1   Entropic polymer elasticity

In the lecture, the force-length relation of a 1D polymer was calculated using the microcanonical ensemble.

a) Now do the calculation in the canonical ensemble. (*2 points*)
HINT: Consider again a chain of N monomers of size a with $x_i = +a$ or $-a$ and $X = \sum_i x_i$ the total length of the polymer (for the given configuration). Note that the polymer is "ideal", i.e. the distribution of bonds does not change the energy of the chain in the force-free case; in turn, under an external force F the energy of this system is given by $E(X) = -FX$.

The partition sum for the canonical ensemble is given by

$$Z = \sum_i e^{-\beta E_i}, \qquad \text{with } \beta := \frac{1}{k_B T}. \tag{1}$$

The sum is performed over all configurations i with energy E_i. Define the length of the polymer as $L = Na$ and the effective length of the polymer,

$$X = \sum_i x_i = (N_+ - N_-)a = (2N_+ - N)a, \tag{2}$$

where N_+ corresponds to the number of monomers with $x_i = +a$ and N_- corresponds to the number of monomers with $x_i = -a$. We used the condition $N = N_+ + N_-$.
We need to take into account that there are

$$\Omega(X) = \frac{N!}{N_+! N_-!} = \binom{N}{N_+} \tag{3}$$

different configurations that lead to the same length X. Thus, the partition sum is given by

$$Z = \sum_X \Omega(X) e^{-\beta E(X)} = \sum_{i=0}^{N} \binom{N}{i} e^{-(N-2i)\beta Fa} = \left(e^{\beta Fa} + e^{-\beta Fa} \right)^N. \tag{4}$$

In the last step, we used the binomial theorem,

$$(x+y)^n = \sum_{i=0}^{n} \binom{n}{i} x^{n-i} y^i, \tag{5}$$

and set $x = e^{-\beta Fa}$ and $y = e^{\beta Fa}$. Therefore, the partition sum is given by

$$Z = 2^N \cosh(\beta Fa)^N \tag{6}$$

$$= \left(2 \cosh(\beta Fa) \right)^N. \tag{7}$$

From the partition sum, we can calculate the system's energy:

$$\langle E \rangle = -\partial_\beta \ln(Z) \tag{8}$$

$$= -N \cdot \partial_\beta \ln \left(2 \cosh(\beta Fa) \right) \tag{9}$$

$$= -N \cdot \frac{1}{2 \cosh(\beta Fa)} \cdot 2 \sinh(\beta Fa) \cdot Fa \tag{10}$$

$$= -NFa \cdot \tanh(\beta Fa) \tag{11}$$

b) Show that your result is identical to the one in the lecture. Discuss the limits $Fa \ll k_B T$ and $Fa \gg k_B T$. (2 points)

Because the system's energy is related to the applied force by $\langle E \rangle = FX$, it follows that

$$FX = -NFa \cdot \tanh(\beta Fa) \tag{12}$$

$$\Rightarrow X = -Na \cdot \tanh(\beta Fa) \tag{13}$$

For large T:
Large temperature values lead to a small β. For small input values x, we can approximate $\tanh(x) \approx x$. Thus, for large temperatures we can rewrite Equation 13 as

$$F \approx -\frac{X}{Na^2} \cdot k_B T, \tag{14}$$

which is the result that we already know from the lecture.

For small T:
In the limit of $x \to \infty$, $\tanh(x) \to 1$. Therefore, we get

$$X \approx -N \cdot a = -L_0, \tag{15}$$

which means that $N_+ = 0$ and $N_- = N$, i.e. the polymer is expanded to its full length.

To further check our results, we can calculate the free energy

$$F = -k_B T \cdot \ln(Z) \tag{16}$$

$$= -k_B T N \cdot \ln\left(2\cosh(\beta Fa)\right) \tag{17}$$

$$= -k_B T N \cdot \ln\left(2\cosh\left(\frac{Fa}{k_B T}\right)\right) \tag{18}$$

$$\tag{19}$$

and from this the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{20}$$

$$= k_B N \cdot \ln\left[2\cosh\left(\frac{Fa}{k_B T}\right)\right] - k_B T N \cdot \frac{1}{2\cosh\left(\frac{Fa}{k_B T}\right)} \cdot 2\sinh\left(\frac{Fa}{k_B T}\right) \cdot \frac{Fa}{k_B T^2} \tag{21}$$

$$= k_B N \cdot \left\{ \ln\left[2\cosh\left(\frac{Fa}{k_B T}\right)\right] - \tanh\left(\frac{Fa}{k_B T}\right) \cdot \frac{Fa}{k_B T} \right\} \tag{22}$$

$$\tag{23}$$

2   Debye model

Consider the Debye model for the specific heat of a crystal as discussed in the lecture.

