ELASTICITY AND THERMOELASTICITY OF CROSSLINKED POLYMER NETWORKS

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ABSTRACT

One of the important assumptions used in deriving the statistical theory of rubber elasticity is free energy additivity. This assumption permits one to write the partition function for the polymer network as a product of the molecular partition functions of individual network chains. The consequence of this assumption is that the interchain interactions in the network must be invariant with deformation. Experimentally it has been noted in the literature that the energy contributions to rubber elasticity \( (f_{s}/f) \) determined by thermoelastic measurements are often not invariant, but may either increase or decrease with increasing deformation. It will be shown that if these data are analysed on the basis of temperature coefficients of shear moduli rather than elastic force, this apparent contradiction with the basic tenet of statistical theory is removed. Thus the theory is self-consistent. Consideration of the thermoelastic behaviour from a continuum mechanical point of view, however, shows that \( f_{s}/f \) is invariant only in the special case where the strain energy function (the equivalent of free energy function in statistical theory) is neo-Hookean (Gaussian). If other forms of strain energy functions are used, such as Mooney–Rivlin or Valanis–Landel functions, \( f_{s}/f \) must change as a function of strain. The implication here is that a more complete molecular theory must take into account the fact that interchain forces, in general, do contribute to the elasticity of cross-linked polymer networks.

INTRODUCTION

Perhaps no substances other than rubber-like materials can lay claim to the fact that they at once partake of the characteristics of solids, liquids and gases. They are solid-like in that the crosslinked rubbers have dimensional stability, and that their elastic response at infinitesimal strains is Hookean. They behave like liquids because their coefficients of thermal expansion and their bulk moduli are of the same order of magnitude as those of liquids, indicating that the intermolecular forces in rubbers are similar to those in liquids. They resemble gases in the sense that stresses in deformed rubbers increase with increasing temperature, much as the pressures in compressed gases do. In fact, this gas-like behaviour provided the first hint that rubbery stresses are dominated by entropy rather than energy effects.\(^1\)

The thermodynamic equation of state for gases is

\[
-P = \left( \frac{\partial E}{\partial V} \right)_{T} - T \left( \frac{\partial S}{\partial V} \right)_{T}
\]  

(1)
where $E$ is internal energy, $S$ is entropy, and $P$, $V$ and $T$ are pressure, volume and absolute temperature, respectively. The kinetic theory of ideal gases assumes that the internal energy of the system is invariant with volume change, and the first term on the right-hand side of equation (1) can be neglected. The molecular model of the ideal gas is a collection of point masses in ceaseless random motion. Pressure can thus be calculated by considering the configurational entropy change of these point masses alone.

The recognition of such analogous behaviour in crosslinked rubbers must be considered a milestone in polymer science. The elastic force was computed by neglecting the first term of the following equation:

$$I = \left( \frac{\partial E}{\partial L} \right)_{T,V} - T \left( \frac{\partial S}{\partial L} \right)_{T,V}$$

where $L$ is the sample length. The molecular model for an ideal rubber is that of a collection of random chains. Configuration entropy of the crosslinked network was then computed by adding the configurational entropies of the individual chains. Because of its similarity to the kinetic theory of gases, the molecular theory of rubber elasticity has often been referred to as the kinetic theory of rubber elasticity.

Despite the apparent oversimplification of this model, however, the theory is an outstanding success in providing a foundation for understanding the physical behaviour of macromolecules. Numerous refinements have been provided by later workers. One of the refinements is based on the realization that the energy effects may not be entirely negligible, so that the $(\partial E/\partial L)_{T,V}$ term in equation (2) must be retained, and

$$f = (\partial A/\partial L)_{T,V}$$

where $A$ is the Helmholtz free energy.

In the derivation of the statistical theory of rubber elasticity, the partition function for the crosslinked network is written as

$$Q = \sum n! \prod q_{i}^{n_{i}}/n_{i}!$$

where $n = \sum n_{i}$ and $n_{i}$ is the number of chains with end-to-end distance $r_{i}$. $q_{i}$s are the molecular partition functions of the network chains. The use of equation (4) in obtaining the free energy expression is tantamount to the assumption of free energy additivity, i.e. the free energy of the crosslinked network is the sum of those of individual chains in the network. In order for this basic tenet to be valid, it is necessary that intermolecular interactions between neighbouring chains be unchanged upon deformation, and the energy effects in rubber elasticity must be attributable to intramolecular interactions within the chain. Experimentally, however, there is some evidence in the literature that the energy effects seem to vary with the degree of deformation. This paper proposes to review this apparent contradiction, and to point out how this contradiction can be resolved.

