Atomic-Level Description of Stress in Dense Polymeric Systems

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ABSTRACT

A new framework is being developed to describe stress production and relaxation in dense polymeric systems. Stress is traditionally defined on the molecular scale, with the chains being regarded as entropic springs. In this view, the polymeric chains are considered to be always in tension and stress is due exclusively to bonded interactions along the chains. Stretching the chains leads to a retractive force of an entropic nature. Non-bonded interactions between atoms belonging to neighboring chains are considered to lead to hydrostatic stress only. The new description is defined on the atomic rather than on the molecular scale. It takes into account all (bonded and non-bonded) interactions, and makes no *apriori* assumption about the behavior of any component of the system. Since it is defined on the atomic scale, the description captures all fast and slow relaxation modes that correspond to short and long wavelength perturbations, respectively. It is therefore equally applicable to small and large volumes of material and to short and long chains. This report presents a brief overview of this new framework. It is discussed which assumptions made in the molecular theory are justified by atomistic simulation results and which are not. It is shown that both theories are in qualitative agreement with the experimentally observed physical picture, while the atomic scale description offers the advantages mentioned above.

Keywords: Polymer dynamics, Stress relaxation, Polymer molecular structure.

1 INTRODUCTION

Most treatments of viscoelasticity in polymeric systems are on the molecular level [1-3], with chains regarded as entropic springs in tension. The deformation of the material leads to chain stretching and hence to preferential orientation of chain segments in the direction of the flow. This leads to a macroscopic deviatoric stress. Thermodynamically, the stress results from the variation of the system entropy associated with the preferential orientation of chains, and from here its (postulated) "entropic" nature. The energetic component of the free energy is usually neglected in these theories. This is rooted in the conjecture that the neighborhood of a representative chain segment does not change during deformation, and only the average segment orientation, and hence the entropy, changes.

Therefore, the chains are regarded as being always in tension and the non-bonded interactions, between atoms that are not covalently bonded, are assumed to contribute to the hydrostatic stress only.

Since this theory is defined on the molecular scale, and since it neglects the role of non-bonded interactions in stress production, it fails to represent phenomena that take place on a scale smaller than the smallest intrinsic length scale of the theory (usually, an ill-defined chain segment length). For example, the theory is unable to represent the fast relaxation modes (β relaxation) which correspond to system perturbations having very small wavelength and which involve localized structural changes only. Furthermore, the theory should not apply to small volumes of material or to polymers confined in nanoscale volumes, if the volume is smaller than the intrinsic length scale of the model.

These observations determined the development of the "intrinsic stress framework."[4-7] In this description, stresses are computed on the atomic scale, scale which imposes the (natural) length scale cut-off for structural problems. Both bonded and non-bonded interactions are considered and it is shown that, in fact, the non-bonded interactions are more significant than the bonded ones. Furthermore, several essential features of the macroscopic system behavior (e.g. the stress-optical coefficient) may be derived from atomic-scale quantities computable in this framework [6-8]. Interestingly, several important regimes of stress relaxation and their time constants may be evaluated from equilibrium simulations based on the fluctuation-dissipation theorem [9]. The entropic nature of stress in the intrinsic model is a result rather than an assumption, as in the entropic spring theory [10].

A brief summary of the definition of the intrinsic stress framework and the main developments associated with this concept is presented next. The reader is referred to the cited literature for further details.

2 THE MODEL

The principal tool in this investigation is the computer simulation of model systems consisting of dense collections of molecules. The molecules are represented by a "pearl necklace" type model in which particles represent atoms linked into chains by stiff linear springs representing covalent bonds. The studied systems are monodisperse. Both short (2 to 4 atoms per chain) and long (200 atoms per chain) are considered. The covalent bond between the pair of atoms of each molecule is represented by the quadratic

potential $u_b(r) = \frac{1}{2}\kappa(r - b_0)^2$, while the interactions between non-covalently bonded atoms are modeled by a purely repulsive 12-6 Lennard-Jones potential. Here r denotes the distance between any pair of atoms and b_0 is the undeformed bond length. The units of the problem are those imposed by the Lennard-Jones potential.

