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THE ELASTICITY OF A NETWORK OF LONG-CHAIN MOLECULES. III.

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THE ELASTICITY OF A NETWORK OF LONG-CHAIN MOLECULES.—III.

By L. R. G. Treloar.

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In the second paper of this series [1] the statistical theory of Wall was developed to take account of the most general type of homogeneous deformation of a rubber, and a simple equation was derived giving the free energy of deformation in terms of the three principal strains. It was pointed out that this equation would not be expected to apply to a real rubber when any of the principal strains was very large, owing to the fact that the formula for the distribution of molecular lengths, on which it is based, is no longer applicable if an important fraction of the molecules are extended to a point approaching their maximum outstretched length. Later experimental work [2] confirmed that the theoretical equations were in reasonably good agreement with experimental data at small or moderate strains, but not at very large strains.

In order to extend the theory to cover the whole range of possible strains which can be applied to rubber, it is necessary to make use of the more accurate distribution functions which have since been worked out.[3] It is the purpose of the present paper to show how this may be achieved, and to present theoretical curves which represent the stress-strain properties of an *ideal* rubber over the whole range of deformations. It is not possible to derive a general algebraical equation covering any type of strain, as was done for the simpler case of small or moderate strains, but it appears to be necessary to work out each type of strain in detail. The types of strain considered are the simple elongation and 2-dimensional extension (or compression).

Two possible lines of attack on the problem of incorporating the effect of the "non-Gaussian" probability distributions of molecular length (or, briefly, "non-Gaussian chains") were considered. The first was on the basis of Wall's [4] theory, and the second on the basis of Flory and Rehner's [5] later theory. The former was not proceeded with, on account of certain difficulties to which no very satisfactory solution was found. It will be sufficient to indicate here that these difficulties were mainly associated with the problem of how to formulate the distribution of chain lengths corresponding to the deformed state. It can no longer be assumed that the chain components change on deformation in the same ratio as the bulk rubber, as was done in the case of Gaussian chains.

Flory and Rehner's model, on the other hand, involves the introduction of no new principle, when applied to non-Gaussian chains, and for this reason was chosen as a basis for the present work.

Before the non-Gaussian case is considered, the original analysis of Flory and Rehner for Gaussian chains will be extended and generalised. It will be shown that the model leads to the same general equation for the free energy of deformation as had previously been obtained on the basis of Wall's theory.

[1] Treloar, *Trans. Faraday Soc.*, 1943, **39**, 241.

[2] Treloar, *ibid.*, 1944, **40**, 59.

[3] Treloar, *ibid.*, *in press.*

[4] Wall, *J. Chem. Physics*, 1942, **10**, 485.

[5] Flory and Rehner, *ibid.*, 1943, **11**, 512.

The Flory-Rehner Model for Gaussian Chains.

The Flory-Rehner method involves the calculation of the entropy of formation of a network of molecules of equal contour or chain length. Four chains are assumed to radiate from each point of cross-linkage, and it is assumed that the restraints imposed on any given junction point by the remainder of the network will not be affected by fixing the four nearest-neighbour junction points at their average positions, *i.e.*, at the corners of a regular tetrahedron, Fig. 1. It is further assumed that the mechanical properties of the network can be computed from those of this "average" cell of four chains, and that the dimensions of this cell are changed by the deformation in the same ratio as the dimensions of the bulk rubber.

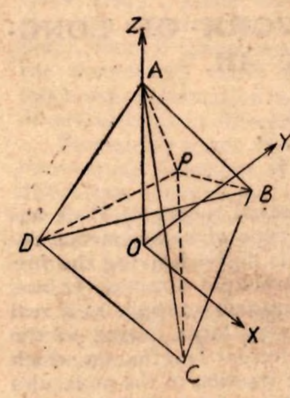

FIG. 1.—The Flory-Rehner tetrahedral model.

The significant step in the calculation of the entropy of formation, in connection with the present problem, is that which concerns the junction of the four chains converging from the fixed corners of the tetrahedron. The probability that these four chains should meet in a given small volume, $\Delta\tau = dx\,dy\,dz$ may be written *

$$\omega(x, y, z)(dx\,dy\,dz)^4 = \prod_{i=1}^{4} W(x_i\,y_i\,z_i)dx_i\,dy_i\,dz_i \quad . \quad . \quad (1)$$

where $x_1 y_1 z_1$ are the co-ordinates of the same volume element $\Delta\tau$ referred, respectively, to the four corners A, B, C, D of the tetrahedron. For Gaussian chains we have

$$W(x, y, z) = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2+y^2+z^2)} dx\,dy\,dz \quad . \quad . \quad . \quad (2)$$

and in this special case, eqn. (1) reduces to the form

$$\omega(x, y, z) = \frac{\beta^{12}}{\pi^6} \exp\left[-\beta^2 \sum_{i=1}^{4} r_i^2\right] \quad . \quad . \quad . \quad (3)$$

The quantity Σr_i^2 has to be evaluated at all points of space. Integration then gives the probability of the four chains meeting anywhere in space and consequently the entropy corresponding to the formation process. This entropy is calculated both for the stretched and unstretched states. The difference is the required entropy of deformation.

