2 Kinetic Theory of Rubber

2.1 Rubber Elasticity is "Entropy Induced"

We start by considering an elastic bar of any solid material, be it steel, aluminium, wood − or rubber. The bar is fixed to the bottom at one end and a tensile load P_λ is applied to the other end slowly, or as we say, *quasistatically*. This means that the deformation of the bar caused by the tensile load P_λ is homogeneous and that the load itself is always equilibrated by the retractive elastic force $\bar{P}_\lambda$ of the bar. Accelerations are negligible and so is the kinetic energy of the bar and the dissipation, or entropy production. The undistorted length of the bar is L_λ^0 and the deformed length under the load P_λ − or $\bar{P}_\lambda$ − is L_λ, see Fig. 2.1. The temperature is equal to T everywhere in the bar and at all times.
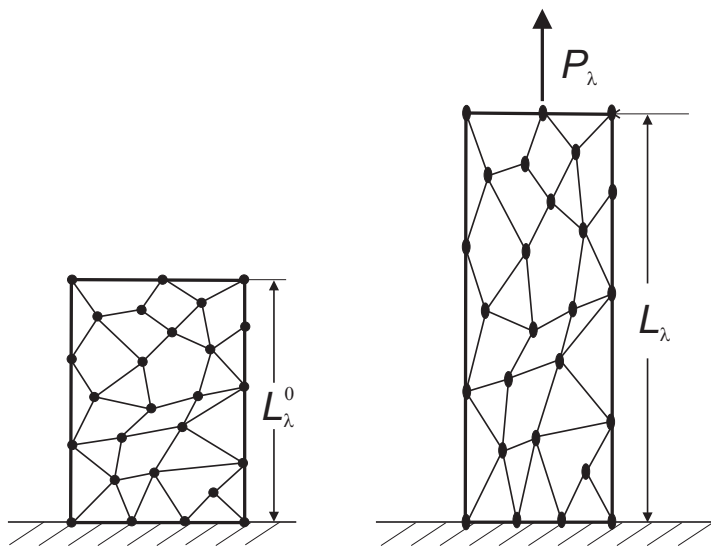

Fig. 2.1. An elastic bar in the undistorted state (left) and deformed by the load P_λ (right)

Under quasistatically applied loads the first and second laws of thermodynamics read

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{Q} + \dot{W} \qquad \text{and} \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\dot{Q}}{T}. \tag{2.1}$$

U and S are the internal energy and entropy respectively and $\dot{W}$ is the working, or power, of the load, i.e.

$$\dot{W} = P_\lambda \frac{\mathrm{d}L_\lambda}{\mathrm{d}t} \qquad \text{or here} \qquad \dot{W} = \bar{P}_\lambda \frac{\mathrm{d}L_\lambda}{\mathrm{d}t}. \tag{2.2}$$

$\dot{Q}$ is the heating needed to maintain the constant temperature T. Both equations (2.1) represent somewhat mutilated forms of the laws of thermodynamics. Thus the first law, or energy balance, has no kinetic energy term because the process is quasistatic. For the same reason the second law, or entropy balance, is an equality rather than an inequality. Indeed, the entropy production vanishes in a quasistatic or reversible process.

Later, in Chap. 3 we shall have to consider rapid, irreversible processes and that will force us to give the complete form of the thermodynamic laws. Also we shall then have to make a distinction between the applied load P_λ, and the elastic force $\bar{P}_\lambda$.

Elimination of $\dot{Q}$ and $\dot{W}$ between (2.1) and (2.2) provides the Gibbs equation for S

$$T\mathrm{d}S = \mathrm{d}U - \bar{P}_\lambda \mathrm{d}L_\lambda, \tag{2.3}$$

or, equivalently, for the free energy $F = U - TS$

$$\mathrm{d}(U - TS) = -S\mathrm{d}T + \bar{P}_\lambda \mathrm{d}L_\lambda. \tag{2.4}$$

The elastic force $\bar{P}_\lambda$ and the internal energy U depend on L_λ and T and so does S, by (2.3). The functions $\bar{P}_\lambda(L_\lambda, T)$ and $U(L_\lambda, T)$ are called thermal and caloric equations of state, respectively, and their specific form is characteristic for a material. The two equations of state are not independent, because (2.4) implies

$$\bar{P}_\lambda = \frac{\partial U}{\partial L_\lambda} - T\frac{\partial S}{\partial L_\lambda} \quad \text{and} \quad \frac{\partial S}{\partial L_\lambda} = -\frac{\partial \bar{P}_\lambda}{\partial T}, \quad \text{hence} \quad \frac{\partial U}{\partial L_\lambda} = \bar{P}_\lambda - T\frac{\partial \bar{P}_\lambda}{\partial T}. \tag{2.5}$$

Equation $(2.5)_2$ results as an integrability condition for the free energy F, cf. (2.4), while $(2.5)_1$ allows us to split the elastic force $\bar{P}_\lambda$ into

