Dilation of rubber on extension

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The theory of volume changes on extension is developed in terms of a strain-energy function *W* of the Ogden type. Experimental values of volume change derived from measurements of dilation coefficients by Allen *et al.* (Trans. Faraday Soc., 1971, **67**, 1278) exceed the values calculated from the theory by an average amount of 22% at the maximum extension ratio $\lambda = 2.0$, but by only 6% at $\lambda = 1.5$. These figures represent a considerably closer agreement between theory and experiment than that obtainable from the Gaussian statistical theory, but the residual discrepancies are still disturbingly large. No reason for these discrepancies can be suggested. It is also shown that the apparent agreement between theory and experiment obtainable on the basis of the Mooney form of *W* is fortuitous.

INTRODUCTION AND OBJECTIVES

The Gaussian statistical theory of the cross-linked network, as presented originally by Flory[1] and later in a slightly modified form by the author[2] enables the changes of volume which which accompany the extension of a rubber to be derived. Measured values of these volume changes, notably by Christensen and Hoeve[3], Penn[4], Allen, Kirkham, Padget and Price[5] and Price and Allen[6], have revealed large divergences from the theoretically predicted values. The question which naturally arises is whether these divergences can be related to the deviations in the form of the stress–strain relations from the corresponding theoretical relations, in which case the substitution of an experimentally more realistic form of strain-energy function might enable the observed volume changes to be more accurately predicted.

In the theory of Flory[1] the response of the rubber to an applied stress is assumed to involve two distinct mechanisms of deformation. The first of these is related to the change of volume, and is associated with the forces *between* the molecules; this mechanism is of the same kind as that which is responsible for the compressibility of an ordinary liquid. The second mechanism is related to the distortion of the rubber-like network, the corresponding change of free energy in this process being related to the configurational entropy of the network.

In the present paper the same basic separation into a compressibility and a network deformation mechanism is retained, but in place of the expression for the free energy of network deformation derived from the statistical theory a general form of network strain-energy function is introduced. General equations may then be derived for the change of volume in a pure homogeneous strain of any type. By the substitution of any particular form of strain-energy function into these equations specific expressions for the changes of volume (e.g. in simple extension) are readily obtained. The advantage of this method of treatment is that it provides a uniform basis for the treatment of volume changes which brings out the relationship between the statistical or thermodynamic approach on the one hand and the phenomenological or purely mechanical approach on the other.

Among the phenomenological theories of rubber elasticity of particular interest are those of Mooney[7] and Ogden[8]; these are the subject of special consideration in the present paper. It will be shown that the Ogden formulation gives a much closer approximation to the experimental volume change data than the Gaussian statistical theory, though it still leaves significant discrepancies to be accounted for.

THEORETICAL

Basic formulation

The theory of volume changes here presented follows the same general lines as the earlier treatment based on the Gaussian network theory (Treloar[2]) except for the substitution of a more general expression for the free energy of network deformation. For a state of pure homogeneous strain defined by three principal extension ratios λ_1, λ_2 and λ_3 with reference to the *stress-free* state the total Helmholtz free energy, A, is expressed by the equation:

$$A = A^* + \Phi(\lambda_1, \lambda_2, \lambda_3) \tag{1}$$

in which A^* represents the contribution of the compressibility (or liquid-like) component and the unspecified function Φ the network deformation contribution. The principal stresses t_1, t_2 and t_3 are obtained by equating the change in free energy δA in an incremental deformation $\delta\lambda_i$ to the work done by the corresponding force. The volume in the strained state being given by $V = \lambda_1\lambda_2\lambda_3 V_u$, where V_u is the unstrained volume; we obtain in this way:

$$\frac{t_i V}{\lambda_i}\delta\lambda_i = \left(\frac{\partial A^*}{\partial \lambda_i} + \frac{\partial \Phi}{\partial \lambda_i}\right)\delta\lambda_i \quad [i = 1, 2, 3] \tag{2}$$

Putting $\partial A^*/\partial V = p^*$, where p^* is equivalent to a hydrostatic pressure, and noting that $\partial V/\partial\lambda_i = V/\lambda_i$, we obtain from equation (2):

$$t_i = -p^* + \frac{\lambda_i}{V}\frac{\partial \Phi}{\partial \lambda_i} \tag{3}$$

The quantity p^* is related to the volume of the system and

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to the compressibility K. As in the earlier paper, let V_1 be the volume for which $p^* = 0$. Then:

$$-p^* = \frac{1}{K} \cdot \frac{V - V_1}{V} \tag{4}$$

To eliminate p^* we consider the stress-free state, for which $V = V_u, \lambda_i = 1, t_i = 0$. Equations (3) and (4) then yield:

$$\frac{V_u - V_1}{KV} + \frac{1}{V_u}\left(\frac{\partial\Phi}{\partial\lambda_i}\right)_{\lambda_i=1} = 0 \tag{5}$$

