Stretching a Polymer

Specific elastic properties of rubber follow from equilibrium properties of just one long polymer, since the rubber is a system of linked polymers. From the statistical-mechanical viewpoint, these properties are totally due to *decrease in entropy* resulting from stretching.—There are no hidden microscopic "springs"! It is also worth noting that the effect is purely classical.

General analysis. Consider a long loose polymer with ends fixed at a distance l. The word 'loose' means that the stretching force is negligible as compared to the molecular forces, so that the polymer by no means should be thought of as a tight string. Under these conditions and at not that small temperatures, the partition function factorizes into a product of two partition functions:

$$Z(T, l) = Z_{\text{int}}(T) \, Z_{\text{conf}}(l) , \qquad (1)$$

where Z_{int} comes from short-ranged degrees of freedom and thus is not sensitive to l, while Z_{conf} comes from summing over all possible larger-scale spatial configurations of the polymer. It turns out that at large enough temperatures Z_{conf} does not depend on T.—Let us understand why. In a general case, the sum over the configurations is written as (we are interested only in high enough temperatures and thus use classical formula)

$$Z_{\text{conf}} = \int \mathrm{d}\vec{\xi}_1 \, \mathrm{d}\vec{\xi}_2 \cdots \mathrm{d}\vec{\xi}_N \, e^{-U_{\text{conf}}(\vec{\xi}_1, \vec{\xi}_2, \ldots, \vec{\xi}_N)/T} , \qquad (2)$$

where we describe a configuration of the polymer by a broken line formed by $N \gg 1$ vectors, $(\vec{\xi}_1, \vec{\xi}_2, \ldots, \vec{\xi}_N)$. More specifically, we break the polymer into N pieces of equal length l_0 by introducing $(N-1)$ intermediate points. The vector $\vec{\xi}_j$ goes from the point $(j-1)$ to the point j, with $j = 0$ corresponding to the beginning of the polymer and $j = N$ corresponding to its end.

The configurational potential energy U_{conf} comes from the Van der Waals interaction between distant (not adjacent to each other) parts of the macro-molecule. At low enough temperature, this interaction is important and leads to the formation of a compact state, the so-called *globule phase*. The properties of the globule phase are basically the same as those of a solid. We are interested in an opposite high-temperature case, when it is energetically favorable to form a loose phase. In this case, the configurational energy is much smaller than temperature, and we can replace the exponential in (2) with unity.—Z_{conf} becomes temperature-independent.

Eq. (18) implies that for the free energy we have

$$F(T, l) = F_{\text{int}}(T) - T S_{\text{conf}}(l) , \qquad (3)$$

where

$$F_{\text{int}}(T) = -T \ln Z_{\text{int}}(T) , \qquad (4)$$

and

$$S_{\text{conf}}(l) = \ln Z_{\text{conf}}(l) . \qquad (5)$$

Here S_{conf} is the configurational entropy.—When all the states are equally probable, then the entropy is just the log of the partition function.

The quantity of our interest is the force, $\mathcal{F}$, exerted by stretched polymer to a support. Employing the same argument that has lead us to the expression for pressure (work of the force equals energy change), we first get

$$\mathcal{F} = -\left\langle \frac{\partial H}{\partial l} \right\rangle , \qquad (6)$$

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and then, utilizing the general relation

$$\left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \left(\frac{\partial F}{\partial \lambda} \right)_T , \tag{7}$$

obtain

$$\mathcal{F} = -\left(\frac{\partial F}{\partial l} \right)_T . \tag{8}$$

Taking into account Eq. (3), we find

$$\mathcal{F} = T \frac{\mathrm{d}S_{\mathrm{conf}}}{\mathrm{d}l} . \tag{9}$$

We see that the force is directly proportional to temperature. That is it *increases* with increasing T, which is rather counterintuitive.

Actually, we can go further with our analysis and get a generic expression for $S_{\mathrm{conf}}(l)$ by mapping our problem onto the random walk problem. If we fix only the left end of the polymer and consider all possible configurations of the rest of the molecule, we get a typical random walk problem in 3D. So that the partition function for the configuration with the fixed right end is nothing else than the probability density of finding the random walk end at this point. With a little trick, the 3D problem can be reduced to a 1D one. Instead of fixing all the three coordinates of the right end, we fix only one of them, say, the coordinate $x = l$. Though the other coordinates of the right end are free, their fluctuations are negligibly small (at $N \gg 1$) as compared to l and do not change the final answer. So, we have a 1D random variable

$$l = \xi_1^{(x)} + \xi_2^{(x)} + \ldots + \xi_N^{(x)} , \tag{10}$$

composed out of x-components of the vectors specifying the polymer configuration. Hence, up to a normalizing factor, the function $Z_{\mathrm{conf}}(l)$ is just the probability density for the random variable l. Assuming that l_0 is large enough, we can treat $\xi^{(x)}$'s as statistically independent variables and use the Central Limiting Theorem:

$$Z_{\mathrm{conf}}(l) \propto \mathrm{e}^{-l^2/2N\sigma_0^2} , \tag{11}$$

where σ_0 is the dispersion of $\xi^{(x)}$'s:

$$\sigma_0 = \Delta\xi_1^{(x)} = \Delta\xi_2^{(x)} = \cdots = \Delta\xi_N^{(x)} . \tag{12}$$

