SAND2013-10044C

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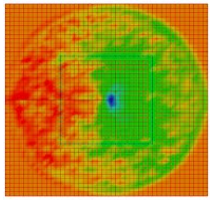
ESP900: Atomistic/Molecular Simulation:

Lecture 10: Monte Carlo methods



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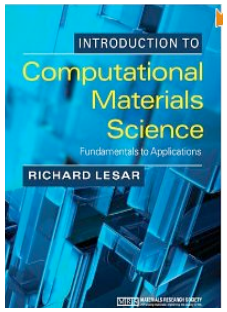


Outline

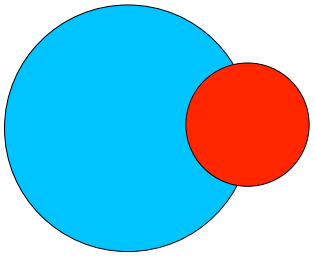
- Introduction
- Monte Carlo integration and importance sampling
- Statistical mechanics background
- The Metropolis Monte Carlo method
- Trial moves
- Monte Carlo in various ensembles

Introduction

- What is a Monte Carlo method?
  - Most generally, refers to a class of methods that use repeated random sampling to generate results
    - By computing on a sufficiently large set of samples, we can make estimates of probabilities or averages for a much larger data set
  - In molecular simulation, usually refers to "Metropolis Monte Carlo" method
    - Idea of *importance sampling* is used to generate a "good" set of sample points
    - Estimates can be computed for various ensemble-average quantities from statistical mechanics

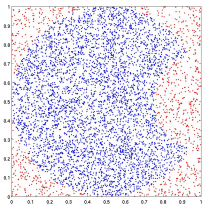
A Simple Example

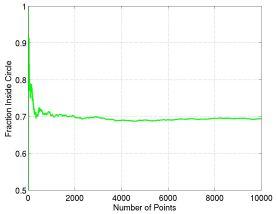
- Suppose we want to compute the area of a complex shape without knowing a formula,
  - e.g. area inside blue circle but outside of red:



A Simple Example

- Monte Carlo strategy:
  - Place points at random inside a square that circumscribes the blue circle, and count the fraction that lie inside





- For some cases (high dimensional spaces, complicated domains) this might be the most efficient way to approximate an integral

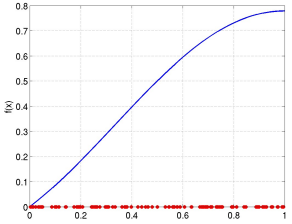
$$A_{shape} = \frac{\text{Points Inside}}{\text{Total Points}} \times A_{square}$$

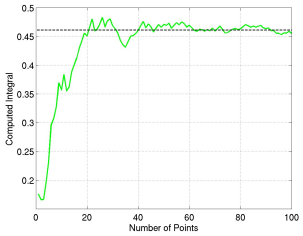
Another Integration Example

- We can compute an integral in 1D by sampling points at random in the domain
  - E.g. compute the average value of a function on the domain [0,1]

$$\langle f(x) \rangle = \int_0^1 f(x)\,dx \approx \frac{1}{N}\sum_{i=1}^{N} f(x_i)$$

$$f(x) = xe^{-(x-0.5)^2/\sigma^2}$$
$$\sigma = 1$$

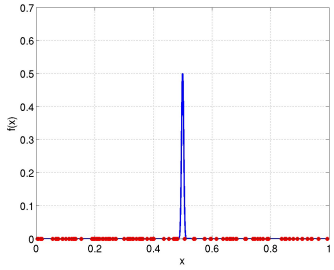


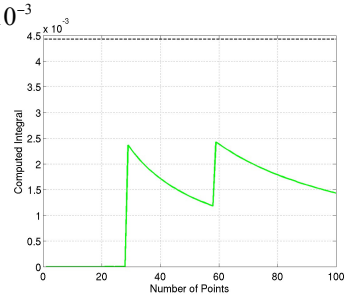


Still Another Integration Example

- But some functions can be very difficult to integrate in this way, especially if they are very localized:

$$f(x) = xe^{-(x-0.5)^2/\sigma^2}$$
$$\sigma = 5\times10^{-3}$$





Importance Sampling

- Suppose we distribute our points unevenly in space, so that they're more concentrated where the integrand is larger. This is called ***importance sampling***
- Distribute points according to some probability density function w(x) that is large where f(x) is large
  - Formally, we can do this through a change of variables: Let:

$$f(x) = g(x)\,p(x)$$
$$\int_0^1 p(x)\,dx = 1$$
$$p(x) = \frac{du}{dx}(x)$$
$$u(0) = 0$$
$$u(1) = 1$$

$$\langle f(x) \rangle = \int_0^1 g(x)\,p(x)\,dx = \int_0^1 g(x)\,du \approx \frac{1}{N}\sum_{i=1}^{N} g(x_i)$$