- an energetic part $\frac{\partial U}{\partial L_\lambda}$ and
- an entropic part $-T\frac{\partial S}{\partial L_\lambda}$. $\tag{2.6}$
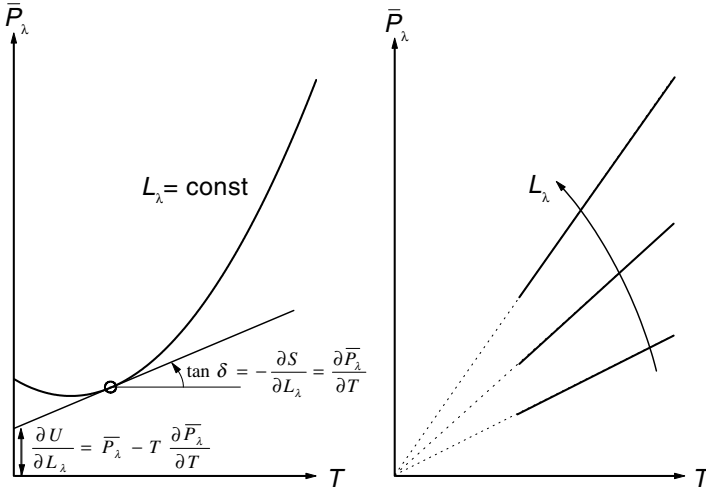
Fig. 2.2. Left: Measured load-temperature graph of a bar of an arbitrary material (schematic). Right: Measured load-temperature graphs of rubber for different constant values of L_λ

Thus we recognize that part of the elastic force is due to a change of energy with length and part is due to a change of entropy.

It is possible to identify the two parts of $\bar{P}_\lambda$ — the energetic and entropic ones — for every L_λ and T from a simple experiment: For different temperatures, we measure the load $\bar{P}_\lambda$ needed to maintain a fixed length L_λ and we plot $\bar{P}_\lambda(L_\lambda, T)$. Let Fig. 2.2$_{left}$ represent such a measured plot for one L_λ. At one point of that curve the slope $\frac{\partial \bar{P}_\lambda}{\partial T}$ determines the entropic part of $\bar{P}_\lambda$ — to within the factor T — because, by $(2.5)_2$, that slope equals $-\frac{\partial S}{\partial L_\lambda}$. Also, the ordinate intercept of the tangent in that point determines the energetic part, because, by $(2.5)_3$, we have $\frac{\partial U}{\partial L_\lambda} = \bar{P}_\lambda - T\frac{\partial \bar{P}_\lambda}{\partial T}$.

When we perform this experiment for rubber, we obtain straight lines as those shown in Fig. 2.2$_{right}$ and, upon extrapolation of these lines down to absolute zero temperature, we see that the ordinate intercept is equal to zero. Accordingly the internal energy U of rubber is independent of L_λ, or we may say that the energy has nothing to do with the elastic force of rubber. That force is *entropy-induced*. Indeed, for rubber $(2.5)_1$ reduces to

$$\bar{P}_\lambda = -T\frac{\partial S}{\partial L_\lambda}. \tag{2.7}$$

Rubber is not the only material with entropy-induced elasticity. Ideal gases have the same property. Let us consider:

The framework of quasistatic or reversible thermodynamics is equally valid for any fluid and for the elastic bar in uniaxial tension considered heretofore. In particular, the first and second laws have the forms (2.1) and the only difference

is the form of the quasistatic working which is $-p\frac{dV}{dt}$ in a fluid, where p is the pressure of the fluid and V is its volume. Thus, in order to convert our formulae to those of a fluid, we need only replace the pair $(\bar{P}_\lambda, L_\lambda)$ by $(-p, V)$. In particular we have, in analogy to (2.5)

$$p = -\frac{\partial U}{\partial V} + T\frac{\partial S}{\partial V} \qquad \text{and} \qquad \frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}.$$

The thermal and caloric functions of state of a fluid are given as $p(V,T)$ and $U(V,T)$.

In an ideal gas with N molecules the thermal equation of state reads $pV = NkT$, so that p is a linearly homogeneous function of T starting with zero at $T = 0$. Therefore U is independent of V. Hence

$$p = T\frac{\partial S}{\partial V},$$

and we conclude that the pressure of an ideal gas is entropy-induced − just like the load $\bar{P}_\lambda$ of rubber is entropy-induced.

It is because of that similarity that we have called gases the closest relatives of rubber in Chap. 1. Or, as a joker with an original turn of mind has once put it: rubbers are the ideal gases among the solids.

2.2 Entropy of a Rubber Molecule

Seeing from (2.7) that the form of the thermal equation of state $\bar{P}_\lambda(L_\lambda, T)$ can be determined by differentiation of the entropy function $S(L_\lambda, T)$ with respect to L_λ, we shall now proceed to calculate S as a function of L_λ. For that purpose we need a model of the molecular structure of rubber.

We rely on the conclusion of the chemists who have classified rubber as a *polymer* whose molecules are long chains of hundreds of isoprene molecules $CH_2 = CH - C(CH_3) = CH_2$ strung together by carbon-carbon bonds. The chain is quite flexible and we may consider it as consisting of N loose links, each of length b, twisting and entangled so that a projection of the chain upon the page may look as shown in Fig. 2.3_{top}.

