chain ends are free. Doi and Edwards[5,20] introduce in this context hypothetical phantom forces, which act upon the end points of the chain. This leads in a first approximation to the picture of a chain, with its first and last monomer being fixed.

In conclusion, I have shown that even the simplest approach to the conformational statistics of a polymer chain, namely, the simulation of the real chain by a Gaussian random walk, bears some unexpected subtleties, which can be discovered in a model where the restriction of phase space available to the polymer is realized in a specific way.

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Concept of Intrinsic Chain Stress in Rubber Elasticity

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ABSTRACT: The concept of the entropic axial force exerted by a long-chain molecule loses its clear-cut physical significance, in a dense system, in the presence of inter- and intrachain noncovalent interactions. In order to generalize this concept, it is shown by means of the virial stress formula that the macroscopic stress tensor in a network may be expressed as a sum of individual chain stress contributions. When the individual chain stress tensor is referred to a local coordinate system, with $\bar{x}_1$ in the chain vector direction, we obtain the intrinsic chain stress tensor, $\bar{\chi}_{rs}$. Under reasonable physical assumptions, the tensor $\bar{\chi}_{rs}$ is cylindrical with only $\bar{\chi}_{11}$ and $\bar{\chi}_{22} = \bar{\chi}_{33}$ as nonzero components. The axial component, $\bar{\chi}_{11}$, may be used to define an effective axial force associated with the chain, while the radial components, $\bar{\chi}_{22} = \bar{\chi}_{33}$, represent the effect of noncovalent chain–chain interactions. These concepts are employed in calculations for the affine uniaxial deformation of a simple tetrafunctional network model. It is found that the interchain noncovalent contribution to the stress is nonhydrostatic in the deformed network and varies with deformation due to the variation in chain orientation. In these model calculations these effects lead to departures from the usual Gaussian chain models, which, in a Mooney–Rivlin-type plot, show qualitative similarity to that observed experimentally.

1. Introduction

If we consider the collection of atoms forming a network of a rubberlike solid, we can identify two principal types of atomic interactions: the covalent interactions responsible for the long-chain molecules and the noncovalent interactions active between pairs of atoms of the same chain or of different chains. There are also important rotational potentials producing energy barriers to rotations about bonds, but we do not consider them in this paper.

In the earlier treatments[1] of rubber elasticity, the covalent and noncovalent interactions are regarded as operating on two completely decoupled systems. The covalently bonded chains are treated as entropic springs in tension. The two-body noncovalent interactions, since they are spherically symmetric, are regarded as capable of producing only a hydrostatic or isotropic contribution to the state of stress in the system, whether it is in its undeformed reference state or in a deformed state. The physical picture that results from this decoupling is that of a network of entropic springs immersed in an incompressible liquid, with no direct interaction between the two systems; there is only indirect coupling through the stress boundary conditions.

In several recent papers[2–6] we have been examining this assumption of decoupled systems by means of the computer simulation of atomistic models of polymer melts and networks. We have found two significant modes of direct coupling between the two types of interactions:[5] (i) The noncovalent interactions produce a significant change in the mean force in the covalent bonds. (ii) The covalent structure causes directional screening of the noncovalent interactions so that the latter make a nonhydrostatic contribution to the stress in the system.

These two coupling mechanisms occur on the atomic scale. In this paper, we present some theoretical considerations underlying a third mechanism, which operates on

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the chain or molecular level. It is based on a recasting of the virial stress formula to exhibit the stress in a network in terms of a sum of stress contributions from the individual chains of the system. This concept of a chain stress, developed in section 2, is a generalization of the usual treatments of rubber elasticity in which only the axial force of the chain is considered. We also introduce in section 2 the concept of intrinsic chain stress; this is obtained by referring the chain stress for a particular chain in the network to a local coordinate system that has one of its axes in the chain vector direction. On the basis of some reasonable physical assumptions, presented in section 3, we conclude that the intrinsic stress tensor is cylindrical and a function only of the end-to-end distance of the chain. This concept is then applied, in section 3, to a simple network model whose characteristics are chosen to facilitate computation but still serve to demonstrate the effect of the change in chain orientation upon deformation. These calculations reveal that this chain orientation change introduces a softening mechanism in the uniaxial extension of the model. The physical significance of these results is discussed in section 4.

2. Concept of Chain Stress

Virial Stress Formula. The starting point of our discussion is the classical virial theorem, which provides an expression for the macroscopic equilibrium state of stress in a collection of interacting atoms at temperature T confined to a volume v. For the case in which all interactions are through pair potentials, it takes the form[2]

$$vt_{ij} = -n_t kT\delta_{ij} + \sum_{\alpha} \langle (r^\alpha)^{-1} u'_\alpha(r^\alpha) r_i^\alpha r_j^\alpha \rangle \qquad (2.1)$$

where t_{ij}, $i, j = 1, 2, 3$, are the components of the stress tensor, force per unit area, referred to a rectangular Cartesian coordinate system x_i; n_t is the number of atoms free to undergo thermal motion; δ_{ij} is the Kronecker delta; α ranges over all pairs of atoms; $\mathbf{r}^\alpha$ is the vector displacement between the α pair with components r_i^α; $r^\alpha = |\mathbf{r}^\alpha|$; $u_\alpha(r^\alpha)$ is the pair potential acting between the α pair; $u'_\alpha = \mathrm{d}u_\alpha/\mathrm{d}r^\alpha$; and brackets denote long-time averages.