Flory and Rehner consider the application of a simple elongation α in two special directions with respect to the cell, namely along OY and OZ (Fig. 1) and show that the resultant entropy is the same in each of these cases. They point out that, strictly, an average should be taken over all possible directions of the elongation, but make the reasonable assumption that the result obtained for the two special directions may be taken to represent this average.

In the following treatment, Flory and Rehner's analysis will be extended in two ways, namely :

(1) By the application of the most general type of homogeneous deformation, and

(2) By establishing that the entropy of deformation is the same for all possible directions of the principal strains with respect to the tetrahedral cell.

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* Flory and Rehner's notation has been slightly modified.

Suppose the positions of the corners A, B, C, D to be defined originally with respect to the co-ordinate system OX, OY, OZ, the origin being at the centre of the tetrahedron, OX parallel to DC and OZ perpendicular to the plane BCD. The average length of each chain in the undeformed state is OA = λ.

The general homogeneous deformation may be described by stretches in the ratio α_1, α_2 and α_3 in three mutually perpendicular directions, OX′, OY′, OZ′—the principal axes of strain. It will be assumed that these axes are related to OX, OY, OZ by the direction cosines (l_1, m_1, n_1), (l_2, m_2, n_2), (l_3, m_3, n_3) respectively. If a point P has co-ordinates (x, y, z) referred to OX, OY, OZ, its co-ordinates (x', y', z') referred to OX′, OY′, OZ′ are given by the relations

$$\begin{aligned} x' &= l_1x + l_2y + l_3z \\ y' &= m_1x + m_2y + m_3z \\ z' &= n_1x + n_2y + n_3z. \end{aligned}$$

The co-ordinates of the points A, B, C, D in the strained state, referred to OX′, OY′, OZ′ may thus be shown to be the following :

For A :

$$x_1/\lambda = \alpha_1 l_3,\ y_1/\lambda = \alpha_2 m_3,\ z_1/\lambda = \alpha_3 n_3.$$

For B :

$$\begin{aligned} x_2/\lambda &= (2\sqrt{2}l_2/3 - l_3/3)\alpha_1 \\ y_2/\lambda &= (2\sqrt{2}m_2/3 - m_3/3)\alpha_2 \\ z_2/\lambda &= (2\sqrt{2}n_2/3 - n_3/3)\alpha_3 \end{aligned}$$

For C :

$$\begin{aligned} x_3/\lambda &= (\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/3 - l_3/3)\alpha_1 \\ y_3/\lambda &= (\sqrt{2}m_1/\sqrt{3} - \sqrt{2}m_2/3 - m_3/3)\alpha_2 \\ z_3/\lambda &= (\sqrt{2}n_1/\sqrt{3} - \sqrt{2}n_2/3 - n_3/3)\alpha_3 \end{aligned}$$

For D :

$$x_4/\lambda = (-\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/3 - l_3/3)\alpha_1, \quad \text{etc.}$$

We have now to take any point P, having co-ordinates (x', y', z') and find $\Sigma r_1^2 = \mathrm{PA}^2 + \mathrm{PB}^2 + \mathrm{PC}^2 + \mathrm{PD}^2$. (*Cf.* eqn. (3).)

$$\begin{aligned} \mathrm{PA}^2/\lambda^2 &= (x'/\lambda - l_3\alpha_1)^2 + (y'/\lambda - m_3\alpha_2)^2 + (z'/\lambda - n_3\alpha_3)^2 \\ \mathrm{PB}^2/\lambda^2 &= [x'/\lambda - (2\sqrt{2}l_2/3 - l_3/3)\alpha_1]^2 + \ldots \\ \mathrm{PC}^2/\lambda^2 &= [x'/\lambda - (\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/\sqrt{3} - l_3/3)\alpha_1]^2 + \ldots \\ \mathrm{PD}^2/\lambda^2 &= [x'/\lambda + (\sqrt{2}l_1/\sqrt{3} + \sqrt{2}l_2/\sqrt{3} - l_3/3)\alpha_1]^2 + \ldots \end{aligned}$$

