Relative Importance of Internal Pressure and Excluded-Volume Effects in Resolution of Network Collapse Problem

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ABSTRACT: A reexamination of the statistical mechanical formulation of rubber elasticity is presented, particularly with regard to the treatment of interactions between atoms of the network which are not covalently bonded to each other. In this formulation these are represented as a sum of two potentials: (i) a deformation-dependent one-body potential and (ii) a deformation-independent two-body potential. The first gives rise to an internal pressure while the second represents the remaining excluded-volume effects. It is argued that the first is more important in preventing network collapse than the second. A simple atomistic model is introduced to illustrate these ideas and results of the computer simulation of the model by the method of Brownian dynamics are presented. The model also has relevance for the problem of a tie molecule between two parallel lamellae in a semicrystalline polymer.

I. Introduction

A convenient starting point for the discussion of rubber elasticity on the basis of equilibrium statistical mechanics is the theory, due to James and Guth,[1,2] of a phantom network of Gaussian chains. Apart from the covalent interactions between neighboring backbone atoms of a given chain, all atomic interactions are neglected in this theory.[3] Therefore distinct atoms of the same chain or of different chains can occupy the same position in space—hence the terminology, due to Flory,[4] of phantom network.

The internal energy of such a network is deformation independent and its thermomechanical equation of state is determined solely by its entropy. We are then led to the undesirable conclusion that the network configuration which corresponds to zero applied load is one in which the entire network contracts to a single point. This defect in the theory is referred to as the collapse problem.

The collapse problem may be avoided in a phenomenological manner by adding the geometric constraint that all deformations from some reference configuration must be volume-preserving or by postulating the existence of an appropriate volume-dependent internal energy. Statistical mechanical approaches to the problem have been presented by Boggs,[5] by Deam and Edwards,[6] and by Eichinger.[7] These theories have stressed the role of the two-body repulsive interactions between the noncovalently bonded atoms of the system in preventing collapse. It is the purpose of this paper to examine the role of the forces exerted by the atoms of the system on its boundary. It presents computer simulation studies of a simple atomistic model which show that for this case these forces, which may be described as exerting an internal pressure, are sufficient to avoid the collapse problem without invoking repulsive interactions between the atoms of the system. When the latter are included as well, they are found to play only a secondary role in the model's behavior.

In order to motivate the viewpoint adopted in this paper we begin, in section II, with a reexamination of the statistical mechanical formulations for the thermomechanical equation of state of deformable substances. A more complete discussion of these formulations and of the viewpoint adopted here is given in ref 8. A simple atomistic model based on these considerations is then described in section III and the behavior of this model, as found by its computer simulation, is summarized in section IV. Conclusions are given in section V.

II. Boundary Interactions in Statistical Mechanics

The basic procedure for obtaining the macroscopic equation of state of a deformable substance from an atomistic model by the use of equilibrium statistical mechanics is well-known. The atomistic model is described by a Hamiltonian $H(q,p;\epsilon)$, where (q,p) denotes all the coordinates and momenta of the atomistic model and the parameter ϵ denotes an appropriate measure of the deformation imposed on the model. The partition function $Z(\epsilon,T)$ is computed on the basis of $H(q,p;\epsilon)$ and the Helmholtz free energy $F(\epsilon,T) = -kT \log Z(\epsilon,T)$. The equation of state is then computed from $F(\epsilon,T)$ by application of the principles of macroscopic thermodynamics.

The question which particularly concerns us here is: How does the deformation parameter ϵ play a role in the description of the atomistic model of the substance and thus enter the Hamiltonian $H(q,p;\epsilon)$? We first consider this question for a gas and for a perfect crystal. The answers in these cases suggest the appropriate formulation for a rubber-like substance.

Gas. Consider a gas confined to a cylinder of volume v (Figure 1). Denote the collection of gas atoms by I (the internal system) and the cylinder and its surroundings by E (the external system). Let (q,p) denote the coordinates and momenta of the gas atoms. Only the gas atoms are treated explicitly in the statistical mechanics of the system. Any interaction between these atoms is described by an internal potential, $V_I(q)$.

It is also necessary to describe the interaction between the atoms of I and those of E. However, since the coordinates and momenta of the atoms of E are not part of the formulation, the state of E must be described in terms of macroscopic parameters. The atoms of E serve both as a heat bath and as a confining vessel for those of I. The state of the atoms of E as far as the first function is concerned is described by their temperature T. The second function is fulfilled by the introduction of a potential $V_{I,E}$ between I and E defined as

$$V_{I,E}(q;v) = 0 \qquad \text{if all atoms are in cylinder} \tag{1a}$$

$$V_{I,E}(q;v) = \infty \qquad \text{if any atom is outside of cylinder} \tag{1b}$$

Note that the actual interactions between the atoms of I and those of E will be time dependent for two reasons: the thermal motion of the atoms of I and the thermal motion of the atoms of E. Only the first time dependence is explicitly introduced into the formulation by the potential $V_{I,E}(q;v)$. The second time dependence is accounted for by regarding E as a heat bath at temperature T; in accord with the general principles of equilibrium statistical

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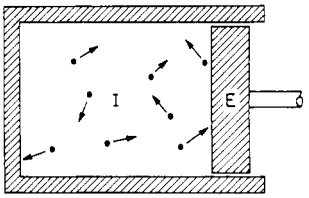

Figure 1. Gas in cylinder. Atoms of gas constitute system I. Cylinder and piston are system E.