For the purpose of our calculation we simplify that figure and consider the chain as a "one-dimensional tangle" as represented in the lower part of Fig. 2.3.[1]

The molecule, or chain, has so many links that all by itself it can be ascribed an entropy S_{Mol}. We consider the one-dimensional model molecule of Fig. 2.3_{bottom} of $N_\pm$ links pointing to the right or left. For an end-to-end distance r, see Fig. 2.3, N_+ and N_- must satisfy the constraints

$$\begin{aligned} N_+ + N_- &= N \\ N_+b - N_-b &= r \end{aligned} \quad \Longleftrightarrow \quad N_\pm = \frac{N}{2}\left(1 \pm \frac{r}{Nb}\right). \tag{2.8}$$

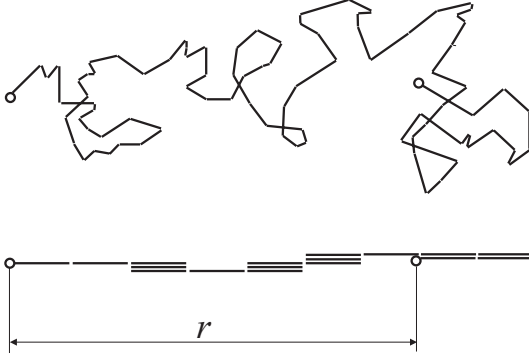[1] In Sect. 2.3 we consider a more realistic model, in which the links are arbitrarily oriented.

Fig. 2.3. Top: Projection of a rubber molecule onto the page. Bottom: One-dimensional "tangle" representing a rubber molecule

The pair of numbers $\{N_+, N_-\}$ is called the *distribution* of links and we conclude from (2.8) that, in the case of the one-dimensional chain, the distribution is fully determined by the end-to-end distance r.

The molecular entropy S_{Mol} is calculated from the Boltzmann formula

$$S_{\text{Mol}} = k \ln W, \tag{2.9}$$

where W is the number of possibilities to realize the distribution $\{N_+, N_-\}$. By the combinatorial rules and (2.8) we have

$$W = \frac{N!}{N_+! N_-!} = \frac{N!}{\left[\frac{N}{2}\left(1 + \frac{r}{Nb}\right)\right]! \left[\frac{N}{2}\left(1 - \frac{r}{Nb}\right)\right]!}. \tag{2.10}$$

Thus W, and hence S_{Mol}, is a function of the end-to-end distance r.

We simplify that function by use of the Stirling formula and by an expansion of the logarithmic function, viz

$$\ln a! \approx a \ln a - a \quad \text{and} \quad \ln\left(1 \pm \frac{r}{Nb}\right) \approx \pm \frac{r}{Nb} - \frac{1}{2}\left(\frac{r}{Nb}\right)^2. \tag{2.11}$$

The former is true for large values of a and we apply it to N as well as N_+ and N_- thus assuming big numbers for all of them. The approximation $(2.11)_2$ holds for $\frac{r}{Nb} \ll 1$ i.e. for a strong degree of entanglement of the chain molecule; after all r is the end-to-end distance and Nb is the contour length of the chain. Introducing the approximations (2.11) into (2.10) we obtain after a brief calculation

$$S_{\text{Mol}} = Nk \left(\ln 2 - \frac{1}{2}\left(\frac{r}{Nb}\right)^2\right). \tag{2.12}$$

Therefore the molecular entropy as a function of the end-to-end distance is represented by a concave parabola with its apex at $r = 0$. We conclude that the entropy of the molecule assumes a maximum when the degree of entanglement is maximal.

2.3 The Rubber Molecule
with Arbitrarily Oriented Links

Replacing a three-dimensional tangle of a rubber molecule by the one-dimensional line-up of links of Fig. 2.3$_{bottom}$ is, of course, quite unrealistic and it might be thought to lead to unrealistic results. This is not so, however. Indeed, for all that counts, which is the entropy of the molecule, the two models are equivalent. We proceed to demonstrate that.

Let there be $N_{\vartheta\varphi}$ links pointing in the direction ϑ, φ, where ϑ is the angle with the direction of the end-to-end distance vector of a molecule and φ is the azimuthal angle of the link. In that case we have two constraints on $N_{\vartheta\varphi}$, namely

$$\sum_{\vartheta\varphi} N_{\vartheta\varphi} = N$$

$$\sum_{\vartheta\varphi} b\cos\vartheta \ N_{\vartheta\varphi} = r. \tag{2.13}$$

The entropy of the molecule is given by

$$S_{\mathrm{Mol}} = k\ln W, \quad \text{where} \quad W = \frac{N!}{\prod_{\vartheta\varphi} N_{\vartheta\varphi}!}. \tag{2.14}$$

It is now not possible − as it was before, cf. (2.8) − to immediately relate the numbers $N_{\vartheta\varphi}$ to the end-to-end distance r; there are too many numbers $N_{\vartheta\varphi}$ for that and still only two constraints. In order to be able to proceed we assume that the distribution $\{N_{\vartheta\varphi}\}$ is such that it maximizes the entropy under the constraints (2.13). For quasi-static deformations of rubber this *maximum entropy assumption* seems reasonable; at least it is frequently invoked by physicists in similar circumstances when dealing with stochastic processes in gases, fluids and solids.

