Significance of cross correlations in the stress relaxation of polymer melts

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Significance of cross correlations in the stress relaxation of polymer melts

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According to linear response theory, all relaxation functions in the linear regime can be obtained using time correlation functions calculated under equilibrium. In this paper, we demonstrate that the cross correlations make a significant contribution to the partial stress relaxation functions in polymer melts. We present two illustrations in the context of polymer rheology using (1) Brownian dynamics simulations of a single chain model for entangled polymers, the *slip-spring* model, and (2) molecular dynamics simulations of a multichain model. Using the single chain model, we analyze the contribution of the confining potential to the stress relaxation and the plateau modulus. Although the idea is illustrated with a particular model, it applies to any single chain model that uses a potential to confine the motion of the chains. This leads us to question some of the assumptions behind the tube theory, especially the meaning of the entanglement molecular weight obtained from the plateau modulus. To shed some light on this issue, we study the contribution of the nonbonded excluded-volume interactions to the stress relaxation using the multichain model. The proportionality of the bonded/nonbonded contributions to the total stress relaxation (after a density dependent "colloidal" relaxation time) provides some insight into the success of the tube theory in spite of using questionable assumptions. The proportionality indicates that the shape of the relaxation spectrum can indeed be reproduced using the tube theory and the problem is reduced to that of finding the correct prefactor. © *2007 American Institute of Physics*.
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I. INTRODUCTION

Time correlation functions reveal relaxation properties of physical systems and consequently are often calculated in computer simulations.[1,2] Alternatively, it is possible to measure the relaxation of the quantity of interest after a perturbation. If the perturbation is "small," then according to linear response theory, the two methods should yield identical relaxation functions.[3] In order to improve the response signal, especially in molecular dynamics simulations of polymer melts, large values of the perturbation field are typically used,[4,5] but then the system may no longer be in the linear regime. In contrast, time correlation functions calculated at equilibrium yield linear response functions. The calculation of time correlation functions frequently consumes significant CPU time and memory resources. Recently developed efficient methods[6–8] have made this computation significantly easier.

Using simulations we can go further than merely calculating the total response function and investigate the different contributions to the response. For example, a question of some significance in dense polymer systems is the bonded versus nonbonded contributions to the deviatoric stress. Gao and Weiner have extensively investigated this issue by using molecular dynamics simulations (see Refs. 5 and 9 and references therein). To the best of our knowledge, the same kind of study at equilibrium, including the analysis of the cross correlations between the bonded and nonbonded contributions, has not yet been addressed in the literature. According to linear response theory, such partial contributions can be obtained using *only* the equilibrium time correlation functions. This obviates the need for the usually more computationally expensive nonequilibrium simulations. In the present paper we intend to clarify, both theoretically and by example, the importance of the cross correlations when calculating partial relaxation functions using time correlation functions.

A single chain model to describe the dynamics and rheology of entangled polymers, the *slip-spring* model, has recently been proposed by Likhtman.[10,11] Inspired by a model to describe rubber elasticity,[12] it contains all the relaxation mechanisms accounted for by most tube theories.[13,14] In addition, the model describes, in a natural manner, the transition between the unentangled (Rouse) and the entangled regimes. In this model, the confinement field due to entanglements is introduced in an explicit, discrete manner using harmonic potentials that connect the polymer chain to the nonfluctuating background. This entanglement potential constitutes an additional set of virtual springs whose one end is fixed in space while the other end is connected to the chain through a slip link which allows reptation-like motion of the chain (see Fig. 1).

