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Statistical Thermodynamics of Rubber. III¹

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A basic postulate used by Treloar and by the author in recent theories of rubber elasticity is reexamined and its equivalent is derived from more fundamental considerations. The postulate dealt with the distribution of molecular lengths in a sample of strained rubber. Equations of state for rubber-like materials are derived by using the conventional methods of statistical mechanics. The results are found to be equivalent to those obtained by other means.

THE kinetic theories of rubber elasticity which have been developed within recent years^{1,2} have grown out of one fundamental idea, namely that the elastic forces involved are due to the thermal motions of the molecules rather than to deformations of valence bonds and angles. In deriving theoretical equations of state for rubber, the usual procedure has been to connect entropy concepts with the probability functions for molecular shapes, assuming that molecules can have different shapes as a result of rotation about some of the valence bonds. Although the various authors^{1,2} started with substantially the same idea their theories differed as to the way in which entropy changes were calculated. Recently, however, Treloar³ has shown that by eliminating certain approximations from Kuhn's treatment,^{2c} then Kuhn's theory gives precisely the same result as does the theory of the present author.¹

A basic postulate of the author's theory and of Kuhn's theory as amended by Treloar is that when a piece of rubber is deformed, the components of the lengths of the molecules will change in the same ratio as the corresponding dimensions of the rubber. To illustrate this specifically, let us consider a one-dimensional problem. If x is the component of the length of a molecule in the direction under consideration, then for a piece of unstrained rubber the probability of finding a molecule with a value of

x in the range x to $x+dx$ will be given by

$$p(x)dx = (\beta/\pi^{1/2}) \exp(-\beta^2 x^2) dx \quad (1)$$

where β is a parameter depending upon the nature of the molecular chains. According to the above-mentioned postulate, when the rubber is stretched by a factor α , then the distribution function becomes

$$p'(x)dx = (\beta/\pi^{1/2}\alpha) \exp(-\beta^2 x^2/\alpha^2) dx. \quad (2)$$

Although Eq. (2) is highly plausible and provides a convenient start for a theory of elasticity, it would be well to look into the reasons underlying it. One of the purposes of the present paper is to derive Eq. (2) from more fundamental considerations. This will be accomplished by showing that (2) is the most probable distribution compatible with the strained condition of the rubber, it being assumed that (1) represents the distribution for the unstrained material.

A rubber network presumably consists of molecules linked together at various places by means of vulcanization bridges. Starting at one end of a piece of bulk rubber one should be able to reach the other end by following a more or less random path of molecules through the network (Fig. 1). Going from one end to the other by a random path involves a large number of molecules and the path will include numerous retrogressions from as well as advancements toward the ultimate goal. It should be recognized that a few conceivable paths might involve a relatively small number of molecules if the paths happen to be fairly straight. Other paths on the other hand can involve an unduly large number of molecules. We shall here consider a typical random path involving, let us say, n molecules.

¹For the first two papers of this series see (a) F. T. Wall, *J. Chem. Phys.* **10**, 132 (1942); (b) F. T. Wall, *J. Chem. Phys.* **10**, 485 (1942).

²(a) K. H. Meyer, G. von Susich and E. Valko, *Kolloid Zeits.* **59**, 208 (1932). (b) E. Guth and H. Mark, *Monats. Chem.* **65**, 93 (1934). (c) W. Kuhn, *Kolloid Zeits.* **68**, 2 (1934); **76**, 258 (1936). (d) E. Guth and H. M. James, *Ind. Eng. Chem.* **33**, 624 (1941); **34**, 1365 (1942).

³L. R. G. Treloar, *Trans. Faraday Soc.* **34**, 36 (1943).