For a material which is isotropic in the unstrained state the strain energy function is symmetrical in the λ_i. We may therefore write:

$$\left(\frac{\partial\Phi}{\partial\lambda_i}\right)_{\lambda_i=1} = g' \tag{5a}$$

where g' is a constant. To a sufficient degree of accuracy it is not necessary to discriminate between V and V_u in the denominators of the terms in equation (5). With this approximation equations (4) and (5) and (5a) give:

$$-p^* = \frac{V - V_u}{KV} - \frac{g'}{V} \tag{4a}$$

Substitution into equation (3) yields finally:

$$t_i = \frac{V - V_u}{KV} + \frac{\lambda_i}{V}\frac{\partial\Phi}{\partial\lambda_i} - \frac{g'}{V} \tag{6}$$

For the case of simple extension (or uniaxial compression) corresponding to an axial stress t_1, with $t_2 = t_3 = 0$, equation (6) yields, on putting $i = 2$:

$$V - V_u = \Delta V = -K[\lambda_2(\partial\Phi/\partial\lambda_2) - g'] \tag{7}$$

where $\lambda_2 \approx \lambda_1{}^{-1/2}$

For an equi-biaxial extension produced by tensile stresses $t_2 = t_3$, with $t_1 = 0$, the corresponding result is:

$$\Delta V = -K[\lambda_1(\partial\Phi/\partial\lambda_1) - g'] \tag{8}$$

Particular forms of strain energy function

As a basis for further development it is convenient to introduce the form of strain energy function proposed by Ogden[8]; other more restricted forms may then be derived from this as special cases. The strain energy, W, per unit volume is represented by Ogden in the form of the following series

$$W = \frac{\Phi}{V} = \sum_n \frac{\mu_n}{\alpha_n}(\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_3^{\alpha_n} - 3) \tag{9}$$

in which the α_n may be any real numbers. This formula was originally applied by Ogden to an incompressible material, but may equally well be applied to a (slightly) compressible material provided that the λ_i are defined with respect to the stress-free dimensions. Differentiation of equation (9) with respect to λ_2 and substitution into equation (7) yields on putting $\lambda_2 = \lambda_1^{-1/2}$ for simple extension (or uniaxial compression) and dropping the subscript 1:

$$\Delta V/V = K\sum_n \mu_n(1 - \lambda^{-\alpha_n/2}) \tag{10}$$

For comparison with experiment it is convenient also to introduce the differential volume change $\partial\ln V/\partial\lambda$, termed the 'dilation coefficient' by Allen *et al.*[5]. Differentiation of equation (10) gives:

$$\partial\ln V/\partial\lambda = \frac{1}{2}K\sum_n \mu_n\alpha_n\lambda^{-\alpha_n/2-1} \tag{11}$$

The result equation (10) has been obtained by Chadwick[9] on the basis of a more general mathematical formulation.

For an equi-biaxial extension the expression for the total volume change, obtained from equations (8) and (9) is:

$$\Delta V/V = K\sum_n \mu_n(1 - \lambda_z^{-2\alpha_n}) \tag{12}$$

This also may be derived from the formulation of Chadwick.

Mooney equation. The Mooney form of strain energy function, namely:

$$W = \Phi/V = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) \tag{13}$$

is a special case of (9) with $\alpha_1 = 2, \alpha_2 = -2, \mu_1 = 2C_1, \mu_2 = -2C_2$. Substitution of these values into equation (10) gives for the volume change in simple extension (or uniaxial compression):

$$\Delta V/V = 2K[C_1(1 - 1/\lambda) + C_2(\lambda - 1)] \tag{14}$$

while for the corresponding differential quantity equation (11) gives

$$\partial\ln V/\partial\lambda = 2K(C_1/\lambda^2 + C_2) \tag{15}$$

Gaussian statistical theory. The Gaussian statistical theory yields the strain-energy function

$$W = \frac{1}{2}G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{16}$$

which corresponds to the first term of the Mooney equation (13), with $G = 2C_1$. Hence for simple extension (or uniaxial compression)

$$\Delta V/V = KG(1 - 1/\lambda) \tag{17a}$$

$$\partial\ln V/\partial\lambda = KG/\lambda^2 \tag{17b}$$

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* Flory[1] applies the term dilation coefficient to the different quantity $(\partial\ln V/\partial\ln l)_{T,p}$ which is equivalent to $\lambda\partial\ln V/\partial\lambda$ in the present notation

