Polymer Science 2024/25

Exercise 6

1. Consider a freely jointed chain constituted from n segments of length a. "Simple" statistical calculations show that the entropy of this chain, S^c, is

$$S^c(\vec{r}) = S_0 - k\left(\frac{3r^2}{2na^2}\right)$$

where k is Boltzmann's constant, S_0 is a constant, and r is the distance between the two ends of the chain. Now suppose that this chain undergoes a deformation. The vector which defines the relative positions of the ends of the chain before the deformation is $\vec{r}_0 = (\vec{x}_0, \vec{y}_0, \vec{z}_0)$ and after the deformation it becomes $\vec{r} = (\vec{x}, \vec{y}, \vec{z}) = (\lambda_x \vec{x}_0, \lambda_y \vec{y}_0, \lambda_z \vec{z}_0)$.

(i) Express 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? Consider an arbitrary direction of the end-to-end distance.

(ii) Consider an elastomeric network where the subchains separated by each crosslinking point contain n segments and where the number of subchains per unit volume is N. What is the change in entropy per unit volume during a uniaxial strain, λ, in the x direction? You can assume that elastomers are incompressible ($\lambda_x \lambda_y \lambda_z = 1$). Why?

(iii) Derive an expression for the stress σ_x as a function of λ for the same uniaxial deformation and find thus an expression for the Young's modulus of the elastomer. What are the limitations of this approach?

(iv) In a crosslinked polymer of density 1.1 g/cm^3 and of very low T_g, the number-average mass, M_{nx}, of the sub-chains connecting two crosslinking points is 6’000 g/mol. What is its elastic modulus at ambient temperature? (k = 1.38 x 10^{-23} J/K.)

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2. Show that the change of entropy of a freely jointed chain during a *small* displacement $\mathrm{d}\vec{r}$ in the direction of the vector between its two ends, $\vec{r}$, is given by

$$\mathrm{d}S^c \approx -\frac{3k\vec{r}\cdot\mathrm{d}\vec{r}}{na^2}$$

and therefore, that the force which acts in the direction of this displacement is

$$f^c = -\frac{3kT\vec{r}}{na^2}$$

Give an analogous expression for the force f^s between two segments of the chain, whose positions relative to the origin are defined by the vectors $\vec{r}_i$ and $\vec{r}_{i+1}$ and which are linked by a subchain containing n_s links. In which direction is this force acting?

A mass, m, is bound to a freely jointed chain containing 100 links of length $a = 1.4 \cdot 10^{-10} m$, which is fixed by one of its ends at the ceiling (the position of which in relation to the earth's surface does not vary).

From the above derived formula for f^c, get an expression for the value of m for which this chain will be fully stretched, if T = 27 °C (you can ignore the mass of the chain).

What would be the average distance between a weight of this mass and the ceiling, if we increased the temperature to 327 °C? (Assuming that the chain does not degrade at this temperature.) What would happen, if we reduced the temperature instead of increasing it?

What would the average position of the second end of the chain be without the weight?

Reading suggestions:

- Lecture Notes of Chapters 4.1