

SOFT MATTER

PRACTICES 1

Soft Matter: Objects and Methods

Rubber elasticity

Rubber is made of long molecules (polymers). We study the strain-stress relation of a unique polymer chain lying in the plane. We suppose that the orientations of the $N \gg 1$ monomers are uncorrelated, and the steric repulsions and interactions between monomers are neglected. The energy of the molecule is then composed exclusively of the kinetic energy of its monomers (purely entropic chain).

The first suppose that the polymer is attached at both ends. We note X the (fixed) abscissa difference between both ends, a the length of each monomer, and E the energy of the polymer chain.

A configuration of the polymer (“micro-state”) is described by the momentum and orientation of every monomer of the chain. Orientation of monomer i is given by polar angles (θ_i, φ_i) , with $\theta_i \in [0, \pi[$ and $\varphi_i \in [0, 2\pi[$ (the angles are measured with respect to the x axis). Its momentum is denoted \mathbf{p}_i .

The system is in contact with a thermostat with temperature T .

1. Show that the probability distribution of the micro-states that satisfy the boundary conditions (attached ends) still follows the Gibbs statistics.
2. Explain why the chosen boundary conditions are not convenient to calculate the partition function Z of this system.

We now replace one of the boundary condition: we suppose that one of the extremities of the molecule is attached to a spring with length at rest l_0 and spring constant k_{sp} , while the other extremity is fixed. We suppose the spring can extend only in the x direction:

$$\mathbf{F}_{sp} = -k_{sp}(l - l_0)\mathbf{e}_x,$$

where $l > 0$ is the length of the spring, l_0 its length at rest, k_{sp} the spring constant, and \mathbf{e}_x the unit vector pointing in the x direction. We consider that the y and z coordinates of the bead are fixed.

experimentally, such a “spring” can be done by grafting the polymer extremity to a dielectric bead and applying a non-uniform external electric field on it: then the bead experiences an attractive force (optical tweezers), which can be idealized by a hookean spring (see Fig. 1).

We note X the (fluctuating) abscissa difference between both ends of the polymer (*projected length*).

3. Write down the potential energy of the spring E_{sp} as a function of X , l_0 and L , the (fixed) distance between the two attached extremities of the system (see Figure 1).
4. Let $\langle X \rangle$ be the average projected length of the polymer. Show that when the fluctuations $\delta X = X - \langle X \rangle$ are small, the potential energy of the spring becomes:

$$E_{sp} = E_0 - \tau X,$$

where E_0 is a constant and τ is the tension exerted by the chain, which you will express as a function of k_{sp} , L , $\langle X \rangle$ and l_0 . What is the physical interpretation of this relation ?

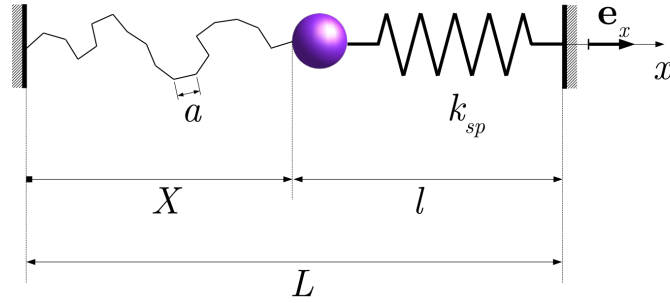


Figure 1: polymer with one end fixed, and the other attached to a spring.

5. Justify that the above approximation becomes increasingly accurate at high tensions.
6. Show that within this approximation, the partition function of the system is:

$$Z = Z_{kinetic} z^N,$$

where $Z_{kinetic}$ denotes the kinetic part of the partition function – **which we will not try to evaluate** – and

$$z = \int \sin \theta d\theta d\varphi e^{\beta \tau a \cos \theta} = 4\pi \frac{\sinh(\beta \tau a)}{\beta \tau a}.$$

7. Calculate the thermodynamic potential $\phi = -k_B T \ln Z$, and show that $\phi = \langle E \rangle - TS - \tau \langle X \rangle$, where E and S are the energy and entropy of the system (polymer + spring), respectively.
8. Deduce the expression of the average chain elongation $\langle X \rangle$ as a function of N , a , T and τ .
9. Show that when $\tau \ll k_B T/a$, the chain behaves like an hookean spring, and give the associate spring constant.
10. What is the value of $\langle X \rangle$ in the limit $\tau \rightarrow \infty$?
11. What happens when a rubber elastic is heated (does it contract or dilate ?)