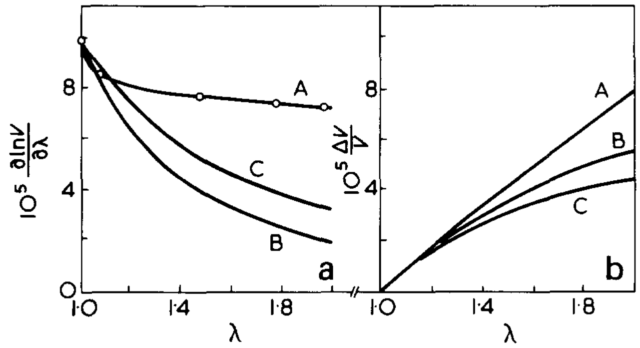

Figure 1 Sample A. (a): Dilation coefficient, (A) experimental; (B) from equations (21) and (22); (C) from equation (11), with scaled parameters from *Table 1* (lower line). (b): Total volume change, (A) by integration of (A)a; (B) by integration of (B)a; (C) from equation (10), with scaled parameters from *Table 1* (lower line). $K = 5.83 \times 10^{-4}$ mm^2 N^{-1}

Equations substantially equivalent to (17a) and (17b) have been given by Flory[1]

For equi-biaxial extension the corresponding volume change, obtained by putting $\alpha = 2, \mu_1 = G$ in equation (12), is

$$\Delta V/V = KG(1 - \lambda_2^{-4}) \tag{18}$$

EXPERIMENTAL DATA CONSIDERED

Ideally, for comparison of calculated and experimental results, it would be desirable to have volume-change data on specimens for which the form of strain-energy function is known. This form can only be established with an adequate degree of generality from extensive biaxial strain experiments such as those reported by Jones and Treloar[10]. In the absence of such data it is desirable at least to have complete data on the form of the force-extension relation in simple extension. The most extensive data which satisfy this more limited requirement are those of Allen, Kirkham, Padget and Price[5]; these data will therefore be used as a basis for comparison with the theoretical deductions given above.

Allen *et al.*[5] examined five vulcanized natural rubber samples, differing in degree of cross-linking and obtained data on the dilation coefficient $\partial \ln V/\partial \lambda$ in both the dry and swollen states. They also obtained values of the Mooney constants by which the form of the force-extension curves could be represented. The present discussion will be limited to their samples A, B, C and D in the *unswollen* state. For these samples the maximum value of λ attained lay between 1.9 and 2.1; their sample E, for which the maximum value of λ was less than 1.5, will not be included. The complete set of numerical results, including those reproduced in the form of graphs in the original paper, has kindly been made available to the author by Dr. C. Price.

The volume changes referred to were not obtained by direct measurement but were derived indirectly from measurements of the pressure dependence of the force at constant length, making use of the thermodynamic identity

$$(\partial V/\partial l)_{p,T} = (\partial f/\partial p)_{l,T} \tag{19}$$

The experimental volume-change data will be compared first with the Gaussian statistical theory and then with the Ogden theory. The bearing of the Mooney theory will be examined later.

COMPARISON WITH GAUSSIAN THEORY

In the attempt to compare the experimental results with the formula (17b) derived from the statistical theory a difficulty immediately arises in assigning an appropriate value to the modulus G in this formula. Since the experimental force-extension curve does not coincide with the form deduced from the Gaussian theory, i.e.,

$$f = G(\lambda - 1/\lambda^2) \tag{20}$$

it is not possible to assign a unique value to the modulus G in equation (17b). To overcome this difficulty Allen *et al.*[5] adopted the common procedure of substituting $f/(\lambda - 1/\lambda^2)$, where f is the measured value of the force, for G in this equation so as to obtain

$$\frac{\partial \ln V}{\partial \lambda} = \frac{Kf}{\lambda^3 - 1} \tag{21}$$

Since the samples studied yielded force-extension relations in close accord with the Mooney equation*

$$f = 2(\lambda - 1/\lambda^2)(C_1 + C_2/\lambda) \tag{22}$$

an equivalent procedure, which will be adopted in the present paper, is to use values of f calculated from equation (22) in conjunction with equation (21), the values of the two Mooney constants for each sample being taken from the original paper. (It must be emphasized that this procedure does not imply acceptance of the Mooney form of *strain-energy* function; it is merely a convenient empirical method of generating the experimental data. See Section 6). For the compressibility the figure used by Allen *et al.*[5] namely 5.83×10^{-10} m^2 N^{-1} (at 45°C), was assumed. (This figure was provided by Dr. Price).