The points are randomly distributed in *u* space, with uniform probability density, but clustered in *x* space where *p*(*x*) is large

Importance Sampling

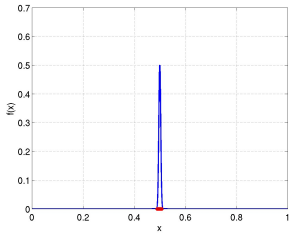
- For our earlier example:

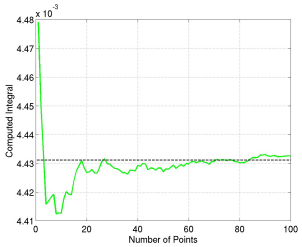
$$f(x) = xe^{-(x-0.5)^2/\sigma^2}$$

$$\sigma = 5\times10^{-3}$$

$$p(x) = Ae^{-(x-0.5)^2/\sigma^2} \quad (A \text{ is a normalization constant})$$

$$g(x) = \frac{x}{A}$$





Importance Sampling

- Unfortunately, computing the functions $p(x)$ and $u(x)$ requires that we can compute the integral of $p(x)$, which is similar in difficulty to computing the original integral!
- For example, in our "simple" example:

$$u(x) = \int_0^x p(x')dx' = \frac{1}{2} + \frac{\text{erf}\left(\frac{2x-1}{2\sigma}\right)}{2\,\text{erf}\left(\frac{1}{2\sigma}\right)}$$

- Importance sampling is useful **IF** we can write things in terms of a normalized distribution $p(x)$ **AND** we have some way of generating sample points with this distribution
  - The latter is what the **Metropolis scheme** will give us
- But why should we even care about computing integrals like this? And what does this have to do with molecular simulation?
  - The answer requires some background in statistical mechanics…

Statistical Mechanics

- Given a set of N atoms in a volume V, assume that we can describe the **state** of the system entirely in terms of the positions and momenta of each atom:

$$r_i \equiv \text{position of atom } i$$

$$p_i \equiv \text{momentum of atom } i$$

$$m_i \equiv \text{mass of atom } i$$

$$v_i \equiv \frac{p_i}{m_i} = \text{velocity of atom } i$$

  - So, (**r**,**p**) gives the state of the system, where **r** and **p** are vectors (with length 3N) of all positions and momenta of all atoms
  - Set of all possible **r** and **p** defines a **phase space**

- Fundamental question of statistical mechanics: What is the probability of finding the system in a given state (**r**,**p**)?

Probability Density

- Define the *probability density* P(**r**,**p**) such that

$$P(\mathbf{r},\mathbf{p})d\mathbf{r}d\mathbf{p} \equiv \text{Probability of finding state between } (\mathbf{r},\mathbf{p}) \text{ and } (\mathbf{r}+d\mathbf{r},\mathbf{p}+d\mathbf{p})$$

- Suppose that we know the energy E of the system
  - The **Hamiltonian** H(**r**,**p**) is the function that returns the system energy

$$H(\mathbf{r},\mathbf{p}) = \frac{1}{2}\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{m_i} + U(\mathbf{r}) = E$$

- Basic assumption of statistical mechanics:

> For a system with given number of atoms N, volume V, and energy E, **all states with energy E are equally probable**

$$P_{NVE}(\mathbf{r},\mathbf{p}) = \begin{cases} \text{constant, if } H(\mathbf{r},\mathbf{p}) = E \\ 0, \quad \text{if } H(\mathbf{r},\mathbf{p}) \neq E \end{cases}$$

Subscript denotes system with given N, V and E

The Partition Function

$$P_{NVE}(\mathbf{r},\mathbf{p}) = \begin{cases} \text{constant, if } H(\mathbf{r},\mathbf{p}) = E \\ 0, \quad \text{if } H(\mathbf{r},\mathbf{p}) \neq E \end{cases} = C\delta\big(H(\mathbf{r},\mathbf{p}) - E\big)$$