Answers

Correction: Rubber elasticity

1. Let p_l be the probability distribution of any configuration l of the polymer, satisfying or not the boundary conditions. The probability distribution for the configurations that satisfy the boundary conditions is:

$$p'_l = \frac{p_l}{\sum_{l \text{ satisfying b.c.}} p_l}.$$

It is then clear that if p_l follows Gibbs statistics, so it is for p'_l .

2. The orientations of the monomers are not independent, as they must satisfy: $\sum_i a \cos \theta_i = X$.
3. The energy is:

$$E = E_{kinetic} + \frac{k}{2} (L - X - l_0)^2,$$

where $E_{kinetic}$ is the kinetic energy of the polymer.

4. If $|\delta X| \ll L - \langle X \rangle - l_0$:

$$E_{sp} = \frac{k}{2} (L - \langle X \rangle - \delta X - l_0)^2 \simeq \frac{k}{2} (L - \langle X \rangle - l_0)^2 - k(L - \langle X \rangle - l_0) \delta X.$$

Since $\delta X = X - \langle X \rangle$: $E_{sp} = E_0 - \tau X$ with $\tau = k(L - \langle X \rangle - l_0)$.

Physical meaning: the projected length of the polymer is free to fluctuate, but it experiences a **constant** tension τ .

5. The condition $|\delta X| \ll L - \langle X \rangle - l_0$ is equivalent $k|\delta X| \ll \tau$. Therefore the approximation becomes increasingly accurate as τ increases.

6. Partition function:

$$Z = \sum_{configs} e^{-\beta(E_i - \tau X_i)} = Z_{kin} \times \int d^2\Omega_1 \dots d^2\Omega_N e^{\beta\tau a \sum_i \cos \theta_i}.$$

Introducing $z = \int \sin \theta d\theta d\varphi e^{\beta\tau a \cos \theta} = 4\pi \frac{\sinh(\beta\tau a)}{\beta\tau a}$, one gets $Z = Z_{kinetic} z^N$.

Note that we integrated over all possible angles, while we required small ΔX . This is justified by the fact that the exponential term is sharply peaked around its max.

7. $\phi(T, \tau, N) = -k_B T \ln Z = \phi_0(T) - N k_B T \ln \left(\frac{\sinh(\beta\tau a)}{\beta\tau a} \right)$.

8. $\langle X \rangle = -\frac{\partial \phi}{\partial \tau}$. Thus:

$$\langle X \rangle = Na \left(\coth(\beta\tau a) - \frac{1}{\beta\tau a} \right).$$

By definition $S = -k_B \sum_l p_l \ln p_l$, with here $p_l = e^{-\beta(E_l - \tau X_l)} / Z$. It comes: $-TS = -\langle E \rangle + \tau \langle X \rangle - k_B T \ln Z$, or equivalently, $\phi = \langle E \rangle - TS - \tau \langle X \rangle$.

9. Since $\coth \epsilon \simeq \epsilon^{-1} + \epsilon/3$, one gets:

$$\langle X \rangle = \frac{Na^2}{3k_B T} \tau.$$

The spring constant is $k = \frac{3k_B T}{Na^2}$.

10. When $\tau \rightarrow \infty$, $\langle X \rangle \rightarrow Na$. That is the maximal length of the chain.

11. When T increases, the spring constant increases. For a given tension applied on the chain, the rubber contracts. (this is counter-intuitive: most materials dilate when heated).