Values of the dilation coefficient calculated in this way are reproduced in *Figures 1a* to *4a* (curves B). The corresponding experimental values (curves A) show increasing divergences from the theoretical curves as the extension is increased, being in excess of the calculated values at λ = 2.0 by amounts varying from 171 to 266% approximately, with an average difference of 212%. (Substantially identical curves for samples A, C and D are given in *Figure 5* of the original paper by Allen *et al.*[5]. These very large divergences, however, are liable to give a somewhat exaggerated impression of the inadequacy of the theory. A more balanced picture is conveyed by comparisons not with the dilation co-

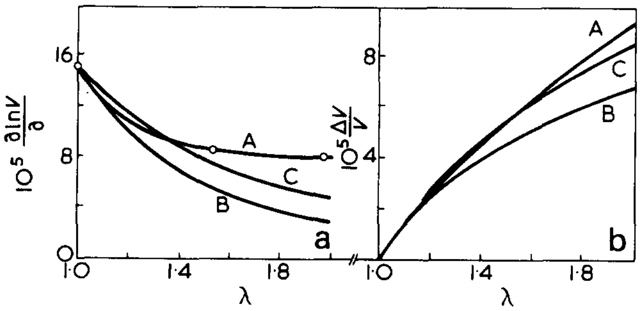

Figure 2 Sample B. Particulars as for *Figure 1*

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* The constants C_1 and C_2 in the notation of Allen *et al.*[5] differ by a factor of 2 from those defined by equation (22)

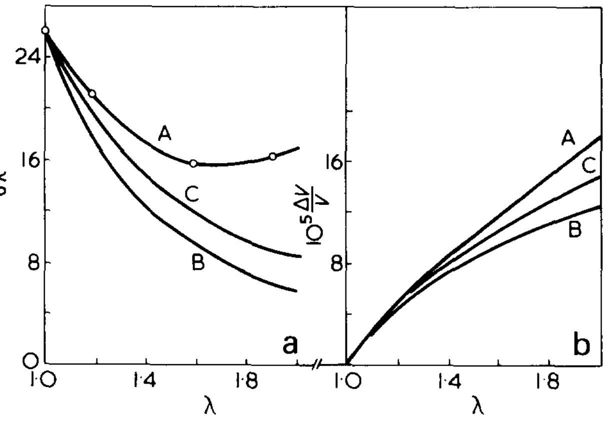

Figure 3 Sample C. Particulars as for *Figure 1*

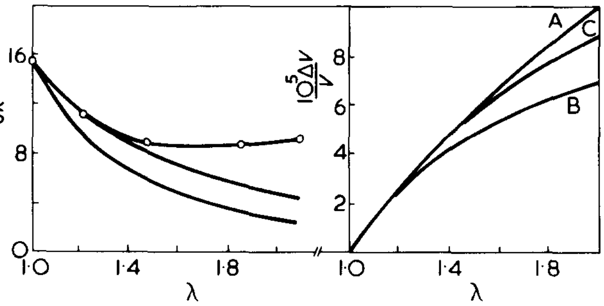

Figure 4 Sample D. Particulars as for *Figure 1*

efficient (i.e. the differential volume change) but with the total volume change ΔV. This was not measured by Allen *et al.* but may be obtained by integration with respect to λ of their experimental dilation coefficient curves. The results so obtained are compared in *Figures 1* to *4* (right) with the calculated curves of total volume change, also obtained (for reasons discussed in the next paragraph) by numerical integration of the corresponding *calculated* dilation coefficient curves. The divergences from the calculated values at λ = 2.0 shown in these figures range from 40% to 75%, the average difference being 53%. These differences are only about a quarter of the corresponding discrepancies in the values of dilation coefficient.

Some comment is desirable here on the application of the theoretical formula (17a) to experimental data for the total volume change. As in the case of the dilation coefficient some authors have introduced the experimental value of $f/(\lambda - 1/\lambda^2)$ into this equation to give

$$\frac{\Delta V}{V} = \frac{Kf(1 - 1/\lambda)}{\lambda - 1/\lambda^2} = \frac{Kf\lambda}{1 + \lambda + \lambda^2}\ . \qquad (23)$$

This procedure suffers from the disadvantage that values of total volume change so calculated, using the experimental values of f, are not consistent with values of dilation coefficient calculated from the analogous equation (21); in other words, equation (21) cannot be derived from equation (23), except in the case when the variation of f with λ is of the form (20) required by the theory. In practice, for values of λ up to 2.0 at least, the effective modulus G defined by equation (20) decreases continuously with increasing strain; the total volume change derived from equation (23) will therefore fall below that derived by numerical integration of the dilation coefficient curve obtained on the basis of equation (21). This conclusion has been verified by direct calculation. Moreover, both methods of calculation yield lower values than would be obtained by the insertion of the small-strain value of modulus G in either equation (21) or equation (23). These inconsistencies arise from the fact that when the force-extension relationship deviates from the theoretical form there is no unambiguous way of interpreting the Gaussian modulus G. The most that can be achieved is consistency between the methods of calculation of the dilation coefficient and of the total volume change, and this is ensured by the method used above, i.e., by the integration of the calculated dilation coefficient curves with respect to λ so as to obtain the total volume change.

