reaction mixture was shaken virogously to achieve mixing and sampled until the concentration of substrate was below the detection limits of the GC.

NMR Experiments. A typical NMR experiment was performed as follows: A solution of methyltrimethoxysilane (1.0 g, 7.3 mM) in acetone-d_6 (2.0 mL) was placed into a NMR tube along with 25–35 mg of $Cr(acac)_3$. Water (0.40 mL) was added by syringe. A spectrum of this solution was obtained and remained unchanged with time. Addition of the catalyst (0.050 mL of a 6.8×10^{-2} M solution of p-TSA in acetone) was followed by rapid mixing and acquisition of spectra over several hours.

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Excluded-Volume Effects in Rubber Elasticity. 1. Virial Stress Formulation[1]

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ABSTRACT: The usual view of stress in rubber elasticity focuses upon the axial force in the component chains as giving rise to stress across an arbitrary interior plane. The virial stress formulation provides a more local view of the stress in a rubber-like system in which both the covalent interactions responsible for the chain bonds and the noncovalent interactions appear on an equal footing. This formulation is applied here to a chain with excluded volume. It is shown that the virial viewpoint corresponds to considering forces across fixed spatial planes and therefore requires inclusion of momentum transport. By contrast, the usual approach treats forces between fixed sets of atoms and momentum transport does not enter. The equivalence of the two viewpoints is demonstrated.

Introduction

From the viewpoint of the thermal motion of its atoms, a rubberlike material occupies a position intermediate between a glassy solid and a fluid. The long-time average positions of its atoms are approximately uniformly distributed in space as is the case for a glassy solid, but the amplitudes of their thermal motion about these mean positions are much larger. One would therefore expect that the atomic interpretation of stress should share features of that for a glass, for which the interatomic forces exerted across an arbitrary internal plane play the primary role, and that for a fluid where momentum transfer becomes important.

The usual view of stress in rubber elasticity, however, bypasses both viewpoints and focuses upon the axial force in the component chains as giving rise to the stress across an arbitrary interior plane. Noncovalent interactions, including those due to excluded volume, are generally not

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treated explicitly[2] but are invoked as the origin of the internal pressure required to prevent collapse of the system.

The purpose of this paper is to use the generalized virial theorem to obtain a more local view of the stress in a rubberlike system, one in which both the covalent interactions responsible for the chain bonds and the noncovalent interactions appear on an equal footing. We present and discuss the virial expression in section 1. In section 2 it is applied to a single ideal chain to obtain a virial expression for the axial force. This is compared there with the usual formula for the axial force based on the chain free energy or, equivalently, on its partition function and it is shown that the two approaches correspond to two different but equivalent physical pictures of the process. Results for the computer simulation of a chain with excluded volume are presented in section 3 and are analyzed there in terms of these two viewpoints. Conclusions are given in section 4.

1. Generalized Virial Stress Formula

The virial formula is most often employed to provide an expression for the pressure in a confined system of atoms interacting with a two-body potential. It has been generalized[3] to yield the full stress tensor in such a system and in this case takes the form for n atoms in volume v at temperature T

$$vt_{ij} = -nkT\delta_{ij} + \sum_{\alpha}\langle r_\alpha^{-1}u'_\alpha(r_\alpha)y_i(\alpha)y_j(\alpha)\rangle \qquad (1.1)$$

where t_{ij}, $i, j = 1, 2, 3$, are the components of the stress tensor, force per unit area in the deformed system, referred to a rectangular Cartesian coordinate system x_i, δ_{ij} is the Kronecker delta, α ranges over all pairs of atoms, $\mathbf{r}_\alpha$ is the vector displacement between the α pair, $r_\alpha = |\mathbf{r}_\alpha|$, $u'_\alpha(r_\alpha)$ is the derivative of the potential for this pair, $y_i(\alpha)$ are the components of $\mathbf{r}_\alpha$ with respect to the coordinate system x_i, and brackets denote long-time averages.

