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Exercise 6 - Solution

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.

before deformation:

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

after deformation:

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

entropy change:

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

with:

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

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

(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 ($c_x\lambda_y\lambda_z = 1$). Why?

$$\lambda_z\lambda_y\lambda = 1 \rightarrow \lambda_z = \lambda_y = \sqrt{\frac{1}{\lambda}} \qquad \Delta S = -\frac{Nk\left(\lambda^2+\frac{2}{\lambda}-3\right)}{2}$$

For the significant difference between compression modulus and elastic modulus (ca. 3 orders of magnitude), see Slide 204.

(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?

with $\Delta A = -T\Delta S$

$$f = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial A}{\partial \lambda}\right)_T = \frac{\partial}{\partial \lambda}\left(\frac{NkT(\lambda^2+2\lambda^{-1}-3)}{2}\right)_T = NkT(\lambda-\lambda^{-2}) = \sigma$$

In terms of the strain ϵ:

$$\epsilon = \lambda - 1 \qquad \sigma = NKT(1+\epsilon-\frac{1}{(1+\epsilon)^2}) = NkT\frac{(1+\epsilon)^3-1}{(1+\epsilon)^2}$$

From the definition of Young's modulus: $E = \left(\frac{d\sigma}{d\epsilon}\right)_{\epsilon\to 0}$

$$\sigma = NkT\frac{\epsilon^3+3\epsilon^2+3\epsilon}{(1+\epsilon)^2} \approx 3NkT\epsilon \quad \longrightarrow \quad E = \frac{\sigma}{\epsilon} = 3NkT$$

The calculations are based on the average behavior of a single chain, assuming that the displacements of its ends are proportional to the macroscopic deformation (affine network). Moreover, we completely ignore the interactions of this chain with its neighbors, that is we consider a

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"phantom" network where the subchains are able to walk through their neighbors as if they weren't there. This limitation is nevertheless minor - most important is that all the statistical distributions that we use are Gaussian-type and predict a finite probability for values of the end-to-end distance greater than *na*, the length of a fully stretched chain, which does not make physical sense. Moreover, in reality, for very large values of *ε*, we observe a significant hardening within this limit (see our example of natural rubber. Why does it show this effect?), which is not taken into account in the microscopic theory presented here. See also Slide 217 and the Lecture Notes!

(iv) In a crosslinked polymer of density 1.1 g/cm³ 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.)

The elastic modulus is given by

$\boldsymbol{E = 3NkT}$.

The number of subchains is equal to the density divided by the mass of a subchain, M_{nx}, divided by Avogadro's number, N_A:

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

Insertion into the above relation for *G* gives us a fairly reasonable value:

$$E = 3\cdot(273\ \mathrm{K} + 20\ \mathrm{K})\cdot 10^{26}\mathrm{m}^{-3}\cdot 1.4\cdot 10^{-23}\mathrm{J\ K}^{-1} \approx 1.35\ \mathrm{MPa}.$$

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

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

The force acting in the direction of displacement = -d*A*/d*r* where *A* is the change in energy (the force is given by the negative gradient of the free energy with respect to the displacement). This force is therefore opposed to positive

displacements. Since we only consider the contribution of entropy here, equal to -*TS*, and since the temperature does not change, we can write

$$\mathrm{d}S^c = \frac{3k}{2na^2}\left(r^2 - (r + \mathrm{d}r)^2\right) = \frac{3k}{2na^2}\left(-2\vec{r}\cdot\mathrm{d}\vec{r} - \mathrm{d}r^2\right) \approx -\frac{3k\vec{r}\cdot\mathrm{d}\vec{r}}{na^2}$$

$$f^c = -\frac{\mathrm{d}A}{\mathrm{d}r} = T\frac{\mathrm{d}S}{\mathrm{d}r} = -\frac{3kT\vec{r}}{na^2}$$

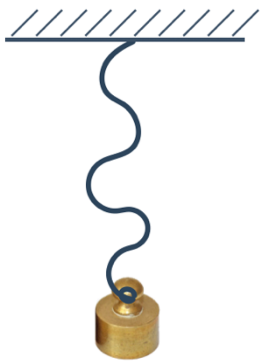
Give an analogous expression for the force f^s between two segments of the chain, whose positions relative to the origin are defined by the vectors $\vec{r}_i$ and $\vec{r}_{i+1}$ and which are linked by a subchain containing n_s links. In which direction is this force acting?

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

The vector $\vec{r} = \vec{r}_i - \vec{r}_{i+1}$ has for origin the segment *i*+1 and points into the direction of the segment *i* and its length corresponds to the separation of the two segments. So, we substitute $\vec{r}_i - \vec{r}_{i+1}$ for $\vec{r}$ and n_s for *n* in the above expression for f^c.

The force acts in the direction of a displacement of the segment *i* along *r*. In other words, there is a positive force in the direction of segment *i*+1. The subchain acts as a spring between the two segments, opposing their spacing.

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).

The chain contains *n* bonds of length *a*, so its length when fully stretched is *na*.

$$f^c = -\frac{3kT\vec{r}}{na^2} = \frac{3kTna}{na^2} = \frac{3kT}{a} = \frac{3 \cdot 1.38 \cdot 10^{-23}\text{J K}^{-1} \cdot 300\text{ K}}{1.4 \cdot 10^{-10}\text{ m}} \approx 10^{-10}\text{N} = m \cdot g$$

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?

Convert temperatures in Kelvin, first. The force is always equal to $m \cdot g$, so

$$m \cdot g = -\frac{3k \cdot 300 \cdot na}{na^2} = -\frac{3k \cdot 600 \cdot \vec{r}}{na^2}$$

$$\vec{r} = \frac{na}{2} = -\frac{100 \cdot 1.4 \cdot 10^{-10}}{2}\text{m} = 7\text{ nm}$$

The weight rises from 14 nm to 7 nm below the ceiling.

If we reduce the temperature, an entropic type spring generally becomes "softer" and the weight drops. However, the chain in question is already fully stretched at 27 °C and there is no possible conformational change that would allow the weight to drop further, even though our expression gives us a force for *r* > *na* (in fact the weight should rise a bit under these conditions due to the thermal contraction of the C-C bonds). This inconsistency is due to the use of a Gaussian distribution for *r* in the model presented on the slides, which therefore admits that a string has a certain probability of being longer than *na*, which does not make sense (in fact the bonds of a polymer are not perfectly rigid, but we implicitly ignore their deformation here because this is negligible compared to *na*). For more realistic models, a truncated distribution at *r* = *na* called the Langevin distribution can be used (see Slide 218).

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

It will obviously be 0. This is an average position, just like the positions you calculated above in the presence of weight. At one point it can be found at any positive or negative height relative to the bar, as long as it does not move away from it more than *na*.