Volume Changes and Mechanical Anisotropy of Strained Rubbers

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The Gaussian network theory, suitably modified to take account of the finite compressibility of an actual rubber, is used to derive the relation between the change of volume and the applied stresses in a pure homogeneous strain of the most general type. The anisotropy of compressibility is also worked out for the case of a pure homogeneous strain maintained by fixed applied forces. The formulae derived can be reduced to those previously given by Flory for the particular case of simple extension. It is further shown that the anisotropy of compressibility for a rubber in equilibrium with a swelling liquid is identical with that for a slightly compressible dry rubber.

THE treatment of the stress/temperature relations for crosslinked rubbers given by Flory[1], which is based on the theory of the Gaussian network, enables certain approximations introduced into the earlier thermodynamic analysis of the stress/temperature relations as given by Gee[2] and by Elliott and Lippmann[3] to be eliminated. This leads to a more precise formulation of the relation between the stress/temperature relations at constant pressure and at constant volume.

The important new departure in Flory's development of the theory was the recognition of the significance of the temperature dependence of the statistical length of the molecule in the uncrosslinked rubber. This temperature dependence arises from energetic interactions *within* the chain. Previously it had been suggested that the internal energy changes observed in the extension of rubber were due to forces *between* molecules, and that these changes should be absent if the extension were carried out at constant volume[2]. However, if the internal energy contribution to the stress is associated either wholly or partially with internal energy changes within the single molecule, it will not disappear under constant volume conditions.

Since the publication of Flory's theory direct measurements of the temperature coefficient of the stress have been carried out by Allen and his colleagues[4,8]. These confirm Flory's analysis in showing a definite energetic contribution to the stress at constant volume.

In the course of his analysis Flory derives expressions for the change of volume in simple extension, and for the relative changes in longitudinal and transverse dimensions due to a superimposed hydrostatic pressure (anisotropy of compressibility). The main purpose of the present paper is to explore in greater detail these mechanical properties of crosslinked rubbers, and to examine types of strain other than simple extension. Expressions will be derived for the change of volume and for the anisotropy of compressibility in a pure homogeneous strain of the most general type. Attention will also be given to the formal similarity between the mechanical properties of a slightly compressible rubber and the corresponding properties of a rubber swollen to equilibrium in a liquid of low molecular weight, which behaves in certain respects as a highly compressible rubber.

STRESS/STRAIN RELATIONS FOR PURE HOMOGENEOUS STRAIN

Helmholtz free energy

In the usual form of the statistical theory of rubber elasticity[5], based on the assumption of constancy of volume, the Helmholtz free energy for a pure homogeneous strain defined by principal extension ratios λ_1, λ_2 and λ_3 takes the form

$$A = \tfrac{1}{2}\nu kT\,(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{1}$$

where ν is the number of chains in the network. In the derivation of this equation it is assumed that the mean-square length $\overline{r_i^2}$ of the chains in the unstrained rubber is equal to the mean-square length $\overline{r_0^2}$ of a corresponding set of free chains. Since the value of $\overline{r_0^2}$ depends, in general, on the temperature, while $\overline{r_i^2}$ is determined by the volume of the rubber, it is apparent that this assumption will not, in general, be valid. To overcome this difficulty Flory introduces a hypothetical volume V_0 at which the assumption $\overline{r_i^2} = \overline{r_0^2}$ would be valid. (V_0 is a function of temperature.) Equation (1) then remains valid if the extension ratios are calculated on the dimensions in the undistorted state of volume V_0.

This device has the disadvantage that the volume V_0, and the corresponding extension ratios λ_1, λ_2 and λ_3, are not observable parameters. It cannot be assumed that V_0 is even approximately equal to the actual volume; its actual value will depend on the temperature of vulcanization, the temperature dependence of $\overline{r_0^2}$ and the mode of network formation (cf. ref. 5, p 81). An alternative method of presentation, which is used in the present paper, is to define the extension ratios with respect to the unstrained state of volume V_u. The network free energy may then be written in the form

$$A = \tfrac{1}{2}\nu kT\,(\overline{r_i^2}/\overline{r_0^2})(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{2a}$$

or

$$A = \tfrac{1}{2}G'\,(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{2b}$$

where†

$$G' = \nu kT\,(\overline{r_i^2}/\overline{r_0^2}) \tag{3}$$

All the quantities in equation (2b) can now be measured, G' being obtained directly from the elastic modulus.

