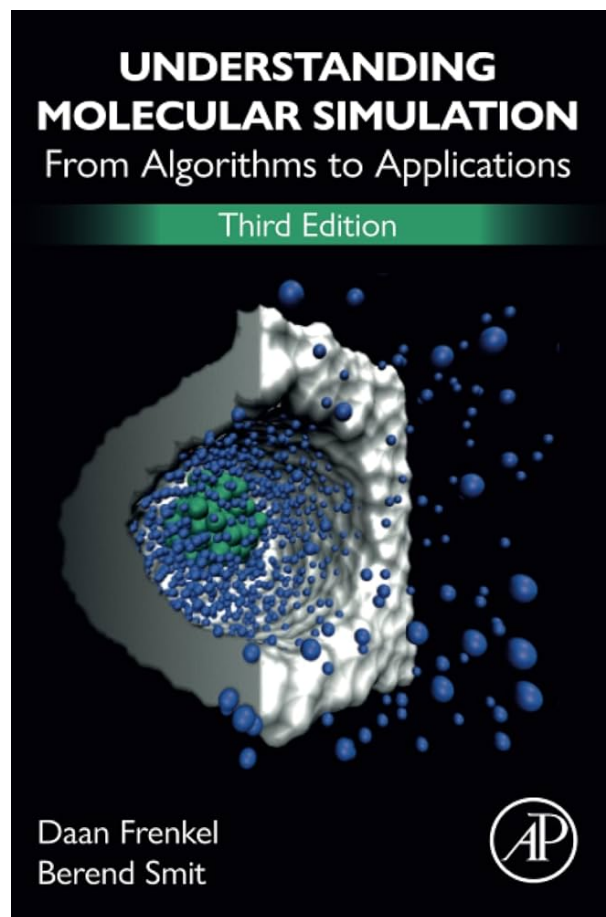# EPFL

CH-420
UNDERSTANDING ADVANCED
MOLECULAR SIMULATION

BLOCK 1
STATISTICAL THERMODYNAMICS

1 Distribution of Particles

Consider an ideal gas of N particles in a constant volume at constant energy. Let us divide the volume in p identical compartments. Every compartment contains n_i molecules such that:

$$N = \sum_{i=1}^{i=p} n_i \tag{1}$$

An interesting quantity is the distribution of molecules over the p compartments. Because the energy is constant, every possible eigenstate of the system will be equally likely. This means that in principle it is possible that one of the compartments is empty.

6	12	12	11	20	15	10	10	10
15	14	18	18	10	13	10	12	11
11	11	10	9	20	12	7	11	16
13	16	8	12	10	18	15	9	10
17	12	12	16	15	13	10	17	12
16	15	12	12	13	12	7	9	16
7	13	12	15	12	14	13	9	9
13	8	13	10	9	14	15	13	13
11	17	13	9	9	14	9	15	10

Figure 1: An ideal gas of $N = 1000$ particles in a constant volume at constant energy. The volume is divided into $p = 81$ compartments. The snapshot is obtained by randomly distributing $N = 1000$ particles over $p = 81$ compartments.

1. Enclosed is a program that calculates the distribution of molecules along the p compartments.
   Step 1: Complete the code first (see the file *distribution.c*);
   Step 2: Run the program; the output of the program is the probability to find x particles in a particular compartment as a function of x (*results.dat*);
   Step 3: Plot the outputs using *python plot.py* or *gnuplot plot*.
   Run the program with different numbers of compartments (p) and total number of gas molecules (N). Describe and discuss the characteristics of the distributions.

2. Why does it (almost) never happen that one of the compartments is empty when $N/P >> 1$?

2 Boltzmann Distribution

Consider a system of N energy levels with energies $0, \epsilon, 2\epsilon, \cdots, (N-1) \times \epsilon$ and $\epsilon > 0$.
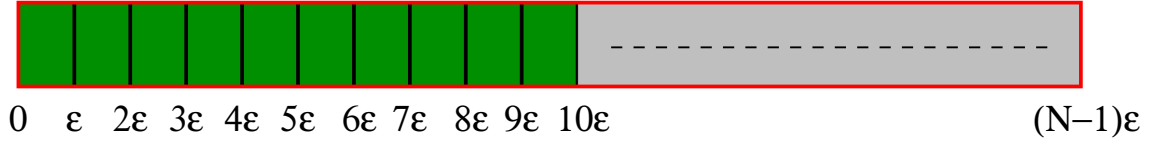

Figure 2: A system of N energy levels with energies $0, \epsilon, 2\epsilon, \cdots, (N-1) \times \epsilon$ ($\epsilon > 0$).

