Monte Carlo Simulation of Liquids

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How to Perform MC Simulation of Liquids

Goal: Perform Metropolis MC on a simple liquid (i.e. Ar)

- Assume pairwise LJ interactions

$$\mathcal{V}_{ij}^{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1}$$

Task: Generate a sequence of configurations for N molecules in volume V that asymptotically samples the probability density of the canonical (NVT) ensemble.

How to Perform MC Simulation of Liquids

Nomenclature:

- Multi-dimensional space $\rightarrow$ configuration space, $(\mathbf{r}_1, \cdots, \mathbf{r}_M)$
- States $\rightarrow$ configurations (atom arrangements)
- $\rho_m \rightarrow \rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)}) d\mathbf{r}^N$
  ($d\mathbf{r}^N$ is an elementary volume element in configuration space)
- $\rho_n / \rho_m \rightarrow \frac{\rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)})}{\rho^{NVT}(\mathbf{r}_1^{(n)}, \cdots, \mathbf{r}_N^{(n)})} = \frac{\rho_n^{NVT}}{\rho_m^{NVT}}$

How to Perform MC Simulation of Liquids

Note that

$$\rho^{NVT}(\mathbf{r}_1^{(m)}, \cdots, \mathbf{r}_N^{(m)}) \equiv \rho_m^{NVT} = \frac{\exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]}{Z(NVT)} \equiv \frac{\exp[-\beta \mathcal{V}_m]}{Z} \quad (2)$$

Thus,

$$\frac{\rho_n^{NVT}}{\rho_m^{NVT}} = \frac{\exp[-\beta \mathcal{V}_n]}{\exp[-\beta \mathcal{V}_m]} = \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m)] = \exp[-\beta \Delta \mathcal{V}_{m \to n}] \quad (3)$$

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Metropolis Algorithm for Liquids

- Assume equal attempt probabilities $\alpha_{mn} = \alpha_{nm}$
- Start with configuration *m*, generate a new configuration *n*
- Compute the energy difference
- if $\mathcal{V}_n \leq \mathcal{V}_m$

$$min\left(1, \frac{\rho_n^{NVT}}{\rho_m^{NVT}}\right) = 1 \tag{4}$$

Accept the new configuration

- if $\mathcal{V}_n > \mathcal{V}_m$

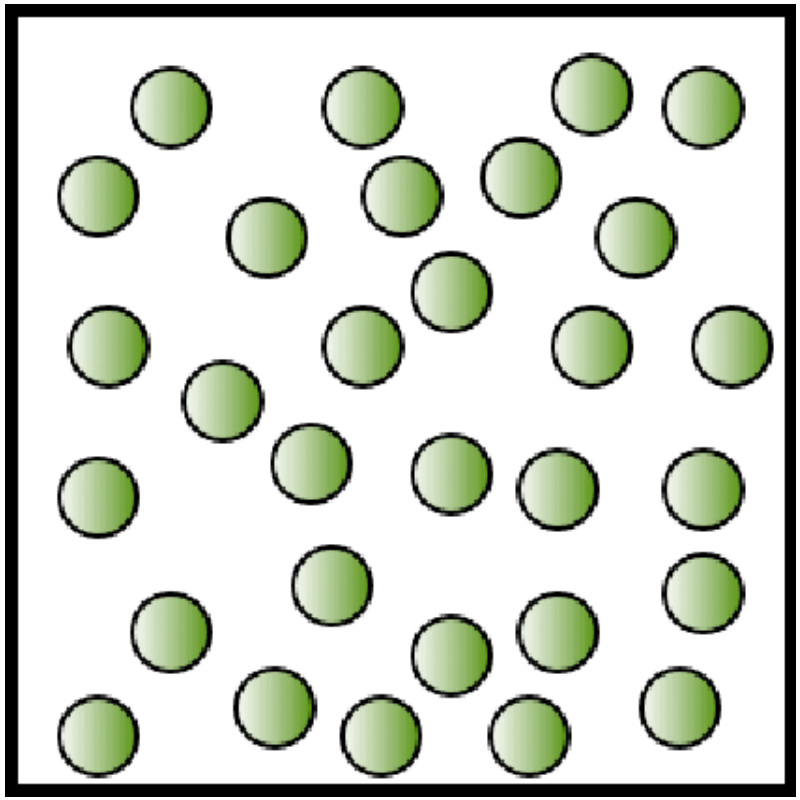
$$min\left(1, \frac{\rho_n^{NVT}}{\rho_m^{NVT}}\right) = \exp[-\beta\Delta\mathcal{V}_{m\rightarrow n}] \tag{5}$$

