9. Monte Carlo Simulations of Molecular Systems

Metropolis-Hastings algorithm for Boltzmann distributions

- for a system with fixed N, V, T, the Boltzmann distribution is

$$p(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \frac{1}{Z} \exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots))$$

- the Metropolis-Hastings algorithm for sampling from the Boltzmann distribution

1. given the sample $\mathbf{r}_o$ at step i, propose a new sample $\mathbf{r}_n$ using a proposal distribution $q(\mathbf{r}_n|\mathbf{r}_o)$ that satisfies $q(\mathbf{r}_n|\mathbf{r}_o) = q(\mathbf{r}_o|\mathbf{r}_n)$
2. calculate the acceptance probability

$$\alpha(\mathbf{r}_n|\mathbf{r}_o) = \min\left(1, \frac{\exp(-\beta U(\mathbf{r}_n))}{\exp(-\beta U(\mathbf{r}_o))}\right) = \min\left(1, \exp(-\beta \Delta U)\right)$$

   where $\Delta U = U(\mathbf{r}_n) - U(\mathbf{r}_o)$
3. $\mathbf{r}_{i+1} = \mathbf{r}_n$ with probability $\alpha(\mathbf{r}_n|\mathbf{r}_o)$; otherwise, $\mathbf{r}_{i+1} = \mathbf{r}_o$

An example system: a box of water molecules

- the system is a box of water molecules
- the system has fixed N, V, T
- periodic boundary conditions are applied to approximate a bulk system
- its potential energy $U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ needs to be specified
- the Metropolis-Hastings algorithm is used to sample from the Boltzmann distribution determined by the potential energy

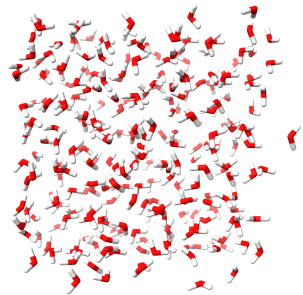
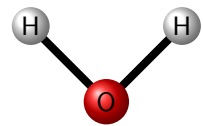


Figure: A box of water

The TIP3P water model

- TIP3P - Transferable Intermolecular Potential with 3 Points
- a simple *rigid* model for water; the bond length of O-H bonds is fixed at 0.09572 nm; the angle between the O-H bonds is fixed at 104.52°
- partial charges: $q_O = -0.834$, $q_H = 0.417$



- Lenard-Jones potential between the O atoms:

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

  where $\epsilon = 0.636\,\text{kJ/mol}$, $\sigma = 0.315\,\text{nm}$

- no Lenard-Jones potential for the O-H and H-H interactions

Proposed moves

- the Metropolis-Hastings algorithm requires a proposal distribution $q(\mathbf{r}_n|\mathbf{r}_o)$
- the acceptance probability $\alpha(\mathbf{r}_n|\mathbf{r}_o) = \min\left(1, \exp(-\beta\Delta U)\right)$ only when the proposal distribution is symmetric, i.e., $q(\mathbf{r}_n|\mathbf{r}_o) = q(\mathbf{r}_o|\mathbf{r}_n)$
- in the case of TIP3P water, each water molecule is a rigid body
- the proposed moves are translations and rotations of an entire water molecule

Proposed moves: translations

- the translation of a water molecule is a move of of the entire molecule
- no change in its orientation or conformation
- a simple proposal is to move a water molecule by a random displacement in each axis

$$\mathbf{r}_n = \mathbf{r}_o + \Delta \cdot \begin{bmatrix} \mathrm{rand}() - 0.5 \\ \mathrm{rand}() - 0.5 \\ \mathrm{rand}() - 0.5 \end{bmatrix},$$

  where $\mathrm{rand}()$ is a random number uniformly distributed between 0 and 1

- Δ, the displacement magnitude, is a parameter that needs to be tuned to achieve a desired acceptance rate (typically 0.2-0.5, depending on the system)

Proposed moves: translations

- what is the proposal distribution $q(\mathbf{r}_n|\mathbf{r}_o)$ for the translation move described in the previous slide?
- is it symmetric, i.e., $q(\mathbf{r}_n|\mathbf{r}_o) = q(\mathbf{r}_o|\mathbf{r}_n)$?