Macromolecules 1991, *24*, 4152–4156

Temperature-Dependent Potentials in the Theory of Rubber Elasticity

J. J. Hermans

Chemistry Department, University of North Carolina, Chapel Hill, North Carolina 27599

Received January 31, 1991

ABSTRACT: The classical theory of rubber elasticity is briefly reviewed because it has recently been criticized. The new theory that aims to replace it is discussed. It is pointed out that the potential used in this theory to describe the effect of a deformation of the rubber is a potential of average force. As a result, it depends on the temperature. When this is taken into account, the objections raised against the classical theory can be shown to be invalid and the results of the new theory become identical with those of the classical one.

1. Introduction

The classical theory of the elasticity of cross-linked rubber was developed in the early 1940s.[1-6] Reviews can be found in refs 7–10. The theory is based on a model that represents the chain molecule between cross-links as a sequence of freely jointed segments. Freely jointed means that the connections between the segments are like hinges that can be bent freely in all directions, as in a ball-bearing. As a result, the orientations of the segments in space are independent of each other, and they obey random-flight statistics. If the number N of segments is large, a molecule can adopt a large number of conformations and it is permissible to attribute to it an entropy S_m, which is a function of the end-to-end distance R. This is usually done by counting the number of ways in which the N steps in the random flight can be oriented when R is fixed, and the result (in the limit of large N, and $R \ll Nb$) is

$$S_m = -3kR^2/2Nb^2 + \text{constant} \tag{1.1}$$

where k is Boltzmann's constant and b^2 is the average square of the end-to-end vector of a single segment. The distribution is, accordingly

$$\psi_0(\mathbf{R}) = (\text{constant}) \exp(-3R^2/2Nb^2) \tag{1.2}$$

Formally it is also possible to speak of a retractive "force" f between the end points

$$f = -T\partial S_m/\partial R = 3kTR/Nb^2 \tag{1.3}$$

T being the Kelvin temperature. This result says that for large N the freely jointed segments behave as a three-dimensional harmonic spring with force constant $\kappa = 3kT/Nb^2$. The origin of this force constant is purely entropic.

It has recently[11,12] been claimed that the above equations are incorrect. One reason is said[12] to be that the Boltzmann formula works for a discrete set of states but is inappropriate for a set of random configurations that vary continuously. A simple way to answer this objection is to derive eq 1.1 from an argument that treats the orientation angle as a continuous variable. To that end, let us apply the relation between entropy and phase volume. We can omit the momenta because they are not relevant. Then, if θ_i is the angle between the ith segment and the vector $\mathbf{R}$ and $u_i = \cos\theta_i$, the phase volume is

$$\Omega = (2\pi)^N \int_{-1}^{1} du_1 \dots \int_{-1}^{1} du_N \delta\left(\sum_{i=1}^{N} u_i - R/b\right) \tag{1.4}$$

where the δ function serves to restrict the phase space to those values of the u's for which $\sum_i u_i = R/b$. Upon replacement of the δ function by its Fourier transform, the integration over the u's gives

$$\Omega = (\text{constant}) \int_{-\infty}^{\infty} d\omega \exp(-iR\omega/b)(\sin\omega/\omega)^N$$

Using the relation $S = k \ln \Omega$, one finds again eq 1.1 when N is large and $R \ll Nb$; see, for example, Chandrasekhar.[13]

Another objection that has been raised against eqs 1.1–1.3 will be dealt with at the end of section 2.

