A dynamic rotational isomeric state approach for extension of the time scale of the local dynamics observed in fully atomistic molecular dynamics simulations: Application to polybutadiene

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The dynamic rotational isomeric state (DRIS) formalism has been utilized to predict the local dynamics of amorphous *cis*- and *trans*-polybutadiene at bulk density from short-time molecular dynamics (MD) simulations at 425 K. The rates for transitions between rotational isomeric states have been calculated from the initial slopes of time-delayed transition (*conditional*) probability curves extracted from the MD simulation. First- (*independent*), second- (*pairwise dependent*), and third- (*triplewise dependent*) order conformational transitions have been incorporated into the DRIS formalism. Conformational and orientational correlation functions have been evaluated. The comparison of DRIS results with MD simulations indicates that this approach may be advantageously used to predict the time evolution of bond isomeric states and the contribution of transitions between these states to conformational correlation functions. The first-order conformational kinetics is the major factor controlling the relaxation in the latter. Cross-correlation functions are not reproduced as well, because they are dominated by torsional librations within rotational isomeric states, and such librations are not incorporated in the DRIS analysis. The prediction of anisotropic character of the segmental motions is also satisfactory to an important extent, but it still awaits some more consideration in the choice of the size of the kinetic segment, along with the accurate input of cooperative motions arising from both intra- and intermolecular interactions in a MD simulation. Information which would otherwise be extracted from the statistical analysis of very long trajectories of MD simulations may become readily obtainable from DRIS. © *1996 American Institute of Physics.* [S0021-9606(96)50212-7]

I. INTRODUCTION

There are basically two broad regimes at which the dynamics of macromolecules may be analyzed, depending on the time and length scale of the observation. (1) The Rouse–Zimm[1,2] regime, where the large scale motions are considered, and (2) the local dynamics regime. The motions in the latter regime can be classified into three groups. (i) High frequency motions such as bond stretching, bond-angle bending and small amplitude oscillations within a single rotational potential energy well; (ii) side chain motions; and (iii) rotational transitions from one rotational isomeric state to another. The use of detailed molecular level structural and conformational features is essential in studying motions belonging to this regime. Molecular dynamics (MD) is the most powerful computational technique in studying local chain dynamics for fully atomistic models of a polymer system. It is accurate to the extent the force field gives a realistic representation of interatomic interactions. However, the attainment of the time scale of relevant experiments for amorphous polymers at bulk density by MD technique is often impossible, due to the large number of degrees of freedom which need to be integrated with a very small time step.

In the present work, the dynamic rotational isomeric state (DRIS) model is utilized to predict the long-time behavior of local chain dynamics of bulk amorphous polybutadiene (*cis*- and *trans*-PBDs), using the information obtained from short-time (ns) MD simulation.[3] First- (*independent*), second- (*pairwise dependent*), and third- (*triplewise dependent*) order interdependence[4] in the conformational transitions are considered in the calculations. The DRIS model renders the problem analytically tractable, but less precise. For example, it focuses attention exclusively on the transitions between discrete rotational isomeric states, and ignores the effect of librational motion within a rotational isomeric state. Also, intermolecular interactions are incorporated only in an indirect fashion, via their influence on the transitions rate employed in the DRIS analysis. Nevertheless, the DRIS model provides an understanding of the mechanism and basic factors controlling the local relaxation in a specific polymer without the necessity for extensive simulations. The torsional autocorrelation functions have been reproduced reasonably well. The DRIS analysis is less successful for the orientational autocorrelation functions. The shortcoming of the technique will be discussed along with the presentation of the results.

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The paper is organized as follows. The two different implementations of the DRIS method that are applied here will be explained. The pertinent results from the recent MD simulation study[3] of bulk amorphous PBD will be summarized very briefly. The formulation of the DRIS model from the data provided by MD trajectories will be presented along with its prediction of different correlation functions.