**Thermoelastic Equations**

From equation (2) the energy component of the elastic force is defined as

$$f_{e} = (\partial E/\partial L)_{T,V} = f + T(\partial S/\partial L)_{T,V}$$

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Since from the thermodynamic identity it can be shown that

\[ (\partial S/\partial L)_{T,V} = -(\partial f/\partial T)_{V,L} \]  \hspace{1cm} (6)

one can readily find the relative energy contribution to rubber elasticity:

\[ f_e/f = 1 - (\partial \ln f/\partial \ln T)_{V,L} \]  \hspace{1cm} (7)

In order to determine \( f_e/f \) from equation (7), not only the sample length but also the sample volume must be maintained constant. Thus hydrostatic pressure must be applied during the thermoelastic measurement in order to nullify the volume change due to thermal expansion. The experiment is a difficult one, but has been accomplished by the excellent work of Allen, Price and co-workers.4-6

Because of the difficulty encountered in constant volume experiments, most thermoelastic data were obtained under constant pressure. For these experiments, equation (7) must be transformed to account for the new constraint of constant pressure. We shall now provide a unified derivation for several of these equations. First we note that

\[ (\partial f/\partial T)_{V,L} = (\partial f/\partial T)_{P,L} + (\partial P/\partial T)_{V,L}(\partial f/\partial P)_{T,L} \]  \hspace{1cm} (8)

Inserting it into equation (7), the energy contribution is now

\[ f_e/f = 1 - (\partial \ln f/\partial \ln T)_{P,L} - (\partial P/\partial T)_{V,L}(\partial f/\partial P)_{T,L} \]  \hspace{1cm} (9)

This equation is exact. Again the thermal pressure coefficient \( (\partial P/\partial T)_{V,L} \) and the force–pressure coefficient \( (\partial f/\partial P)_{T,L} \) are not easy to measure. Attempts in this regard have nevertheless been made.4-6

To simplify the experimental difficulties, one can further develop equation (9) by using the following relation:

\[ (\partial f/\partial P)_{T,L} = (\partial V/\partial L)_{T,P} \]

\[ = (\mu L \beta')(\partial f/\partial L)_{T,P} \]  \hspace{1cm} (10)

where

\[ \beta' = - (\partial \ln L/\partial P)_{T,f} \]  \hspace{1cm} (11)

and

\[ \mu = 3(\partial \ln L/\partial \ln V)_{T,f} \]  \hspace{1cm} (12)

\( \mu \) is the Elliott–Lippmann anisotropy factor, which is a measure of linear compressibility anisotropy of deformed solids. At small deformations, however, the material can be considered approximately isotropic and \( \mu = 1 \). Assuming that \( (\partial P/\partial T)_{V,L} \approx \alpha/\beta' \), where \( \alpha \) is the thermal expansion coefficient and \( \beta \) is the isothermal compressibility, one obtains

\[ f_e/f = 1 - (\partial \ln f/\partial \ln T)_{P,L} - (\alpha T/3)(\partial \ln f/\partial \ln L)_{T,P} \]  \hspace{1cm} (13)

which is for infinitesimal strains and was first derived by Gee.10

Since rubbers are highly extensible, the Elliott–Lippmann anisotropy
factor is, in general, not unity. One can express $\mu$ in terms of the equation of state for rubber elasticity obtained by the statistical theory\textsuperscript{11–13}:

$$f = GA_0(\lambda - V/V_0\lambda^2)$$

where

$$G = (NkT/V_0)\langle r^2 \rangle /\langle r^2_f \rangle$$

In equations (14) and (15), $\lambda$ is $L/L_0$; $L_0$, $A_0$ and $V_0$ are the length, cross-sectional area and volume of the rubber at zero force, zero pressure and temperature $T$; $L$ and $V$ are the length and volume at force $f$, pressure $P$ and temperature $T$; $N$ is the number of network chains in the sample; $k$ is the Boltzmann constant; $\langle r^2 \rangle$ is the mean square end-to-end distance of the network chain in volume $V_0$; and $\langle r^2_f \rangle$ is that of the corresponding free chain. From equation (14) it can be readily shown\textsuperscript{8,14,15} that, by setting $V/V_0 = 1$,

$$\frac{\partial f}{\partial L}_{T,P} = \frac{(f/L)(\lambda^3 + 2)}{\lambda^3 - 1}$$

and

$$\mu = \frac{3}{\lambda^3 + 2}$$

Combining equations (9), (10), (16) and (17), one obtains

$$fe/f = 1 - (\partial \ln f / \partial \ln T)_{P,L} - \alpha T / (\lambda^3 - 1)$$

Equation (18) was first derived by Flory, Hoeve and Ciferri\textsuperscript{16}, and has been used by most workers in obtaining values of $fe/f$. 

Figure 1 shows the thermoelastic data carried out under constant pressure for a crosslinked natural rubber\textsuperscript{17}. Equations (9) and (18) were used in computing values of $fe/f$ for elongation ratios up to $\lambda = 2$. These computed values\textsuperscript{7} are shown in Figure 2. In using equation (9), the thermal pressure coefficient and the force-pressure coefficient were taken from the data of Allen, Bianchi and Price\textsuperscript{4}. Also shown in Figure 2 are the constant volume thermoelastic data by Allen et al.\textsuperscript{4}, which were used in calculating $fe/f$ by equation (7). It is apparent from these data that $fe/f$ appears to be a function of strain in the region of low strains, but becomes approximately constant at higher strains.

In applying equation (13), low strain data ($\lambda \leq 1.1$) were used. Figure 3 again shows the strain-dependence of $fe/f$ in the region of low strains\textsuperscript{7}. However, it is clear that the level of strain above which $fe/f$ becomes independent of $\lambda$ is not the same as that indicated in Figure 2. This discrepancy provides a strong hint that the observed strain-dependence, which is contrary to the basic assumption of the statistical theory, may be an experimental artifact rather than an inherent character of rubbers in general.

Equation (18) is most suitable for a more detailed examination of the observed strain-dependence of $fe/f$. In Figure 3 the same infinitesimal thermoelastic data\textsuperscript{7} were calculated by equation (18). The computed values appear to decrease with decreasing strain; in contrast, those computed by equation (13) increase with decreasing strain. Apparently, in the low-strain regions, the data are highly sensitive to experimental errors. Because of the $(\lambda^3 - 1)^{-1}$ term in equation (18), a small error in the determination of elongation ratio can be greatly amplified. In Figure 3 we show the two dotted
Figure 1. Force–temperature data of natural rubber crosslinked with dicumyl peroxide. Numerals indicate the elongation ratios (After Shen, McQuarrie and Jackson17).

Figure 2. Energy contribution to rubber elasticity for natural rubber computed from the data in Figure 1 with equation (9) (solid line) and equation (18) (broken line)7. Solid circles are the constant volume data of Allen, Bianchi and Price4.
curves which were calculated by using $\lambda$s that are factors of 1.001 and 0.999, respectively, of the measured quantities. It can be seen that a change of 0.1 per cent in $\lambda$s produces dramatic deviations from the original data.

One can appreciate the magnifying effect of the inverse third-power term in equation (18) by examining its differential:

$$
\frac{d(f_e/f)}{df} = -\frac{d}{df} \ln f \frac{d}{d\ln T} + 3\lambda^2 \alpha T d\lambda / (\lambda^3 - 1)^2
$$

(19)
The second term in equation (19) is plotted in Figure 4. It can be seen here that, in the region of low strains, a small error \( (d^2 = 0.01) \) can easily distort the calculated values. Of course, if \( d^2 = -0.01 \) were used, a mirror image of the curve in Figure 4 would have been obtained which would have produced negative deviations as noted in Figure 3.

