Contribution to a liquid-like theory of rubber elasticity: 2. Existence of a $(\lambda_x\lambda_y + \lambda_y\lambda_z + \lambda_z\lambda_x)$ term*

Edmund A. Di Marzio
National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
(Received 20 May 1993)

We first show that the classical gas-like theory of rubber elasticity is incorrect because the force–extension relation for an individual polymer chain is dependent on the interaction of its chain segments with segments of other chains in its neighbourhood. Two previous attempts by the author to formulate a liquid-like theory are discussed and improved. It is then argued that chain entanglements result in the value of the number of segments N in the expression $f=3kTx/N$ increasing with chain extension x or with increasing force f. The entropic contribution to the free energy of a rubber from this effect is then shown to be given by $B(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$, where B is proportional to kT and to the number of chains per unit volume. In order to facilitate comparison with experiment, the stress–strain equations for simple extension, biaxial extension and for pure shear are displayed for three different choices of strain invariants: those of Rivlin, those of this paper, and those of the localization model of Gaylord, Douglas and McKenna. Comparisons with experiment are discussed.

(Keywords: rubber theory; elastomers; strain energy)

INTRODUCTION

The classical theory of rubber elasticity consists of an analysis on a network of linear polymer chains connected at their two ends to the other chains in a (usually) tetrafunctional manner. Each chain is given a free energy which is a quadratic function of the separation between the ends, and the ends are assumed to move affinely. The theory is a gas-like theory because the segments of each chain are assumed not to interact with the segments of other chains, except for the connection at the ends. The assumption of non-interaction is a poor one in view of the fact that the volume spanned by a chain of N segments varies as $N^{3/2}$ so that (segments of at least) $N^{1/2}$ other chains occupy this same volume. Experimental data are found to deviate systematically from the classical James and Guth expression[1] $F=\rho kT(\lambda_x^2+\lambda_y^2+\lambda_z^2)$. Data for simple extension seem always to fall significantly below the theoretical curve in a plot of force *versus* extension[2]. Clearly then, the classical theory needs improvement.

The author used an extension of the Flory–Huggins theory that evaluates orientation dependent entropy to calculate the change in configurational entropy when stretching a rubber[3]. This orientation dependent packing entropy reduces the force when the rubber is stretched uniaxially but for biaxial stretch there is very little change. Qualitatively, it has just the right behaviour but quantitatively the effect was originally thought to be too small. Subsequently, Tanaka and Allen[4] showed that the problem done self-consistently resulted in an effect twice as large as originally estimated. An attractive feature of these calculations is that they are independent of parameters, the only assumptions being those inherent in the lattice model. However, the effect seems too small to account for the deviations from classical theory. A modification that leads to a much larger effect is to model the N-step polymer as a sequence of K connected freely rotating sticks of aspect ratio N/K. (If the force–length (f–x) relation for a chain of N bonds is $f=3kTx/Nl^2$, where l is the length of a bond, then for a chain of N/C_N rigid rods each of length C_Nl the force–length relation is $f=3kTx/C_NNl^2$. So, for the same force the rigid rod chain will be stretched more. On the other hand it is easy to show that if each chain is stretched to the same value of x then the probability of the bond making an angle θ with the stretch direction is proportional to $\exp(+fC_Nl\cos(\theta)/kT)$ which is the same for both cases. However, even when the distribution of orientation function is the same, the change in packing entropy during stretch can be much greater for the longer rods.) Since the persistence length can be determined by other considerations no new parameters are introduced. This will not be done here because it is only part of the explanation for the deviation. We think it better to gather the various parts before combining them into a total explanation. A separate contribution is the focus of this paper.

Another approach is to model the rubber by considering that each chain is hemmed in by the chains

---

* Presented at 'International Polymer Physics Symposium Honouring Professor John D. Hoffman's 70th Birthday', 15–16 May 1993, Washington, DC, USA

0032-3861/94/09/1819–08

that surround it[5]. One imagines that the surrounding chains and their cross-links form a web or cocoon that constrains the enclosed chain from wandering beyond the confines of the cocoon. This has obvious connections with tube models and the localization model[6,7]. (Tube models, cocoon or web models, slip-ring or hoop models, and localization models are different ways of looking at the one phenomenon; they emphasize different aspects of the problem.) The Gaussian distribution for end-to-end length that characterizes a free chain is replaced by an infinite sum of Gaussians if we replace the web by a rectangular cage and use the method of images (see below). Specifying that the cage dimensions change during stretch results in a correction to the theory of rubber elasticity. The sum can be evaluated numerically. This will not be done here for reasons explained below.

Gao and Weiner, in a series of papers[8–11], argued that the force transmitted to the rest of the network by a single chain is not properly taken into account in the classical theory. The assumption that the total energy stored in a chain is given by $3kTx^2/2Nl^2$ is found to be a gross oversimplification. These papers rely extensively on computer calculations and are consequently hard to verify. The general thrust of their work is, however, obviously correct, as are their qualitative conclusions. The functional form of their equation for simple elongation is different from ours.

Gaylord and Douglas[6,7], Douglas and McKenna[12] and McKenna *et al.*[13–17] have argued for an extra term of the form $(\lambda_x+\lambda_y+\lambda_z)$ based on the basic cocoon picture mentioned above. They determine the change of network chain confinement through an argument emphasizing chain packing. They show that in fitting to the experimental data the contributions from this term can be considerably greater than that from the classical $(\lambda_x^2+\lambda_y^2+\lambda_z^2)$ term. They also stress that one must test rubber theories simultaneously for the three kinds of strain and for their predictions of swelling experiments and of the effects of cross-link density variations in order to have a believable theory. Earlier, Varga had suggested this form based on phenomenological considerations[18]. The work of Edwards and Stockmayer[19] is also relevant.

Tube models[20–25] and slip-ring models[26–29] have been used to model both excluded volume effects and entanglement effects. A relatively recent review by Edwards and Vilgis[30] deserves special mention.

In this paper we will develop an insight as to why the entropy contribution to the total free energy arising from a chain of N monomers tied to the network by its end monomers is not $3kTx^2/2Nl^2$. We will do this by showing how the presence of the chain near a plane surface modifies the stored energy, by showing the equivalence between a configurational and a kinetic view of stored energy and by observing that the chain does not sample all its configurations during the timescale of the experiment.

Next, we replace the chain anchored at its two end points which move affinely, by a chain anchored at its two end points and threaded through a slip-ring: the end points and the slip-ring are assumed to move affinely. This leads naturally to the term $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$. The connection with other slip-ring models is discussed.