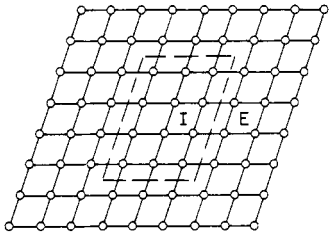

Figure 2. Deformed crystal. Atoms of central portion, surrounded by dashed lines, constitute system I. Remainder of crystal constitutes system E.

mechanics, it is not otherwise explicitly included in the formulation.

The Hamiltonian for the gas is therefore given by

$$H(q,p;\upsilon) = K_I(p) + V_I(q) + V_{I,E}(q;\upsilon) \qquad (2)$$

where $K_I(p)$ is the kinetic energy of the gas atoms. We see, therefore, that the gas volume υ, the appropriate deformation measure for this case, enters the Hamiltonian through the potential of interaction $V_{I,E}$.

Crystal. Consider next a perfect crystal whose atoms interact with a short-range force law and which is subjected to a deformation described by a suitable measure ϵ. If we were to regard the entire crystal as the atomic system to be treated explicitly, then it would be necessary to consider the nature of the loading device which imposes the deformation upon the crystal. This would also introduce difficulties associated with the inhomogeneous deformations near the surface which are introduced by the particular loading device.

For these reasons, it is simpler to treat explicitly only an interior portion I of the crystal and to regard the remainder of the crystal as the external system E (Figure 2).

The macroscopic deformation of the crystal is described by an affine transformation of a reference lattice to a deformed lattice. We regard the sites of the deformed lattice as completely specified[8] by the deformation measure ϵ. The atoms of I (coordinates q) and of E (coordinates q') are executing thermal motion in the vicinities of their respective deformed lattice sites. The interaction between the atoms of I is given by a potential $V_I(q)$. In addition, the atoms of I and the atoms of E near the boundary separating the two systems interact with a potential $V_{I,E}(q,q')$. As in the discussion of the gas, it is necessary to eliminate from the formulation the explicit time dependence of this interaction due to the thermal motion of the atoms of E. Let x' denote the positions of the deformed lattice sites of E and write

$$V_{I,E}(q,q') = V_{I,E}(q,x') + \Delta V_{I,E}(q,q')$$

so that $V_{I,E}(q,x')$ is the interaction between the atoms of I and those of E if the latter were fixed at their deformed lattice sites, and $\Delta V_{I,E}$ is the additional time-dependent interaction due to the thermal motion of the atoms of E. The latter term is treated as a weak interaction in the sense of equilibrium statistical mechanics and is neglected in the formulation.[9] Instead, its role is accounted for by describing E as a heat bath at temperature T.

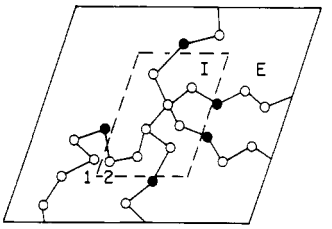

Figure 3. Deformed amorphous long-chain network. Atoms of central portion, surrounded by dashed lines, constitute system I. Remainder of network constitutes system E. (●) Atoms of E which interact covalently with atoms of I. Atom 1 is an example of an atom of E which interacts noncovalently with an atom of I (atom 2).

Since the deformed lattice sites x' are completely defined[10] by the deformation measure ϵ, $V_{I,E}(q,x') = V_{I,E}(q;\epsilon)$ and we can write the Hamiltonian for the atoms of the portion I of the deformed crystal as

$$H(q,p;\epsilon) = K_I(p) + V_I(q) + V_{I,E}(q;\epsilon) \qquad (3)$$

Amorphous Network. We consider next a deformed amorphous network of long-chain molecules as shown schematically in Figure 3. This system has some features in common with those of a gas and those of a crystal and we attempt to parallel as far as possible their treatment. As for the crystal, we divide the network into systems I and E. In our discussion of atomic interactions, it is necessary to distinguish between the covalent interactions, i.e., the interactions between neighboring backbone atoms, and interactions between atoms which are not covalently bonded.[3] The covalent interaction potentials will be denoted by $V^c_I(q)$ and $V^c_{I,E}(q,q')$ and the noncovalent interactions by $V^n_I(q)$ and $V^n_{I,E}(q,q')$, where, as before, q denotes the coordinates of the atoms of I and q' the coordinates of the atoms of E.

System E again serves the dual function of heat bath and the means of imposing the deformation ϵ upon I. It is again necessary that these functions be described without explicit introduction of q', the thermal motion of the atoms of E. The heat bath aspect is described by the temperature T. For the second function, consider first $V^c_{I,E}(q,q')$. Because of the nearest-neighbor character of covalent bonding, this interaction takes place only between backbone atoms, one of which is in I and the second in E (Figure 3). We refer to the latter set of atoms as boundary junctions. As in our discussion of the crystal we assume that we may regard the boundary junctions as fixed[11] at positions x' which are obtained from their reference positions by the affine deformation characterized by ϵ. That is, for the purposes of the statistical mechanical formulation, we assume that we can replace $V^c_{I,E}(q,q')$ by $V^c_{I,E}(q,x') = V^c_{I,E}(q;\epsilon)$.