Thus all of the thermoelastic equations shown here are in fact sound on a theoretical basis. However, because of the experimental difficulties encountered in the strain measurements, apparently contradictory data were obtained. The observed \( f_e/f \) dependence on strain is not limited to natural rubber. Figure 5 shows literature data on a number of other elastomers\(^1\)\(^9\)\(^2\)\(^3\). These values were all calculated by equation (18). These observed trends in the strain dependence of the energy contribution to rubber elasticity became a source of concern in that they cast doubt on the validity of the free energy additivity principle used in statistical theory.

**Figure 5.** Energy contributions to rubber elasticity for styrene–butadiene rubber\(^1\)\(^9\), Viton\(^2\)\(^0\), ethylene–propylene rubber\(^2\)\(^1\), elastomeric wool fibre\(^2\)\(^2\) and polybutadiene\(^2\)\(^3\) computed with equation (18).

**VERIFICATION OF THE FREE ENERGY ADDITIVITY PRINCIPLE**

It has been demonstrated in the preceding section that experimental uncertainties in the low-strain region tend to produce the observed strain-dependence of the energy contribution. Equation (18) was particularly amenable for quantitatively displaying this difficulty. However, this difficulty is not limited to equation (18), but is shared with the other constant pressure thermoelastic equations (equations 9 and 13). Essentially in all three equations one is required to determine a small number from the difference of three larger numbers, one of which is particularly sensitive to the strain.

The resolution of this difficulty turns out to be quite simple. We note that the equation of state for rubber elasticity (equation 14) at small strains is

\[
3G = \frac{f/A_0}{\varepsilon}
\]

Equation (20) is obtained by setting \( \lambda = 1 + \varepsilon \) and \( V/V_0 = 1 \) and expanding to first order. The right-hand side of equation (20) is the definition for the
tensile modulus. It is well known that for rubbers the tensile modulus is three times the shear modulus. Therefore \( G \) is the shear modulus of the rubber. In the context of statistical theory, \( G \) is given by equation (15). It is seen to be proportional to \( V^{-1} \), since \( \langle r_0^2 \rangle \) is proportional to \( V^3 \) and all other quantities are independent of volume. But \( V_0 \) is the initial volume of the sample at zero force and zero pressure. Thus the shear modulus is independent of the current volume \( V \), and consequently also independent of any applied hydrostatic pressure. Experimentally, it has been found that the modulus of natural rubber increased by 0.0075 per bar (10^6 dyn/cm^2) of pressure increase\(^24\). It was found in the work of Allen et al.\(^14\) that a maximum of 150 bar is applied in carrying out thermoelastic measurements under constant volume. Thus, even if the modulus of the real rubber is not constant as required by the statistical theory, the error introduced by accepting the independence of modulus of pressure is only about 1 per cent.

The insensitivity of shear modulus to pressure allows us to directly use equation (7). At constant volume and length, the use of equation (14) gives

\[
(\partial \ln f / \partial \ln T)_{V, L} = (d \ln G / d \ln T) + \alpha T/3 \tag{21}
\]

Combining equations (7) and (21), one immediately gets\(^7,18\)

\[
f_f/f = 1 - (d \ln G / d \ln T) - \alpha T/3 \tag{22}
\]

In equation (22) total differentials are used for the temperature coefficient of shear modulus because \( G \) is not subject to the constraints of constant \( V \) and \( L \). Since \( G \) at different temperatures are the initial slopes of stress–strain plots at respective temperatures, all quantities on the right-hand side of equation (22) are independent of strain. Thus equation (22) automatically satisfies the free energy additivity principle so essential to the foundations of the statistical theory of rubber elasticity.

It is of interest to note that in his recent modulus–temperature study of natural rubber cured by varying amounts of dicumyl peroxide, Wood\(^25\) found an empirical relationship for his data that is identical with equation (22) except for the lack of the \(-\alpha T/3\) term. Treloar\(^26\) investigated stress–temperature relations for rubbers in torsion, and was able to derive the following relationship:

\[
f_f/f = 1 - (\partial \ln M / \partial \ln T)_{P, L, \psi} + \alpha T \tag{23}
\]

where \( M \) is the torsional couple and \( \psi \) is the angular displacement.

