Intrinsic Chain Stress Model for the Mooney Effect in Swollen Networks

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ABSTRACT: The concept of the axial force exerted by a given chain in a network loses its clear physical significance in the presence of interchain noncovalent interactions because the chain is subject to forces along its length as well as at its ends. The concept of intrinsic chain stress is a generalization of the concept of chain force which retains its significance in the presence of noncovalent interactions and reduces to the concept of chain force in their absence. In a recent paper we have applied the intrinsic chain stress concept to an idealized network model and have shown that it implies a nonhydrostatic stress contribution by the noncovalent interactions that varies with deformation because of the change in chain orientation. Furthermore, it was shown that, as a consequence, the stress–strain relation in a simple extension of this model exhibited the strain-softening or Mooney effect characteristic of dry rubberlike solids. In this paper, the analysis is extended to swollen networks and it is shown that the model predicts a decrease in the magnitude of the Mooney effect with a degree of swelling that is characteristic of real systems.

1. Introduction

The classical molecular theory of rubber elasticity provides the following simple expression for the stress in a rubberlike solid undergoing uniaxial extension in the x_1 direction:

$$t_{11} = G(\lambda^2 - \lambda^{-1}) \qquad (1.1)$$

where t_{11} is the normal stress (force per unit deformed area) acting on a plane perpendicular to the x_1 direction, λ is the extension ratio, and the constant G is discussed further below. A deviation from this theoretical prediction, which may be termed strain softening and is sometimes called the Mooney effect,[1] occurs in most rubbers and rubberlike solids, and in the range of $1.1 \lesssim \lambda \lesssim 2$, experimental data are better fitted by the expression

$$t_{11} = G(\lambda^2 - \lambda^{-1})\left(1 + \frac{c}{\lambda}\right) \qquad (1.2)$$

where the constant $c = C_2/C_1$ in the traditional notation and typically is in the range $0.2 \lesssim c \lesssim 1.0$ in dry samples.

A continuing focus of research over the years has been the search for a molecular explanation for the empirical portion of eq 1.2. Current theories include those that deal with the effect of deformation on the fluctuation of network junctions,[1,2] with entanglement effects,[3] and with the confinement or localization of chains by their interaction with the rest of the system.[4]

In our work, we have been focusing on the role of the noncovalent interactions between the nonbonded atoms of the system. We regard these to be of the same type considered in the study of simple liquids—namely, as two-body interactions with a short-range strongly repulsive portion corresponding to the excluded-volume interaction together with a longer range attractive van der Waals interaction.

In most treatments of rubber elasticity, it is assumed that these noncovalent liquidlike interactions make only a hydrostatic or isotropic contribution to the stress and that, therefore, they do not require a detailed discussion. However, we have found in our computer simulation of polymer melts and networks that, at realistic densities, there is strong coupling between the covalent bond structure and the noncovalent interactions and that, as a consequencce, the latter make a significant nonhydrostatic or anisotropic contribution to the stress.[5] In a recent paper,[6] employing a concept we call the intrinsic chain stress, we have shown that this nonhydrostatic contribution, which depends upon the degree of deformation, provides a strain-softening mechanism of the type described by the empirical portion of eq 1.2.

As a further probe of the mechanical behavior of rubberlike solids, extensive tests have been performed on swollen networks.[7] The results for uniaxial tension in the stated deformation range are again well-fitted by eq 1.2, but it is found that c decreases with a swelling ratio increase, becoming negligible when the volume fraction of the polymer, $v_2 \simeq 0.2$. At this swelling ratio, therefore, the classical theory of eq 1.1 applies, and the process is sometimes described by the statement that the behavior of the network becomes ideal when it is sufficiently swollen.

In this paper we show that our previous discussion for dry networks[6] can be extended in a natural way to swollen networks and that this treatment provides an explanation for the observed approach to ideal behavior. The general theory, which is based on the virial stress formula[8] and the concept of intrinsic chain stress,[6] is developed in section 2. It is applied in section 3 to the model network previously introduced in ref 6 in order to obtain explicit formulae. Conclusions and physical interpretation of the results are given in section 4.

2. Concept of Chain Stress in the Presence of Solvent

We consider a polymer network interacting with a solvent. For simplicity, the chains of the network are taken as freely jointed and the solvent or diluent is regarded as monatomic. The discussion may be generalized, however, to more realistic chain models and to molecular solvents.