The potential energy in the slip-spring model has two contributions: one due to the chain and the other due to the confining potential (virtual springs). According to the tube theory,[13,14] the stress originates within the probe chain inside the tube and all the intermolecular chain interactions are discarded. Similarly, in the slip-spring model, the stress tensor at any instant of time can be calculated from the current

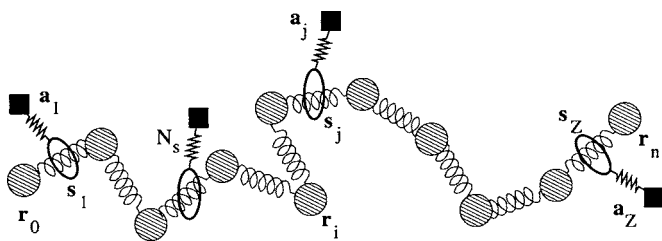a)Electronic mail: jorge@maths.leeds.ac.uk

FIG. 1. Slip-spring model of entangled polymers: a standard Rouse chain of $N+1$ beads is constrained by Z discrete virtual springs. The virtual springs have one end attached to anchoring points $\mathbf{a}_j$ (black squares) and the other is linked to the chain through slip links. The average distance between slip links is N_e segments, and the strength of the confining potential is measured by N_s, the equivalent number of segments of each virtual spring.

FIG. 2. Stress relaxation moduli from the slip-spring model for a chain with $N=64$, $N_e=4$, $N_s=0.5$, and $\xi_s=0.1$. (a) Real-chain relaxation modulus. Symbols: calculation at equilibrium using $\langle\sigma_{xy}^R(t)\sigma_{xy}^R(0)\rangle$. Lines: relaxation after step shear, $\sigma_{xy}^R(t,\gamma)/\gamma$. (b) Total relaxation modulus. Symbols: calculation at equilibrium using $\langle\sigma_{xy}^T(t)\sigma_{xy}^T(0)\rangle$. Lines: relaxation after step shear. $\sigma_{xy}^T(t,\gamma)/\gamma$. Values of the shear strain are indicated in the legend.

conformation of the chains using Kramer's expression.[15] In this expression, the stress depends only on the coordinates of the beads of the chain and there are no contributions from the virtual springs. Another reason for discarding the contribution from the confining potential is to avoid double counting when calculating the stress tensor. Virtual springs represent neighboring chains that are entangled with the probe chain. Their contribution to the stress is accounted for by applying Kramer's expression to all the other chains in the melt. Therefore, the $\alpha\beta$ component of the real-chain stress tensor ($\alpha,\beta=x,y,z$) of a slip-spring chain of N segments is

$$\sigma_{\alpha\beta}^R = c\frac{3k_BT}{b^2}\sum_{i=1}^{N}\langle(r_{\alpha,i}-r_{\alpha,i-1})(r_{\beta,i}-r_{\beta,i-1})\rangle. \quad (1)$$

Here, $r_{\alpha,i}$ is the α coordinate of bead i, k_B is the Boltzmann constant, T is the temperature, b is the Kuhn length of the chain segments, c is the chain concentration, and the average is taken over an ensemble of chains. Similarly, we can define the virtual springs' stress tensor to be

$$\sigma_{\alpha\beta}^V = c\frac{3k_BT}{N_sb^2}\sum_{j=1}^{Z}\langle(s_{\alpha,j}-a_{\alpha,j})(s_{\beta,j}-a_{\beta,j})\rangle, \quad (2)$$

where N_s measures the strength of the entanglement potential, Z is the number of slip links in a chain, and $\mathbf{s}$ and $\mathbf{a}$ are the position vectors of the slip link and the corresponding anchoring point, respectively (see Fig. 1). The total stress then is given as the sum $\sigma_{\alpha\beta}^T(t)=\sigma_{\alpha\beta}^R(t)+\sigma_{\alpha\beta}^V(t)$.

As mentioned earlier, the shear relaxation modulus can be calculated in two different ways: either by applying a "small" deformation to the sample or by measuring the autocorrelation of the shear stress at equilibrium. In Fig. 2, the results using these two approaches to the real stress and the total stress are shown. Both methods should agree in the linear regime. From Fig. 2 it is clear that this is the case for the total modulus [Fig. 2(b)]. However, the partial contributions to the modulus calculated by the two methods disagree at intermediate times [Fig. 2(a)], even as $\gamma\rightarrow0$. This suggests that, even if one assumes that the virtual springs do not contribute to the instantaneous shear stress of the real chains, they contribute to the real-chain response function calculated using time correlation functions.