Accept if $\zeta < \exp[-\beta(\mathcal{V}_n - \mathcal{V}_m)]$

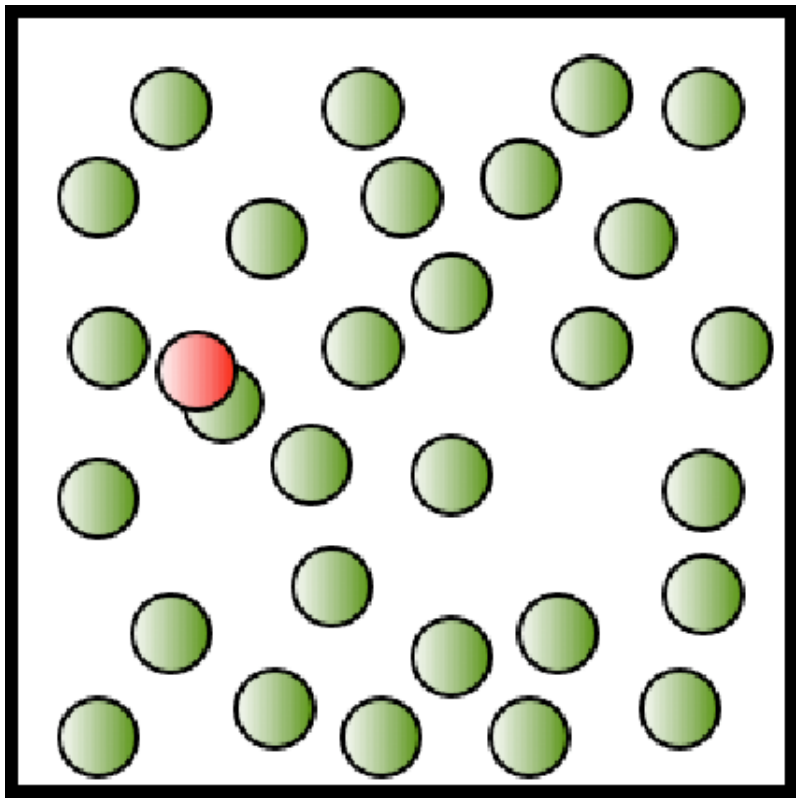
- Notice the Metropolis selection criterion *only involves potential energy*

Details, details...

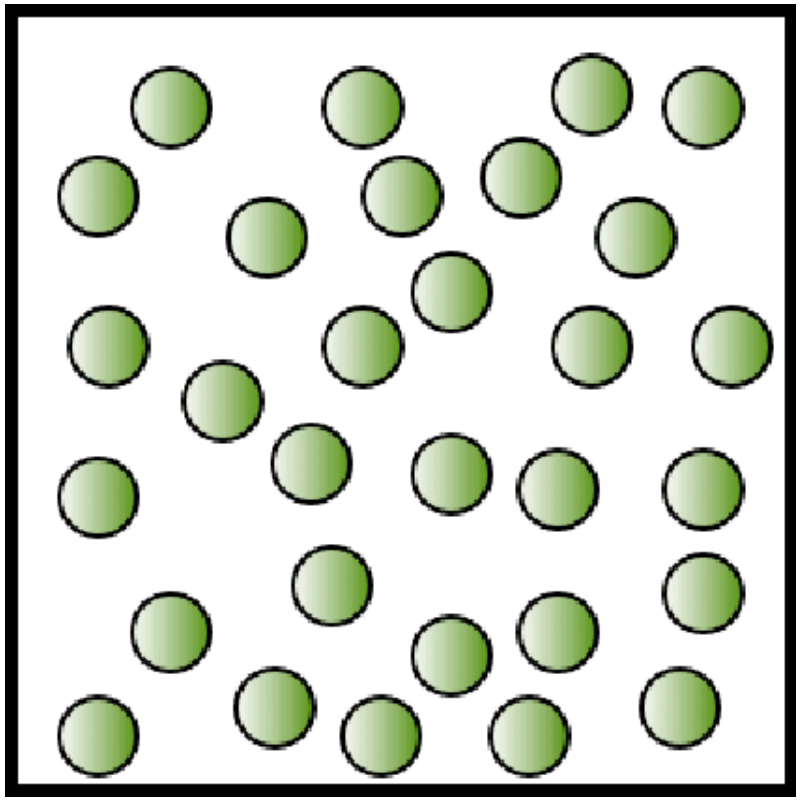
- Decide on form of α, the underlying stochastic matrix
- If moving between *m* and *n* is equally probable, $\alpha_{mn} = \alpha_{nm}$ and previous acceptance rules are OK
- Turns out small “local” moves are typically preferred over large “bold” moves. Why?



