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According to the kinetic theory of elasticity of rubber-like materials, originally propounded by Meyer, v. Susich and Valko,[1] and subsequently developed by Guth and Mark [2] and by Kuhn,[3] the retractive force in stretched rubber is due to the thermal motions of the carbon atoms of the molecular chain. On the assumption of free (or effectively free) rotations about each of the C—C bonds, it is shown that in the absence of external restraints the molecule will take up a randomly-kinked form in which its average length (measured by the distance between its ends) is only a small fraction of the length of the fully extended chain. The statistical treatment of the problem [2, 3] leads to a formula defining the probability of a given length in terms of the molecular parameters.

An extension of the treatment to a three-dimensional network of molecules, in order to account for the properties of a rubber in bulk, has been attempted by various authors, notably by Kuhn [3] and by Wall. [4, 5] Their results, however, are not in agreement. In the present paper the methods of Kuhn and of Wall are critically examined, and the source of the discrepancies between their results is demonstrated.

Wall's Treatment of Elongation.

In this discussion the historical order will be reversed, and Wall's work will be considered before that of Kuhn which appeared 8 years earlier.

Working on the basis of Kuhn's statistics of the individual molecule Wall set out to calculate the entropy of a network of N_0 equal molecules making up a cylinder of length l_0 in the undeformed and l in the deformed state. For this structure the distribution of lengths (*i.e.* distances between

[1] Meyer, v. Susich and Valko, *Koll. Z.*, 1932, **59**, 208.

[2] Guth and Mark, *Monats. Chem.*, 1934, **65**, 93.

[3] Kuhn, *Koll. Z.*, 1934, **68**, 2 ; 1936, **76**, 258.

[4] Wall, *J. Chem. Physics*, 1942, **10**, 132.

[5] Wall, *ibid.*, 1942, **10**, 485.

junction points) of the molecules in the undeformed state was assumed to be that given by Kuhn's formula, which may be written

$$p(x, y, z)\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z = \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2(x^2+y^2+z^2)}\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \quad . \quad (1)$$

In this equation x, y and z represent the components of length of a given molecule along each of the three co-ordinate axes, and

$$\frac{1}{\beta^2} = \frac{2}{3} l_c^2 Z \frac{1 + \cos\theta}{1 - \cos\theta} \quad . \quad . \quad . \quad . \quad (1a)$$

l_c being the C—C bond distance, Z the number of links in the molecular chain, and θ the supplement of the valence angle. To describe the deformation Wall assumed that the volume remains unchanged, and that the components of length of each molecule change in the same ratio as the corresponding dimensions of the bulk rubber. Thus, writing α for l/l_0, x, y and z are changed to αx, $\alpha^{-\frac{1}{2}} y$ and $\alpha^{-\frac{1}{2}} z$ respectively,[*] and the corresponding distribution function is

$$p'(x, y, z)\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z = \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/\alpha^2+\alpha(y^2+z^2)]}\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \quad . \quad (2)$$

The problem is to determine the probability P that the assembly of N_0 molecules should be found in the state represented by equation (2), when the probability that a given molecule has components of length x, y and z is given by equation (1). The result found by Wall is

$$\ln\frac{P}{P_0} = -\frac{N_0}{2}\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \quad . \quad . \quad . \quad . \quad (3)$$

where P_0 is the probability of the most probable distribution. The entropy change due to the extension is therefore

$$S - S_0 = k \ln P/P_0 = -\tfrac{1}{2} N_0 k\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \quad . \quad . \quad (4)$$

The tension F is then obtained by applying the thermodynamic relation

$$F = \left(\frac{\partial W}{\partial l}\right)_T = -T\left(\frac{\partial S}{\partial l}\right)_T$$

giving, for a cylinder of original cross-sectional area 1 cm.^{2},

$$F = NkT\left(\alpha - \frac{1}{\alpha^2}\right) = \rho\frac{RT}{M}\left(\alpha - \frac{1}{\alpha^2}\right) \quad . \quad . \quad (5)$$

where N is the number of molecules per c.c., M the molecular weight and ρ the density.

Equation (5) applies for a uni-directional compression as well as for an elongation.

2. Wall's Treatment of Shear.

A simple shear may be defined by a change of the dimensions of the specimen from x, y and z to αx, y/α and z.[†] As before Wall assumed that the molecular components of length change in the same ratio as the external dimensions. The function representing the distribution of molecular lengths in the state of shear is therefore

$$p'(x, y, z)\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z = \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/\alpha^2+\alpha^2y^2+z^2]}\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \quad . \quad (6)$$

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[*] In his earlier paper[4] Wall took account only of changes in the x components of length. His later treatment,[5] which is obviously the more correct, is here considered.

[†] Love, *Mathematical Theory of Elasticity*, Cambridge University Press, 2nd Ed. p. 34.