The tube theory assumes that all the chains besides the probe chain impose topological constraints on the probe chain (thereby confining it) and contribute additional friction
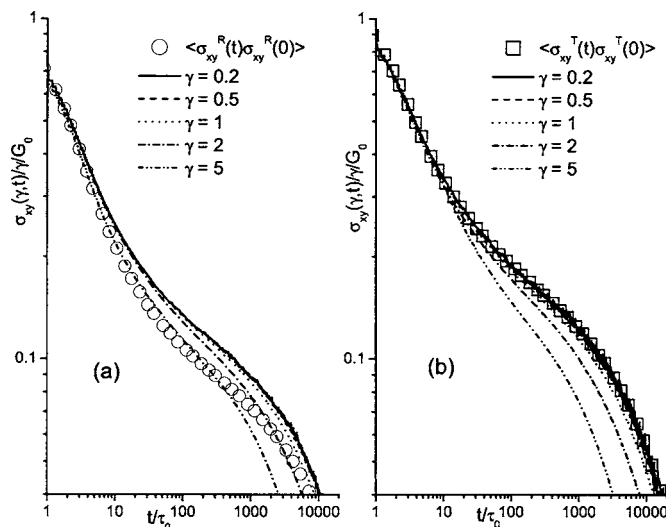
through their frequent collisions with the probe chain. The intermolecular interactions are assumed to decorrelate rapidly and consequently do not contribute to the plateau modulus. However, recent molecular dynamics simulations suggest that chain confinement within a tube-like region can be represented by a potential.[16] The observed potential is approximately quadratic, similar to the confining potential of the slip-spring model. The effect of such confinement potentials on the plateau modulus has not been addressed in the literature. In the present paper, we will explore this issue by studying the contribution of the cross correlations to the plateau modulus in the slip-spring model. The starting point for our discussion is a known result from linear response theory,[3] which refers to the calculation of a partial response function in a system with several additive contributions to the Hamiltonian. In the specific case of shear deformation (shear strain γ) for a system comprising real and virtual springs as described above, the shear relaxation modulus due to the real chain only is

$$G^R(t) = \frac{\overline{\sigma_{xy}^R(t)}}{\gamma} = \frac{V}{k_BT}(\langle\sigma_{xy}^R(t)\sigma_{xy}^R(0)\rangle + \langle\sigma_{xy}^R(t)\sigma_{xy}^V(0)\rangle).$$

$$(3)$$

This result states that the partial contribution to the linear relaxation function from the real chains is given by the sum of the autocorrelation function of the contribution to the shear stress from the real chains and the cross correlation between the contributions to the stress from the real and virtual chains. Although this result is not new and can be found in a more general form in standard textbooks,[3] it was overlooked in the past (for instance, see Ref. 10) and leads to interesting results that we will discuss in the remaining sections of this article. In Sec. II, we analyze the contribution to the relaxation modulus from the confining potential in single chain models. In Sec. III, we study the contribution of non-
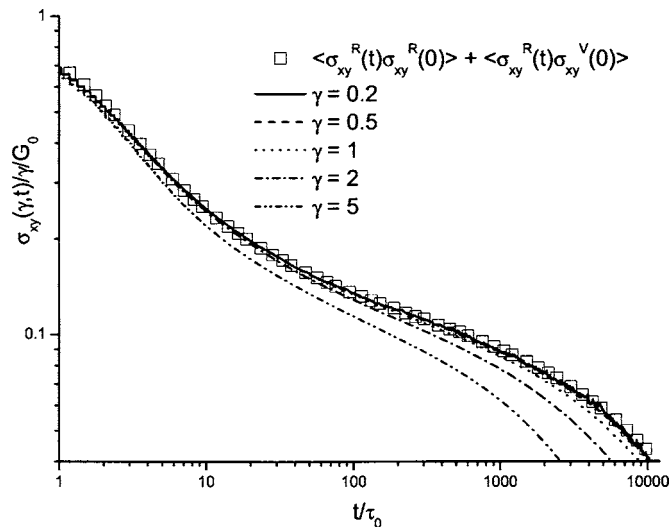
FIG. 3. Stress relaxation modulus from the slip-spring model (same parameters as in Fig. 2). Symbols: calculation at equilibrium using Eq. (3). Lines: relaxation after step shear, $\sigma^R_{xy}(t, \gamma)/\gamma$. Values of the shear strain are indicated in the legend.

