Nature of Stress on the Atomic Level in Dense Polymer Systems

Jianping Gao and Jerome H. Weiner

Stress in dense polymer systems is classically viewed as being molecular in character and is based on the entropic spring concept. A description on the atomic level has been developed on the basis of extensive computer simulations. An important new concept is the intrinsic monomer stress (IMS), the individual monomer contribution to the macroscopic stress referred to a local moving coordinate system in which the backbone bonds attached to that monomer are fixed. The IMS is time-independent and, for a given polymer system at fixed density, has the same value in the equilibrium melt, with the melt undergoing stress relaxation, and in the deformed cross-linked system.

Dense polymer systems above their glass transition temperatures, whether cross-linked as in rubber and other elastomers or uncross-linked as in polymer melts, play important roles in technology and biology. As with all classes of materials, a clear understanding of the microscopic character of stress is essential. Almost since the inception of polymer physics more than 60 years ago, the microscopic description of the nature of stress in polymer systems has been on a molecular level—that is, with the long-chain molecule as the basic unit and with the molecules behaving as entropic springs as the central concept. In this article we present a description of stress on the atomic level, in terms of the interactions of the atoms of the system with their neighbors.

To provide some historical background and explain the entropic spring concept, we begin on the macroscopic level with a rubber thread of length l subjected to a tensile force f. Neglecting any change in volume in the extension process, we can apply the principles of macroscopic thermodynamics and write

$$f = \left.\frac{\partial A}{\partial l}\right|_T \tag{1}$$

where $A(l, T)$ is the Helmholtz free energy at absolute temperature T; that is, $A(l, T) = U(l, T) - TS(l, T)$, with U the internal energy and S the entropy of the system. Therefore,

$$f = \left.\frac{\partial U}{\partial l}\right|_T - T\left.\frac{\partial S}{\partial l}\right|_T \tag{2}$$

This result, known already to Kelvin (*1*) in 1857, has an important physical interpretation: The force required to extend the thread serves in part to produce a change in internal energy and in part to produce a change in entropy. This result applies equally well to all elastic materials; for almost all of these materials, the first term is dominant. An exception, studied experimentally by Joule (*2*) in 1859, is rubber. For this material, the tensile force is found to be almost entirely entropic, with little dependence of internal energy on l. [This conclusion is easily deduced (*3*) from the relation

$$\left.\frac{\partial U}{\partial l}\right|_T = f - T\left.\frac{\partial f}{\partial T}\right|_l$$

obtained from macroscopic thermodynamics and from the experimentally observed proportionality to temperature of the force at constant l.]

With the work of Kelvin and Joule, the entropic character of rubber elasticity was firmly established on a macroscopic level. A microscopic explanation had to await the understanding of the macromolecular character of rubber and rubberlike solids, a view that became clear in the 1920s largely through the efforts of Staudinger (*4*). Not long afterward, Guth and Mark (*5*) demonstrated that a macromolecule with an end-to-end distance fixed at l behaved as a molecular entropic spring in tension. For a long linear chain of N freely jointed links each of length a, they found that its entropy is (for $l << Na$)

$$S(l) = -\frac{3k_B l^2}{2Na^2} + C \tag{3}$$

where k_B is Boltzmann's constant and C is a constant. Therefore (with U again independent of l), the tensile force required to maintain the length l was determined to be

$$f = \frac{3k_B Tl}{Na^2} \tag{4}$$

The concept of a linear macromolecule as an entropic spring has since played a central role in polymer science. For example, by modeling a rubberlike solid (that is, an elastomer) as a macroscopically amorphous cross-linked network of entropic springs satisfying the relation in Eq. 4, one is led quickly (*3*), with few assumptions, to the classical formula of rubber elasticity for a network subject to a constant volume extension, λ, in the x_1 direction, namely

$$t_{11} - t_{22} = \upsilon k_B T(\lambda^2 - \lambda^{-1}) \tag{5}$$

where υ is the number of chains per unit volume and $t_{ij}(i, j = 1, 2, 3)$ is the stress tensor (force per unit current area). Note that Eq. 5 provides only the value of the stress difference, $t_{11} - t_{22}$. The mean stress in the constant-volume system is not determined by the constitutive relation but through the imposed boundary conditions, such as $t_{22} = t_{33} = 0$; therefore, we are interested only in explaining the deviatoric or anisotropic portions of the stress.