II. DYNAMIC ROTATIONAL ISOMERIC STATE (DRIS) APPROACH

The dynamics rotational isomeric state approach,[4–12] which is the dynamic extension of the rotational isomeric state model,[13,14] considers the discrete conformational space $\Omega=\{\Omega_\alpha,\Omega_\beta,...,\Omega_{\nu N-2}\}$ of a chain of n bonds having ν states accessible to each bond. The stochastic process of $\nu^{n-2}\times\nu^{n-2}$ transitions between those conformations is the object of the method. The DRIS model is based on the Markov assumption which implies that the state of the system at a given time $\tau_0+\tau$ is prescribed entirely by its state at time τ_0. Mean dynamic properties associated with conformational transitions are evaluated by assigning a stochastic weight $\Omega_t[\{\Omega_\alpha;\Omega_\beta\}]$ to each transition occurring at time τ as

$$\langle f(\tau)\rangle=\sum_\alpha\sum_\beta \Omega_\tau[\{\Omega_\alpha;\Omega_\beta\}]f(\Omega_\alpha;\Omega_\beta), \tag{1}$$

where $f(\Omega_\alpha;\Omega_\beta)$ is the value of the investigated property when the transition takes place from conformation β to α, and the summation is performed over all conformational space. Here, $\Omega_t[\{\Omega_\alpha;\Omega_\beta\}]$ can be evaluated as

$$\Omega_\tau[\{\Omega_\alpha;\Omega_\beta\}]=\prod_{i=x}^{N-1} v_i(abc\ldots;a'b'c'\ldots), \tag{2}$$

where $v_i(abc,\ldots;a'b'c'\ldots)$ denotes the stochastic weight corresponding to the transition $abc\ldots\rightarrow a'b'c'...$ at time τ by the groups of the bonds $i-(x-1),\ldots,i-1,i$, with the order of the interdependence restricted to x consecutive bonds. $v_i(abc\ldots;a'b'c'\ldots)$ may be determined[11] from time-dependent probabilities according to

$$\begin{aligned}&v_i(abc\ldots;a'b'c'\ldots)\\&\quad=p_i(abc\ldots d_{x-1}e_x;a'b'c'\ldots d'_{x-1}e'_x)/\\&\qquad p_{i-1}(abc\ldots d_{x-1};a'b'c'\ldots d'_{x-1}),\end{aligned} \tag{3}$$

where $p_i(abc\ldots d_{x-1}e_x;a'b'c'\ldots d'_{x-1}e'_x)$ indicates the time-delayed probability of the joint occurrence of isomeric states $\{abc\ldots d_{x-1}e_x\}$ and $\{a'b'c'\ldots d'_{x-1}e'_x\}$ within the time interval τ. This time-delayed probability can be evaluated from

$$\begin{aligned}&p_i(abc\ldots d_{x-1}e_x;a'b'c'\ldots d'_{x-1}e'_x)\\&\quad=c_i(a'b'c'\ldots d'_{x-1}e'_x|abc\ldots d_{x-1}e_x)\\&\quad\times xp_i^0(abc\ldots d_{x-1}e_x),\end{aligned} \tag{4}$$

where $p_i^0(abc\ldots d_{x-1}e_x)$ is the equilibrium probability of the state $(abc\ldots d_{x-1}e_x)$ for bonds $i,i-1,\ldots i-(x-1)$, and $c_i(a'b'c'\ldots d'_{x-1}e'_x|abc\ldots d_{x-1}e_x)$, which is the conditional probability for the indicated transition. Equation (4) may be rewritten in matrix notation for all of the possible ν^{2x} transitions of the segment of x bonds as $\mathbf{P}_\tau=\mathbf{C}_\tau\mathbf{P}_0$, where $\mathbf{P}_\tau$ and $\mathbf{C}_\tau$ represent the joint probability and conditional probability matrices of order ν^x, and $\mathbf{P}_0$ is the vector of the equilibrium probabilities of the ν^x states. For a chain of n bonds with x-wise interdependent transitions, use of Eqs. (2)–(4) in Eq. (1) yields

$$\langle f(\tau)\rangle=\sum_\alpha\sum_\beta C_\tau(\Omega_\alpha|\Omega_\beta)P_0(\Omega_\beta)f(\Omega_\alpha,\Omega_\beta). \tag{5}$$