FIG. 4. ϕ_T [Eq. (4)] as a function of N_e/N_s from the slip-spring model, $N = 32$, $\xi_s = 0.1$, and $N_e = 0.5, 1, 2, 4, 8$. N_s values are shown in the legend. Line: prediction of the Warner-Edwards model for a chain of infinite length [note that when $N_e/N_s \to 0$, $\phi_T = 0.5$, and when $N_e/N_s \to \infty$, $\phi_T \sim (N_e/N_s)^{-1}$].

bonded interactions to the stress relaxation in unentangled multichain models. In both sections, we will discuss the implications of the results for theories of polymer rheology. Following that, we will provide a summary of the results and briefly conclude. For the sake of completeness, a brief derivation of Eq. (3) is included in the Appendix.

II. STRESS RELAXATION IN THE SLIP-SPRING MODEL

In Fig. 3, the relaxation of the stress from the real chain in the slip-spring model after a step shear is shown, along with the results from Eq. (3). These results correspond to the same parameters used in the data shown in Fig. 2. The agreement between the equilibrium and nonequilibrium calculations is now excellent at all time scales. Similar plots have been produced for different chain lengths and different sets of the slip-spring model parameters (N_e, N_s, and ξ_s). In all cases, the nonequilibrium relaxation modulus for small shear deformation agrees exactly with the equilibrium value calculated using Eq. (3). We have also checked that it is possible to obtain the relaxation of the cross correlations from nonequilibrium simulations. For that purpose, we need to apply a perturbation to one of the parts of the system (i.e., the virtual springs) and then track the relaxation of the response from the other part (i.e., the stress tensor from the real chain).

The plateau modulus in a melt of linear polymers is defined in the limit of infinitely long chains. For chains of finite length, the relaxation modulus never shows a true plateau regime. Alternatively, the plateau modulus can be determined by preventing the chains from reptating out of their tubes. This is possible in the slip-spring model because reptation is determined by discrete first-passage events in the simulation. In practice, this is accomplished by substituting the disentanglement event by a reflecting boundary at the ends. The relaxation modulus now shows a horizontal plateau after the Rouse time of the chain. Any chain end effects, due to the
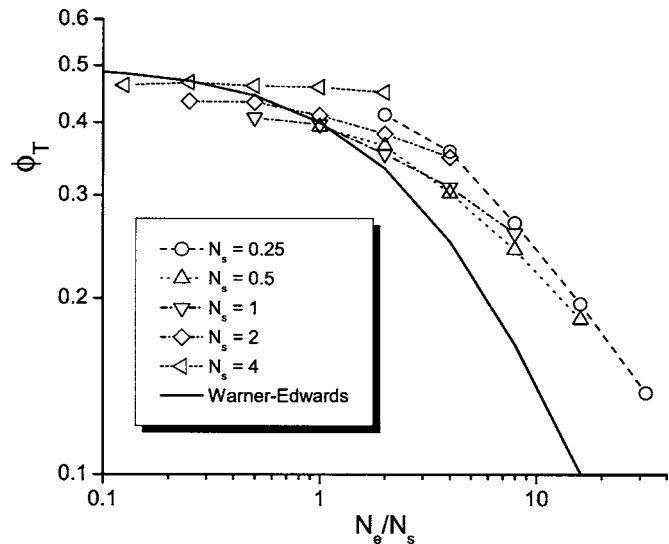
finite length of the chains, can be removed by calculating the plateau modulus for different chain lengths and extrapolating the results for $N \to \infty$.