We display and develop the stress–strain equations for simple elongation, biaxial stretch and pure shear for three different choices of strain invariants. Comparison with experiment is discussed.

THEORY

Insights into the forces on a single chain

The stress–strain relation for a polymer near a surface. A polymer placed above the $z=0$ plane, which is viewed as an energy neutral barrier to segments being below the plane, has a number of configurations Ps^N given by[31]:

$$P=(2\pi Nl^2/3)^{-3/2}\exp\{[-(z_2-z_1)^2-(x_2-x_1)^2-(y_2-y_1)^2]/(2Nl^2/3)\}-(2\pi Nl^2/3)^{-3/2}\times\exp\{[-(z_2+z_1)^2-(x_2-x_1)^2-(y_2-y_1)^2]/(2Nl^2/3)\} \tag{1}$$

where 1, 2 label the ends, l is the segment or bond length and s measures the configurational freedom of one bond. The reflection principle[32] which was used to derive equation (1) states that the number of walks from 1 to 2 in the presence of a plane boundary is equal to the number of walks from 1 to 2 in the absence of a boundary minus the number of walks from the image of 1 in the plane to 2 in the absence of a boundary. This number is obviously very different from the free chain case. In the limit $z_1\to 0$ we have (dropping the subscript 2 and starting the chain at (0, 0, 0)):

$$P=2\pi l(2\pi Nl^2/3)^{-5/2}z\exp[(-z^2-x^2-y^2)/(2Nl^2/3)] \tag{2}$$

The entropy associated with this chain is:

$$S=k\ln W=k(\ln z-3R^2/2Nl^2) \tag{3}$$

and the associated force is[33]:

$$f=\mathrm{grad}(TS)$$
$$f_z=kT(1/z-3z/Nl^2),\quad f_x=-3x/Nl^2,\quad f_y=-3y/Nl^2 \tag{4}$$

The force is composed of the usual Hookean force which is proportional to the distance between end points, always tending to pull the ends together, plus a force perpendicular to the plane, varying inversely to z and always tending to push the point away from the plane. To obtain further insight into the nature of these forces, imagine the plane plus the one chain tethered to the plane at one end to be isolated from all other matter. The monomer units are constantly bombarding the surface because of Brownian motion. But we know the system cannot accelerate continuously in space so this means the chain is tugging at the surface with a force equal and opposite, on average, to the impulse from Brownian bombardment. This tugging arises from the monomer units bouncing away from the surface and then being decelerated by the inextensible chain. The tension in the chain is certainly not constant and it is different at the two ends.

The energy stored in the stretched chain depends then on the chain end-to-end length as well as on the separation of the end points from the plane. If surfaces are used to represent the confinement of the chain by the other chains in a rubber, then the total stored energy will depend on these surfaces as well as on the end-to-end length of the polymer being confined. A particularly appealing geometry for the cage is to imagine that every chain is within a rectangular parallelepiped, as in *Figure 1*. The method of images can be used to construct

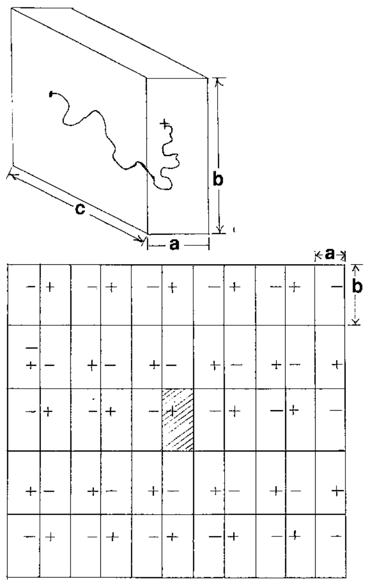

Figure 1 A polymer in a box with adsorbing boundary conditions has a probability P given by a sum of Gaussian sources. Notice that $P=0$ for every vertical and horizontal plane shown as lines in this figure. The $z=$constant planes are treated similarly

the following infinite sum, which gives the probability for the end-to-end distribution for absorbing boundary conditions on the walls:

$$\begin{aligned}P=&[\Sigma(-1)^j(\beta^2/\pi)^{1/2}\exp\{-\beta^2[x_2-(-1)^jx_1-ja]^2\}]\\&\times[\Sigma(-1)^j(\beta^2/\pi)^{1/2}\exp\{-\beta^2[y_2-(-1)^jy_1-jb]^2\}]\\&\times[\Sigma(-1)^j(\beta^2/\pi)^{1/2}\exp\{-\beta^2[z_2-(-1)^jz_1-jc]^2\}]\end{aligned}\tag{5}$$

where $\beta^2=3/2Nl^2$, and the origin of coordinates is at the centre of the parallelepiped and the summation over j in each of the sums is over all real integers. This is a generalization of a formula given previously[5]. See also the work of Gaylord[34–36]. Fourier methods[37] can also be used to give:

$$\begin{aligned}P=&\{(2/a)\Sigma\exp[-(j\pi l/a)^2Nl^2/6]\sin(j\pi x_2/a)\sin(j\pi x_1/a)\}\\&\{(2/b)\Sigma\exp[-(j\pi l/b)^2Nl^2/6]\sin(j\pi x_2/b)\sin(j\pi x_1/b)\}\\&\{(2/c)\Sigma\exp[-(j\pi l/c)^2Nl^2/6]\sin(j\pi x_2/c)\sin(j\pi x_1/c)\}\end{aligned}\tag{6}$$

Either of these two expressions can be used to replace the single Gaussian representing the probability of end-to-end length of a chain in free space. We shall not carry the treatment further because the box dimensions are parameters that could be used to fit the data. If the stress–strain curves had lots of structure, as for example in one of the various spectroscopies, then we might argue that this is a useful procedure, but because the stress–strain curves are rather featureless such a procedure would be tantamount to curve fitting. However, the equations may be useful in assessing the effects of varying cross-links or volume fraction of solvent.

Another way to model the cocoon is to employ a harmonic oscillator potential about the axis of the tube, as was done by Gaylord and Douglas[6,7].

