

06-640: Molecular Simulations

Homework 4

Due date: Thursday 3/15

1. We showed in class that the partition function for a classical N-body system in the canonical ensemble is

$$Q = \frac{1}{N! h^{3N}} \int \dots \int d\bar{p}_1 \dots d\bar{p}_N d\bar{r}_1 \dots d\bar{r}_N \exp\left(-\frac{E}{k_B T}\right).$$

In this problem, we will examine an ideal monatomic gas of N atoms confined in a volume V at temperature T. In an ideal gas, the potential energy due to interactions between atoms is neglected, so the total energy of the system in a particular state is

$$E = \frac{m}{2} \sum_{i=1}^N (v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2).$$

Show that the partition function of this system can be written as $Q = q^N / N!$, where q is the partition function of a single atom in volume V at temperature T. Then show that q (and therefore Q) can be evaluated explicitly. Use the resulting expression for the partition function to evaluate the Helmholtz free energy, A, the thermodynamic energy, E, and pressure, P, of an ideal gas as a function of N, V, and T.

Finally, extend your results to an ideal binary mixture containing N_1 atoms of mass m_1 and N_2 atoms of mass m_2 . The total partition function for this mixture can be written as

$$Q = (q_1^{N_1} q_2^{N_2}) / (N_1! N_2!).$$

[Hint: The result you find for the pressure should look familiar.]

2. If we define $f(x,y) = 1$ for $x^2 + y^2 \leq 1$ and $f(x,y) = 0$ for $x^2 + y^2 > 1$, then

$$\int_{-1}^1 \int_{-1}^1 f(x,y) dx dy = \pi. \text{ Write a MATLAB code to compute } \pi \text{ by evaluating this double}$$

integral using Monte Carlo sampling. Compute π by using $N = 10, 100, 1000,$ and $10,000$ samples. In each case, run your code 5 times and report the average value of π and the estimated uncertainty. Based on your results, predict how many samples you would need to compute π to 20 significant figures.

3. Write a MATLAB code to evaluate $I = \int_0^1 \exp(-50x) \sin(x) dx$ using (a) brute force

Monte Carlo sampling and (b) importance sampling. Compare the accuracy of these two schemes using the same numbers of samples as in problem 1. Briefly describe why the accuracy of the two schemes differ.

4. In this problem we will use Monte Carlo simulations to study the properties of a single diatomic molecule. We will assume that the potential energy of a diatomic molecule can

be expressed as a function of only the distance between the two atomic centers, r .

Specifically, we will assume that $U(r) = \frac{1}{2} K(r - r_0)^2$, where r_0 is the equilibrium bond length and K is a constant.

- (a) Using $r_0 = 0.15$ nm and $K = 2 \times 10^7$ K.nm⁻², write a MATLAB code that uses Metropolis Monte Carlo to compute $\langle U \rangle_T$ for $T = 100, 200, 300$ K. Make sure you describe how you debugged your code and how you chose the parameters you used to collect your data.
- (b) Repeat part (a) but use $r_0 = 0.15$ nm and $K = 1 \times 10^7$ K.nm⁻². How do your results differ from those of part (a)? Explain your observations.
- (c) We noted in class that the Metropolis acceptance/rejection criterion is not unique. In other words, there are other acceptance/rejection criteria that also can be used to perform Monte Carlo calculations in the NVT ensemble. Demonstrate this fact by repeating part (a) using the following criterion: compute the acceptance

$$\text{probability for all moves by } acc(old \rightarrow new) = \frac{\exp(-\beta\delta E / 2)}{\exp(-\beta\delta E / 2) + \exp(\beta\delta E / 2)},$$

where $\delta E = U(new) - U(old)$. Simulations performed with this criterion are often referred to as Kawasaki Monte Carlo. In addition to implementing Kawasaki Monte Carlo in your MATLAB code, you should show analytically that this criterion satisfies detailed balance.