The formal solution of the Master equation which governs the stochastics of transitions gives

$$\mathbf{P}_\tau(\Omega)=\exp\{\mathbf{A}\tau\}\mathbf{P}_0(\Omega)=\mathbf{B}\exp\{-\Lambda\tau\}\mathbf{B}^{-1}\mathbf{P}_0(\Omega), \tag{6}$$

where $\mathbf{A}$ is the transition rate matrix for the kinetics of the transitions. The diagonalization of $\mathbf{A}=\mathbf{B}\Lambda\mathbf{B}^{-1}$ leads to the respective matrices of eigenvectors and the eigenvalues, $\mathbf{B}$ and Λ. From the physical meaning of Eq. (6), the time-delayed conditional probability matrix $\mathbf{C}_\tau$ equals the term

$$\mathbf{C}_\tau=\mathbf{B}\exp\{-\Lambda\tau\}\mathbf{B}^{-1}. \tag{7}$$

Knowledge of $\mathbf{C}_\tau$ together with the equilibrium probabilities, $\mathbf{P}_0(\Omega)$, gives a complete description of the stochastics of conformational transitions. Any correlation function $f(\tau)$ which depends on conformational transitions may be evaluated by using the elements of $\mathbf{C}_\tau$ and $\mathbf{P}_0(\Omega)$ in Eq. (5).

In the present study, two alternative approaches have been undertaken to compute, in general, any transient property, $\langle f(\tau)\rangle$, as expressed in Eq. (5).

(a) The rate matrix $\mathbf{A}$ for a polymer chain of n bonds can be formed[12] by suitable combination of transition rate matrices ascribed to x-wise interdependent bonds, $\mathbf{A}^x$. This matrix governs the conformational kinetics of n x-wise interdependent bonds. Similarity transformation of $\mathbf{A}^x$ and substitution of the results in Eq. (7) leads to the conditional probabilities and thus joint probabilities of occurrence of conformations Ω_a and Ω_b with a time delay of τ. Details can be found in the Ref. 4–12. Using Eq. (7), Eq. (5) can be written as

$$\langle f(\tau)\rangle=\sum_\gamma k_\gamma\exp\{\lambda_\gamma\tau\}, \tag{8}$$

where λ_γ is the γth eigenvalue of Λ. k_γ is the amplitude factor which is a static quantity expressed as a function of the specified investigated property and given by

$$k_\gamma=\sum_\alpha\sum_\beta B_{\alpha\gamma}[B^{-1}]_{\gamma\beta}P_0(\Omega_\beta)f(\Omega_\alpha;\Omega_\beta). \tag{9}$$

From Eqs. (5), (8), and (9), any transient property may be evaluated. Some examples will be presented in the calculations part.

(b) Alternatively, it is possible to evaluate $\langle f(\tau)\rangle$ without going through the Eqs. (8) and (9), thereby avoiding matrix manipulations which might sometimes be very cumbersome. $\langle f(\tau)\rangle$ may be directly computed by using Eqs. (1) and (2). The summations in Eq. (1) are performed over all the initial and final states of the rotatable bonds in the chain. This method incorporates an enormous number of transitions for a given τ. The most probable conformational transition subspace can be separated from the complete conformational transition space simply by using the Monte Carlo (MC) simulation method. This method provides a convenient way of calculating any property of interest from the ensemble of generated chains for a given time, as based on the time-delayed conditional probability values predicted by the DRIS model.

III. MD SIMULATION OF BULK AMORPHOUS POLYBUTADIENE

In a recent MD simulation of bulk amorphous *cis*- and *trans*-PBDs, the local dynamics above the glass transition temperature were studied for the simulation time of 0.8–1 ns.[3] The local motions are found to be different in the two polymers as a result of the structural differences imposed by the different conformational states at the double bond. Different time correlation functions have been evaluated to study the mechanism and intramolecular cooperative motions controlling the local relaxation.

In the present study, the above simulation trajectories have been utilized to acquire the time-delayed conditional probabilities, based on first-, second-, and third-order conformational transition statistics, between possible conformational states of $CH_2–CH_2$ and $CH–CH_2$ bonds in both PBDs. The $CH{=}CH$ bond is ignored in this analysis because it only experiences librational motion within a single rotational isomeric state, and the present implementation of the DRIS model does not incorporate such librational motions.