An important conceptual problem with the model of an elastomer as a cross-linked network of entropic springs soon became apparent. Because such springs are always in tension with $f > 0$ when $l > 0$, why does the network not simply collapse to a point when free of external forces? The answer lies, of course, in the strong repulsive interactions that occur when two atoms approach each other closely, so that to first approximation each atom may be regarded as a hard sphere of diameter σ, where the value of σ is characteristic of its chemical species. There is also a weaker attractive interaction that becomes dominant at greater distances, but in the present discussion [as in the van der Waals picture of simple and molecular liquids (*6*)] we focus on the strong, short-range, repulsive interaction. This short-range interaction is often referred to as the excluded volume (EV) or steric interaction, both terms referring to the hard-sphere interpretation.

To first approximation, therefore, we can regard a dense polymer system such as a cross-linked elastomer as a collection of atoms interacting through two types of potentials. Most important are the covalent interactions responsible for the bonds between backbone atoms along each chain and their connected side groups. In addition, there are the EV interactions between any two atoms in close proximity in space. The first type represents inherently intrachain interactions that are frequently referred to as bonded interactions. The second type may act between intrachain or

---

The authors are with the Division of Engineering, Brown University, Providence, RI 02912, USA.

interchain atoms and are termed nonbonded interactions. (A third type of intrachain interactions is due to rotational potentials; for simplicity, we neglect them in this discussion.)

With this background, we are now ready to pose a basic question regarding stress on the atomic level in these materials: In a constant-volume deformation such as that leading to Eq. 5, what are the relative contributions of the bonded and nonbonded interactions to the deviatoric stress? The classical answer on the molecular level is straightforward and unequivocal: The deviatoric stress is due solely to the system of chains acting as entropic springs in tension. Nonbonded interactions, as in a simple atomic liquid, make only an isotropic contribution to the stress in the deformed polymer system. Because the principal nonbonded interaction is that due to EV, we refer to the latter statement as the excluded volume hydrostatic hypothesis (EVHH). It underlies almost all work to date (*7*) in the mechanics of polymer systems above their glass transition temperatures. It is important to emphasize that the EVHH refers only to the contribution of stress made by EV for a given set of atom configurations; it is clearly recognized (*7*) that EV has strong effects on the atom dynamics, through entanglements or other confining effects.

Computer Simulation

The use of high-speed digital computers to simulate atomistic models of condensed-matter systems has proved to be a valuable new way to understand phenomena (in particular, stress) on the atomic or monomer level and to check the validity there of the EVHH. In our simulations, we have used what are commonly termed "united-atom" models in which all side-group atoms are collapsed onto the backbone atom and the entire monomer is represented as a single "atom" of appropriate size. In that sense our description is on the monomer level. We believe that simulations with all atoms explicitly modeled (*8*) would give an atomic-level picture that would differ only in details from the present monomer-level discussion. Below we use the terms "atom" and "monomer" interchangeably to denote the united-atom entity of our simulation.

Our simulations have used the technique of molecular dynamics, together with the usual periodic boundary conditions (*9*). Chain models have ranged from the highly idealized freely jointed case to more realistic ones involving bond-angle and rotational potentials. In all of the studies, intra- and interchain nonbonded interactions have been included; the latter have generally been represented by the repulsive part of a Lennard-Jones potential (with parameters σ and ϵ), although in some cases the effect of an attractive tail has been studied.

An important aspect of our simulation studies has been the use of the generalized virial formula (*10*) to compute the macroscopic stress tensor, t_{ij}, in terms of atomic interactions. For the case of freely jointed chains, in which both the bonded interaction potential, $u_b(r)$, and the nonbonded potential, $u_{nb}(r)$, are two-body, the virial formula is

$$
\begin{aligned}
vt_{ij} = & -nk_BT\delta_{ij} \\
& + \sum_{\alpha \in b} \langle (r^{\alpha})^{-1} u_b'(r^{\alpha}) r_i^{\alpha} r_j^{\alpha} \rangle \\
& + \sum_{\alpha \in nb} \langle (r^{\alpha})^{-1} u_{nb}'(r^{\alpha}) r_i^{\alpha} r_j^{\alpha} \rangle \qquad (6)
\end{aligned}
$$

where n is the number of atoms in volume v; $\mathbf{r}^{\alpha}$ is the vector displacement between a pair, α, of interacting atoms; $r^{\alpha} = |\mathbf{r}^{\alpha}|$; r_i^{α} are the components of $\mathbf{r}^{\alpha}$ with respect to the coordinate system x_i; the notations $\alpha \in$ b and $\alpha \in$ nb indicate that these sums range over all pairs of atoms interacting by way of the potential, u_b or u_{nb}, respectively; u_b' and u_{nb}' denote derivatives of these potentials; and brackets denote long-time averages in equilibrium systems or ensemble averages in nonequilibrium studies. Further details regarding the use of the virial stress formula and its generalization to cases in which three-body angle potentials and four-body rotational potentials are present may be found in (*11–13*). The use of the virial formula permits a rigorous decomposition of the deviatoric stress into that portion due to bonded interactions and that due to nonbonded interactions.