Virial Stress Formula. As in our previous work, the starting point of our discussion is the classical virial theorem that provides an expression for the macroscopic equilibrium state of stress in a collection of interacting atoms

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at temperature T confined to a volume v. For the case in which all interactions are through pair potentials it takes the form[8]

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

where t_{ij} ($i, j = 1, 2, 3$) are the components of the stress tensor, force per unit present area, referred to a fixed rectangular Cartesian coordinate system x_i which we term the laboratory frame, 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 appropriate subdivision of the pair interactions in eq 2.1, the virial formula can be written as a sum over all of the atoms of the system in the form

$$\frac{vt_{ij}}{kT} = \sum_{\beta \in \mathrm{ch}} \langle \sigma_{ij}(\beta) \rangle + \sum_{\beta \in \mathrm{so.}} \langle \sigma_{ij}(\beta) \rangle \tag{2.2}$$

where the notations $\beta \in$ ch and $\beta \in$ so. denote an atom β belonging to the chains or to the solvent, respectively. The definitions of $\sigma_{ij}(\beta)$ for these two systems are as follows:

$$\sigma_{ij}(\beta) = -\delta_{ij} + \frac{1}{2kT} \sum_{\alpha_{\mathrm{ch}}(\beta)} (r^\alpha)^{-1} u_\alpha'(r^\alpha) r_i^\alpha r_j^\alpha + \frac{1}{kT} \sum_{\alpha_{\mathrm{so.}}(\beta)} (r^\alpha)^{-1} u_\alpha' r_i^\alpha r_j^\alpha \quad \text{for } \beta \in \text{ch} \tag{2.3}$$

$$\sigma_{ij}(\beta) = -\delta_{ij} + \frac{1}{2kT} \sum_{\alpha_{\mathrm{so.}}(\beta)} (r^\alpha)^{-1} u_\alpha'(r^\alpha) r_i^\alpha r_j^\alpha \quad \text{for } \beta \in \text{so.} \tag{2.4}$$

where the notation $\alpha_{\mathrm{ch}}(\beta)$ indicates that the sum ranges over all those atoms of the chains that interact with the atom β and correspondingly for $\alpha_{\mathrm{so.}}(\beta)$.

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. 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.

Two points regarding the definitions of $\sigma_{ij}(\beta)$ should be noted. (i) The terms of the virial formula corresponding to the chain–solvent interaction are assigned completely to $\sigma_{ij}(\beta)$ for $\beta \in$ ch. (ii) If β corresponds to an atom that is not free to undergo thermal motion, i.e. if it is a fixed node in the network, then the term $-\delta_{ij}$ is omitted in eq 2.3.

Covalent and Noncovalent Interactions. We have, thus far, left the nature of the two-body interactions u_α between the α pair of atoms unspecified. They are of two categories: (a) the covalent potential $u_{\mathrm{c}}(r)$ that acts only between neighboring atoms along a chain and serves to keep their distance nearly constant at the equilibrium bond length and (b) the noncovalent potential $u_{\mathrm{nc}}(r)$ that acts between all nonbonded atoms. The latter has a strongly repulsive part due to the excluded-volume interaction and an attractive tail arising from a van der Waals interaction. The parameters characterizing $u_{\mathrm{nc}}(r)$ may be different for chain–chain, chain–solvent, or solvent–solvent noncovalent interactions. In eq 2.3, the sum over $\alpha_{\mathrm{ch}}(\beta)$ involves both u_{c} and u_{nc}; the other sums in eqs 2.3 and 2.4 involve only u_{nc}.

Tensor Character of $\langle \sigma_{ij}(\beta) \rangle$. From the nature of its definition, it appears reasonable to assume that $\langle \sigma_{ij}(\beta) \rangle$ for $\beta \in$ so. is an isotropic tensor, that is

$$\langle \sigma_{ij}(\beta) \rangle = \sigma_1 \delta_{ij} \quad \text{for } \beta \in \text{so.} \tag{2.5}$$