Equation 1.2 gives the distribution of end-to-end vectors for an assembly of freely dispersed molecules. It is assumed that it is valid also for the cross-linked polymer before it is deformed. When a deformation takes place, a new distribution $\psi(\mathbf{R})$ is generated, and to find the free energy for this distribution, the classical theory assumes that the internal energy does not change. If $\nu_i = \psi(\mathbf{R}_i)\, d^3R_i$ is the number of chains that after the deformation have end-to-end vector $\mathbf{R}_i$, the number of ways in which this distribution can be achieved is $W_1 = \nu!/\Pi_i\nu_i!$. However, for each distribution we must also count the number of ways in which the segments can be oriented, because this number is restricted by the end-to-end distances R_i. In view of the fact that for the N segments in a chain with end-to-end vector $\mathbf{R}_i$ this number is proportional to $\psi_0(R_i)$, it is clear that W_1 must be multiplied by the factor $\Pi_i[\psi_0(R_i)]^{\nu_i}$ so that the total number of configurations is

$$W = (\nu!/\Pi_i\nu_i!)\Pi_i[\psi_0(R_i)]^{\nu_i} \tag{1.5}$$

Taking the logarithm and replacing the sum by an integral

$$S_m = \text{constant} - k\int d^3R\psi(\mathbf{R}) \ln [\psi(\mathbf{R})/\psi_0(R)] \tag{1.6}$$

Our argument here was basically the same as that given by previous authors,[10,14] but it was deemed necessary to briefly repeat it because eq 1.6 has also been criticized. In ref 11 the authors claim that the correct expression is

$$S_m = \text{constant} - k\int d^3R\psi(\mathbf{R}) \ln \psi(\mathbf{R}) \tag{1.7}$$

However, it will be shown in section 3 that this well-known equation for the entropy is not appropriate for the problem in hand.

The deformation to be considered in the present work is a uniaxial extension in the direction of the x axis, but the reasoning can be applied also to other types of deformation. Experience shows that when no solvent is present, the volume of the rubber remains unaltered. This is attributed to the strong interaction between neighboring molecules in the network, and a rigorous theory should from the very beginning take this interaction into account. Such a theory, however, would be quite difficult, and in the classical theory this difficulty is circumvented by

0024-9297/91/2224-4152$02.50/0

simply assuming that the new distribution is the one that is obtained when the cross-links follow the macroscopic dimensions of the test piece ("affine deformation"). If the extension ratio is α, this means that the x-component of the end-to-end vectors is increased in the ratio α while the y and z components are reduced by the factor $\alpha^{1/2}$. The distribution becomes

$$\psi = (\text{constant}) \exp\left[-\frac{3}{2Nb^2}\left(\frac{x^2}{\alpha^2} + \alpha y^2 + \alpha z^2\right)\right] \tag{1.8}$$

where x, y, and z are the components of $\vec{R}$. The constant in eq 1.8 is the same as that in eq 1.2. One clear advantage of the expression 1.8 is its symmetry. In particular, the averages $\langle y\rangle$ and $\langle z\rangle$ remain zero, as they should. We note further that with this distribution

$$\langle x^2\rangle = \alpha^2\langle x^2\rangle_0;\quad \langle y^2\rangle = \alpha^{-1}\langle y^2\rangle_0;\quad \langle z^2\rangle = \alpha^{-1}\langle z^2\rangle_0 \tag{1.9}$$

where the subscript 0 refers to the undeformed state. If now one applies eq 1.6, one finds that the change in the Helmholtz free energy per molecule between cross-links, as a result of the stretching, is

$$\Delta F_{\mathrm{m}} = -T\delta S_{\mathrm{m}} = {}^1/_2kT(\alpha^2 + 2/\alpha - 3) \tag{1.10}$$

The free energy of deformation of the rubber is found by multiplying the result (eq 1.10) by the number of molecules in the sample, and the retractive force on the cross section is obtained by partial differentiation with respect to the length of the test piece.

2. A New Approach to Rubber Elasticity

An interesting new theory has recently been developed by Dahler and co-workers.[11,12] This theory is discussed in the following; the interpretation of the results is quite different from that given by the authors. In their theory it is assumed that the effect of the deformation can be described by introducing a spatially uniform force **E** that acts on the end points of the chain molecules. This adds the term **E**·**R** to the Hamiltonian of the molecule. The procedure is reminiscent of earlier work by the present author,[5] who postulated a distribution $\psi(\mathbf{R})$ = constant $\psi_0(R)\exp(\gamma x/kT)$, where γ was identified with the external force acting on the rubber. In contrast, **E** is not the external force applied to the system but (quoting from ref 11) "the force transmitted to the end of a representative chain by the macroscopic network of chains". It turns out that **E** is complex: some of its components are imaginary. It will also become clear that **E** must be considered as a function of the temperature.

