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

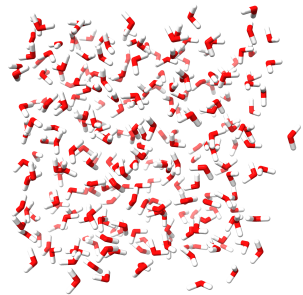
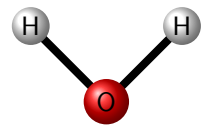


Figure: A box of water

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., $q(\mathbf{r}_n|\mathbf{r}_o) = q(\mathbf{r}_o|\mathbf{r}_n)$?

Proposed moves: rotations

- rotations with respect to the center of mass of a water molecule
- different ways to define a rotation, e.g., Euler angles, quaternions, etc.
- here the rotation is defined by an axis and an angle
- the axis u is a random unit vector in 3D space is a random unit vector in 3D space, around which the molecule is rotated
- the angle θ is a random number uniformly distributed between $-\theta_{\mathsf{max}}$ and θ_{max}
- θ_{max} needs to be tuned to achieve a desired acceptance rate

Proposed moves: rotations

two ways of sampling a random unit vector $u = (u_x, u_y, u_z)$

1. – generate a pair of random numbers ϵ_1, ϵ_2 indendently and uniformly distributed between -1 and 1 until $s = \epsilon_1^2 + \epsilon_2^2 < 1$
   – set $(u_x, u_y, u_z) = (2\epsilon_1\sqrt{1-s}, 2\epsilon_2\sqrt{1-s}, 1-2s)$

2. – generate three random numbers $\epsilon_1, \epsilon_2, \epsilon_3$ independently from a standard normal distribution
   – let $s = \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2}$
   – set $(u_x, u_y, u_z) = (\epsilon_1/s, \epsilon_2/s, \epsilon_3/s)$

Proposed moves: rotations

- given the axis $u = (u_x, u_y, y_z)$ and the angle θ, the rotation matrix is

$$R = (\cos\theta)I + (1 - \cos\theta)uu^T + (\sin\theta)S,$$

where I is the identity matrix, S is the skew-symmetric matrix

$$S = \begin{bmatrix} 0 & -u_z & u_y \\ u_z & 0 & -u_x \\ -u_y & u_x & 0 \end{bmatrix}$$

- to rotate around its center of mass, r_{cm}, the proposed r_n for each atom is

$$r_n = R(r_o - r_{\text{cm}}) + r_{\text{cm}},$$

where r_o is the original position of the atom.

Putting it all together

the Metropolis-Hastings algorithm for sampling from the Boltzmann distribution of a system of rigid water molecules at fixed N, V, T.

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given the initial configuration $\mathbf{r}_{\text{init}} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$, the potential energy function $U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$, and the temperature T. Let $\mathbf{r}_{\text{o}} = \mathbf{r}_{\text{init}}$ and $S = \{\mathbf{r}_{\text{o}}\}$.

repeat

1. pick a random water molecule i
2. pick a random move: translation or rotation
3. propose a new configuration $\mathbf{r}_{\text{n}}$ by applying the chosen move to the molecule i in $\mathbf{r}_{\text{o}}$
4. calculate the acceptance probability $\alpha(\mathbf{r}_{\text{n}}|\mathbf{r}_{\text{o}}) = \min\left(1, \exp(-\beta(U(\mathbf{r}_{\text{n}}) - U(\mathbf{r}_{\text{o}})))\right)$
5. with probability $\alpha(\mathbf{r}_{\text{n}}|\mathbf{r}_{\text{o}})$, accept the move, add $\mathbf{r}_{\text{n}}$ to S, and set $\mathbf{r}_{\text{o}} = \mathbf{r}_{\text{n}}$;
   otherwise, reject the move and add $\mathbf{r}_{\text{o}}$ to S

until a desired number of samples is generated

return S

Sampling conformations at constant NPT

- the Metropolis-Hastings algorithm described earlier can be extended to sample conformations at constant NPT.
- at constant NPT, the system is allowed to change its volume
- a new proposal move is needed: changing volume by scaling the periodic box
- the acceptance probability for changing volume needs to be calculated

Proposed moves: changing volume

- changing volume by scaling the periodic box and the coordinates of each water molecule's center of mass by a factor s
- assume V and $\mathbf{r}_1, \mathbf{r}_2, \ldots$ are the current volume and coordinates, respectively
- the volume is proposed to change to $V + \Delta V$ with $\Delta V = A \cdot r$, where A is a scaling factor and r is a random number uniformly distributed between -1 and 1
- the scaling factor is

$$s = \left(\frac{V + \Delta V}{V} \right)^{1/3}$$

Proposed moves: changing volume

- the acceptance probability for changing volume is

$$\alpha = \min\left(1, \exp\left(-\frac{\Delta W}{k_B T}\right)\right),$$

where

$$\Delta W = \Delta U + P\Delta V - N k_B T \ln\left(\frac{V + \Delta V}{V}\right)$$

- ΔU is the change in potential energy
- P is the pressure of the system

Putting it all together for constant NPT

the Metropolis-Hastings algorithm for sampling conformations of rigid water molecules at constant NPT.

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given the initial configuration $\mathbf{r}_{\text{init}} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots\}$, the potential energy function $U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$, the temperature T, the pressure P and the initial periodic box vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$.

Let $\mathbf{r}_{\text{o}} = \mathbf{r}_{\text{init}}, \mathbf{a}_{\text{o}} = \mathbf{a}, \mathbf{b}_{\text{o}} = \mathbf{b}, \mathbf{c}_{\text{o}} = \mathbf{c}$ and $S = \{(\mathbf{r}_{\text{o}}, \mathbf{a}_{\text{o}}, \mathbf{b}_{\text{o}}, \mathbf{c}_{\text{o}})\}$.

repeat

1. fix the periodic box vectors at $\mathbf{a}_{\text{o}}, \mathbf{b}_{\text{o}}, \mathbf{c}_{\text{o}}$ and attempt the translation and rotation moves described earlier; include the periodic box vectors when adding $\mathbf{r}_{\text{o}}$ or $\mathbf{r}_{\text{n}}$ to S
2. **every** k **steps**, attempt a volume change move: $(\mathbf{r}_{\text{o}}, \mathbf{a}_{\text{o}}, \mathbf{b}_{\text{o}}, \mathbf{c}_{\text{o}}) \rightarrow (\mathbf{r}_{\text{n}}, \mathbf{a}_{\text{n}}, \mathbf{b}_{\text{n}}, \mathbf{c}_{\text{n}})$
   if the volume change is accepted, set $\mathbf{r}_{\text{o}} = \mathbf{r}_{\text{n}}, \mathbf{a}_{\text{o}} = \mathbf{a}_{\text{n}}, \mathbf{b}_{\text{o}} = \mathbf{b}_{\text{n}}, \mathbf{c}_{\text{o}} = \mathbf{c}_{\text{n}}$ and add $(\mathbf{r}_{\text{o}}, \mathbf{a}_{\text{o}}, \mathbf{b}_{\text{o}}, \mathbf{c}_{\text{o}})$ to S; otherwise, add $(\mathbf{r}_{\text{o}}, \mathbf{a}_{\text{o}}, \mathbf{b}_{\text{o}}, \mathbf{c}_{\text{o}})$ to S

until a desired number of samples is generated

return S