In the present case we maximize

$$k\ln\frac{N!}{\prod_{\vartheta\varphi} N_{\vartheta\varphi}!} - \alpha\left(\sum_{\vartheta\varphi} N_{\vartheta\varphi} - N\right) - \beta\left(\sum_{\vartheta\varphi} b\cos\vartheta \ N_{\vartheta\varphi} - r\right)$$

without constraints, where α and β are Lagrange multipliers. We invoke the Stirling formula (2.11)$_1$ on N and on all $N_{\vartheta\varphi}$ and obtain after a short calculation

$$N_{\vartheta\varphi} = \mathrm{e}^{-\left(1+\frac{\alpha}{k}\right)}\mathrm{e}^{-\frac{\beta}{k}b\cos\vartheta}.$$

This is the distribution $N_{\vartheta\varphi}$ that maximizes S_{Mol}. The multipliers α and β must be determined from the constraints (2.13) and thus we get

$$N_{\vartheta\varphi} = \frac{\mathrm{e}^{-\frac{\beta}{k}b\cos\vartheta}}{\sum\limits_{\vartheta\varphi}\mathrm{e}^{-\frac{\beta}{k}b\cos\vartheta}} \quad \text{and} \quad \frac{r}{Nb} = \frac{\sum\limits_{\vartheta\varphi}\cos\vartheta \ \mathrm{e}^{-\frac{\beta}{k}b\cos\vartheta}}{\sum\limits_{\vartheta\varphi}\mathrm{e}^{-\frac{\beta}{k}b\cos\vartheta}}. \tag{2.15}$$

Once $N_{\vartheta\varphi}$ is known by $(2.15)_1$ we may use it to calculate the entropy

$$S_{\mathrm{Mol}} = k \ln \frac{N!}{\prod_{\vartheta\varphi} N_{\vartheta\varphi}!} \approx -k \sum_{\vartheta\varphi} N_{\vartheta\varphi} \ln \frac{N_{\vartheta\varphi}}{N}$$

and obtain

$$S_{\mathrm{Mol}} = \beta r + Nk \ln \left(\sum_{\vartheta\varphi} \mathrm{e}^{-\frac{\beta}{k} b \cos \vartheta} \right). \tag{2.16}$$

Of course β follows from $(2.15)_2$ as a function of r, if only we could invert that relation which, however, is impossible, $-$ at least exact inversion is impossible.

In order to invert $(2.15)_2$ approximately we first write that relations as

$$\frac{r}{Nb} = -\frac{\partial}{\partial \beta} \left(\ln \sum_{\vartheta\varphi} \mathrm{e}^{-\frac{\beta}{k} b \cos \vartheta} \right)$$

and then convert the sum into an integral by virtue of the assumption that the number of orientations in the interval ϑ, φ and $\vartheta + \mathrm{d}\vartheta, \varphi + \mathrm{d}\varphi$ is proportional to the solid angle element $\sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi$ traced out by orientations in that interval. We assume that the number equals $Z \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi$, where Z is the factor of proportionality.[2] With all this we may write

$$\sum_{\vartheta\varphi} \mathrm{e}^{-\frac{\beta}{k} b \cos \vartheta} = Z \int_0^{2\pi} \int_0^\pi \mathrm{e}^{-\frac{\beta}{k} b \cos \vartheta} \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi = +4\pi Z \frac{\sin \mathrm{h} \frac{\beta b}{k}}{\frac{\beta b}{k}} . \tag{2.17}$$

Insertion into $(2.15)_2$ gives

$$\frac{r}{Nb} = - \left(\coth \frac{\beta b}{k} - \frac{1}{\frac{\beta b}{k}} \right). \tag{2.18}$$

The expression in brackets is called the Langevin function. This function passes through the origin of a $\left(\frac{r}{Nb}, \frac{\beta b}{k} \right)$-plane with the slope $1/3$. Unfortunately the function cannot be inverted analytically except for small values of $\frac{r}{Nb}$, i.e. for a strong degree of entanglement. If $\frac{r}{Nb} \ll 1$ holds, we have

$$\frac{r}{Nb} \approx -\frac{1}{3} \frac{\beta b}{k}, \quad \text{hence} \quad \frac{\beta}{k} = -3 \frac{r}{Nb^2} \tag{2.19}$$

and that is the desired approximate relation between β and r.

Insertion into (2.16) determines the molecular entropy for a strongly entangled chain, namely

$$S_{\mathrm{Mol}} = Nk \left(\ln 4\pi Z - \frac{r^2}{\frac{1}{3} N^2 b^2} \right). \tag{2.20}$$

Comparison with (2.12) shows an essential agreement: both formulae show that S_{Mol} depends linearly on r^2. To be sure, the value of S_{Mol} for $r = 0$ is different, but that is unimportant for our argument. Also the numerical factor of the r^2-term is different which is again of little account, since N, the number of links, is to be adjusted to observed elastic properties anyway.

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[2] In effect this means that the orientations are quantized; but that aspect need not concern us at present since the value of Z is unimportant for our argument.

2.4 Entropy and Disorder, Entropic Elasticity

The one-dimensional chain of N loose links of length b provides the most instructive arguments concerning the character of entropy: its growth property, its relation to disorder and the nature of entropic forces. Let us consider:

First of all, order or disorder: Why is it said that entropy is a measure of disorder? Well, a fully stretched-out chain with end-to-end distance Nb — so that all links point in the same direction — is perfectly well ordered. Such a situation can only be realized in one single manner, so that $W=1$ holds, and the entropy $S = k\ln W$ is zero. If only one link points in the opposite direction, there is less order; that situation can be realized in N ways and the entropy S equals $k\ln N$. Rather obviously the disorder is biggest when $N/2$ links point in either of the two directions. The entropy in that case equals

$$S = k \ln \frac{N!}{N_+!N_-!} \quad \text{with} \quad \{N_+, N_-\} = \left\{\frac{N}{2}, \frac{N}{2}\right\}$$

and it can easily be shown that this value is the biggest one among all distributions $\{N_+, N_-\}$. Thus entropy is properly linked to disorder.