In a canonical ensemble for classical particles and the Boltzmann distribution in this case is the following (eq.2):

$$P_i = g_i \times \exp\{-E_i/k_B T\} \tag{2}$$

Where g_i is the degeneracy of energy levels, i is the energy level, E_i is its energy, k_B is the Boltzmann constant.

1. Modify the problem and calculate the occupancy of each level for different values of the temperature when all levels are non-degenerate. You can consider $\epsilon = 1$ for convenience. What happens at high temperatures? (Note that the temperature T is expressed in reduced units, that is, $k_B = 1$).

2. Change the program in such a way that the degeneracy of energy level i equals $i+1$. What do you see?

3. i. Modify the program in such a way that the occupation of the energy levels as well as the partition function (q) is calculated for a linear rotor with moment of inertia I. Note that the energy levels of a linear rotor are

$$U = i\,(i+1)\,\frac{\hbar^2}{2I} \qquad \frac{I}{\hbar^2} = 1 \tag{3}$$

where i are the energy levels, with $i = 0, 1, 2, \cdots, \infty$. The degeneracy of level i equals $2i+1$.

ii) Compare your result with the approximate result for different temperatures (eq. 4).

$$q = \frac{2I}{\beta\,\hbar^2} \qquad \frac{I}{\hbar^2} = 1 \tag{4}$$

3 Coupled Harmonic Oscillators

Consider a system of N harmonic oscillators with a total energy U. A single harmonic oscillator has energy levels $0, \epsilon, 2\epsilon, \cdots, \infty$ $(\epsilon > 0)$. All harmonic oscillators in the system can exchange energy.
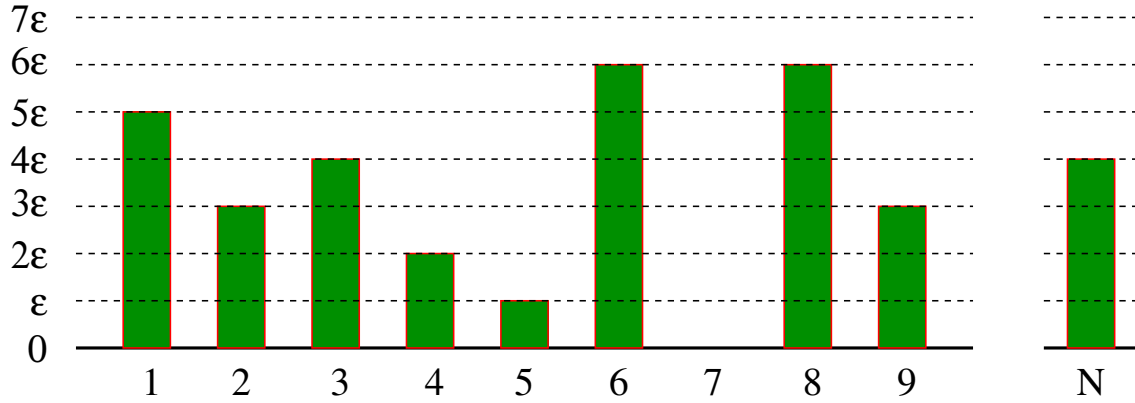

Figure 3: A system of N harmonic oscillators with a total energy U.

1. Invent a computational scheme for the update of the system at constant total energy (U). Compare your scheme with the scheme that is incorporated into the given computer code (see the file *harmonic.c*).

2. Make a plot of the energy distribution (*result.dat*) of the first oscillator as a function of the number of oscillators for a constant value of U/N. Which distribution is recovered when N becomes large? What is the function of the other $N-1$ harmonic oscillators? Explain.

3. Compare this distribution metioned in 2 with the canonical distribution (Use the option NVT) of a single oscillator at the same average energy.