so that

$$\begin{aligned} \frac{1}{\lambda^2}\Sigma r_1^2 = {} & 4x'^2/\lambda^2 + 2\alpha_1 x'[- l_3 - (2\sqrt{2}l_2/3 - l_3/3) \\ & - (\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/3 - l_3/3) + (\sqrt{2}l_1/\sqrt{3} + \sqrt{2}l_2/3 - l_3/3)] \\ & + \alpha_1^2[l_3^2 + (2\sqrt{2}l_2/3 - l_3/3)^2 + (\sqrt{2}l_1/\sqrt{3} - \sqrt{2}l_2/3 - l_3/3)^2 \\ & + (\sqrt{2}l_1/\sqrt{3} + \sqrt{2}l_2/3 + l_3/3)^2] \end{aligned}$$

+ similar expressions in y' and z', leading to

$$\begin{aligned} \Sigma r_1^2 &= 4x'^2 + \tfrac{4}{3}\alpha_1^2\lambda^2(l_1^2 + l_2^2 + l_3^2) + \ldots \\ &= 4[(x'^2 + y'^2 + z'^2) + \lambda^2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)/3] \end{aligned}$$

since

$$l_1^2 + l_2^2 + l_3^2 = 1, \text{ etc.}$$

Thus

$$\Sigma r_1^2 = 4[s^2 + \lambda^2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)/3] \quad . \quad . \quad . \quad (4)$$

where s is the distance of P from the origin.

The expression (4) replaces eqn. (17) in Flory and Rehner's paper.[5] If this is inserted in eqn. (3) and the integration is carried out in the manner described in their paper, taking $\lambda^2 = 3/2\beta^2$ the expression for the entropy of deformation becomes

$$\Delta S = -\tfrac{1}{2}Nk(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) \quad . \quad . \quad . \quad (5)$$

in which N is the number of molecular chains. The entropy of deformation is thus proved to be independent of the direction cosines of the principal axes of strain. Flory's expression (19′) is a special case of the more general form (5), obtained by putting $\alpha_1 = \alpha$, $\alpha_2 = \alpha_3 = \alpha^{-\frac{1}{2}}$. The free energy of deformation, W, is obtained directly from (5), *i.e.*,

$$W = \tfrac{1}{2}NkT(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) \quad . \quad . \quad . \quad (6)$$

This formula is identical with that derived in II on the basis of Wall's theory. In the previous derivation, however, it was necessary to assume that the volume remained constant under deformation. This assumption is not involved in the present argument.

Having now established the equivalence of the methods of Flory and Rehner and of Wall with regard to Gaussian chains, and having shown that the geometrical relation of the elementary cell to the axes of strain makes no difference to the results, we may proceed with more confidence to the application of Flory and Rehner's model to the more complex case of non-Gaussian chains.

The Flory-Rehner Model for Non-Gaussian Chains.

The only difference involved in the application to non-Gaussian chains is that in place of the distribution represented by equation (2), we have

$$W(x, y, z) = \frac{1}{4\pi r^2}P(r),$$

where $P(r)$ is the distribution function for the random chain, evaluated in the preceding paper.[3] In the non-Gaussian region eqn. (1) no longer reduces to (3), and consequently $\omega(x, y, z)$ is not simply a function of Σr_i^2.

In principle, it is necessary to find $\omega(x, y, z)$, which is the product of the separate probabilities that each of the four chains should terminate in the volume element at P, at all points in space, and to integrate over the whole volume. The result would give the required probability of the four chains meeting anywhere in space. If it was desired to obtain a complete stress-strain relation, it would be necessary to carry out this calculation at a number of different strains.

Such a procedure might well appear impossibly laborious, but in practice it is possible to introduce approximations which greatly reduce the amount of work involved. The principle adopted was to locate by trial the point at which the probability density $\omega(x, y, z)$ was a maximum, and then to explore the variation of ω along the directions of the three co-ordinate axes, taking this point as origin. In the case of Gaussian chains, as will be seen from eqn. (4), the point of maximum probability density is at the centre of the tetrahedron, and the variation of ω may be expressed in terms of the maximum probability density ω_0 and the distance s from the centre by the Gaussian formula

$$\omega = \omega_0 \, \mathrm{e}^{-4\beta^2 s^2} \quad . \quad . \quad . \quad . \quad (7)$$

which shows the variation of probability to be spherically symmetrical and independent of strain. For non-Gaussian chains, on the other hand, it is found, when the calculations are carried out, that the variation is no longer spherically symmetrical. The variation along any one direction, however, remains approximately Gaussian, even though the rate of fall is different along the three directions chosen. In this way there are obtained three equations of the type

$$\omega_x = \omega_0' \, \mathrm{e}^{-4\beta_1^2 x^2} \quad . \quad . \quad . \quad . \quad (8)$$

