

Polymer Science 2025/26

Exercise 7 – Solution

1. A freely jointed chain consists of n segments of length a . Simple statistical considerations show that its conformational entropy S^c is

$$S^c(\vec{R}_n) = S_0 - \frac{3kR_n^2}{2na^2} ,$$

where k is Boltzmann's constant, S_0 is a constant, and R_n is the end-to-end distance of the chain.

- (i) Suppose the chain undergoes a macroscopic deformation. The vector defining the positions of the chain ends before deformation is $\vec{R}_{n,0} = (\vec{x}_0, \vec{y}_0, \vec{z}_0)$ and after deformation it becomes $\vec{R}_n = (\vec{x}, \vec{y}, \vec{z}) = (\lambda_x \vec{x}_0, \lambda_y \vec{y}_0, \lambda_z \vec{z}_0)$, where λ_x , λ_y , and λ_z are the principal stretch ratios.

Derive an expression for the change in entropy associated with this deformation as a function of λ_x , λ_y , and λ_z . What is the corresponding change in free energy? Assume an arbitrary chain orientation.

before deformation:

$$S^c = S_0 - \frac{3kR_n^2}{2na^2} = S_0 - \frac{3k(x_0^2 + y_0^2 + z_0^2)}{2na^2}$$

after deformation:

$$S_d^c = S_0 - \frac{3k(\lambda_x^2 x_0^2 + \lambda_y^2 y_0^2 + \lambda_z^2 z_0^2)}{2na^2}$$

entropy change:

$$\Delta S = S_d^c - S^c = - \frac{3k((\lambda_x^2 - 1)x_0^2 + (\lambda_y^2 - 1)y_0^2 + (\lambda_z^2 - 1)z_0^2)}{2na^2}$$

For a randomly oriented chain population:

$$\langle R_n^2 \rangle = \langle x_0^2 \rangle + \langle y_0^2 \rangle + \langle z_0^2 \rangle \rightarrow \langle x_0^2 \rangle = \langle y_0^2 \rangle = \langle z_0^2 \rangle = \frac{na^2}{3}$$

Averaging gives the free-energy change for one chain:

$$\langle \Delta A^c \rangle = -T \langle \Delta S \rangle = \frac{kT \left((\lambda_x^2 - 1) + (\lambda_y^2 - 1) + (\lambda_z^2 - 1) \right)}{2} = \frac{kT (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)}{2}$$

- (ii) Consider an elastomeric network in which each subchain between two crosslinks contains n segments and the number of subchains per unit volume is N . Calculate the change in entropy per unit volume during a uniaxial strain λ in the x -direction. You may assume that elastomers are incompressible (i.e., $\lambda_x \lambda_y \lambda_z = 1$). Explain this assumption.

For a uniaxial deformation along x , incompressibility implies:

$$\lambda_x = \lambda, \quad \rightarrow \quad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

The entropy change per unit volume is therefore:

$$\Delta S = - \frac{Nk \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)}{2}$$

Rubbers are effectively incompressible because the bulk modulus K is ca. ca. 3 orders of magnitude larger than the shear modulus G or tensile modulus E . Thus, deformations occur primarily by shape change, not by volume change.

- (iii) Derive an expression for the stress $\sigma_x(\lambda)$ for the same uniaxial deformation and show how to obtain Young's modulus of the elastomer. Discuss the limitations of this approach.

The Helmholtz free energy change per unit volume is:

$$\Delta A = -T \Delta S = \frac{NkT \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)}{2}$$

The nominal stress in uniaxial tension follows from:

$$\sigma_x = \left(\frac{\partial \Delta A}{\partial \lambda} \right)_T = NkT (\lambda - \lambda^{-2})$$

In terms of strain $\varepsilon = \lambda - 1$:

$$\sigma_x = NkT \left(\varepsilon + 1 - \frac{1}{(\varepsilon + 1)^2} \right) = NkT \frac{(\varepsilon + 1)^3 - 1}{(\varepsilon + 1)^2} .$$

For small deformations ($\varepsilon \ll 1$):

$$\sigma_x = NkT \frac{(\varepsilon + 1)^3 - 1}{(\varepsilon + 1)^2} \approx 3NkT \rightarrow E = \frac{\sigma}{\varepsilon} = 3NkT.$$

The model assumes a Gaussian chain and therefore fails at large stretches: chain extensibility is limited by the contour length, but the Gaussian distribution predicts a finite probability for end-to-end distances greater than na .

