Understanding Molecular Simulation
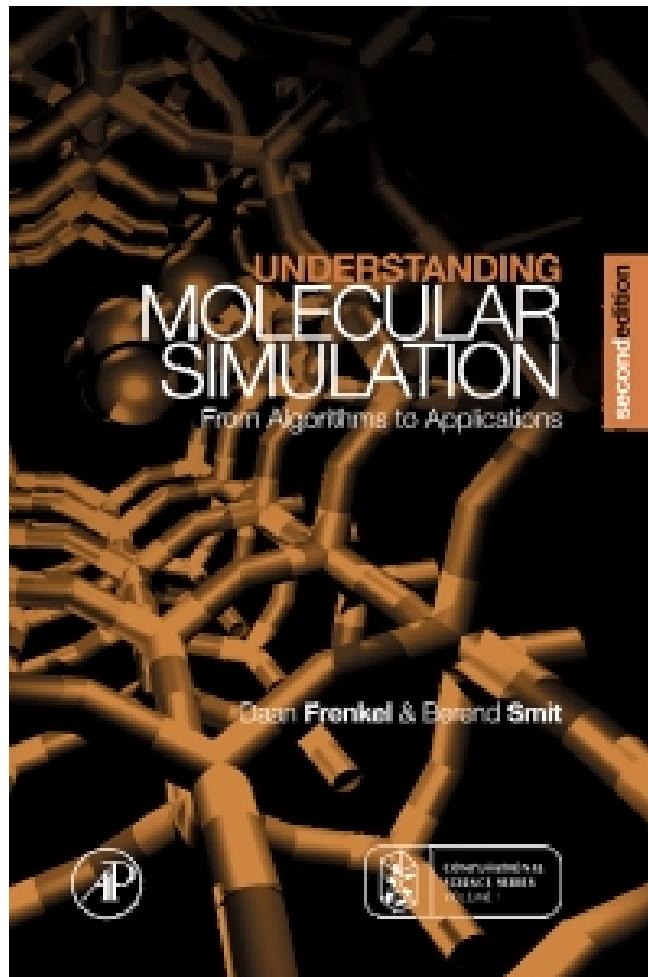
Seyed Mohamad Moosavi, Andres Guerrero and Berend Smit [*]
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[*]berend.smit@epfl.ch

Block 4

Phase equilibrium and free-energy calculations

4.1   Vapour-liquid equilibrium

In this exercise, we will use Widom's test particle method (see Page 175 of the book) to locate a vapour-liquid equilibrium. This is compared with a Gibbs-ensemble simulation.

Questions:

1. Modify the Monte Carlo program of Lennard-Jones particles in the NVT ensemble (only in the file *mc_nvt.f* or *mc_nvt.c*) in such a way that the chemical potential can be calculated using Widom's test particle method:

$$\mu = \mu_0 - \frac{\ln\left(\rho^{-1}\left\langle\exp\left[-\beta\Delta U^+\right]\right\rangle\right)}{\beta} \tag{4.1}$$

   in which ρ is the number of particles per volume, U^+ is the energy of a test particle and

$$\mu_0 = \frac{\ln\left(\Lambda^3\right)}{\beta} \tag{4.2}$$

   - Compute μ_0 and make a plot of the excess chemical potential and pressure as a function of the density for $T = 0.8$. Use the following densities: 0.001, 0.003, 0.006, 0.009, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9.
   - Why is it more difficult to calculate the chemical potential at high densities than at low densities?
   - How can you locate the vapour-liquid coexistence densities?

2. Perform a Gibbs-ensemble simulation of the system at $T = 0.8$. In the Gibbs ensemble, the chemical potential of box i is equal to

$$\mu_i = \mu_0 - \frac{\ln\left\langle\frac{V_i}{n_i+1}\exp\left[-\beta\Delta U_i^+\right]\right\rangle}{\beta} \tag{4.3}$$

   in which n_i is the number of particles in box i and V_i is the volume of box i. Do the vapour-liquid density and chemical potential agree with your previous results?

4.2 Umbrella sampling

Generally, it may be difficult to sample high free energy regions of phase space. If one would like to obtain an accurate ensemble average including such regions, we can force the simulation to stay within these regions using an additional biasing (umbrella) potential. Below we will consider a very simple case of such a potential: a zero potential constrained by two hard walls, that divides the space into overlapping slices.

Consider a single particle on a one-dimensional energy landscape. The energy as a function of the position is given by

$$U(x) = \epsilon x^2 \tag{4.4}$$

One would like to calculate the probability distribution of finding the particle at a position x ($p(x)$) using a Monte-Carlo scheme (we will use $\beta = \epsilon = 1$).

Questions:

1. Why is this distribution difficult to calculate for large values of x when a conventional MC scheme is used ?

2. Alternatively, one can divide the x axis in overlapping slices and calculate the distribution $p(x, i)$ in all slices i. This scheme is often referred to as umbrella sampling. Show that $p(x, i) \propto p(x, j)$ when $i \neq j$ (This also means that $\ln(p(x, i)) = \ln(p(x, j)) + C$ in which C is a constant).

3. Compare the results from the conventional MC algorithm with the results from the umbrella-sampling simulations, especially at large values of x. Different slices can be combined using *xmgr* or *gnuplot*.

   Note that in practice we use a fitting procedure to link the different slices together. One can increase the accuracy of such a fitting procedure by putting more weight on the most frequently sampled data points, which is commonly referred to as the Weighted Histogram Analysis Method (WHAM).