Simulation Results

The sequence of computer simulations that we have performed has yielded a surprisingly detailed picture of stress on the monomer level, one that is greatly different from the classical molecular view.

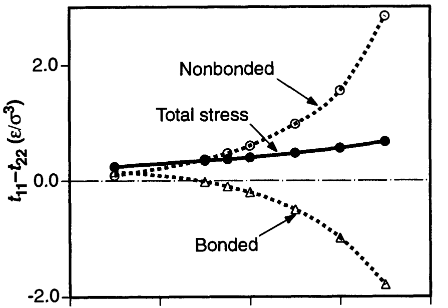

Fig. 1. Contributions to stress difference, $t_{11} - t_{22}$, made by nonbonded and bonded potentials [after (*14*)]. Results are from a simulation of a model network of freely jointed chains with bond length a, $\sigma = a$, and $N = 10$ bonds, subjected to a constant-volume uniaxial extension, $\lambda = 2$. Reduced density, $\rho = n\sigma^3/v$, is varied by change in system volume, v.

Nonbonded contribution to deviatoric stress. An important parameter in the study of the role of EV interactions in dense polymer systems is the reduced density, $\rho = n\sigma^3/v$, where σ is the effective hard-sphere diameter of each of n atoms confined to volume v. For dense polymer systems, such as elastomers or polymer melts, $\rho \sim 1$. The reduced density or the packing fraction, $\phi = \pi\rho/6$, is central to the theoretical treatment of liquids; it is symptomatic of the subsidiary role assigned to EV in classical discussions of stress in dense polymer systems that these parameters or their values are absent from theoretical consideration.

We have performed simulations with many different models in the study of this question. As an example, we show in Fig. 1 the stress difference $t_{11} - t_{22}$ and the separate contributions made by bonded and nonbonded interactions obtained by simulating (*14*) the extension of a model network. At low reduced density ($\rho = 0.6$) the two contributions are approximately equal; this result already contradicts the EVHH. Even more surprising, however, is the behavior of the model as ρ increases: The nonbonded contribution grows and becomes dominant while the bonded contribution becomes negative.

Steric shielding. The EVHH is based on the reasoning that the nonbonded interactions are two-body and spherically symmetric and can therefore make only an isotropic contribution to the stress, as in a simple atomic liquid. A careful examination of the simulation results, however, reveals a new feature of the nonbonded interaction in the presence of a covalently bonded structure that is missing in simple liquids. We term this feature steric shielding.

From an examination of Fig. 2, it is clear that atom A can interact more readily with B than with C because the atoms bonded to A sterically shield A from the close approach of C. In a macroscopically isotropic system, the nonbonded interactions remain statistically isotropic with respect to a fixed laboratory coordinate system. However,

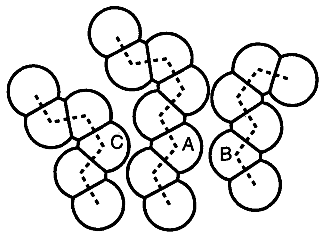

Fig. 2. Steric shielding of nonbonded interactions [after (*36*)]. For the conformations shown, monomer C is shielded from close interaction with mer A by the mers bonded to A, while mer B is not shielded from close interaction with mer A.

when the system is subject to a macroscopic deformation, the bonds attached to A assume a statistically anisotropic orientation with respect to the laboratory frame, and so the nonbonded interaction makes an anisotropic contribution. The effect of steric shielding clearly becomes more important with increased ρ, which makes close, strongly repulsive interactions become more frequent.

Entropic character of stress. As we have noted, the entropic character of rubber elasticity has been well established from the macroscopic viewpoint since the work of Kelvin and Joule in the late 1850s. When Guth and Mark (5) introduced the picture of a linear macromolecule acting as an entropic spring, it was natural to put the two ideas together and to regard the Guth and Mark entropic spring concept as the unique explanation of the macroscopic entropic character of rubber elasticity. It should be emphasized, therefore, that a system of hard spheres connected by geometric constraints representing covalent bonds is also a purely entropic system and that the monomer-level picture based on steric shielding in no way contradicts the classic results of Kelvin and Joule.

Covalent bonds in compression. The concept of steric shielding explains the mechanism through which the nonbonded interaction makes a positive contribution to the stress difference $t_{11} - t_{22}$ (Fig. 1). We now turn to explaining the negative contribution made by the bonded interaction. For simplicity, consider a freely jointed chain with bond length a. For a collection of such chains with no EV interactions (neither intra- nor interchain interactions), the force in each bond is positive, which corresponds to the bonds in tension (*15*). This tensile force may be traced (*16*, *17*) to the "centrifugal force" acting on the bond from the thermal motion of the atoms of the chain. Furthermore, this tensile bond force is compatible with the molecule acting as an entropic spring in tension, although the distinction between the bond force and the axial force must be emphasized.

