E6: Free energy and entropic springs

Week 10. Due Wed 17 Mar 23:59, reviewed Thu 18 Mar

About 2 hours. Theory: Entropy, free energy and entropic forces and Nelson chapter 6.

1. The ideal gas law from the free energy

A cylinder with cross-section A contains N molecules of an ideal gas in the length x between the bottom and a piston. A spring with potential energy $U_s(x)$ pushes the piston down; there is no gas above the piston. The cylinder stands on a heat reservoir at temperature T (Nelson, Figure 6.4b).

a. Write down the Helmholtz free energy $F(x)$ of the system gas + spring. Use that the gas has $F_{\text{gas}} = -Nk_BT \ln V + (\text{terms independent of } V)$.
b. The system goes to the x that minimizes F. Show that at this point the force from the spring per area equals Nk_BT/V, so that you have derived the ideal gas law.
c. Which part of the force on the piston is energetic and which is entropic?

2. Entropy change when two boxes equilibrate

Two boxes each hold N molecules of an ideal gas in the same volume V, at temperatures T_A and T_B. They are isolated from the world, and are then put in thermal contact with each other (Nelson, Problem 6.2).

a. What is the final temperature?
b. Show that the total entropy changes by $\Delta S = \frac{3}{2}Nk_B \ln \dfrac{(T_A+T_B)^2}{4T_AT_B}$. *Hint:* at fixed V and N, the entropy of an ideal gas depends on T as $S = \frac{3}{2}Nk_B \ln T + \text{const}$.
c. Write ΔS as a function of $X = T_A/T_B$ and plot it. Show that $\Delta S \geq 0$. When is it zero, and why?

3. A polymer as an entropic spring

Model a polymer as a chain of N segments of length L, each pointing either left ($-L$) or right ($+L$) along x. Its end-to-end extension is $x = \sum_i \pm L$. We pull on the end with a force f in the $+x$ direction, so a segment pointing right has energy $-fL$ and one pointing left $+fL$.

a. Each segment is a two-state system. Use the Boltzmann distribution to find the probability that a segment points right, and show that $\langle x \rangle = NL \tanh(fL/k_BT)$.
b. Show that for small forces the chain is a linear spring, and find its stiffness k. How does k depend on temperature? Why is that the opposite of a metal spring?
c. Check (a) numerically: for $N = 100$ and a range of fL/k_BT between 0 and 4, draw many random chains with the right Boltzmann probability for each segment, and compare the mean extension with tanh. Plot both.
d. At $f = 0$, show that $\langle x^2 \rangle = NL^2$ and that $k = k_BT/\langle x^2 \rangle$. This is equipartition, $\frac{1}{2}k\langle x^2 \rangle = \frac{1}{2}k_BT$.
e. D. Discher measured the stiffness of the polymer network under the membrane of a red blood cell in this way, by tracking a 40 nm bead attached to it (Nelson, Problem 6.6). The rms displacement was $\sqrt{\langle \Delta x^2 \rangle} = 35$ nm at room temperature. What is the spring constant?