We thus have

$$S_{\mathrm{conf}} = \mathrm{const} - \frac{l^2}{2N\sigma_0^2} , \tag{13}$$

and

$$\mathcal{F} = -\frac{Tl}{N\sigma_0^2} . \tag{14}$$

This expression contains some arbitrariness associated with the choice of the length l_0. We can easily get rid of it. Introducing the total length of the polymer, L, we have $N = L/l_0$, and

$$\mathcal{F} = -\frac{Tl}{L} \frac{l_0}{\sigma_0^2} . \tag{15}$$

The ratio σ_0^2/l_0 is actually l_0-independent for exactly the same reasons that lead to the Δt-independence of the ratio $\sigma_0/\Delta t$ in the theory of Brownian motion. Hence, $\sigma_0^2/l_0 = a$, where a is some microscopic length, and we ultimately have

$$\mathcal{F} = -\frac{Tl}{aL} . \tag{16}$$

What is the range of applicability of this relation? The criterion is simply

$$l \ll L \; . \tag{17}$$

Below we will see it with a particular example.

Simple model. The simplest model for a polymer is just N rigid vectors of the length a, so that the integral (2) is over the orientations of the vectors.

This model is readily solvable by the following trick. Instead of looking for the force as a function of l, we will apply a constant force $\mathcal{F}$ to one end of the polymer keeping the other end fixed. With the x axis along the force direction, the partition function reads

$$Z = \int \mathrm{d}\vec{\xi}_1 \, \mathrm{d}\vec{\xi}_2 \cdots \mathrm{d}\vec{\xi}_N \; \mathrm{e}^{-U(x)/T} \; , \tag{18}$$

where

$$x = \xi_1^{(x)} + \xi_2^{(x)} + \ldots + \xi_N^{(x)} \tag{19}$$

is the x-coordinate of the end to which the force is applied (the other end is fixed at the origin), and

$$U(x) = -\mathcal{F}x \tag{20}$$

is the potential corresponding to the coordinate-independent force $\mathcal{F}$. We want to find the average distance between the ends,

$$l = \langle x \rangle \; . \tag{21}$$

And this is easily due to the linearity of the external potential. Indeed, the exponential $\mathrm{e}^{-U(x)/T}$ factorizes into the product of identical exponentials for each particular element, so that

$$\langle x \rangle = N \langle \xi^{(x)} \rangle \; , \tag{22}$$

with

$$\langle \xi^{(x)} \rangle = \frac{\int \mathrm{d}\vec{\xi}\, \xi^{(x)} \, \mathrm{e}^{\mathcal{F}\xi^{(x)}/T}}{\int \mathrm{d}\vec{\xi}\, \mathrm{e}^{\mathcal{F}\xi^{(x)}/T}} = T \frac{\partial}{\partial \mathcal{F}} \ln Z_0 \; , \tag{23}$$

where

$$Z_0 = \int \mathrm{d}\vec{\xi}\, \mathrm{e}^{\mathcal{F}\xi^{(x)}/T} \; . \tag{24}$$

The integral over $\vec{\xi}$ is over the directions of $\vec{\xi}$ only, since $|\vec{\xi}| = a$. This means that in spherical coordinates we have

$$\mathrm{d}\vec{\xi} = -\mathrm{d}\varphi \, \mathrm{d}(\cos\theta) \; , \qquad \xi^{(x)} = a\cos\theta \; . \tag{25}$$

Performing the integral we find (we do not care about constant factors since these do not affect the final answer)

$$Z_0 \propto \frac{T}{\mathcal{F}a} \sinh\left(\frac{\mathcal{F}a}{T}\right) \; , \tag{26}$$

which in accordance with (22), (23) leads to

$$l = -\frac{NT}{\mathcal{F}} + aN \coth \frac{\mathcal{F}a}{T} \; . \tag{27}$$

It is reasonable to introduce dimensionless scaling variables for l and $\mathcal{F}$. The natural unit for l is the total length of the polymer, $L = aN$. As follows from (27), the natural unit for $\mathcal{F}$ is T/a. We thus introduce the variables (not to be confused with the coordinates):

$$x = \frac{l}{L} \; , \qquad y = \frac{\mathcal{F}a}{T} \; , \tag{28}$$

and rewrite Eq. (27) as

$$x = -1/y + \coth y \ . \tag{29}$$

There are two characteristic cases: (i) $y \ll 1 \Leftrightarrow x \ll 1$ and (ii) $y \gg 1 \Leftrightarrow 1 - x \ll 1$. The case (i) corresponds to the generic random-walk limit (14). The case (ii) corresponds to the limit of strong stretching and is model-specific. At $y \ll 1$ we expand the hyperbolic cotangent up to the second term (the first term will be cancelled by $-1/y$) and get