We can now define the Hamiltonian $H_P(q,p;\epsilon)$ used to describe a phantom network:

$$H_P(q,p;\epsilon) = K_I(p) + V^c_I(q) + V^c_{I,E}(q;\epsilon) \qquad (4)$$

It is seen that the phantom network formulation omits $V^n_I(q)$ and $V^n_{I,E}(q,q')$. The first represents the repulsive, liquid-like interactions between the noncovalently bonded atoms of I. It is these which have been included in the formulations of Boggs,[5] Deam and Edwards,[6] and Eichinger.[7] We turn next to the consideration of $V^n_{I,E}$, which does not appear in their formulations.

By analogy to the procedure followed in the formulation for the gas and for the crystal, it is necessary to approximate $V^n_{I,E}(q,q')$ as $V^n_{I,E}(q;\epsilon)$ so as to eliminate the explicit dependence upon q' and to display the role of $V^n_{I,E}(q;\epsilon)$,

along with $V^c_{I,E}(q;\epsilon)$ of imposing the deformation ϵ upon I. As we have seen, the potential $V^c_{I,E}(q,\epsilon)$ represents the effects of the relatively few atoms of E which are covalently bonded to atoms of I. The potential $V^n_{I,E}(q;\epsilon)$ represents the tendency of all of the atoms of E to keep all of the atoms of I in the region assigned to I through a simple excluded-volume effect; the atoms of I cannot stray outside of that region because its exterior is already occupied by the atoms of E. The effect of $V^n_{I,E}(q;\epsilon)$ may also be described as representing the gas-like or internal pressure forces exerted by the atoms of I upon its boundary.

The relative importance of $V^c_{I,E}$ and $V^n_{I,E}$ depends upon the deformation. For states of deformation in which most of the chains are highly extended, the topological constraints imposed by V^c_I prevent most of the atoms of I from approaching its boundary and $V^n_{I,E}$ is unimportant. On the other hand, for states of deformation in which the mean end-to-end distance of the chains is very small, the atoms of I can move through that region with relatively little hindrance from V^c_I and the effect of $V^n_{I,E}$, that is, of the gas-like forces on the boundary of I, becomes important.

Two general points about our discussion of the statistical mechanics of deformable media should be noted here. The first is that our treatment is based on an ansatz as to the general mechanical behavior of the system under consideration. Thus the formulation of crystal elasticity assumes that the atoms execute thermal motion in the vicinity of the sites of a perfect lattice. In a similar way our formulation for an amorphous network assumes sufficient cross-linking so that the network behaves like a solid, which can resist shear, and not like a liquid. It is this assumption which permits us to define an idealized boundary, as in Figure 3, which separates the distinct systems I and E and which deforms according to the prescribed macroscopic deformation. The actual boundary between the atoms of I and the atoms of E may undergo some temporal fluctuations, but it is part of our ansatz that the time average of this boundary behaves like the assumed idealized boundary.

The second point to recognize is that our discussions correspond to the use of a strain ensemble; that is, the Hamiltonian $H(q,p;\epsilon)$ contains the deformation measure as imposed external parameter. It is also possible to formulate the statistical mechanics of a deformable substance on the basis of a stress ensemble[8] in which the Hamiltonian takes the form $H(q,p;\sigma)$, with the stress σ as imposed external parameter. The nature of the resolution of the collapse problem takes a different form for the two ensembles. For the strain ensemble it is necessary to show that there is a prescribed value ϵ_0 which gives rise, through the macroscopic equation of state computed on the basis of the strain ensemble, to zero applied load and which corresponds to a reasonable (i.e., noncollapsed) configuration. It will then be convenient, generally, to regard this zero load configuration as the reference configuration for further deformation descriptions. For the stress ensemble, on the other hand, it would be necessary to show that setting $\sigma = 0$ leads to a noncollapsed configuration. The latter problem appears to be the more difficult of the two and is not treated here.

III. Model System

In order to illustrate and to make quantitative the treatment of amorphous networks given in section II, we consider here a simple atomistic model. It consists of a single freely jointed chain with N bonds. Let the positions of the atoms be denoted by $\mathbf{x}_j$, $j = 0, ..., N$, with $\mathbf{x}_0 = 0$ and $\mathbf{x}_N = \mathbf{r}$, the prescribed end-to-end displacement.

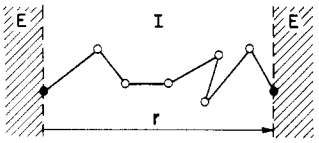

Figure 4. Model system.

The atoms $j = 1, ..., N-1$ constitute the system I and are regarded as confined to the infinite strip of width $|\mathbf{r}|$ between the planes passing through $\mathbf{x}_0$ and $\mathbf{x}_N$ perpendicular to $\mathbf{r}$ (Figure 4). The exterior of this strip is regarded as occupied fully by system E, which consists of atoms $j = 0$ and N, and many other atoms which are not covalently bonded to the atoms of I.

We may think of this model as representing very schematically a single chain which traverses completely a network of the type shown in Figure 3. A closer physical realization of the model is provided by a tie molecule between two parallel crystalline lamellae.

Rigid and Flexible Models. In recent years, two distinct approaches to the modeling of the strong covalent bonds between adjacent backbone atoms have been distinguished and studied.[12-21] They lead to what are generally referred to as rigid and flexible models, and the terminology describes two methods for the computation of the model partition function.

For a rigid model, strong covalent bonds are modeled by geometric constraints (e.g., fixed bond length a) in the Hamiltonian H_r of the model. The partition function, Z_r, is then computed on the basis of H_r.