The generalized virial stress formula has been used primarily in computer studies of crystalline solids.[4] It has also been employed recently by Theodorou and Suter[5] in their study of atomic models of polymeric glasses; in this case thermal motion plays a relatively unimportant role and was not included explicitly. The virial formula may be extended further to three-body and other many-body potentials.[6] However, in this paper we restrict attention to models described by two-body potentials and, in our computer simulations, treat the simplest system which has both the covalent bonding characteristic of macromolecules and the attribute of excluded volume. This model, the hard-sphere, freely jointed model, consists of a set of freely jointed chains whose atoms interact with a hard-sphere potential. For computational and conceptual convenience, the covalent potential is represented by a stiff linear spring and the hard-sphere potential is replaced by a truncated Lennard-Jones potential. That is, the covalent potential $u_c(r)$ is

$$u_c(r) = \tfrac{1}{2}\kappa(r - a)^2 \qquad (1.2)$$

where r is the distance between adjacent atoms on a given chain, and the noncovalent potential is

$$\begin{aligned} u_{nc}(r) &= 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \qquad \text{for } r \leq r_0 \\ &= u_{nc}(r_0) \qquad \text{for } r \geq r_0 \end{aligned} \qquad (1.3)$$

where r denotes the distance between any nonadjacent pair of atoms on a given chain or between any pair of atoms on different chains and $r_0 = 2^{1/6}\sigma$. The results reported in this paper were carried out for $\kappa a^2/kT = 202$ and $\epsilon/kT = 0.05$. Test calculations for $\sigma = 0$ showed that the former parameter value led to results for the axial force f which differed from the theoretical large κ limit results by 3% for $L/Na = 0.3$ (where L is the imposed end-to-end distance) increasing to 11% for $L/Na = 0.8$. All calculations with nonzero σ employed the value $\sigma/a = 0.8$.

For this class of models we may rewrite eq 1.1 in the form

$$vt_{ij} = -nkT\delta_{ij} + \sum_{\alpha\in c}\langle r_\alpha^{-1}u'_c(r_\alpha)y_i(\alpha)y_j(\alpha)\rangle + \sum_{\alpha\in nc}\langle r_\alpha^{-1}u'_{nc}(r_\alpha)y_i(\alpha)y_j(\alpha)\rangle \qquad (1.4)$$

where the notations $\alpha \in c$ or $\alpha \in nc$ indicate that the sums range over all pairs of covalently or non-covalently interacting atoms, respectively.

Pressure and Deviatoric Stress. Consider a material that is macroscopically isotropic in its reference state and is subject to a deformation with principal stretches λ_i, $i = 1, 2, 3$. The principal values t_i of the stress tensor t_{ij} may be determined from the Helmholtz free energy per unit reference volume, $F(\lambda_1,\lambda_2,\lambda_3,T)$ as[7]

$$t_i = J^{-1}\lambda_i(\partial F/\partial\lambda_i) \qquad (i = 1, 2, 3) \qquad (1.5)$$

where

$$J = \lambda_1\lambda_2\lambda_3 \qquad (1.6)$$

is the ratio of deformed to undeformed volume. Note that the summation convention on repeated indices is not employed in this paper.

In treating certain classes of deformation, such as uniaxial extension, in the theory of rubber elasticity it is convenient and accurate to make the isochoric assumption, i.e., that the deformation takes place at constant volume. In this case, the three principal stretches λ_i are no longer independent but must satisfy the constraint $J = 1 = \lambda_1\lambda_2\lambda_3$. As a consequence, eq 1.5 is replaced by[7]

$$t_i = \lambda_i(\partial F/\partial\lambda_i) - c \qquad (i = 1, 2, 3) \qquad (1.7)$$

where c is an arbitrary constant. It follows that with the isochoric assumption the mean stress or pressure is not determined from the constitutive relation, that is from the function $F(\lambda_1,\lambda_2,\lambda_3,T)$, but must be determined in a given case from the imposed stress boundary conditions. If the coordinate system x_i is taken to lie in the directions of the principal stretches and principal stresses, we may write $t_i = t_{ii}$ and we assume that this is the case in what follows.

In view of this situation it is convenient to express the stress tensor t_{ij} as a sum of a hydrostatic pressure p and a deviatoric stress τ_{ij} by the relations

$$t_{ij} = \tau_{ij} - \delta_{ij}p \qquad (1.8)$$

where

$$p = -\tfrac{1}{3}\sum_{i=1}^{3} t_{ii} \qquad (1.9)$$

Then, from eq 1.7, we find that

$$p = -\frac{1}{3}\sum_{i=1}^{3}\lambda_i\frac{\partial F}{\partial\lambda_i} + c \qquad (1.10)$$

and, from eq 1.8 and 1.9,

$$\tau_{11} = \frac{2}{3}\lambda_1\frac{\partial F}{\partial\lambda_1} - \frac{1}{3}\left(\lambda_2\frac{\partial F}{\partial\lambda_2} + \lambda_3\frac{\partial F}{\partial\lambda_3}\right) \qquad (1.11)$$

with analogous expressions for τ_{22} and τ_{33}.