Atomic Level Stress. By dividing any pair interaction in eq 2.1 equally between each of the atoms in the pair, the virial formula can be written as a sum over all of the atoms of the system in the form

$$vt_{ij}/kT = \sum_{\beta} \langle \sigma_{ij}(\beta) \rangle \qquad (2.2)$$

where

$$\sigma_{ij}(\beta) = -\delta_{ij} + \frac{1}{2kT} \sum_{\alpha(\beta)} (r^\alpha)^{-1} u'_\alpha(r^\alpha) r_i^\alpha r_j^\alpha \qquad (2.3)$$

with the sum ranging over all interacting pairs to which the β atom belongs. (If β corresponds to an atom that is not free to undergo thermal motion, e.g., if it is a fixed node in a network, then the term $-\delta_{ij}$ is omitted in eq 2.3.)

If we wish to treat chain models with valence angle restrictions and with rotational potentials, it is necessary to generalize the virial theorem accordingly. It is still possible to write it in the form of eq 2.2, although, of course, the definition of $\sigma_{ij}(\beta)$ changes.[7]

The quantity vt_{ij}/kT is nondimensional and extensive (since it is proportional to the system volume) and we term it the extensive stress factor.[8] Then $\langle \sigma_{ij}(\beta) \rangle$ is the contribution that atom β makes to the extensive stress factor and is termed the atomic level stress. The atomic level stress is studied further in ref 6 for systems of chains with valence angle constraints. There we refer the tensor $\sigma_{ij}(\beta)$ to a local coordinate system that maintains a fixed orientation to the covalent bond structure attached to atom β; this leads to what we term the intrinsic atomic level stress.

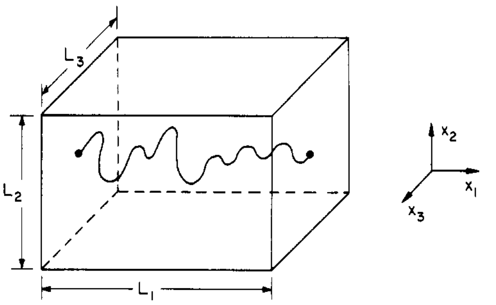

Figure 1. Schematic of a long-chain molecule confined to a box with ends fixed in faces perpendicular to the x_1 axis.

Chain Stress. As a simplification we now restrict attention to networks of chains in which the junctions are fixed; that is, the junctions or nodes are treated as atoms that interact with the other atoms of the system, but they do not engage in thermal motion. A macroscopic affine deformation of the network is accomplished by applying this deformation to its junctions.

We now consider the contribution to the extensive stress made by each chain of the network and we write eq 2.2 as

$$vt_{ij}/kT = \sum_{\gamma} \chi_{ij}(\gamma) \qquad (2.4)$$

where

$$\chi_{ij}(\gamma) = \sum_{\beta(\gamma)} \langle \sigma_{ij}(\beta) \rangle$$

with the sum carried out over all the atoms $\beta(\gamma)$ belonging to chain γ. Terms $\langle \sigma_{ij}(\beta) \rangle$ corresponding to a junction at which several chains meet are assigned in equal proportions to these chains.

We term $\chi_{ij}(\gamma)$ the chain stress. It is the contribution to the extensive stress factor that is made by the γ chain.

Single Chain in a Box. In order to gain some familiarity with the chain stress concept, we consider a single chain in a box of dimensions L_1, L_2, and L_3 in the x_1, x_2, and x_3 directions respectively, with the chain-end atoms fixed in the centers of the faces perpendicular to the x_1 direction, Figure 1. Let $L_2 = L_3$ and suppose first that $L_2 \gg L_1$ and $L_2 \gg S$, the fully extended length of the chain. Under these conditions, the chain atoms can interact only with the faces of the container that are perpendicular to x_1 so that the only nonzero stress component is

$$t_{11} = f/L_2L_3 \qquad (2.5)$$

where f is the force in the x_1 direction exerted by the chain on the face perpendicular to the x_1 direction. It then follows from eq 2.4 that

$$vt_{11}/kT = fL_1/kT = \chi_{11} \qquad (2.6)$$

We next consider the case in which $L_2 = L_3$ is sufficiently small so that atoms of the chain interact with all of the walls of the container. By symmetry, $t_{ij} = 0$ for $i \neq j$, but t_{11}, $t_{22} = t_{33}$ will be non-zero and, from eq 2.4, corresponding statements apply to χ_{ij}.