Dirac delta function

- So, what is the value of the constant?
- Let's make use of the fact that the probability density has to be normalized; i.e. the total probability of finding the state *somewhere* in phase space has to be unity:

$$\iint P_{NVE}(\mathbf{r},\mathbf{p})\,d\mathbf{r}d\mathbf{p} = 1$$

$$\Rightarrow C = \frac{1}{\iint \delta\big(H(\mathbf{r},\mathbf{p}) - E\big)\,d\mathbf{r}d\mathbf{p}}$$

- Define this normalization factor as the **partition function** $\Omega(N,V,E)$

$$\Omega(N,V,E) \equiv \iint \delta\big(H(\mathbf{r},\mathbf{p}) - E\big)\,d\mathbf{r}d\mathbf{p}$$

$$P_{NVE}(\mathbf{r},\mathbf{p}) = \frac{\delta\big(H(\mathbf{r},\mathbf{p}) - E\big)}{\Omega(N,V,E)}$$

Microcanonical Ensemble, Entropy, and Temperature

- The set of states with a given *N, V,* and *E* is called the **microcanonical ensemble**
- The microcanonical ensemble partition function $\Omega(N,V,E)$ is a measure of the number of possible states with a fixed (N,V,E)
  - Gives a measure of a surface in phase space:

$$\Omega(N,V,E) \equiv \iint \delta\big(H(\mathbf{r},\mathbf{p}) - E\big)\,d\mathbf{r}d\mathbf{p}$$

  - Note that the definition of the partition function sometimes includes a constant of proportionality to give correct units, but this is unimportant for our purposes here
- The **entropy** of a state is related to the microcanonical ensemble partition function

$$S(N,V,E) = k_B \ln \Omega(N,V,E)$$

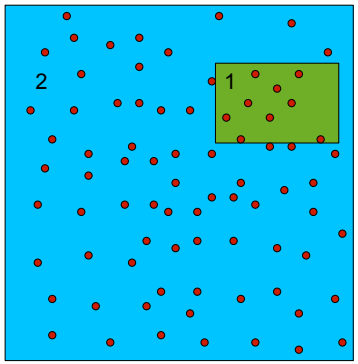
where k_B is Boltzmann's constant

- The **temperature** is in turn related to the entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V=\text{const.}}$$

The Canonical Ensemble

- Suppose that we know the temperature *T* of a system, not the energy *E*
- The ensemble of states with common *N, V,* and *T* is called the **canonical ensemble**
- How do we compute the probability of a given state $(\mathbf{r},\mathbf{p})$ in the canonical ensemble?
- To do this, consider a small system (system 1) that is in thermal contact with a much larger system (system 2)
  - Because they are in thermal contact, the two systems have the same temperature: $T_1 = T_2$
  - But the energy of system 2 is much larger



Canonical Ensemble

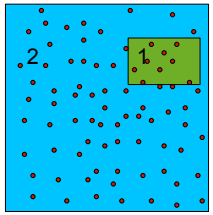
- Suppose the energy of the combined system is fixed:

$$E_{1+2} = E_1 + E_2 = \text{const.}$$

  - Note that the two systems can exchange energy, so neither E_1 nor E_2 alone is constant; both may fluctuate
- What's the probability that system 1 has a given energy E_1?
  - Same as probability that system 2 has energy E_{1+2}-E_1
  - Remember that $\Omega(E)$ is a measure of the number of states with a given energy, so:

$$P_{NVT} = \frac{\#\text{ of states where system 2 has energy } (E - E_1)}{\text{total \# of possible states}}$$

$$= \frac{\Omega(E - E_1)}{\int_0^E \Omega(E - E_1')\,dE_1'} = \frac{\Omega(E - E_1)}{\text{constant}}$$



$T_1 = T_2$

$(N_1,V_1,E_1) = (N_2,V_2,E_2)$

Canonical Ensemble

- So we have: $P_{NVT}(\mathbf{r},\mathbf{p}):\ \Omega\left(E-E_1(\mathbf{r},\mathbf{p})\right)$
- To compute this, remember that $E>>E_1$, and expand the logarithm of Ω about E_1=0:

$$\ln\Omega(E-E_1)\approx\ln\Omega(E)-E_1\frac{\partial}{\partial E}\left(\ln\Omega(E)\right)$$
$$=\frac{S(E)}{k_B}-\frac{E_1}{k_BT}$$
$$\Rightarrow\Omega(E-E_1)=\exp\left(\frac{S}{k_B}\right)\exp\left(-\frac{E_1}{k_BT}\right)$$

and so

$$P_{NVT}(\mathbf{r},\mathbf{p})=C\exp\left(-\frac{E_1(\mathbf{r},\mathbf{p})}{k_BT}\right)$$