The temperature coefficient of elastic force at constant pressure and constant length can be shown from equation (14) to be\(^18\)

\[
(\partial \ln f / \partial \ln T)_{P, L} = d \ln G / d \ln T + \frac{1}{3} \alpha T \left( \lambda^3 - 4 \right) / \left( \lambda^3 - 1 \right) \tag{24}
\]

Inserting equation (24) into equation (22), we recover equation (18). Thus equation (22) is in fact consistent with equation (18). The transformation to temperature coefficient of shear modulus from that of the elastic force allows averaging out of the experimental uncertainties over the whole region of strain before calculating the value of \( f_f/f \). Both equation (18) and equation (22) are based on the statistical theory, and are thus subject to the same constraints required by the theory. The form of equation (22) is such,
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however, that it emphasizes the insensitivity of $f_e/f$ to strain and thus satisfies the free energy additivity principle.

Experimentally equation (22) has been applied to data obtained from thermoelastic measurements carried out in tension under the conditions of constant pressure and length$^7$; in compression under the conditions of

<table>
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<th>Polymer</th>
<th>$f_e/f$</th>
<th>Experimental method</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Natural rubber</td>
<td>0.14</td>
<td>Constant $P, L$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>Tension $L$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>Constant $P, f$</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>Tension $L, \psi$</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>Constant $V, L$</td>
<td>30</td>
</tr>
<tr>
<td>Poly(n-butyl acrylate)</td>
<td>-0.35</td>
<td>Constant $P, f$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>-0.36</td>
<td>Tension $L$</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Constant $P, L$</td>
<td>29</td>
</tr>
</tbody>
</table>

constant pressure and length$^7$; in tension under the conditions of constant pressure and load$^{18, 28}$; and in simple shear under the conditions of constant pressure$^{29}$. These are to be compared with data obtained at constant volume in tension$^6$, and at constant pressure in torsion$^{30}$. A summary of these results is given in Table 1.

In thermoelastic measurements under the conditions of constant pressure and length, shear modulus is determined from the slope of a plot of $f/A_0$.

Figure 6. Shear modulus—temperature data of natural rubber crosslinked with dicumyl peroxide carried out under the conditions of constant pressure and length. Open circles: tension$^7$; closed circles: compression$^{27}$.  

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against \((\lambda - 1/\lambda^2)^{-1}\). This has been done for crosslinked natural rubber both in tension\(^7\) and in compression\(^27\), the data of which are illustrated in Figure 6.

The alternative condition of keeping the tension constant and determining the variations of the sample lengths as a function of temperature at constant

\[
\alpha_L = \alpha^0_L - \left(\frac{\lambda^3 - 1}{\lambda^3 + 2}\right) \left(\frac{\ln G}{\text{d}T} + \frac{2\alpha^0}{3}\right)
\]

Figure 7. Plot of the linear thermal expansion coefficients\(^{18}\) of strained natural rubber as a function of \((\lambda^3 - 1)/(\lambda^3 + 2)\) according to equation (25).

Figure 8. Shear modulus–temperature data\(^{29}\) of poly(n-butyl acrylate) determined by simple shear at various shear stresses \((10^6 \text{ dyne/cm}^2)\): \(\circ 0.23; \Box 0.42; \triangle 0.62; \bullet 0.80\).
The direct measurement of shear moduli as a function of temperature has been carried out in simple shear for poly(butyl acrylate). As shown in Figure 8, the data are independent of load (and thus length) over the range of applied constant stresses.

It can be seen in *Table 1* that the energy contributions to rubber elasticity for natural rubber and for poly(butyl acrylate) determined by the above-described techniques and calculated by equation (22) are in good agreement with each other. For natural rubber, the agreement is also good with the values of \( f_e/f \) determined in tension at constant volume (equation 7) and in torsion at constant pressure (equation 23). Thus these data provide an experimental indication of the free energy additivity principle for the statistical theory of rubber elasticity.

**THERMOELASTICITY OF RUBBERS AT LARGE DEFORMATIONS**

The vindication of the free energy additivity principle proves the self-consistency of the statistical theory of rubber elasticity. However, it is well known that the theory is only valid up to about \( \lambda \approx 1.3 \). At large deformations equation (14) cannot be used to describe the stress–strain behaviour of real crosslinked rubbers. Thus it would be instructive to examine the thermoelastic behaviour in the light of the phenomenological theories of finite elastic deformations.