The authors investigate a number of cases in which the polymer molecule can be treated as a sequence of N freely jointed elements. The Hamiltonian $V(r)$ of one of these elements in the undeformed state will in general be a function of the extension r of such an element. It may also depend on other coordinates, but it is assumed that the contribution of these other coordinates is not affected by the deformation. The Hamiltonian of the entire molecule is written as

$$H = \sum_{i=1}^{N} V(r_i) + \mathbf{E}\cdot\mathbf{R} \tag{2.1}$$

and we have

$$\mathbf{R} = \sum_{i=1}^{N} \mathbf{r}_i \tag{2.2}$$

One does not have to consider the contribution of the kinetic energy because it has no effect on the retractive force. It suffices, therefore, to consider the partition function

$$Z = \int d^3r_1 \ldots \int d^3r_N \exp[-\beta\sum_{i=1}^{N} V(r_i) - \beta\mathbf{E}\cdot\mathbf{R}] \tag{2.3}$$

where

$$\beta = 1/kT \tag{2.4}$$

From eq 2.3 we can compute averages such as $\langle x\rangle$ and $\langle x^2\rangle$, namely

$$\langle x\rangle = -kT\,\partial \ln Z/\partial E_x \tag{2.5}$$

$$\langle x^2\rangle = (kT)^2[\partial^2 \ln Z/\partial E_x^{\,2} + (\partial \ln Z/\partial E_x)^2] \tag{2.6}$$

with similar equations for the y and z directions. When the deformation is an extension in the x direction, it follows from symmetry that $E_y = E_z$ and likewise $\langle y\rangle = \langle z\rangle$. As an obvious weakness of the theory, we note that $\langle y\rangle$ and $\langle z\rangle$ are not zero.

The Helmholtz free energy of the system, which consists of a polymer molecule plus the load that serves to stretch it, is $-kT\ln Z$, and of this free energy the amount $\mathbf{E}\cdot\langle\mathbf{R}\rangle$ resides in the load. An obvious way to find the free energy F_{m} of the molecule is, therefore, to simply subtract the contribution $\mathbf{E}\cdot\langle\mathbf{R}\rangle$ of the load:

$$F_{\mathrm{m}} = -kT\ln Z - \mathbf{E}\cdot\langle\mathbf{R}\rangle \tag{2.7}$$

This equation determines F_{m} as a function of E and T. For a comparison with experimental data, it is necessary to find the relation between E and the extension ratio α. This is done on the basis of eq 1.9. The procedure is illustrated by examples in sections 3 and 4, but before doing so we return to eqs 1.1 and 1.2 of the Introduction. In ref 12 the authors consider the partition function Z_{c} for an ensemble of constrained molecules, constrained meaning that the end-to-end vector **R** is fixed. This partition function is

$$Z_{\mathrm{c}} = \int d^3r_1 \ldots \int d^3r_N\,\delta(\mathbf{R} - \sum_{i=1}^{N}\mathbf{r}_i)\exp[-\beta\sum_{i=1}^{N} V(r_i) - \beta\mathbf{E}\cdot\mathbf{R}] \tag{2.8}$$

It is claimed[12] that this does not lead to the equations 1.1–1.3. On the contrary, one can derive these equations from eq 2.8 in a straightforward manner. We observe that in this case the factor $\exp(-\beta\mathbf{E}\cdot\mathbf{R})$ can be placed in front of the integral. Evaluating the free energy and subtracting the term **E**·**R**, we find that the free energy of the constrained molecule is $F_{\mathrm{cm}} = -kT\ln Z_{\mathrm{cm}}$ where

$$Z_{\mathrm{cm}} = \int d^3r_1 \ldots \int d^3r_N\,\delta(\mathbf{R} - \sum_{i=1}^{N}\mathbf{r}_i)\exp[-\beta\sum_{i=1}^{N} V(r_i)] \tag{2.9}$$