In order to quantify the effect of the confining potential on the plateau modulus in the slip-spring model, the plateau modulus has been determined for different values of N_e and N_s, according to the method described above, both with and without the cross-correlation term in Eq. (3). We can measure the relative contribution from the cross correlations to the plateau modulus as

$$\phi_T = \lim_{t \to \infty} \frac{\langle \sigma^R_{xy}(t) \sigma^V_{xy}(0) \rangle}{\langle \sigma^R_{xy}(t) \sigma^R_{xy}(0) \rangle + \langle \sigma^R_{xy}(t) \sigma^V_{xy}(0) \rangle}. \qquad (4)$$

In Fig. 4, ϕ_T is plotted as a function of the ratio N_e/N_s. In the tube limit ($N_e/N_s \to 0$, many soft confining springs distributed along the chain), the cross correlations between the real and the virtual chains contribute to about 50% of the value of the plateau modulus. This is in agreement with a theoretical calculation of ϕ_T using the Warner-Edwards model for networks.[17,18] If $N_e/N_s > 1$, the contribution from the cross correlations to the plateau modulus in the model decreases monotonically but less rapidly than the corresponding Warner-Edwards calculation. This difference is most likely due to the longitudinal movement of the monomers in the slip-spring model, which is absent in the Warner-Edwards network. This reptation-like movement relaxes stress but does not affect the tube itself. Therefore, the relative contribution of the cross correlations to the plateau modulus is larger. In the opposite limit where $N_e/N_s \to \infty$, where we have long strands whose ends are strongly localized, we recover the limit of "Gaussian" network theories, with no contribution from the cross correlations to the stress.

In the particular case discussed in Figs. 2 and 3, $N_e/N_s = 8$. For that value, we can read in Fig. 4 that the relative contribution of the tube to the plateau modulus is about 30%. The same set of parameters was used for most of the results

included in the original slip-spring publication.[10] The contribution of the cross correlations to the stress relaxation function was not included in that paper, so all the results in that reference related to the plateau modulus and viscosity should be multiplied by a factor of 1.3.

As mentioned in the Introduction, a recent simulation suggests a particular form for the soft entropic potential that restricts the chain inside a tube.[16] The reported tube potential can be approximated by a quadratic potential at all times for excursions $r/\sigma < 5$, where σ is the unit of length in the simulation. For larger excursions, the potential is softer than quadratic and softens further as time progresses due to constraint release events. The tube radius obtained from this potential is similar to the one obtained by looking at crossovers in $g_2(t)$ (mean square monomer displacement with respect to the center of mass of the chain). In the slip-spring model, this would correspond to a small value of N_e/N_s (many slip links per chain, with fluctuations from the tube axis of the order of the tube radius). In that limit (see Fig. 4), the cross correlation with the confining potential of the tube is responsible for about half the plateau modulus.

From the above, it appears that, in any theoretical model where an explicit potential energy is used to confine the dynamics of a probe chain (in other words, to represent the tube), the tube itself contributes to the stress relaxation via cross correlations, even if the confining potential does not enter in the expression for the stress tensor. The classical expression for the plateau modulus as a function of the entanglement molecular weight is [see Eq. (7.128) in Ref. 13]

$$G_N^0 = \frac{4}{5}\frac{\rho_m RT}{M_e},\qquad(5)$$

where ρ_m is the mass density, M_e, the entanglement molecular weight, is defined in analogy with the classical theories of rubber elasticity, and the factor of 4/5 is due to the longitudinal stress relaxation. If the contribution from the cross correlations to the plateau modulus is not negligible, the meaning of M_e in the previous expression ceases to be clear.