In terms of the virial stress expression of eq 1.1, we can express the hydrostatic pressure p and the deviatoric stress τ_{ij} as

$$pv = nkT - \tfrac{1}{3}\sum_{\alpha} \langle r_\alpha u'(r_\alpha) \rangle \tag{1.12}$$

and

$$\tau_{ij}v = \frac{1}{3}\sum_{\alpha} \left\langle u'_\alpha(r_\alpha) \left[\frac{3y_i(\alpha)y_j(\alpha) - \delta_{ij}r_\alpha^{\,2}}{r_\alpha} \right] \right\rangle \tag{1.13}$$

Consider a term $\langle ru'_c(r) \rangle = \langle rf \rangle$ corresponding to a particular covalent bond in the sum of eq 1.12, where $f(r) = u'_c(r)$ is the force in the bond when its length is r. Let $\Delta A = A - \langle A \rangle$ for any fluctuating quantity. Then

$$\langle rf \rangle = \langle r \rangle \langle f \rangle + \langle \Delta r \Delta f \rangle \tag{1.14}$$

By use of the relation $f = \kappa(r - a)$, it is then readily shown that

$$\langle r \rangle = \kappa^{-1}\langle f \rangle + a \tag{1.15}$$

and

$$\langle \Delta r \Delta f \rangle = 2\langle e \rangle - \kappa^{-2}\langle f \rangle^2 \tag{1.16}$$

where

$$e = \tfrac{1}{2}\kappa(r - a)^2 \tag{1.17}$$

is the bond energy. Therefore, if $\langle f \rangle$ remains bounded, in the large κ limit we have

$$\langle rf \rangle = a\langle f \rangle + 2\langle e \rangle \tag{1.18}$$

Substitution of eq 1.18 into eq 1.12 leads to

$$pv = nkT - \tfrac{1}{3}Na\langle\langle f \rangle\rangle - \tfrac{2}{3}N\langle\langle e \rangle\rangle + \tfrac{1}{3}\sum_{\alpha \in \mathrm{nc}} \langle r_\alpha u'_{\mathrm{nc}}(r_\alpha) \rangle \tag{1.19}$$

where we have assumed N covalent bonds in the system with $\langle\langle f \rangle\rangle$ the mean bond force and $\langle\langle e \rangle\rangle$ the mean bond energy (double brackets denote an average both over time and over all covalent bonds in the system). It will be seen that eq 1.19 is equivalent to eq 11 of ref 8 with some changes in notation. The derivation given in that reference shows that it remains valid in the presence of covalent bond angle constraints and rotational energy barriers.

As noted in ref 8 and as observed in our computer simulation results, the mean bond energy $\langle\langle e \rangle\rangle = kT/2$ to good approximation. Then eq 1.19 can be written in the form

$$p = p_{\mathrm{int}} + p_{\mathrm{c}} + p_{\mathrm{hs}} \tag{1.20}$$

where

$$p_{\mathrm{int}} = (n - N/3)kT/v \tag{1.21}$$

is the internal pressure in the system due to the thermal motion of the atoms, with the coefficient $n - N/3$ reflecting the loss in atomic mobility due to the N covalent bonds;

$$p_{\mathrm{hs}} = \tfrac{1}{3}\sum_{\alpha \in \mathrm{nc}} \langle r_\alpha u'_{\mathrm{nc}}(r_\alpha) \rangle / v \tag{1.22}$$

is the additional contribution to the pressure due to the noncovalent, hard-sphere interaction, and

$$p_{\mathrm{c}} = -\tfrac{1}{3}Na\langle\langle f \rangle\rangle / v \tag{1.23}$$

is the balancing negative pressure due to the tensile bond forces $\langle\langle f \rangle\rangle$.

2. Virial Formulation for a Single Chain

Ideal Chain. In order to gain familiarity with the virial stress formulation, we consider first in this section the simple example of a single freely jointed chain with no excluded volume. For the case of fixed end-to-end displacement (strain ensemble[9]) we determine the required mean axial force on the basis of the usual partition function formulation and compare this with a calculation based on the virial stress formulation.

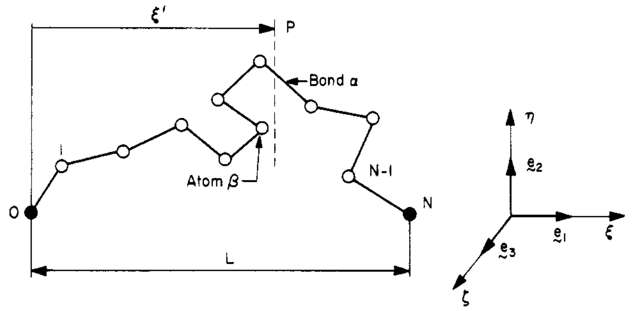

Figure 1. Hard-sphere, freely jointed model. Shown schematically is plane P, $\xi = \xi'$, with bond α crossing plane and atom β at the point of crossing P in forthcoming time interval Δt and transporting momentum into the region $\xi > \xi'$.