Network. We turn now to a cross-linked network of chains in which the nodes do not undergo thermal motion, Figure 2. As we have seen in the previous example, for an isolated chain in a box with an end-to-end vector in the x_1 direction, the chain stress component χ_{11} is proportional to the axial force f exerted by the chain. In order to introduce the corresponding concept of the axial force $f(\gamma)$ exerted by the γ chain into the formulation for the network, it is convenient therefore to refer its chain stress to

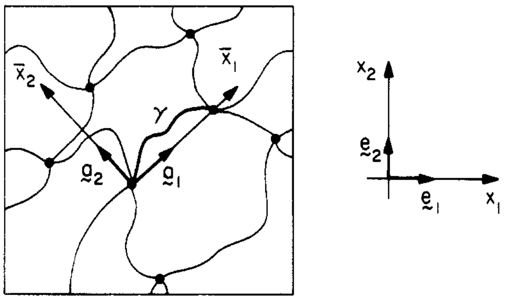

Figure 2. Local coordinate system $\bar{x}_i(\gamma)$ with unit base vectors $\mathbf{a}_i(\gamma)$ used to define intrinsic stress $\bar{\chi}_{rs}(\gamma)$ for chain γ. $\bar{x}_1(\gamma)$ is taken in the direction of the end-to-end chain vector, with $\bar{x}_2(\gamma)$, $\bar{x}_3(\gamma)$ in arbitrary orthogonal directions.

a local Cartesian coordinate system $\bar{x}_j(\gamma)$ with $\bar{x}_1(\gamma)$ in the direction of the end-to-end vector of the γ chain and with $\bar{x}_2(\gamma)$, $\bar{x}_3(\gamma)$ in a plane perpendicular to $\bar{x}_1(\gamma)$, Figure 2. We briefly recall here the appropriate transformation laws. Let $\mathbf{e}_i$ be a set of unit vectors in the x_i coordinate directions (the laboratory frame) and let $\mathbf{a}_j(\gamma)$ be a set of unit vectors in the $\bar{x}_j(\gamma)$ directions. Then any vector $\mathbf{f}$ can be written in terms of components with respect to either frame as $\mathbf{f} = f_i\mathbf{e}_i = \bar{f}_j\mathbf{a}_j$, where we are adopting throughout the summation convention with respect to repeated latin indices, i.e.

$$\mathbf{f} = f_i\mathbf{e}_i \triangleq \sum_{i=1}^{3} f_i\mathbf{e}_i \tag{2.7}$$

and the convention that overhead bars (e.g., $\bar{f}_j$) denote components with respect to the local frame $\mathbf{a}_j$. The vector components with respect to the two frames are related as

$$f_i = \bar{f}_j\mathbf{a}_j\cdot\mathbf{e}_i = \bar{f}_j a_{ji} \tag{2.8}$$

where $a_{ji}(\gamma) = \mathbf{a}_j(\gamma)\cdot\mathbf{e}_i$ with inverse relation

$$\bar{f}_j = f_i a_{ij}^{-1} \tag{2.9}$$

with $a_{ij}^{-1}(\gamma) = \mathbf{e}_i\cdot\mathbf{a}_j(\gamma) = a_{ji}(\gamma)$. Similarly, the chain stress can be expressed in terms of components with respect to either frame as $\chi(\gamma) = \chi_{ij}\mathbf{e}_i\mathbf{e}_j = \bar{\chi}_{rs}\mathbf{a}_r\mathbf{a}_s$ with the tensor components related as

$$\chi_{ij}(\gamma) = \bar{\chi}_{rs}(\gamma)a_{ri}a_{sj} \tag{2.10}$$

$$\bar{\chi}_{rs}(\gamma) = \chi_{ij}(\gamma)a_{ir}^{-1}a_{js}^{-1} \tag{2.11}$$

with $a_{ri} = a_{ri}(\gamma) = \mathbf{a}_r(\gamma)\cdot\mathbf{e}_i$ as above. We refer to the components $\bar{\chi}_{rs}$ as intrinsic chain stresses in analogy to the intrinsic atomic level stresses introduced in ref 6. We may then rewrite eq 2.4 with the aid of eq 2.10 in the form

$$vt_{ij}/kT = \sum_{\gamma}\bar{\chi}_{rs}(\gamma)a_{ri}a_{sj} \tag{2.12}$$

This expression for the extensive stress factor in terms of intrinsic chain stresses is rigorously correct only for networks in which the nodes are not subject to thermal motion, the case to which we are restricting attention in this paper. If the nodes are in thermal motion, then χ_{ij}, $\bar{\chi}_{rs}$, and a_{ri} are all fluctuating quantities and eq 2.12 is replaced by

$$vt_{ij}/kT = \sum_{\gamma}\langle\chi_{ij}(\gamma)\rangle = \sum_{\gamma}\langle\bar{\chi}_{rs}(\gamma)a_{ri}a_{sj}\rangle \tag{2.13}$$

We regard the tensor $\bar{\chi}_{rs}(\gamma)$, together with the orientation of chain γ, as the fundamental mode of description of that chain's contribution to the macroscopic stress in the network. In order to make contact with treatments that give primacy to the axial force exerted by a chain, it is convenient to define the effective axial force $f(\gamma)$ associated with the γ chain by means of a relation analogous to eq 2.6

$$f(\gamma) = kT\bar{\chi}_{11}(\gamma)/\rho(\gamma) \tag{2.14}$$

where $\rho(\gamma)$ is the end-to-end distance of the γ chain. However, in the presence of both inter- and intrachain noncovalent interactions, it is important to emphasize that we can no longer visualize the axial force $f(\gamma)$ as simply transmitted through the covalent bonds of the γ chain since, as we have observed,[3,5,6] the covalent and noncovalent interactions are strongly coupled on the atomic level.