A kinetic versus *phase space view.* In explaining the forces on a chain near a plane surface we *qualitatively* discussed the Brownian motion of monomers impinging on the plane and the resulting tugging by the attached chain end as the segments are restrained by the inextensible chain. Discussing the problem via its kinetics added insight. A simple problem that illustrates *quantitatively* the duality is a trimer held at its two ends so that the only motion is the middle monomer moving about a circle whose centre bisects the straight line connecting the two end monomers and whose plane is perpendicular to this line[38]. If the radius of the circle is r, the separation between ends is x and the bond length $l/2$ so that $r^2=(l/2)^2-(x/2)^2$, then the phase space available to the centre monomer is $2\pi r$. The force f along the x axis is by standard argument:

$$F=-kT\ln(2\pi r),\quad f=-\partial F/\partial x=kTx/(l^2-x^2)\tag{7}$$

We can get this same result by a kinetic argument. The centrifugal force is mv^2/r and we must have:

$$\begin{aligned}f\,\mathrm{d}x=(mv^2/r)\,\mathrm{d}r,\quad \mathrm{d}r/\mathrm{d}x=x/4r,\quad f=(mv^2/r)\,\mathrm{d}r/\mathrm{d}x\\=mv^2x/4r^2=kTx/(l^2-x^2)\end{aligned}\tag{8}$$

The last equality makes use of the equipartition theorem. The above development is strictly analogous to the two ways to calculate the equation of state for an ideal gas: the phase space approach and the kinetic approach. The generalization of the kinetic approach to higher molecular weight has not yet been accomplished, but we can solve the problem approximately. (For an N-segment polymer we imagine the polymer to rotate rigidly about the axis drawn through the end points of the polymer that are fixed in space. We use Kubo's expression[37], which is $f=[2x/(l^2-x^2)](p_\varphi^2/I)=kTx/(l^2-x^2)$, where the second bracketed term is the rotational energy about the axis, I is the moment of inertia, and $l/2$ is the distance to the centre of mass. For very small x we can treat our system as a ring so that $(l/2)^2$ is the square of the radius of gyration of a ring which is $Nl_1^2/12$ where N_1 is the bond segment length. Substituting we obtain $f=3kTx/Nl_1^2$. Although the formula is correct this derivation is approximate because we have not calculated the contributions from the other modes of motion.)

The kinetic approach suggests that the neighbours to the segments of a given chain influence strongly the stress–strain relation since they interfere with the motion of the chain.

Accessibility of phase space. If a monomer unit has say four different locations relative to its preceding segments in the chain, and if the chain length is 100, then we have $4^{100}=1.6\times10^{60}$ distinct conformations, each of which must be sampled in order for statistical mechanics to be applicable. Now if we assume the rather generous sampling rate of 10^{15} per second per monomer then the chain is visiting 10^{17} configurations per second. Since there are 3.156×10^7 s in a year we see that it would take at least 5×10^{35} years for each chain shape to be visited. We can also ask the question: how small would the chain length have to be so that there is a reasonable expectation that the configurations of a chain can be sampled in the timescale of the experiment, which we take to be 1 s? A simple calculation shows that the chain length is less than 28. The problem of accessibility of phase space is common to many statistical mechanics problems[39,40], but the suggestion in the context of rubber elasticity is that perhaps we can obtain an insight into the behaviour of rubber by considering portions of the chain that are less than the full distance between cross-links.

Insights from general phenomenological principles

Stability. One would expect that for infinitesimal strains the strain energy function of an isotropic block of rubber would be subsumed under the general form:

$$F=(\lambda/2)(x_x+y_y+z_z)^2+\mu[x_x^2+y_y^2+z_z^2+(x_y^2+y_z^2+z_x^2)/2] \tag{9}$$

which is the most general form possible for an isotropic material which is both quadratic in the strain and positive definite (see, for example, ref. 41). However, the classical expression for rubber elasticity:

$$F=kTN_c(\lambda_x^2+\lambda_y^2+\lambda_z^2) \tag{10}$$

is neither quadratic in the strain nor is it positive definite. Using:

$$\lambda_x=1+x_x, \quad \lambda_y=1+y_y, \quad \lambda_z=1+z_z \tag{11}$$

and choosing principal axes for the strain we obtain:

$$F/kTN_c=(\lambda_x^2+\lambda_y^2+\lambda_z^2)=x_x^2+y_y^2+z_z^2+2(x_x+y_y+z_z)+3 \tag{12}$$

Dropping the '3', since it can be of no importance for free energy, we see that choice of negative infinitesimal strains gives a free energy that is opposite in sign to that for positive strains. This violates thermodynamic stability requirements. Also, the expression is manifestly not quadratic.

However, if we assume constant volume, as we shall now do, the expression is positive definite. The condition for constant volume is $\lambda_x\lambda_y\lambda_z=1$ or using equation (11):

$$x_x=-(y_y+z_z+y_yz_z)/(1+y_y+z_z+y_yz_z) \tag{13}$$

The condition for constant volume can also be written as:

$$x_x+y_y+z_z=-(x_xy_y+y_yz_z+x_xz_z)-x_xy_yz_z \tag{14}$$

which, when we substitute from equation (13) for x_x on the right-hand side and expand in ascending powers of y_y and z_z, gives:

$$x_x+y_y+z_z=y_y^2+z_z^2+y_yz_z+\text{higher order terms} \tag{15}$$

Now the condition for a quadratic form to be positive definite is that the determinant formed by the coefficients of $Ax^2+Bxy+Cy^2$ be positive; or

$$\begin{vmatrix} A,B & B/2 \\ B/2, & C \end{vmatrix}>0 \tag{16}$$

Since $A=B=C=1$, the value of the determinate is 0.75. So $x_x+y_y+z_z$ is positive definite and therefore from equation (12) so is $(\lambda_x^2+\lambda_y^2+\lambda_z^2)$, provided that we assume constant volume. In like manner we can show that $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$ is positive definite, so all three terms are permissible candidates for free energy insofar as they do not violate stability conditions when constant volume is assumed.

Expansion in strain invariants. Because the unstressed rubber is isotropic, the free energy needs to be a symmetric function of the λs. Any symmetric function of the λs can be expressed as a function of three independent strain invariants. A choice recommended by Rivlin[42] is:

$$\begin{aligned} I_1&=(\lambda_x^2+\lambda_y^2+\lambda_z^2)\\ I_2&=(\lambda_x\lambda_y)^2+(\lambda_y\lambda_z)^2+(\lambda_z\lambda_x)^2\\ I_3&=\lambda_x^2\lambda_y^2\lambda_z^2 \end{aligned} \tag{17}$$

We shall argue for use of the invariants:

$$I'_1=I_1, \quad I'_2=(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x), \quad I'_3=I_3 \tag{18}$$

while Gaylord and Douglas[6,7] and Douglas and McKenna[12] have used I_1, I_3 and

$$I''_2=\lambda_x+\lambda_y+\lambda_z \tag{19}$$

A function of one set of invariants can always be expressed as a function of another set. For example, the relation

$$I_2=(I'_2)^2-2I_3^{1/2}(I_1+2I'_2)^{1/2} \tag{20}$$

allows us to re-express the free energy, which was originally expressed in terms of I_1 and I_2, in terms of the invariants of equation (18). Naturally we would hope to find that the expansion for free energy is a linear combination of I_1 and I'_2 (or I_1 and I_2).