In a flexible model, the strong covalent bonds are modeled first by stiff linear springs whose spring constant is scaled by a parameter κ, leading to a Hamiltonian H_f. For the freely jointed chain with link size a, these springs have the length a as the equilibrium length under zero load. The partition function for the flexible model, Z_f, is then computed on the basis of H_f. Finally, the spring-constant scaling factor is regarded as arbitrarily large.

Based on the results of recent studies, we use here a flexible model to represent the freely jointed chain. Therefore, in the terminology of section II

$$V^c_I(\mathbf{x}_1,...,\mathbf{x}_{N-1}) = \frac{1}{2}\kappa_c \sum_{j=2}^{N-1} (|\mathbf{x}_j - \mathbf{x}_{j-1}| - a)^2 \qquad (5a)$$

$$V^c_{I,E}(\mathbf{x}_1,\mathbf{x}_{N-1};\mathbf{r}) = \frac{1}{2}\kappa_c[(|\mathbf{x}_1| - a)^2 + (|\mathbf{r} - \mathbf{x}_{N-1}| - a)^2] \qquad (5b)$$

where a is the unstretched bond length and κ_c is the large spring constant representing the covalent bonds.

For the interactions between noncovalently bonded atoms of I we will use a hard-sphere potential of diameter ba:

$$V^n_I(\mathbf{x}_j,\mathbf{x}_k) = 0 \quad \text{if} \quad |\mathbf{x}_j - \mathbf{x}_k| \geq ba$$
$$= \infty \quad \text{if} \quad |\mathbf{x}_j - \mathbf{x}_k| < ba, \qquad j, k = 1, ..., N-1 \qquad (6)$$

Finally, to model the interaction between the atoms of I and system E we introduce the potential

$$V^n_{I,E}(\mathbf{x}_1,...,\mathbf{x}_{N-1};\mathbf{r}) = \sum_{j=1}^{N-1} [g_1(x_j) + g_2(x_j)] \qquad (7)$$

where $x_j = \mathbf{x}_j \cdot \mathbf{r}/|\mathbf{r}|$ is the component of $\mathbf{x}_j$ in the $\mathbf{r}$ direction and

$$g_1(x_j) = \tfrac{1}{2}\kappa_n x_j^2 \quad \text{for} \quad x_j < 0$$
$$= 0 \quad \text{for} \quad x_j > 0 \qquad (8a)$$

$$g_2(x_j) = \tfrac{1}{2}\kappa_n(x_j - |\mathbf{r}|)^2 \quad \text{for} \quad x_j > |\mathbf{r}|$$
$$= 0 \quad \text{for} \quad x_j < |\mathbf{r}| \qquad (8b)$$

It is seen that for large κ_n, $V_{I,E}$ models elastic collisions with rigid walls confining system I.

IV. Computer Simulation of Model[22]

Computation Procedure. The behavior of the model under conditions of thermal equilibrium is simulated by use of the technique of Brownian dynamics. Detailed descriptions of this technique as applied to models of long-chain molecules may be found, for example, in ref 23 and 24. Briefly, it involves the numerical solution of the Langevin equation of the model:

$$m\ddot{\mathbf{x}}_j = -\nabla_j V - \eta\dot{\mathbf{x}}_j + R_j; \qquad j = 1, \ldots N-1 \tag{9}$$

where m is the atomic mass, $V = V^c_I + V^c_{I,E} + V^n_I + V^n_{I,E}$ is the total potential energy, ∇_j is the gradient with respect to x_j, η is the viscosity, and R_j is the random force acting on the j'th atom whose statistical characteristics depend upon m, η, and the temperature T as in the theory of Brownian motion.[25] For a given set of sample functions $R_j(t)$, generated so as to satisfy these statistical characteristics, the numerical solution of eq 9 leads to the functions $\mathbf{x}_j(t)$ and to the time-dependent values of any properties of the model which depend on these atomic positions. Time averages over a sufficiently long period then lead to the expected equilibrium values of these properties. In particular, the force exerted by the left-half portion of E on I through the covalent bond between atoms $j = 0$ and 1 is

$$\mathbf{f}_c^- = -\nabla_1 V^c_{I,E} \tag{10}$$

and that exerted by the left-half portion of E on I through the noncovalent potential $V^n_{I,E}$ is (see eq 7 and 8)

$$\mathbf{f}_n^- = -\sum_{j=1}^{N-1} \nabla_j g_1(x_j) \tag{11}$$

The corresponding forces exerted by the right-hand portions of E on I are

$$\mathbf{f}_c^+ = -\nabla_{N-1} V^c_{I,E} \tag{12a}$$

$$\mathbf{f}_n^+ = -\sum_{j=1}^{N-1} \nabla_j g_2(x_j) \tag{12b}$$

It may be seen from the definition of $V^n_{I,E}$, eq 7 and 8, that $\mathbf{f}_n^-$ acts in the direction $+\mathbf{r}$, and $\mathbf{f}_n^+$ acts in the direction $-\mathbf{r}$; that is they are compressive forces. We set

$$f_n = \tfrac{1}{2}\langle \mathbf{f}_n^+ - \mathbf{f}_n^- \rangle \cdot \mathbf{r}/|\mathbf{r}| \tag{13}$$

where the angular brackets denote a long-time average. It is seen that $f_n \leq 0$ and $-f_n$ is the pressure force exerted by system I on the boundaries between I and E.