Next consider this collection of polymer chains with all EV interactions (intra- and interchain) turned on. Our simulations (*16–18*) show that as the reduced density of the system increases, the covalent bond force decreases. At realistic densities, this force becomes negative; that is, the bonds are in compression, which helps explain the negative contribution to the stress difference that is made by the bonded interactions. The mechanism whereby the bonds are put into compression may be explained in terms of the concept of intrinsic forces discussed below.

Intrinsic forces. Consider, for example, a polymer melt of chains with bond-angle potential included. We have stated that when such a melt is undeformed and therefore macroscopically isotropic, steric shielding leaves the nonbonded interactions statistically isotropic with respect to the laboratory frame. However, steric shielding renders the interaction with atom A anisotropic with respect to a moving local coordinate system in which the bonds attached to A are fixed. As a result, the time-averaged components of the force, **f**, acting on A that are referred to this intrinsic coordinate system at each instant are nonzero. The character of these intrinsic forces has been determined by simulation (Fig. 3). If the macromolecule in a particular conformation is visualized as a long curved cylinder, the intrinsic forces are distributed over its surface, including its capped ends, directed inward and approximately normal to the surface. It is tempting to think of these forces as due to the macroscopic pressure in the melt. However, these forces are relatively insensitive to the melt pressure, p; they are present and have the same character even when $p = 0$ (*19*). From the character of these intrinsic forces (Fig. 3), it is clear that their tendency is to put the backbone bonds of the chain into compression, which occurs at realistic system densities (*20*).

Chain force in systems of interacting chains. The results described so far, derived mainly from computer simulation, present a radically different physical picture of the nature of stress on the atomic level from the picture, based on entropic springs in tension and the EVHH, that underlies the classical molecular theory of rubber elasticity, as exemplified by Eq. 5. A natural question that arises is why the classical theory agrees as well as it does with experimental data for moderate extensions, $\lambda \lesssim 2$. [For $\lambda \gtrsim 2$, experimental results show a decrease of the stress (*21*) below that predicted by Eq. 5; this softening is sometimes called the Mooney effect.] We have examined this question in (*22*).

Consider first a network of noninteracting chains in which, for simplicity of discussion, we assume that the junctions do not undergo thermal motion. The stress, t_{ij}, in such a system can be written in the form

$$v t_{ij} = \sum_{\gamma} f_i(\gamma) R_j(\gamma) \qquad (7)$$

where $\mathbf{f}(\gamma)$ with components $f_i(\gamma)$ is the force required to maintain the chain vector $\mathbf{R}(\gamma)$ with components $R_j(\gamma)$ of chain γ, and the sum is carried out over all chains of the system occupying the volume, v. This expression for the stress may be derived, for example, by application of the principle of virtual work (*23*). Use of Eqs. 4 and 7 together with the affine assumption (that is, that the chain vectors all undergo the same linear transformation that characterizes the macroscopic deformation) and assumptions on the distribution of chain vectors in the reference state leads very quickly to Eq. 5.

In (*22*), we sought to determine the extent to which this type of derivation can be used in the presence of intra- and interchain EV interaction. For this purpose, we generalized the concept of chain force, derived by Guth and Mark (5) for an isolated chain with no EV (ideal chain), to one with EV in interaction with many surrounding chains. First we found that in this case it is again necessary to apply tensile forces, **f** and −**f**, to the two end atoms of the chain to maintain a fixed chain vector **R**. However, the physical mechanism underlying the need for this force depends strongly on the system density, ρ. At low values of ρ, the forces **f** and −**f** are needed because the end atoms are being pulled inward by the adjoining atoms of the chain; this is the same physical picture that underlies the kinetic view (*24*) of the Guth and Mark entropic spring. However, as ρ increases and approaches realistic values (ρ ~ 1), the tensile forces are needed because the end atoms are being pushed inward by interchain EV interactions.