Partition Function Formulation. Let the positions of the atoms of the chain be denoted by $\mathbf{x}_k$, $k = 0, ..., N$ with $\mathbf{x}_0 = 0$ and $\mathbf{x}_N = L\mathbf{e}_1$ (Figure 1); the chain thus has N bonds and $n = N - 1$ atoms free to undergo thermal motion. The covalent bonds are represented by stiff linear springs, i.e., by the potential $u_c(r)$ defined in eq 1.2, so that the potential energy of the system is

$$V(\mathbf{x}_0,...,\mathbf{x}_N) = \sum_{\alpha=1}^{N} u_c(r_\alpha) \tag{2.1}$$

with $r_\alpha = |\mathbf{x}_\alpha - \mathbf{x}_{\alpha-1}|$.

The configurational partition function is

$$Z(L, T) = \int_{\Gamma_x} e^{-\beta V}\, d\mathbf{x}_1 ... d\mathbf{x}_n \tag{2.2}$$

where $\beta = (kT)^{-1}$.

The mean axial force f is then obtained from the relation

$$f = -kT\frac{\partial}{\partial L} \log Z \tag{2.3}$$

If we carry out this differentiation, noting that the prescribed length L appears in V only through the argument $\mathbf{x}_N$, we find that

$$f = Z^{-1} \int_{\Gamma_x} r_N^{-1} u'_c(r_N) y_1(N) e^{-\beta V}\, d\mathbf{x}_1 ... d\mathbf{x}_n \tag{2.4}$$

or, if we equate phase and time averages,

$$f = \langle y_1(N) r_N^{-1} u'_c(r_N) \rangle \tag{2.5}$$

Virial Stress Formulation. In order to apply the virial stress formula of eq 1.4 to this case the chain is regarded as enclosed in a rectangular parallelepiped with area A perpendicular to the axial direction $\mathbf{e}_1$, so that $v = LA$. The mean axial force f required to maintain the length L can then be obtained from the stress tensor t_{ij} as $f = t_{11}A$ and eq 1.4 then becomes, since $u_{\mathrm{nc}} \equiv 0$,

$$f = \frac{-nkT}{L} + \frac{1}{L}\sum_{\alpha=1}^{N} \langle y_1^{\,2}(\alpha) r_\alpha^{-1} u'_c(r_\alpha) \rangle \tag{2.6}$$

and we see that the cross-sectional area of the enclosing parallelepiped drops out of the formulation as it should. However, the two expressions for the mean axial force f, eq 2.5 and 2.6, appear quite different. Two points may be made regarding their relation.

(1) The virial axial force expression may be derived directly from the partition function formulation as follows: Let the components of $\mathbf{x}_k$ in the $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ directions be denoted by ξ_k, η_k, ζ_k, respectively. Introduce a coordinate transformation $\mathbf{x}_k$ to $\bar{\mathbf{x}}_k$ by the relations

$$\xi_k = (L/L_0)\bar{\xi}_k \qquad \eta_k = \bar{\eta}_k \qquad \zeta_k = \bar{\zeta}_k \qquad k = 0, ..., N \tag{2.7}$$

where L_0 is an arbitrary but fixed length. Then

$$Z(L, T) = (L/L_0)^n \int_{\Gamma_\xi} e^{-\beta V(\mathbf{x}_0,\ldots,\mathbf{x}_N)}\, \mathrm{d}\bar{\mathbf{x}}_1 \ldots \mathrm{d}\bar{\mathbf{x}}_n \quad (2.8)$$

where now *all* of the arguments of V depend on L through eq 2.7. Use of $Z(L, T)$ in this form in eq 2.3 then leads to the virial axial force expression of eq 2.6.

(2) Although we have thus demonstrated the mathematical equivalence of the two expressions, the physical interpretation of the force f is different in the two cases. That given by eq 2.5 and derived from the partition function in the usual way has a straightforward interpretation. It is seen that $y_1(N)/r_N = \cos\theta$, where θ is the angle between the Nth bond and the axis, so that f in eq 2.5 is simply the time average of the axial component of the fluctuating force $u'_c(r_N)$ in the Nth bond.