COMPARISON WITH OGDEN THEORY

The effectiveness of the strain-energy function represented by equation (9) for the interpretation of the stress-strain relations of rubber was first demonstrated by Ogden[8] who used a 3-term expression of this type to account for data by the writer[11] for natural rubber in simple extension, equibiaxial extension and pure shear. The values of the parameters which he used are given in the top line of *Table 1*. A more extensive study, involving general biaxial strain measurements, was carried out by Jones and Treloar[10]; this also yielded a 3-term function, with parameters closely similar to those found by Ogden (*Table 1*). Confirmation of this same general form is also provided by the recent work of Vangerko and Treloar[12]. Furthermore, comparable biaxial strain data obtained by Obata, Kawabata and Kawai[13] yielded a function which, though not represented in terms of an algebraic series, was of very similar form to that obtained by Jones and Treloar[10], except for a scale factor. This evidence encourages the hope that a function of the same general form as that represented by either set of parameters in *Table 1* may reasonably be assumed to apply to vulcanized rubbers in general, with appropriate numerical scaling.

In applying these considerations to the data of Allen *et al.* the constants of Jones and Treloar given in *Table 1* were preferred, and a scaling factor (S.F.) was applied to the μ_n such that the limiting value of the shear modulus at zero strain ($\lambda \rightarrow 1$), namely $\frac{1}{2}\Sigma\mu_n\alpha_n$, was equal to the corresponding value of $2(C_1 + C_2)$, as given by Allen *et al.*, for the samples under consideration. For the Jones and Treloar constants we have then

$$\tfrac{1}{2}\Sigma\mu_n\alpha_n \times \text{Scaling Factor} = 2(C_1 + C_2) \qquad (24)$$

Taking values of C_1 and C_2 from *Table 5* of Allen *et al.*, and putting $\frac{1}{2}\Sigma\mu_n\alpha_n = 0.4807\ \text{Nmm}^{-2}$ from Jones and Treloar[10] the values of S.F. shown in *Table 2* are obtained. As previously, K was taken as $5.83 \times 10^{-10}\ \text{m}^2\ \text{N}^{-1}$. The values of dilation coefficient calculated in this way from equation (11) are compared with the previous experimental results in *Figures 1* to *4* (*a* curves C). The latter are in excess of the calculated values at λ = 2.0 by amounts varying from 63% to 121%, the mean difference for the four samples being 90%.

Table 1 Parameters in strain-energy function (19) found by Ogden[8] and by Jones and Treloar[10]. (μ_n in N mm^{-2})

	α_1	α_2	α_3	μ_1	μ_2	μ_3
Ogden	1.3	5.0	−2.0	0.61_8	0.0011_8	-0.009_8
J and T	1.3	4.0	−2.0	0.69	0.01	−0.0122

Table 2 Scaling factors for elastic parameters

Sample	$2(C_1 + C_2)$ N mm^{-2}	S.F.
A	0.1697	0.3530
B	0.259	0.5388
C	0.450	0.9361
D	0.264	0.5492

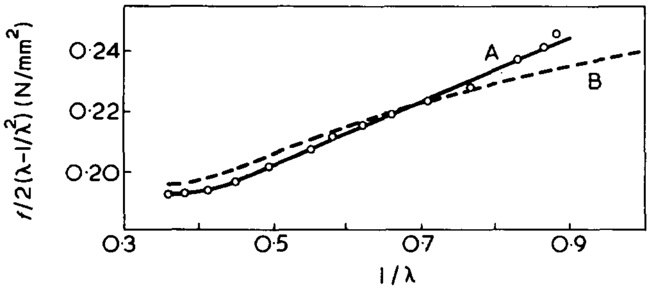

Figure 5 Mooney plot for simple extension. A, Experiments of Jones and Treloar[10]. B, Calculated from Ogden theory, with parameters from *Table 1* (lower line).

The corresponding curves for $\Delta V/V$ calculated from equation (10) are shown in *Figures 1b* to *4b*. The difference between theory and experiment is now reduced to the range 11% to 40%, with a mean value of 22%. This is less than half the discrepancy (53%) calculated on the basis of the statistical theory.