Gaussian Network. We next present a derivation based on eq 2.12 of the elementary formula for the stress t_{11} in the uniaxial deformation of a network. That is, we are considering the deformation of a macroscopic body formed from the network in which a cube with faces perpendicular to the x_1, x_2, and x_3 axes is subject to a stress t_{11} on the faces perpendicular to the x_1 axis, while the transverse faces perpendicular to the x_2 and x_3 axes are maintained free of stress, $t_{22} = t_{33} = 0$. Since the body is macroscopically homogeneous, the macroscopic stress tensor t_{ij} is constant throughout the body with t_{11} the only nonzero stress component. Let $\mathbf{R}(\gamma)$, with components $R_i(\gamma)$, be the end-to-end vector of chain γ before deformation, with the length of this vector denoted by $R(\gamma) = |\mathbf{R}(\gamma)|$. The network is subjected to an affine deformation at constant volume corresponding to an elongation λ in the x_1 direction. Then, after deformation, the components of the end-to-end vector of chain γ are $\lambda R_1(\gamma)$, $\lambda^{-1/2}R_2(\gamma)$, $\lambda^{-1/2}R_3(\gamma)$ and its length is $\rho(\gamma)$, with $\rho^2 = \lambda^2R_1^2 + \lambda^{-1}R_2^2 + \lambda^{-1}R_3^2$. It follows that in the deformed state

$$a_{11}(\gamma) = \lambda R_1(\gamma)/\rho(\gamma); \quad a_{12} = \lambda^{-1/2}R_2(\gamma)/\rho(\gamma); \quad a_{13} = \lambda^{-1/2}R_3(\gamma)/\rho(\gamma) \tag{2.15}$$

Let $R_0^2(\gamma)$ be the mean-square end-to-end distance of the γ chain when it is free of force, i.e., with one end free. By the assumption that all chains are Gaussian and putting aside the caveat after eq 2.14, the axial force $f(\gamma)$ of the γ chain is

$$f(\gamma) = 3kT\rho(\gamma)/R_0^2(\gamma) \tag{2.16}$$

Because of the constant volume assumption the mean stress or pressure p in the deformed system is not determined from the molecular theory but by the imposed stress boundary conditions. In the elementary Gaussian theory this pressure p is regarded as the sole manifestation of any noncovalent interactions in the system. The deviatoric stress (i.e., the difference between the total and mean stress) is taken as due only to the axial force $f(\gamma)$. In terms of the intrinsic chain stress concept, this is equivalent to treating explicitly only the component $\bar{\chi}_{11}$ of the tensor $\bar{\chi}_{rs}$ and assuming that the other components together give rise to a hydrostatic pressure p, so that

$$vt_{ij}/kT = \sum_{\gamma}\bar{\chi}_{11}a_{1i}a_{1j} - p\delta_{ij} \tag{2.17}$$

From eq 2.14 and 2.16, we see that for a Gaussian chain

$$\bar{\chi}_{11}(\gamma) = 3\rho^2(\gamma)/R_0^2(\gamma) \tag{2.18}$$

Furthermore, for uniaxial extension in the x_1 direction, t_{11} is the only nonzero stress component. Therefore, writing eq 2.17 for t_{11} and for $t_{22} = 0$ and eliminating p lead to the equation

$$\frac{vt_{11}}{kT} = \sum_{\gamma}\bar{\chi}_{11}(\gamma)(a_{11}^2 - a_{12}^2) = 3\lambda^2\sum_{\gamma}\frac{R_1^2(\gamma)}{R_0^2(\gamma)} - 3\lambda^{-1}\sum_{\gamma}\frac{R_2^2(\gamma)}{R_0^2(\gamma)} \tag{2.19}$$

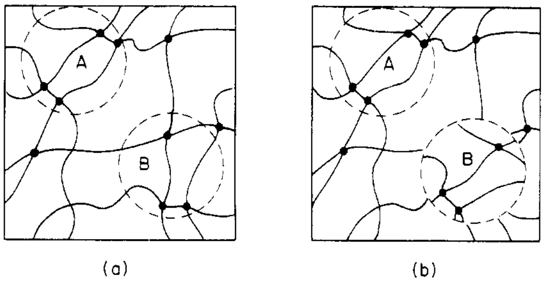

Figure 3. Schematic of a cross-linked network. (a) Chains A and B have equal end-to-end distances but nonparallel end-to-end chain vectors. Circles represent spheres enclosing portions of the network with which chains A and B are in noncovalent interaction. (b) Chain B, together with its interacting sphere, has been rotated so that end-to-end chain vectors are parallel.

where we have used eq 2.15 and 2.18.