The interpretation of eq 2.6 is less straightforward. Consider the plane P, $\xi = \xi'$, which is fixed in space and the region R, $\xi > \xi'$, Figure 1. Select an arbitrary instant t and a time interval Δt, $t \leqslant \tau \leqslant t + \Delta t$ where Δt is short enough so that atom velocities change little in it. The conservation of linear momentum in the $\mathbf{e}_1$ direction for the region R then leads to the equation

$$(1/\Delta t)\sum_\beta m\dot{x}_\beta - \sum_\alpha u'_c(r_\alpha)y_1(\alpha)/r_\alpha + \hat{f} = (1/\Delta t)\sum_\gamma [m\dot{x}_\gamma(t + \Delta t) - m\dot{x}_\gamma(t)] \quad (2.9)$$

where the first term represents the net flux of momentum into R by those atoms β which cross P in Δt, the second term represents the mean force over Δt exerted by the bonds α which cross P, $\hat{f}$ is the mean over Δt of the axial component of the fluctuating force which must be applied to the Nth atom to keep it fixed, and the right-hand side is the rate of change of momentum of those atoms γ in R throughout Δt.

We consider a continuous distribution of planes P uniformly spaced in the inverval $0 \leqslant \xi \leqslant L$ and average eq 2.9 over this set of planes. In so doing, it is necessary to recognize that atom β travels the distances $\dot{x}_\beta \Delta t$ during Δt and therefore the first term must be weighted by this factor and similarly the covalent force associated with bond α must weighted by $y_1(\alpha)/L$. The ξ'-averaged form of eq 2.9 then becomes

$$\frac{1}{L}\sum_{\beta=1}^{n} m\dot{x}_\beta^2 - \frac{1}{L}\sum_{\alpha=1}^{N} u'_c(r_\alpha)y_1^2(\alpha)r_\alpha^{-1} + \hat{f}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{L}\int_0^L \sum_{\gamma(\xi')} m\dot{x}_\gamma \,\mathrm{d}\xi'\right) \quad (2.10)$$

where we have, after averaging over ξ', taken the limit $\Delta t \to 0$.

We next take the long-time average of this equation. In this process the right-hand side vanishes since the momenta are bounded, $\langle \hat{f}(t) \rangle = f$ and $\langle m\dot{x}_\beta^2 \rangle = kT$ by the equipartition theorem; we are thus led to eq 2.6.

Although, as we have seen, both eq 2.5 and 2.6 lead to the same value of f, they represent time averages of different functions. The first is the time average of the axial component of the fluctuating force in the Nth bond. Since this is the force in a single bond, the magnitudes of its fluctuations are large regardless of the length of the chain.[10] The value of f based on the virial formulation, however, is a suitably weighted average of force components in all of the bonds in the chain. As such we may expect the relative fluctuations in this quantity to decrease as $N^{-1/2}$. An example of the two time-dependent functions as obtained by computer simulation of chains with 20 and 100 bonds is shown in Figure 2.

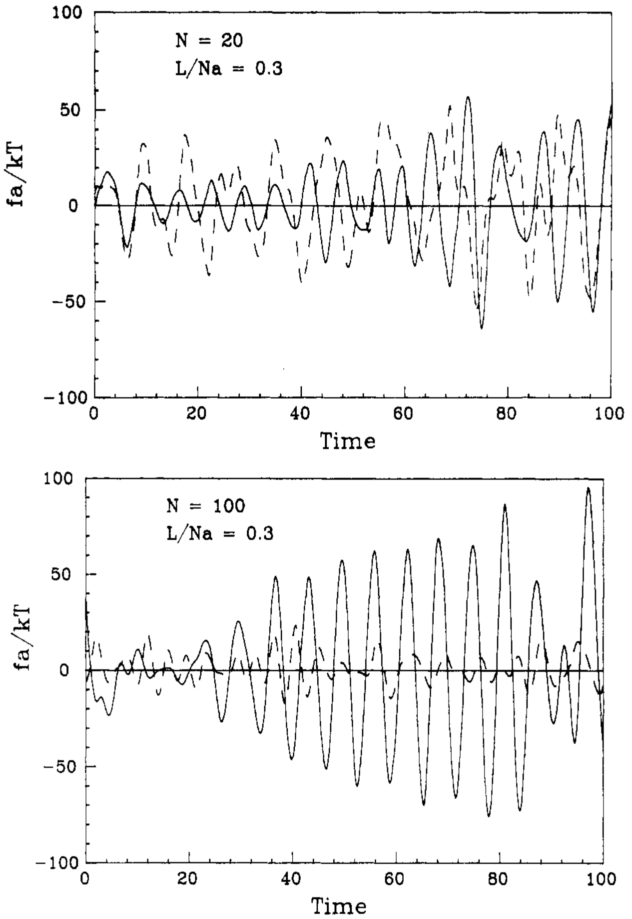

Figure 2. Comparison of time-dependent axial force, $\hat{f}(t)$, for an ideal chain as computed on the basis of the partition function, leading to the axial component of force in the Nth bond, (solid curve) and as computed on the basis of virial formula (dashed curve): (top) chain with $N = 20$ bonds and (bottom) chain with $N = 100$ bonds. The time scale is in units in which $(m/\kappa)^{1/2} = 1$.