4. Can you explain the phenomenon you see in Question 3? How does this exercise relate to the derivation of the Boltzmann distribution for a system at temperature T on page 27-28 of reference[1]?

4 Random Walk on a 1D Lattice

Consider the random walk of a single particle on a line. The probability that after N jumps the particle is at a position n with respect to its origin is:

$$\ln\left(P\left(n, N\right)\right) \approx \frac{1}{2}\ln\left(\frac{2}{\pi N}\right) - \frac{n^2}{2N} \tag{5}$$
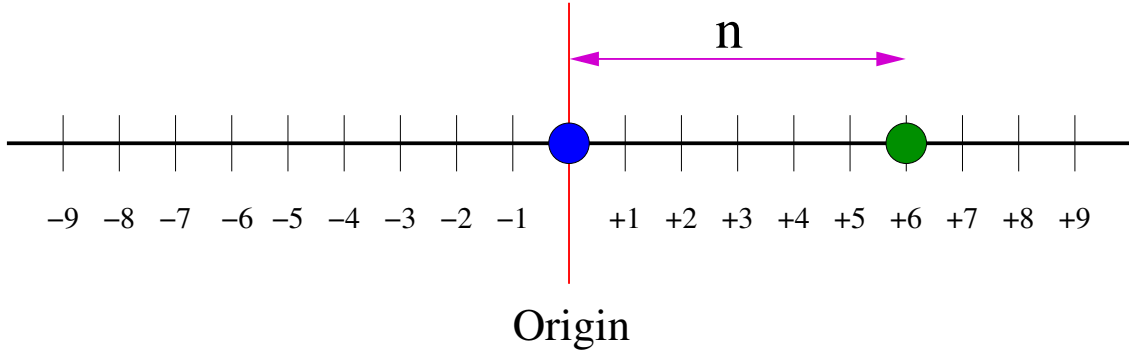

Origin

Figure 4: A random walk of a single particle on a line. After N jumps the particle that started at the origin has travelled a distance n. We are interested in $\langle n^2 \rangle$ as function of time. The update frequency $\tau = 1$ (jump per time) and the lattice spacing $\lambda = 1$. Hence, time is equal to the number of jumps N.

1. Derive equation 5. Useful information:

   i) Consider that the probability to jump to one direction equals the probability to jump to the other direction.

   ii) To get the probability of finding a particle at n after N jumps, you can calculate the binomial coefficient and relate it with the probabilities to jump in each direction.

   iii) For large values of y, $y!$ can be approximated by (Stirling's approximation):

   $$\ln\left(x!\right) \approx x \ln x - x \ln\left(\sqrt{2\pi x}\right) \tag{6}$$

   iv) You might find it handy to use the Taylor series expansion for ln(1+x):

   $$\ln(1 + x) \approx x \tag{7}$$

   v) It can be useful to note that $N > n \therefore \frac{n^2}{N} << \frac{n^2}{N^2}$.

   (Hint: Note that equation you derived might not be normalized. The standard Gaussian integral might be useful).

2. Run the code for a determined number of cycles and a determined number of jumps per cycle (e.g.: 10000 cycles and 10 jumps/cycle). The code computes the distribution based on sampling, and the probability based on the equation you derived. Plot and compare the two: are they similar?

3. We are now interested in the diffusivity of our system. From the concentration profile (eq.8, see book), we can relate the mean square displacement (which can also be computed by sampling) with the diffusion coefficient D (eq.9) in the case of 1D (d=1). Compare the theoretical prediction in eq.9 with the numerical result you get from running the program. What is the diffusivity of the system? (see also page 86-88 in the book, or 148-151 in the 3rd edition).

$$c(x,t) = \frac{1}{(4\pi Dt)^{d/2}} e^{\frac{-x^2}{4Dt}},$$ (8)

$$\frac{\partial \langle x^2 \rangle}{\partial t} = 2dD$$ (9)

4. Modify the program in such a way that the probability to jump in one direction equals 0.8. What happens?

(Note: you might need to install the scipy library on python to plot a Gaussian fit. To do so, activate your environment with conda activate molsim and then do conda install scipy)

References

[1] Daan Frenkel and Berend Smit. *Understanding molecular simulation: from algorithms to applications*, volume 1. Elsevier, 2001.