By expanding the free energy as a power series in $\delta\lambda_i$:

$$F=F_0+\partial F/\partial\lambda_i\partial\lambda_i+\partial^2F/\partial\lambda_i\lambda_j\partial\lambda_i\partial\lambda_j \tag{21}$$

and using the constant volume relation $\delta I_3=0$, and the fact that F is symmetric in the λs it is easily shown that the forces are all zero when the λs are each equal to 1 and also that the quadratic term is positive definite.

The stresses in a rubber can easily be calculated in terms of derivatives of the free energy function. Rivlin[42] obtains the equations:

$$p_j=2\lambda_j^2\partial F/\partial I_1-2\lambda_j^{-2}\partial F/\partial I_2-P, \quad j=x,\ y,\ z \tag{22}$$

These three equations plus $\lambda_x\lambda_y\lambda_z=1$ determine the λ_x, λ_y, λ_z in terms of the p_x, p_y, p_z and conversely. P is an undetermined multiplier. (If one minimizes a function F subject to the constraint condition $V=c$ then the value of the undetermined multiplier depends on the specific form of F. That is to say $V=c$ can be substituted into F to give various forms for F and these various forms give different undetermined multipliers. Thus, giving a physical interpretation to an undetermined multiplier is dangerous. The physics of the three equations (22) is obtained by eliminating P. Similar statements apply to equations (23) and (24).)

The analogous equations for the set of equations (18) are:

$$p_j=2\lambda_j^2\partial F/\partial I_1-\lambda_j^{-1}\partial F/\partial I'_2-P', \quad j=x,\ y,\ z \tag{23}$$

while the set of equations (19) gives:

$$p_j=2\lambda_j^2\partial F/\partial I_1-\lambda_j\partial F/\partial I''_2-P'', \quad j=x,\ y,\ z \tag{24}$$

These equations give different expressions for the cases of simple elongation, biaxial stretch and pure shear (equivalent to simple shear).

The appearance of the stress equations depends on which set of invariants we use. For three different sets of invariants we have, for the case of simple elongation:

$$\begin{gathered} \lambda_y=\lambda_z=1/\sqrt{\lambda}, \quad \lambda_x=\lambda, \quad p_y=p_z=0, \quad I_1=\lambda2+2/\lambda,\\ I_3=1 \quad \text{(simple elongation)}\\ p_x=2(\lambda^2-1/\lambda)(\partial F/\partial I_1+\lambda^{-1}\partial F/\partial I_2), \quad I_2=2\lambda+1/\lambda^2 \end{gathered} \tag{25}$$

$$p_x=2(\lambda^2-1/\lambda)\partial F/\partial I_1+(\sqrt{\lambda}-\lambda^{-1})\partial F/\partial I'_2,\quad I'_2=2\sqrt{\lambda}+1/\lambda \tag{26}$$

$$p_x=2(\lambda^2-1/\lambda)\partial F/\partial I_1+(\lambda-\lambda^{-1/2})\partial F/\partial I''_2,\quad I''_2=\lambda+2/\sqrt{\lambda} \tag{27}$$

For pure shear we have

$$\lambda_y=1,\quad \lambda_x=1/\lambda_z,\quad p_z=0,\quad I_1=\lambda^2+1+1/\lambda^2,$$
$$I_3=1\quad \text{(pure shear)}$$

$$p_x=2(\lambda^2-\lambda^{-2})(\partial F/\partial I_1+\partial F/\partial I_2),\quad I_2=\lambda^2+1+1/\lambda^2 \tag{28}$$

$$p_y=2(1-\lambda^{-2})\partial F\partial I_1+(\lambda^2-1)\partial F/\partial I_2 \tag{29}$$

$$p_x=2(\lambda^2-\lambda^{-2})\partial F/\partial I_1+(\lambda-1/\lambda)\partial F/\partial I'_2,\quad I'_2=\lambda+1+1/\lambda \tag{30}$$

$$p_y=2(1-\lambda^{-2})\partial F\partial I_1+(\lambda-1)\partial F/\partial I'_2 \tag{31}$$

$$p_x=2(\lambda^2-\lambda^{-2})\partial F/\partial I_1+(\lambda-1/\lambda)\partial F/\partial I''_2,\quad I''_2=\lambda+1+1/\lambda \tag{32}$$

$$p_y=2(1-\lambda^{-2})\partial F\partial I_1+(1-1/\lambda)\partial F/\partial I''_2 \tag{33}$$

For biaxial stress one could have different stretch ratios, but we will assume:

$$\lambda_x=\lambda_y=\lambda,\quad p_z=0,\quad I_1=2\lambda^2+\lambda^{-4},$$
$$I^3=1\quad \text{(biaxial stretch)}$$

$$p_x=p_y=2(\lambda^2-\lambda^{-4})(\partial F/\partial I_1+\lambda^2\partial F/\partial I_2),\quad I_2=\lambda^4+2\lambda^{-2} \tag{34}$$

$$p_x=p_y=2(\lambda^2-\lambda^{-4})\partial F/\partial I_1+(\lambda^2-\lambda^{-1})\partial F/\partial I_2,$$
$$I'_2=\lambda^2+2\lambda^{-1} \tag{35}$$

$$p_x=p_y=2(\lambda^2-\lambda^{-4})\partial F/\partial I_1+(\lambda^2-\lambda^{-2})\partial F/\partial I_2,$$
$$I''_2=2\lambda+\lambda^{-2} \tag{36}$$

Notice how closely equations (34)–(36) and equations (25)–(27) are related through the transformation $\lambda^2\rightarrow 1/\lambda$.

A free energy which is linear in the first two invariants of equation (17) or of equation (18) or of equation (19) would obey the Valanis–Landel[43] separability condition. Note that equation (30) for pure shear, which is derived from the invariants of equation (18), is identical to equation (32), which is derived from the invariants of equation (19). Thus a free energy that is linear in I_1 and I''_2 cannot be distinguished from a free energy that is linear in I_1 and I''_2 by pure shear measurements of p_x alone. Note that it makes good sense to test these relations for the free energy against experiment since it is known that AI_1+AI_2 does not accurately represent experiments[44,45].