From (7) the total probability, in the Gaussian case, is proportional to

$$\Omega = \omega_0 \int 4\pi s^2 \, \mathrm{e}^{-4\beta^2 s^2} \mathrm{d}s = \omega_0 \cdot \frac{\pi^{3/2}}{8\beta^3} \quad . \quad . \quad . \quad (9)$$

The comparable expression for the non-Gaussian case was assumed to be

$$\Omega' = \omega_0' \frac{\pi^{3/2}}{8\beta_1\beta_2\beta_3} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

corresponding to an ellipsoidal distribution of probability density. The entropy change in deformation is thus dependent on two terms, *i.e.*,

$$\frac{\Delta S}{k} = \ln\frac{\omega_0'}{\omega_0} - \ln\frac{\beta^3}{\beta_1\beta_2\beta_3} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

of which the first represents the probability at the maximum, which may be called the "intensity factor," whilst the second, or "volume factor" represents the rate at which the probability falls away on moving outwards from the maximum.

The foregoing analysis of the spatial distribution of probability density, though admittedly only approximate, is quite adequate for the purpose. The reason is that the second term in (11) is found to be, in all cases, very small compared with the first. Thus for 25-link chains, the "volume factor" never accounted for more than 3 % of the total entropy change, whilst for 100-link chains its maximum contribution was always less than 1 % of the whole. The amount of work involved in calculating the spatial distribution, even in this approximate manner, is thus justified rather by the desire for theoretical completeness than on account of its practical significance.

Simple Elongation.

In the non-Gaussian case it is no longer true that the entropy change will be independent of the direction of the elongation with respect to the tetrahedron, and the choice of this direction has to be made arbitrarily.

TABLE I.—SIMPLE ELONGATION.

Calculated values of $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ for 4-chain cell. $n = 25$ and 100.

$n = 25$.		$n = 100$.	
α.	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$.	α.	$\frac{-\Delta S}{2k(\alpha^2 + 2/\alpha - 3)}$.
1·5	$1{\cdot}00_0$	2 0	$1\ 00_0$
2 0	$1{\cdot}02_0$	2·5	$1{\cdot}00_6$
2·5	$1{\cdot}04_6$	3·0	$1{\cdot}01_7$
3·0	$1{\cdot}07_4$	4·0	$1{\cdot}03_2$
3·5	$1{\cdot}11_4$	5·0	$1{\cdot}05_4$
4·0	$1{\cdot}16_7$	6·0	$1{\cdot}08_3$
4·5	$1{\cdot}25_2$	7·0	$1{\cdot}12_4$
4·75	$1{\cdot}31_0$	8·0	$1{\cdot}17_9$
5·0	$1{\cdot}38_2$	9·0	$1{\cdot}25_5$
5·25	$1{\cdot}48_0$	10·0	$1{\cdot}39_4$
5·5	1·63	11·0	1·63
5·75	1·88	11·5	1·89
5·85	2·03		

A few calculations were, however, made from which some idea of the effect of stretching in other directions may be obtained.

The stretching direction chosen was along OX (Fig. 1). The corners of the tetrahedral cell were assumed to move in such a way that their *x*-co-ordinates changed in the ratio α whilst their *y*- and *z*-co-ordinates changed in the ratio $\alpha^{-\frac{1}{2}}$. The entropy was calculated at a number of values of α. For the Gaussian region this entropy has the value $-2k(\alpha^2 + 2/\alpha - 3)$; it is convenient, therefore, to express the calculated entropy ΔS in the form of the ratio which it bears to the quantity $2k(\alpha^2 + 2/\alpha - 3)$. These ratios are given in Table I.