a) *Corrections to classical limit:* **In the lecture it was shown that the Debye model yields** $E = 3Nk_BT$ **in the classical limit as expected. Calculate the first two corrections from a Taylor expansion in** T_D/T **of the integrand of the energy formula and discuss the resulting heat capacity. (*4 points*)**

The specific heat is given by

$$c_v(T) = \frac{9Nk_B}{u_m^3} \cdot \int_0^{u_m} \frac{e^u \cdot u^4}{(e^u - 1)^2} \cdot du \qquad \text{with } u := \beta\hbar\omega = \frac{\hbar\omega}{k_BT} = \frac{\hbar\omega}{k_BT_D} \cdot \frac{T_D}{T}, \tag{24}$$

where $u_m = \beta\hbar\omega_D = T_D/T$ because $T_D = \hbar\omega_D/k_B$. This integral can not be solved analytically, which is why we approximate the integrand via Taylor expansion up to the second order for small u, i.e. for large T:

$$\frac{e^u \cdot u^4}{(e^u - 1)^2} \approx u^2 + \frac{u^4}{12} + \frac{u^6}{240}. \tag{25}$$

Thus, the specific heat can be approximated by

$$c_v(T) \approx \frac{9Nk_B}{u_m^3} \cdot \int_0^{u_m} u^2 + \frac{u^4}{12} + \frac{u^6}{240} \cdot du = 3Nk_B \cdot \left[1 + \frac{1}{20}\left(\frac{T_D}{T}\right)^2 + \frac{1}{560}\left(\frac{T_D}{T}\right)^4\right]. \tag{26}$$

With the formula $c_v(T) = \mathrm{d}E/\mathrm{d}T$, we find for the energy corrections

$$E = 3Nk_B \cdot \left[T - \frac{1}{20}\frac{T_D^2}{T} - \frac{1}{1680}\frac{T_D^4}{T^3}\right]. \tag{27}$$

b) *Number of phonons:* **Write the mean number of phonons** $\langle N \rangle$ **in the Debye model as an integral (similar but different to the integral formula for the energy) and evaluate it for low and high temperatures. (*4 points*)**

In the script, we had the following formula for the mean energy:

$$E = \sum_{\text{modes}} \hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right) \overset{!}{=} \hbar\omega\left(N + \frac{1}{2}\right). \tag{28}$$

We conclude that the formula for the mean particle number will be given by:

$$N = \sum_{\text{modes}} \frac{1}{e^{\beta\hbar\omega} - 1} = 3N \int_0^{\omega_D} \mathrm{d}\omega \, \frac{3\omega^2}{\omega_D^3} \frac{1}{e^{\beta\hbar\omega} - 1} \tag{29}$$

For low T (large β):

$$N \approx 3N \int_0^{\omega_D} \mathrm{d}\omega \, \frac{3\omega^2}{\omega_D^3} \frac{1}{e^{\beta\hbar\omega}} \longrightarrow 0. \tag{30}$$

For large T (small β):

$$N \approx 3N \int_0^{\omega_D} \mathrm{d}\omega \, \frac{3\omega^2}{\omega_D^3} \frac{1}{\beta\hbar\omega} = \frac{9NT}{2T_D}. \tag{31}$$

3   Molecular zipper

Consider a zipper consisting of N units. Each unit can either be in the closed state with energy 0 or in the open state with energy $\varepsilon > 0$. The zipper can open only from the left, that is, a given unit can only switch to the open state when all units to its left are already open.

a) Calculate the canonical partition sum. *(1 point)*

Recall the definition of the partition sum:

$$Z = \sum_i e^{-\beta E_i}, \qquad \text{with } \beta := \frac{1}{k_B T}. \tag{32}$$

For each configuration i, there is only one possible state (due to the fact that a given unit can only switch to the open state if all units to its left are open). The energy of a given configuration with i open bonds is given by $E_i = \varepsilon \cdot i$. The partition sum can then be written as

$$Z = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \dots \tag{33}$$

$$= \sum_{i=0}^{N} e^{-i\beta\varepsilon} \tag{34}$$

$$= \frac{e^{-(N+1)\beta\varepsilon} - 1}{e^{-\beta\varepsilon} - 1}. \tag{35}$$

Starting with the configuration were all units are closed and sum up until all units are open.

b) Determine the average number of open units. Discuss the limit $\beta_\varepsilon \gg 1$. *(2 points)*

The average number of open units is given by

$$\langle n \rangle = \frac{1 \cdot 0 + e^{-\beta\varepsilon} \cdot 1 + e^{-2\beta\varepsilon} \cdot 2 + \dots}{Z} \tag{36}$$

$$= \frac{1}{Z} \sum_{i=0}^{N} i e^{-i\beta\varepsilon} \tag{37}$$

$$= -\frac{1}{\varepsilon} \partial_\beta \ln Z \tag{38}$$

$$= \frac{N+1}{1 - e^{(N+1)\beta\varepsilon}} - \frac{1}{1 - e^{\beta\varepsilon}}. \tag{39}$$