Equation 2.9 shows that F_{cm} does not depend explicitly on **E**, only implicitly, because **R** depends on **E**. The same thing is true for eq 1.1. In particular, for the special case of a sequence of N freely jointed segments, eq 2.9 leads to the result (eq 1.4) which for large values of N gives eq 1.1. It is also easily verified that for a sequence of freely jointed harmonic springs with force constant κ (compare section 3), the result (eq 2.9) reduces to $Z_{\mathrm{cm}} = \exp(-\beta\kappa R^2/2N)$, in agreement with the well-known fact that such a sequence is equivalent to a harmonic spring with force constant κ/N. Thus eqs 1.1 and 1.2 are completely vindicated.

3. Harmonic Chain

The harmonic chain[11] is a sequence of N freely jointed harmonic springs: $V(r)$ in eq 2.3 is equal to ${}^1/_2\kappa r^2$. The partition function for a single spring is

$$\zeta = \int \mathrm{d}^3 r \exp[-\beta(^1/_2\kappa r^2 + \vec{\mathbf{E}}\cdot\vec{\mathbf{R}})], \text{ and } Z = z^N \tag{3.1}$$

It follows that $z = z_{E=0} \exp(\beta E^2/2\kappa)$ and hence the free energy of deformation

$$\Delta F = -kT(\ln Z - \ln Z_{E=0}) = -NE^2/2\kappa \tag{3.2}$$

Further, from eqs 2.5 and 2.6

$$\langle \vec{R} \rangle = -N\vec{E}/\kappa;\ \ \langle x^2 \rangle = N(kT/\kappa)(1 + NE_x^{\,2}/\kappa kT);$$
$$\langle y^2 \rangle = N(kT/\kappa)(1 + NE_y^{\,2}/\kappa kT) \tag{3.3}$$

The application of eq 1.9 gives

$$E_x^{\,2} = \kappa kT(\alpha^2 - 1)/N;\ \ E_y^{\,2} = E_z^{\,2} = \kappa kT(1/\alpha - 1)/N \tag{3.4}$$

from which it follows that

$$E^2 = \kappa kT(\alpha^2 + 2/\alpha - 3)/N \tag{3.5}$$

We note in passing that E_y and E_z are imaginary when $\alpha > 1$. This is true also for other models. If, instead of an extension, we would have considered a uniaxial compression in the x direction, we would have found that E_y and E_z are real but E_x is imaginary.

Subtracting the free energy $\vec{\mathbf{E}}\cdot\langle\vec{R}\rangle = -NE^2/\kappa$ of the load from the result eq 3.2, one finds that the free energy of deformation of the rubber molecule is $\Delta F_{\mathrm{m}} = NE^2/2\kappa = {}^1/_2kT(\alpha^2 + 2/\alpha - 3)$, which is identical with the answer eq 1.10 of the classical theory. For the entropy this gives

$$\Delta S_{\mathrm{m}} = -\partial(NE^2)/2\kappa\partial T = -^1/_2k(\alpha^2 + 2/\alpha - 3) \tag{3.6}$$

It follows that the internal energy U_{m} of the molecule has not changed. Altenberger and Dahler[11] ignore the temperature dependence of E and claim that $\Delta U_{\mathrm{m}} = \Delta F_{\mathrm{m}} = NE^2/2\kappa$; i.e., $\Delta S_{\mathrm{m}} = 0$. This is in conflict with eq 3.5 and with the result for ΔF_{m}, and these conflicts are removed when one recognizes that E is a function of the temperature. The matter is related to the problem of entropy touched upon in the introduction; see eq 1.7. This relation is well-known in statistical mechanics, but it must be kept in mind that it is restricted to Hamiltonians that are independent of the temperature. Indeed, suppose that the Hamiltonian of a system contains parameters that are functions of T. This will be true, for example, for electric charges in a medium with a temperature-dependent dielectric constant or for a spring with a temperature-dependent force constant. Even a weight in air is temperature-dependent because the buoyancy is. The partition function for such a system is $Z = \int \mathrm{d}q \exp[-\beta H(q,T)]$ where q stands for the coordinates over which one must integrate. The distribution is given by $\psi = Z^{-1} \exp(-\beta H)$ so that

$$-k\int \mathrm{d}q\, \psi \ln \psi = k \ln Z + \langle H \rangle / T \tag{3.7}$$

