Simulating Matter with Molecular Dynamics

(Straightforward, Obvious, Ridiculously Effective)

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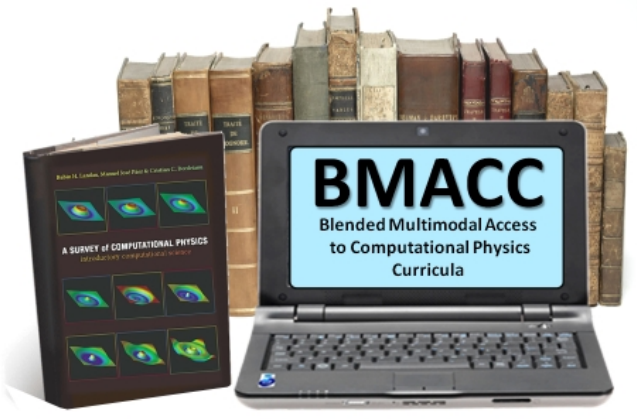
Based on *A Survey of Computational Physics* by Landau, Páez, & Bordeianu

with Support from the National Science Foundation

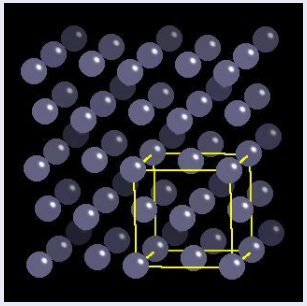
Course: **Computational Physics II**



What Can You Do with Molecular Dynamic?