And why is it that entropy grows? In order to explain this we rely on the reasonable assumption that, — in the course of the thermal motion of the chain links, — all chain realizations occur equally frequently. Thus for instance the fully stretched chain of length $r = Nb$ occurs just as frequently as the chain shown in Fig. 2.3$_{\text{bottom}}$ which has a much shorter length. However, the shorter length occurs more frequently, since it can be realized in so many more ways than $r = Nb$, which can only be done in one way. Therefore, if we start with $r = Nb$, we will most likely soon see the chain with a shorter length as the thermal motion of the links kicks it around. Therefore we will in all likelihood see the chain contract and the entropy grow.

If we wish to prevent the contraction and maintain a non-zero length r, we need to apply a force to the ends each time when the thermal motion tries to shorten the chain. And, if there are 10^{12} kicks to the chain per second by the thermal motion, the force needs to be applied constantly. That is the nature of entropic forces! As the temperature becomes higher the thermal motion becomes more virulent and the entropic force must grow to maintain the length r. That is why the elastic force at a given length grows with T as shown in Fig. 2.2.

2.5 Entropy of a Rubber Bar

Modeling a rubber molecule as a chain of loose links is only the first step in modeling a rubber bar. For the bar we assume that it consists of a network of n such chains as shown in Fig. 2.1. The lines in that figure represent the chains and the dots represent joints between them. The joints are points of entanglement of a molecule with itself or with neighbouring ones. Therefore a chain may be considerably shorter than a molecule. All chains are supposed

to have N links, but their orientations are different and they are given by the cartesian components $(\vartheta_1, \vartheta_2, \vartheta_3)$ of their end-to-end distance vector. Thus the length r − or end-to-end distance − of a chain is $r = \sqrt{\vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2}$. By (2.12) the entropy of a molecule is thus given by

$$S_{\text{Mol}}(\vartheta_1, \vartheta_2, \vartheta_3) = Nk\left(\ln 2 - \frac{\vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2}{2N^2 b^2}\right). \tag{2.21}$$

The entropy of the bar is the sum of the chain entropies so that in the undistorted and in the deformed states of the bar we may write the entropies as

$$S_0 = \int S_{\text{Mol}}(\vartheta_1, \vartheta_2, \vartheta_3)\, z_0(\vartheta_1, \vartheta_2, \vartheta_3)\, d\vartheta_1 d\vartheta_2 d\vartheta_3 \quad \text{and}$$
$$S = \int S_{\text{Mol}}(\vartheta_1, \vartheta_2, \vartheta_3)\, z(\vartheta_1, \vartheta_2, \vartheta_3)\, d\vartheta_1 d\vartheta_2 d\vartheta_3. \tag{2.22}$$

$z_0 d\vartheta_1 d\vartheta_2 d\vartheta_3$ and $z d\vartheta_1 d\vartheta_2 d\vartheta_3$ are the numbers of distance vectors in the interval between $\vartheta_1, \vartheta_2, \vartheta_3$ and $\vartheta_1+d\vartheta_1, \vartheta_2+d\vartheta_2, \vartheta_3+d\vartheta_3$ in the undistorted and deformed states respectively.

We proceed to determine the distribution functions $z_0(\vartheta_1, \vartheta_2, \vartheta_3)$ and $z(\vartheta_1, \vartheta_2, \vartheta_3)$ and start with $z_0(\vartheta_1, \vartheta_2, \vartheta_3)$. Rubber in the undistorted state is isotropic so that we may assume that z_0 depends only on the distance r. If that distance is small, it can be realized in many ways and if it is large it can be realized in few ways only. We assume that the number of distance vectors of length r in the network is proportional to the number of possibilities to realize r. And that number of realizations is given by

$$W = e^{\frac{1}{k} S_{\text{Mol}}}$$

according to the Boltzmann formula for entropy. Therefore we have by (2.12)

$$z_0(\vartheta_1, \vartheta_2, \vartheta_3)\, d\vartheta_1 d\vartheta_2 d\vartheta_3 = C\, e^{-\frac{\vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2}{2Nb^2}}\, d\vartheta_1 d\vartheta_2 d\vartheta_3. \tag{2.23}$$

C is a factor of proportionality whose value may be calculated from the knowledge that the number of chains equals n. Thus

$$\int z_0 d\vartheta_1 d\vartheta_2 d\vartheta_3 = n, \quad \text{hence}^3 \quad C = \frac{n}{\sqrt{2\pi N b^2}^3}. \tag{2.24}$$

Having determined the distribution function in the undistorted state $z_0(\vartheta_1, \vartheta_2, \vartheta_3)$ we still need $z(\vartheta_1, \vartheta_2, \vartheta_3)$ in the deformed state and we proceed to determine it from the assumption that the end-to-end distance vector of each chain deforms in the same manner as the bar itself. For the bar under uniaxial tension the length L_λ is in the direction of the load and the lengths L_μ, L_ν are perpendicular to the load. All lengths are related to the original lengths L_λ^0, L_μ^0, L_ν^0 by

