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Cross-Correlation Contributions to Orientational Relaxations
in Primitive Chain Network SimulationsYuichi MASUBUCHI^{*†} and Sathish K. SOKUMARAN^{**†}^{*}*Institute for Chemical Research, Kyoto University, Gokasyo, Uji 611-0011, Japan*^{**}*Graduate School of Science and Engineering, Yamagata University, Jyonan4-3-16, Yonezawa 992-8510, Japan*

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Models for entangled polymer dynamics can be conveniently thought of as belonging to two major categories – multichain models, such as the Kremer-Grest model simulated using molecular dynamics and single chain models, such as the tube and sliplink models. The single chain models typically assume that each polymer chain moves essentially independently of the other chains in the system. Hence they also assume that the cross-correlations between the different chains make negligible contribution to the various physical quantities (for e.g., the time-dependent relaxation modulus). However, Cao and Likhtman [Phys Rev Lett 104, 207801 (2010)] using molecular dynamics simulations have shown that there exist significant cross-correlation contributions to the time-dependent orientational relaxation function. In this study, the effect of cross-correlation was investigated using the primitive chain network model, a multi-chain sliplink model. Orientational relaxation functions for both the subchain vectors between entanglements and also for the end-to-end vector of whole chain were evaluated. In the case of the subchain relaxation function (and which corresponds to the time-dependent relaxation modulus by the stress-optical rule), the cross-correlation contribution to the total relaxation function appears to progressively increase with time. Further, the ratio of the cross-correlation function to the total relaxation function reaches a maximum value of approximately 40 % in the terminal region. Besides indicating that the cross-correlation contributions to the total relaxation function are non-negligible, this also demonstrates that the relaxation spectrum itself is modified if the cross-correlation contribution is neglected from the total relaxation. Specifically, the cross-correlation contribution affects the relaxation spectrum in the time range where the effect of the constraint release process is expected to be important. On the other hand, the results indicate that effect of cross-correlations on the shape of the relaxation curve is not significant at long times around the terminal region and that the autocorrelation and the total correlation functions can be superimposed by rescaling the unit of modulus. In contrast, the contribution from cross-correlation to the end-to-end relaxation (that corresponds to the dielectric relaxation of type-A polymers) is less significant than that for the subchain relaxation. In fact, no significant difference was found in the prediction of dielectric relaxation between the end-to-end relaxation functions with and without the contribution of the cross-correlations.

Key Words: Entangled polymers / Sliplink simulations / Orientational relaxation / Cross-correlation

1. INTRODUCTION

Despite the fact that both tube and sliplink models offer excellent descriptions of the dynamics of entangled polymers^{1,2)}, there still remain several unresolved issues. In most theories for entangled polymer dynamics, single chain modeling is employed, which assumes that the dynamics of each chain is essentially independent of the other chains in the system. This single chain assumption can only be valid if the cross-correlations between the different polymer chains are negligible in the time range of model description. However, non-negligible contributions from the cross-correlations

between the different chains have been reported for some physical measures in both experiments and molecular simulations. For instance, Graf et al³⁾ investigated chain dynamics in a polybutadiene melt using H double-quantum NMR and found that the residual orientation of the bonds undergoing stress relaxation is significantly larger than that expected from the conventional reptation picture. They suggested that this is due to intermolecular orientational correlations arising from pronounced local packing effects. Cao and Likhtman⁴⁾ performed Kremer-Grest type molecular dynamics (MD) simulations and showed that the segment orientation auto-correlation function (that corresponds to the linear relaxation modulus) includes contribution from cross-correlation of approximately 50 % in the time range beyond τ_e (Rouse time of the subchain between entanglements).