Calculations of total volume change were also made on the basis of Ogden's numerical parameters, given in the first row of *Table 1*, (with appropriate adjustments of the scaling factors). The results so obtained were in all cases within 1.0% of those obtained on the basis of the Jones and Treloar figures. This confirms the immediate impression that the differences between the two sets of parameters in *Table 1* are relatively unimportant.

The differences between calculated and experimental values of dilation coefficient shown in *Figures 1* to *4* are consistent with the calculations made by Price[14] on the basis of Ogden's numerical values of parameters.

THE MOONEY THEORY

It has been shown by Price and Allen that the Mooney theory, as represented by equation (15), yields moderately close agreement with experimental data for the dilation coefficients of both natural and polybutadiene rubbers[6,14]. A similar conclusion is arrived at from calculations of $\Delta V/V$ using equation (14) together with the values of Mooney constants given by Allen *et al.*[5] for the natural rubber samples under discussion in the present paper. The discrepancies between experimental and calculated values of $\Delta V/V$ so obtained ranged from +11% for sample A to −14% for D, with an average of −1%. Before this close agreement is accepted as an explanation, however, it is necessary to examine the logical basis of this application of the Mooney theory.

The constants in the Mooney equation are normally derived from experiments confined exclusively to simple extension. It has been shown unambiguously by Rivlin and Saunders[15], and more recently by Obata *et al.*[13] and by Jones and Treloar[10], that agreement with the Mooney equation in simple extension (equation 22) cannot be taken to imply that the *general* strain-energy function is of the Mooney form (equation 9). These authors have clearly demonstrated that the use of the Mooney strain-energy function, with values of C_1 and C_2 derived from simple extension experiments, is not consistent with data for other types of strain (e.g. uniaxial compression). In the general analysis given in Section 2 it is seen that the volume change in simple extension is determined not by the tensile stress directly, but by $\partial\Phi/\partial\lambda_2$, the derivative of the strain-energy function with respect to the *transverse* direction, i.e. for $\lambda_2 < 1$. This quantity cannot be obtained from the force-extension relation in simple extension alone, but necessitates a comprehensive study of the biaxial strain behaviour, as in the work of Jones and Treloar[10].

The argument may be illustrated more specifically by considering the data for simple extension obtained by Jones and Treloar, and reproduced in *Figure 5*. These data are in agreement with the Mooney equation from about $1/\lambda = 0.45$ to $1/\lambda = 0.88$. They may also be represented to an accuracy of 4% or better by an Ogden series, with values of parameters obtained from experiments involving the general biaxial strain (*Table 1*). These respective forms of strain-energy – Mooney and Ogden – while yielding closely similar force-extension curves, give very different values of $\partial\Phi/\partial\lambda_2$, and hence of the volume change in simple extension. This is illustrated in *Figure 6* which shows the curves for ΔV calculated from the Ogden formula and from the corresponding Mooney formula, using values of the constants obtained from the Mooney line in *Figure 5* for the latter. The difference between these two calculated values of ΔV at $\lambda = 2.0$ for this particular case amounts to 35%.

It must therefore be concluded that the apparent satisfactory agreement with the volume changes predicted by the Mooney formula which was obtained by Price is open to serious objection.

DISCUSSION AND CONCLUSIONS

Experimental

The foregoing analysis establishes that the use of the Ogden form of strain-energy function in place of that derived from the statistical theory leads to a considerable reduction

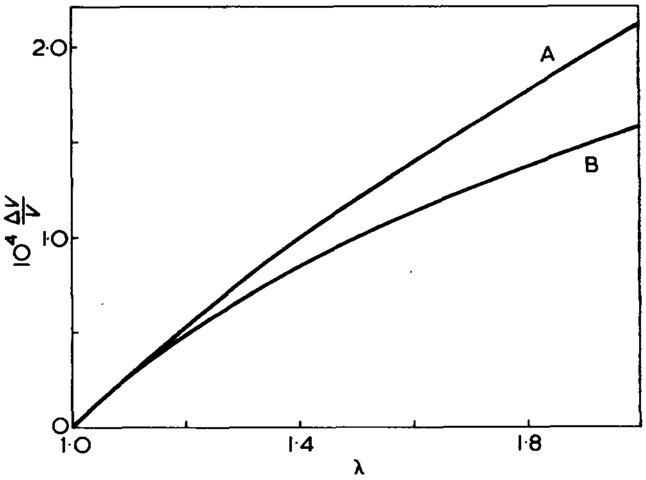

Figure 6 Calculated total volume change. (A) From equation (14), with $C_1 = 0.148$ N mm^{-2}, $C_2 = 0.108$ N mm^{-2}. (B) From equation (10),with parameters from *Table 1* (lower line). $K = 5.83 \times 10^{-4}$ mm^2 N^{-1}

