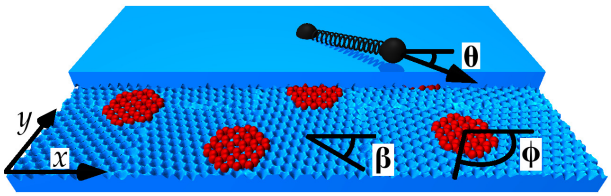
5 Exercises lectures 10 and 11 (due March 5th)

5.1 Applying thermostats sensibly

When you perform MD simulations in the canonical ensemble, or where for some other reason temperature must be controlled with a thermostat, it is important to consider what sort of dynamics would be realistic.

a) Suppose you would like to know if you can turn your Argon simulation into a crystalline solid. To achieve this, you would have to cool it down very slowly, changing the temperature of the system slowly. This means you would have to apply a thermostat. Would you use the Nosé-Hoover thermostat or a stochastic thermostat like the Langevin thermostat? Why?

b) Consider another simulation of a non-equilibrium system. The setup would be similar to the figure below (taken from my own work). Two parallel rigid surfaces (blue) are made of regularly placed atoms. There are other particles (red) embedded between the two surfaces, keeping them seperated. These could be single atoms, or larger molecules (like in the figure). The interactions between the red particles and atoms in the blue surfaces is governed by some sort of effective interaction, for example Lennard-Jones. The surfaces are kept parallel and orthogonal to the z-axis. One is kept completely fixed. The other surface is forced to slide with respect to the first. This will inject energy into the system. Without any additional measures, the system would heat up. How would a real system cool down? In the simulation a thermostat is necessary to model this. How would you thermostat this system and why?



c) Consider the same system as in b), but now with several layers of particles between the two surfaces. Suppose the particles cannot move from one layer to the other. How would you thermostat this system and why?

5.2 Importance sampling in the Ising model

a) Consider, for example, the three-dimensional Ising model. How many possible states does the system have if it has $N \times N \times N$ sites? Make some simple guesses about computer speeds and the number of operations needed to calculate the terms in the sum. Give an estimate of the order of magnitude of time it would take to numerically calculate the partition function for $N = 5$ with today's computers.

$N = 5$ is nowhere near the thermodynamic limit. Obviously, for large systems, it is not a good idea to consider every state. We can get around this problem by using me thods which estimate thermodynamic properties by sampling a small subset of all configurations. Suppose we attempt to estimate the partition function by randomly sampling B states, and calculating their contributio n. Let α_1 through α_k be the results of the sampling. Consider the estimator

for a quantity X

$$X_{\text{estimate}} = \frac{\frac{1}{B}\sum_{k=1}^{B} X(\alpha_k)\exp[-\beta E(\alpha_k)]}{\frac{1}{B}\sum_{k=1}^{B}\exp[-\beta E(\alpha_k)]} \ , \tag{9}$$

where $E(\alpha)$ and $X(\alpha)$ are the energy and relevant quantity respectively.

b) Argue that, if $B \gg 1$, the expectation value of X_{estimate} is equal to the thermal average of X.

c) Recall what happens to the Ising model at low temperatures. What happens to the terms in the sums in equation (9)? How many states (compared to the total number) would you have to sample to get the results to converge to something sens ible when the temperature approaches 0?

The reason for the difficulties with the estimator in equation (9) is that all states are equally likely to be sampled, even though some hardly contribute to the partition function. The variance of the terms in the sum is large. Suppose instead that we sample from the range of possible states with some probability $\rho(\alpha)$ that depends on the state α.

d) Write down an estimator for the quantity X, making sure that the expectation value of the estimate is equal to the thermodynamic average. The estimator should be of the form

$$X_{\text{estimate}} = \frac{1}{B}\sum_{k=1}^{B}\xi(\alpha_k) \ . \tag{10}$$

e) The right choice of $\rho(\alpha)$ can greatly improve the convergence of the sum. So far in this problem, $\rho(\alpha)$ has been constant. By calculating the variance of $\xi(\alpha)$, show that $\rho(\alpha) \propto \exp[-\beta E(\alpha_k)]$ is an efficient choice of probability density that works well for physical quantities.

5.3 Metropolis

While we know we wish to sample the distribution according to the Boltzmann factor, we do not know the normalisation constant. In Markov-chain Monte-Carlo methods, rather than just selecting a random configuration, a new configuration is generated from an old one in a random way, thus producing a string of pseudo-random states.

Let the associated transition probability from configuration α to configuration α' be denoted by $P(\alpha \to \alpha')$. If the transition probabilities are chosen appropriately, then the states are distributed according to the correct ensemble distribution. Two conditions need to be satisfied for this to be the case, accessibility and detailed balance.

a) Write down the condition for detailed balance and substitute the equilibrium distribution.

b) Use induction to show that if the accessibility and above detailed balance conditions are satisfied, the distribution of elements of a long Markov chain approaches the correct distribution.

The Metropolis algorithm is a commonly used implementation that achieves this. The first step is to randomly generate a new state from the old one (trial move). In the Ising model for instance

this could be by flipping a random spin. The state is then accepted with some probability. The transition probability from the old state to the new one in the Metropolis algorithm is:

$$P(\alpha \to \alpha') = \begin{cases} & \text{if} \quad E(\alpha') < E(\alpha) \\ \exp[-\beta(E(\alpha) - E(\alpha')] & \text{if} \quad E(\alpha') > E(\alpha) \end{cases} . \tag{11}$$

In a practical implementation one would generate a random number between 0 and 1, and accept the new state if the random number is less than the transition probability.

c) Show that this algorithm satisfies the detailed balance condition you have obtained in a), and that in the above described scheme for the Ising model, it satisfies the accessibility assumption as well.