If the finite compressibility of the rubber is taken into account the volume V in the strained state will differ from V_u, and the expression for the free energy will contain a term A^*, associated with the volume occupied by the molecules, in addition to the network free energy term (2b). This additional term is of the same form as for an ordinary liquid: it is a function of volume and temperature only, and is independent of the presence of cross-

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†G' is to be distinguished from G in Flory's paper[1] which is defined as νkT.

linkages and of network deformation. The complete expression for the free energy thus becomes

$$A = A^* + \tfrac{1}{2}G'(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{4}$$

It will also be necessary to refer to a set of extension ratios α_1, α_2, α_3 defined with respect to an isotropic state having a volume V equal to the final *strained* volume, the relation between the αs and the λs being of the form

$$\lambda_1 = \alpha_1 (V/V_u)^{1/3} \text{ etc.} \tag{5}$$

Principal stresses

Consider a specimen (containing ν chains) of cubic form in the unstressed state and subjected to normal (tensile) forces f_1, f_2, f_3 on pairs of opposite faces. The corresponding strained dimensions being $V_u^{1/3}\lambda_1$ etc., the area on which the force f_1 acts is $V_u^{2/3}\lambda_2\lambda_3$. Since

$$V/V_u = \lambda_1\lambda_2\lambda_3 \tag{6}$$

the principal *stress* t_1 corresponding to the force f_1 is given by

$$t_1 = f_1/V_u^{2/3}\lambda_2\lambda_3 = f_1\lambda_1 V_u^{1/3}/V \tag{7}$$

The relation between t_1 and λ_1 may be obtained by equating the change in free energy in a further deformation $\delta\lambda_1$ (at constant λ_2, λ_3 and T) to the work done by the applied force. For the latter we have, from the definition of λ_1, together with equation (7)

$$\delta W = f_1 V_u^{1/3}\,\delta\lambda_1 = (t_1 V/\lambda_1)\,\delta\lambda_1 \tag{8}$$

From equation (4) the corresponding change in free energy is

$$\delta A = (\partial A/\partial\lambda_1)\,\delta\lambda_1 = (\partial A^*/\partial\lambda_1 + G'\lambda_1)\,\delta\lambda_1 \tag{9}$$

Since A^* is a function of V (and T) only we have

$$(\partial A^*/\partial\lambda_1)_T = (\partial A^*/\partial V)_T\,(\partial V/\partial\lambda_1) \tag{10}$$

Further, since A^* has the same form as for an ordinary liquid we may write

$$(\partial A^*/\partial V)_T = -p^* \tag{11}$$

where p^* is an effective pressure; $-p^*$ represents that part of the applied stress not borne by the network. Also from equation (6)

$$\partial V/\partial\lambda_1 = V/\lambda_1 \tag{12}$$

Hence equation (9) becomes

$$\delta A = (-p^* V/\lambda_1 + G'\lambda_1)\,\delta\lambda_1 \tag{13}$$

Equating δA to δW, as given by equation (8), we obtain

$$t_1 = -p^* + (G'/V)\,\lambda_1^2 \tag{14a}$$

and similarly

$$t_2 = -p^* + (G'/V)\,\lambda_2^2 \tag{14b}$$

$$t_3 = -p^* + (G'/V)\,\lambda_3^2 \tag{14c}$$

The principal stress *differences* do not contain p^*, i.e.