On the other hand, consider an atom β that belongs to chain γ with end-to-end vector $\mathbf{R}(\gamma)$. Because of the covalent bonding, this atom is constrained to move, in terms of long-time averages, in an axisymmetric fashion with respect to $\mathbf{R}(\gamma)$. We may therefore assume that $\langle \sigma_{ij}(\beta) \rangle$ is a cylindrical tensor with axis $\mathbf{R}(\gamma)$. That is, if we utilize a local Cartesian coordinate system $\bar{x}_j(\gamma)$ with $\bar{x}_1(\gamma)$ in the direction of $\mathbf{R}(\gamma)$, then $\langle \bar{\sigma}_{11}(\beta) \rangle$, $\langle \bar{\sigma}_{22}(\beta) \rangle = \langle \bar{\sigma}_{33}(\beta) \rangle$ are the only nonzero components of $\langle \bar{\sigma}_{rs}(\beta) \rangle$. Here the notations $\langle \sigma_{ij}(\beta) \rangle$ and $\langle \bar{\sigma}_{rs}(\beta) \rangle$ denote components of the same tensor referred to the fixed laboratory frame x_i and to the local frame $\bar{x}_r(\gamma)$, respectively. By the customary laws of tensor transformation

$$\langle \sigma_{ij}(\beta) \rangle = \langle \bar{\sigma}_{rs}(\beta) \rangle a_{ri} a_{sj} \tag{2.6}$$

where $a_{ri}(\gamma)$ are the direction cosines between $\bar{x}_r(\gamma)$ and x_i and the summation convention $r, s = 1, 2, 3$ is employed here and in what follows.

Chain Stress. We next define the chain stress $\chi_{ij}(\gamma)$ as

$$\chi_{ij}(\gamma) = \sum_{\beta(\gamma)} \langle \sigma_{ij}(\beta) \rangle \tag{2.7}$$

with the sum carried out over all the atoms $\beta(\gamma)$ belonging to chain γ. Its components $\bar{\chi}_{rs}(\gamma)$ with respect to the local coordinate system $\bar{x}_r(\gamma)$ are, correspondingly

$$\bar{\chi}_{rs}(\gamma) = \sum_{\beta(\gamma)} \langle \bar{\sigma}_{rs}(\beta) \rangle \tag{2.8}$$

and, from the preceding discussion, $\bar{\chi}_{rs}(\gamma)$ is a cylindrical tensor, with $\bar{\chi}_{11}$, $\bar{\chi}_{22} = \bar{\chi}_{33}$ as the only nonzero components. As in eq 2.6

$$\chi_{ij}(\gamma) = \bar{\chi}_{rs}(\gamma) a_{ri} a_{sj} \tag{2.9}$$

We may now rewrite eq 2.2 as

$$\frac{vt_{ij}}{kT} = \sum_\gamma \chi_{ij}(\gamma) + \sigma\delta_{ij} \tag{2.10}$$

where $\sigma = n_{\mathrm{so.}}\sigma_1$ with $n_{\mathrm{so.}}$ the number of solvent atoms in v, and we have employed eqs 2.5 and 2.7. We may also use eq 2.9 and write

$$\frac{vt_{ij}}{kT} = \sum_\gamma \bar{\chi}_{rs}(\gamma) a_{ri}(\gamma) a_{sj}(\gamma) + \sigma\delta_{ij} \tag{2.11}$$

or, using the fact that $\bar{\chi}_{11}$, $\bar{\chi}_{22} = \bar{\chi}_{33}$ are the only nonzero components of $\bar{\chi}_{rs}$, the expressions for the normal stress components t_{11}, t_{22}, t_{33} take the form

$$\frac{vt_{11}}{kT} = \sum_\gamma \bar{\chi}_{11} a_{11}^2 + \sum_\gamma \bar{\chi}_{22}(a_{21}^2 + a_{31}^2) + \sigma \tag{2.12}$$

$$\frac{vt_{22}}{kT} = \sum_\gamma \bar{\chi}_{11} a_{12}^2 + \sum_\gamma \bar{\chi}_{22}(a_{22}^2 + a_{32}^2) + \sigma \tag{2.13}$$

$$\frac{vt_{33}}{kT} = \sum_\gamma \bar{\chi}_{11} a_{13}^2 + \sum_\gamma \bar{\chi}_{22}(a_{23}^2 + a_{33}^2) + \sigma \tag{2.14}$$

where the dependence of the summands' dependence on γ is understood.