On the other hand, $F = -kT \ln Z$, from which it follows that

$$S = -\partial F/\partial T = k \ln Z + \langle H \rangle/T - \partial\langle H \rangle/\partial T \tag{3.8}$$

The results (eqs 3.7 and 3.8) differ by the amount $\partial\langle H \rangle/\partial T$. For the harmonic chain (if κ is independent of T) we have $\partial H/\partial T = \vec{R}\cdot\partial\vec{E}/\partial T$ and thus

$$\partial\langle H \rangle/\partial T = \langle\vec{R}\rangle\cdot(\partial\vec{E}/\partial T) = -\partial(NE^2)/2\kappa\partial T$$

which is exactly equal to the entropy, eq 3.6.

In hindsight it is not difficult to see why E is a function of the temperature. It is true that the origin of E lies in the external force, which stretches the rubber, but its value is, to a large extent, determined by interactions with neighboring molecules. In other words, E is the result of averaging over many configurations in the rubber. The potential $\vec{E}\cdot\vec{R}$ therefore is *a potential of average force*, and it is well-known that such potentials are functions of the temperature.[15] One might argue that the effect of the averaging seems uncommonly large: it reduces the internal energy of deformation to zero! However, also the interaction between neighbors in the rubber is large. It is this interaction that forces us to introduce the condition of constant volume, which is precisely the condition that was used to determine the value of E (see eq 3.4).

4. Freely Jointed Segments

This is the model considered in the classical theory. One way to handle the problem starts with eq 2.3. We can first carry out the integration over $\mathbf{r}_1...\mathbf{r}_N$ under the condition that $\sum_i \mathbf{r}_i = \mathbf{R}$. We know already that this gives

$$Z = \int \mathrm{d}^3R\, \Omega(\mathbf{R}) \exp(-\mathbf{E}\cdot\mathbf{R}/kT) \tag{4.1}$$

where $\Omega(\mathbf{R})$ is the degree of degeneracy for given $\mathbf{R}$ and is determined by eq 1.4. When N is large, $\Omega(\mathbf{R})$ is proportional to $\psi_0(\mathbf{R})$ in eq 1.2, so that the problem has been reduced to that of the harmonic chain, with the understanding that the force constant κ is now a function of the temperature, namely $\kappa = 3kT/Nb^2$. However, there is nothing in eqs 3.1–3.5 that requires κ to be independent of T, and, therefore, when N is large, the result for ΔF_{m} is again eq 1.10.

An alternative treatment[12] of the freely jointed segments is to consider the partition function ζ for a single segment. If the segment has length b and if ϕ is the angle between $\mathbf{r}$ and $\mathbf{E}$

$$\zeta = 2\pi\int_0^{\pi} \mathrm{d}\phi \sin\phi \exp(-\beta Eb\cos\phi) = 4\pi(\sinh X_0)/X_0 \tag{4.2}$$

where

$$X_0 = Eb/kT \tag{4.3}$$

Consequently, for the entire system $Z = (4\pi)^N[(\sinh X_0)/X_0]^N$. Using eq 2.5 to find $\langle\mathbf{R}\rangle$ and evaluating $\mathbf{E}\cdot\langle\mathbf{R}\rangle$, one gets

$$\mathbf{E}\cdot\langle\mathbf{R}\rangle = -kTN(X_0 \coth X_0 - 1) \tag{4.4}$$

so that the free energy of deformation of the molecule is

$$\Delta F_{\mathrm{m}} = kTN(X_0 \coth X_0 - 1) - kTN \ln[(\sinh X_0)/X_0] \tag{4.5}$$