Consider the sum

$$\sum_\gamma \frac{R_1^2(\gamma)}{R_0^2(\gamma)} = \sum_\gamma \frac{R_1^2(\gamma)}{R^2(\gamma)}\,\frac{R^2(\gamma)}{R_0^2(\gamma)} = \nu v\left[\frac{R_1^2}{R^2}\right]\left[\frac{R^2}{R_0^2}\right] \qquad (2.20)$$

where, in the last form of the equation, ν is the number of chains per unit volume, brackets indicate averages over the network, and we have assumed that chain vector length and orientation are uncorrelated. A similar calculation can be made for the second sum in eq 2.19. It follows from the isotropy of the network in the stress-free reference configuration that

$$\left[\frac{R_1^2}{R^2}\right] = \left[\frac{R_2^2}{R^2}\right] = \left[\frac{R_3^2}{R^2}\right] = \frac{1}{3} \qquad (2.21)$$

Substitution of eq 2.20 and 2.21 into eq 2.19 then leads to the usual result[9]

$$t_{11} = \nu kT\left[\frac{R^2}{R_0^2}\right](\lambda^2 - \lambda^{-1}) \qquad (2.22)$$

for the stress due to uniaxial extension based on the affine deformation of a Gaussian network.

3. Equivalent Chain Stress Assumption

In this section we use the chain stress concept in order to reexamine the usual assumption that the noncovalent interactions in a rubberlike system make only a hydrostatic contribution to the stress.

Consider a cross-linked network with fixed nodes and two chains A and B with the same end-to-end distance ρ but with different orientations, Figure 3a. Each chain interacts with some portion of the surrounding network, shown schematically as enclosed in a sphere. We now make the assumption that if the sphere containing chain B were rotated so that both chains A and B had the same orientation, as well as end-to-end distance, Figure 3b, then both chains would make the same contribution to the extensive stress factor, vt_{ij}/kT; i.e., after rotation, $\chi_{ij}(\mathrm{A}) = \chi_{ij}(\mathrm{B})$. An equivalent statement of this assumption, which refers only to the original configuration in Figure 3a, is $\bar\chi_{rs}(\mathrm{A}) = \bar\chi_{rs}(\mathrm{B})$, where the bars denote intrinsic chain stress components. Since chains A and B are alike only in terms of having the same end-to-end distance ρ, the final form of this assumption is that for a given network, $\bar\chi_{rs} = \bar\chi_{rs}(\rho)$; the intrinsic stress contribution of any chain is a function only of its end-to-end distance ρ.

It is clear that this assumption cannot apply strictly to a particular pair of chains A and B, since their immediate surroundings may differ somewhat as to monomer density, junction density, etc. Rather the assumption is being made in some averaging or mean-field sense and regards the effective environment of chains A and B as homogeneous and isotropic. Accordingly, we add to the assumption the statement that the only nonzero components of $\bar\chi_{rs}$ are $\bar\chi_{11}$ and $\bar\chi_{22} = \bar\chi_{33}$; i.e., $\bar\chi_{rs}$ are the components of a cylindrical tensor with $\bar\chi_{11}$ its axial component and $\bar\chi_{22} = \bar\chi_{33}$ its radial component. As we have seen in our previous discussion of a single chain confined in a box and its generalization to a chain in a network subject to noncovalent interactions, it is natural to relate the component $\bar\chi_{11}(\gamma)$ to the effective axial force $f(\gamma)$ associated with the γ chain, as in eq 2.14, and to regard the radial component $\bar\chi_{22} = \bar\chi_{33}$ as due to the interaction of the chain with it surroundings, in this case to the noncovalent interactions of the chain with the surrounding network.

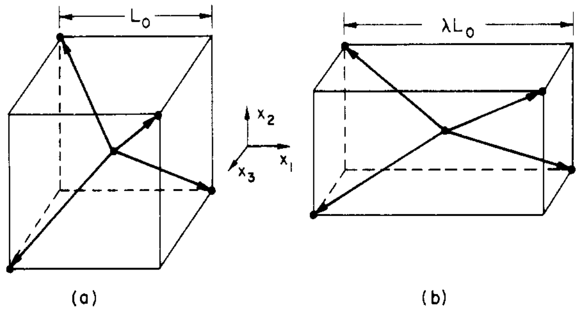

Figure 4. Basic cell of the four-chain model with a fixed, tetrafunctional node at center. Shown are end-to-end chain vectors. (a) In the reference, stress-free state, all chain vectors have components with respect to the x_i system of equal magnitude, $|R_1| = |R_2| = |R_3|$. (b) When subjected to a uniaxial, constant-volume deformation, the magnitudes of these components become $|\lambda R_1|$, $|\lambda^{-1/2}R_2| = |\lambda^{-1/2}R_3|$.

With the aid of the equivalent chain stress assumption, eq 2.12 can be rewritten in the following form for the diagonal stress components t_{11}, t_{22}, and t_{33}:

$$vt_{11}/kT = \sum_\gamma \bar\chi_{11}(\rho_\gamma)a_{11}^2(\gamma) + \sum_\gamma \bar\chi_{22}(\rho_\gamma)(1 - a_{11}^2(\gamma))$$

$$vt_{22}/kT = \sum_\gamma \bar\chi_{11}(\rho_\gamma)a_{12}^2(\gamma) + \sum_\gamma \bar\chi_{22}(\rho_\gamma)(1 - a_{12}^2(\gamma))$$

$$vt_{33}/kT = \sum_\gamma \bar\chi_{11}(\rho_\gamma)a_{13}^2(\gamma) + \sum_\gamma \bar\chi_{22}(\rho_\gamma)(1 - a_{13}^2(\gamma)) \qquad (3.1)$$

In putting the equations in this form, we have used the assumption that $\bar\chi_{11}$ and $\bar\chi_{22} = \bar\chi_{33}$ are the only nonzero components of $\bar\chi_{rs}$ and the relation $a_{ri}a_{rj} = \delta_{ij}$.