Physical Picture. Equations 2.12–2.14 provide a clear physical picture of the deformation of swollen networks. We begin with a discussion of the physical significance of the components $\bar{\chi}_{rs}$. As discussed in ref 6, for an isolated ideal chain (no noncovalent interactions)

$$\bar{\chi}_{11} = \frac{f\rho}{kT} \tag{2.15}$$

where f is the axial force required to maintain an end-to-end chain distance ρ and $\bar{\chi}_{22} = \bar{\chi}_{33} = 0$. For a chain in a network subject to inter- and intrachain noncovalent interactions, $\bar{\chi}_{22} = \bar{\chi}_{33}$ will no longer be zero and the value of $\bar{\chi}_{11}$ may also be changed. The radial components $\bar{\chi}_{22} = \bar{\chi}_{33}$ are therefore completely due to the existence of noncovalent interactions and may be thought of as the response of the chain to its confinement by the rest of the system. Since we are dealing with a chain of atoms subjected to external forces along the chain as well as at its ends, the concept of a chain axial force loses its clear physical significance in the presence of noncovalent interactions. Nevertheless, we may use eq 2.15 to define an effective axial force f in terms of $\bar{\chi}_{11}$.

Consider next a swollen network under zero applied stress. We may expect $\bar{\chi}_{11} > 0$, $\bar{\chi}_{22} < 0$, $\sigma < 0$, corresponding to chains in axial tension but exerting radial pressure and the solvent exerting a pressure, with such magnitudes that eq 2.12–2.14 lead to $t_{11} = t_{22} = t_{33} = 0$.

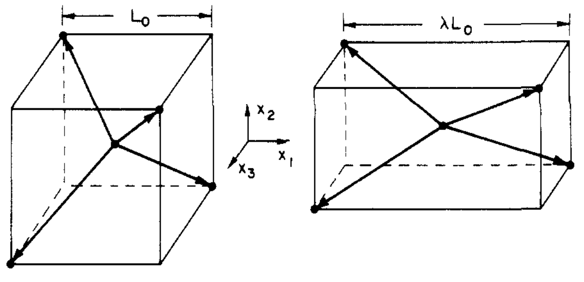
We now subject the swollen network to a uniaxial extension stretch λ in the x_1 direction, corresponding to $t_{11} > 0$, while the transverse surfaces are kept free of stress, $t_{22} = t_{33} = 0$. We make the affine deformation assumption so that the end-to-end chain vectors change in a corresponding fashion. The components $\bar{\chi}_{11}$, since they reflect the covalently bonded chain topology, are most sensitive to the chain end-to-end distance, and their values will change accordingly. Therefore, in eqs 2.13 and 2.14, the values of $\bar{\chi}_{22}$ and σ must change accordingly in order to meet the transverse boundary conditions, $t_{22} = t_{33} = 0$. At the liquidlike densities we are considering here, the strongly repulsive excluded-volume interactions play a dominant role, and the required readjustment of $\bar{\chi}_{22}$ and σ can take place with only a very small volume change. The latter, as usual, can be neglected in the description of the affine deformation. In summary, therefore, the components $\bar{\chi}_{11}$ are determined by the end-to-end chain distances, but $\bar{\chi}_{22}$ and σ are determined by the stress boundary conditions.

Uniaxial Constant-Volume Deformation. For convenience, we collect here the relevant geometrical quantities that describe the change in a chain end-to-end vector when it undergoes an affine deformation corresponding to a uniaxial constant-volume deformation. 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 $\rho^2 = \lambda^2 R_1^2 + \lambda^{-1}R_2 + \lambda^{-1}R_3^2$. It follows that, in the deformed state

$$a_{11}(\gamma) = \frac{\lambda R_1(\gamma)}{\rho(\gamma)} \qquad a_{12} = \frac{\lambda^{-1/2}R_2(\gamma)}{\rho(\gamma)}$$
$$a_{13} = \frac{\lambda^{-1/2}R_3(\gamma)}{\rho(\gamma)} \tag{2.16}$$

3. Model Network

In order to make quantitative predictions based on the formalism of eqs 2.12–2.14, we apply them to the simple model network used in ref 6. This network, in the stress-free swollen reference configuration, has end-to-end chain vectors $\mathbf{R}$ 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 1), 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 2.16 that



(a) (b)

Figure 1. Basic cell of four-chain model with 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 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 $|\lambda R_1|$, $|\lambda^{-1/2}R_2| = |\lambda^{-1/2}R_3|$.

$$a_{11}^2 = \lambda^2(\lambda^2 + 2\lambda^{-1})^{-1} \qquad a_{12}^2 = a_{13}^2 = (\lambda^3 + 2)^{-1} \tag{3.1}$$

for all chains. The chain length $\rho(\gamma)$ after deformation is the same for all chains; its square is

$$\rho^2 = \frac{1}{3}(\lambda^2 + 2\lambda^{-1})R^2 \tag{3.2}$$

where R is the common chain length before deformation. As discussed in ref 6, we assume that all of the chains are equivalent, except for their differing orientations, and therefore that $\bar{\chi}_{11}$ and $\bar{\chi}_{22}$ have the same value for all chains. We can then rewrite eqs 2.12–2.14 in the form

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

where ν is the number[9] of chains in the (swollen) volume v. In rewriting eqs 2.12–2.14 in the form of eq 3.3, we have also made use of the relation $a_{ri}a_{rj} = \delta_{ij}$ governing direction cosines, so that $a_{21}^2 + a_{31}^2 = 1 - a_{11}^2$, etc.