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[3] The integration over ϑ_i $(i = 1, 2, 3)$ is carried from $-\infty$ to $+\infty$ without essential mistake.

$$
\begin{bmatrix} L_\lambda \\ L_\mu \\ L_\nu \end{bmatrix} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{\lambda}} \end{bmatrix} \begin{bmatrix} L^0_\lambda \\ L^0_\mu \\ L^0_\nu \end{bmatrix}. \tag{2.25}
$$

L_μ/L^0_μ and L_ν/L^0_ν are equal by isotropy and $L_\lambda L_\mu L_\nu = L^0_\lambda L^0_\mu L^0_\nu$ holds, because of the incompressibility of rubber; λ is called the stretch. If indeed all distance vectors in the network suffer the same deformation as the bar itself, namely (2.25), we must have

$$
z\left(\vartheta_1, \vartheta_2, \vartheta_3\right) = z_0\left(\frac{1}{\lambda}\vartheta_1, \sqrt{\lambda}\vartheta_2, \sqrt{\lambda}\vartheta_3\right), \tag{2.26}
$$

because a distance vector $\vartheta_1, \vartheta_2, \vartheta_3$ in the deformed state originally had the components $\frac{1}{\lambda}\vartheta_1, \sqrt{\lambda}\vartheta_2, \sqrt{\lambda}\vartheta_3$. With this relation between the functions z and z_0 and the knowledge of $z_0\left(\vartheta_1, \vartheta_2, \vartheta_3\right)$ from (2.23), (2.24) we conclude that

$$
z\left(\vartheta_1, \vartheta_2, \vartheta_3\right) = \frac{n}{\sqrt{2\pi N b^2}^3}\, e^{-\frac{\frac{1}{\lambda^2}\vartheta_1^2 + \lambda\left(\vartheta_2^2 + \vartheta_3^2\right)}{2Nb^2}}. \tag{2.27}
$$

Insertion into (2.22) and simple integrations provide the entropy as a function of the stretch λ in the direction of the load. We obtain

$$
S = nk\left(N\ln 2 - \frac{1}{2}\left(\lambda^2 + \frac{2}{\lambda}\right)\right). \tag{2.28}
$$

The graph of this function is shown on the left hand side of Fig. 2.4. It has a maximum in the undistorted state for $\lambda = 1$. For $\lambda \to 0$ the entropy tends to $-\infty$ asymptotically and for $\lambda \to \infty$ it approaches a concave parabola.

2.6 Uniaxial Force-Stretch Curve

Having determined S as a function of the stretch $\lambda = L_\lambda/L^0_\lambda$ we need only introduce that function into the equation (2.7) to obtain the force-stretch relation. We get

$$
\bar{P}_\lambda = \frac{nkT}{L^0_\lambda}\left(\lambda - \frac{1}{\lambda^2}\right). \tag{2.29}
$$

The graph of that function is shown on the right hand side of Fig. 2.4. For $\lambda = 1$ we have $\bar{P}_\lambda = 0$, as it must be, and for $\lambda \to 0$ we must apply a compressive force tending toward infinity. For large values of λ the force asymptotically tends to a linear function of λ.[4] The force is linear in T which must be expected; actually the proportionality of $\bar{P}_\lambda$ and T was our starting point, cf. Fig. 2.2$_{right}$, when we identified the elasticity of rubber as entropic.

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[4] The kinetic theory of rubber of the present simple form is restricted in validity to $\lambda \lesssim 3.5$, because for larger stretches crystallization occurs and the elasticity is no longer purely entropic. See Chap. 10 for a qualitative treatment of the range of large stretches.
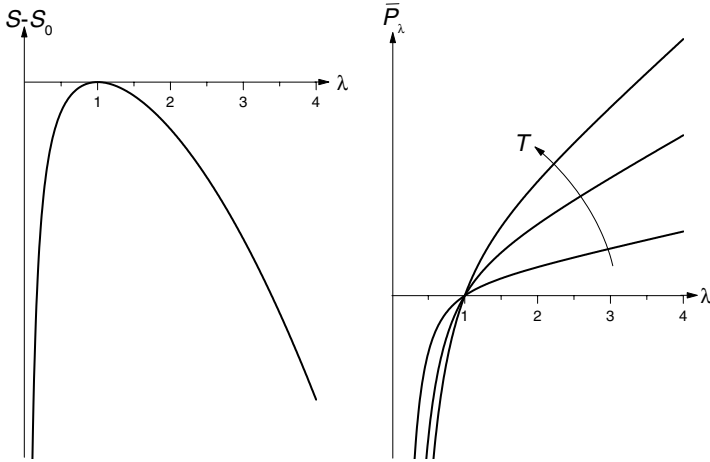
Fig. 2.4. Left: Entropy $S-S_0$ as a function of stretch λ. Right: Force-stretch curves