Finally, we do not accept the argument used previously[42] that the free energy needs to be an even function of the λs. Negative λs have no physical meaning.

Derivation of the $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$ term

If we examine the stress–strain curve for simple extension and compression we see that the experiments fall below the theoretical curve in the extension range, but in the compression or biaxial extension range the fit is very good[2]. From equation (4) we see that if the number of chain segments were somehow to increase as we stretched the chain, the forces would be less than the classical value. Is there anything going on within a rubber that can be interpreted as increasing N? *Figure 2* gives five possible ways to increase N as we stretch. The first way is to imagine N_1 segments to be adsorbed in a sphere and N_2 segments to comprise the portion of the chain outside of the sphere ($N_1+N_2=N$). Stretching pulls out some segments from the sphere, increasing the number of segments in the elastic portion of the chain.

This is a disguised form of the zippering–unzippering model used originally to gain insight into the helix–random coil transition in DNA[46]. It can result in constant force as a function of elongation[32]. Higgs and Ball[27] treat a slightly different model in the context of gels. These models are useful for modelling the non-entropic part of the stress–strain curves. The second figure has N_1 chains

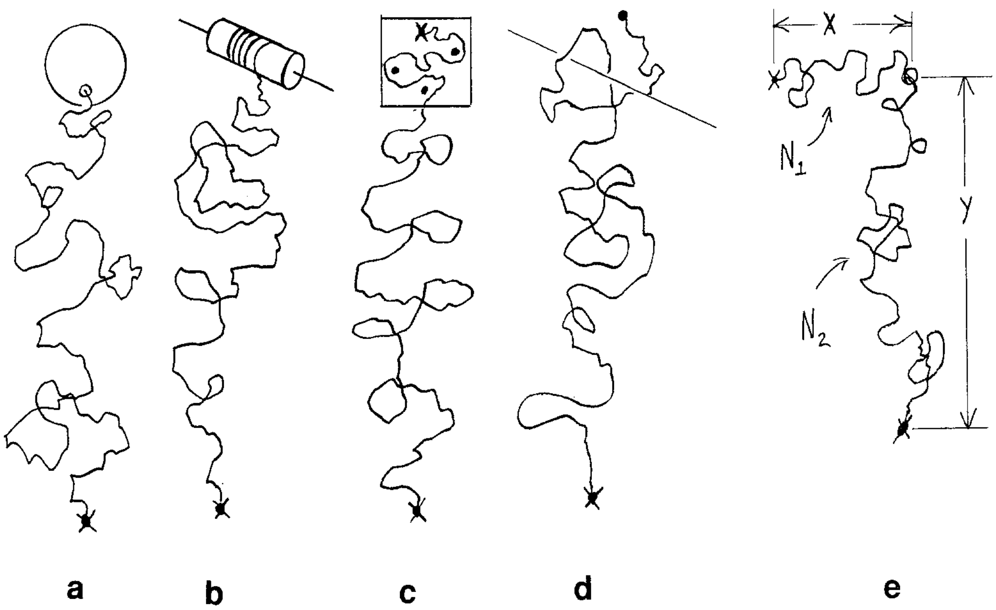

Figure 2 A progression of ideas suggested in (a) to (d) shows that the effective value of the number of segments in a chain increases when the chain is stretched. The model we settle on is that of (e), where the end points and slip-ring move affinely and the numbers of segments in each of the two legs adjust themselves to minimize the chain free energy

wrapped on a spool and as x is increased they are pulled off into the free part of the chain. The spool has a rotary spring constant α. The relevant equations are:

$$f=3kTx/(N_2+\Delta N_1),\quad f=\alpha\Delta N_1 \tag{37}$$

$$\begin{aligned} f&=-\alpha N_2/2+[(\alpha N_2)^2+3kT\alpha x]^{1/2},\\ &\approx 3kTx/N_2l^2-9(kTx)^2/N_2^3\lambda^4\alpha \end{aligned} \tag{38}$$

so that the force is diminished by a pulling out of the segments into the Gaussian portion of the chain. However, there are no hollow spheres or spools in a rubber. *Figure 2b* suggests *Figure 2c*. When the chain end is pulled, the slack that resides about the three pivot points (cylinders perpendicular to the plane of the drawing) is reduced and the value of N_2, the number of segments in the chain between the two xs, is increased. This picture may well be a meaningful characterization of the constraints suffered by a typical polymer chain. In *Figure 2d* the horizontal chain that threads through the loop of the vertical chain represents a more realistic situation, which must occur often considering that there are at least $N^{3/2}-N$ segments from other chains in the vicinity of segments of the one chain. Here, too, the slack around the horizontal chain can increase N_2 during stretching of the vertical chain.

We model these constraints with the model of *Figure 2e*. The xs indicate cross-links and the ring is a slip-ring that allows the values of N_1 and N_2 to change when the cross-links *and* the slip-ring move affinely. One line connecting the cross-link to the slip-rings lies in the x direction, the other line in the y direction. We imagine equal numbers of each of the possible pairs to represent a real isotropic rubber. There are 12 distinct pairs not counting the xx, yy and zz pairs. The force in the x direction equals the force in the y direction. The problem is much like the problem of a rope running over a pulley. If we neglect friction then we have equal tension in both legs of the rope.

$$f_x=3kTx/N_1,\quad f_y=3kTy/N_2,\quad \mathrm{f}_x=f_y,\quad N_1+N_2=1 \tag{39}$$

from which we find that:

$$x/N_1=y/N_2=(x+y)/N \tag{40}$$

Now

$$\begin{aligned}(3kT/N)\,\mathrm{d}F&=f_x\,\mathrm{d}x+f_y\,\mathrm{d}y=(x+y)(\mathrm{d}x+\mathrm{d}y)\\ &=(x+y)\,\mathrm{d}(x+y)=\mathrm{d}(x+y)^2/2\end{aligned} \tag{41}$$