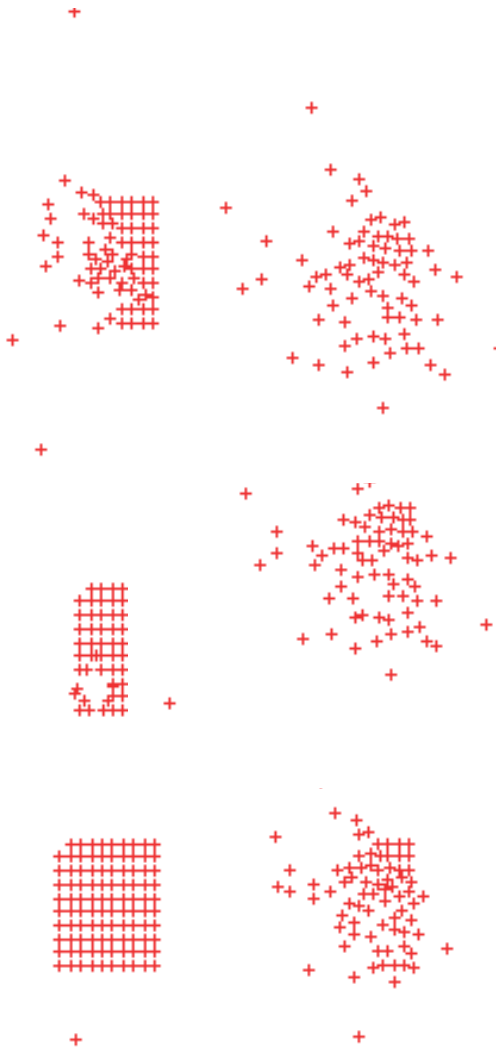
Problem

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

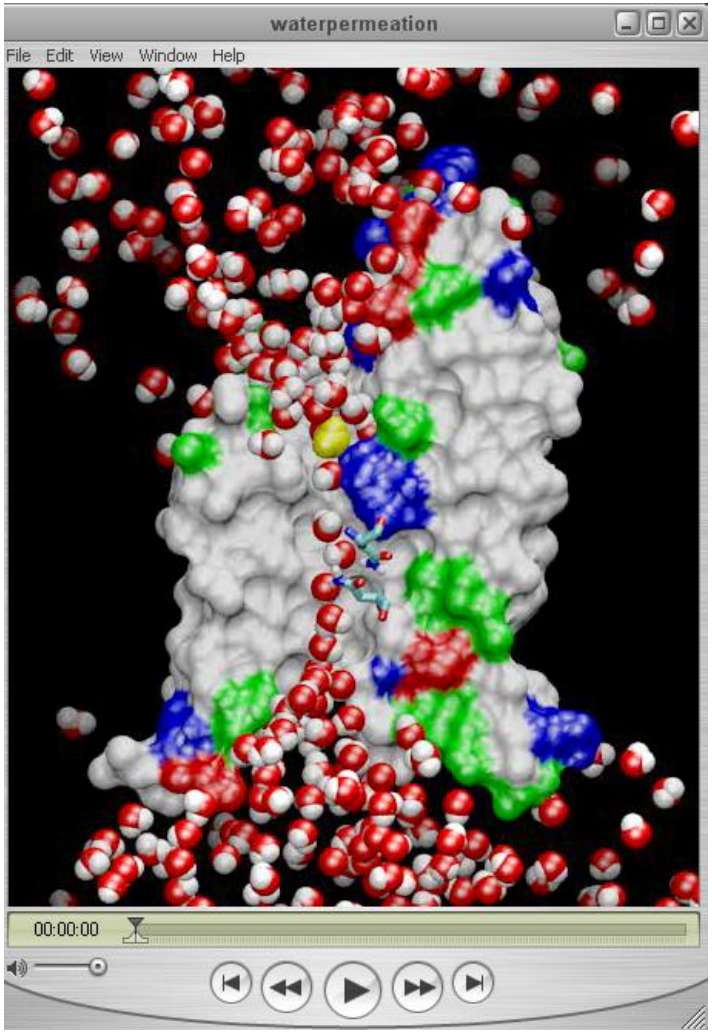


MD Overview

- 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

waterpermeation.mpg

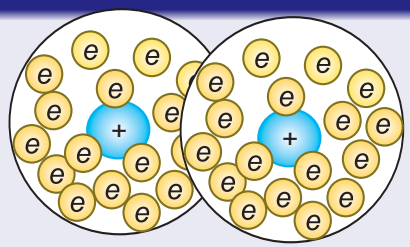


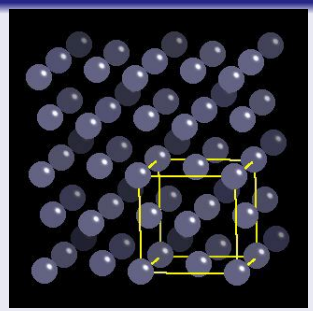
2 Powerful Simulation Techniques

- 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 Visiblitity)

Atom-Atom Interactions





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

$$m\frac{d^2\mathbf{r}_i}{dt^2} = \boldsymbol{F}_i(\mathbf{r}_0, \ldots, \mathbf{r}_{N-1}) \quad (1)$$

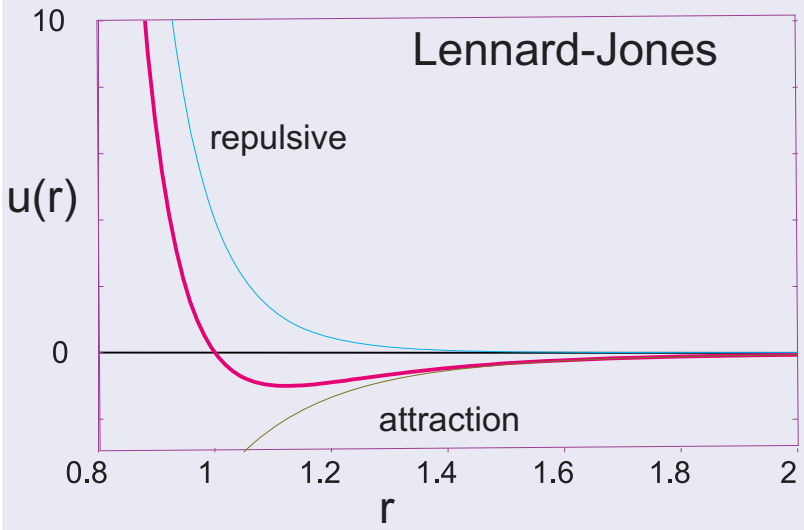
$$\boldsymbol{F}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}_0, \mathbf{r}_1, \ldots) \quad (2)$$

$$U = \sum_{i<j} u(r_{ij}) \quad (3)$$

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\sum_{i<j=0}^{N-1} \frac{du}{dr_{ij}} \quad (4)$$

