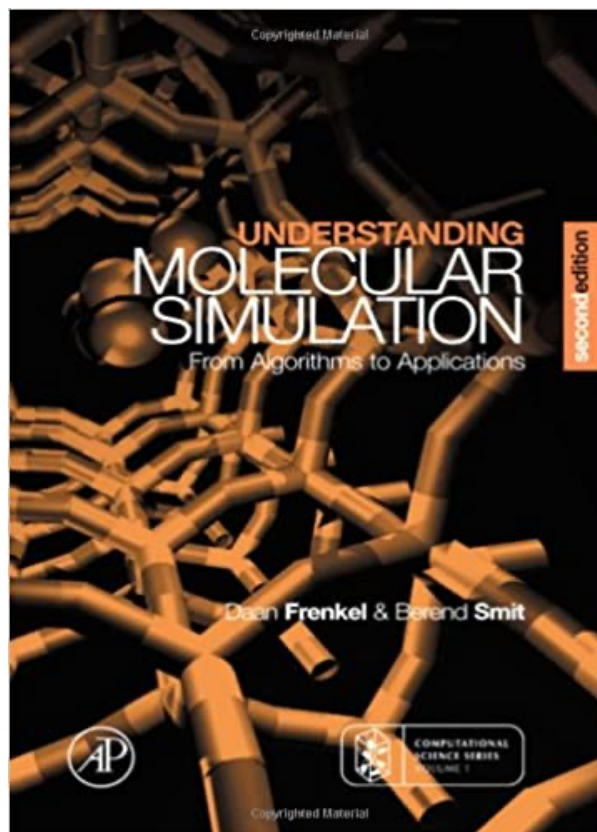*CH-420 EXERCISE NOTES*

Understanding Advanced Molecular Simulation

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Block 3

MD and MC in various ensembles

3.1 Barrier crossing

Consider the movement of a single particle that moves on a 1D potential energy surface with the following functional form:

$$U(x) = \begin{cases} \epsilon B x^2 & x < 0 \\ \epsilon(1 - \cos(2\pi x)) & 0 \leq x \leq 1 \\ \epsilon B (x - 1)^2 & x > 1 \end{cases} \tag{3.1}$$

The energy, force and the derivative of the force are continuous functions of the position x and $\epsilon > 0$.

Questions:

1. Derive an expression for B. Make a sketch of the energy landscape.

2. A program is provided that integrates the equation of motion of the particle starting at $x(t = 0) = 0$ using several methods. What do you expect the phase space trajectories to look like in the following situations?

   (a) No thermostat (NVE ensemble).

   (b) The Andersen thermostat. In this method, the velocity of the particle is coupled to a stochastic heat bath which leads to a canonical distribution.

   (c) A Nosé-Hoover chain . In this method, the motion of the particle is coupled to a chain of thermostats. The equations of motion are integrated using an explicit time-reversible algorithm that might look a little-bit complicated at first sight , see *integrate_res.f* or *integrate_res.c*. One can prove that this method yields a canonical distribution provided that the system is ergodic.

   (d) No molecular dynamics, but a simple Monte Carlo scheme.

3. The Andersen thermostat and the NVE integration algorithm are not implemented yet, so you will have to do this yourself (see *integrate_nve.f* and *integrate_and.f*, or *integrate_nve.c* and *integrate_and.c*). Try to use all methods for a low temperature, $T = 0.05$, for which the system behaves like a harmonic oscillator. Pay special attention to the following:

   (a) Why does the phase space distribution of the MC scheme look so much different at low temperatures ?

(b) Why does the phase space distribution of the NVE scheme look like a circle ?

(c) Compare the phase space distributions of the Nosé-Hoover chain method with distribution generated by the Andersen thermostat. How long has the Nosé-Hoover chain to be to obtain a canonical distribution ?

4. Investigate at which temperature the particle is able to cross the energy barrier.

5. Another widely used algorithm is the temperature coupling of Berendsen , which provides a fast adaptation of the system to the target temperature. In this algorithm the temperature of the system is controlled by scaling the velocities every timestep with a factor λ.

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right) \right]^{\frac{1}{2}} \tag{3.2}$$

in which T_0 is the desired temperature, T is the actual temperature, Δt is the time step on the integration algorithm and τ_T is a constant. The temperature coupling can be used in combination with a leap-frog algorithm:

$$
\begin{aligned}
v \left(t + \frac{\Delta t}{2} \right) &= \lambda \left(t - \frac{\Delta t}{2} \right) \times \left(v \left(t - \frac{\Delta t}{2} \right) + \frac{F(t)}{m} \Delta t \right) \\
x(t + \Delta t) &= x(t) + v \left(t + \frac{\Delta t}{2} \right) \Delta t
\end{aligned}
\tag{3.3}
$$

This method does not produce a canonical ensemble. Recently, an improvement was suggested to this thermostat by including a stochastic term to the scaling factor.

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right) + 2 \sqrt{\frac{T_0 \Delta t}{T \tau_T}} dW \right]^{\frac{1}{2}} \tag{3.4}$$

with dW a so-called Wiener noise (*i. e.* a zero mean Gaussian distributed random noise).

Program the Berendsen term and the stochastic term in *integrate_ber.c* or *integrate_ber.f*.

What happens to the sampling of the phase space, without the stochastic term?

3.2 MC in the NPT ensemble

Enclosed is a program to simulate hard spheres of diameter $\sigma = 1$ in the NPT ensemble using MC.

Questions:

1. Why is it impossible to calculate the virial for this system directly?

2. In the current code, a random walk is performed in $\ln(V)$ instead of V. Change the code in such a way that a random walk in V is performed. Check that the average densities calculated by both algorithms are equal.