The instantaneous values of $\mathbf{f}_c^+$ and $\mathbf{f}_c^-$ do not, in general, act in the $\mathbf{r}$ direction. However, this will be the case for their long-time averages, and we write

$$f_c = \tfrac{1}{2}\langle \mathbf{f}_c^+ - \mathbf{f}_c^- \rangle \cdot \mathbf{r}/|\mathbf{r}| \tag{14}$$

It will be seen that, in general, $f_c \geq 0$ and f_c is the tensile force exerted by system E on I. Finally, we set

$$f = f_c + f_n \tag{15}$$

f is therefore the resultant average force, acting in the $+\mathbf{r}$ direction, which is exerted by the right half of E on the system I (or the negative of that force exerted by the left half of E).

Model Parameters. The model parameters were taken to be representative of a carbon backbone chain. The value of κ_c was chosen so that $\omega_0 = (\kappa_c/m)^{1/2} = 1.3 \times 10^{14}\ s^{-1}$. Test calculations showed that, as long as κ_c and κ_n were of the same order of magnitude, the results were insensitive to the ratio κ_c/κ_n and the calculations reported used $\kappa_n = \kappa_c$. The value of η corresponded to $\eta/(\kappa_c m)^{1/2} = 0.1$, i.e., to underdamped conditions. For the numerical integration of eq 9, a time step $\Delta t = 7.5 \times 10^{-16}$ s was employed. The temperature $T = 400$ K and $N = 10$.

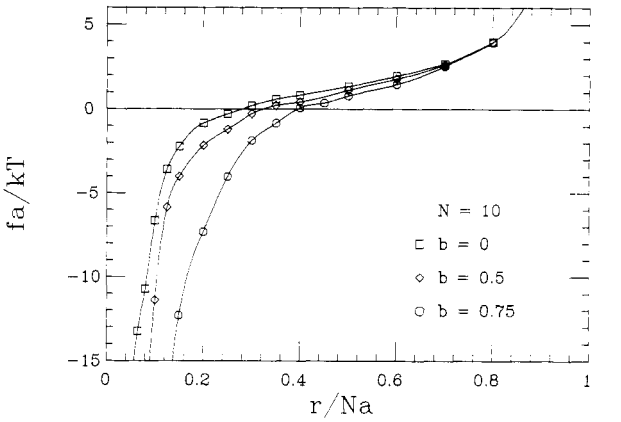

Figure 5. Force required to maintain chain at fixed length for chain of 10 bonds ($N = 10$) with confining walls and various hard-sphere diameters. Data points obtained from time average of computer simulation over a period of 300 ps. Lines connecting simulation points obtained by computer-smoothing routine.

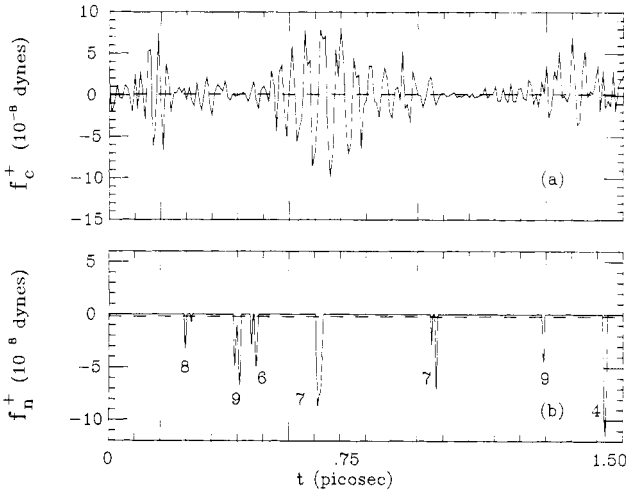

Figure 6. Time dependence of components of (a) $\mathbf{f}_c^+$ and (b) $\mathbf{f}_n^+$ in the $\mathbf{r}$ direction for a representative time period with $b = 0$. Numerals in (b) indicate which atom is interacting with wall. Dashed lines show time-averaged f_c and f_n.

Numerical Results. $b = 0$. We first discuss the behavior of the model for the case in which the hard-sphere potential paramter $b = 0$ so that, as seen from eq 6, the potential $V^n_I \equiv 0$.

The general behavior of the model in this case is shown in Figure 5. It is seen that the model exhibits a zero-load configuration at $r/(Na) \simeq 0.27$; i.e., the inclusion of $V^n_{I,E}$ is sufficient to prevent collapse, even if V^n_I is omitted.

We can gain insight into the model by considering some detailed aspects of its behavior. The time-dependent forces $\mathbf{f}_c^+$ and $\mathbf{f}_n^+$ exerted by the right-hand portions of E on I are defined in eq 12. In Figure 6, we show f_c^+ and f_n^+, the components of these forces in the $\mathbf{r}$ direction, for a short representative time period. We see that f_c^+, the $\mathbf{r}$ component of the force in the covalent bond between atoms 9 and 10, is highly oscillatory, while f_n^+ behaves like an impact force.