Relationship between $\bar{\chi}_{22}$ and σ. In order to proceed further in the solution of eq 3.3, it is necessary to postulate a relationship between σ and $\bar{\chi}_{22}$. We do so on the basis of the following reasoning: Both σ and $\bar{\chi}_{22}$ represent noncovalent contributions to the extensive stress factor as given by the virial equation (2.2). If we postulate that an individual solvent atom and an individual chain atom will make an equal contribution, then the total contributions of solvent and chain systems will be proportional to their numbers, i.e.

$$\frac{\sigma}{\nu\bar{\chi}_{22}} = \frac{n_{\mathrm{so.}}}{n_{\mathrm{ch}}} \tag{3.4}$$

where $n_{\mathrm{so.}}$ and n_{ch} are the number of solvent and chain atoms, respectively, in the volume v. Furthermore, we assume that the van der Waals volumes of the solvent and chain atoms (or solvent molecules and chain monomers) are comparable so that, at liquidlike densities

$$\frac{v_{\mathrm{so.}}}{v_{\mathrm{ch}}} = \frac{n_{\mathrm{so.}}}{n_{\mathrm{ch}}} \tag{3.5}$$

where $v_{\mathrm{so.}}$ and v_{ch} are volumes occupied by the solvent and chain atoms, respectively, with $v = v_{\mathrm{so.}} + v_{\mathrm{ch}}$. It then follows from eqs 3.4 and 3.5 that

$$\sigma + \nu\bar{\chi}_{22} = v_2^{-1}\nu\bar{\chi}_{22} \tag{3.6}$$

where

$$v_2 = \frac{v_{\mathrm{ch}}}{v} = \frac{\text{dry volume}}{\text{swollen volume}} \tag{3.7}$$

as in the usual notation employed for swelling phenomena. We note that eqs 3.4 and 3.5 represent only rough estimates which could be refined by more extensive analysis. Their purpose here is only to establish orders of magnitude and modes of variation.

Stress–Elongation Relation. By the substitution of eq 3.6 into eq 3.3, they become

$$\frac{vt_{11}}{\nu kT} = \bar{\chi}_{11}a_{11}^{2} + \bar{\chi}_{22}(v_2^{-1} - a_{11}^{2}) \tag{3.8}$$

$$\frac{vt_{22}}{\nu kT} = \bar{\chi}_{11}a_{12}^{2} + \bar{\chi}_{22}(v_2^{-1} - a_{12}^{2}) \tag{3.9}$$

$$\frac{vt_{33}}{\nu kT} = \bar{\chi}_{11}a_{13}^{2} + \bar{\chi}_{22}(v_2^{-1} - a_{13}^{2}) \tag{3.10}$$

It is seen that these equations are of the same form as eq 3.3 of ref 6 and reduce to them for $v_2 = 1$. Their solution proceeds in the same manner. We can determine $\bar{\chi}_{22}$ in terms of $\bar{\chi}_{11}$ from eq 3.9 and the boundary condition that $t_{22} = 0$ and then substitute into eq 3.8 to obtain

$$\frac{vt_{11}}{\nu kT} = \bar{\chi}_{11}\left[\frac{a_{11}^{2} - a_{12}^{2}}{1 - v_2 a_{12}^{2}}\right] \tag{3.11}$$

By use of eq 3.1, eq 3.11 may be written as

$$\frac{vt_{11}}{\nu kT} = \bar{\chi}_{11}\left[\frac{\lambda^3 - 1}{\lambda^3 + 2 - v_2}\right] \tag{3.12}$$