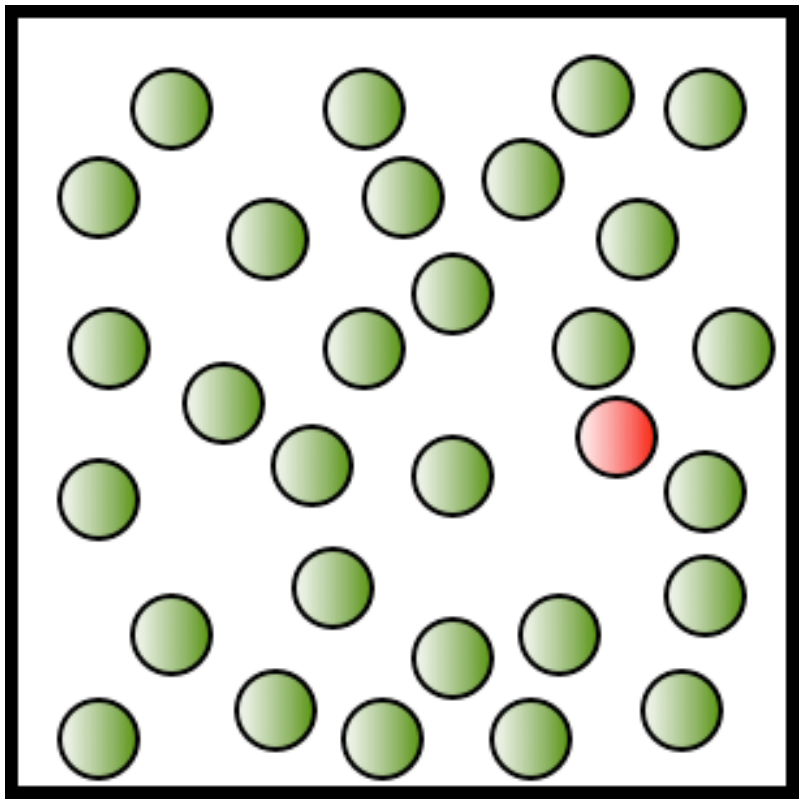
Initial configuration
Dense fluid



Move a molecule at random. High probability of overlap. *Move rejected*

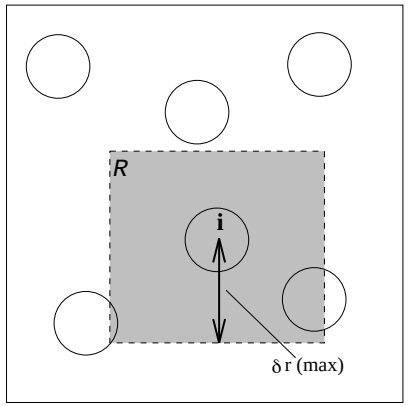


Initial configuration
Dense fluid



Local move reduces overlap probability *Adjust* α *to achieve desired acceptance rates*