The result was obtained in terms of the work required to produce a shear deformation $\sigma\left(= \alpha - \frac{1}{\alpha}\right)$, namely

$$W = \tfrac{1}{2}NkT\sigma^2 = \tfrac{1}{2}G\sigma^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from which it is seen that the modulus of rigidity G appears as a constant. That is to say, the network obeys Hooke's law under shear, though not under elongation.

3. Kuhn's Treatment of Elongation.

Kuhn made the same fundamental assumptions as Wall, but worked from a consideration of the entropy of the single molecule, integrating over the whole assembly of molecules in order to obtain the total entropy. From equation (1) the entropy s of a single molecule is given by Kuhn as

$$s = k \ln p = c_1 - k\beta^2(x^2 + y^2 + z^2) = c_1 - k\beta^2 r_1^2 \quad . \quad . \quad (8)$$

where r_1 is the distance between its ends. The contribution to the total entropy per c.c. due to molecules having length components between x and $x + \mathrm{d}x$, y and $y + \mathrm{d}y$, z and $z + \mathrm{d}z$ is obtained by multiplying this entropy s by the appropriate number of molecules, *i.e.*

$$s \,.\, Np(x \,.\, y \,.\, z)\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \,.$$

N being the number of molecules per c.c. Integration gives the total entropy S_1 corresponding to the unstretched state,

$$S_1 = \iiint_{-\infty}^{+\infty} N[c_1 - k\beta^2(x^2 + y^2 + z^2)]\frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2(x^2+y^2+z^2)}\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \quad . \quad (9)$$

For the deformed state corresponding to an extension in the x direction of amount γ $(= l/l_0 - 1)$ the entropy S'_1 is represented by the integral

$$S'_1 = \iiint_{-\infty}^{+\infty} N[c_1 - k\beta^2(x^2+y^2+z^2)]\frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2[x^2/(1+\gamma)^2+(y^2+z^2)(1+\gamma)]}\, \mathrm{d}x \,.\, \mathrm{d}y \,.\, \mathrm{d}z \quad (10)$$

in which the exponential term represents the distribution of molecular lengths after deformation. Integration of expressions (9) and (10) leads to the *approximate* relation

$$S'_1 - S_1 = -\frac{3}{2}Nk\gamma^2 \quad . \quad . \quad . \quad . \quad (11)$$

Entropy due to r_2 and r_3 Values.—The entropy thus determined, referred to by Kuhn as the partial entropy due to the r_1 values, was not considered to represent the whole of the entropy change on extension. He argued that besides having a "length" r_1, the molecule may be considered to have a "breadth" r_2 and a "thickness" r_3, and that it is necessary to take into account also the partial entropies associated with the r_2 and r_3 values. If Z is the number of links in the chain, r_2 is defined as the distance of the middle link from the line joining the ends, and r_3 as the distance of links numbered $Z/4$ and $3Z/4$ (counting from one end of the chain) from the plane containing r_1 and r_2. Kuhn's method of calculating the entropy due to the r_2 and r_3 values will not be considered here. The result is that an additional entropy of amount $-Nk\gamma^2$ is introduced for each of these values, so that the total entropy change on extension becomes

$$S' - S_0 = -\frac{3}{2}Nk\gamma^2 - 2Nk\gamma^2 = -\frac{7}{2}Nk\gamma^2 \quad . \quad . \quad . \quad (12)$$

This leads directly to the stress-strain relation

$$F = 7NkT\gamma = 7NkT(\alpha - 1) \quad . \quad . \quad . \quad (13)$$

This result does not agree with that of Wall (equation (5)), the one relation being linear and the other non-linear. The reasons for this discrepancy will now be considered.

4. Criticism of Kuhn's Treatment.

The r_2 and r_3 Values.—The probability function (1) is derived by considering the number of possible configurations of the molecule when one end is fixed at the origin of co-ordinates and the other is contained within a small volume element $dx \, . \, dy \, . \, dz$. On Kuhn's basis the entropy is reduced on extension because the number of possible configurations is reduced. In stating the probability in terms of r_1 he includes all possible configurations, and therefore all possible values of r_2 and r_3. The r_2 and r_3 values cannot be considered to have an existence independently of r_1 and to attribute a separate entropy to them is incorrect.

If the r_2 and r_3 values are omitted, equation (13) becomes

$$F = 3NkT\gamma \quad . \quad . \quad . \quad . \quad (14)$$

Wall's equation (5) gives for the modulus at zero extension

$$\left(\frac{dF}{d\gamma}\right)_{\gamma=0} = 3NkT \quad . \quad . \quad . \quad . \quad (15)$$

The modified formula (14) thus agrees with Wall's equation for sufficiently small elongations.

It will now be shown that the remaining difference between the results of Wall and of Kuhn is due to the introduction of an approximation by the latter author.