The time averages of these forces, f_c and f_n as defined in eq 14 and 13, are shown in Figure 7. They are com-

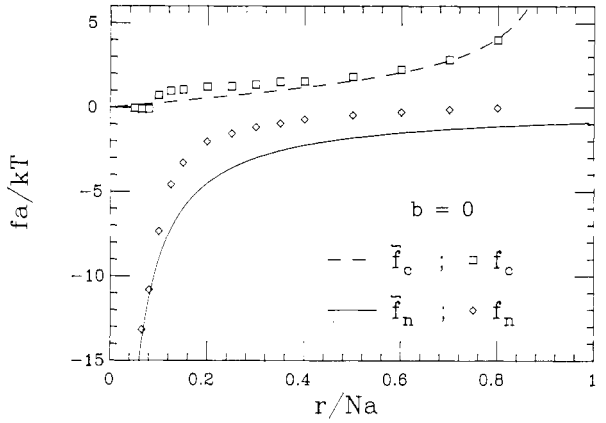

Figure 7. Comparison of time-averaged f_c with $\tilde{f}_c$, the required force in absence of confining walls, eq 16–18, and comparison of f_n with $\tilde{f}_n$, the ideal gas pressure force of $N - 1$ particles confined between walls a distance r apart, eq 19. Hard-sphere parameter $b = 0$.

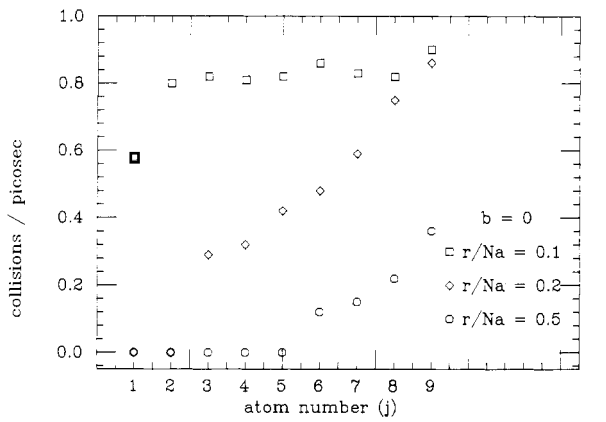

Figure 8. Collision frequency of atoms with right wall for $b = 0$ and various wall separations. No collisions occur for atoms 1 and 2 at $r/(Na) = 0.2$.

pared there to the forces $\tilde{f}_c$ and $\tilde{f}_n$; these are defined as follows:

(i) $\tilde{f}_c(r)$ is the required applied force for chain end-to-end distance r if the effect of the confining walls is neglected. Under these conditions[21]

$$\tilde{f}_c = -kT \frac{\partial}{\partial r} \log p \tag{16}$$

where $p(r)$ is the probability density computed on the basis of the random walk corresponding to a freely jointed chain of bond length a. For a chain of N bonds, with N small, it is most convenient to use Treloar's formula[21,26] for $p(r)$:

$$p(r) = (8\pi ra^2)^{-1}N(N-1)\sum_{k=0}^{m}\frac{(-1)^k}{k!(N-k)!}\left[\frac{N-(r/a)-2k}{2}\right]^{N-2} \tag{17}$$

where m is the integer in the interval[27]

$$[(N - r/a)/2] - 1 \leq m < (N - r/a)/2 \tag{18}$$

(ii) $\tilde{f}_n(r)$ is the average force which would be exerted on either of the two confining walls by the $N - 1$ atoms of I if these atoms were free of all other restraints, i.e., if $V^c_I \equiv V^n_I \equiv V^c_{I,E} \equiv 0$. As in the elementary kinetic theory of gases, it is readily computed that

$$\tilde{f}_n = (N - 1)kT/r \tag{19}$$

It is seen in Figure 7 that f_c approaches $\tilde{f}_c$ at large extensions and f_n approaches $\tilde{f}_n$ at small extensions. The increasing divergence between f_n and $\tilde{f}_n$ as the extension increases is easily understood to be a consequence of the increasing effectiveness of the topological constraints imposed by the covalent bonding, V^c_I and $V^c_{I,E}$, in preventing collisions between the atoms of I and the walls E. This point is demonstrated in Figure 8, which shows the collision frequency of the atoms of I with the right wall. At low extensions, the collision frequency is substantially equal along the chain; as the extension increases, however, the atoms along the chain which are further from the wall collide less frequently.

It is, on the other hand, less easy to understand the increasing divergence shown in Figure 7 between f_c and $\tilde{f}_c$ as the extension decreases. The analysis given in ref 20 to demonstrate the validity of eq 16 for flexible-chain models does not apply in the presence of confining walls. Whether it can be extended to this case and, if so, what is the proper probability density to replace that of eq 17 and 18 remain subjects for future study.

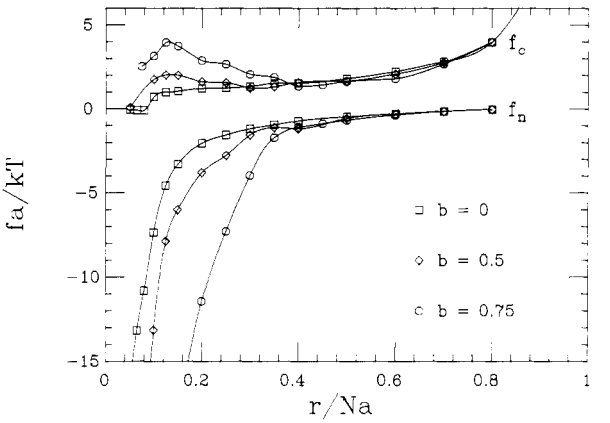

Figure 9. Effect of excluded-volume on time-averaged f_c and f_n for various hard-sphere diameters. Curves through simulation points obtained by computer-smoothing routine.

b > 0. The general behavior of the model for $b = 0.5$ and $b = 0.75$ is shown in Figure 5. It is seen that the inclusion of V^n_I does not affect the qualitative appearance of the force–displacement curve. However, the excluded-volume effect does result in a larger value for the zero-load extension and requires larger compressive forces at small extensions.