Move Algorithm



To move from state *m* to state *n*

1. Choose atom at random; assume atom *i* at position $\mathbf{r}_i^{(m)}$
2. Define a "local" or "neighboring" environment by a square (cube or sphere in three dimensions) centered on *i*. Edge length (or radius) of the local region is δr_{max}
3. Denote local region by $\mathcal{R}$. Note that if we use a cube (as done below), the sides are $2\delta r_{max}$ long.
4. There is a large but finite set of new configurations, $N_{\mathcal{R}}$ within the cube $\mathcal{R}$. If each is of equal probability

$$\alpha_{mn} = 1/N_{\mathcal{R}};\ \mathbf{r}_i^{(n)} \in \mathcal{R} \tag{6}$$

$$\alpha_{mn} = 0;\ \mathbf{r}_i^{(n)} \notin \mathcal{R} \tag{7}$$

- To implement: an atom is chosen at random and given a uniform, random displacement along each Cartesian axes.
- An adjustable parameter, δr_{max}, controls the "boldness" of the attempted move: small displacements give high acceptance rates but slow evolution; large displacements yield large configurational changes, but get rejected more often.
- δr_{max} is typically adjusted during equilibration so that about 50% of the attempted moves are successful

```
rxnew = rx(i) + (2.0 * rranf(iseed) - 1.0) * drmax
rynew = ry(i) + (2.0 * rranf(iseed) - 1.0) * drmax
rznew = rz(i) + (2.0 * rranf(iseed) - 1.0) * drmax
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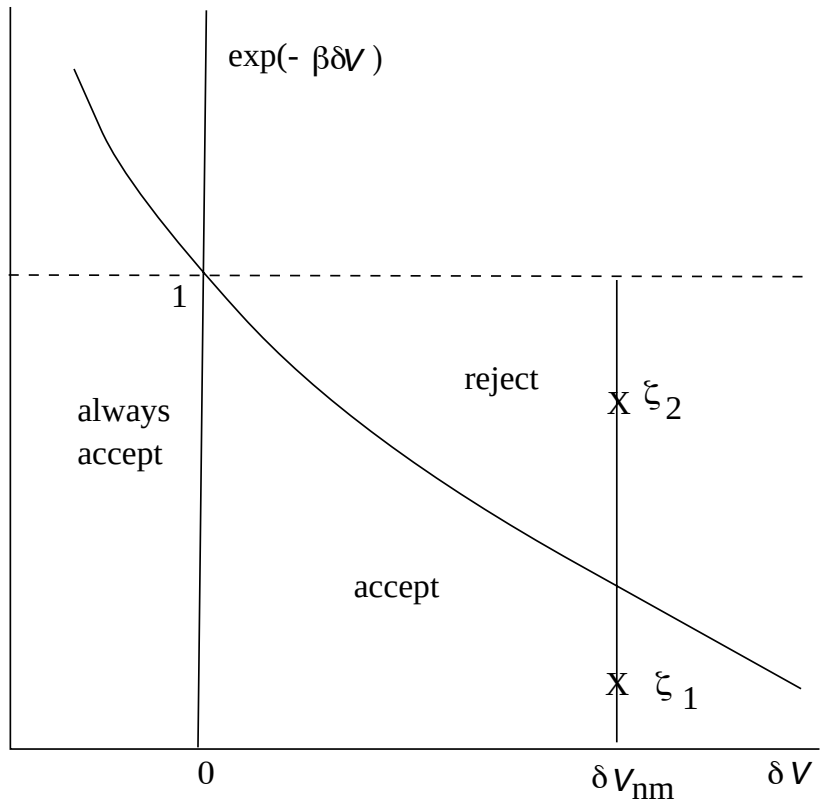
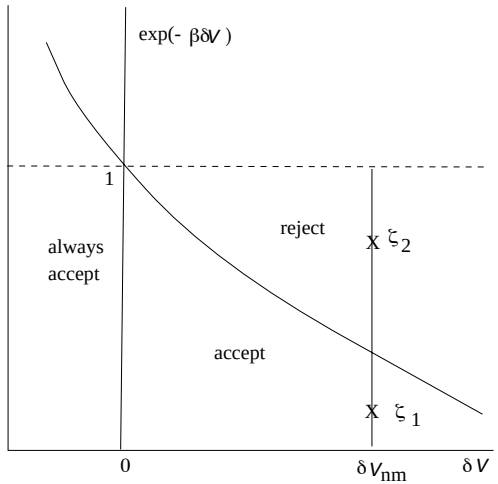
- After displacement is made, energy of the new state is compared to the energy of the old state.
- The Metropolis selection rule is used to decide whether or not this new state is accepted





- If move from *m* to *n* is downhill, $\delta\mathcal{V}_{nm} \leq 0$ and the move is always accepted. $\pi_{mn} = \alpha_{nm}/\alpha_{mn} = 1$
- For "uphill" moves, a random number ζ is generated uniformly on (0,1)
- If $\zeta < \exp[-\beta\mathcal{V}_{nm}]$, ($\zeta_1$ in the figure), the move is accepted
- Otherwise, (ζ_2), the move is rejected
- Over the course of the simulation, the net result is that energy changes such as $\delta\mathcal{V}_{nm}$ are accepted with probability $\exp[-\beta\delta\mathcal{V}_{nm}]$

Using Cassandra

Use Cassandra to reproduce the properties of the LJ equation of state

- Study a series of cases to explore the effect of various simulation parameters
- Potential cutoff
- System size
- Uniqueness of trajectories
- Computing averages

Stochastic Matrix

- What if $\alpha_{mn} \neq \alpha_{nm}$?
- Recall acceptance rule that satisfies detailed balance

$$\pi_{mn} = min(1, \frac{\alpha_{nm}\rho_n}{\alpha_{mn}\rho_m}) \tag{8}$$