III. RELAXATION MODULUS FROM MOLECULAR DYNAMICS

In this section we illustrate the role of cross correlations in molecular dynamics simulations by analyzing bonded/nonbonded and intra-/interchain contributions to the linear stress relaxation function. We use the standard Kremer-Grest model[19] of a dense polymer system. It consists of purely repulsive Lennard-Jones spheres connected by finitely extensible nonlinear elastic springs (for details see Ref. 19). We perform a series of *NVT* simulations with 20 chains of length $N=25$, at temperature $T=1$. We vary the density from $\rho=0.1$ to $\rho=1.15$, which is close to the glass transition. At each step we calculate the total shear stress of the system as well as the bonded/nonbonded and intra-/interchain contributions. Using a new algorithm for the calculation of correlation functions "on the fly" without a significant loss of CPU time,[6,7] we calculated the autocorrelations of each component as well as the cross correlations. For the "standard" density, $\rho=0.85$, the results are presented in Fig. 5.
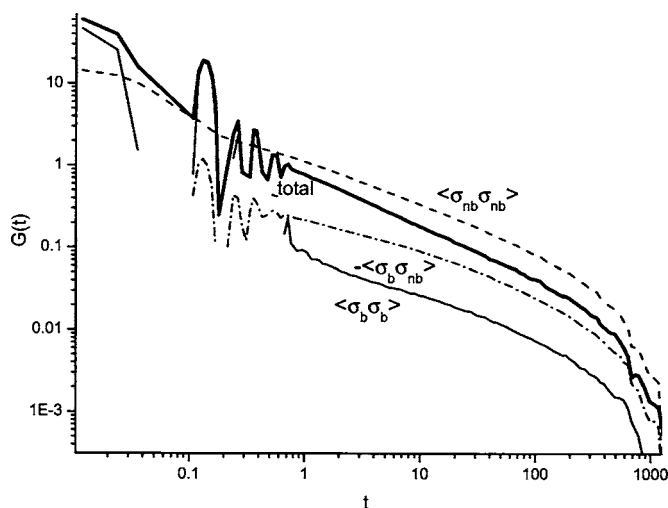

FIG. 5. Stress relaxations from the Kremer-Grest model ($N=25$, $\rho=0.85$). Total relaxation modulus is indicated as a thick line. Also shown are the autocorrelation functions of the bonded (σ_b, thin line) and the nonbonded (σ_{nb}, dashed) stresses, as well as their cross correlation (dot-dashed line).

From Fig. 5, we can see that the nonbonded stress autocorrelation function is higher than the total stress by about factor of 2 at long times, whereas the bonded stress autocorrelation is five times lower than the total stress. Qualitatively, the negative cross correlation can be explained by the fact that for any given orientation of a bond, the corresponding nonbonded forces are predominantly perpendicular to this orientation. In order to calculate bonded and nonbonded contributions to the stress relaxation after a small step deformation, we add the cross correlation to each of the autocorrelation functions following Eq. (3). The results in Fig. 6 indicate qualitatively different interplays between the bonded and the nonbonded interactions at the three different densities.

First of all, one should notice that the curves for each
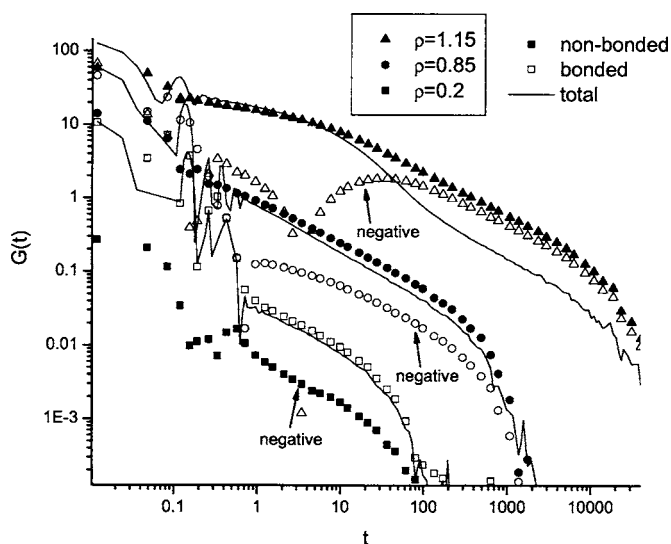

