Problems

1. Show that the velocity Verlet scheme for integrating Newton's equations of motion produces identical trajectories to the Verlet scheme.

2. Calculate the expected error in the value of π obtained by Monte Carlo approach on p. 23 when the circle has diameter d and lies within a square of size l. Show that this error is minimized when $d/l = 1$

   Formulate a Markov chain Monte Carlo version of this approach to calculate π.

3. Suppose you wanted to calculate the integral $\int_0^1 (1+x^2)$ by MC simulation.

   (a) What would the standard deviation be for a straightforward calculation using M points

   (b) What would the standard deviation be if you used $1+x$ as your importance sampling function.

4. Revision of classical statistical mechanics

   Consider a system interacting with a pair potential. Its canonical partition function has the form:

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} Z(N,V,T) \tag{1}$$

   where the de Broglie thermal wavelength is $\Lambda = (2\pi mkT/h)^{1/2}$ and the configurational partition function is given by

$$Z(N,V,T) = \int \exp\left[-\beta \mathcal{V}\left(\mathbf{r}^N\right)\right] d\mathbf{r}^N \tag{2}$$

   (a) Show that for an ideal gas $Z(N,V,T) = V^N$

   (b) Show that the free energy per particle is given by

$$\frac{\beta A_{id}}{N} = \log\left[\rho\Lambda^3\right] - 1. \tag{3}$$

   (c) From this derive the pressure $\beta P(\rho)$

   (d) Derive an expression for the chemical potential $\mu = (\partial A/\partial N)_{V,T}$

   (e) The grand-canonical partition function can be written as

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \exp\left[N\beta\mu\right] Q(N,V,T). \tag{4}$$

   Hence, derive the form of grand-canonical partition function for an ideal gas. As $\beta PV = \log[\Xi(\mu,V,T)]$, then derive an expression for the pressure of an ideal gas in terms of μ. Is this result consistent with the results of (c) and (d)?

(f) Do the same for the isobaric ensemble, where the variables are N, P, T.

(g) For low-density gases, the pressure can be approximated with a second virial coefficient:

$$\beta P = \rho + B_2\rho^2. \tag{5}$$

For such a system what is the excess free-energy defined by $A = A_{id} + A_{ex}$ and the excess chemical potential.

5. The heat capacity can be calculated from fluctuations in the total energy in the canonical ensemble:

$$C_v = \frac{\langle E^2\rangle - \langle E\rangle^2}{kT^2} \tag{6}$$

However, in NVT MC only the potential energy is calculated. Derive an expression for the heat capacity in terms of fluctuations in the potential energy.

6. Consider a system for which the energy is a function of only one variable (x) and is given by:

$$\exp[-\beta E(x)] = \begin{cases} 1 & 0 \leq x < 1 \\ 0 & x < 0 \text{ or } x \geq 1 \end{cases} \tag{7}$$

We wish to use Monte Carlo to simulate this system, and consider two algorithms that differ in the types of moves used.

(a) Add a random displacement between $[-\delta, \delta]$ to x.

(b) Generate a random number ϕ between $[1, 1+\delta]$. With probability of 0.5 invert the value of ϕ. Scale x by ϕ.

Derive the correct acceptance criteria for both schemes. [One way to check that you have got the right answers is to write a short MC program to calculate the average value of x using the above schemes.]

What will happen if the acceptance criterion for (i) is used for (ii)

7. Calculate expressions for the tail correction for the energy and pressure for a truncated LJ potential.

8. Widom insertion is a much more efficient method for calculating the excess chemical potential than Widom deletion in which trial particle deletion moves are probed. For Widom deletion, derive an expression for the excess chemical potential that is analogous to that for Widom insertion. Suggest why Widom deletion is not as efficient? What happens if one applies it to hard spheres?

Computational Exercises

1. Write an MC program to simulate the 2D Ising model on a square lattice with nearest-neighbour ferromagnetic interactions. Use single spin flips as the basic MC move.

   Compute the temperature dependence of the magnitude of the magnetization, heat capacity and magnetic susceptibility. Explore the dependence of the results on the system size and comment on the trends.

   Estimate the transition temperature at zero field.

2. Write either a molecular dynamics or Monte Carlo program to simulate a Lennard-Jones fluid.

   Use reduced units (i.e. measure energy in ϵ, distance in σ, time in $(m\sigma^2/\epsilon)^{1/2}$), periodic boundary conditions, a cut-and-shifted potential (include tail corrections) for a system of 108 atoms.

   If using MD, explore how the time-step affects the conservation of energy. If using MC, explore how the acceptance ratio depends on step size.

   Compute the equation of state of the Lennard-Jones fluid at $T = 2.0\,\epsilon k^{-1}$ and compare to the equation of state in Johnson *et al.* (Molecular Physics, **78**, 591-618 (1993).

3. Adapt your 2D Ising program to compute the free-energy barrier as a function of the magnetization using umbrella sampling. (Generating the biasing distribution is easier for smaller system sizes and the relative free energy of the two stable states can be used to check convergence.)

   Explore the temperature dependence of the free energy barrier, and hence again estimate the transition temperature. Is this consistent with your previous estimates?

   What is the lowest-energy state with zero magnetization? Hence, calculate the free-energy barrier at $T = 0$. Do your computational results extrapolate to this value?