Likewise, the Gaussian assumption breaks down for short subchains, i.e. when the crosslinking density is too high.

The affine network treats chains as non-interacting (“phantom network”) and assumes that the displacements of their ends are proportional to the macroscopic deformation.

Finally, energetic contributions and strain-induced crystallization (relevant for natural rubber, see our Chapter on Polymer Crystallization for why this effect occurs) are neglected.

- (iv) A crosslinked polymer of density 1.1 g/cm^3 and very low T_g has a number-average molar mass of network strands M_{nx} = is $6'000 \text{ g/mol}$. Estimate its elastic modulus at room temperature ($k = 1.38 \times 10^{-23} \text{ J/K}$).

Each network strand (the polymer segment between two crosslinks) contributes one “spring” to the elastic response. To determine the number of such strands per unit volume (N), we first divide the density by M_{nx} , which gives the *moles* of subchains per cubic meter. Multiplying by Avogadro’s number (the number of subchains per mole) then converts this to the *number* of subchains per cubic meter.

Thus, the number density of network strands is:

$$N = \frac{N_A \rho}{M_{nx}} = \frac{6 \cdot 10^{23} \text{ mol}^{-1} \cdot 1.1 \cdot 10^6 \text{ g m}^{-3}}{6000 \text{ g mol}^{-1}} = 1.1 \cdot 10^{26} \text{ m}^{-3}$$

At room temperature (298 K):

$$E = 3NkT = 3 \cdot 10^{26} \text{m}^{-3} \cdot 1.38 \cdot 10^{-23} \text{J K}^{-1} \cdot 298 \text{K} \approx 1.4 \cdot 10^6 \text{Pa} = 1.4 \text{MPa}$$

2. A freely-jointed chain contains $n = 100$ links of length $a = 1.4 \cdot 10^{-10}$ m. Show that for a small displacement $d\vec{R}_n$ in the direction of its end-to-end vector \vec{R}_n :

$$dS^c \approx -\frac{3k\vec{R}_n \cdot d\vec{R}_n}{na^2},$$

and therefore the internal (restoring) force exerted by the chain is

$$f^c = -\frac{3kT}{na^2} \vec{R}_n.$$

What is the direction of this force relative to \vec{R}_n ?

Start from the chain entropy

$$S^c(\vec{R}_n) = S_0 - \frac{3kR_n^2}{2na^2}.$$

For a small change $d\vec{R}_n$:

$$dS^c = S^c(\vec{R}_n + d\vec{R}_n) - S^c(\vec{R}_n) = \frac{3k}{2na^2} (R_n^2 - (\vec{R}_n + d\vec{R}_n)^2) \approx -\frac{3k\vec{R}_n \cdot d\vec{R}_n}{na^2}.$$

Here, we expanded $(\vec{R}_n + d\vec{R}_n)^2$ and neglected the small second-order term dR_n^2 . This gives the differential form asked for:

$$\frac{dS^c}{d\vec{R}_n} = -\frac{3k\vec{R}_n}{na^2}$$

The Helmholtz free energy is $A = U - TS$. The internal restoring force is defined as the negative gradient of the free energy:

$$f^c = -\frac{\partial A}{\partial \vec{R}_n}$$

For entropic elasticity, U is constant (independent of \vec{R}_n):

$$f^c = -\frac{\partial(U - TS^c)}{\partial \vec{R}_n} = T \frac{\partial S^c}{\partial \vec{R}_n} = T \left(-\frac{3k\vec{R}_n}{na^2} \right) = -\frac{3kT\vec{R}_n}{na^2}$$

Direction: f^c points opposite to \vec{R}_n (restoring, pulling the ends together), as indicated by the negative sign in the relation between f^c and \vec{R}_n . By contrast, in our treatment of the molecular theory of rubber elasticity (see Slide 229), we considered the external force needed to hold the chain at a given extension, which is positive by convention:

$$f_{\text{ext}} = -f^c = \frac{\partial A}{\partial \vec{R}_n}$$

Give an analogous expression for the restoring force f^s of a subchain containing n_s links whose end positions are \vec{r}_i and \vec{r}_{i+1} . Into which direction does this force act?