FIG. 6. Total relaxation modulus and the bonded/nonbonded contributions from molecular dynamics simulations at different densities using the Kremer-Grest model, $N=25$. Absolute values are shown whenever a contribution is negative (see labels in the plot). At late times, both contributions are proportional to the total modulus.
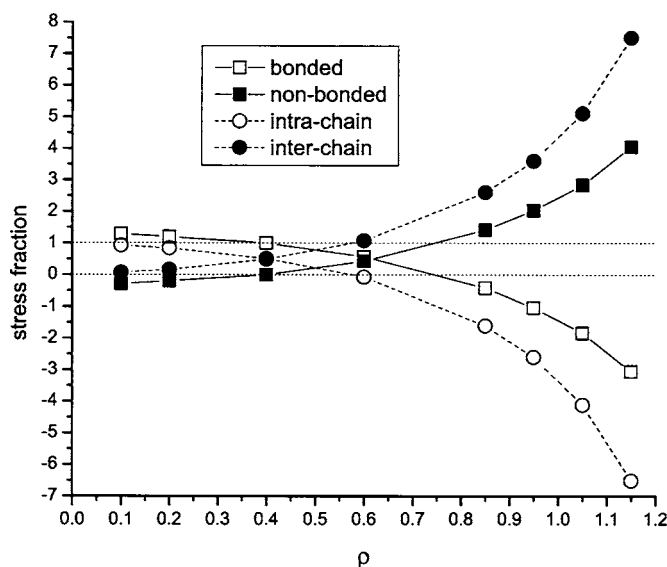
FIG. 7. Decomposition of the shear modulus into complementary partial contributions as a function of the density: bonded and nonbonded (squares), and intra- and interchain (circles).

density become exactly proportional to each other (at least within 1%) after some "colloidal relaxation" time, ranging from 1 at low density to 300 for $\rho=1.15$. This suggests that after the equilibration of the monomers surrounding a particular bond, there is only one relaxation process left, associated with the segmental orientation relaxation. The bonded and the nonbonded contributions at long times are shown in Fig. 7 as a function of density, together with the intrachain and interchain contributions calculated similarly.

One can see that at low density $\rho<0.4$ the contribution from the nonbonded stress is negative, whereas for high densities $\rho>0.75$ or so the contribution from the bonded stress becomes negative. The fact that the nonbonded contribution is almost always comparable to the bonded contribution led some researchers[20] to question the validity of the tube or Rouse theory for polymer melts since they both assume that only bonded forces contribute to the stress relaxation. Indeed, our results confirm that, at least for the standard Kremer-Grest polymer, the assumption of Doi and Edwards that only the bonded forces contribute to the stress relaxation at long times is invalid, at least if taken literally. However, as both the bonded and the nonbonded contributions are exactly proportional to the total stress relaxation, only the prefactor in the tube theory must be questioned rather than the shape of the relaxation spectrum. In fact, this prefactor is analogous to the stress-optical coefficient: we have found that the stress relaxation curve is proportional to the bond orientation relaxation. Also, in the context of Eq. (5), this would suggest that the prefactor of 4/5 might have to be modified.

IV. CONCLUSION

In this work, we have demonstrated the importance of including cross correlations while calculating partial relaxation functions and the corresponding transport coefficients using equilibrium time correlation functions. We have provided the appropriate expressions to obtain the correct partial

relaxation functions in equilibrium simulations using linear response theory. The derived expressions are not new but, to the best of our knowledge, have not been used before in equilibrium simulations of polymers.