Canonical Ensemble Partition Function

- Once again we can use the fact that P_{NVT} must be normalized:

$$P_{NVT}(\mathbf{r},\mathbf{p})=\frac{1}{Z(N,V,T)}\exp\left(-\frac{E(\mathbf{r},\mathbf{p})}{k_BT}\right)$$
$$Z(N,V,T)\equiv\iint\exp\left(-\frac{E(\mathbf{r},\mathbf{p})}{k_BT}\right)d\mathbf{r}d\mathbf{p}$$

- $Z(N,V,T)$ is the **canonical ensemble partition function**
- It's common to define the quantity $\beta=1/k_BT$, so that we can simply write:

$$P_{NVT}(\mathbf{r},\mathbf{p})=\frac{1}{Z}\exp\left(-\beta E(\mathbf{r},\mathbf{p})\right)$$
$$Z=\iint\exp\left(-\beta E(\mathbf{r},\mathbf{p})\right)d\mathbf{r}d\mathbf{p}$$

Ensemble Averages

- Suppose we're interested in knowing the expected value of some property of the system (e.g. the total energy or momentum)
- To compute this, we need to average over all of the possible states of the system (i.e. the ensemble)
  - But some states are much more like than others, so we need to compute a *weighted* average, where each state is weighted by its probability
  - For the canonical ensemble (*N,V,T*), this is:

$$\langle A\rangle=\iint A(\mathbf{r},\mathbf{p})P_{NVT}(\mathbf{r},\mathbf{p})d\mathbf{r}d\mathbf{p}$$
$$=\frac{\iint A(\mathbf{r},\mathbf{p})\exp\left(-\beta E(\mathbf{r},\mathbf{p})\right)d\mathbf{r}d\mathbf{p}}{\iint\exp\left(-\beta E(\mathbf{r},\mathbf{p})\right)d\mathbf{r}d\mathbf{p}}$$
$$=\frac{1}{Z}\iint A(\mathbf{r},\mathbf{p})\exp\left(-\beta E(\mathbf{r},\mathbf{p})\right)d\mathbf{r}d\mathbf{p}$$

- The bracket notation <*A*> denotes an ensemble average

The Metropolis Method

- For some molecular systems, the partition function and ensemble averages can be computed analytically
  - E.g. ideal gases (with no potential energy), harmonic systems (linear spring potential energy)
- But usually, ensemble averages can only be computed numerically
- We can recognize the integral in the ensemble average as a good candidate for importance sampling, because it has the form:

$$\langle A\rangle=\iint A(\mathbf{r},\mathbf{p})P(\mathbf{r},\mathbf{p})d\mathbf{r}d\mathbf{p}$$

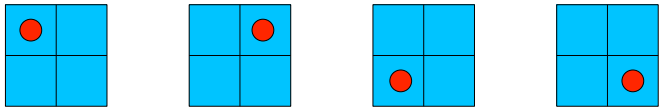
where *P* is already normalized:

$$\iint P(\mathbf{r},\mathbf{p})d\mathbf{r}d\mathbf{p}=1$$

  - Note that this integral would be hard to compute without importance sampling, since *P* is very localized because of the exponential function
- So we need a way of generating a large number of sample points in phase space (**r**,**p**) with a density *P*(**r**,**p**)

The Metropolis Method

- The Metropolis method generates a set of sample points through a simple algorithm using **trial moves**
- Let's work with a simple example: Consider a very simple system with only 4 possible states.



A B C D

- Each state has a different energy: E_A, E_B, E_C, E_D
- The probability of finding the system in each state is related to the energy:

$$P(A) = \frac{\exp(-\beta E_A)}{\sum_i \exp(-\beta E_i)}$$

The Metropolis Method

- We want to generate a sequence of states, e.g. (*A,C,C,A,B,C,D,D,D,A,*…), so that the frequency of each state is proportional to the canonical ensemble probability for that state:

$$\frac{N_A}{N_B} = \frac{P(A)}{P(B)} = \frac{\exp(-\beta E_A)}{\exp(-\beta E_B)} = \exp\left(-\beta\left(E_A - E_B\right)\right)$$

- Each item in the sequence can be thought of as a move from one state to another
  - This includes the possibility that a "move" results in the system remaining in the same state, e.g. (*A,A,A,*…)
- How do we compute the probability of moving from one state to another?
  - Call this the **transition probability:**