So that

$$F=(3kT/N)(x_0\lambda_x+y_0\lambda_y)^2 \tag{42}$$

x_0 and y_0 being the unstretched values of x and y. Equation (42) obtains when the two legs lie one in the x and one in the y directions. There are 12 distinct pairs not counting the xx, yy and zz pairs. We imagine equal numbers of each of the possible pairs. Averaging over the initial separations we obtain:

$$\begin{aligned}F/kT=\Sigma\{g(r_{0j})[(x_0\lambda_x+y_0\lambda_y)^2+(y_0\lambda_y+z_0\lambda_z)^2\\ +(z_0\lambda_z+x_0\lambda_{xy})^2]\}\end{aligned} \tag{43}$$

where g is the distribution function for the legs. Combining equation (43) with the classical term we see that our final expression for the free energy is:

$$F/kT=A(\lambda_x^2+\lambda_y^2+\lambda_z^2)+B(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)=AI_1+BI_2' \tag{44}$$

One might want to estimate the extent to which the segments are concentrated in the lengthening leg during stretch. As an example, if we assume simple elongation then $x\propto\lambda_x$, $y\propto\lambda_y$, and using equation (40) we obtain:

$$N_1/N=\lambda/(\lambda+1/\sqrt{\lambda}) \tag{45}$$

Thus the model verifies our intuition. However, although equating forces in each leg is permissible for a macroscopic situation, such as in ropes over a pulley, one might question it for the case where the force arises from Brownian fluctuations. To answer this question we discuss the partition function for *Figure 2e*.

$$Q_s=\sum_{N_1+N_2=N}Q(x,N_1)Q(y,N_2) \tag{46}$$

$$Q(x,N_1)=(2\pi N_1l^2)^{-3/2}\exp(-3x^2/2N_1l^2) \tag{47}$$

Figure 3 is a plot of the partition function before summation *versus* N_1 for various values of x and y. When x and y have values near their average dimensions, $\langle x^2\rangle=\langle y^2\rangle=N/3$, the curve is symmetrical and reaches a maximum at $N_1=N/2$, as the bottom-most symmetrical figure shows. For smaller $x=y$ the curve is bipolar, as the top-most figure shows. The asymmetrical curves show that the segments tend to migrate to the longer leg. Thus our intuition is verified also by the more accurate description of equation (46) as well as the more approximate view of equation (40).

The bimodal characteristic of the distribution function for a chain pinned at a middle position was first used to justify the chain-folded model of polymer crystallization[47]. It was argued that the size of an amorphous loop connecting two crystal stems would be very small because the segments preferred being in the amorphous chain end that had not yet incorporated into the crystal. Mansfield[49] and Rieger[50] have more complete discussions of the statistics of pinned chains.

As soon as it is recognized that equation (46) is a convolution, one can generalize it to include any number of slip-rings. Higgs and Ball[27], Aldolf[28] and Kosc[29] have slip-ring theories but they do not reach the same conclusions on the functional form of the stress–strain laws. In an interesting paper, Higgs and Ball[26] obtain a cross term $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$. However, there are three

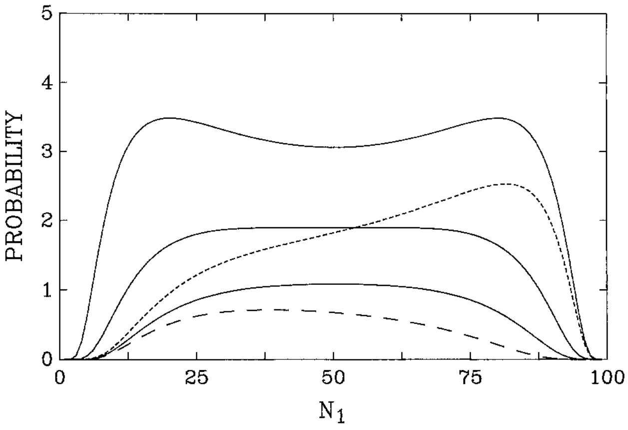

Figure 3 Probability that a chain has N_1 statistical lengths in a leg of length x and 100-N_1 statistical lengths in the leg of length y. For the symmetrical curves starting from the top: $x/l=4$, $y/l=4$; $x/l=4.9$, $y/l=4.9$; $x/l=5.77$, $y/l=5.77$. For the upper asymmetrical curve $x/l=5.77$, $y/l=4$ while for the lower curve $x/l=5.77$, $y/l=7$. For the bimodal curves there is an entropy barrier impeding transfer of segments between the maxima. But stretching can drive the segments into the longer leg, as the asymmetric curves show

difficulties that render the convolution approach less than definitive. First, the integration over N_i is from x_i/l to N, not from 0 to ∞. Second, the system cannot possibly sample all allowed configurations, as discussed in the previous section. Third, the steepest descents method does not treat the bifurcation of the stationary point. Nevertheless, the convolution approach strongly suggests that the important variable of slip-ring theory is $(\lambda_x+\lambda_y+\lambda_z)^2$ and equation (44) is suggested as a first approximation.

DISCUSSION AND CONCLUSION

The gas-like theory of rubber elasticity in which the polymer chains constituting the rubber do not interact with each other except through the cross-links is wrong. It is wrong because the statistics of a polymer chain depend very strongly on the other polymer chains that intertwine with it. Three improvements to the gas-like theory are discussed.

The first improvement is to modify a liquid-like theory proposed previously, which computes the orientation dependent packing entropy. This entropy was shown to contribute a qualitatively correct correction but it was too small. It is observed that the magnitude of the effect will be much larger if the chain is modelled as N/l segments (rigid rods) of length l rather than N segments of unit length.

The second improvement is to modify a theory proposed earlier in which each chain is imagined to be enclosed in a cocoon formed by the chains and cross-links that surround the central chain. This cocoon is modelled as a rectangular parallelepiped rather than as a rectangular cylinder. Equations are given for the statistics of the central chain.

The third improvement arises from entanglements, and is different from the cocoon effect. We arrived at our improvement by assuming that the effective value of the number of segments per chain is increased as the chain is stretched. This effect arises from a picture in which the chain is constrained by slip-rings. The result is equation (44), which contains, in addition to the classical $(\lambda_x^2+\lambda_y^2+\lambda_z^2)$ term, a term linear in $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$. This model has much in common with the work of Higgs and Ball, who treated the slip-ring model and showed that it is not always equivalent to the tube model. A tube model in which one tube is entangled in another tube, as in *Figure 2d* (imagine a tube around each of the two chains), gives results different from non-entangled tubes. In the cocoon model some of the chains can be modelled as the threads of the cocoon, but the chains that are entangled cannot; which of the entangled chains would one place as threads of the cocoon and which as the central chain? So, we must complicate *Figure 1* by imagining (at least) one other chain entangling with the central chain in the manner of *Figure 2d.*

We do not implement all three improvements simultaneously in this paper because we do not know the relative weights of the three contributions. Since the sum of the relative weights adds up to 1, this would introduce two unknown parameters. Additionally, the dimensions of the parallelepiped are two unknown parameters. Thus we would have introduced four parameters to explain relatively featureless stress–strain curves. We think it best to refrain from combining all three effects until we can do it with fewer parameters.