The system is evolved by molecular dynamics, with the forces being computed based on both bonded and non-bonded interactions. The algorithm used to integrate the equations of motion as well as the thermostat are those due to Berendsen *et al* [11]. Periodic boundary conditions are used in the simulations as is customary in molecular dynamics. The basic cell referred to a Cartesian system is, in the equilibrium state, a cube of dimensions L. There are N atoms per unit cell, which leads to a reduced density $\rho = N/L^3$. The initial configuration of the system of chains is obtained by performing self-avoiding random walks on a dummy BCC lattice that fills the undeformed simulation cell. Only configurations with a random bond orientation are retained. Then, a high temperature equilibration is performed by molecular dynamics, in order to obtain a proper melt structure.

Both equilibrium and non-equilibrium simulations are performed. In non-equilibrium simulations, the system undergoes a constant volume elongational deformation. The relaxation, both stress and structural, is observed after the deformation is completed, with the simulation cell size and shape being kept unchanged.

In order to reduce the noise in measured quantities, the simulation is repeated a large number of times (usually about 200 times) and the results are obtained by averaging over all replicas.

3 THE INTRINSIC STRESS FRAMEWORK

3.1 Global Atomic Level Stress

The stress t_{ij} expressed in the global coordinate system x_i tied to the simulation cell is computed using the virial stress formula as

$$Vt_{ij} = -NkT\delta_{ij} + \frac{1}{2}\sum_{m=1}^{N}\left\langle \sum_{n=1}^{N_m} r_{mn}^{-1} u'_{mn}(r_{mn}) r_{mni} r_{mnj} \right\rangle \qquad (1)$$

Here, $V = L^3$ is the volume of the unit cell, r_{mn} is the length of the vector $\mathbf{r}_{mn}$ between interacting atoms m and n and has components r_{mni}. The first sum is taken over all atoms in the system while the second is over all N_m atoms interacting with atom m at time t in a given simulation. The contribution to stress of both bonded and non-bonded interactions is considered, with u_{mn} representing the respective potential. The kinetic contribution -NkT is assumed to contribute to the hydrostatic stress only since the thermal velocities are much higher than those due to the deformation of the simulation cell. The angular bracket represents averaging over all replicas. Hence, the non-kinetic contribution to global stress of a representative atom m, at time t and in a given simulation, is therefore

$$\sigma_{ij}^{m} = \frac{1}{2V}\sum_{n=1}^{N_m} r_{mn}^{-1} u'_{mn}(r_{mn}) r_{mni} r_{mnj} \qquad (2)$$

3.2 Intrinsic Atomic Level Stress

The stress may also be computed in the intrinsic coordinate system, $\tilde{x}_i$ ($\tilde{\sigma}_{ij}$). This frame is chosen for each atom such that the axis $\tilde{x}_1$ is always tied to the covalent bond between atoms j and j+1. Hence, the intrinsic frames associated with each bead are mobile and rotate in space during deformation. The intrinsic stress computed for atom m is related to the contribution of the same atom to the global stress by a simple rotation of the coordinate system from global to intrinsic axes. The intrinsic stress is computed by averaging the stress tensor components over the whole population of intrinsic frames. The intrinsic stress so obtained is a cylindrical tensor in which the only non-zero components are $\tilde{\sigma}_{11}$ and $\tilde{\sigma}_{22} = \tilde{\sigma}_{33}$.

The most striking property of the intrinsic stress tensor is its invariance during system deformation at temperatures above the glass transition.

Figure 1a shows typical stress variation during the loading and relaxation periods for a system of density $\rho = 1$ and at temperature T = 1 (a dense melt). Here, only the non-bonded contribution to the global deviatoric stress is shown. The relaxation period begins at time t = 2. Various relaxation regimes are labeled in the Figure and are discussed in Section 4. The variation of the intrinsic stress during the same simulation is shown in Fig. 1b. It is seen that, except a small oscillation during loading, all components of the intrinsic stress tensor are insensitive to the deformation of the system of chains.

The insets show by shades of gray the non-bonded neighbor number density about a representative atom at two instants of time, at the end of the loading period, and later, during relaxation. The distribution is shown up to the cut-off radius of the potential. In the close neighborhood of the representative atom (RA), the neighbor number density vanishes due to the excluded volume effect and hence the interacting neighbors are located in a thin spherical layer about RA. The intrinsic distribution vanishes in the direction of the $\tilde{x}_1$ axis due to the steric shielding.