$\pi_{AB} \equiv$ probability of moving from state A to state B (assuming we start at state A)

Detailed Balance

- Thought experiment: Imagine a large number of simulations running simultaneously, with some number of simulations (N_A, N_B, N_C, N_D) simultaneously in each state
- For equilibrium, we need the number of simulations leaving state *A* to equal the number of simulations entering state *A*
  - Remember that π_{AB} is the transition probability from state *A* to *B*, so:

$$\boxed{\begin{array}{c}\text{number leaving state } A \;=\; \text{number entering state } A \\ N_A\pi_{AB} + N_A\pi_{AC} + N_A\pi_{AD} = N_B\pi_{BA} + N_C\pi_{CA} + N_D\pi_{DA}\end{array}}$$

- It's easiest to enforce this by imposing a much stronger condition: the number of moves going from state *A* to *B* is exactly canceled by the number from *B* to *A* (and likewise for all other pairs):

$$\boxed{N_A\pi_{AB} = N_B\pi_{BA}}$$

  - This condition is called **detailed balance**
    - Sometimes called **microscopic reversibility**
  - If detailed balance is enforced, so is the more general condition above

Transition Probabilities

- Enforcing detailed balance gives us the ratio of transition probabilities:

$$N_A\pi_{AB} = N_B\pi_{BA}$$

$$\frac{\pi_{AB}}{\pi_{BA}} = \frac{N_B}{N_A} = \frac{\exp(-\beta E_B)}{\exp(-\beta E_A)} = \exp\left(-\beta\left(E_B - E_A\right)\right)$$

  - So, if the energy of state *B* is higher than state *A* ($E_B > E_A$), the ratio is less than 1 and the transition from *B* to *A* is more likely
  - The system is more likely to move to lower energy
- In the Metropolis method, transitions are implemented in two steps:
  - Pick a trial move, a transition from one state to another
  - Randomly decide whether to accept the move (with some probability); if accepted, the move to the new state, but if rejected, remain in the old state
- Let α_{AB} be the probability that the transition AB is chosen as the trial move
- Let a_{AB} be the probability that this transition is accepted
- Then the total transition probability is the product of these two:

$$\pi_{AB} = \alpha_{AB} a_{AB}$$

Acceptance Probabilities

- In many cases, we can choose the trial moves with symmetric probabilities, so that $\alpha_{AB}=\alpha_{BA}$
- So the ratio of transition probabilities is controlled by the ratio of acceptance probabilities:

$$\frac{\pi_{AB}}{\pi_{BA}} = \frac{\alpha_{AB}a_{AB}}{\alpha_{BA}a_{BA}} = \frac{a_{AB}}{a_{BA}} = \exp\left(-\beta\left(E_B - E_A\right)\right)$$

- The method introduced by Metropolis et al. (1953) satisfies this ratio by choosing:

$$a_{AB} = \begin{cases} 1, & \text{if } E_B \le E_A \\ \exp\left(-\beta\left(E_B - E_A\right)\right), & \text{if } E_B > E_A \end{cases}$$

  - So, a trial move is always accepted if it leads to a decrease in energy
  - But there is still a finite probability of accepting a move if it increases the energy
  - The acceptance probability goes to zero if $\beta(E_B-E_A)$ is very large, i.e. if the energy change is large compared to k_BT

Implementation

$$a_{AB} = \begin{cases} 1, & \text{if } E_B \le E_A \\ \exp\left(-\beta\left(E_B - E_A\right)\right), & \text{if } E_B > E_A \end{cases}$$

- To implement this, we need to generate of a random number if $E_B>E_A$
  - Generate a random number ***r*** between 0 and 1

$$\rightarrow \begin{cases} \text{accept move}, & \text{if } r < \exp\left(-\beta\left(E_B - E_A\right)\right) \\ \text{reject move}, & \text{if } r \ge \exp\left(-\beta\left(E_B - E_A\right)\right) \end{cases}$$

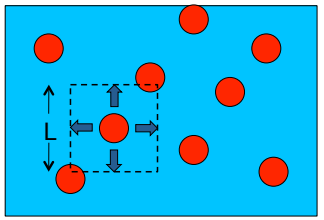
Summary: The Metropolis Algorithm

The Metropolis Monte Carlo algorithm:

- Suppose we want to compute some averaged quantity <*F*>, where *F* is a function of the state of the system.
- Specify the temperature of the system, and compute $\boldsymbol{\beta}=1/k_BT$
- Beginning from some known state:
  1. Compute the energy of the current state, $E_{current}$
  2. Choose a new state at random; this is the trial move
  3. Compute the energy of the new state, E_{new}
  4. If Enew<=Ecurrent, accept the trial move (current state = new state) and go to step 6
  5. Else, choose a random number *r* between 0 and 1
     - If $r < \exp(-\beta(E_{new}-E_{current}))$, accept the trial move
     - Else, reject the trial move
  6. Compute *F* at the current state and update statistics
  7. Go to step 1

Metropolis Method for Molecular Simulation

- The algorithm is the same for a system of atoms as for our simple example
- Now, the state of the system is defined by positions and momenta, (**r,p**)
- A trial move from one state to another therefore changes the position or momentum of one or more particles
- Usually these are incremented by a random amount less than some maximum:



$$x_{new} = x_{old} + \frac{L}{2}\left(random - 0.5\right)$$

$$y_{new} = y_{old} + \frac{L}{2}\left(random - 0.5\right)$$

$$z_{new} = z_{old} + \frac{L}{2}\left(random - 0.5\right)$$

Metropolis Method for Molecular Simulation

- Momentum can be changed in a similar way
- However, very often we can work with position changes only. Why?
  - The energy function is usually *separable* into kinetic (depending only on momenta) and potential (depending only on positions)
  - The statistics we care about are often only functions of positions, so:

$$\langle A(\mathbf{r})\rangle = \frac{\iint A(\mathbf{r})\exp\left(-\beta\left(K(\mathbf{p})+U(\mathbf{r})\right)\right)d\mathbf{r}d\mathbf{p}}{\iint \exp\left(-\beta\left(K(\mathbf{p})+U(\mathbf{r})\right)\right)d\mathbf{r}d\mathbf{p}}$$
$$= \frac{\left(\int A(\mathbf{r})\exp\left(-\beta U(\mathbf{r})\right)d\mathbf{r}\right)\left(\int \exp\left(-\beta K(\mathbf{p})\right)d\mathbf{p}\right)}{\left(\int \exp\left(-\beta U(\mathbf{r})\right)d\mathbf{r}\right)\left(\int \exp\left(-\beta K(\mathbf{p})\right)d\mathbf{p}\right)}$$
$$= \frac{\int A(\mathbf{r})\exp\left(-\beta U(\mathbf{r})\right)d\mathbf{r}}{\int \exp\left(-\beta U(\mathbf{r})\right)d\mathbf{r}}$$

- Algorithms proceed as before, but trial moves only change atom positions, and we can work with $U(\mathbf{r})$ instead of $E(\mathbf{r},\mathbf{p})$

Example: A Very Early Application

- Metropolis et al., *J Chem Phys* **21**:1087 (1953)
  - Introduced the method
  - Computed radial distribution function of rigid spheres
  - Energy of rigid sphere system is either 0 (for no overlap between spheres) or infinity (if there's overlap)

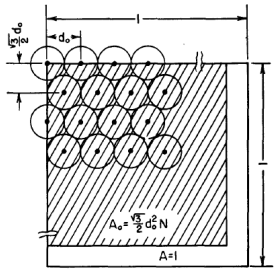


FIG. 3. The close-packed arrangement for determining A_0.

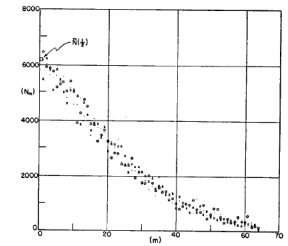
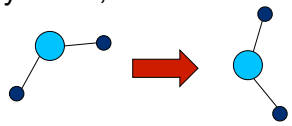


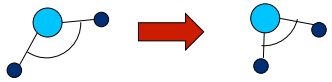
FIG. 5. The radial distribution function N_m for $\nu=5$, $(A/A_0)=1.31966$, $K=1.5$. The average of the extrapolated values of N_m in $N_1=6301$. The resultant value of $(PA/NkT)-1$ is $6KN_1/N^2(K-1)$ or 6.43. Values after 16 cycles, ●; after 32, ×; and after 48, ○.