The equation for E is obtained, as before, from the condition eq 1.9. This leads to a relation between E and the extension ratio α. Eliminating E from this relation and eq 4.5, we finally obtain ΔF_{m} as a function of α. This cannot be done in closed form, but we can proceed by successive approximations, expanding in powers of X_0. It is then found that

$$\Delta F_{\mathrm{m}} = {}^1/_2kT(\alpha^2 + 2/\alpha - 3)[1 + O(N^{-1})] \tag{4.6}$$

In other words, in the limit of large N we again recover the result eq 1.10 of the classical theory. This is not demonstrated in detail because we can derive the result eq 4.6 for a much wider class of systems. This is done in the next section.

5. Freely Jointed Elements of an Arbitrary Nature

It will be shown that the result eq 4.6 is valid for any molecule that is made up of freely jointed elements, irrespective of their nature. These elements may be springs, harmonic, or anharmonic,[11] they may be segments or extendible dumbbells,[12] or they may be elements for which the Hamiltonian has more than one minimum,[12] etc. If the partition function ζ for a single element is integrated over the angular coordinates, one obtains

$$\zeta = 4\pi \int_0^\infty \mathrm{d}r\, r^2 \exp[-\beta V(r)] \sinh(\beta E r)/\beta E r \quad (5.1)$$

This shows that ζ is a function of the modulus E of $\vec{E}$. What is more, it is an even function of E, and it is reasonable to assume that $V(r)$ increases sufficiently rapidly at large r to allow a series expansion in powers of E^2. Thus we write

$$\ln Z = N \ln \zeta = N \sum_{j=0}^{\infty} a_j E^{2j} \quad (5.2)$$

where the a's are functions of the temperature. When we apply eq 2.5, we find that

$$\langle \vec{R} \rangle = -kT\vec{E} \sum_{j=1}^{\infty} 2 j a_j E^{2j-2}; \quad \vec{E}\cdot\langle \vec{R} \rangle = -kT \sum_{j=1}^{\infty} 2 j a_j E^{2j} \quad (5.3)$$

It follows that the free energy of the molecule is

$$F_\mathrm{m} = kTN \sum_{j=0}^{\infty} (2j-1) a_j E^{2j}, \quad \text{i.e., } \Delta F_\mathrm{m} = kTN \sum_{j=1}^{\infty} (2j-1) a_j E^{2j} \quad (5.4)$$

Next, from eq 2.6 and the condition eq 1.9

$$[N^2(\sum_{j=1}^{\infty} 2 j a_j E^{2j-2})^2 + N \sum_{j=2}^{\infty} 2j(2j-2) a_j E^{2j-4}] E_x{}^2 + N \sum_{j=1}^{\infty} 2 j a_j E^{2j-2} = \beta^{-2} \langle x^2 \rangle_0 \alpha^2 \quad (5.5)$$

and the same equation for $E_y{}^2$ and $E_z{}^2$, except that the right-hand side becomes $\beta^{-2}\langle y^2 \rangle_0 \alpha^{-1}$. The subscript 0 refers to the polymer before deformation. We find from eq 5.5 that

$$\langle x^2 \rangle_0 = \langle y^2 \rangle_0 = \langle z^2 \rangle_0 = 2Na_1/\beta^2 \quad (5.6)$$

Further, by adding the equations for $E_x{}^2$, $E_y{}^2$, and $E_z{}^2$ to each other, we find the relation between E^2 and α:

$$NE^2(\sum_{j=1}^{\infty} 2 j a_j E^{2j-2})^2 + \sum_{j=2}^{\infty} 2j(2j+1) a_j E^{2j-2} = 2a_1(\alpha^2 + 2/\alpha - 3) \quad (5.7)$$

E^2 can be eliminated from eqs 5.4 and 5.7 by successive approximations; we first consider the terms with E^2 and find

$$E^2 = \frac{1}{2a_1} \frac{\alpha^2 + 2/\alpha - 3}{N + 5a_2/a_1{}^2} = \frac{\alpha^2 + 2/\alpha - 3}{2a_1 N}[1 + O(N^{-1})] \quad (5.8)$$

$$\Delta F_\mathrm{m} = kTNa_1E^2 = {}^1\!/_2 kT(\alpha^2 + 2/\alpha - 3)[1 + O(N^{-1})] \quad (5.9)$$