The second term in each of eq 3.1 represents the contribution of the noncovalent chain–chain interaction since, in the absence of the latter, $\bar\chi_{22} = \bar\chi_{33} \equiv 0$. In order to draw firm conclusions regarding the character of these contributions, it is necessary to specify the nature of the network. Here we consider only a model network for which the calculations are particularly simple.

Model Network. We treat a model network that, in the stress-free reference configuration, has end-to-end chain vectors **R** with components R_i such that $|R_1| = |R_2| = |R_3|$ for all chains. We may model such a network by placing tetrafunctional nodes at the centers of like-oriented cubes, Figure 4, but we do not make use in our calculations of the precise nodal structure of the network. Under uniaxial constant-volume deformation in the x_1 direction, we then find from eq 2.15 that

$$a_{11}^2 = \lambda^2(\lambda^2 + 2\lambda^{-1})^{-1};\quad a_{12}^2 = a_{13}^2 = (\lambda^3 + 2)^{-1} \qquad (3.2)$$

for all chains. Furthermore, $\bar\chi_{11}$ and $\bar\chi_{22}$ have the same values for all chains, since their length $\rho(\gamma) = (\lambda^2 +$

$2\lambda^{-1})^{1/2}|R_1|$ is the same for all chains. We can then rewrite eq 3.1 in the form

$$\begin{aligned} t_{11}/\nu kT &= \bar{\chi}_{11}a_{11}^2 + \bar{\chi}_{22}(1 - a_{11}^2) \\ t_{22}/\nu kT &= \bar{\chi}_{11}a_{12}^2 + \bar{\chi}_{22}(1 - a_{12}^2) \\ t_{33}/\nu kT &= \bar{\chi}_{11}a_{13}^2 + \bar{\chi}_{22}(1 - a_{13}^2) \end{aligned} \tag{3.3}$$

where ν is the number of chains per unit volume. It is now clear from eq 3.2 and 3.3 that for this model network, the noncovalent interchain contribution to the stress (the second terms in eq 3.3) is nonhydrostatic for $\lambda \neq 1$.

For uniaxial deformation in the x_1 direction, the second and third equations of (3.3) are equivalent. From the boundary conditions $t_{22} = t_{33} = 0$ we may then determine $\bar{\chi}_{22}$ in terms of $\bar{\chi}_{11}$ as

$$\bar{\chi}_{22} = \frac{-\bar{\chi}_{11}a_{12}^2}{1 - a_{12}^2} \tag{3.4}$$

or, if we substitute from eq 3.2

$$\bar{\chi}_{22} = \frac{-\bar{\chi}_{11}}{\lambda^3 + 1} \tag{3.5}$$

By substitution of eq 3.4 into the first equation of (3.3), we find

$$t_{11}/\nu kT = \bar{\chi}_{11}\left(\frac{a_{11}^2 - a_{12}^2}{1 - a_{12}^2}\right) \tag{3.6}$$

(We may compare eq 3.6 with the first form of eq 2.19, derived on the assumption that the noncovalent interchain contribution is hydrostatic, which for the present model takes the form $t_{11}/\nu kT = \bar{\chi}_{11}(a_{11}^2 - a_{12}^2)$.)

By use of eq 3.2, eq 3.6 takes the form

$$\frac{t_{11}}{\nu kT} = \bar{\chi}_{11}\left(\frac{\lambda^3 - 1}{\lambda^3 + 1}\right) \tag{3.7}$$

If all of the chains are Gaussian, then $\bar{\chi}_{11} = 3\rho^2/R_0^2$ from eq 2.18, with

$$\rho^2 = R_1^2(\lambda^2 + 2\lambda^{-1})$$

then eq 3.7 takes the form

$$t_{11} = \nu kT\left(\frac{R^2}{R_0^2}\right)(\lambda^2 - \lambda^{-1})\left(1 + \frac{1}{\lambda^3 + 1}\right) \tag{3.8}$$

with $R^2 = 3R_1^2$; this may be compared with the usual expression for an affinely deformed Gaussian network, eq 2.22. It is seen that the explicit inclusion of interchain interactions for this model through the agency of the terms $\bar{\chi}_{22} = \bar{\chi}_{33}$ introduces a multiplicative factor $1 + (\lambda^3 + 1)^{-1}$, which has a 2-fold effect relative to the usual result. (i) At $\lambda = 1$ the effective front factor or equivalent shear modulus is increased by a factor of $^3/_2$. (ii) The additional multiplying factor decreases with increasing λ and thus produces a softening effect at higher strains.