Although the physical mechanisms for the chain force are therefore quite different between the ideal case and that with EV, our simulations show that as ρ increases, the force-length relation for $\lambda \lesssim 2$ approaches the relation for the ideal case. This result is in accord with what has come to be known as the Flory theorem (*25*). Furthermore, the use of Eq. 7 agrees well with the stress in the system of interacting chains as determined by computer simulation. These results help explain why the classical theory of Eq. 5 agrees well with experimental results for λ

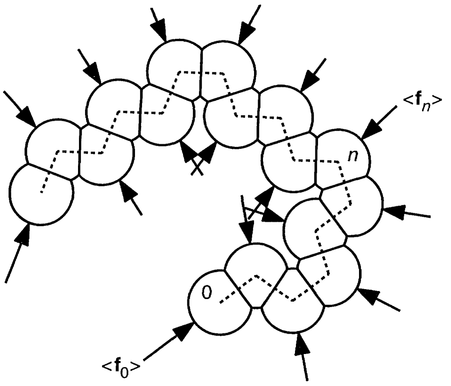

Fig. 3. Intrinsic forces acting on a long-chain molecule in a dense polymer system [after (*19*)]. Arrows represent the time-averaged resultant force, $\langle \mathbf{f}_n \rangle$, of all nonbonded forces acting on mer n. At each instant, force components are taken with respect to an intrinsic coordinate system for mer n in which covalent bonds attached to this mer are fixed. The intrinsic force $\langle \mathbf{f}_n \rangle$ is nonzero and is in the direction shown because of steric shielding.

$\lesssim 2$, although it is based on a radically different picture than what is observed on the atomic level in our simulations. As λ increases beyond $\lambda \cong 2$, however, a new feature appears in the interacting chain case. The simulations show that the forces **f** and $-$**f** cease to be coaxial with the chain vector **R**; that is, they become equivalent to an axial force plus end moments **M**, and the magnitude of these moments may be determined from the simulation results. The origin of the moments may be understood as follows: The required end forces **f** and $-$**f** are, as we have noted, due to the EV interactions of the given chain with the surrounding chains. For small λ, the surrounding chains are isotropically distributed and the force **f** is coaxial with **R**. However, for $\lambda \gtrsim 2$, anisotropy in these interactions produces the need for end moments in addition to an axial force. Furthermore, it is found by application of Eq. 7 that these moments are in a direction such that they cause a softening in the predicted stress-extension relation, a softening in qualitative and semiquantitative accord with the experimentally observed Mooney effect (*22*). This softening mechanism, based on anisotropic interchain interactions, is related to that put forth some time ago by DiMarzio (in *26*) that is based on the change of packing entropy with deformation. In a recent paper (*27*), DiMarzio concludes that the packing entropy effect is only one of three important effects in rubber elasticity [the other two being the chain confinement effect, often modeled by tubes (*28*), and the entanglement effect, sometimes modeled by slip rings (*29*)] and that a unified theory incorporating all three effects in a consistent manner is needed.

Intrinsic stresses. Along with the discussion of intrinsic forces given above, we have also found it useful to introduce the concept of intrinsic stresses. These are defined in the following way: As a consequence of the virial theorem, the stress t_{ij} in a system of interacting atoms at temperature T can be written in the form

$$\frac{vt_{ij}}{kT} = \sum_{\beta} \langle \sigma_{ij}(\beta) \rangle \qquad (8)$$

where the sum is over all of the atoms in the basic cell of volume v. The quantity $\langle \sigma_{ij}(\beta) \rangle$ is the time average of the instantaneous contribution that atom β makes to the dimensionless stress, vt_{ij}/kT. The explicit form of $\sigma_{ij}(\beta)$ depends, of course, on the nature of the interactions among the atoms of the system. For an ideal gas, $\sigma_{ij}(\beta) = -\delta_{ij}$. For a system with general pair interactions, the expression for $\sigma_{ij}(\beta)$ can be deduced directly from Eq. 6; for a polymer model with three-body potentials used to express valence angle constraints, the explicit form of $\sigma_{ij}(\beta)$ is given in (*11, 12*).

Both $\sigma_{ij}(\beta)$ and t_{ij} in Eq. 8 are referred to the same fixed laboratory frame, x_i, $i = 1, 2, 3$. Because we are interested in the effect of the covalent structure upon the interactions at each time step of the simulation, we refer the tensor $\sigma_{ij}(\beta)$ to a local coordinate system, $\bar{x}_r(\beta)$, where $r = 1, 2, 3$, which moves so that it always bears a fixed relation to the covalent bonds attached to mer β. The components of the mer stress that are referred to $\bar{x}_r(\beta)$ are denoted by $\bar{\sigma}_{rs}(\beta)$, and the time average of $\bar{\sigma}_{rs}(\beta)$ over all of the monomers of the system is denoted by $^*\sigma_{rs}$. We refer to $^*\sigma_{rs}$ as the intrinsic monomer stress (IMS). As is the case for the macroscopic stress, we find that at liquid-like densities the nonbonded interactions make the dominant contribution to the deviatoric part of the IMS.