Phenomenological Lennard-Jones Potential

$\sum$ Short-Range Repulsion + Long Attraction



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

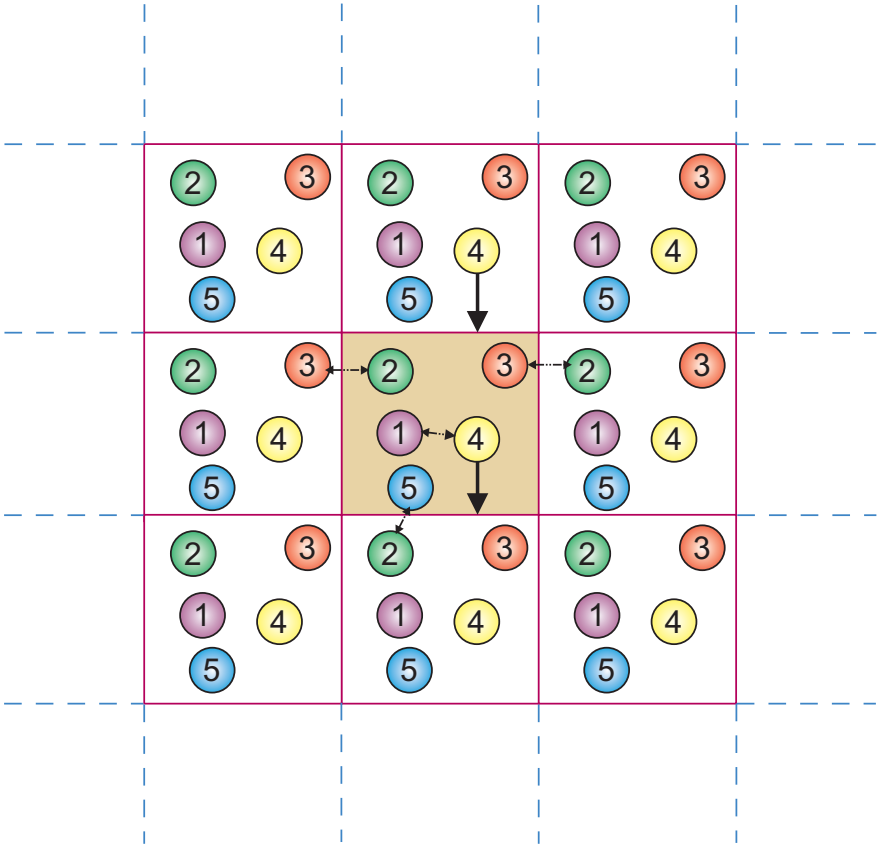
$$\mathbf{f}(r) = -\frac{du}{dr}$$

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

- $\epsilon \leftrightarrow$ strength
- $\sigma \leftrightarrow$ length scale
- Repulsive r^{-12}
- e-e small r overlap

- Attractive r^{-6}
- Large r van der Waals
- Weak induced dipole–dipole
- $\Leftarrow$, $\Leftarrow$, $\Leftarrow\Leftarrow$

Time for A Break



Calculation of Thermodynamic Variables from MD

Large N, Use Statistical Mechanics

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

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

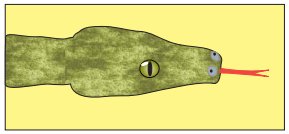
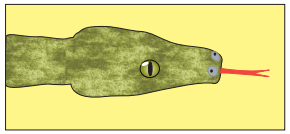
- Time average KE (3^o freedom)

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

- Pressure via Virial theorem, w = <force>

$$P = \frac{\rho}{3N} \left(2 \langle \mathrm{KE} \rangle + w \right), \quad \rho = \frac{N}{V} \tag{3}$$

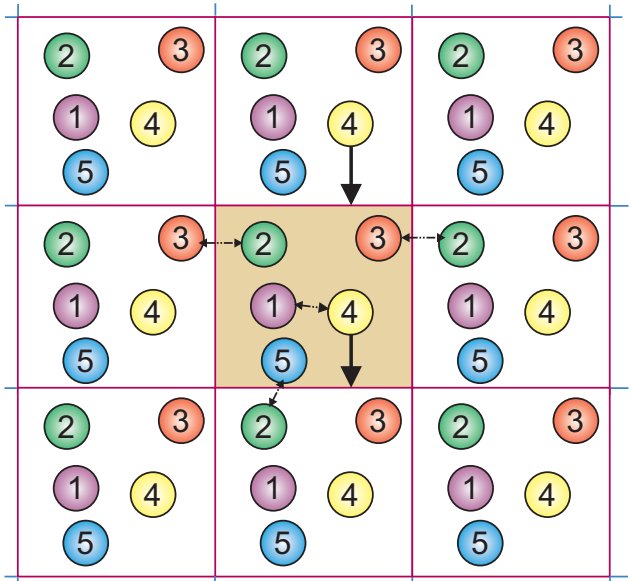
Setting Initial Velocities for Molecules