3. Chain with Excluded Volume

As an extension of the single ideal chain we consider next a single chain with excluded volume effects as represented by the potential $u_{nc}(r)$ of eq 1.3 and study its behavior by molecular dynamics. The atoms of the principal chain have, as before, positions $\mathbf{x}_k$, $k = 0, \ldots, N$ with $\mathbf{x}_0 = 0$ and $\mathbf{x}_N = L\mathbf{e}_1$. In addition, to avoid end effects in the noncovalent interactions, all atoms in the principal chain are also assumed to interact with image atoms at positions $\mathbf{x}_k + mL\mathbf{e}_1$, $k = 1, \ldots, N$, $m = \pm 1, \pm 2, \ldots$

An outline of the molecular dynamics procedure employed is contained in the Appendix of ref 2. The program computes $f_c(j)$, the time average of the axial component of the covalent force transmitted across the jth bond that is exerted by atom j on atom $j - 1$, as well as $f_{nc}(j)$, the corresponding noncovalent force transmitted by the atoms $k \geq j$ on the atoms $k \leqslant j - 1$, with image atom interactions included. Typical results for $f_c(j)$ and $f_{nc}(j)$ are shown in Figure 3. It is seen that the use of periodic boundary conditions removes the end effects in these distributions found in previous work on finite chains (cf. Figure 7 of ref 11), and within computational scatter, f_c and f_{nc} are independent of j. Also shown in Figure 3 is the axial force f,

$$f = f_c + f_{nc} \quad (3.1)$$

The decomposition of the axial force f into its covalent and noncovalent portions given in eq 3.1 is expressed in terms of forces f_c and f_{nc}, which are time averages of forces

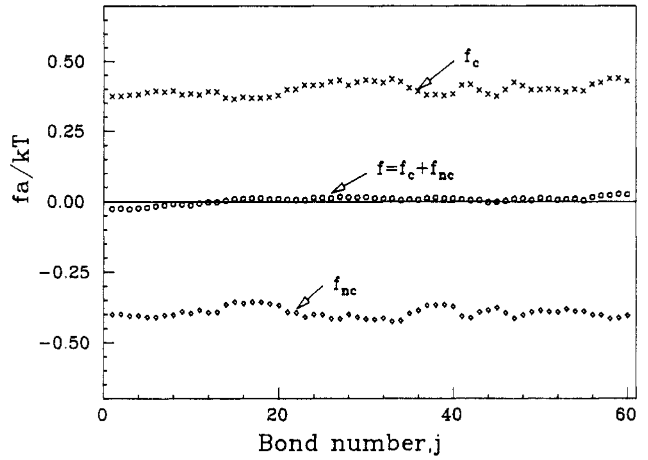

Figure 3. Covalent, $f_c(j)$, and noncovalent $f_{nc}(j)$, time-averaged axial force components exerted by the atoms $k \geq j$ on the atoms $k \leq j - 1$. Calculations performed for $N = 60$ and $L/Na = 0.15$.

between fixed set of atoms; for this reason, momentum transfer need not be considered. A second decomposition may be obtained from the virial stress formula, eq 2.6 as generalized to include the noncovalent interactions, so that it becomes

$$f = f^*_c + f^*_{nc} \tag{3.2}$$

where

$$f^*_c = \frac{1}{L}\sum_{\alpha=1}^{N}\langle y_1{}^2(\alpha)r_\alpha{}^{-1}u'_c(r_\alpha)\rangle - \frac{nkT}{L}$$

$$f^*_{nc} = \frac{1}{L}\sum_{\beta}\langle y_1{}^2(\beta)r_\beta{}^{-1}u'_{nc}(r_\beta)\rangle \tag{3.3}$$

and where the sum over β ranges over all pairs of atoms within the range of u_{nc}, with at least one atom of the pair belonging to the principal chain.

As we have seen in section 2, the virial stress formula relates to the force exerted across a plane fixed in space by variable sets of atoms. As such it does require consideration of momentum transfer, and in eq 3.3, we have found it convenient to include this term, nkT/L, in the expression for f^*_c.