Trial Moves

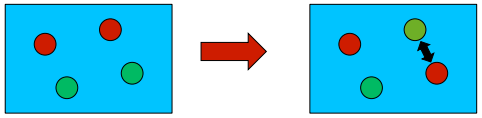
- We've already looked at **translational** moves, where the position of an atom is perturbed
- For molecular systems, **orientational** moves are also possible:
  - Rotational:



  - Internal molecular degrees of freedom:



- For mixed systems, identity swaps are also allowed:



Trial Moves

- Other important points about trial moves:
  - **Symmetry**
    - The probability of choosing (NOT accepting!) a trial move from one state to another must equal the probability of the reverse move

$$\alpha_{AB} = \alpha_{BA}$$

  - **Ergodicity**
    - The set of allowed trial moves must allow all regions of phase space to be reached in a finite number of moves from any point
  - **Step size**
    - If the step (e.g. the translation distance) is too large, the energy change may be so large that very few moves are accepted
    - If the step size is too small, phase space is explored too slowly
    - Good rule of thumb: aim for about 50% acceptance of trial moves
  - **Equilibriation**
    - The initial configuration may not be near equilibrium, so as in MD, we often allow the system some time to reach equilibrium before taking statistics

Monte Carlo in Other Ensembles

- We've been looking at the canonical ensemble: constant (N,V,T)
- Other ensembles can be used, by modifying the probability density (the partition function) and the types of trial moves
- **Isobaric-Isothermal Ensemble**
  - Constant (N,P,T) – number, pressure and temperature
  - Volume can change
- **Grand-Canonical Ensemble**
  - Constant (μ,V,T) – chemical potential, volume and temperature
  - Number of particles can change

Isobaric-Isothermal Ensemble

- Constant (N,P,T)
- Trial moves:
  - Particle displacements (translations and rotations)
  - Volume changes
    - Particle positions are written in terms of *relative* coordinate **s:**
    - **s** remains constant when V (and L) are changed

$$\mathbf{s}_i = \frac{\mathbf{r}_i}{L}$$

$$V = L^3$$

- Probability distribution:

$$P_{NPT}(\mathbf{s},V) \propto \exp\left(-\beta\left[U(\mathbf{s},V) + PV - N\beta^{-1}\ln V\right]\right)$$

Grand Canonical Ensemble

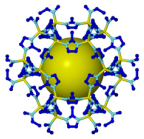
- Constant (μ,V,T)
- Trial moves:
  - Particle displacements (translations and rotations)
  - Particle insertion and removal
    - A particle is inserted at a random position, or a randomly selected particle is removed
- Probability distribution:

$$P_{\mu VT}(\mathbf{r},N) \propto \frac{\exp(\beta\mu N)}{\Lambda^{3N}N!}\exp\left(-\beta U(\mathbf{r})\right)$$

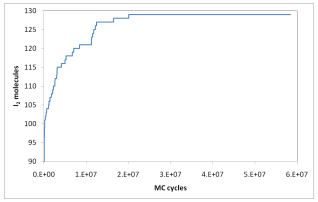
$$\Lambda \equiv \sqrt{\frac{h^2}{2\pi m k_B T}} = \text{thermal de Broglie wavelength}$$

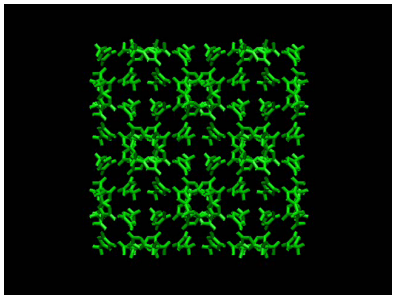
Example: Grand Canonical MC Simulation of Iodine Uptake in Metal-Organic Framework

GCMC of I2 in ZIF (Zeolitic Imidazolate Framework) [P. Crozier]



Crystal structure of ZIF-8 with void space shown in yellow. (*Figure credit: Praveen K. Thallapally)*

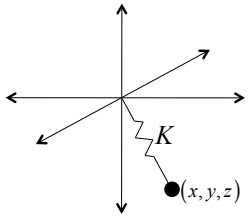




Further Reading

- Books
  - D. Frenkel and B. Smit, Understanding Molecular Simulation, Academic Press, 1996.
    - A great summary of the MC technique, with lots of details on statistical mechanics and MC in other ensembles
- Papers
  - N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, "Equation of state calculations by fast computing machines", *J. Chem Phys.* **21**(6):1087
    - The original reference for the Metropolis method, and a very readable paper

Homework



- Consider a 1-particle system with a harmonic spring, with spring constant K
- Potential energy:

$$U(r) = \frac{1}{2}Kr^2$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

- Given temperature T, and $\beta = 1/k_B T$

1. Compute the expected mean values of r and U **analytically**, as functions of K and β (assume the canonical ensemble)
2. Using the python script provided, use Metropolis Monte Carlo to compute <r> and <U> for K=1.0, and β = 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0. Compare with the analytical values.

