School of Engineering
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and Organic Materials

Polymer Science 2025/26

Exercise 7

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

$$S^c(\vec{R}_n) = \mathrm{S}_0 - \frac{3\mathrm{k}{R_n}^2}{2na^2} \ ,$$

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.

(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.

(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.

(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 g/mol. Estimate its elastic modulus at room temperature (k = 1.38 x 10^{-23} J/K).

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

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

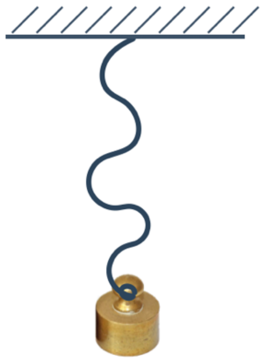
and therefore the internal (restoring) force exerted by the chain is

$$f^c = -\frac{3\mathrm{k}T}{na^2}\vec{R}_n \quad .$$

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

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?

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 °C (ignore the chain's mass). Use k = 1.38 x 10^{-23} J/K and g = 9.81 m/s^2).



The temperature is raised to T = 327 °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.

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

Reading suggestion:

- Reader on Rubber Elasticity.

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

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