2.7 Biaxial Loading

So far for simplicity we have developed the kinetic theory of rubber for a bar under uniaxial loading, but it is an easy matter to apply the same ideas to the biaxial loading of a rectangular rubber membrane, see Fig. 2.5. Let the surfaces of the membrane be perpendicular to the λ-, μ-, and ν-directions and let the corresponding lengths be L_λ, L_μ, L_ν — or L_λ^0, L_μ^0, L_ν^0 in the undistorted state. We assume that the membrane is loaded quasistatically by $\bar{P}_\lambda$ and $\bar{P}_\mu$ in the λ- and μ-directions while there is no load in the ν-direction. The working $\dot{W}$ in that case is given by $\bar{P}_\lambda \frac{dL_\lambda}{dt} + \bar{P}_\mu \frac{dL_\mu}{dt}$ and the Gibbs equation reads

$$\mathrm{d}F = -S\mathrm{d}T + \bar{P}_\lambda \mathrm{d}L_\lambda + \bar{P}_\mu \mathrm{d}L_\mu. \tag{2.30}$$

Since rubber elasticity is entropy-induced it follows that

$$\bar{P}_\lambda = -T\frac{\partial S}{\partial L_\lambda} \quad \text{and} \quad \bar{P}_\mu = -T\frac{\partial S}{\partial L_\mu}. \tag{2.31}$$

The arguments concerning rubber molecules and the network of rubber chains are unchanged from before and that includes the calculation of the distribution function $z_0\left(\vartheta_1, \vartheta_2, \vartheta_3\right)$ in the undistorted state. What needs modification is the calculation of the distribution function $z\left(\vartheta_1, \vartheta_2, \vartheta_3\right)$ in the deformed state. Indeed, since in biaxial loading the deformation is given by

$$\begin{bmatrix} L_\lambda \\ L_\mu \\ L_\nu \end{bmatrix} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \frac{1}{\lambda\mu} \end{bmatrix} \begin{bmatrix} L_\lambda^0 \\ L_\mu^0 \\ L_\nu^0 \end{bmatrix} \tag{2.32}$$
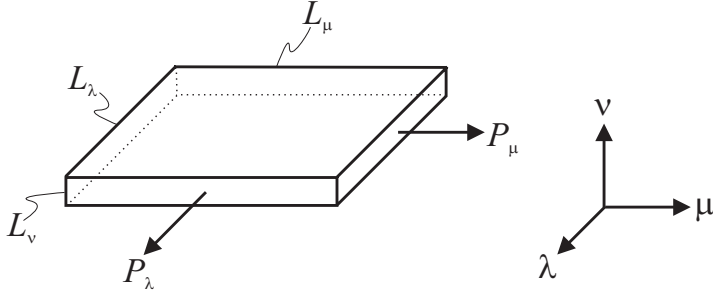
Fig. 2.5. Rectangular rubber membrane

instead of (2.25), the analogue to (2.26) reads

$$z\left(\vartheta_1, \vartheta_2, \vartheta_3\right) = z_0\left(\frac{1}{\lambda}\vartheta_1, \frac{1}{\mu}\vartheta_2, \lambda\mu\vartheta_3\right). \tag{2.33}$$

Therefore, by (2.23), (2.24), the distribution function in the deformed state is given by

$$z\left(\vartheta_1, \vartheta_2, \vartheta_3\right) = \frac{n}{\sqrt{2\pi Nb^2}^3}\, \mathrm{e}^{-\frac{\frac{1}{\lambda^2}\vartheta_1^2 + \frac{1}{\mu^2}\vartheta_2^2 + \lambda^2\mu^2\vartheta_3^2}{2Nb^2}}$$

and the entropy for biaxial loading may then be calculated from $(2.22)_2$ as a function of the two stretches λ and μ. We obtain

$$S = nk\left(N\ln 2 - \frac{1}{2}\left(\lambda^2 + \mu^2 + \frac{1}{\lambda^2\mu^2}\right)\right). \tag{2.34}$$

The resulting biaxial force-stretch relation is obtained from (2.31). We have

$$\bar{P}_\lambda = \frac{nkT}{L_\lambda^0}\left(\lambda - \frac{1}{\lambda^3\mu^2}\right), \qquad \bar{P}_\mu = \frac{nkT}{L_\mu^0}\left(\mu - \frac{1}{\lambda^2\mu^3}\right). \tag{2.35}$$

The normal stresses $t_{\lambda\lambda}$ and $t_{\mu\mu}$ in the surfaces perpendicular to the λ- and μ-directions are given by

$$t_{\lambda\lambda} = \frac{\bar{P}_\lambda}{L_\mu L_\nu} = \lambda\frac{\bar{P}_\lambda}{L_\mu^0 L_\nu^0} = \frac{nkT}{V}\left(\lambda^2 - \frac{1}{\lambda^2\mu^2}\right) = \rho\frac{k}{m}T\left(\lambda^2 - \frac{1}{\lambda^2\mu^2}\right)$$

$$t_{\mu\mu} = \frac{\bar{P}_\mu}{L_\lambda L_\nu} = \mu\frac{\bar{P}_\mu}{L_\lambda^0 L_\nu^0} = \frac{nkT}{V}\left(\mu^2 - \frac{1}{\mu^2\lambda^2}\right) = \rho\frac{k}{m}T\left(\mu^2 - \frac{1}{\mu^2\lambda^2}\right), \tag{2.36}$$