The two types of forces, f_c, f_{nc} and f^*_c, f^*_{nc} are compared in Figure 4. It is seen that they agree well at large values of L/Na where atomic mobility is limited; however, there are substantial differences between the two at small values of L/Na where momentum transfer becomes important. The fact that the differences $f^*_c - f_c$ and $f^*_{nc} - f_{nc}$ vary differently with L/Na indicates that the relative effect of momentum transport upon f^*_c and f^*_{nc} depends upon L/Na. The appearance in eq 3.3 of the term $-nkT/L$ in the definition of f^*_c is a matter of convenience, chosen to produce agreement between f^*_c and f_c at large values of L/Na; it does not indicate that momentum transfer affects only f^*_c. Finally, the total axial force $f = f_c + f_{nc} = f^*_c + f^*_{nc}$ is shown in Figure 5 and it is seen that the two types of decomposition are in excellent agreement.

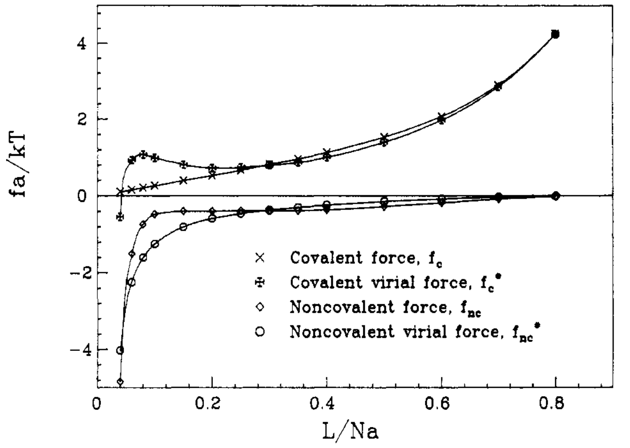

Figure 4. Comparison of covalent and noncovalent forces f_c and f_{nc} transmitted between fixed sets of atoms, averaged over all bonds, and covalent and noncovalent virial forces f^*_c and f^*_{nc} as defined in eq 3.3. Calculations performed for $N = 60$.

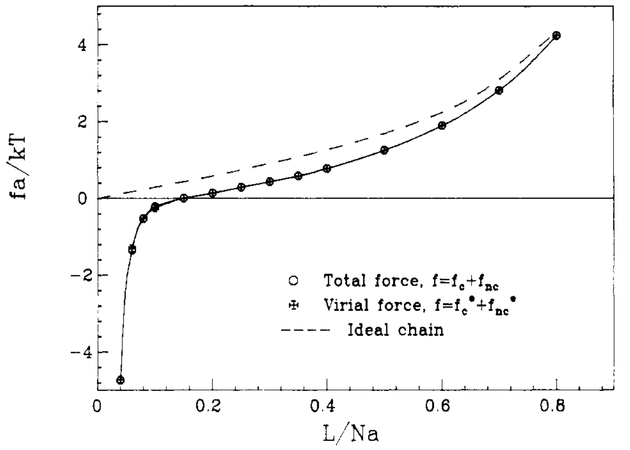

Figure 5. Total axial force f as computed by $f = f_c + f_{nc}$ and $f = f^*_c + f^*_{nc}$; ideal chain corresponds to $\sigma = 0$. Calculations performed for $N = 60$.

4. Conclusions

a. Local versus Chain View of Stress. We have seen that the virial stress formula provides a different physical picture of stress in a macromolecular system than the usual one which focuses on the entropy (or more generally, on the free energy) of the individual chains. In the latter approach, which we term the chain view of stress, the axial forces on each chain contribute to the stress tensor and therefore the chain, particularly the time dependence of its end-to-end displacement, is the significant unit. The virial stress formula, on the other hand, gives a more local view of the state of stress in a macromolecular system and, as far as the covalent interactions are concerned, focuses on $u'_c(r_\alpha) = f_\alpha$, the bond force in a link of the chain, and on the time dependence of $\mathbf{r}_\alpha$, the orientation of that link.

The chain view of stress leads naturally to the assigning of an important role to the topology of a cross-linked network and how it affects the statistical characteristics of the end-to-end vector $\mathbf{R}(t)$ of individual chains. For the virial stress formulation, the statistical characteristics of $\mathbf{r}_\alpha(t)$ with $\alpha \in c$, i.e., the covalent bond vectors, are the significant quantities and the role of cross-linking is to permit the transfer of a global deformation to the bond behavior so that $\langle\langle \mathbf{r}_\alpha \rangle\rangle \neq 0$ as it would be in a melt or in an undeformed network.

b. Traction. A key concept in understanding the mechanical behavior of a material from the continuum viewpoint is the transmission of force across an arbitrary interior planar element of area P, with unit normal $\mathbf{n}$. This force expressed per unit area is referred to as the traction $\mathbf{t}(\mathbf{n})$ across this plane and is regarded as exerted by the material (P_+) on the positive side of $\mathbf{n}$ on the material (P_-) on the negative side of $\mathbf{n}$. An important result in the subject of continuum mechanics is that this traction can be expressed in terms of the stress tensor $\mathbf{T}$ by the relation $\mathbf{t}(\mathbf{n}) = \mathbf{n}\cdot\mathbf{T}$.