$$t_1 - t_2 = (G'/V)(\lambda_1^2 - \lambda_2^2) \text{ etc.} \tag{15}$$

while for simple extension, with

$$\lambda_2^2 = \lambda_3^2 = V/V_u\lambda_1 \; ; \; t_2 = t_3 = 0 \tag{16}$$

$$t_1 = (G'/V)\,(\lambda_1^2 - V/V_u\lambda_1) \tag{17}$$

VOLUME CHANGE DUE TO STRESS

Equations (14) above are formally similar to the corresponding stress/strain relations for an incompressible rubber, which are of the form[5]

$$t_1 = p + (G'/V)\,\lambda_1^2 \tag{18}$$

where p is an arbitrary constant, equivalent to a hydrostatic pressure. Equation (18) implies that for an incompressible rubber, for which V is constant, the stresses corresponding to a given state of strain are indeterminate. However, if one of the principal stresses is known (as in simple extension) this determines p and hence also the remaining stresses. In a compressible rubber, on the other hand, the specification of λ_1, λ_2 and λ_3 (and hence of V) automatically fixes p^* and hence uniquely determines the principal stresses.

The relation between p^* and V involves the compressibility K. For the small volume changes with which we are concerned ($\Delta V/V \approx 10^{-4}$) we may assume a linear relation of a form similar to that for a liquid, i.e.

$$p^* = -(1/K)(V - V_1)/V \tag{19}$$

in which V_1 is the volume at which $p^* = 0$. This volume is not the stress-free volume V_u of the crosslinked rubber, but the volume which would be occupied by the uncrosslinked molecules at zero pressure. [This follows from the definition of A^*, from which p^* is derived, see equation (11)]. Unlike V_u, the quantity V_1 is not accessible to direct measurement; its value can, however, be derived from V_u by the application of equations (14) to the *crosslinked* rubber in the stress-free state. For this state $t_1 = t_2 = t_3 = 0$, $\lambda_1 = \lambda_2 = \lambda_3 = 1$ and $V = V_u$. Thus, from equation (14a)

$$-p^* + G'/V_u = 0 \; ; \; p^* = G'/V_u \tag{20}$$

Insertion of this value of p^* into equation (19) then gives

$$V_1 = V_u + KG' \tag{21}$$

Equation (19) may now be used, with this value of V_1, to determine p^* in any other state of strain, i.e.

$$p^* = (V - V_u)/KV + G'/V \tag{22}$$

The resulting principal stresses [equations (14)] may thus be written in the form

$$t_1 = (V - V_u)/KV + (G'/V)(\lambda_1^2 - 1) \tag{23}$$

with corresponding expressions for t_2 and t_3.

Equations (23) etc. relate the principal stresses to the change of volume which accompanies the application of the stress. Alternatively, given the value of the stress, they may be used to calculate the change of volume. This may be illustrated by the case of simple elongation considered below.

Application to simple extension

For a simple extension λ_1, we have $t_2 = t_3 = 0$. Application of the equation for t_2 corresponding to (23) gives (putting $V - V_u = \Delta V$),

$$t_2 = 0 = \Delta V / KV + (G'/V)(\lambda_2^2 - 1)$$

or, from equation (16)

$$\Delta V / V = (KG'/V)(1 - V/V_u\lambda_1) \tag{24}$$

In terms of the extension ratio α_1 defined by equation (5) this becomes

$$\Delta V / V = (KG'/V)\left[1 - (V/V_u)^{2/3}(1/\alpha_1)\right] \tag{25}$$

This may be compared with Flory's expression[1]

$$\Delta V / V = (K_L \nu kT / V)(V/V_0)^{2/3}(1 - 1/\alpha_1) \tag{26}$$

in which K_L is the compressibility at constant length. This is related to K by the equation[1]

$$K_L - 1 = K^{-1} + \nu kT / 2V \tag{27}$$

For typical rubbers the term $\nu kT/2V$ is of the order of 10^{-4} of K^{-1}, hence $K_L \approx K$. The quantity $(V/V_0)^{2/3}$ is by definition equal to $\overline{r_i^2}/\overline{r_0^2}$. Bearing in mind the definition of G' [equation (3)] Flory's expression is equivalent to

$$\Delta V / V = (K_L G'/V)(1 - 1/\alpha_1) \approx (KG'/V)(1 - 1/\alpha_1) \tag{26a}$$

Comparing this with (25), we note that $V/V_u - 1 \longrightarrow 0$ as $\alpha_1 \longrightarrow 1$, and that $V/V_u - 1 \approx 10^{-4}$ at $\alpha_1 = 2{\cdot}0$ (ref. 4). Hence, for practical purposes,

$$1 - (V/V_u)^{2/3}(1/\alpha_1) \approx 1 - 1/\alpha_1$$

and expressions (25) and (26a) are substantially equivalent.