1D  2D 

Initial Conditions Should Not Matter

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

Periodic Boundary Conditions (PBC)

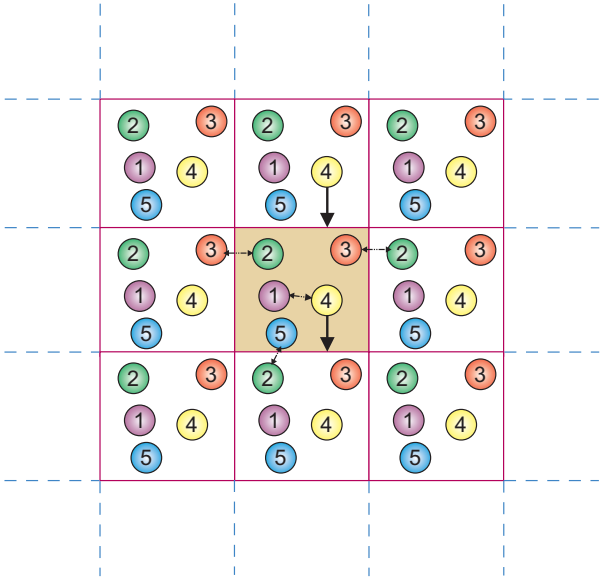


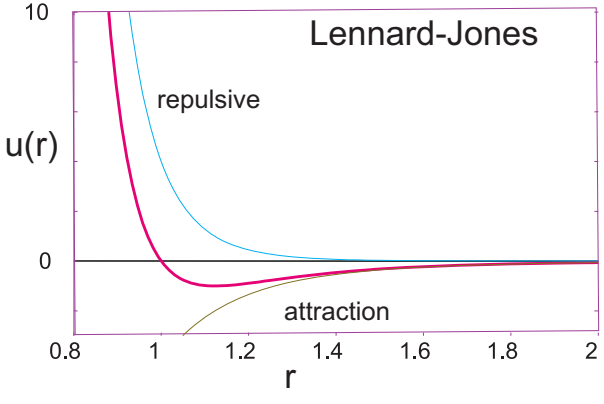
- $N = 10^3$–10^6 = bulk?
- *Must have box!*
- Walls: surface effects
- $\downarrow N \Rightarrow \uparrow$ surface/volume

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

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

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: $f = \frac{-du(r_{\text{cut}})}{dr} = -\infty$
- Small effect since $V(r)$ small

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*''

$$\boldsymbol{f}_i[\mathbf{r}(t),t] = m(=1)\frac{d^2\mathbf{r}_i}{dt^2} \simeq \frac{\mathbf{r}_i(t+h)+\mathbf{r}_i(t-h)-2\mathbf{r}_i(t)}{h^2} \tag{1}$$

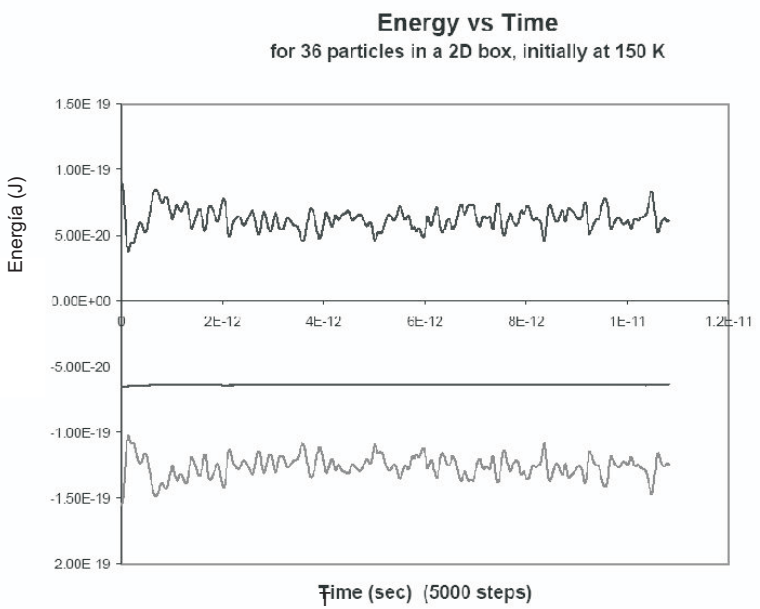
$$\Rightarrow \quad \mathbf{r}_i(t+h) \simeq 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + h^2\boldsymbol{f}_i(t) + \mathrm{O}(h^4) \tag{2}$$