The most often used phenomenological equation of state for rubber elasticity is the Mooney–Rivlin equation:

\[
\frac{f}{A_0} = (2C_1 + 2C_2 V_0/V)(\lambda - V/V_0\lambda^2)
\]

where \( 2C_1 \) and \( 2C_2 \) are constants. At small strains, it can be easily shown that equation (26) reduces to equation (20), and

\[
G = 2C_1 + 2C_2
\]

We can rewrite these constants as

\[
2C_1 = \phi G \\
2C_2 = (1 - \phi)G
\]

where \( \phi \) can be taken as that fraction of the shear modulus attributable to \( 2C_1 \). Equation (26) can now be rewritten as

\[
f = GA_0[\phi + (1 - \phi)V_0/V\lambda](\lambda - V/V_0\lambda^2)
\]

By differentiating equation (29) with respect to temperature and under the conditions of constant volume and length, and inserting the resulting expression into equation (7), the following equation is obtained:

\[
(f_e/f)^{mr} = 1 - (\text{d} \ln G/\text{d} \ln T) - \alpha T/3
\]

\[
- \frac{T}{1 - (1 - \lambda)\phi} \left[ (\lambda - 1) \frac{\text{d} \phi}{\text{d} T} + \frac{4\alpha}{3} (1 - \phi) \right]
\]

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The superscript mr refers to the Mooney–Rivlin equation that was used in arriving at equation (30). Note that the first three terms on the right-hand side of this equation are identical with those of equation (22). The difference between the Mooney–Rivlin expression for energy contribution and the statistical theory expression is the last term in equation (30), which will be designated as $\Delta (f_e/f)^{mr}$:

$$
\Delta (f_e/f)^{mr} = \frac{T}{1 - (1 - \lambda)\phi} \left( \frac{1}{\lambda - 1} \frac{d\phi}{dT} + \frac{4\alpha(1 - \phi)}{3} \right)
$$  \hspace{1cm} (31)

Equation (31) indicates that $f_e/f$ is not constant with $\lambda$ for a rubber obeying the Mooney–Rivlin equation at large deformations.

Another useful phenomenological equation of state for natural rubber was proposed by Valanis and Landel\textsuperscript{35}:

$$
f = G A_0 \left[ 2 \ln \lambda + \left( \frac{V}{V_0} \lambda^3 \right)^\frac{1}{3} \ln \left( \frac{V}{V_0} \lambda \right) \right] \hspace{1cm} (32)
$$

Now by using the same technique as in obtaining equations (22) and (30), it can be shown that, for a rubber obeying the Valanis–Landel equation,

$$
\Delta (f_e/f)^{VL} = - \left( \frac{\alpha T}{3} \right) \left[ 1 - \frac{2\lambda^\frac{1}{3} + 2}{(2\lambda^\frac{1}{3} + 1) \ln \lambda} \right] \hspace{1cm} (33)
$$

Again the energy contribution is expected to depend on strain.

The $\lambda$-dependent portions of $f_e/f$ for natural rubber calculated for both Mooney–Rivlin and Valanis–Landel equations are plotted as a function of the elongation ratio in Figure 9. It is apparent that when an equation of state other than that derived from statistical theory is used, $f_e/f$ will be found to vary as a function of strain. Since the intramolecular interactions in rubber elasticity are presumably due to the rotational energy barriers along the chain backbone\textsuperscript{36}, they should be independent of the applied strain. Thus

![Figure 9. The $\lambda$-dependent terms of energy contributions to rubber elasticity at large deformations](After Shen\textsuperscript{34})

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it follows that the $\lambda$-dependent portion of the relative energy contribution should be attributable to the intermolecular interactions. It should be emphasized that neither the Mooney–Rivlin nor the Valanis–Landel equation was derived on the basis of any molecular model. However, they do conform to the stress–strain behaviour of real rubbers up to very large deformations. The implication is that if a more complete molecular theory is to be found that will more closely describe the elasticity of crosslinked rubbers over a wider range of strains, intermolecular interactions should probably be not neglected in constructing the molecular model and the validity of assuming free energy additivity must be re-evaluated.

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