In order to proceed further with the evaluation of the stress–strain relation, we make the assumption that $\bar{\chi}_{11}$ corresponds to a Gaussian chain force–length relation, that is

$$f = \frac{3kT\rho}{R_0^{2}} \tag{3.13}$$

where f is the axial force in a chain with end-to-end distance ρ and R_0^{2} is the mean-square end-to-end distance when the chain is free of force. It then follows from eq 2.15 that

$$\bar{\chi}_{11} = \frac{3\rho^2}{R_0^{2}} = \frac{R^2}{R_0^{2}}(\lambda^2 + 2\lambda^{-1}) \tag{3.14}$$

where we have used eq 3.2. Substitution of eq 3.14 into eq 3.12 then leads to the result

$$t_{11} = \frac{\nu kT}{v}\left(\frac{R^2}{R_0^{2}}\right)(\lambda^2 - \lambda^{-1})\left(1 + \frac{v_2}{\lambda^3 + 2 - v_2}\right) \tag{3.15}$$

In this relation, $R = R_{\mathrm{s}}$, $v = v_{\mathrm{s}}$, where we now use the subscript s for the swollen state, d for the dry state, and t_{11} is the force per unit area in the deformed, swollen state. It is customary, in this literature, to refer various quantities of eq 3.15 to the dry state, although λ retains its significance as the ratio of a length in the x_1 direction in the swollen deformed state to its length in the swollen undeformed state. We make use of the following relations:[10]

$$\begin{aligned} R_{\mathrm{s}}^{2} &= R_{\mathrm{d}}^{2}v_2^{-2/3} \\ v_{\mathrm{s}} &= v_{\mathrm{d}}v_2^{-1} \\ f' &= t_{11}\lambda^{-1}v_2^{-2/3} \end{aligned} \tag{3.16}$$

where, in the last equation, f' is the force per unit undeformed, unswollen area; eq 3.15 may then be rewritten as

$$f' = Gv_2^{-1/3}(\lambda - \lambda^{-2})\left(1 + \frac{v_2}{\lambda^3 + 2 - v_2}\right) \tag{3.17}$$

where

$$G = \frac{\nu kT}{v_{\mathrm{d}}}\frac{R_{\mathrm{d}}^{2}}{R_0^{2}} \tag{3.18}$$

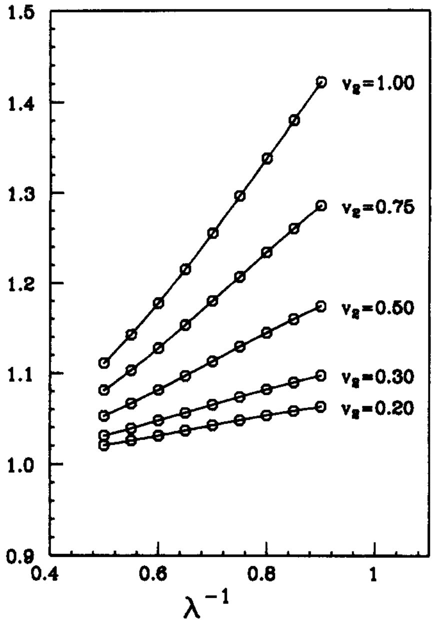


Figure 2. Mooney–Rivlin plot of model behavior: ϕ is the reduced force (eq 3.19), v_2^{-1} is the volume swelling ratio (eq 3.7), and λ is the extension ratio (Figure 1).

We can now consider the effect of swelling on deformation behavior of this model in a Mooney–Rivlin type of plot of the quantity

$$\phi = \frac{f'v_2^{1/3}}{G(\lambda - \lambda^{-2})} \tag{3.19}$$

where, from eq 3.17

$$\phi = 1 + \frac{v_2}{\lambda^3 + 2 - v_2} \tag{3.20}$$

The results are shown in Figure 2. It is seen that the behavior of the model is quite similar in appearance to that observed in real systems.[7]

4. Conclusions

If the single parameter in the classical molecular theory of rubber elasticity (eq 1.1) is used to fit the data for small strains in the uniaxial extension of rubberlike solids, then it is found that the experimental stress at larger strains falls below the theoretical prediction, with the difference becoming significant for extensions $\lambda \gtrsim 2$. This strain softening relative to the theory is sometimes referred to as the Mooney effect, and the search for its molecular mechanism has long been an important part of research in rubber elasticity. In recent years several alternate theories that exhibit this effect have been put forward; among these are theories that deal with the variation of junction fluctuation with deformation,[1,2] with the effects of chain entanglements,[3] and with chain localization effects.[4]

In the classical molecular theory of rubber elasticity, attention is almost exclusively given to the covalent interactions responsible for the bonds of the long-chain molecules. Noncovalent interactions between atoms of the system are assumed to give rise only to a hydrostatic pressure and therefore regarded as of little interest. The molecular theories for the Mooney effect to which we have just referred build on the classical molecular theory and continue to treat the covalent interactions as primary, with the role of the noncovalent interactions limited respectively to constraining junction fluctuation,[1,2] making possible chain entanglements[3] or localizing chains.[4]