Effect of superimposed hydrostatic pressure

In the preceding analysis the principal stresses t_1, t_2, t_3 and the corresponding forces f_1, f_2, f_3 are the *total* stresses and *total* forces acting. When a superimposed hydrostatic pressure, e.g. the atmospheric pressure, is present, the derivation of the volume change in terms of the forces actually applied (or the corresponding *partial* stresses) requires further examination. The analysis, which is given in the Appendix, shows that, in fact, the results are not significantly affected.

ANISOTROPY OF COMPRESSIBILITY

In the general thermodynamic treatment of the stress/temperature relations for rubbers in simple extension as developed by Gee[2], an important quantity is the anisotropy of compressibility under constant tensile force. Gee assumed as a first approximation that the material remained isotropic with respect to a superimposed hydrostatic pressure, i.e. that the relation between changes of length l and volume V is

$$\frac{V}{l}\left(\frac{\partial l}{\partial V}\right)_f = \left(\frac{\partial \ln l}{\partial \ln V}\right)_f = \frac{1}{3} \tag{28}$$

as for the unstrained state.

On the basis of Flory's theory the anisotropy of compressibility arises solely from the properties of the crosslinked network and may readily be calculated. For simple extension the result obtained by Flory is

$$(\partial \ln l/\partial \ln V)_f = 1/(\alpha_1^3+2) \tag{29}$$

which can be reduced to equation (28) in the limit when $\alpha_1 \longrightarrow 1$.

In the treatment given below, the anisotropy of compressibility is calculated for the case of a pure homogeneous strain of the most general type.

Consider as before a specimen in the form of a cube in the stress-free state which is deformed to dimensions $\lambda_1 V_u^{1/3}$, $\lambda_2 V_u^{1/3}$, $\lambda_3 V_u^{1/3}$ by normal forces f_1, f_2, f_3 acting in the directions of the principal extensions together with a superimposed hydrostatic pressure p. Since the force f_1 acts on an area $V/V_u^{1/3}\lambda_1$, the stress acting in the direction λ_1 is (cf. Appendix).

$$t_1 = f_1\lambda_1 V_u^{1/3}/V - p \tag{30a}$$

and similarly

$$t_2 = f_2\lambda_2 V_u^{1/3}/V - p \tag{30b}$$

whence

$$t_1 - t_2 = (V_u^{1/3}/V)(f_1\lambda_1 - f_2\lambda_2) \tag{31}$$

But from equation (15) the difference of principal stresses is given by

$$t_1 - t_2 = (G'/V)(\lambda_1^2 - \lambda_2^2) \tag{32}$$

Equating the right-hand sides of (31) and (32) we obtain

$$f_1 = f_2\lambda_2/\lambda_1 + G'V_u^{-1/3}(\lambda_1 - \lambda_2^2/\lambda_1) \tag{33}$$

We require the relation between the changes in λ_1 and λ_2 produced by a change in p at constant f_1, f_2 and f_3. We therefore write

$$\mathrm{d}f_1 = (\partial f_1/\partial\lambda_1)_{f_2,f_3,\lambda_2}\mathrm{d}\lambda_1 + (\partial f_1/\partial\lambda_2)_{f_2,f_3,\lambda_1}\mathrm{d}\lambda_2 = 0 \tag{34}$$

From equation (33) we have

$$(\partial f_1/\partial\lambda_1)_{f_2,f_3,\lambda_2} = -f_2\lambda_2/\lambda_1^2 + G'V_u^{-1/3}(1+\lambda_2^2/\lambda_1^2) \tag{35}$$

$$(\partial f_1/\partial\lambda_2)_{f_2,f_3,\lambda_1} = f_2/\lambda_1 - 2G'V_u^{-1/3}\lambda_2/\lambda_1 \tag{36}$$