Formulas are given for the behaviour of a rubber in terms of $(\lambda_x^2+\lambda_y^2+\lambda_z^2)$ and $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x)$ viewed as strain invariants when constant volume is assumed; for simple elongation, for biaxial stretch and for pure shear. For comparison purposes, analogous expressions are given for the classical I_1, I_2 invariants and also when the invariants I_1, and $I_2''=(\lambda_x+\lambda_y+\lambda_z)$ are used. It should be noted that we do not accept the statement that the free energy needs to be an even function of λ_x, λ_y, λ_z.

The question naturally arises as to whether the added term results in better fits to experiments. We can compare the three sets of equations for simple elongation and compression. Assuming linearity of free energy in the strain invariants and use of equations (25)–(28) results in:

$$f_1=A_1(\lambda-\lambda^{-2})+B_1(1-\lambda^{-2}),\quad I_2=(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x) \tag{48}$$

$$f_2=A_2(\lambda-\lambda^{-2})+B_2(\lambda^{-1/2}-\lambda^{-2}),\quad I_2'=(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_z\lambda_x) \tag{49}$$

$$f_3=A_3(\lambda-\lambda^{-2})+B_3(1-\lambda^{-3/2}),\quad I_2''=(\lambda_x+\lambda_y+\lambda_z) \tag{50}$$

These are plotted as $[f_j-A_j(\lambda-\lambda^{-2})]/B_j(\lambda-\lambda^{-2})$ in *Figure 4*. Because the curves are so different it seems that we should have no trouble in deciding which curve best fits the data. From the work of Rivlin and Saunders[44,45], and Gumbrell *et al.*[51], which were limited to $0.5<\lambda^{-1}<1$, we see that the data can be represented as a straight line. Only two of the curves in *Figure 4* seem able to fit the data; however, we need data over a wider range of λ to decide. Treloar displays a composite curve as Figure 5.3 of his book on rubber elasticity[2] in which the data cover a range of λ from less than 0.4 to 2. This curve definitely agrees with the classical form in the compressive range. This means that the straight line curve of our *Figure 4* is a poor representation and that the more horizontal curves will represent the data better in this region of λ. Higgs and Gaylord[52] give a detailed comparison of experiment to the various theories. Their general conclusion is that entanglement theories fit the data much better than non-entanglement theories.

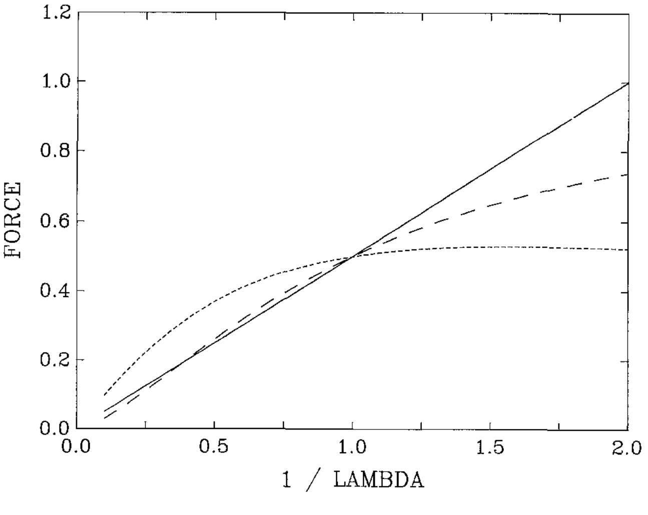

Figure 4 Reduced force *versus* $1/\lambda$ for simple elongation–compression. See text for definition of reduced force: ——, the Mooney version; ···, the localization model; – – –, the formula suggested in the text. The classical formula is represented by a horizontal line

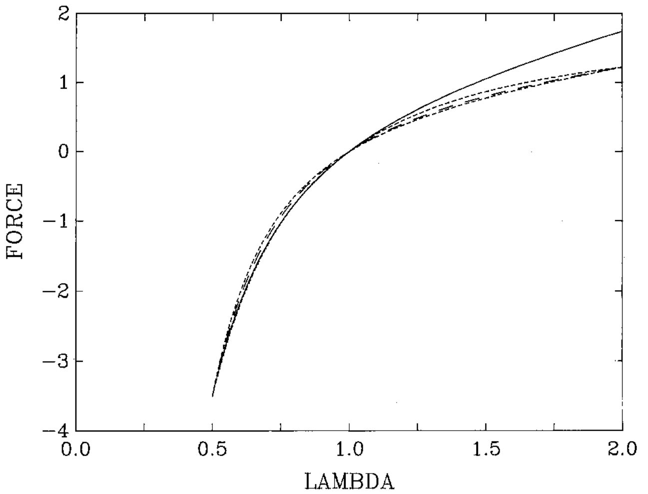

Figure 5 Force *versus* extension: ——, classical curve; – – –, ···, Mooney form (lower curve on right, upper curve on left) and localization model (upper curve on right, lower curve on left). These three curves are sufficiently coincident to adequately represent the data within this range of λ. They suggest that questions of reversibility, relaxation times and subtle experimental questions need to be addressed if one is to favour one over the other

Douglas and McKenna[12] have compared their expression, which is linear in the I_1 and I_2'' invariants, to experiments for simple shear and obtained an excellent fit. This means that our equations also give an excellent fit for this set of experiments, since our equations are virtually the same as theirs for pure shear. To see this, compare equations (30) and (32), which are identical. Equations (31) and (33) differ in the coefficients $(\lambda-1)$ and $(1-1/\lambda)$. If we expand them in $\delta=\lambda-1$ we obtain δ and $(\delta-\delta^2+\delta^3-\cdots)$ which are the same to first order in δ. Thus the equations are very much alike for pure shear and therefore also for simple shear. However, equations (28) and (29) coupled with the assumption that the free energy is linear in I_2 do not do as well.