In our computer simulation studies of polymers systems[5] we have found, contrary to the usual assumption, that the noncovalent interactions do make a large nonhydrostatic contribution to the stress, one which increases with system density and, at the liquidlike densities of real materials, is comparable to the stress contribution made by the covalent interactions. The mechanism whereby the spherically symmetric noncovalent interactions make an anisotropic stress contribution is found, in the computer simulation studies, to be the directional screening of the noncovalent interactions by the covalent structure of the network.

In the classical molecular theory, the concept of the force exerted by a chain on the cross-links which tie it to the network plays a central role. As a result, much effort has been expended on determining how this force varies with end-to-end distance for various types of chain models. This concept loses its clear physical significance, however, in the presence of nonhydrostatic, noncovalent interactions since now the atoms of the chain are subject to forces along its length as well as at its end points. To deal with this difficulty we have recently introduced the concept of intrinsic chain stress[6] as a natural generalization of the concept of chain force. It retains its significance in the presence of noncovalent interactions and reduces to the concept of chain force in their absence.

With the aid of the intrinsic chain stress concept, we have been able to show analytically, on the basis of a simple network model, that the nonhydrostatic noncovalent contribution to the stress in simple extension changes with stretch because of the change in chain orientation and that this change in noncovalent contribution gives rise to a strain softening comparable to the Mooney effect.[6]

A second important experimental observation regarding the Mooney effect is the decrease in its magnitude when the network is swollen by intake of a small molecule organic liquid which we refer to as solvent. This decrease in the Mooney effect (or equivalently of the parameter c in eq 1.2 with swelling is such that $c \simeq 0$, and the classical theory of eq 1.1 applies, when the system has swollen to about 5 times its original volume.

Clearly, any proposed mechanism for the Mooney effect must also explain its behavior in a swollen system. Here the explanation is quite natural. We are proposing that the effect is due to the nonhydrostatic stress contribution made by noncovalent interactions. In the dry network, all of the atoms of the system are associated with covalent structure and therefore all of their noncovalent interactions make a nonhydrostatic stress contribution. However, when solvent atoms are present, solvent–solvent interactions make only a hydrostatic contribution. This hydrostatic solvent contribution serves therefore to dilute and to decrease the effect of the nonhydrostatic noncovalent contribution of the atoms belonging to the network.

In this paper we have made these physical ideas quantitative by analytical computations on a simple network model. This model exhibits the effects on the stress–strain relation of swelling in terms of Mooney–Rivlin plots that are quite similar in appearance (Figure 2) to those describing experiments on real materials.[7] We hope, in future work, to supplement these calculations by computer simulation of more realistic models.

An important, well-established, experimental fact in rubber elasticity (perhaps the most important) is that the force of retraction is primarily (on the order of 90%) entropic in origin. Since the force–length relation of an ideal freely jointed long-chain molecule is purely entropic, it appears natural to ascribe most of the deviatoric, or nonhydrostatic, portion of the stress in rubberlike solids to the covalent or intrachain interactions and to assume that the noncovalent or interchain interactions contribute primarily to the hydrostatic portion of the stress as in an ordinary liquid. However, a network model in which the covalent bonds are represented by geometric constraints and the noncovalent excluded-volume interactions are modelled by hard-sphere interactions will also exhibit purely entropic elasticity.[11] Such a model will also exhibit, at liquidlike densities, a large noncovalent contribution to the deviatoric stress due to the directional screening of the hard-sphere excluded volume interactions by the covalent or bond structure of the network. Therefore, a large noncovalent contribution to the deviatoric stress is not incompatible with the primarily entropic character of rubber elasticity. In particular, for the model employed in this paper, the resulting stress–elongation relation, eq 3.15, exhibits its purely entropic character by the fact that the stress t_{11}, for fixed λ, is linearly dependent on T.

Note Added in Proof. An assumption made in the model employed in this paper and in ref 6 is that the intrinsic chain stress, $\bar{\chi}_{rs}$, is a cylindrical tensor with $\bar{\chi}_{11}$, $\bar{\chi}_{22} = \bar{\chi}_{33}$ as the only nonzero components. In computer simulations of an atomistic four-chain model (with no solvent) now in progress here, we find in contradiction that $\bar{\chi}_{rs}$ has systematic nonzero off-diagonal terms in the stretched state. These are apparently due to the anisotropic character of the system when deformed. Details of these computer simulations and their implications will be discussed in a future publication.