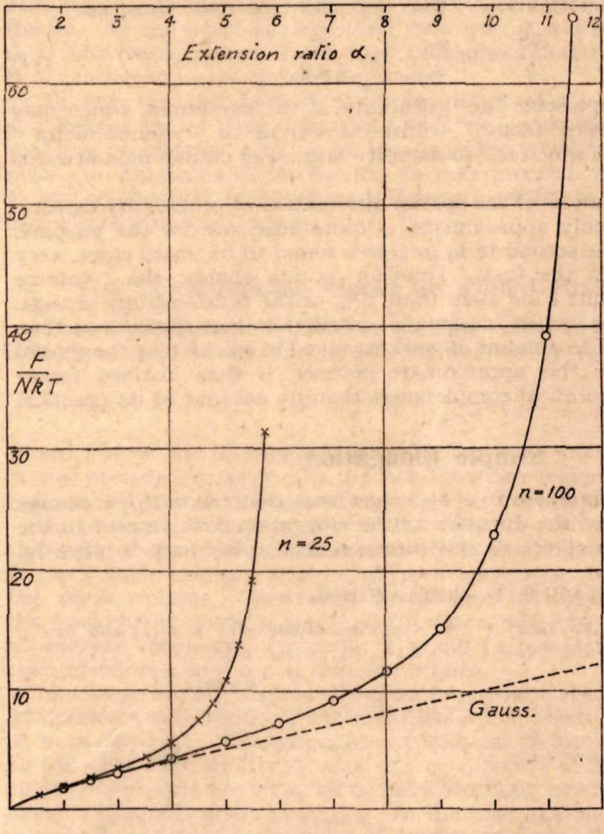

FIG. 2.

Simple elongation. The function F/NkT for a network of random chains of 25 and 100 links.

It is interesting to notice that the functions $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ for the two different chain lengths are of similar form and differ only in the range of α covered. Especially is this true when α is large, the value of the function for $n = 25$ at a given value of α being almost exactly the same as for $n = 100$ and twice that value of α. This property would be useful if it were required to interpolate for other values of n.

The tensile force is proportional to $-\,\mathrm{d}\Delta S/\mathrm{d}\alpha$, and the most direct way of obtaining this is from the slope of the curve of ΔS plotted against α. However, it is more accurate to derive the force indirectly, from a plot of the above function $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ against α. If this function is denoted by σ it is easy to show that

$$\frac{1}{k}\frac{\mathrm{d}\Delta S}{\mathrm{d}\alpha} = 2(\alpha^2 + 2/\alpha - 3)\frac{\mathrm{d}\sigma}{\mathrm{d}\alpha} + 4(\alpha - 1/\alpha^2)\sigma \quad . \quad . \quad (12)$$

The values of $\mathrm{d}\sigma/\mathrm{d}\alpha$ were obtained by drawing a smooth curve through the points given in Table I, and finding its slope at these points. The advantage of this method is that $\mathrm{d}\Delta S/\mathrm{d}\alpha$ is obtained as the sum of two terms, of which only the first (which is generally the smaller) involves the slope taken from the curve. If F is the tensile force per square cm.

of the original cross-section of the bulk rubber, and if N is the number of molecular chains per c.c., we have then

$$\frac{F}{NkT} = -\frac{1}{4k}\frac{d\Delta S}{d\alpha} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

since the tetrahedron contains four chains.

The functions F/NkT are reproduced in Fig. 2.

Effect of Different Directions of Extension.—Differences between different directions of extension become increasingly significant with increasing extension. However, these differences affect only the detail of the stress-strain curve, and not its general shape. For the z-direction, which differs most seriously from the x-direction, the value of $\Delta S/k$ at $\alpha = 5{\cdot}5$, $n = 25$, was found to be 80·5 compared with 89·8 for the x-direction. The same value of $\Delta S/k$ (80·5) would be given a stretch of about $\alpha = 5{\cdot}37$ in the x-direction. This indicates the kind of maximum divergence between the different directions of stretching. Since, ideally, it is the average entropy for stretching in all directions which is required, it is considered that any error introduced by considering only the x-direction is likely to be very slight.

Two-Dimensional Extension.

In the 2-dimensional extension the x-dimension of the tetrahedron was reduced in the ratio α (where $\alpha < 1$) while the y and z dimensions were increased in the ratio $\alpha^{-\frac{1}{2}}$. As before, the entropy may conveniently be represented by $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ or σ which is given in Table II, as a function of the linear extension ratio $\alpha^{-\frac{1}{2}}$.

TABLE II.—TWO-DIMENSIONAL EXTENSION.

Calculated values of $\Delta S/2k(\alpha^2 + 2/\alpha - 3)$ for 4-chain cell. $n = 25$ and 100.

$n = 25$.		$n = 100$.	
Linear extension ratio $1/\sqrt{\alpha}$.	$\frac{-\Delta S}{2k(\alpha^2+2/\alpha-3)}$.	Linear extension ratio $1/\sqrt{\alpha}$.	$\frac{-\Delta S}{2k(\alpha^2+2/\alpha-3)}$.
1·414	$1{\cdot}00_0$	2·0	$1{\cdot}00_5$
2·0	$1{\cdot}03_1$	3·0	$1{\cdot}01_6$
2·45	$1{\cdot}05_8$	4·0	$1{\cdot}03_8$
3·0	$1{\cdot}09_3$	5·0	$1{\cdot}06_7$
3·46	$1{\cdot}14_0$	6·0	$1{\cdot}10_4$
4·0	$1{\cdot}22_6$	7·0	$1{\cdot}16_2$
4·47	$1{\cdot}33_5$	8·0	$1{\cdot}24_0$
5·0	1·56	9·0	$1{\cdot}36_5$
5·25	1·75	10·0	1·59
		10·5	1·78

Once again, it is seen that the entropy curves for the two chain lengths are very similar, but in the present case it is the scale of $\alpha^{-\frac{1}{2}}$ which is doubled on multiplying n by 4.