where $V = L_\lambda L_\mu L_\nu$ is the volume of the membrane, ρ is the mass density of rubber and m is the molecular mass of a chain.
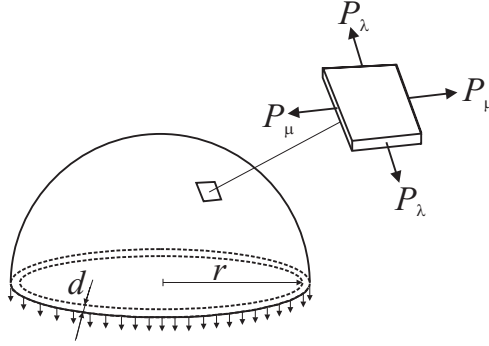
Fig. 2.6. Left: Force balance on the half-balloon. Right: Tangential forces on a square clipping of the membrane

2.8 Application to a Balloon

We consider a spherical balloon of radius r with the membrane thickness d. In the undistorted state these quantities shall have the values r_0 and d_0. We focus attention upon a small square cut from the balloon membrane, cf. Fig. 2.6, whose edges are perpendicular to the λ- and μ-directions. On those edges we have normal stresses which are much bigger than the pressure difference $[p]=p-p_0$ across the membrane so that we ignore that pressure difference for the purpose of calculating the stresses $t_{\lambda\lambda}$ and $t_{\mu\mu}$. In other words, we use the relations (2.36) to relate the stresses to the stretches λ and μ.

The stretches λ and μ are obviously given by the ratio r/r_0 of the circumferences of the balloon in the inflated and uninflated states so that, by (2.36), we have

$$t_{\lambda\lambda} = t_{\mu\mu} = \rho \frac{k}{m} T \left(\left(\frac{r}{r_0}\right)^2 - \left(\frac{r_0}{r}\right)^4 \right). \tag{2.37}$$

The pressure difference across the balloon surface is now most easily calculated from a balance of forces on the half balloon, see Fig. 2.6$_{left}$. The tangential force $t_{\lambda\lambda}2\pi rd$ on the equatorial circular ring must be equal to the force of the pressure jump $[p]$ on the cross section πr^2. Thus

$$[p]\pi r^2 = t_{\lambda\lambda}2\pi rd. \tag{2.38}$$

Because of incompressibility we have $dr^2 = d_0 r_0^2$ and then we may use (2.37) to calculate

$$[p] = 2 \underbrace{\rho \frac{k}{m} T}_{s_+} \frac{d_0}{r_0} \left(\frac{r_0}{r} - \left(\frac{r_0}{r}\right)^7 \right). \tag{2.39}$$
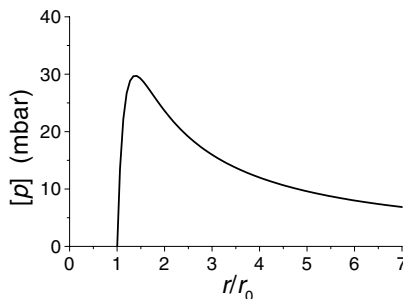
Fig. 2.7. Pressure-radius characteristic of a balloon according to the kinetic theory of rubber

We abbreviate the coefficient by s_+ as indicated in (2.39) and note that for a typical rubber this coefficient has a value of approximately 3 bar for $T = 300$ K. The ratio $\frac{d_0}{r_0}$ for a typical balloon may be given by $0.8 \cdot 10^{-2}$. For these values the pressure jump $[p]$ as a function of $\frac{r}{r_0}$ has been plotted in Fig. 2.7. We obtain a non-monotonic graph which has a zero value − of course − at $\frac{r}{r_0} = 1$ and a maximum at $\left([p], \frac{r}{r_0}\right) = (29.7 \text{ mbar}, 1.38)$. The maximal pressure jump lies at 29.7 mbar which is small indeed compared to 4.89 bar, the value of $t_{\lambda\lambda}$ for $\frac{r}{r_0} = 1.38$ according to (2.37). Therefore we were justified in neglecting the pressure difference in comparison with the normal stresses $t_{\lambda\lambda} = t_{\mu\mu}$.

2.9 Criticism of the Kinetic Theory of Rubber

The kinetic theory of rubber has given us a pressure-radius characteristic with only *one* ascending branch and this is bad! Indeed, we have measured that characteristic for a balloon, cf. Fig. 1.4, and found it to have *two* ascending branches.

Thus it turns out that the kinetic theory of rubber is deficient. It is true that the theory provides a deep insight into the mechanics and thermodynamics of rubber − and of other polymers − but it is not good enough for balloons, either quantitatively or qualitatively.

And yet, knowing that $s_+ \approx 3$ bar holds for a typical rubber, and $\rho \approx 10^3 \frac{\text{kg}}{\text{m}^3}$, we may use (2.39) to calculate the molecular mass m of a chain to be $m \approx 1.38 \cdot 10^{-23}$kg. This mass corresponds to the mass of 121 isoprene units so that we obtain a reasonable estimate for the length of the chains. It is true that a polymer molecule is usually much longer than 120 units. But then such a molecule is entangled with itself and others; it forms knots and joints and the present number, viz. 121, is the number of isoprene units between such joints or the length of a chain.

We shall now turn to the non-linear theory of elasticity to provide us with an improved pressure-radius characteristic.