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In this paper we will focus on the effect of the cross-correlations between different chains on the dynamics of entangled polymers. We have examined the cross-correlation between different chains in the primitive chain network (PCN) model⁵⁾, a multi-chain sliplink model. Owing to its multi-chain nature and coarse-graining at the level of an entanglement segment, the PCN model occupies a niche between single chain models and multi-chain MD simulations. To establish a theoretical path between the models, attempts have been made to compare the relaxation modulus of a single chain model with that of the PCN⁶⁾, and the structure of the entanglement network as seen in MD simulations to that in the PCN.⁷⁾ However, multi-chain effects on the various physical observables (for e.g., relaxation moduli, orientational relaxation function etc.) have hitherto not been elucidated. Cao and Likhtman⁴⁾ mentioned that the cross-correlations seen in MD reflect the cooperative motion of the chains realized via the excluded volume interactions. Since the cross-correlation function does not decay away even in the time range beyond τ_e , it has been suggested that the cooperativity in the chain dynamics is not only due to the local collision between the chain segments but also includes contributions from the entanglements. In PCN, although interactions of the excluded volume type do exist (in the form of the chemical potential that prevents network collapse), as they are rather weak, one can expect to observe the cooperativity in the long time dynamics arising due to entanglements.

In order to better elucidate multi-chain effects in entangled polymer dynamics, we have investigated cross-correlations in the orientational relaxation functions of both the subchain vector and the end-to-end vector of whole chain. The contribution of the cross-correlation was estimated and compared to that in the MD simulation.⁴⁾ Since the examined relaxation functions are proportional to the stress and the dielectric relaxation functions respectively, comparison to experimental data will be also presented to discuss possible effects of the cross-correlation between the different chains on the experimental measures (i.e. stress and dielectric relaxations).

2. MODEL AND SIMULATION

The model and the simulation code are identical to those used in earlier studies.⁶⁻⁸⁾ The PCN model is a sliplink model where the effect of entanglements is replaced by sliplinks distributed along the polymer chain with the spacing between sliplinks corresponding to the dimension of the subchain of entanglement molecular weight. The distinguishable feature

of the PCN model from the other sliplink models⁹⁻¹²⁾ is the multi-chain modeling in real space, which is realized by the formation of a network consisting of many chains bundled together by the sliplinks. The motion of polymers is described by time development of the sliplink position, number of monomers between sliplinks and the number of sliplinks per chain. The sliplink position obeys a Langevin-type equation of motion describing the force balance between the drag force, local tension, osmotic force and random force. The number of monomers between sliplinks develops in time according to the sliding motion of the chain, and the corresponding monomer transport through the sliplink is described by the kinetic equation including the forces that affect the sliplink motion. The number of sliplinks per chain fluctuates due to the entanglement and disentanglement processes occurring around the chain ends. If the number of monomers at the end segment becomes larger than a certain critical maximum value, a new sliplink is created on the segment and another segment is randomly chosen from the surroundings to be hooked by the created sliplink. On the contrary if the number of monomers becomes less than a certain minimum, the sliplink adjacent to the subjected end segment is removed and the bundled segments are released. Further details can be found in the earlier publications.⁶⁻⁸⁾

Simulations were performed with unit of length, a (the average distance between connected sliplinks), unit of energy, kT and unit of time $\tau_0 = \zeta a^2 / kT$ (where ζ is the friction coefficient of the sliplink) using a cubic box of size $(8a)^3$ subject to periodic boundary conditions.

3. SELF AND CROSS CORRELATION FUNCTIONS

The subchain orientational correlation function $S_s(t)$ is defined (in non-dimensional form) as

$$S_s(t) = N_b \left(\frac{1}{N_b} \sum_{j=1}^{N_c} O_j^{xy}(t) \right) \left(\frac{1}{N_b} \sum_{j=1}^{N_c} O_j^{xy}(0) \right) \quad (1)$$

$$O_j^{xy}(t) = \sum_{i=1}^{Z_j} \frac{r_{ij}^x(t) r_{ij}^y(t)}{n_{ij}(t)}$$

Here, $\mathbf{r}_i = (r_i^x, r_i^y, r_i^z)$ is the bond vector of subchain i , n_i is the number of monomers on the corresponding subchain, Z_j is the number of subchains for chain J , N_c is the number of chains and N_b is the total subchain number. x , y and z stands for the normal axes, and no specific direction exists in this study because all the simulations were made under quiescent conditions to discuss linear responses. Note that