Since there is assumed to be no change of volume of the rubber, a strain of the kind considered may be regarded either as a unidirectional compression or as a 2-dimensional extension. From the entropy it is possible to calculate either the compressive force in the first case, or the tensile force in the second. For the compressive force, per cm.^{2} of the original section, we have

$$f = -Td\Delta S/d\alpha. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The tensile force per cm. in a sheet of original thickness 1 cm., stretched in two dimensions is [2]

$$t = \alpha^2 f. \qquad (15)$$

The second is the more convenient quantity for graphical representation.

The compressive force is formally equivalent to the tensile force in a simple elongation, hence from (12) and (13)

$$-\frac{4f}{NkT} = 2(\alpha^2 + 2/\alpha - 3)\frac{d\sigma}{d\alpha} + 4(\alpha - 1/\alpha^2)\sigma.$$

Hence, introducing (15), the tension in the equivalent 2-dimensional extension is

$$-\frac{4t}{NkT} = 2\alpha^2(\alpha^2 + 2/\alpha - 3)\frac{d\sigma}{d\alpha} + 4(\alpha^3 - 1)\sigma \qquad (16)$$

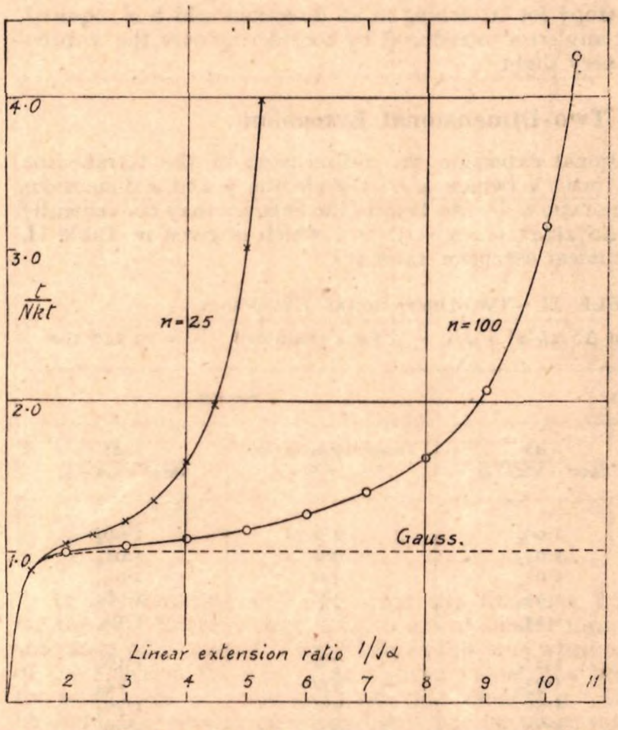

FIG. 3.

Two-dimensional extension. The function t/NkT for a network of random chains of 25 and 100 links.

The quantity $d\sigma/d\alpha$ in this expression is not obtainable accurately from a direct plot of σ against α because of the rapid variation of σ with α. It is more satisfactory to plot σ against $\alpha^{-\frac{1}{2}}$ and thus to obtain $d\sigma/d(\alpha^{-\frac{1}{2}})$. This is converted to $d\sigma/d\alpha$ by the relation

$$\frac{d\sigma}{d\alpha} = -\frac{1}{2\alpha^{3/2}} \cdot \frac{d\sigma}{d(\alpha^{-\frac{1}{2}})},$$

so that (16) becomes

$$\frac{4t}{NkT} = \alpha^{\frac{1}{2}}(\alpha^2 + 2/\alpha - 3)\frac{d\sigma}{d(\alpha^{-\frac{1}{2}})} + 4(1 - \alpha^3)\sigma \qquad (17)$$

The result of the application of this equation is shown in Fig. 3.

Application to Polyisoprene Rubber.

So far the work has been concerned with a network of randomly-linked chains. The resultant stress-strain relations, shown in Figs. 2 and 3, give the stresses divided by NkT where N is the number of chains per c.c.