This concept provides a clear picture, on the atomic level, of the nature of stress in a rubberlike solid. As an illustration, we have performed computer simulations (*30*) of a network model and of the corresponding melt in which all chains are allowed to move freely with all other parameters unchanged. In the melt, the macroscopic state of stress in equilibrium is purely isotropic; the network model, when extended, shows the expected behavior of the deviatoric stress, or stress difference $t_{11} - t_{22}$, as a function of the extension ratio, λ. However, the IMS $^*\sigma_{rs}$ is identical, within numerical error, in the melt and deformed networks and is independent of λ in the latter. We may think of each mer of either network or melt and its associated covalent bonds as a carrier of an IMS whose principal directions bear a fixed relation to the covalent structure. In the melt the covalent structure rotates freely in space, and therefore the effect of the IMS, when referred back to the laboratory frame, is purely isotropic. The mobility of the covalent structure in the network is restricted because of the chain cross links. In the reference configuration of the network, the covalent structure orientations are isotropically distributed in space and the resultant of the IMS contributions remains isotropic. However, when the network is stretched, the covalent structure becomes anisotropic and the resultant of the IMS contributions gains an anisotropic component (Fig. 4). Therefore, the word "intrinsic" in the terminology for $^*\sigma_{rs}$ is seen from these simulations to have dual significance: It is the monomer stress referred to a coor-

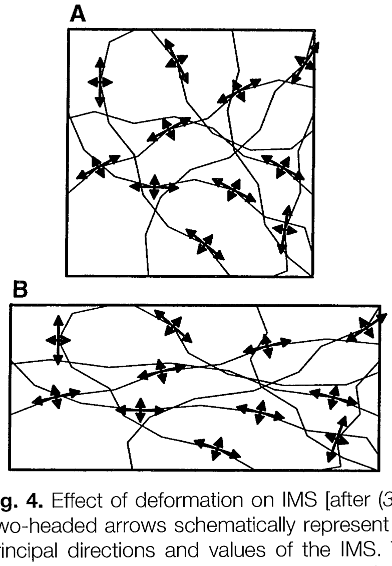

Fig. 4. Effect of deformation on IMS [after (*36*)]. Two-headed arrows schematically represent the principal directions and values of the IMS. The principal values are the same for all mers in the system [except for chain ends (*36*)]. (**A**) In the undeformed system, principal directions are isotropically distributed. (**B**) When the system is deformed, the principal direction distribution becomes anisotropic.

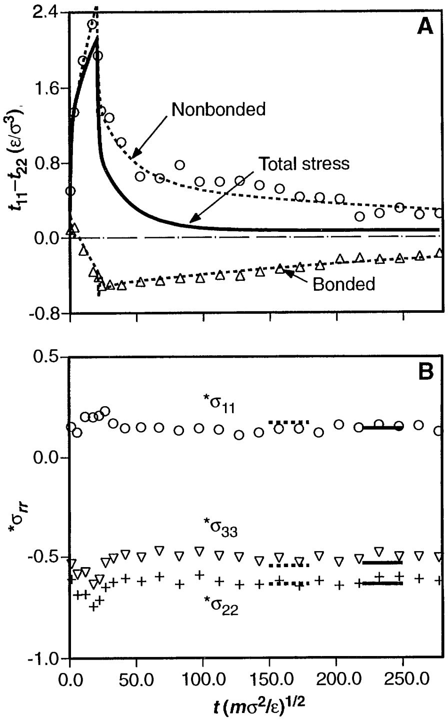

Fig. 5. Time history of macroscopic stress and of IMS during a loading and unloading process [after (*36*)]. Results of a nonequilibrium molecular dynamics simulation of a melt of freely rotating chains with $N = 40$ bonds each and with parameter values of the freely rotating chain model of Takeuchi and Roe (*39*) at $T = 172$ K. For these parameter values, $(m\sigma^2/\epsilon)^{1/2} = 2$ ps, where m is the monomer mass. Melt is subjected to a constant-volume strain in the x_1 direction at the rate of $\dot{\epsilon}_0 = 0.01$ ps^{-1} for $t \leq 42$ ps, followed by unloading with $\dot{\epsilon}_0 = 0$. (**A**) Macroscopic stress difference, $t_{11} - t_{22}$, together with separate contributions made by bonded and nonbonded interactions. (**B**) IMS history during the same loading and unloading process. By definition (Eq. 8), IMS components $^*\sigma_{rr}$ (no sum) are nondimensional. Solid lines represent values of $^*\sigma_{rr}$ for the corresponding equilibrium melt; dashed lines represent simulation results for the values of $^*\sigma_{rr}$ in the stretched model network of the same chain system.

dinate system that bears a fixed relation to the covalent structure, and it has the same value in a stretched network that it has in the corresponding polymer melt.