Hence, from (34) for constant f_1 (as well as constant f_2 and f_3)

$$[(-f_2\lambda_2/\lambda_1^2 + G'V_u^{-1/3}(1+\lambda_2^2/\lambda_1^2)]\,\mathrm{d}\lambda_1 = -(f_2/\lambda_1 - 2G'V_u^{-1/3}\lambda_2/\lambda_1)\,\mathrm{d}\lambda_2$$

which gives, on simplification

$$\left(\frac{\partial\lambda_1}{\partial\lambda_2}\right)_{f_1,f_2,f_3} = \frac{f_2\lambda_1 - 2G'V_u^{-1/3}\lambda_1\lambda_2}{f_2\lambda_2 - G'V_u^{-1/3}(\lambda_1^2+\lambda_2^2)} \tag{37}$$

This, with the corresponding expression for $\partial\lambda_1/\partial\lambda_3$, gives the relative changes in dimensions for variations of p at constant f_1, f_2 and f_3. The change in volume corresponding to a change of pressure $\mathrm{d}p$ is

$$\mathrm{d}V/V = \mathrm{d}\lambda_1/\lambda_1 + \mathrm{d}\lambda_2/\lambda_2 + \mathrm{d}\lambda_3/\lambda_3$$

Hence

$$\frac{\mathrm{d}V}{V} = \left(1 + \frac{\lambda_1}{\lambda_2}\frac{\partial\lambda_2}{\partial\lambda_1} + \frac{\lambda_1}{\lambda_3}\frac{\partial\lambda_3}{\partial\lambda_1}\right)\frac{\mathrm{d}\lambda_1}{\lambda_1} \tag{38}$$

With the help of equations of the type (37) this enables $\partial V/\partial\lambda_1$, etc. to be obtained. The full expressions will not be written out.

Two-dimensional extension

For the particular case when $f_3 = 0$, corresponding to a two-dimensional extension under forces f_1 and f_2, we write the equation for $(\partial\lambda_1/\partial\lambda_3)_{f_1,f_2,f_3}$ corresponding to (37) and put $f_3 = 0$. The result is

$$(\partial\lambda_1/\partial\lambda_3)_{f_1,f_2} = 2\lambda_1\lambda_3/(\lambda_1^2 + \lambda_2^2) \quad (f_3 = 0) \tag{39a}$$

and similarly,

$$(\partial\lambda_2/\partial\lambda_3)_{f_1,f_2} = 2\lambda_2\lambda_3/(\lambda_2^2 + \lambda_3^2) \quad (f_3 = 0) \tag{39b}$$

and therefore

$$(\partial\lambda_1/\partial\lambda_2)_{f_1,f_2} = \lambda_1(\lambda_2^2 + \lambda_3^2)/\{\lambda_2(\lambda_1^2 + \lambda_3^2)\} \quad (f_3 = 0) \tag{39c}$$

Unlike equation (36), these expressions do not involve the forces directly. This is because when $f_3 = 0$ the stress $t_3 = -p$, and the remaining stresses can be directly related to the extension ratios [equations (14)].

If λ_1 and λ_2 are both large, λ_3^2 is small compared with λ_1^2 or λ_2^2. Equation (39c) then gives the approximation

$$(\partial\lambda_1/\partial\lambda_2)_{f_1,f_2} \approx \frac{\lambda_1\lambda_2^2}{\lambda_2\lambda_1^2} \approx \frac{\lambda_2}{\lambda_1} \quad (f_3 = 0) \tag{39d}$$

Simple extension

For simple extension in the direction λ_1, $f_2 = f_3 = 0$ and $\lambda_2^2 = \lambda_3^2 = V/V_u\lambda_1$. Equation (39c) can then be reduced to

$$\left(\frac{\partial\lambda_1}{\partial\lambda_2}\right)_{f_1} = \left(\frac{\partial\lambda_1}{\partial\lambda_3}\right)_{f_1} = \frac{2\lambda_1\lambda_2}{\lambda_1^2 + \lambda_2^2} \tag{40}$$

