \sigma \leftrightarrow \text{length scale} \)
- Repulsive \( r^{-12} \)
- e-e small \( r \) overlap
Time for A Break
Calculation of Thermodynamic Variables from MD

Large $N$, Use Statistical Mechanics

- Equipartition, equilibrium $@ T$, $E = \frac{1}{2} k_B T$ /°F
- Simulation: just translational KE (no rotate, vibrate)

$$KE = \frac{m}{2} \left\langle \sum_{i=0}^{N-1} v_i^2 \right\rangle$$

- Time average KE (3° freedom)

$$\langle KE \rangle = \frac{3}{2} k_B T \Rightarrow T = \frac{2\langle KE \rangle_{MD}}{3k_B N}$$

- Pressure via Virial theorem, $w = <\text{force}>$

$$P = \frac{\rho}{3N} (2\langle KE \rangle + w), \quad \rho = \frac{N}{V}$$
Setting Initial Velocities for Molecules

- Start: velocity distribution characteristic some $T \propto \langle KE \rangle$
- $\neq$ true $T$ since not equilibrium (KE ↔ PE)
- Randomness: just to speed up calc
- Random Gaussian $= \frac{1}{12} \sum_{i=1}^{12} r_i$
Periodic Boundary Conditions (PBC)

- EG: 1000 particles $10 \times 10 \times 10$ cube
- $\Rightarrow 10^3 - 8^3 = 488$ surface
- $10^6$ particles $\rightarrow 6\%$
- PBC: min surface effects
- Replicate box to infinity
- Continuous at edges
- Each $\Delta t$, outside box?
- Bring image in opposite side:

$$x \Rightarrow \begin{cases} 
  x + L_x, & \text{if } x \leq 0, \\
  x - L_x, & \text{if } x > L_x
\end{cases}$$

- $N = 10^3 - 10^6 = \text{bulk}$?
- Must have box!
- Walls: surface effects
- $\downarrow N \Rightarrow \uparrow$ surface/volume
Potential Cutoff

Computers & Boxes are Finite

- $m_i$ interacts with all $m_j$
- $\Rightarrow \infty$ interactions
- Yet $V(r >> \sigma) \simeq 0$
- $V(r = 3\sigma) \simeq V(1.13\sigma)/200$
- Cut off: $u(r > 2.5\sigma) \equiv 0$
- $\Rightarrow$ only nearest image interaction
- Problem: $f = \frac{-du(r_{cut})}{dr} = -\infty$
- Small effect since $V(r)$ small

Lennard-Jones

![Lennard-Jones Potential](image-url)
Verlet & Velocity-Verlet Algorithms: Integrate Eq of Mtn

Realistic MD: 3-D Eq of M, $10^{10}$ t’s, $10^3$–$10^6$ particles

- rk4 ODE solver good; need quicker, simpler, built-in
- **Verlet**: central-difference $f''$

$$f_i[r(t), t] = m(=1) \frac{d^2r_i}{dt^2} \simeq \frac{r_i(t+h) + r_i(t-h) - 2r_i(t)}{h^2}$$ (1)

$$\Rightarrow r_i(t+h) \simeq 2r_i(t) - r_i(t-h) + h^2f_i(t) + O(h^4)$$ (2)

- Efficient: no solve for $v$’s; Determine $v$ at end
- **Velocity-Verlet** ($>$ stable); FD $r$ & $v$ together:

$$r_i(t+h) \simeq r_i(t) + hv_i(t) + \frac{h^2}{2}f_i(t) + O(h^3)$$ (3)

$$v_i(t+h) \simeq v_i(t) + h\overline{a(t)} + O(h^2)$$ (4)
1-D Implementation: PE, KE, E vs Time

Energy vs Time
for 36 particles in a 2D box, initially at 150 K

Energy vs Time
for 300 particles 2D box, initially at 150 K

MD.py

1. Start FCC lattice site: $V_{LJ}$ equilibrium
2. FCC particles/cell: $4N^3 = 32, 108, \ldots$
3. Start Maxwellian velocity distribution
4. Highlight: ODE, PBC, image, cut off
5. $\sim 10^4–10^5$ steps equilibrate ($10^{-9}$ s)
6. Choose largest $h$ that’s stable
7. Compare to Figures
8. Evaluate $<E>_t$, final $T$
9. Relation final and initial $T$’s?
Trajectory Analysis (Time To Get To Work)

Output Several Particles’ x & v for Every 100 Steps

1. Start with 1-D, \( T = 0 \) @ equilibrium, then 2-D
2. \( PV = NRT \) for ideal (\( V = 0 \)) gas
3. Increase \( T \), note motion, interactions
4. Create an animation
5. Plot displacements \( R_{\text{rms}} \) vs \( T \)
6. Test for time-reversal invariance