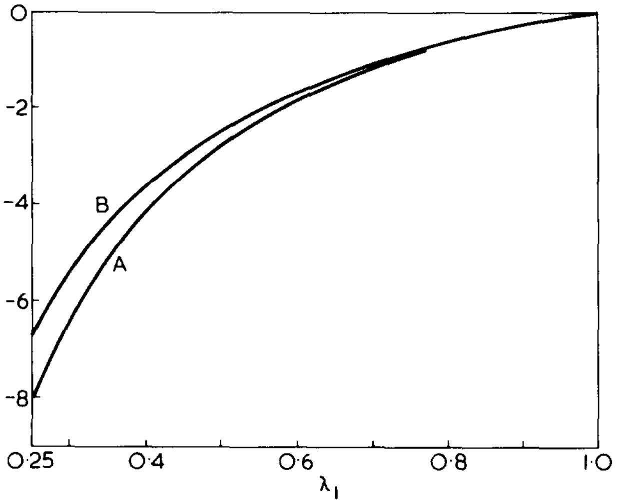

Figure 7 Calculated volume change for uniaxial compression. (A) Statistical theory (equation 17a), with $G = 0.4807$ N mm^{-2}. (B) Ogden theory (equation (10) with parameters from *Table 1* (lower line). $K = 5.83 \times 10^{-4}$ mm^2 N^{-1}

of the discrepancy between observed and calculated volume changes. From the curves presented it is seen that this discrepancy decreases rapidly with decreasing strain. Thus, for example, the mean discrepancy (for the 4 samples) between calculated and observed values of $\Delta V/V$ falls from 22% at $\lambda = 2.0$ to 9% at $\lambda = 1.6$ and to only 6% at $\lambda = 1.5$.

The most serious uncertainty in the calculations lies in the absence of direct experimental data on the values of the Ogden parameters for the particular rubber samples examined, though from the evidence presented in Section 5 it seems unlikely that this could account for the whole of the observed differences.

Theoretical

In addition to the Mooney equation, Price[14] has also considered the application of the early theory due to Elliott and Lippmann[16] and Gee[17], which relates the dilation coefficient to the slope of the force-extension curve at any point. This theory, which neglects the anisotropy of compressibility of the strained rubber arising from the network deformation, gives the result

$$\left(\frac{\partial \ln V}{\partial \lambda}\right)_{p,T} = \frac{K}{3V}\, l_i \left(\frac{\partial f}{\partial l}\right)_{p,T} \qquad (25)$$

where l_i is the unstrained length. This formula was found by Price to give a fairly satisfactory representation of the data of Allen and co-workers for both natural and polybutadience rubbers. However, it is difficult to believe that this agreement is significant, since the anisotropy of compressibility is a property of the network which has been explicitly calculated by Flory on the basis of the Gaussian theory and is implicit in the theory presented in Section 2 of the present paper and in the specific form of this theory incorporating the Ogden form of strain-energy function. The omission of this fact in Gee's theory was due to the absence at that time of any method of evaluating it.

The present theory, based on the Ogden form of strain-energy function, contains a minimum of arbitrary assumptions. This form of strain-energy function has been established experimentally up to values of λ of 2.6 at least, and the only uncertainty, already emphasized, is in the values to be assigned to the parameters for the particular rubbers for which volume-change data are available. The only other physical assumption is that the 'liquid-like' properties of the rubber may be represented by a normal compressibility term. A closely related theory of volume changes has been developed by Ogden[18] which discusses this aspect of the problem in a more general way and arrives at an identical solution for the particular case when the 'liquid' compressibility is isotropic and independent of the distortional strain (i.e. of the network deformation in the present theory). If this restriction is relaxed, i.e. if there is a 'coupling' between the distortional strain and the compressibility term, then the 'liquid-like' component develops anisotropic properties and the situation becomes much more complicated. (Such anisotropy of the liquid-like component is to be distinguished from the anisotropy of compressibility discussed above, which is associated directly with the network anisotropy). The compressibility of the liquid-like component is determined by the intermolecular forces, which in the unstrained rubber are isotropic; it is possible in principle for the orientation of chain segments resulting from the network deformation to confer some degree of anisotropy on the system of the intermolecular forces and hence on the compressibility. However, there are reasons for believing that any such induced anisotropy would not be significant, at least for strains up to, say, $\lambda = 2$. Without going very deeply into this question, the work of Hennig[19], which discusses the strain-induced anisotropy of a number of properties of polymers (e.g. compressibility, thermal expansion, thermal conductivity, etc.) which are related to the intermolecular forces but are not directly dependent on network structure, may be quoted. Hennig succeeded in measuring a difference in thermal conductivity of 3% between longitudinal and transverse directions in a natural rubber vulcanizate extended to $\lambda = 3$. At $\lambda = 2$ the difference would be less than half this value. Differences of this order in the compressibility would have an insignificant effect on the calculated values of the volume changes in the region of strain covered by the experimental measurements of Allen *et al.*[5].