In polymer rheology, we have presented two illustrations of the significant contribution from the cross correlations to the partial relaxation functions at equilibrium using (1) a single chain model for entangled polymers, the slip-spring model, and (2) molecular dynamics simulations using the multichain Kremer-Grest model. In the single chain model, the non-negligible contribution of the cross correlations with the tube potential to the stress relaxation prompts us to question the validity of some of the assumptions underlying the tube model. In particular, it appears that the analogy with classical rubber elasticity in defining the entanglement molecular weight is lost and, consequently, the meaning of the entanglement molecular weight becomes unclear. In contrast, the proportionality of the partial (bonded and nonbonded) contributions to the total stress relaxation (after a density dependent "colloidal" relaxation time) in the multichain model sheds some light on the success of the tube theory in spite of using incorrect assumptions. The proportionality indicates that the shape of the relaxation spectrum can be calculated using tube theory, but the problem of determining the correct prefactor remains.

APPENDIX: PARTIAL RELAXATION FUNCTIONS

In classical statistical mechanics, the canonical ensemble average of any dynamical quantity, $A(t)$, can be written as an integral over phase space as[3]

$$\langle A(t)\rangle = \frac{\int d\mathbf{r}^N d\mathbf{p}^N \exp(-H(\mathbf{r}^N,\mathbf{p}^N)/k_B T)A(t;\mathbf{r}^N,\mathbf{p}^N)}{\int d\mathbf{r}^N d\mathbf{p}^N \exp(-H(\mathbf{r}^N,\mathbf{p}^N)/k_B T)}$$
$$= \frac{\mathrm{Tr}(e^{-\beta H}A(t))}{\mathrm{Tr}(e^{-\beta H})}, \tag{A1}$$

where the Tr( ) in the last term symbolically represents the integral over the phase space of the system. An external field a conjugate to A is applied to the system and the system is allowed to equilibrate under the action of the field. As we are interested in the partial contributions to the response, it is useful to write the perturbation to the Hamiltonian as a sum of the partial contributions,

$$\Delta H(t) = -a(t)(A_1(t) + A_2(t)). \tag{A2}$$

Here, A_i, with $i=1,2$, is the dynamical variable corresponding to the ith contribution and conjugate to a. For example, if A_1 is the intrachain stress and A_2 is the interchain stress, then a is proportional to the strain. The field is disabled at time $t=0$. The time-dependent relaxation of the ensemble average of A_i can be written as

$$\overline{A_i}(t) = \frac{\mathrm{Tr}(e^{-\beta(H+\Delta H(0))}A_i(t))}{\mathrm{Tr}(e^{-\beta(H+\Delta H(0))})}. \tag{A3}$$

$\overline{A_i}$ is used to indicate the ensemble average in the perturbed case to distinguish it from $\langle\cdot\cdot\rangle$, the average in the unperturbed case. For linear response, the perturbation to the Hamiltonian is assumed to be small compared to the original Hamiltonian. Let us focus on one of the two contributions, say, A_1. Expanding to linear order in $\Delta H(0)$ and substituting for the value of $\Delta H(0)$ from Eq. (A2), we get

$$\overline{A_1}(t) = \langle A_1(t)\rangle + \beta a\{\langle A_1(0)A_1(t)\rangle + \langle A_2(0)A_1(t)\rangle\}$$
$$- \beta a\{\langle A_1(t)\rangle\langle A_1(0)\rangle + \langle A_1(t)\rangle\langle A_2(0)\rangle\}. \tag{A4}$$

Equation (A4) indicates that the relaxation function $\overline{A_1}(t)$ can be evaluated as a sum of equilibrium autocorrelation and cross-correlation functions. The above result can be easily extended to an arbitrary number of partial contributions to the perturbation. These contributions can arise under the action of multiple external fields on the system or if the total Hamiltonian can be decomposed into a sum of partial Hamiltonians (e.g., kinetic/potential, bonded/nonbonded, etc.).

Let us consider the specific case of shear deformation (shear strain, γ) for the system comprising real and virtual chains as discussed in the Introduction. To obtain the time-dependent macroscopic shear stress, the corresponding applied field is $a = \gamma V$, where V is the volume of the system under consideration. Also, the unperturbed average shear stress, $\langle\sigma_{xy}^i(t)\rangle$ is zero, $i=R$, V. Using these we can simplify Eq. (A4) to give Eq. (3) in the text.

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