The work of sections 2 and 3 has shown that for a rubberlike material there are two distinct microscopic analogues for the definition of the two sets of atoms P_+ and

P_- which interact with each other and transmit traction.

For a given plane P, (i) we can take the set P_+ as that fixed set of atoms whose long-time average positions lie on the positive side of $\mathbf{n}$, and similarly for P_-, or (ii) we can take the set P_+ as the variable set of atoms which at a given instant lie on the positive side of $\mathbf{n}$. We refer to (i) as the material description and to (ii) as the spatial description. We employed the material descriptions in ref 11 and 12 and have employed both here. It is important to note that the momentum transfer across the fixed plane must be included when the spatial description is employed.

In the present paper we have focused on the nature of the generalized virial stress formula and the insights it provides into the character of stress and traction in a rubberlike material. In the following paper we will use this formula as a means for studying the validity of the ideal chain assumption in rubber elasticity.

References and Notes

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Excluded-Volume Effects in Rubber Elasticity. 2. Ideal Chain Assumption[1]

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ABSTRACT: A key assumption in most theories of rubber elasticity is that the network can be regarded as a system of noninteracting ideal chains. Excluded-volume effects enter only as the agency responsible for maintaining the material at constant volume. As a test of this approach, molecular dynamics calculations are performed for a three-chain model using freely jointed chains and a truncated Lennard-Jones approximation to hard-sphere excluded volume. The state of stress in this model when subjected to constant volume uniaxial extension is determined from the molecular dynamics calculations by use of the virial stress formula and compared with the stress predicted on the basis of the ideal chain assumption. Significant, density-dependent differences are found. Molecular dynamics calculations for a polymer melt show that the force–length relation for a chain in the melt approaches the ideal relation as the melt density is increased, in accord with the Flory theorem, but they also show that this is due to large intermolecular noncovalent contributions to the force. Since noncovalent interactions do not contribute to the deviatoric stress in the model studied, the observed nonideal behavior is not inconsistent with the Flory theorem.

Introduction

The concept of an ideal chain,[2] which occupies a central position in polymer physics, may be described as follows. The covalent bonds between the backbone atoms and side groups of a linear macromolecule are primarily responsible for its characteristic behavior. There are, in addition, noncovalent interactions; these act between atoms which are neighboring along the chain (i.e., nearby side–group interactions) as well as between atoms which are widely separated along the chain but happen to be in close proximity because of the chain's long-range flexibility. A linear chain model which may include the former noncovalent interactions but omits the latter is said to be ideal. In particular, an ideal chain model omits the repulsive excluded-volume interaction which prevents the chain from doubling back on itself and causing two atoms, widely separated along the chain, to occupy the same place in space.

Ideal chain models exhibit some universal characteristics that are independent of the local chain structure, i.e., of bond angle restrictions and local noncovalent interactions. For example the probability density $p(\mathbf{R})$ for an end-to-end displacement $\mathbf{R}$ becomes Gaussian as N, the number of bonds, becomes sufficiently large and $\langle R^2 \rangle \sim N$. In contrast, for an isolated chain model with excluded volume interactions, $\langle R^2 \rangle \sim N^{1.2}$, and the latter prediction has been well confirmed by experiment for linear macromolecules in dilute solution.

For a dense uncross-linked system of like molecules, a polymer melt, Flory[3] has predicted that the excluded-volume potential for any given molecule would be screened by the others and that $p(\mathbf{R})$ for an individual molecule would be ideal. This remarkable result, sometimes termed[2] the Flory theorem, has been confirmed experimentally[4] and by computer simulation[5] as far as the scaling behavior of $\langle R^2 \rangle$ is concerned.

In the subject of rubber elasticity we are concerned with the mechanical behavior of a cross-linked amorphous network of long-chain molecules. The long-time behavior of the end-to-end displacement vector $\mathbf{R}$ of a particular chain of the system provides an important distinction between a melt, in which $\langle \mathbf{R} \rangle = \mathbf{0}$, and a network in which

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