If l equals the over-all length of the rubber, then

$$l = x_1 + x_2 + x_3 + \cdots x_n \quad (3)$$

where the x 's denote the components of the lengths of the molecules in the direction considered. It should be noted that the x 's can have positive or negative values and that l is measured by their algebraic sum and not by the sum of their absolute values. Squaring (3) there is obtained

$$\begin{aligned} l^2 = & x_1^2 + x_2^2 + x_3^2 + \cdots x_n^2 \\ & + 2(x_1x_2 + x_2x_3 + \cdots x_{n-1}x_n) \\ & + 2(x_1x_3 + x_2x_4 + \cdots x_{n-2}x_n) + \cdots \end{aligned} \quad (4)$$

Since n is large we can simplify (4) by introducing averages, thus obtaining

$$\begin{aligned} l^2 = & n\langle x^2 \rangle_{Av} + 2(n-1)\langle x_i x_{i+1} \rangle_{Av} \\ & + 2(n-2)\langle x_i x_{i+2} \rangle_{Av} + \cdots \end{aligned} \quad (5)$$

But because n is large and the path is random all of the averages appearing in (5) except $\langle x^2 \rangle_{Av}$ will approach zero since the x 's are divided almost equally between positive and negative values. Making use of this fact it is seen that

$$l^2 = n\langle x^2 \rangle_{Av}. \quad (6)$$

Equation (6) is not exact but is an excellent approximation for the purpose in mind. As a matter of fact, Eq. (6) will give exactly the mean square length of a large number of chains of n members, the average square lengths of the members being $\langle x^2 \rangle_{Av}$, providing the chains are not subject to any boundary constraints. Since for the problem at hand the chains must begin and end in certain planes and cannot have any portions outside the boundaries of the bulk rubber, some degree of randomness is lost thereby rendering (6) an approximation.

From Eq. (6) we conclude that the over-all length of a piece of rubber is proportional to the root mean square length of the molecules, referring of course to components in the specified direction. Accordingly if a piece of rubber is stretched from a length l to αl , then the root mean square length of the molecules must be increased by a factor α . This statement is considerably more general than saying that *each*

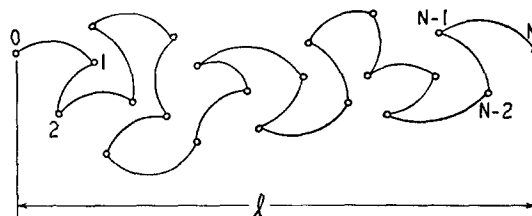


FIG. 1. Random molecular path involving n molecules passing through network of rubber of length l . Small circles denote vulcanization bridges each of which probably link together four "molecules." (To avoid confusion no side links are shown in the figure.)

molecule has its length component changed by a factor α , for there are obviously many other ways of changing the root mean square length by a given factor.

There will now be derived the most probable distribution of molecular lengths consistent with a given macroscopic length for the piece of rubber. For convenience the one-dimensional problem will be considered first and the extension to three dimensions made later.

Let us divide the x space of the molecules into a number of cells of size Δx_i , each cell being located in the neighborhood of x_i . Let the probability that a molecule have an x value in the range of Δx_i be p_i . Then from (1) we have

$$p_i = (\beta/\pi^{\frac{1}{2}}) \exp(-\beta^2 x_i^2) \Delta x_i. \quad (7)$$

Let N_i equal the number of molecules with x values in the range Δx_i and N equal the total number of molecules. Then the number of permutations associated with the statistical state specified by N_0, N_1, N_2, \dots , etc. will be given by

$$W = \frac{N!}{N_0! N_1! N_2! \cdots} p_0^{N_0} p_1^{N_1} p_2^{N_2} \cdots \quad (8)$$

Two conditions of constraint can be applied to Eq. (8), namely:

$$N = \sum_i N_i \quad (9)$$

and

$$l^2 = C \sum_i N_i x_i^2. \quad (10)$$

Condition (9) simply requires the correct sum for the total number of molecules and condition (10), in which C is a constant, is equivalent to (6).