The excluded-volume effect upon the component forces f_c and f_n is shown in Figure 9. In both cases its effect is important only at relatively small extensions. The effect of b upon the pressure force f_n may be interpreted with the aid of the equation of state for a hard-sphere gas:[28]

$$p = kT\left\{\frac{N}{V} + \frac{2\pi c^3}{3}\left(1 - \frac{1}{N}\right) \times \left(\frac{N}{V}\right)^2 + \frac{5\pi^2 c^6}{18}\left(1 + \frac{1}{5N} - \frac{6}{5N^2}\right)\left(\frac{N}{V}\right)^3 + \ldots\right\} \tag{20}$$

for a gas of N atoms of diameter c confined to a volume V. By analogy, we may conjecture that the appropriate generalization[29] of eq 19 for $b > 0$ is

$$\tilde{f}_n = kT\left\{\frac{N-1}{r+ba} + \frac{2\pi(ba)^3}{3}\left(1 - \frac{1}{N-1}\right)\frac{(N-1)^2}{(r+ba)^2} + \frac{5\pi^2(ba)^6}{18}\left(1 + \frac{1}{5(N-1)} - \frac{6}{5(N-1)^2}\right)\frac{(N-1)^3}{(r+ba)^3} + \ldots\right\} \tag{21}$$

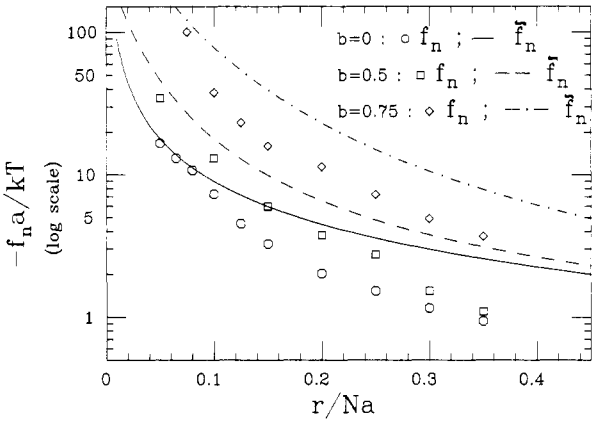

Figure 10. Comparison of time-averaged f_n with $\tilde{f}_n$, the hard-sphere gas pressure force, eq 21, for $b = 0.5$ and $b = 0.75$.

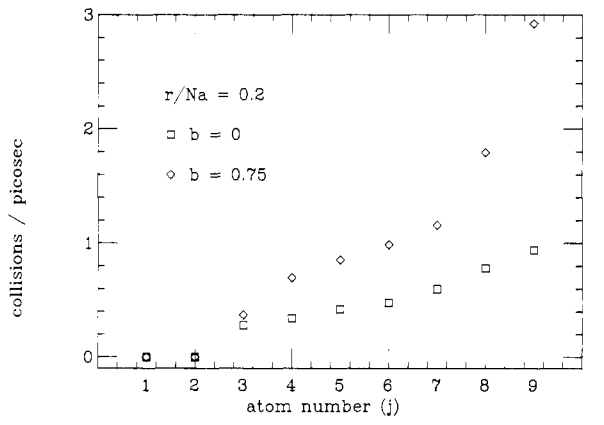

Figure 11. Effect of b on frequency of collision with right wall for $r/(Na) = 0.2$.

The comparison of f_n and $\tilde{f}_n$ as defined in eq 21 is shown in Figure 10, and the effect of b upon the collision frequency is shown in Figure 11. It appears that the effect of intersphere collisions, i.e., the effect of V^n_I, is to increase the collision frequency with the walls. This, in turn, is responsible for the increase in f_n noted in Figure 9.

The nature of the excluded-volume effect upon f_c is more difficult to interpret. In the absence of confining walls, the strain ensemble and stress ensemble are expected[21] to give essentially the same result for the force–length relation for values of $r/(Na) < 0.3$. Furthermore, it is known that in the absence of confining walls, the excluded volume has no effect upon the stress-ensemble relation in this extension range. In fact, in this range, the force–length relation for the unconfined chain is essentially linear with a slope that follows directly[30] from the isotropy of the probability density $p(r)$. This isotropy is disrupted by the confining walls.

V. Conclusions

The potentials $V^n_I(q,q')$ and $V^n_{I,E}(q;\epsilon)$ both arise from the same physical basis: the interactions between the noncovalent-bonded atoms of the network. However, they enter the statistical mechanical formulation of the problem in quite different ways, introduce different complexities, and have different physical interpretations. The potential $V^n_I(q,q')$ requires, in its simplest form, a representation as the sum of two-body potentials and leads to the class of difficulties encountered in the theory of liquids or of imperfect gases. The potential $V^n_{I,E}(q;\epsilon)$, on the other hand, may be taken as a simple one-body potential which confines the system to the interior of a prescribed region as in the theory of perfect gases.

The physical picture of the resolution of the collapse problem which emerges from a formulation based solely on $V^n_I(q,q')$ is expressed clearly in the conclusion of Eichinger:[31] "The elastic restoring forces in a network act to pull the junctions to the center of the elastic body, but they are prevented from doing so by the incompressibility of the atoms." On the other hand, the potential $V^n_{I,E}(q;\epsilon)$ leads naturally to the physical interpretation of an internal pressure in the system which prevents collapse. This picture was put forward in the early paper of James and Guth,[32] who stated: "Under equilibrium conditions...every surface of the model must of course be in equilibrium under all the forces which act on it—the push of the hydrostatic forces, the pull of the network, and any external forces." They also attributed[32] this internal pressure to "the outward forces of the jostling molecules".