- Simply retain α in the acceptance rule
- Key: In this case *you must know what* α_{mn} *and* α_{nm} *are!*
- If $\alpha_{mn} \neq \alpha_{nm}$ and you think they are equal, standard Metropolis algorithm will give you the wrong answer *and you will not know it!*

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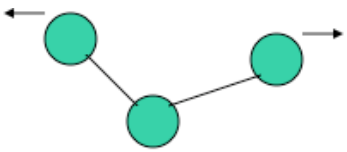
Demonstration of Violation of Detailed Balance

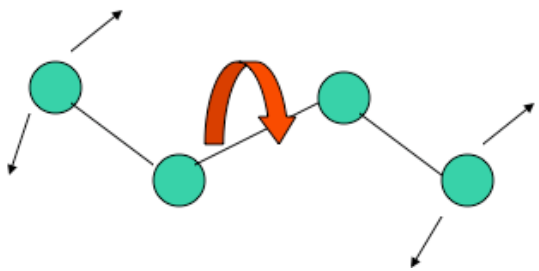
Run demo to see what happens when $\alpha_{mn} \neq \alpha_{nm}$ but you assume it is.

Molecular Liquids

- For molecular systems, the elementary moves must change all the configurational degrees of freedom
  - rigid translation
  - rigid rotation
  - rotation about bonds
  - bond distortion
- More on this later

bond distortions





bond rotations

Initial Configuration

- Final result should be independent of initial configuration
- But how do you start a simulation?
  - Want to start in high probability (low energy) state, to minimize time spent in equilibration
  - Traditional approach: start from an fcc lattice and “melt” to obtain a liquid. This ensures none of the molecules are initially overlapping.
  - Alternative: Randomly shoot molecules into a box and the do energy minimization to relax overlaps.
  - Last configuration of a MC run can be used as starting point if conditions are similar.

Equilibration

- Initial configuration is “far” from equilibrium
- Do not count in averages
- Simulations performed in two stages
  1. “Equilibration” phase: Markov chain asymptotically approaches limiting distribution
  2. “Production” phase: collect averages of “equilibrium” state
- At the end of the equilibration period, *all memory of the starting configuration should be lost*.

Equilibration

- To check whether the system has in fact reached equilibrium:
  - Monitor the potential energy and pressure. Run equilibration until there is no systematic drift in either quantity, only fluctuations about a mean.
  - If you started from a lattice, make sure all indications of initial order have vanished. (Translational and orientational order parameters show no order in fluid).
  - For fluid simulations, the mean–square displacement should grow linearly with time, indicating”diffusive” behavior.
- Rule of thumb is: low–molecular weight systems require 500N – 1000N steps to equilibrate.

Equilibration and the Ising Lattice

Go back and re-run Ising lattice simulation but run an equilibration and then restart the production run from the ending configuration. Do you see much difference? Why or why not?