Note that, to first order, E^2 contains the factor N^{-1}. This has its origin in the term $(\partial \ln Z/\partial E)^2$ in eq 2.6. In the second-order approximation we add to the result eq 5.9 a term of order N^{-1} plus terms of order N^{-2}, N^{-3}, etc. It is easily verified that the term of order N^{-1} inside the brackets of eq 5.9 is a linear function of $\alpha^2 + 2/\alpha$, which means that this term plays a more important role at large than at small degrees of stretch.

We have thus shown that the results of the classical theory are fully confirmed for all polymer molecules that can be represented by a sequence of freely jointed elements, irrespective of the nature of these elements. This does not mean that all polymers are rubberlike. For many polymers the freely jointed elements are not a good model. Moreover, the interaction between the molecules may not allow them to adjust to a deformation of the material without greatly altering the internal energy. Finally, if N is not large, the range of extensions over which the classical result is valid will be small. In the first approximation there is no change in internal energy, but the term of order N^{-1} in the free energy contains the T-dependent coefficients a_1, a_2, and a_3 and this will lead to a nonzero value of ΔU_m.

6. Other Procedures of a Similar Nature

The introduction of the potential $\mathbf{E}\cdot\mathbf{R}$ to describe the effect of a deformation is not free from arbitrariness, and also the use of eq 1.9 is arbitrary. One might for example be inclined to replace eq 1.9 by the condition

$$\langle |x| \rangle = \alpha \langle |x| \rangle_0; \quad \langle |y| \rangle = \alpha^{-1/2} \langle |y| \rangle_0; \quad \langle |z| \rangle = \alpha^{-1/2} \langle |z| \rangle_0 \quad (6.1)$$

but in three-dimensional problems this leads usually to rather unwieldy mathematics. Fortunately for the theory, certain other potentials lead to identical or similar results. A potential of some interest is one in which the force $\mathbf{E}$ is a function of the components x, y, and z of $\mathbf{R}$. The simplest of these would be to assume that E_y and E_z are proportional to y and z, respectively. This gives a potential that contains the term $\mu(y^2 + z^2)$, where μ would then be a function of the temperature. This is the potential that was postulated by Doi and Edwards[16] in their theory of reptation to account for the effect of neighboring molecules in a concentrated solution. Marucci[22] applied this idea in his theory of rubber elasticity. If we make the same assumption for the x component of E, we get a Hamiltonian $V(R) + \lambda x^2 + \mu(y^2 + z^2)$, where λ and μ are functions of T. Let us pursue this for a moment for the sequence of N freely jointed harmonic springs with force constant κ. We know already that for large N this also describes the chain consisting of freely jointed segments. The distribution will be

$$\psi(x,y,z) = Z^{-1} \exp[-\beta({}^1\!/_2\kappa R^2 + \lambda x^2 + \mu y^2 + \mu z^2)] \quad (6.2)$$

with

$$Z = \int \mathrm{d}^3R \exp[-\beta({}^1\!/_2\kappa R^2 + \lambda x^2 + \mu y^2 + \mu z^2)] \quad (6.3)$$

One determines λ and μ from the condition eq 1.9, as explained in the previous sections; the result for the free energy of deformation is again eq 1.10. However, we can also take a shortcut, because from the condition eq 1.9 it follows immediately that the distribution eq 6.2 can be written

$$\psi = Z^{-1} \exp[-c(x^2/\alpha^2 + \alpha y^2 + \alpha z^2)] \quad (6.4)$$

with

$$c = \alpha^2 \beta({}^1\!/_2\kappa + \lambda) = (\beta/\alpha)({}^1\!/_2\kappa + \mu) \quad (6.5)$$