James and Guth[1] made the phenomenological assumption of incompressibility in their discussion and did not provide a statistical mechanical formulation which lead to the existence of an internal pressure in a rubber-like system. Perhaps for this reason, this concept appears to have received decreasing attention in the later literature. As seen from the computer simulations of the model of sections III and IV, this pressure plays a more important role in preventing collapse than do the excluded-volume effects represented by $V^n_I(q,q')$. The model treated here consists not of a network but of a single chain and is intended only to illustrate the general principles discussed in section II. The results do suggest, however, that in the progression from simple to more realistic network models in the statistical mechanics of rubber elasticity, the most reasonable next step beyond the phantom network is the inclusion of the potential $V^n_{I,E}(q;\epsilon)$. We hope to consider network models from this viewpoint in future work.

In addition to its relevance to the collapse problem, the model of sections III and IV may also be taken to represent a tie molecule between two parallel lamellae in a semicrystalline polymer, a subject of current research interest.[33-35] The results of the computer simulation of this model raise questions which require further study regarding the appropriate theoretical basis for the determination of the force–length relation for such molecules.

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dinates to macroscopic control. While this criticism would be justified if the boundary junctions were elements of the system I, from the present viewpoint they belong to the system E and therefore must be described in macroscopic terms.
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Effect of Polystyrene Molecular Weight on the Fluorescence of Molecular Rotors

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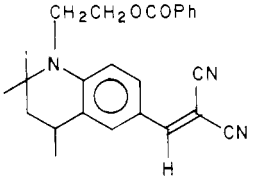
ABSTRACT: The effect of polystyrene molecular weight on the fluorescence intensity of a molecular rotor, [*p*-(dialkylamino)benzylidene]malononitrile derivative **1**, has been studied. The fluorescence intensity of **1** increases gradually with the molecular weight of the host polymer up to a critical M_n of 10^4. This increase in fluorescence was attributed to a decrease in the polymer free volume. An abrupt rise in the fluorescence of **1** in PS with $M_n > 10^4$ was attributed to a change in the bulk morphology of PS due to polymer chain contraction or coiling as Θ conditions.

Polymer chain interpenetration has been extensively studied by luminescence spectroscopy.[1-8] Morawetz et al.[1] described the characterization of polymer compatibility by nonradiative energy transfer between suitably chosen fluorescence labels attached to the polymeric species. Another popular approach involves the use of excimer emission of polymers with aromatic side chains. In solutions of polystyrene, the ratio of excimer to monomer fluorescence intensity (I_e/I_m) increases with increasing polymer molecular weight[2,3] and concentration, since intermolecular chromophore interaction becomes increasingly important.[4] The molecular weight effect on I_e/I_m is not confined to polystyrene; dilute solutions of poly(1-naphthyl methacrylate,[5] poly(α-vinylnaphthalene),[6] and poly(2-vinylnaphthalene)[7] exhibit similar behaviors. Similar increases in I_e/I_m were observed with polymeric fluorescence probes such as poly(2-vinylnaphthalene)[8] or poly(vinylcarbazole)[9] dissolved in glassy films of nonfluorescent host polymers. This change is interpreted as signaling immiscible behavior on a small distance scale. As the host matrix becomes a thermodynamically poorer solvent for the guest probe, the extent of mutual interpenetration of the guest and host chains will decrease, causing the local concentration of the guest aromatic rings to rise and increasing the number of intermolecular excimer sites.

The versatility and sensitivity of luminescence as a technique to probe polymer chain interpenetration and polymer blend miscibility stem from the multiple aspects of the inter- and/or intramolecular interaction of electronically excited state with their immediate environment.[1-10]

This paper reports studies of the effect of the molecular weight of monodisperse atactic polystyrene as nonfluorescent host polymer on the fluorescence yield of a molecular rotor, [*p*-(dialkylamino)benzylidene]malononitrile **1**.[11,12] This system was selected for several reasons.



Narrow-distribution polystyrene samples of different molecular weight are commercially available. The luminescence properties of polystyrene in solution as a function of molecular weight, concentration, and solvents have been studied.[2-4] In addition, polystyrene has been previously used as a host polymer for several polymeric fluorescent probes[7-9] but not for a molecular rotor probes. Finally, the glass transition temperatures of the polystyrene samples used are all above room temperature, making it possible to "freeze in" and study the chain conformation distribution when films are cast at room temperature.[13] The molecular rotor dyes used exhibit an exceptionally high rate of internal conversion, $\sim 10^{11}$ s^{-1}, attributed to torsional relaxation,[12] and this rate is media free-volume dependent. These dyes are therefore, excellent microscopic probes for measuring the torsional rigidity of the surrounding polymer, and the fluorescence yield is very sensitive to polymer structure and conformation.

The polystyrene samples were standards with narrow molecular weight distribution, ($M_w/M_n \leq 1.04$) from Pressure Chemical Co. Dye **1** was purified as described previously.[11] The spectroscopic measurements were made at relatively low dye concentration (≤0.5%) to avoid dye aggregation or dimer formation. Films of dye **1** (0.5 wt %)

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