Thus, from (38)

$$\frac{\mathrm{d}V}{V} = \left[1 + \frac{2\lambda_1}{\lambda_2}\left(\frac{\lambda_1^2 + \lambda_2^2}{2\lambda_1\lambda_2}\right)\right]\frac{\partial\lambda_1}{\lambda_1} = \left(2 + \frac{\lambda_1^2}{\lambda_2^2}\right)\frac{\mathrm{d}\lambda_1}{\lambda_1}$$

With (16) this becomes

$$\frac{\mathrm{d}V}{V} = \left[2 + \lambda_1^3\left(\frac{V_u}{V}\right)\right]\frac{\mathrm{d}\lambda_1}{\lambda_1} = (2 + \alpha_1^3)\frac{\partial\lambda_1}{\lambda_1} \tag{41}$$

from equation (5). This is equivalent to Flory's result [equation (29)].

COMPARISON WITH SWOLLEN INCOMPRESSIBLE RUBBER

An interesting analogy exists between the mechanical properties, and in particular the anisotropy of compressibility, for a slightly compressible dry rubber and the corresponding properties of a rubber swollen to equilibrium in a liquid of low molecular weight. In the treatment of swelling it is customary to assume that the volumes of the rubber and liquid components are additive and independent of applied stress, i.e. for a fixed composition the system is treated as incompressible. If, however, the further condition is introduced that the swollen rubber is in equilibrium with the surrounding liquid, the liquid content becomes a function of the stress, the effect of a hydrostatic pressure, for example, being to reduce the liquid content, i.e. the swollen volume. Under these conditions the swollen rubber is formally analogous to a highly compressible dry rubber.

As in the case of the unswollen rubber, we consider a specimen maintained in a state of pure homogeneous strain, defined by extension ratios λ_1, λ_2, λ_3 referred to the unstrained unswollen state of volume V_u by forces f_1, f_2, f_3.

Stress/strain relations

The total free energy of the system is the sum of two components, of which the first, A_m, represents the free energy of mixing of the liquid and polymer molecules in the uncrosslinked state, while the second, A_e, represents the free energy of network deformation in the combined swelling and straining. Thus

$$A = A_m + \tfrac{1}{2}G'\,(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{42}$$

where G' is defined by (3), as before. Carrying out the analysis in a manner entirely analogous to that given previously, the principal stresses may be expressed by equations of the type

$$t_1 = A_{0m}/V_1 + (G'/V)\lambda_1^2 \tag{43}$$

in which V_1 is the molar volume of the swelling liquid, V is the volume of the swollen rubber and A_{0m} is the *molar* free energy of dilution $\partial A_m/\partial n_0$, where n_0 is the number of moles of liquid in the mixture. The quantity A_{0m}/V_1 is thus the free energy change per unit volume of the liquid component which, assuming additivity of volumes, is equal to $\partial A_m/\partial V$. For A_{0m} it is usual to assume the Flory–Higgins formula[6]

$$A_{0m} = RT\,[\ln(1 - v_2) + v_2 + \chi v_2^2] \tag{44}$$

where v_2 is the volume fraction of rubber (V_u/V) in the swollen state and χ is an interaction parameter whose value depends on the particular rubber and liquid considered. For the present purpose, however, the form of A_{0m} is irrelevant.

Comparison of equation (43) with (14a) shows the formal similarity to the corresponding equation for an unswollen rubber, taking into account compressibility effects. The only difference is the replacement of $-p^*$ by

A_{0m}/V_1. The *differences* of principal stresses, derived from equations of type (43), are given by identical expressions, i.e.

$$t_1 - t_2 = (G'/V)(\lambda_1^2 - \lambda_2^2) \tag{45}$$

Anisotropy of compressibility

As in the case of an unswollen rubber, we now consider the sample subjected to applied forces f_1, f_2, f_3, swollen to equilibrium in a liquid at the hydrostatic pressure p. The stress t_1 will now be the resultant of the contribution due to f_1 and the pressure p. Hence, if V_u is the unstrained unswollen volume

$$t_1 = f_1\lambda_1 V_u^{1/3}/V - p \text{ etc.} \tag{46}$$

The relation between t_1 and f_1 is thus formally identical to that for an unswollen rubber [equation (30a)], and since the principal stress differences are also described by identical relations [cf. (15) and (45)], all the subsequent relations derived from equations (15) and (30) remain valid. Hence the results represented by equations (36) to (41) are equally applicable to the case of a swollen rubber.