Viscoelasticity of polymer melts. The work described so far has focused on systems in equilibrium. We have, more recently, developed a nonequilibrium molecular dynamics (*12*, *31*, *32*) algorithm for the simulation of the viscoelasticity of polymer melts. This algorithm can be used, for example, to determine the stress relaxation in a melt after it has been subjected to a shear or a constant-volume elongation that rises rapidly to a peak value and is then maintained constant. Among the main results from these studies are the following:

1) Nonbonded interactions make the dominant contribution to the deviatoric stress throughout the relaxation process, except for a very brief initial period (Fig. 5A). This finding is contrary to the generally accepted view that adopts the EVHH and entropic spring physical picture but is in agreement with recent results of Fixman (*33*), who uses a different model and algorithm.

2) For systems in equilibrium we found that, although the stresses were due to nonbonded interactions on the atomic level, the entropic spring concept provided an effective computational device for these stresses. In contrast, for the stress relaxation process the simulations (*32*) reveal that the entropic spring concept, as embodied in the Rouse chain model (*34*), greatly underestimates the actual stress until it has decayed to the rubbery regime.

3) The simulations (*12*) satisfy the time-temperature equivalence principle, and the required temperature-dependent shift factors obey the William-Landel-Ferry (WLF) equation as observed in real systems (*35*).

4) The concept of IMS developed earlier for equilibrium systems was also found to apply to these nonequilibrium processes. During the stress relaxation process in which the macroscopic deviatoric stress decays by a factor of 20, the IMS values are found to remain substantially constant (Fig. 5B). We are thus led to still another interpretation of the term "intrinsic." This definition leads to a new monomer-level view of the later stages of stress relaxation through the randomization of the orientation of the IMS tensors (that is, from Fig. 4B to Fig. 4A), which parallels completely a corresponding view of birefringence decay for polymers in which the polarizability tensor is also an intrinsic monomer tensor. This new view leads to a simple expression for the stress-optical coefficient in the rubbery regime in terms of the monomer polarizability and the IMS (*36*).

Conclusions

The view of stress in dense polymer systems on the atomic or monomer level that arises from computer simulations reveals some unexpected features: (i) The process of steric shielding renders anisotropic the contribution that the two-body nonbonded interactions make to the stress in deformed systems. (ii) At liquidlike densities, the covalent bonds of the backbone chains are in compression. As a result of this compression, these bonds make a negative contribution to the tensile stress difference in an elongational deformation. (iii) IMS plays an important role in undetstanding the stress in dense polymer systems.

In spite of the great differences between this monomer-level picture and the classical molecular-level description based on entropic springs and the EVHH, simulations show that the latter serves as an accurate method for computing the stress in moderately deformed cross-linked systems in equilibrium and in the later stages of stress relaxation in melts. Calculations based on the classical picture become less accurate for cross-linked systems at larger elongations and greatly underestimate the stress in the earlier stages of stress relaxation in melts. A theoretical analysis that would clearly delineate the conditions under which the classical molecular approach is accurate would be most valuable.

The central role played by EV interactions in stress production as illustrated in this monomer-level description makes clear the importance of ρ, the reduced density, or ϕ, the packing fraction of the system. The importance of these parameters, in turn, helps to explain the dramatic effects of high pressure (*37*, *38*) on the mechanical behavior of polymeric systems, effects that are difficult to explain solely in terms of the entropic spring plus EVHH picture.