$S_s(t)$ is proportional to the linear relaxation modulus $G(t)$ via the stress-optical law. The total orientation relaxation can be decomposed into auto-correlations (that is within the same chain) $A_s(t)$ and cross-correlations (that is between the different chains) $C_s(t)$;

$$\begin{aligned} A_s(t) &= N_b \frac{1}{N_c^2} \sum_J^{N_c} O_J^{xy}(t) O_J^{xy}(0) \\ C_s(t) &= N_b \frac{1}{N_c^2} \sum_{i \neq J}^{N_c} O_i^{xy}(t) O_J^{xy}(0) = S_s(t) - A_s(t) \end{aligned} \quad (2)$$

Following Cao and Likhtman⁴⁾, the coupling parameter $\kappa_s(t)$ is defined as

$$\kappa_s(t) \equiv \frac{C_s(t)}{S_s(t)} = 1 - \frac{A_s(t)}{S_s(t)} \quad (3)$$

In this study, we also examined the orientational correlation function for the end-to-end vector of whole chain, $S_c(t)$, defined as

$$\begin{aligned} S_p(t) &= N_c \left(\frac{1}{N_c} \sum_{J=1}^{N_c} P_J^x(t) \right) \left(\frac{1}{N_c} \sum_{J=1}^{N_c} P_J^x(0) \right) \\ P_J^x(t) &= \sum_{i=1}^{Z_J} r_{iJ}^x(t) / \sum_{i=1}^{Z_J} n_{iJ}(t) \end{aligned} \quad (4)$$

$S_c(t)$ is proportional to the dielectric relaxation of type-A polymers such like polyisoprene. The auto and cross-correlation functions are defined as

$$\begin{aligned} A_p(t) &= N_c \frac{1}{N_c^2} \sum_J^{N_c} P_J^x(t) P_J^x(0) \\ C_p(t) &= N_c \frac{1}{N_c^2} \sum_{i \neq J}^{N_c} P_i^x(t) P_J^x(0) = S_p(t) - A_p(t) \end{aligned} \quad (5)$$

The coupling parameter for the end-to-end relaxation $\kappa_p(t)$ is correspondingly defined in analogy with Eq. 3.

4. RESULTS AND DISCUSSION

Figure 1 (a) shows $S_s(t)$ (solid curve) and $A_s(t)$ (dashed curve) for Z values ranging from 5 to 40. Due to the contribution of C_s , S_s is considerably different from A_s . Indeed, as shown in Figure 1 (b), κ_s (symbols) increases with time and becomes greater than 0.3 in the long time region, while being only weakly dependent on the molecular weight. Similar behavior is observed in the MD simulation as shown in Figure 1 (b) (where κ_s from the MD simulation is indicated by dotted and broken curves). Here, τ_0 in the PCN simulation is estimated to be 3000 τ_{MD} (τ_{MD} is the unit time of the MD simulation) since τ_e in the MD simulation is reported as 5800 τ_{MD} ¹³⁾ while τ_e in the PCN simulation is roughly

estimated as $2\tau_0$ from the relation between M_e and M_0 .⁸⁾ The MD data are for chain lengths 100 and 350 beads per chain. These chain lengths roughly correspond to Z values of 3 and 9 for PCN. It is believed that the coupling parameter, κ_s , in the MD simulation has its origin in the Lennard-Jones interaction between beads especially at short times. Hence, the time development of κ_s in the time range below τ_0 reflects the local collisions between beads. If the value of κ_s saturates around τ_e ($\sim 2\tau_0$), it can be assumed that each chain moves independently and the contribution of the cross-correlation can be embedded into the unit of modulus. However, as mentioned by Cao and Likhtman⁴, κ_s does not saturate around τ_e and it is difficult to discern any saturation in the value of κ_s from the MD data due to the noise in the long time region. On the other hand, in the PCN data, a saturation of κ_s is clearly observed but the time range is clearly significantly larger than τ_e . At first glance, this suggests that cross-correlations due to entanglements