5. Amendment of Kuhn's Treatment.

(*a*) **Elongation.**—From Kuhn's equations (9) and 10) the entropy change on extension may be written

$$\frac{\pi^{\frac{3}{2}}}{Nk\beta^5}(S'_1 - S_1) = \iiint_{-\infty}^{+\infty} (x^2 + y^2 + z^2)\, e^{-\beta^2(x^2+y^2+z^2)}\, dx \, . \, dy \, . \, dz \, .$$
$$- \iiint_{-\infty}^{+\infty} (x^2 + y^2 + z^2)\, e^{-\beta^2[x^2/(1+\gamma)^2 + (y^2+z^2)(1+\gamma)]}\, dx \, . \, dy \, . \, dz \quad . \quad (16)$$

Insertion of the appropriate values of the definite integrals * gives

$$\frac{\pi^{\frac{3}{2}}}{Nk\beta^5}(S'_1 - S_1) = \frac{3}{2}\,\frac{\pi^{\frac{3}{2}}}{\beta^5} - \frac{\pi^{\frac{3}{2}}}{2\beta^5}\left[(1+\gamma)^2 + \frac{2}{1+\gamma}\right]$$

or $$\frac{1}{Nk}(S'_1 - S_1) = \frac{3}{2} - \left[\frac{(1+\gamma)^2}{2} + \frac{1}{1+\gamma}\right] = -\frac{1}{2}\left(\alpha^2 + \frac{2}{\alpha} - 3\right). \quad (17)$$

Equation (17) *is identical with Wall's eqn.* (4), and leads directly to the stress-strain relation (5), without any approximation. The approximation introduced by Kuhn (valid for small values of γ) was evidently to write

$$\frac{1}{1+\gamma} = 1 - \gamma + \gamma^2,$$

and thus to obtain

$$\frac{1}{Nk}(S'_1 - S_1) \simeq -\frac{3}{2}\gamma^2 \quad . \quad (cf.\ \text{equation (11)})$$

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* Jeans, *Dynamical Theory of Gases*, 3rd Ed. p. 435.

It is obvious that the formula of Kuhn is valid only for elongations of considerably less than 100 %. It is unfortunate that Kuhn did not emphasise the fact that an approximation was involved in the derivation of his apparently linear stress-strain relation.

(*b*) **Shear.**—Although Kuhn did not deal with the shear deformation, this problem also may be dealt with by his method. Writing the total entropy after shearing in the form

$$S'_1 = \iiint_{-\infty}^{+\infty} N[c_1 - k\beta^2(x^2 + y^2 + z^2)]\frac{\beta^3}{\pi^{\frac{3}{2}}}e^{-\beta^2[x^2/\alpha^2 + \alpha^2 y^2 + z^2]}\,dx\,.\,dy\,.\,dz \quad (18)$$

and following exactly the same process as in the case of elongation, we obtain

$$\frac{1}{Nk}(S'_1 - S_1) = -\frac{1}{2}\left(\alpha^2 + \frac{1}{\alpha^2} - 2\right) \quad . \quad . \quad . \quad (19)$$

which, on substitution of σ for $\alpha - \frac{1}{\alpha}$ leads to Wall's result (equation (7))

$$W = \tfrac{1}{2}NkT\sigma^2.$$

6. Some General Considerations.

The more accurate application of Kuhn's method thus leads to the same stress-strain relations as those derived by Wall. The two methods may be considered to be equivalent mathematically, since they differ only in the particular stage of the argument at which the conception of the entropy is introduced. Wall considered only the entropy to be associated with the whole assembly of molecules; Kuhn, on the other hand, considered that an entropy could be associated with the individual molecule. Wall's treatment must be considered the more satisfactory because it avoids the difficulties encountered in attempting to assign a physical meaning to the entropy of a single molecule.

An equation of similar form to (5) has been derived independently by Guth and James,[6] who state that it represents the experimental data for both elongation and compression of rubber to a close approximation. In using the equations of the kinetic theory, however, it is important to keep in mind the assumptions which form their basis. In Kuhn's statistical treatment of the paraffin molecule, from which all the later developments have proceeded, it is assumed that the distance r is small compared with the outstretched length of the chain. The formulæ derived from the network theory would therefore not be expected to apply to a state of deformation in which any important fraction of the molecules were nearly fully extended. They cannot therefore be expected to account accurately for the whole of the stress-strain curve of rubber.

It is interesting to note that equations (5) and (7) contain, implicitly, M, the " molecular weight " between junction points, but do not specifically contain Z, the number of links, or θ, the supplement of the valence angle (which are included in the parameter β (equation (1*a*)). The equations would therefore not be affected if the freedom of rotation about bonds were imperfect, since, as Kuhn has shown,[3] a chain of Z links possessing hindered rotation is equivalent to a chain containing a smaller number Z/s of freely rotating links (where s is a small number), provided, of course, there are still enough effective links to justify the application of statistical methods. The same argument shows that the elastic properties of the network will not be affected by the presence of a proportion of non-rotating bonds, such as the C = C bond in rubber.

Summary.

The treatment of the elasticity of a molecular network by the method of Wall is discussed and compared with the earlier treatment of Kuhn. It is shown that a more accurate application of Kuhn's method leads to formulæ for elongation and shear in agreement with those of Wall.

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