Both the global and the intrinsic stresses are directly related to this distribution. The distribution computed in the global coordinate system (tied to the simulation cell and fixed during loading and relaxation) changes. At the end of the loading period, a low density region is observed along the simulation cell stretch direction, with a corresponding increase in density along the equatorial plane normal to the stretch direction. When computed in the intrinsic frame, the

neighbor number density is seen to be an invariant of deformation. In fact, this is the physical origin of the invariance of the intrinsic stress tensor. Furthermore, the intrinsic stress and distribution shown here for the system in non-equilibrium are identical to those computed in equilibrium at the same density and temperature.

The situation described above allows a fundamental insight into the physics of stress production in the global coordinate system (and hence on the mesoscopic scale). The intrinsic frames carry a constant neighbor number density and a non-zero deviatoric stress tensor. In equilibrium, these frames (covalent bonds) are randomly oriented in space. The global stress and distribution may be

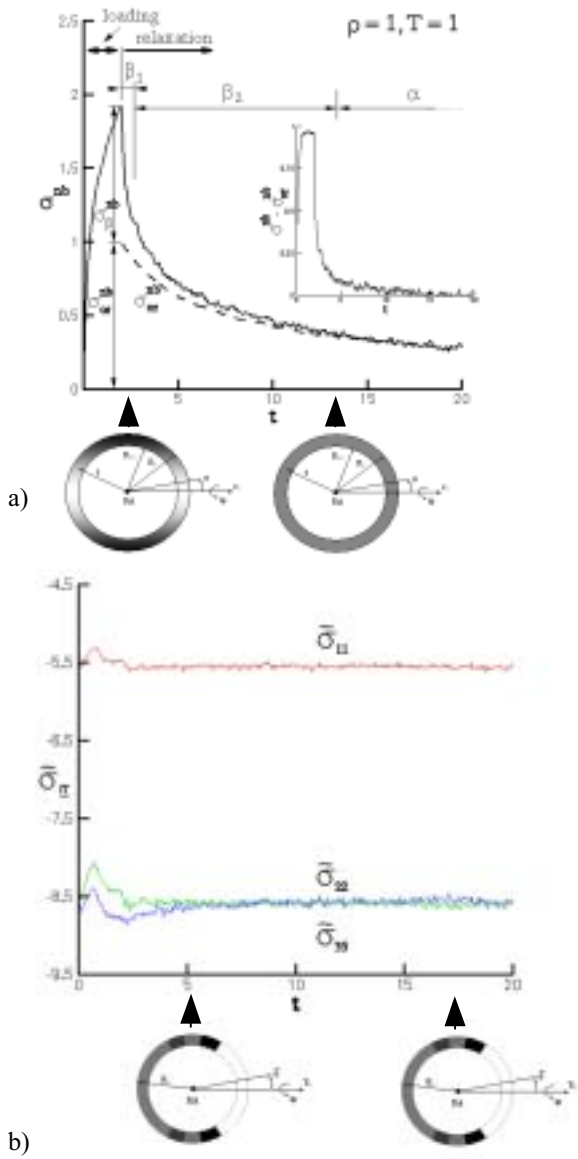

Figure 1. Evolution of the global deviatoric stress (a) and intrinsic stress components (b) due to non-bonded interactions during loading and relaxation. The insets show by shades of gray the neighbor number density about the representative atom (RA) at the end of loading and during relaxation.

obtained by averaging the intrinsic quantities over all spatial orientations. This leads to an isotropic neighbor number density and to a hydrostatic stress only.

The deformation of the system leads to preferential bond orientation. The same averaging process leads in this case, to a global deviatoric stress. Hence, the global deviatoric stress may be obtained as a function of a measure of the average bond orientation and the intrinsic stress components.