3. Make a plot of the acceptance ratio for volume displacements as a function of the maximum volume displacement for both algorithms. Why could it be advantageous to sample in $\ln(V)$?

3.3 Parallel tempering

The method of parallel tempering is a Monte Carlo scheme that has been derived to achieve good sampling of systems that have a free energy landscape with many local minima.
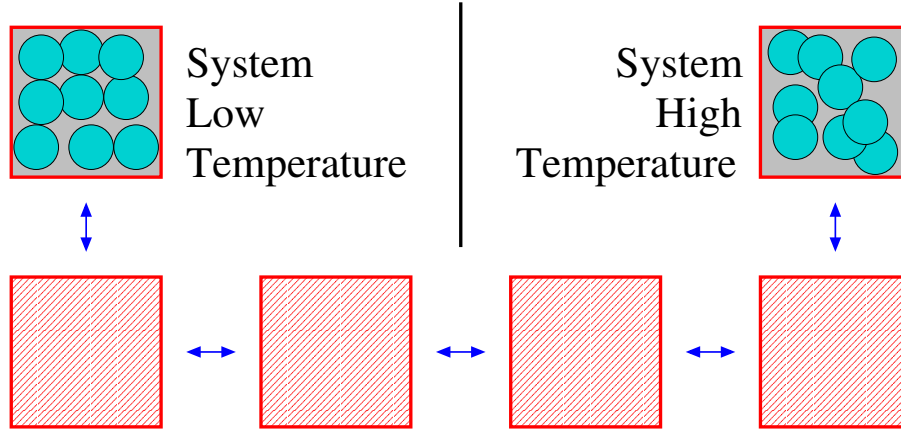

Figure 3.1: Parallel tempering. The low temperature systems suffers from ergodicity problems. At low temperatures, the particles are not able to pass one another and therefore a particle is confined at its original position.

In parallel tempering we consider N systems. In each of these systems we perform a simulation in the canonical ensemble, but each system is in a different thermodynamic state. Usually, but not necessarily, these states differ in temperature. In what follows we assume that this is the case. Systems with a sufficiently high temperature pass all barriers in the system. The low-temperature systems, on the other hand, mainly probe the local energy minima. The idea of parallel tempering is to include MC trial moves that attempt to "swap" systems that belong to different thermodynamic states, *e.g.*, to swap a high temperature system with a low temperature system. If the temperature difference between the two systems is very large, such a swap has a very low probability of being accepted. This is very similar to particle displacement in ordinary Monte Carlo. If one uses a very large maximum displacement a move has a very low probability of being accepted. The solution to this problem is to use many small steps. In parallel tempering we use intermediate temperatures in a similar way. Instead of making attempts to swap between a low and a high temperature, we swap between systems with a small temperature difference. In principle the distribution of the position of a particle should be symmetrical. The high-temperature system *does* show this symmetrical distribution.

The total partition function of a system with N canonical subsystems (Q) equals

$$Q = \prod_{i=1}^{i=N} Q_i \tag{3.6}$$

in which Q_i is the canonical partition function of the individual system i

$$Q_i = \sum_{x_i} \exp\left[-\beta_i U\left(x_i\right)\right] \tag{3.7}$$

where $\beta_i = 1/\left(k_B T_i\right)$. For each of these systems, individual trial moves are performed. After a randomly selected number of trial moves, an attempt is made to exchange configurations. Two

systems (i and j, $|i - j| = 1$) are selected at random, the systems are exchanged by choosing $x_i(n) = x_j(o)$ and $x_j(n) = x_i(o)$. The ratio of acceptance probabilities equals

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \exp\left[(\beta_i - \beta_j) \times (U(x_i(o)) - U(x_j(o)))\right] \tag{3.8}$$

Such trial moves will be accepted when there is enough overlap between the energies of systems i and j. To demonstrate this technique, consider a two-dimensional system of 9 particles that are confined in a square ($\rho = 2.5$). Each particle pair interacts with a soft repulsive potential:

$$U(r) = \begin{cases} \epsilon(r-1)^2 & r \leq 1 \\ 0 & r > 1 \end{cases} \tag{3.9}$$
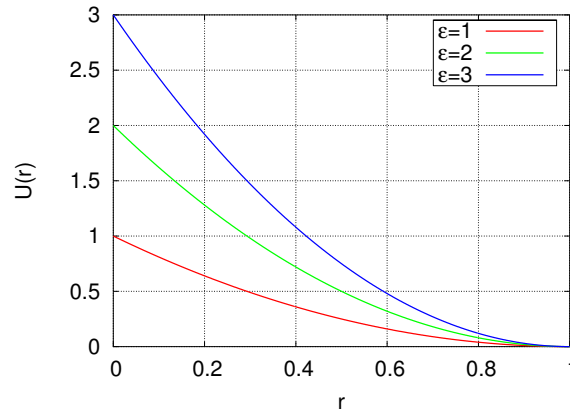

Figure 3.2: The soft repulsive potential $U(r)$ for $\epsilon = 1, 2, 3$. The particles are allowed to overlap completely. At low temperature this becomes more and more unlikely and diffusion is prohibited.

We will use $\epsilon = 1$. At low temperatures, the particles are not able to pass one another and therefore a particle is confined at its original position. However, in principle the distribution of the position of a particle should be symmetrical.

Questions:

1. Derive equation 3.8.

2. Compute the distribution of the position of the first particle as well as the distribution of the total energy for $T = 0.001$ when no exchange moves are allowed ($N = 1$). At which temperature are the particles allowed to diffuse?

3. Complete the code for the exchange moves and find out how many systems are needed to ensure that for $T = 0.001$ the particle is allowed to diffuse. You will have to check the distribution of the total energy to ensure that there is enough overlap between the systems.

4. At high temperature, confirm that the equilibrium distributions with and without exchange moves are identical.