The statistical problem can now be carried

out in the usual way.⁴ To find the most probable distribution we make use of Stirling's approximation and note that

$$\begin{aligned}\delta \ln W &= \sum_i (-\ln N_i + \ln p_i) \delta N_i = 0, \\ \delta N &= \sum_i \delta N_i = 0\end{aligned}\quad (11)$$

and

$$\delta l^2 = C \sum_i x_i^2 \delta N_i = 0.$$

Introducing Lagrangian multipliers in the conventional manner and solving for N_i there is obtained

$$N_i = p_i \exp (\lambda + \mu x_i^2) \quad (12)$$

where the multiplier μ has absorbed the constant C . Putting in the value for p_i it is seen that

$$N_i = (\beta/\pi^{\frac{1}{2}}) \exp \{ \lambda - (\beta^2 - \mu) x_i^2 \} \Delta x_i \quad (13)$$

or in a differential form

$$dN = (\beta/\pi^{\frac{1}{2}}) \exp \{ \lambda - (\beta^2 - \mu) x^2 \} dx. \quad (14)$$

From (14) it follows that

$$N = \frac{\beta e^\lambda}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} \exp \{ -(\beta^2 - \mu) x^2 \} dx = \frac{\beta e^\lambda}{(\beta^2 - \mu)^{\frac{1}{2}}}. \quad (15)$$

Eliminating e^λ from (14) and (15) we see that

$$dN = \frac{N(\beta^2 - \mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \exp \{ -(\beta^2 - \mu) x^2 \} dx. \quad (16)$$

But from (10) and (16) it follows that

$$\begin{aligned}l^2 &= \frac{CN(\beta^2 - \mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \\ &\times \int_{-\infty}^{\infty} x^2 \exp \{ -(\beta^2 - \mu) x^2 \} dx = \frac{CN}{2(\beta^2 - \mu)}. \quad (17)\end{aligned}$$

It is clear from (16) that the piece of rubber must be in its natural unstrained state when $\mu = 0$, under which condition $l = l_0$. Hence from (17),

$$l_0^2 = CN/2\beta^2 \quad (18)$$

from which it follows that

$$\alpha^2 = (l/l_0)^2 = \beta^2/(\beta^2 - \mu). \quad (19)$$

⁴ See for example Tolman, *Statistical Mechanics* (Oxford University Press, 1938), p. 79, or Mayer and Mayer, *Statistical Mechanics* (John Wiley, 1940), p. 113.

Combining (19) with (16) there is obtained the equivalent of (2), namely:

$$dN = (N\beta/\pi^{\frac{1}{2}}\alpha) \exp (-\beta^2 x^2/\alpha^2) dx. \quad (20)$$

The foregoing treatment shows that (2) or (20) must be the most probable distribution compatible with an increase in root mean square length by a factor α . Although (2) was a very plausible postulate, the present treatment strengthens it by showing what ideas are implicit in it. For one thing it is not necessary to suppose that each molecule is extended in the same way as the mass of rubber. Thus the postulatory basis of the theory of rubber elasticity has been pushed back at least one step toward more fundamental concepts such as are illustrated in Fig. 1 and expressed by Eqs. (3) to (6).

It is important that one deal with the root mean square length rather than with the average of the absolute values of the molecular lengths. If condition (10) were replaced by

$$l = C \sum_i |x_i| N_i \quad (21)$$

then Eq. (20) would not be obtained. Instead one would arrive at a less neat distribution function which would ultimately lead to an unwieldy equation of state for rubber. Conditions of type (21) would also make the three-dimensional problem intractable with respect to change of coordinates because the total length of a molecule cannot be taken as the sum of the three components whereas the square of the total length is equal to the sum of the squares of the components. It should not be supposed, however, that (10) is more correct than (21) simply because it is easier to handle, for the theoretical considerations outlined earlier show that (10) is to be expected.