Our final figure (*Figure 5*) shows how difficult it is to decide on the correct formula with one kind of stress–strain data alone. Since there are two parameters in each of the equations (48)–(50) we can choose them to give the experimental values at $\lambda=0.5$ and $\lambda=2$. The results in *Figure 5* suggest that it is difficult to decide on a best equation. A comparison of theory with measurements made on the same, well-characterized material for the three different modes of strain is needed to decide which of the three expressions best fits experiment. Relaxation effects also need to be considered.

It must be remembered that the three separate improvements by the author treat separate effects and that a real rubber contains these effects in an as yet undeciphered synergism. The local packing term which arises from bond orientation is distinctly different from the combined effect of caging and entanglements. Also, the cocoon or web or cage or tube model is different from the entanglement model in that different aspects of the topology are being considered. The cocoon model does not account for entanglements within the cocoon. So we conclude that a correct theory of rubber elasticity must incorporate all three effects. This view has as its corollary the observation that a good fit of experimental data to a theory that incorporates only one of the effects is probably fortuitous.

REFERENCES

1 James, H. M. and Guth, E. *J. Chem. Phys.* 1943, **11**, 455
2 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Oxford University Press, London, 1949
3 Di Marzio, E. A. *J. Chem. Phys.* 1962, **36**, 1563
4 Tanaka, T. and Allen, G. *Macromolecules* 1977, **10**, 426
5 Di Marzio, E. A. *Am. Chem. Soc. Polym. Prepr.* 1968, **9** (1), 256
6 Gaylord, R. J. and Douglas, J. F. *Polym. Bull.* 1987, **18**, 347
7 Gaylord, R. J. and Douglas, J. F. *Polym. Bull.* 1990, **23**, 529
8 Gao, J. and Weiner, J. H. *Macromolecules* 1989, **22**, 979
9 Gao, J. and Weiner, J. H. *Macromolecules* 1991, **24**, 1519
10 Gao, J. and Weiner, J. H. *Macromolecules* 1991, **24**, 5179
11 Weiner, J. H. and Gao, J. *Macromolecules* 1989, **22**, 4544
12 Douglas, J. F. and McKenna, G. B. *Macromolecules* 1993, **26**, 3282
13 McKenna, G. B., Douglas, J. F., Flynn, K. M. and Chen, Y. *Polymer* 1991, **32**, 2128
14 McKenna, G. B., Flynn, K. M. and Chen, Y.-H. *Polym. Commun.* 1988, **29**, 272
15 McKenna, G. B., Flynn, K. M. and Chen, Y.-H. *Macromolecules* 1989, **22**, 4507
16 McKenna, G. B., Flynn, K. M. and Chen, Y.-H. *Polymer* 1990, **31**, 1937
17 McKenna, G. B., Flynn, K. M. and Chen, Y.-H. in 'Molecular Basis of Polymer Networks' (Eds A. Baumgartner and C. E. Picot), Springer Proceedings in Physics 42, Springer Verlag, Berlin, 1989
18 Varga, O. H. 'Stress–Strain Behavior of Elastic Materials', Interscience, New York, 1966
19 Edwards, S. F. and Stockmayer, W. H. *Proc. R. Soc. Lond. A.* 1973, **332**, 439
20 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. II* 1978, **74**, 1789
21 Marrucci, G. *Rheol. Acta* 1979, **18**, 193
22 Marrucci, G. *Macromolecules* 1981, **14**, 434
23 Graessley, W. W. *Adv. Polym. Sci.* 1982, **46**, 357
24 Ball, R. C., Doi, M., Edwards, S. F. and Warner, M. *Polymer* 1980, **22**, 1010
25 Ball, R. C. and Edwards, S. F. *Macromolecules* 1980, **13**, 748
26 Higgs, P. G. and Ball, R. C. *Europhys. Lett.* 1989, **8** (4), 357
27 Higgs, P. G. and Ball, R. C. 'Physical Networks, Proceedings of the 9th Polymer Network Group Meeting, February 1988' (Eds W. Borchard and S. B. Ross-Murphy), Elsevier, London, 1989
28 Aldolf, D. *Macromolecules* 1988, **21**, 228
29 Kosc, M. *Colloid Polym. Sci.* 1988, **266**, 105
30 Edwards, S. F. and Vilgis, T. A. *Rep. Prog. Phys.* 1988, **51**, 243
31 Di Marzio, E. A. *J. Chem. Phys.* 1965, **42**, 2101
32 Feller, W. 'An Introduction to Probability Theory and its Applications' 2nd Edn, John Wiley and Sons, New York, 1961
33 Di Marzio, E. A. and Guttman, C. M. *J. Chem. Phys.* 1991, **95**, 1189
34 Gaylord, R. *Polym. Eng. Sci.* 1979, **19**, 263
35 Gaylord, R. *Polym. Bull.* 1982, **8**, 325
36 Gaylord, R. *Polym. Bull.* 1983, **9**, 181
37 Churchill, R. 'Fourier Series and Boundary Value Problems', McGraw-Hill, New York, 1941
38 Kubo, R. 'Statistical Mechanics', North-Holland, Amsterdam, 1971, pp. 131, 140
39 Zwanzig, R., Szaboand, A. and Bagchi, B. *Proc. Natl Acad. Sci. USA* 1992, **89**, 20
40 Di Marzio, E. A. and Guttman, C. M. *J. Phys. Chem.* 1989, **93**, 7004
41 Love, A. E. H. 'Treatise on the Mathematical Theory of Elasticity' 4th Edn, Dover Publications, New York, 1944
42 Rivlin, R. S. in 'Rheology, Theory and Applications', Vol. 1, Academic Press, New York, 1956
43 Valanis, K. C. and Landel, R. F. *J. Appl. Phys.* 1967, **28**, 2997
44 Rivlin, R. S. and Saunders, D. W. *Phil. Trans. R. Soc. A* 1951, **243**, 251
45 Rivlin, R. S. and Saunders, D. W. *Trans. Faraday Soc.* 1952, **48**, 200
46 Gibbs, J. H. and Di Marzio, E. A. *J. Chem. Phys.* 1959, **30**, 271
47 Di Marzio, E. A. 1967, **47**, 3451
48 Sanchez, I. C. and Di Marzio, E. A. *J. Chem. Phys.* 1971, **55**, 893
49 Mansfield, M. L. *Macromolecules* 1991, **24**, 3395
50 Rieger, J. *Macromolecules* 1989, **22**, 4540
51 Gumbrell, S. M., Mullins, L. and Rivlin, R. S. *Trans. Faraday Soc.* 1953, **49**, 1495
52 Higgs, P. G. and Gaylord, R. J. *Polymer* 1990, **31**, 71