To proceed further, in order to derive the actual stresses in kg./cm.² on the rubber, it is necessary to find a way of introducing N numerically. For this purpose our mathematical chain must be given a mass. The quantity NkT is then equal to $\rho RT/M$, where M is the " molecular " weight of the chain, and ρ the density of the bulk rubber.

For the appropriate value of M, the random chain may be compared with the polyisoprene chain. The last paper showed that the polyisoprene chain is statistically equivalent to a random chain of 1·42 links per isoprene unit. The 25-link random chain is therefore equivalent to a chain of 17·6 isoprene units, which would have a molecular weight of 1200. Similarly the 100-link random chain is equivalent to a polyisoprene of molecular weight 4800. Introduction of the appropriate factors gives, then, the force in kg./cm.². The resulting curves are shown in Figs. 4 and 5, for a temperature of 25° C.

Comparison with Experiment.

In Figs. 4 and 5 the experimental stress-strain relations for the latex rubber, reported in a previous paper,[2] are plotted for comparison with the theoretical curves. The value of NkT for this rubber was 6·3, which corresponds to a " molecular " weight of 4100. (The temperature in these experiments was 50° C.) Its extensibility, for both simple and 2-dimensional extension, should therefore be about 8 % lower than for the theoretical rubber corresponding to $M = 4800$, since the extensibility varies approximately as the square root of the chain length. Its actual extensibility, judging by the position of the upward bend in the curve, appears to be about 80 % in the simple extension, and 55 % in the 2-dimensional

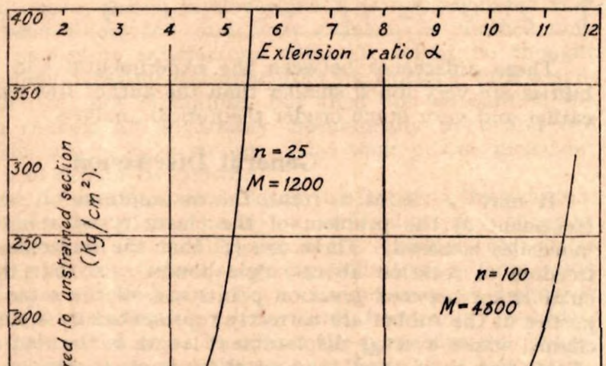

FIG. 4.

Simple elongation. Stress-strain curves for polyisoprene rubber.

M = molecular weight between points of cross-linkage.

extension, of the extensibility for the theoretical $M = 4800$, or about 87 and 60 % respectively of the theoretical for $M = 4100$.

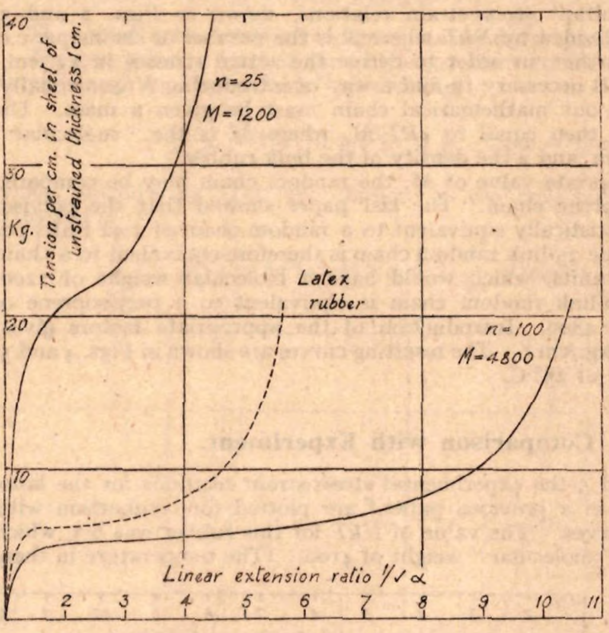

FIG. 5.

Two-dimensional extension. Stress-strain curve for polyisoprene rubber.

M = molecular weight between points of cross-linkage.

These differences between the experimental and theoretical extensibilities are very much smaller than the author was led to expect from an earlier and very much cruder theoretical analysis.[6]

General Discussion.

It may be useful to recall the assumptions on which the theoretical treatment of the problem of the elasticity of a network of long-chain molecules is based. These are (1) that the molecules are endowed with freedom of rotation about single bonds; (2) that the lengths of molecular chain between junction points are all the same; (3) that the properties of the rubber are correctly represented by a simple " cell " of four chains, whose average displacement length is the root-mean-square length of the free chain, and (4) that there is no change in internal energy on deformation at constant temperature, so that the work of deformation may be equated to the entropy. The additional assumption of no volume change on deformation is not really an assumption but a well-established experimental fact.