3.3 The Stress-Optical Coefficient (SOC)

The last statement may be made more specific. The SOC, or the ratio of birefringence to stress is defined here as the ratio of P_2, the second moment of the bond orientation distribution, to the atom-based stress. The global stress difference defined by $\sigma = t_{11} - (t_{22} + t_{33})/2 = (3/2)^D t_{11}$, may be expressed in terms of the deviatoric intrinsic stresses ${}^D\tilde{\sigma}_{ii} = \tilde{\sigma}_{ii} - (\tilde{\sigma}_{11} + \tilde{\sigma}_{22} + \tilde{\sigma}_{33})/3$ as

$$\sigma = \sigma^b + \sigma^{nb} = CP_2(\theta_b)\,. \tag{3}$$

Here, the coefficient C is the inverse of the stress-optical coefficient SOC (C = 1/SOC), and is expressed as

$$C = \frac{3}{2}\left[\rho_b\, {}^D\tilde{\sigma}^b_{11} + \rho_a D\, {}^D\tilde{\sigma}^{nb}_{11}\right]. \tag{4}$$

${}^D\tilde{\sigma}^b_{11}$ and ${}^D\tilde{\sigma}^{nb}_{11}$ represent the deviatoric intrinsic stresses due to bonded and non-bonded interactions, respectively.

It results that the SOC, which is a macroscopically measurable quantity describing the non-equilibrium state of the polymeric system, may be expressed in terms of atomic scale parameters computable from equilibrium simulations!

3.4 Stress Due to Bonded Interactions

Given the specific choice of the orientation of the intrinsic coordinate system, the intrinsic stress induced by bonded interactions has only one non-zero component, $\tilde{\sigma}^b_{11}$. Similar to the situation depicted in Fig. 1b, this component is essentially insensitive to the deformation of the material, and is negative. This shows that the bonds are in compression. The observation contradicts the traditional view of the entropic spring model in which the chains are considered to be, by definition, in tension.

The global stress due to bonded interactions may be obtained from the intrinsic bonded stress $\tilde{\sigma}^b_{11}$ as

$$\sigma^b = \rho_b \tilde{\sigma}^b_{11} P_2(\theta_b)\,, \tag{5}$$

where, as before, $P_2 = \frac{1}{2} < 3\cos^2\theta_b - 1 >$ (θ_b is the angle defining bond orientation) is the second moment of the bond orientation distribution. This relationship shows that the global bonded stress is negative, and the total global stress results by its summation with the non-bonded contribution shown in Fig. 1a (which is positive).

4 STRESS RELAXATION

A typical relaxation of the non-bonded global stress is shown in Fig. 1a. The dashed line in the figure shows the predictions of eqn. (3), with the constant C computed based on intrinsic stresses evaluated in equilibrium. It is apparent that, at later times, the global non-bonded stress becomes proportional to P_2, fact that allows the definition of the stress-optical coefficient. It is noted that the bonded global stress is always proportional to P_2, by definition. The global stress departs from this proportionality rule at early times, right after the end of the loading period. This observation allows for the definition of two relaxation regimes, α and β, which are in direct correspondence to the experimentally observed "slow" and "fast" relaxation modes in polymeric melts.

The fast β modes in this system encompasses two regimes: $\beta 1$ and $\beta 2$. The β relaxation is best viewed if the stress component proportional to P_2 (the dashed line in Fig. 1a) is subtracted from the global stress. This residual is shown in the inset to Fig. 1a and the two regimes appear clearly. The $\beta 1$ regime accounts for about 50% of the total stress drop during relaxation. Since it is very fast, it is not of significant importance to the rheology of the system. This was shown to be a quasi-elastic rebound, with the magnitude of the stress drop being proportional to the magnitude of the perturbation imposed during loading (defined in terms of the structural changes in the melt during loading).

The $\beta 2$ mode is slower and accounts for the relaxation of a smaller fraction of the total stress. Hence, the mode is rheologically important. It was shown that, by contrast to $\beta 1$, the $\beta 2$ mode is exponential and the associated mechanism is diffusional.

Most interestingly, its time constant may be derived from equilibrium, based on a continuum model of diffusion in the neighborhood of the representative atom and on the fluctuation dissipation theorem. This finding shows that the system is in the non-equilibrium linear response regime during $\beta 2$. Furthermore, since the system is in "close non-equilibrium" during $\beta 2$, i.e. relatively early during the stress relaxation history, it results that the same state prevails during the whole subsequent α relaxation. This, in turn, implies that the time constant of the exponential relaxation modes active during the α regime may be derived from equilibrium simulations.

This set of observations shed a new light on the nature of stress production and relaxation in polymeric system above the glass transition, and define procedures for the evaluation of the associated time constants from relatively short equilibrium simulations. This topic is discussed at length in Ref. [9] and in two upcoming publications.

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