$$y = 3x \ , \qquad (x \ll 1) \ , \tag{30}$$

that is

$$\mathcal{F} = \frac{3lT}{La} \qquad (l \ll L) \ . \tag{31}$$

At $y \gg 1$ we have $\coth y \approx 1$, and

$$y = \frac{1}{1-x} \ , \qquad (1 - x \ll 1) \ , \tag{32}$$

that is

$$\mathcal{F} = \frac{T}{a} \frac{1}{1 - l/L} \qquad (L - l \ll L) \ . \tag{33}$$

Problem 31. Perform carefully all the calculations leading to Eqs. (26), (27), and (30).

Problem 32. Make sure that Eq. (31) exactly corresponds to the generic Eq. (14).

Role of the short-range repulsion *(Honors Section material).*
Our general analysis of the polymer was based on the assumption

$$|U_{\text{conf}}| \ll T \ . \tag{34}$$

In reality, this assumption cannot be satisfied at *any* temperature because of the strong repulsive core of the interatomic potential. At high enough temperature we can neglect only the attractive (Van der Waals) part of interaction. A good news, however, is that at high temperature the short-range repulsive interaction is equivalent to a purely geometric constraint that the two fragments of the polymer cannot approach each other at a distance smaller than some characteristic microscopic scale a. This means that the relations (3)-(9) remain true, where $Z_{\text{conf}}(l)$ is some T-independent configurational partition function. A direct calculation of $Z_{\text{conf}}(l)$ is a quite difficult mathematical problem. Nevertheless, its generic properties can be established from the following analysis. The quantity Z_{conf} is a dimensionless function of three variables: l, a, and the total length L. From purely dimensional argument we can reduce the number of independent variables from three to two, by writing, say, $Z_{\text{conf}}(l, L, a) \equiv Z_{\text{conf}}(l/a, L/a)$. We can go further by employing the *similarity* argument. Namely, we once again interpret $Z_{\text{conf}}(l)$ as a (non-normalized) distribution over distances l and note that in the limit of $L \gg a$ the form of this distribution should saturate a*one and the same function*, up to a scaling factor for the variable l:

$$Z_{\text{conf}}(l, L, a) \equiv \mathcal{Z}(l/R(L, a)) \ . \tag{35}$$

The geometrical meaning of the scaling factor $R(L, a)$ is the typical size of the polymer. From now on we will be interested only in the limit of

$$l \ll R(L, a) \ , \tag{36}$$

and thus will be expanding the function $\mathcal{Z}$ in the Taylor series:

$$\mathcal{Z}(x) \;=\; \mathcal{Z}(0) \;+\; (1/2)\mathcal{Z}''(0)\,x^2 \;+\ldots . \tag{37}$$

The linear term is absent because at $x = 0$ our function is supposed to have a maximum.—Physically, $l = 0$ is the most probable configuration of a polymer with a free end. This also implies $\mathcal{Z}''(0) < 0$. With the same accuracy,

$$S_{\text{conf}} \;=\; \ln Z_{\text{conf}} \;\approx\; \text{const} - Cl^2/2R^2 \;, \tag{38}$$

where $C = \mathcal{Z}''(0)/\mathcal{Z}(0)$ is just a constant of the order unity. Without loss of generality, we can set $C = 1$, by re-defining R:

$$R \;\to\; \sqrt{C}\,R \;. \tag{39}$$

For the force $\mathcal{F}$ we then get

$$\mathcal{F} \;=\; T\,\frac{\mathrm{d}S_{\text{conf}}}{\mathrm{d}l} \;=\; -\frac{Tl}{R^2(L,a)} \;. \tag{40}$$

We see that as in the case of the random-walk approximation, the force is proportional to l, but now the dependence of the proportionality coefficient on L and a is supposed to be different.

What can we say about this dependence from general principles? Dimensional analysis says that we can always write

$$R(L,a) \;=\; a f(L/a) \;, \tag{41}$$

where f(x) is some dimensionless function. We are interested in $L \gg a$, which means large x, and thus some *asymptotic behavior* of the function $f(x)$. It is natural to expect that this asymptotic behavior is given by some power-law function:

$$f(x) \;\propto\; x^{\nu} \;. \tag{42}$$

It is impossible to establish the exponent ν from general considerations. Numerical analysis of this problem has established that

$$\nu \;\approx\; 0.588 \;. \tag{43}$$

Our final expression for the force is

$$\mathcal{F} \;=\; -\frac{Tl}{a^2(L/a)^{2\nu}} \qquad\qquad (\,l \;\ll\; a(L/a)^{\nu}\,) \;. \tag{44}$$

A numeric coefficient is absent in this formula, since we can always absorb it into the definition of a.