Homework

- Syntax for the example problem: `mmc.py [K] [beta]`
- Integrals of spherically symmetric functions can be rewritten in terms of r :

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f(x,y,z)\,dxdydz = \int_0^{+\infty} 4\pi r^2 f(r)\,dr$$

- The following integrals may be useful:

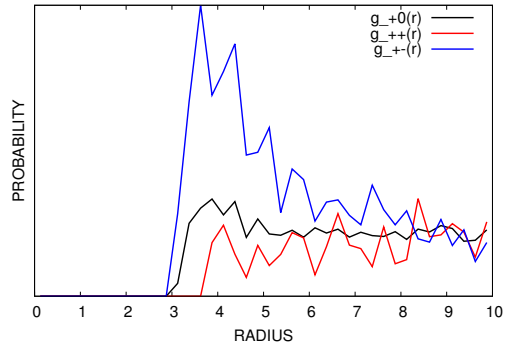
$$\int_0^{+\infty} 4\pi r^2 \exp\left(-\frac{1}{2}\beta K r^2\right) dr = \left(\frac{2\pi}{\beta K}\right)^{3/2}$$

$$\int_0^{+\infty} 4\pi r^3 \exp\left(-\frac{1}{2}\beta K r^2\right) dr = \frac{8\pi}{\beta^2 K^2}$$

$$\int_0^{+\infty} 2\pi K r^4 \exp\left(-\frac{1}{2}\beta K r^2\right) dr = \frac{3\sqrt{2}\pi^{3/2}}{\beta^{5/2} K^{3/2}}$$

Script

```
pair_style lj/cut/coul/cut 10.
dielectric 80.0
read_data      relax.data
group NEUTRAL  type 1
group POSITIVE type 2
group NEGATIVE type 3
pair_coeff * * 0.2381 3.405
pair_modify shift yes
mass      * 39.948
timestep      1.0
fix     NVE all nve
thermo 100
thermo_style custom step temp pe
compute RDF all rdf 40 2 1 2 2 2 3
fix RDF all ave/time 1000 1 1000 c_RDF file
rdf.dat mode vector
run 100000
```

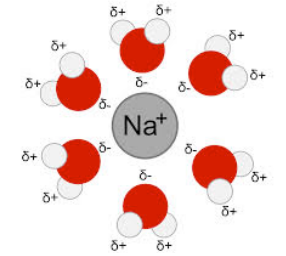


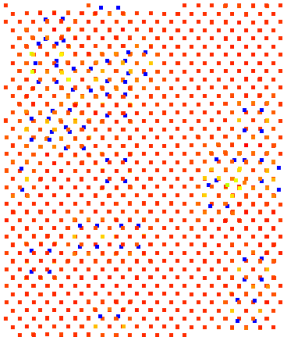
- Do these distributions make sense?
- Why is there a gap?
- Why is the blue curve peaked?
- Why are the curves ordered the way they are?
- Is this data converged?
- Does the system size matter?

BONUS

- Change the neutral species in the fluid system for a water model like TIP4P and observe the differences in the solvation structure
- Make a fluid confined by two walls. Will the RDF change? Will it be uniform?

- Observe the differences in point defect structures obtained using a Stillinger-Weber potential vs Tersoff
- Reverse the loading of the nanobeam , will the response change?
- Add stress as an output does it tell you anything?





Lecture 11

Week 7: **Analyzing Inhomogeneous Systems**

- Identification and visualization of defects and structures
- Metrics, e.g. radial distribution function, common neighbor analysis, centrosymmetry
- Available tools
- Homework: Calculation of centrosymmetry and slip vector around a defect

Week 8 : **Molecular Dynamics**

- Newton's 2nd Law
- Time integration algorithms (Verlet, SHAKE, Gear)
- Conserved quantities
- Ensembles (NVE, NVT, NPT, NPH) & equations of motion
- Thermostats, e.g. Nose-Hoover
- Initial conditions and velocity distributions
- *Homework*: NVT average of pressure.

Reading Suggestions for Lec. 11

- Chapter 6 of LeSar
- Chapter 4 of Frenkel & Smit
- Chapter 3 & 6 of Evans & Morriss
- http://en.wikipedia.org/wiki/Molecular_dynamics
- http://lammps.sandia.gov/