For a subchain of n_s links whose end-to-end vector is $\vec{R}_s = \vec{r}_{i+1} - \vec{r}_i$ (pointing from bead i to bead $i+1$), the identical derivation yields

$$f^s = -\frac{3kT\vec{R}_s}{n_s a^2} = -\frac{3kT(\vec{r}_{i+1} - \vec{r}_i)}{n_s a^2} .$$

The negative sign indicates that the restoring force acts opposite to the chain extension vector, i.e. it pulls bead $i+1$ back towards bead i . Equivalently, the force on bead i due to bead $i+1$ (i.e., bead i feels a force directed toward bead $i+1$) is

$$f^s = \frac{3kT(\vec{r}_i - \vec{r}_{i+1})}{n_s a^2} .$$

The two forces are hence equal in magnitude and opposite in direction (consistent with Newton's third law).

Remark: the explicit sign convention becomes important later, when we describe how chains or "beads" move under such restoring forces in dynamic models of polymers. For now, it is enough to remember that the force always acts to reduce the extension of the subchain.

A mass m is attached to the free end and the other end is fixed to the ceiling and exerts a downward force mg . Determine m for which the chain is fully stretched at $T = 27^\circ\text{C}$ (ignore the chain's mass). Use $k = 1.38 \times 10^{-23} \text{ J/K}$ and $g = 9.81 \text{ m/s}^2$.

At mechanical equilibrium, the external weight of the mass provides a downward force mg balanced by the chain's restoring force. To avoid sign confusion, we use magnitudes in the force balance:

$$m \cdot g = |f^c| = \frac{3kT|\vec{r}_{i+1} - \vec{r}_i|}{na^2} = \frac{3kTna}{na^2} = \frac{3kT}{a}$$

For m , it follows:

$$m = \frac{3kT}{ag} = \frac{3 \cdot 1.38 \cdot 10^{-23} \text{ J K}^{-1} \cdot 300 \text{ K}}{1.4 \cdot 10^{-10} \text{ m} \cdot 9.81 \text{ m/s}^2} = \frac{1242 \cdot 10^{-23} \cdot 10^3 \text{ g m}^2/\text{s}^2}{1.4 \cdot 10^{-10} \text{ m} \cdot 9.81 \text{ m/s}^2} \approx 9 \cdot 10^{-9} \text{ g}$$

Remark: the independence of n at full stretch is an unphysical artifact of applying the Gaussian approximation beyond its domain of validity. Physically, one may switch to a finite-extensibility (Langevin) form.



The temperature is raised to $T = 327 \text{ }^\circ\text{C}$, while keeping that mass. What is the new average extension $|\vec{R}_n|$ predicted by the Gaussian model? Comment on what happens if the temperature is lowered instead.

At equilibrium, the same weight balances the chain's restoring force at both temperatures $T_1 = 300 \text{ K}$ and $T_2 = 600 \text{ K}$:

$$m \cdot g = \frac{3kT_1na}{na^2} = \frac{3kT_2\vec{R}_n}{na^2} \rightarrow \vec{R}_n = na \frac{T_1}{T_2} = \frac{1}{2}na$$

$$\vec{R}_n = \frac{1}{2} \cdot 100 \cdot 1.4 \cdot 10^{-10} \text{ m} = 7 \cdot 10^{-9} \text{ m} = 7 \text{ nm}$$

Thus, raising T reduces the equilibrium extension for the same load because the entropic restoring force scales with T . Lowering T increases the extension for a fixed load. However, if the predicted extension approaches the contour length na the Gaussian model is no longer valid and finite extensibility and energetic bond stretching control the response.

For the free chain end with no attached weight, what is the vector average of \vec{R}_n and the root-mean-square size?

**The vector average of \vec{R}_n for a freely jointed chain is zero (no preferred direction).
The typical size is expressed by the root-mean-square end-to-end distance:**

$$\langle \vec{R}_n^2 \rangle^{1/2} = \sqrt{na} = \sqrt{100} \cdot 1.4 \cdot 10^{-10} \text{ m} = 1.4 \cdot 10^{-9} \text{ m} = 1.4 \text{ nm}$$

This is an average position: at one moment in time, it can be found at any positive or negative height relative to the bar (as long as it does not exceed na).

Reading suggestion:

- Reader on Rubber Elasticity.

(You can download this document from the Moodle-folder 'Reading Recommendation'.)