THE EQUATION OF STATE FOR RUBBER

From Eq. (20) it is possible to deduce an equation of state for rubber by using the methods of the author¹ or of Kuhn as amended by Treloar.³ However another derivation will now be given which parallels the conventional statistical methods. Making use of Boltzmann's relation, the entropy will be given by the expression

$$S = k \ln W_{\max}. \quad (22)$$

Putting in the expression for W and making use of Stirling's approximation, we obtain from (22)

$$S = Nk \ln N - k \sum_i N_i \ln (N_i/p_i). \quad (23)$$

Taking cognizance of (9), (10), and (12) it is found that

$$S = Nk \ln N - Nk\lambda - k\mu l^2/C. \quad (24)$$

Eliminating λ , C , and μ from (24) by use of Eqs. (15), (18), and (19), it is found that

$$S = Nk \ln \alpha - Nk(\alpha^2 - 1)/2. \quad (25)$$

Equation (25) gives that portion of the entropy which can be associated with deformation effects and is not to be regarded as the total entropy of the rubber. But just as it is possible to deduce a correct equation of state for an ideal gas by considering volume effects alone, so too an equation of state for rubber can be derived by investigating the relationship between entropy and length. Differentiating (25) with respect to length there is obtained

$$dS = -(Nk/l_0)(\alpha - 1/\alpha)dl. \quad (26)$$

From the fundamental thermodynamic relation

$$f = -T(\partial S/\partial l)_E \quad (27)$$

where f is the force applied, it follows that

$$f = (NkT/l_0)(\alpha - 1/\alpha). \quad (28)$$

Equation (28) is not complete, of course, because only one dimension was considered. However it is precisely the same equation as was derived by the author's earlier method applied to the one-dimensional problem.^{1a} Hence the equivalence of the two methods of attack has been demonstrated.

The extension to three dimensions can be carried out immediately. The entropy of the deformed rubber will be given by the sum of expressions of type (25) using α_x , α_y and α_z as the relative stretchings in the x , y and z directions. Thus we see that

$$S = Nk \ln (\alpha_x \alpha_y \alpha_z) - Nk(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)/2. \quad (29)$$

Assuming that rubber is incompressible, it follows that $\alpha_x \alpha_y \alpha_z = 1$ which introduces some simplification in (29). If a force is applied in one direction only (say the x direction), then $\alpha_y = \alpha_z = 1/(\alpha_x)^{1/2}$ from which it is seen that

$$S = -Nk(\alpha^2 + 2/\alpha - 3)/2 \quad (30)$$

where the subscript x has been dropped from α . From (30) the stretching force is readily calculated to be

$$f = (NkT/l_0)(\alpha - 1/\alpha^2) \quad (31)$$

which result is the same as has been derived earlier.^{1b,3} The function (31) is also similar to an equation derived by Guth and James.^{2d}

By using the methods indicated above it is also possible to show that rubber should obey Hooke's law with respect to shear. A simple shear of amount γ is obtained⁵ by taking $\gamma = \alpha - 1/\alpha$ where $\alpha = \alpha_x = 1/\alpha_y$ and $\alpha_z = 1$. From (29) the entropy of shear is calculated to be

$$S = -Nk\gamma^2/2. \quad (32)$$

Hence the shearing moment (L) will be given by

$$L = -T(\partial S/\partial \gamma)_E = NkT\gamma. \quad (33)$$

From (33) it is seen that L is proportional to γ ; in other words, Hooke's law is obeyed.

Equations (31) and (33) can be regarded as ideal equations of state for rubber-like substances. This view is justified because of the high degree of correspondence between the derivation and the limitations of Eqs. (31) and (33) and those of the ideal gas law. Actual samples of rubber will not obey the above-mentioned equations exactly for two principal reasons. First the distribution functions (1) and (2) are not valid for large values of x and second the van der Waals interactions have been neglected in the calculations. The errors introduced thereby will increase with increasing deformation. Even if exact distribution functions were used in place of (1) and (2), the equations of state so derived would not be correct for large deformations because of intermolecular attractions and repulsions.

⁵ A. E. H. Love, *Mathematical Theory of Elasticity*, (Cambridge University Press), second edition, p. 34.