Fig. 1. (a) Subchain orientational relaxation function for various Z ranging as 5, 10, 20 and 40 from left to right. Solid and broken curves shows the full relaxation function $S_s(t)$ and the autocorrelation function $A_s(t)$. (b) Coupling parameter $\kappa_s(t)$ for $Z = 5, 7, 10, 15, 20, 30$ and 40. PCN results are shown by symbols. Dotted and broken curves are MD results for chain lengths 100 (broken curve) and 350 (dotted curve) extracted from Ref. 4.

exist. This is perhaps not surprising because one expects the constraint release process to induce cross-correlations (i.e., between different chains) beyond τ_e . However, as κ_s is roughly independent on Z , it is likely that the cross-correlations reflect the local force balance at the entanglements rather than any coupling due to constraint release. The difference in the magnitude of κ_s may be attributed to the Lennard-Jones interactions not incorporated in the PCN model.

In relation to the excluded volume interaction (the main source of coupling in the MD simulations), it is fair to mention that the osmotic force in the PCN simulations plays a similar role and prevents the network from collapsing. The contribution from the osmotic force to the stress is much smaller than that from the subchain tension and thus it is neglected in the analysis. However, the effect of osmotic force on the subchain orientation is implicitly involved in the effect of force balance around sliplink. Unfortunately, it is difficult to isolate this effect due to the nature of the present sliplink model.¹⁴⁾

Figure 2 (a) displays $S_p(t)$ (solid curve) and $A_p(t)$ (dashed curve) for the melts shown in Figure 1. It is clear from the figure that in the case of the end-to-end orientational relaxation function, the contribution from the cross-correlations is significantly less when compared with that for S_s . Figure 2 (b) shows κ_p and indicates that the magnitude of the contribution from the cross-correlations in S_p is similar to that in S_s at $t = \tau_0$, but then decreases with time to be a value significantly smaller than κ_s in the long time region. This result is consistent with earlier studies on the dielectric relaxation of type-A polymers.^{15,16)} The difference in the magnitude between κ_s and κ_p in the long time region may be phenomenologically explained by the tube dilation relationship¹⁷⁾ where $S_s(t)$ ($= A_s + C_s$) is proportional to $S_p(t)^2 = A_p^2 + C_p^2 + 2A_pC_p$. (Note that $S_s(t) \propto S_p(t)^2$ corresponds to the relation between stress relaxation and end-to-end relaxation, and it has been argued in the literature¹⁸⁾ that this relation can be thought of as due to the contribution of the constraint release process to the total segment relaxation.) Since C_p is significantly smaller when compared to A_p and it being unlikely that C_p contributes to A_s , it can be argued that the most significant contribution to C_s is from the cross term A_pC_p . This could potentially explain why κ_s ($= C_s/S_s$) becomes larger than κ_p ($= C_p/S_p$). This reasoning, however, cannot explain the observed antithetical time variation of κ_s (increasing with time) and κ_p (decreasing with time).

To discuss possible effects of the cross-correlations on the comparison between theoretical models and experiments, Figure 3 shows literature data¹⁹⁾ for the viscoelastic and the

dielectric relaxations from a monodisperse polyisoprene melt of molecular weight 94K and fits to the PCN model for $Z = 27$.⁸⁾ Here the relaxations for subchain and whole chain are assumed to be proportional to the stress and the dielectric relaxations respectively, and the proportionality factor is determined by fitting to the experimental data. (Thus the proportionality factor for the total relaxation S_s and S_p is different from that for the auto-correlations A_s and A_p due to the contribution from the cross-correlations.) The time constant τ_0 for all the relaxation functions is fixed at $\tau_0 = 3.5 \times 10^{-5}$ sec.