In order to examine the behavior of this model in a Mooney–Rivlin type of plot, we define a reduced stress t^*_{11} by the relation

$$t^*_{11} = t_{11}/\nu kT\left(\frac{R^2}{R^0}\right)(\lambda^2 - \lambda^{-1}) = \left(1 + \frac{1}{\lambda^3 + 1}\right) \tag{3.9}$$

and show the behavior of t^*_{11} as a function of λ^{-1} in Figure 5. While the model is too simplified to make quantitative comparison significant, it is of interest to note that it produces the usual qualitative features found experimentally.

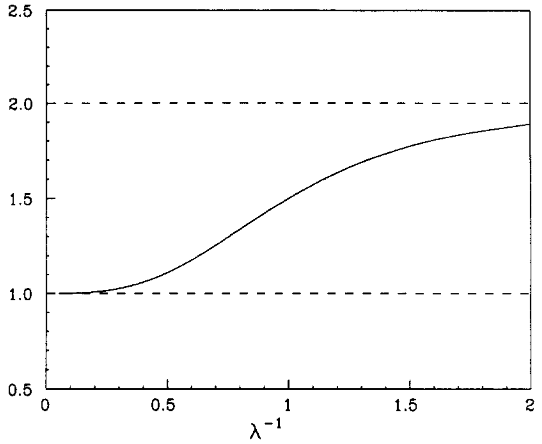

Figure 5. Mooney–Rivlin plot for reduced stress t^*_{11}, eq 3.9.

4. Discussion

In previous work we have considered atomistic mechanisms that result in coupling between the covalent and noncovalent interactions in polymer melts and networks. In this paper we have proposed a coupling mechanism that operates on the molecular (or chain) level in polymer networks.

The basic physical idea that underlies this coupling is easily stated and visualized: A typical chain of a polymer network has an end-to-end vector **R** whose long-time average $\langle \mathbf{R} \rangle \neq 0$. Therefore, the noncovalent interaction of this chain with its surroundings should bear some relation to the vector $\langle \mathbf{R} \rangle$. Since when the network is deformed, the distribution of the set of average chain vectors $\{\langle \mathbf{R} \rangle\}$ of the network becomes anisotropic, it is reasonable to expect that the same will be the case for the noncovalent contribution to the stress. For simplicity, in this paper we have confined attention to networks in which the nodes do not undergo thermal fluctuations and in which there are no topological entanglements. We believe that the first assumption does not affect seriously the basic ideas presented here; the second clearly does and requires further study.

In order to make the physical idea just presented quantitative, we have proceeded as follows: The generalized virial theorem provides an expression for the stress t_{ij} in a network occupying volume v at temperature T. It is a rigorous consequence of this theorem that the extensive stress factor $t_{ij}v/kT$ can be written, eq 2.4, as a sum of contributions by the individual chains, termed here $\chi_{ij}(\gamma)$, the chain stress of the γ chain. These components are then transformed to a local coordinate system $\bar{x}_i(\gamma)$ appropriate to the γ chain, with $\bar{x}_1(\gamma)$ in the chain vector direction; these transformed components, $\bar{\chi}_{rs}(\gamma)$, are termed the intrinsic chain stresses.

Normally, discussions of rubber elasticity focus on the axial force $f(\gamma)$ exerted by the γ chain. In terms of the intrinsic chain stress concept, this is equivalent to considering only the component $\bar{\chi}_{11}$ of the $\bar{\chi}_{rs}$ tensor. To go beyond this simplification, we make the assumption that $\bar{\chi}_{rs}(\gamma)$ depends only on ρ_γ, the end-to-end distance of the γ chain, and that $\bar{\chi}_{rs}$ is a cylindrical tensor; i.e., its only non-zero components are $\bar{\chi}_{11}$ and $\bar{\chi}_{22} = \bar{\chi}_{33}$. As noted, the axial component $\bar{\chi}_{11}$ may be regarded as proportional to the usual axial force concept, or more precisely, $\bar{\chi}_{11}$ provides a means of defining the effective axial force, eq 2.14, in the presence of noncovalent interactions. On the other hand, the radial components, $\bar{\chi}_{22} = \bar{\chi}_{33}$, arise solely from the interchain noncovalent interactions, and they vanish if these interactions are neglected.

Although we have arrived at this view along a different road, it appears that this formulation has close correspondence to approaches based on enclosing a typical chain of the network in a tube in order to represent the confining effect of the other chains.[10] Our assumption regarding the cylindrical character of $\bar{\chi}_{rs}(\gamma)$ is equivalent to the assumption that if there are no permanent topological entanglements on chain γ, then for sufficiently long time averages, the appropriate confining tube is a circular cylinder with the chain vector as the axis. The components $\bar{\chi}_{22} = \bar{\chi}_{33}$ then correspond to the pressure exerted by atoms of chain γ on the tube.

If we accept this time-averaged straight confining tube picture, then it becomes quite clear on physical grounds, apart from any mathematical considerations, that the interchain noncovalent interactions should make a nonhydrostatic contribution in the deformed state of the network, since the confining tubes, along with the chains, then assume an oriented state.