In this case λ and μ remain real. The distribution eq 6.4

was also assumed in the classical theory, so that eq 1.10 follows at once. It may also be noted in passing that the gaussian distribution (eq 6.4) has an additional advantage, namely that the averages of $|x|^n$ and $|y|^n$ have the property

$$\langle|x|^n\rangle = \alpha^n\langle|x|^n\rangle_0; \quad \langle|y|^n\rangle = \alpha^{-n/2}\langle|y|^n\rangle_0 \quad \text{for all } n$$

For $n = 1$ this is eq 6.1. It is not difficult to show that also somewhat different potentials may be used. In other words, many theories of this type lead to similar results. They also have in common two serious shortcomings: the topology of the network and the existence of entanglements are completely ignored, and the only way in which these theories account for the interaction of the molecules with their surroundings is by adding a constraint to the volume of the rubber. Some of the attempts to correct for these effects can be found in refs 17–25. Another important correction concerns the correlation between the orientations of elements that are close enough to each other to interact; see, for example, refs 22–25. All such effects, however, fall outside the scope of the present article.

Acknowledgment. I am grateful to E. T. Samulski and M. L. Berkowitz (Chapel Hill, NC) for helpful discussions and encouragement.

References and Notes

(1) Kuhn, W.; Grün, F. *Kolloid Z.* **1942**, *101*, 248.
(2) Wall, F. T. *J. Chem. Phys.* **1942**, *10*, 485; **1943**, *11*, 527.
(3) Treloar, L. R. G. *Trans. Faraday Soc.* **1943**, *39*, 36, 241.
(4) James, H. M.; Guth, E. *J. Chem. Phys.* **1943**, *11*, 455; *J. Appl. Phys.* 1944, *15*, 294.
(5) Hermans, J. J. *Kolloid Z.* **1943**, *103*, 209; *J. Colloid Sci.* **1946**, *1*, 235.
(6) Flory, P. J.; Wall, F. T. *J. Chem. Phys.* **1951**, *19*, 1435.
(7) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 11.
(8) Vol'kenshtein, M. V. In *Configurational Statistics of Polymer Chains*; Interscience: New York, 1963; Chapter 8.
(9) Smith, K. J. In *Polymer Science*; Jenkins, A. D., Ed.; North Holland: Amsterdam, The Netherlands, 1972; Chapter 5.
(10) Hill, T. L. In *An Introduction to Statistical Thermodynamics*; Dover: New York, 1986; Chapter 21.
(11) Altenberger, A. R.; Dahler, J. S. *J. Chem. Phys.* **1990**, *92*, 3100.
(12) Altenberger, A. R.; Rosa, E., Jr.; Dahler, J. S. Manuscript kindly made available to the author.
(13) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(14) Kuhn, W.; Grün, F. *J. Polym. Sci.* **1946**, *1*, 183.
(15) Hill, T. L. In Reference 10, Chapter 19, p 349.
(16) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, 1802.
(17) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(18) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(19) Gaylord, R. J.; Lohse, D. J. *J. Chem. Phys.* **1976**, *65*, 2779.
(20) Ball, R. C.; Doi, M.; Edwards, S. F.; Warner, M. *Polymer* **1981**, *22*, 1010.
(21) Staverman, A. J. *Adv. Polym. Sci.* **1982**, *44*, 73.
(22) Marrucci, G. *Macromolecules* **1981**, *14*, 434.
(23) Kovac, J.; Crabb, C. C. *Macromolecules* **1986**, *19*, 1744.
(24) Ullman, R. *Macromolecules* **1986**, *19*, 1748.
(25) Adolf, D. *Macromolecules* **1988**, *21*, 228.
(26) de Gennes, P.-G. *C. R. Acad. Sci. B* **1975**, *281*, 101.
(27) Tanaka, T.; Allen, G. *Macromolecules* **1977**, *10*, 426.
(28) Deloche, B.; Samulski, E. T. *Macromolecules* **1981**, *14*, 575; **1988**, *21*, 3107.
(29) Erman, B.; Bahar, I.; Kloszkowski, A.; Mark, J. E. *Macromolecules* **1990**, *23*, 5335, 5341.