It is to be noted that these relations do not involve the absolute values of the dimensional changes for a given change of pressure (or other stress components), which would, of course, be very different in the two cases. They are concerned only with *relative* changes in dimensions. The conclusion that these relative changes are the same for a highly swollen rubber as for a slightly compressible dry rubber is a consequence of the assumption that in both cases we are concerned with the free energy of network deformation, irrespective of the mechanism by which the *volume* of the system is determined. It is this aspect of the problem which is represented mathematically by the identical expressions for the network free energy in equations (4) and (42).

DISCUSSION

It is important to recognize the limitations of the general method of approach used in the present work. Being based on a physical model, the conclusions arrived at do not have the universal validity of a purely thermodynamic analysis of the type given in Gee's original paper[2]. The most significant assumption, in the present context, is that the anisotropy of compressibility is purely a network property. It would be surprising if this were strictly true, particularly at high degrees of orientation, where some degree of anisotropy of intermolecular force fields would be expected to arise. However, the accurate prediction by the network theory of the effects of strain on the degree of swelling[7] suggests that these effects are probably not very important in practice.

APPENDIX

EFFECT OF SUPERIMPOSED HYDROSTATIC PRESSURE

Let us suppose, as before, that f_1, f_2, f_3, are now the actual forces applied, and that p is the added pressure. We will denote by t'_1, t'_2, t'_3 the part of the stress due to the applied forces, while retaining t_1, t_2, t_3 for the total (tensile) stresses. Then

$$t_1 = t'_1 - p \text{ etc.} \tag{46}$$

Equation (23) then gives

$$t'_1 - p = (V - V_u)/KV + (G'/V)(\lambda_1^2 - 1) \tag{47}$$

where, as before, V_u is the volume at zero (total) stress. Introducing the isotropic volume V'_u at the pressure p, we have, from (47), in the absence of other applied forces, i.e. for $t'_1 = 0$

$$-p = \frac{V'_u - V_u}{KV'_u} + \frac{G'}{V'_u}\left[\left(\frac{V'_u}{V_u}\right)^{2/3} - 1\right] \tag{48}$$

For pressures of about one atmosphere $(V'_u - V_u)/V \approx 10^{-4}$, hence we may put

$$(V'_u - V_u)/V'_u \approx (V'_u - V_u)\,V_u \approx (V'_u - V_u)/V$$

and similarly

$$G'/V'_u \approx G'/V$$

Elimination of p between (47) and (48) then gives

$$t'_1 = \frac{V - V'_u}{KV} + \frac{G'}{V}\left[\lambda_1^2 - \left(\frac{V'_u}{V_u}\right)^{2/3}\right] \tag{49}$$

In terms of the extension ration λ'_1 referred to the isotropic state at the pressure p, where

$$\lambda'_1 (V'_u)^{1/3} = \lambda_1 V_u^{1/3}$$

this becomes

$$t'_1 = \frac{V - V'_u}{KV} + \frac{G'}{V}\left(\frac{V'_u}{V_u}\right)^{2/3} (\lambda_1'^2 - 1) \tag{50}$$

The factor $(V'_u/V_u)^{2/3}$ is not significantly different from unity. Hence we may write

$$t'_1 \approx \frac{V - V'_u}{KV} + \frac{G'}{V}(\lambda_1'^2 - 1) \tag{51}$$

This equation is of the same form as equation (23). Thus the relation between the partial stress (calculated as if p were absent) and the change of volume due to the applied forces is, to a close approximation, unaffected by the presence of a hydrostatic pressure.

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