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(9) Note that this is a change in notation from ref 6; there ν represented the number of chains per unit volume.
(10) We make this recasting of eq 3.15 in terms of quantities referring to the dry state in order to conform to usual practice, even though it requires the affine assumption of the first of eq 3.16 whose validity has been placed into question recently; cf. Geissler, E.; et al. *J. Chem. Phys.* **1989**, *90*, 1924. The conclusions regarding the effect of swelling on the predicted strain softening can also be deduced directly from eq 3.15.
(11) To see this result, consider uniaxial extension at constant volume, although the argument is readily extended to general three-dimensional deformations. The partition function Z for the freely jointed, hard-sphere model, or for any model described solely in terms of geometric constraints, takes the form $Z(\lambda, T) = a(T)g(\lambda)$. It then follows that the internal energy $U = kT^2 (\partial/\partial T) \log Z = U(T)$; i.e. the internal energy is independent of the extension λ and the elasticity is purely entropic.

Monte Carlo Simulation of Polymers Confined between Flat Plates

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ABSTRACT: The behavior of polymers (modeled as a pearl necklace of $n = 20$ freely jointed hard spheres) between hard walls is studied by using a canonical ensemble Monte Carlo method. Simulation results for the density profiles and configurational properties are presented for wall separations varying from 4 to 16 hard sphere diameters and for volume fractions of 0.1, 0.2, and 0.3. It is found that the chains are depleted at the wall at the lower density but enhanced at the wall (relative to the center of the pore) at the higher density. The density of end sites of the chain at the wall is higher than it is for middle sites. Near the wall the chains are found to be flattened against the wall; in the large pore the fluid in the middle of the pore is uniform. In the bulk region, the distribution of sites about the center of mass is Gaussian; near the wall it is asymmetric and sharply peaked. In the smallest pore the chains are almost two dimensional. The force on the walls as a function of wall separation is calculated by using a superposition approximation to obtain the density profile for a fluid in small pores from the density profile for a fluid in a large pore at the same chemical potential. At high densities the force is an oscillatory function of wall separation with a period of oscillation of about one bead diameter, but at low densities it is monotonic and attractive.

1. Introduction

In an earlier paper[1] we investigated the behavior of mixtures of short chains (model alkanes) and hard spheres (model methane) confined between plates. In this article we extend the work to pure polymers confined between plates, a problem that is of practical and theoretical interest, which has been the focus of analytical,[2-5] computer simulation,[6-13] and experimental investigations[14,15] in recent years. One objective of this work is to determine if the behavior of long chains is qualitatively different from the behavior we observed earlier for short-chain molecules between plates.[1] Another objective is to gain insight at the molecular level into the behavior of polymers between surfaces.

In this article we use continuous-space Monte Carlo simulation to study the behavior of polymers confined between flat plates. Each polymer molecule is modeled as a pearl necklace of 20 freely jointed hard spheres, long enough to behave like polymer molecules but short enough to allow for intensive computer study. The choice of 20 as a sufficient length for polymeric behavior is supported by recent surface forces apparatus measurements on polybutadiene,[15] which reported a transition from alkane-like to polymer-like behavior at a chain length of $n \geq 20$. The walls of the pore are taken to be hard walls impenetrable to the centers of the sites on the chains. By modeling the walls and segments as hard bodies, we eliminate enthalpic effects and focus instead on the entropic effects associated with chain confinement. We might emphasize that, unlike that of bulk fluids, the structure of confined fluids is sensitive to the attractive part of the interactions, especially at low densities. In other words, enthalpic effects, which we eliminate, can be important in real systems.

The simulations of chains between hard walls are performed by using a modified version of an algorithm developed by Dickman and Hall[9] and later used by Yethiraj and Hall.[1] The wall separation is varied from 4σ to 16σ (where σ is the hard-sphere diameter). Three volume fractions, 0.1, 0.2, and 0.3, are considered. At ambient conditions, the volume fraction of polyethylene is approximately 0.31.[16] We report the density profiles of the fluid, the conformations of the chain in large and small pores, and the force on the walls as a function of the wall separation. We find that the behavior of 20-mers between walls is qualitatively similar to the behavior of short chains that we reported earlier.[1] At low densities, the chains are depleted at the wall relative to the middle; at high densities the chains are enhanced at the wall relative to

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