Given the geometrical construction of the molecular chains, which determines their statistical distribution of displacement length, it is possible, on the basis of the above four assumptions, to derive the stress-strain relationships for any type of strain. In this process, there is, for a given rubber, only one variable parameter—the chain contour length. This determines quantitatively both the vertical and horizontal scales. It is found that, for moderate strains the vertical scale (*i.e.* stress) is inversely proportional to the chain contour length, whilst the horizontal range, or maximum strain is a function of the extensibility of the molecule, and for simple elongation or 2-dimensional extension is proportional to the square root of the chain length. Though the paper is concerned with the polyisoprene chain, these general properties will be the same

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[6] Treloar, *Rep. Prog. Physics*, 1943, 9, 113.

for molecules of different geometrical construction. The general features of the stress-strain relations are fundamental and would be expected from any form of network theory, since they are derived directly from the fundamental statistical properties of long-chain molecules. The *exact* form of the stress-strain curves, is, however, less firmly established, owing to the arbitrary features of a simplifying nature necessarily introduced in any chosen model. Thus, for example, the assumption that the nearest-neighbour junction points to a given junction point may be regarded as fixed in their average positions, and the difficulty, referred to by Flory and Rehner,[5] of knowing which kind of average should be chosen in this connection, are arbitrary features which other possible models might avoid or improve on. The same applies also to the obviously inaccurate assumption that all the chains are of the same length.

A further source of error is connected with the derivation of the statistical distribution of molecular displacement lengths. In this derivation the volume occupied by the chain atoms has been neglected. If these defects were removed, the average chain displacement length would be increased, and since the maximum length would be unchanged, it follows that the extensibility of the molecule and consequently of the network would be reduced. This factor may very well be the main reason for the discrepancy between the experimental and theoretical extensibilities discussed above.

The difficulties are, however, not all on the theoretical side. The determination of a real equilibrium stress-strain curve for rubber is a matter of very considerable difficulty, particularly at large strains, where such effects as crystallisation and mechanical relaxation are very serious. In the experimental curves shown in this paper it is not suggested that these effects have been eliminated, and their inclusion is justified only by the absence of any more satisfactory data. It might be thought possible to remove these experimental difficulties by working with a synthetic rubber which does not crystallise, but then one encounters the difficulty that such rubbers are invariably mechanically weak and will not permit the application of large strains. Also their precise molecular constitution is not, and cannot be known.

A further difficulty, of a related kind, lies in the fact that the deformation, particularly when large, may result in internal energy changes. Such changes may arise from the modification of the intermolecular forces by orientation (leading in the extreme case to crystallisation) or from forces between the atoms of a single chain. Such changes may be estimated experimentally and the contribution to the total free energy resulting from them may be subtracted so as to obtain the pure entropy change, as has been attempted by Anthony, Caston and Guth,[7] but the experimental difficulties involved are here also likely to prove very serious at large strains.

For the reasons advanced in this paragraph, it is evident that caution must be exercised in making a quantitative comparison between the theoretical stress-strain curves and the experimental data available. In spite of the difficulties, however, it is clear that the theory leads to stress-strain relations comparable with the experimental curves in all their characteristic features. This is particularly well shown for the case of a 2-dimensional extension (Fig. 5). It seems justifiable to conclude that the *main elastic properties of a well-vulcanised rubber, even at large strains, are related primarily* (*though not necessarily exclusively*) *to the statistical configurations of molecules in a 3-dimensional network.*

Summary.

The accurate functions representing the distribution of length of long-chain molecules are introduced into the Flory-Rehner model, by means

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[7] Anthony, Caston and Guth, *J. Physic. Chem.*, 1942, **46**, 826.

of which the mechanical properties of a network of such molecules, corresponding to a vulcanised rubber, may be calculated. Stress-strain curves are obtained for (*a*) simple elongation and (*b*) 2-dimensional extension, using chain lengths corresponding to polyisoprene rubbers of molecular weight (M) between junction points of the network of 1200 and 4800 respectively. These curves show all the essential features of the corresponding experimental curves for natural rubber, right up to the breaking point, though the extensibility of the real rubber is significantly less than the theoretical. They show also that the stress for a given small or moderate deformation is inversely proportional to M, whilst the range of extensibility is directly proportional to $M^{\frac{1}{2}}$.

Though an exact agreement between the theoretical and experimental stress-strain relations is not to be expected, on account of the many difficulties encountered in matters of detail both on the theoretical and on the experimental side, the degree of agreement revealed is considered to warrant the conclusion that the main elastic properties of vulcanised rubber are essentially statistical properties of a network of long-chain molecules.

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