To make these physical ideas quantitative, we have considered a model network in which all chains have equal end-to-end distance and, in the unstressed reference state, have chain vectors with all three components with respect to an x_1, x_2, x_3 system of equal magnitude. This is the case, for example, for the network with tetrafunctional fixed nodes at the sites of a diamond lattice, which we have studied previously by computer simulation.[11] Equivalently, we can meet the conditions of our model by using a basic cubic cell with one fixed node at the center and four chains to cube vertices in the tetrahedral pattern, Figure 4. We can therefore refer to the model we treat in this paper as a four-chain model. It may be contrasted with the familiar three-chain model, which contains one chain in each of the coordinate directions. The drawback of the latter model for the purposes of the present discussion is that the chain orientations do not change for uniaxial deformation in the x_1 direction, and therefore the same is true for the orientation of chain-confining tubes. The four-chain model appears to be the simplest extension beyond the three-chain model that allows consideration of the effect of the change of chain orientation upon uniaxial deformation.

For this four-chain model, it is possible to use the condition of stress-free transverse surfaces in uniaxial extension in order to compute $\bar{\chi}_{22} = \bar{\chi}_{33}$ in terms of $\bar{\chi}_{11}$; the result is $\bar{\chi}_{22} = \bar{\chi}_{33} = -\bar{\chi}_{11}(\lambda^3 + 1)^{-1}$, eq 3.5, with λ the extension ratio. Some aspects of this relation warrant discussion: (a) Since $\bar{\chi}_{11}$ is generally positive, corresponding to a positive chain axial force, eq 3.5 implies that $\bar{\chi}_{22} = \bar{\chi}_{33}$ corresponds to a pressure exerted by the chain on its surroundings through interchain noncovalent interactions. (b) The specific values of $\bar{\chi}_{22} = \bar{\chi}_{33}$ thus obtained are independent of any specific form of the noncovalent potential. All that is required is that this potential and the system packing both be liquidlike. Then the stress-free condition on the transverse boundaries can be met through very small changes in the transverse dimensions from constant volume of the system upon change of λ. The changes required, for liquidlike conditions, are so small that the assumption that uniaxial deformation takes place at constant volume is a good one. (c) These considerations also make clear the reason for the decrease in $\bar{\chi}_{22} = \bar{\chi}_{33}$ with increasing extension. As the cube is extended in the x_1 direction, the chains become more nearly parallel to that direction. Then the intrinsic chain stress components $\bar{\chi}_{22} = \bar{\chi}_{33}$ contribute more heavily (relative to $\bar{\chi}_{11}$) to the macroscopic stress components $t_{22} = t_{33}$. Since the latter are zero in uniaxial deformation, the components $\bar{\chi}_{22} = \bar{\chi}_{33}$ must decrease accordingly.

In order to make contact with more familiar results, we have evaluated the behavior of this model in uniaxial deformation under the assumption that the chain axial force is Gaussian. However, it should be emphasized that this is not likely to be the case in the presence of both inter- and intrachain noncovalent interactions. Nevertheless the resulting behavior of the model with Gaussian axial force is instructive. The predicted behavior of the macroscopic tensile stress t_{11} is that obtained in the usual Gaussian affine theory, with an additional multiplying factor of $(1 + (\lambda^3 + 1)^{-1})$. The latter has a 2-fold effect relative to the usual result; at $\lambda = 1$ the effective front factor is increased, followed by a softening effect at larger values of λ. Both may be understood in terms of the role of the components $\bar{\chi}_{22} = \bar{\chi}_{33}$; initially they make a contribution to t_{11}, but this contribution decreases as the chains become more nearly aligned in the x_1 direction. In a Mooney–Rivlin type of plot, this model shows the expected qualitative behavior. Other mechanisms for the observed softening with strain have been proposed in the literature, including the enhanced fluctuations of junctions with strain in the constrained junction models[12,13] and the role of confinement in tube models.[10] The relationship between these different mechanisms requires further study.

In summary, therefore, the concept of intrinsic chain stress appears to provide a consistent way to incorporate noncovalent interactions into the theory of rubber elasticity. We have applied it in this paper to a simple four-chain network model. Its utilization in the treatment of more realistic network models remains the subject of future research.

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References and Notes

(1) See, for example: James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *11*, 455, in particular p 461.

(2) Gao, J.; Weiner, J. H. *Macromolecules* **1987**, *20*, 2520.

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(6) Gao, J.; Weiner, J. H. *J. Chem. Phys.* **1989**, *90*, 6749.

(7) See ref 6 where this is carried through explicitly for chains with valence angle restrictions.

(8) The negative of the corresponding expression in the theory of liquids with $t_{ij} = -p\delta_{ij}$ is termed the compressibility factor: cf. McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976; p 283.

(9) See, for example: Ciferri, A.; Hoeve, C. A. J.; Flory, P. J. *J. Am. Chem. Soc.* **1961**, *83*, 1015, in particular eq 2 on p 1016. To obtain the applied tensile force it is, of course, necessary to multiply the stress t_{11} by the deformed cross-sectional area $\lambda_{-1}L_0^2$, where the reference cube has edge L_0.

(10) See, for example: Gaylord, R. J.; Douglas, J. F. *Polym. Bull. (Berlin)* **1987**, *18*, 347, and references to other tube model discussions contained therein.

(11) Weiner, J. H.; Gao, J. Proceedings of 5th IFF-ILL Workshop, Molecular Basis of Polymer Networks, Julich, F. R. Germany, 1988, in press.

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