Thus, no plausible theoretical reason can be advanced for the observed discrepancy between calculated and observed volume changes, and it seems to the author that the problem is more likely to be clarified by further experimental studies than by modifications to the theoretical treatment. In a discussion of the problems involved Price[14] suggests among other things measurements of volume changes under types of strain

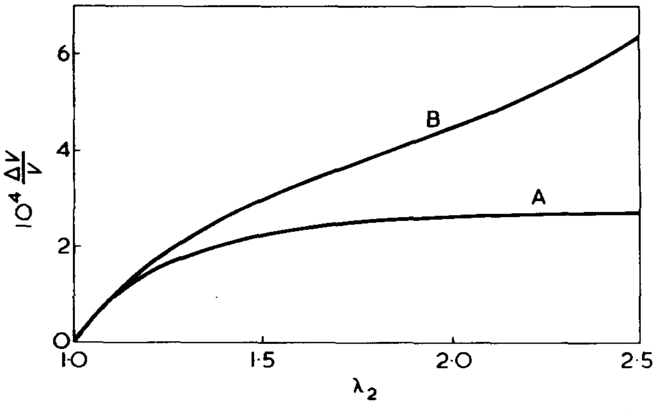

Figure 8 Calculated volume change for equi-biaxial extension. (A) Statistical theory (equation 18) with $G = 0.4807$ N mm^{-2}. (B) Ogden theory (equation 12), with parameters from *Table 1* (lower line). $K = 5.83 \times 10^{-4}$ mm^2 N^{-1}

other than simple extension as an alternative line of development. With this in mind, numerical calculations have been made of the volume changes for uniaxial compression and for equi-biaxial extension for both the statistical theory and the Ogden theory, using the equations derived in Section 2(b). The results show that for uniaxial compression the Ogden theory, using the parameters given in *Table 1*, lower line, yields *smaller* values of $\Delta V/V$ than the statistical theory (*Figure 7*), whereas for equi-biaxial extension, as for simple extension, it yields larger values (*Figure 8*). Experimental work on either of these lines, if it could be shown to be practicable, would be of great interest. Another possibility is torsion, which might be experimentally more tractable. This has been examined theoretically by Treloar[20] and by Ogden[21].

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REFERENCES

1 Flory, P. J. *Trans. Faraday Soc.* 1961, **57**, 829
2 Treloar, L. R. G. *Polymer* 1969, **10**, 279
3 Christensen, R. G. and Hoeve, C. A. J. *J. Polym. Sci.* 1970, **A-1 8**, 1503
4 Penn, R. W. *Trans. Soc. Rheology* 1970, **14**, 509
5 Allen, G., Kirkham, M. J., Padget, J. and Price, C. *Trans. Faraday. Soc.* 1971, **67**, 1278
6 Price, C. and Allen, G. *Polymer* 1973, **14**, 576
7 Mooney, M. *J. Appl. Phys.* 1940, **11**, 582
8 Ogden, R. W. *Proc. Roy. Soc.* 1972, **A326**, 565
9 Chadwick, P. *Phil. Trans. Roy. Soc.* 1974, **276**, 371
10 Jones, D. F. and Treloar, L. R. G. *J. Phys. (D)* 1975, **8**, 1285
11 Treloar, L. R. G. *Trans. Faraday Soc.* 1944, **40**, 59
12 Vangerko, H. and Treloar, L. R. G. *J. Phys. (D)* 1978, **11**, 1969
13 Obata, Y., Kawabata, S. and Kawai, H. *J. Polym. Sci.* 1970, **A-2 8**, 903
14 Price, C. *Proc. Roy. Soc.* 1976, **A351**, 331
15 Rivlin, R. S. and Saunders, D. W. *Phil. Trans. Roy. Soc.* 1951, **A241**, 379
16 Elliott, D. A. and Lippmann, S. A. *J. Appl. Phys.* 1945, **16**, 50
17 Gee, G. *Trans. Faraday Soc.* 1946, **42**, 585
18 Ogden, R. W. *J. Mech. Phys. Solids* 1976, **24**, 323
19 Hennig, J. *J. Polym. Sci.* 1967, **C16**, 2751
20 Treloar, L. R. G. *Polymer* 1969, **10**, 291
21 Ogden, R. W. *J. Mech. Phys. Solids* 1978, **26**, 37