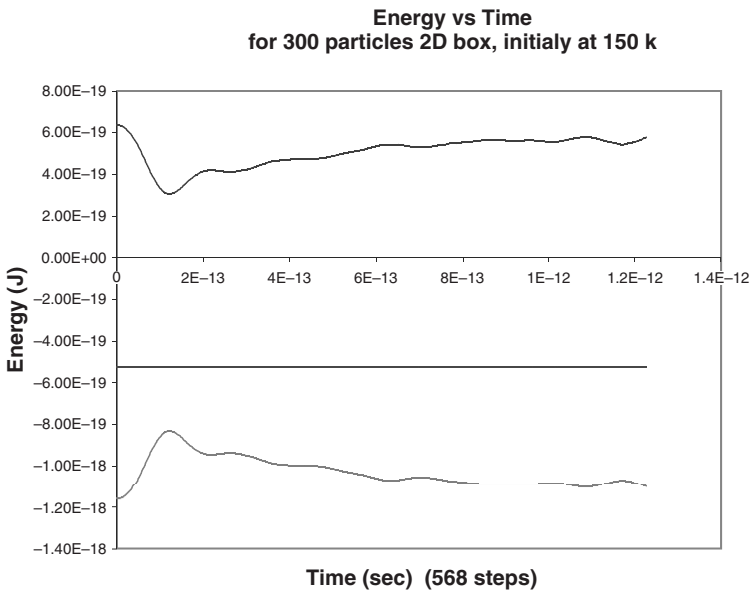
- Efficient: no solve for *v*'s; Determine *v* at end
- Velocity-Verlet (> stable); FD *r* & *v* together:

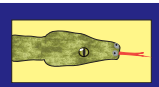
$$\mathbf{r}_i(t+h) \simeq \mathbf{r}_i(t) + h\mathbf{v}_i(t) + \frac{h^2}{2}\boldsymbol{f}_i(t) + \mathrm{O}(h^3) \tag{3}$$

$$\mathbf{v}_i(t+h) \simeq \mathbf{v}_i(t) + h\overline{\mathbf{a}(t)} + \mathrm{O}(h^2) \tag{4}$$

1-D Implementation: PE, KE, E vs Time

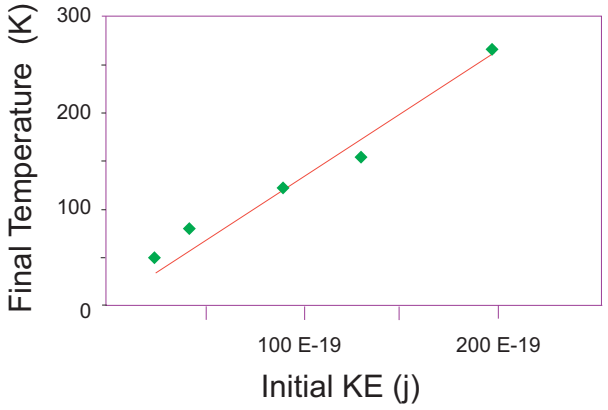


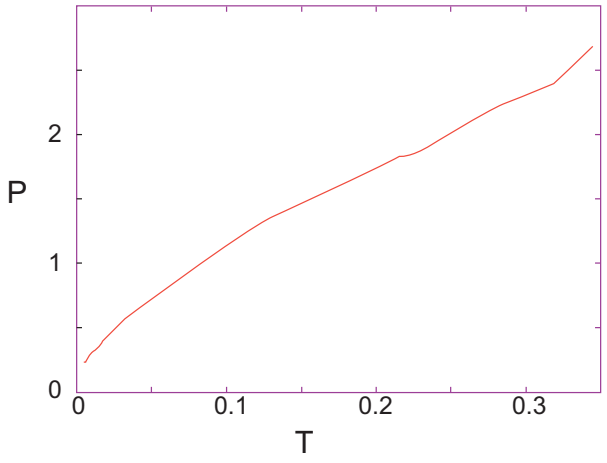


MD.py  CODE $V, T \Rightarrow$ liquid, solid

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_{rms} *vs* T
6. Test for time-reversal invariance