REFERENCES AND NOTES

1. W. Thomson (later Lord Kelvin), *J. Pure Appl. Math.* **1**, 57 (1857).
2. J. P. Joule, *Philos. Trans. R. Soc. London* **149**, 91 (1859).
3. See, for example, L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon, Oxford, ed. 3, 1975).
4. H. Morawetz, *Polymers: The Origins and Growth of a Science* (Wiley, New York, 1985).
5. E. Guth and H. Mark, *Monatsh. Chem.* **65**, 93 (1934).
6. D. Chandler *et al.*, *Science* **220**, 787 (1983).
7. See, for example, M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986), p. 111; J. E. Mark and B. Erman, *Rubberlike Elasticity: A Molecular Primer* (Wiley, New York, 1988), p. 12.
8. D. Y. Yoon, G. D. Smith, T. Matsuda, *J. Chem. Phys.* **98**, 10037 (1993).
9. See, for example, M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
10. R. J. Swenson, *Am. J. Phys.* **51**, 940 (1983); J. Gao and J. H. Weiner, *Macromolecules* **20**, 2520 (1987).
11. J. Gao and J. H. Weiner, *J. Chem. Phys.* **90**, 6749 (1989).
12. ———, *ibid.* **97**, 8698 (1992).
13. D. N. Theodorou, T. D. Boone, L. R. Dodd, K. F. Mansfield, *Makromol. Chem. Theory Simul.* **2**, 191 (1993); J. H. Weiner and J. Gao, *Modelling Simul. Mater. Sci. Eng.* **2**, 755 (1994).
14. J. Gao and J. H. Weiner, *Macromolecules* **24**, 1519 (1991).
15. J. H. Weiner and D. H. Berman, *J. Chem. Phys.* **82**, 548 (1985).
16. J. Gao and J. H. Weiner, *Macromolecules* **22**, 979 (1989).
17. ———, *Mol. Phys.* **70**, 299 (1990).
18. ———, *J. Chem. Phys.* **91**, 3168 (1989).
19. ———, *ibid.* **98**, 8256 (1993).
20. Steric shielding has the same bond compression effects in small molecular systems. See (*17*); G. P. Morriss, P. J. Daivis, D. J. Evans, *J. Chem. Phys.* **94**, 7420 (1991); T. Tominaga and S. Yip, *ibid.* **100**, 3747 (1994). It also appears possible that some of the monomer aspects of stress presented here for polymer melts belong also to polymers in solution in a small molecule solvent; we have not explored such systems as yet.
21. See, for example, figure 1 in P. J. Higgs and R. J. Gaylord, *Polymer* **31**, 78 (1990).
22. J. Gao and J. H. Weiner, *Macromolecules* **24**, 5179 (1991).
23. R. J. J. Jongschaap, *Rep. Prog. Phys.* **53**, 1 (1990).
24. J. H. Weiner, *Am. J. Phys.* **55**, 746 (1987).
25. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979). [The Flory theorem states that $p(\mathbf{R})$, the probability distribution for the end-to-end chain vector **R**, approaches the probability for the ideal chain in a sufficiently dense melt. The result for the chain force follows from the relation

$$\mathbf{f} = -kT\frac{\partial}{\partial \mathbf{R}}\log p(\mathbf{R})$$

which, as shown in (*22*), is valid for a chain in interaction with a melt as well as for an isolated chain.]
26. E. A. DiMarzio, *J. Chem. Phys.* **36**, 1563 (1962). See also J. L. Jackson, M. C. Shen, D. A. McQuarrie, *ibid.* **44**, 2388 (1966); T. Tanaka and G. Allen, *Macromolecules* **10**, 426 (1977). The related question of residual nematic interactions is treated by M. Warner and X. J. Wang, *ibid.* **24**, 4932 (1991).
27. E. A. DiMarzio, *Polymer* **35**, 1822 (1994).
28. S. F. Edwards, *Proc. Phys. Soc. London* **92**, 9 (1967); G. Marrucci, *Macromolecules* **14**, 434 (1981); R. J. Gaylord, *Polymer Bull.* **8**, 325 (1982); R. J. Gaylord and J. F. Douglas, *ibid.* **18**, 347 (1978); J. F. Douglas and G. B. McKenna, *Macromolecules* **26**, 3282 (1993).
29. D. Adolf, *Macromolecules* **21**, 228 (1988); P. G. Higgs and R. C. Ball, *Europhys. Lett.* **8**, 357 (1989). The review by S. F. Edwards and T. A. Vilgis [*Rep. Prog. Phys.* **51**, 243 (1988)] deals with slip link and other models of rubber elasticity and contains an extensive bibliography.
30. J. H. Weiner and J. Gao, in *Computer Simulation of Polymers*, R. J. Roe, Ed. (Prentice-Hall, Englewood Cliffs, NJ, 1991), p. 255.
31. J. Gao and J. H. Weiner, *Macromolecules* **25**, 1348 (1992).
32. ———, *ibid.*, p. 3462.
33. M. Fixman, *J. Chem. Phys.* **95**, 1410 (1991).
34. P. E. Rouse, *ibid.* **21**, 1272 (1953).
35. J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, ed. 3, 1983).
36. J. Gao and J. H. Weiner, *Macromolecules* **27**, 1201 (1994).
37. H. N. Yoon, K. D. Pae, J. A. Sauer, *J. Polym. Sci. Polym. Phys. Ed.* **14**, 1611 (1976).
38. A. L. Kovarskii, Ed., *High-Pressure Chemistry and Physics of Polymers* (CRC Press, Boca Raton, FL, 1994).
39. H. Takeuchi and R.-J. Roe, *J. Chem. Phys.* **94**, 7446 (1991); *ibid.*, p. 7458.

40. This research has been supported by the Gas Research Institute. The computer simulations have been performed at the Pittsburgh Supercomputer Center.