For the viscoelastic relaxation, S_s and A_s gives similar $G^*(\omega)$ around the terminal region. Thus for the prediction in this time domain the contribution from the cross-correlations can be neglected as long as one can adjust the proportionality factor between the correlation functions and the modulus. For example, in this specific case, the proportionality factor for A_s is 50 % larger than that for S_s in order to obtain a reasonable fit to the $G^*(\omega)$ data. It is germane to note that the modification

Fig. 2. (a) End-to-end orientational relaxation function for various Z at 5, 10, 20 and 40 from left to right. Solid and broken curves shows the full relaxation function $S_p(t)$ and the autocorrelation function $A_p(t)$. (b) Coupling parameter $\kappa_p(t)$ for $Z = 5, 7, 10, 15, 20, 30$ and 40.

in the prefactor has been related to the nature of entanglement network such as the fluctuations and the functionality of network nodes.²⁰⁾ The discussion above suggests that cross-correlations may be an additional mechanism contributing to modifying the prefactor from its classically expected values.

In the high frequency region, the $G^*(\omega)$ calculated from A_s differs from that calculated from S_s . As discussed earlier, this is due to the fact that in this frequency region, the relaxation spectrum of A_s is different from that of S_s due to the contribution from C_s . (Note that the proportionality factor to fit the data for A_s is larger than S_s and thus in Figure 3 the $G'(\omega)$ and $G''(\omega)$ calculated from A_s appear larger than those from S_s .) Usually, the dominant contribution to the relaxation spectrum in this region of time is from the relaxation modes attributed to the constraint release process. However, the result of this study suggests another mechanism that is the contribution of the cross-correlations between chains, to which the force balance enforced at the entanglements in the PCN model contributes.

On the other hand, for the dielectric relaxation, the results from S_p and A_p are indistinguishable (and indeed overlap with each other) and is again consistent with earlier studies.^{15, 16)}

5. CONCLUSION

The effect of the cross-correlations between different chains on both the orientational relaxations for subchain vector between entanglements and the end-to-end vector of whole chain was investigated using simulations of the primitive chain

network model. For the subchain relaxation (that corresponds to the viscoelastic relaxation) the contribution of the cross-correlations to the total is non-negligible with ratio of the cross-correlation term to the total relaxation reaching around a maximum value of approximately 40 %. Due to the cross-correlations being time dependent, the relaxation spectrum is modified if the contribution from the cross-correlations is neglected from the total relaxation. In particular, cross-correlations affect the relaxation spectrum in the time range where the effect of constraint release is also expected to be significant. On the other hand, the effect of cross-correlations can be ignored at long times around the terminal region, as long as the unit of modulus is allowed to compensate for the effect of cross-correlations. For the end-to-end relaxation (that corresponds to the dielectric relaxation of type-A polymers) the contribution from cross-correlation is significantly lower when compared to the subchain relaxation. In fact, no significant difference was found in the prediction of dielectric relaxation between the end-to-end relaxation functions with and without the contribution of cross-correlation.

The obtained results suggest that it would be necessary to understand the cross-correlations between chains in order to obtain a quantitative description of the relaxation of subchain orientation. We will further investigate these effects vis-à-vis the relaxations in the single chain model, the multi-chain sliplink model without the real-space coupling and especially molecular dynamics simulations.

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Fig. 3. Viscoelastic (top) and dielectric (bottom) relaxations obtained from the subchain and the end-to-end relaxation functions, respectively. Thick and thin curves are obtained from the total relaxation function ($S_s(t)$ and $S_p(t)$) and the contribution of auto-correlation ($A_s(t)$ and $A_p(t)$). Symbols are the experimental data from Ref. 19.

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