IV. CALCULATIONS

A. The transition rate matrices

Depending on the order of the interdependence of conformational transitions, the elements of $\mathbf{A}^x$, which represents the rate of transition from one rotational isomeric state to another, may be estimated from the kinetics of one or more bonds. Three isomeric states are accessible to both $CH–CH_2$ and $CH_2–CH_2$ bonds in PBDs. They are *trans* (t), *gauche*$^+$ (g^+), and *gauche*$^-$ (g^-) for $CH_2–CH_2$; t, *anticlinical*$^+$ (s^+), *anticlinical*$^-$ (s^-) for $CH–CH_2$ in *cis*-PBD, and t,g^+,g^-, for $CH_2–CH_2$; *cis* (c), s^+,s^- for $CH–CH_2$ in *trans*-PBD. The three rotational isomeric states at each rotatable bond lead to an $\mathbf{A}^x$ matrix of dimensions 3×3 in first-order, $x=1$; 9×9 in second order, $x=2$; and 27×27, $x=3$, in third order transitions. The transition rate matrix $\mathbf{A}$ operating in a chain of n bonds can be found[12] from the convolution of the rate matrices $\mathbf{A}^x$.

The initial slopes of time-delayed transition probability $\mathbf{C}_\tau$ curves, which have directly been calculated from MD simulation trajectories, give the transition rates to be implemented in $\mathbf{A}^x$. The rates from the simulation reflect molecular level structural and conformational information, including the perturbation that results from intra- and intermolecular interactions, independent of whether these interactions appear formally in the subsequent analysis using the DRIS model. The accurate estimation of those rates is very important to obtain a quantitative relation between theory and simulation.

B. Time-delayed conditional probabilities

The time-delayed conditional probabilities of conformational transitions of first, second, and third order have been calculated for each type of bond in both *cis*- and *trans*-PBDs from the trajectories. The first objective is to reproduce those curves using the DRIS model. The rate matrix $\mathbf{A}^x$ operates as the core of the DRIS calculations. The conditional probability matrix $\mathbf{C}_\tau$ for a given τ is calculated from Eq. (7), by similarity transformation of $\mathbf{A}^x$. Calculations are performed for first-, second-, and third-order interdependent conformational transitions. The resulting transition probability curves will be used later in the evaluation of intermolecular cooperativity effects on different correlation functions. The curves comparing DRIS calculations and MD simulation for a few isomeric pairs of interest are depicted in Figs. 1–3.

Figure 1 presents first-order transition probabilities with respect to time for all possible transitions between three isomeric states, c, s^+, and s^-, of the $CH–CH_2$ bond in *trans*-PBD at 425 K. The curves in that figure are organized to present the history of each specific state towards its equilibrium. At infinite time, all three curves in each panel must approach a common value, which is the equilibrium probability for the final state. This condition is obtained in reasonable approximation for all three panels in Fig. 1. The symmetry of the torsion potential energy functions requires that identical limits be obtained in the second and third panels. This requirement is also met in reasonable approximation. Conceivably the accuracy of the DRIS analysis might be improved somewhat by combining symmetry-related sets (such as $s^+|s^+$ and $s^-|s^-$) in the evaluation of the slopes. The DRIS model captures the time dependence quite well when the transitions involve only the anticlinical states. It is less successful when the transitions involve the *cis* state, as can be seen by inspection of the open circles in all three panels in Fig. 1. The origin of this problem may lie in the very low probability for the *cis* state, as shown by the limiting value of C_τ in the top panel. The small probability for the *cis* state means that the rates had to be evaluated from a relatively small number of observations. Of course, the low probability of the *cis* state also suggests that the correlation functions calculated later in this article may not be very sensitive to errors in the estimation of the time dependence of the occupancy and escape from the *cis* state.

Figure 2 depicts first-order transition probabilities for three isomeric pairs of $CH–CH_2$ bond in *cis*-PBD at 425 K. The curves involving only anticlinical states must have a common limit, which is nearly achieved in 400 ps. Second-order transition probabilities for the $CH–CH_2$ bond pair at the two ends of the double bound in *trans*-PBD at 425 K are depicted in Fig. 3 for three out of 9×9 isomeric pairs.

The DRIS calculations provide a reasonably successful reproduction of transition probabilities for PBDs at 425 K. However, at lower temperatures, 353 K and 300 K, which

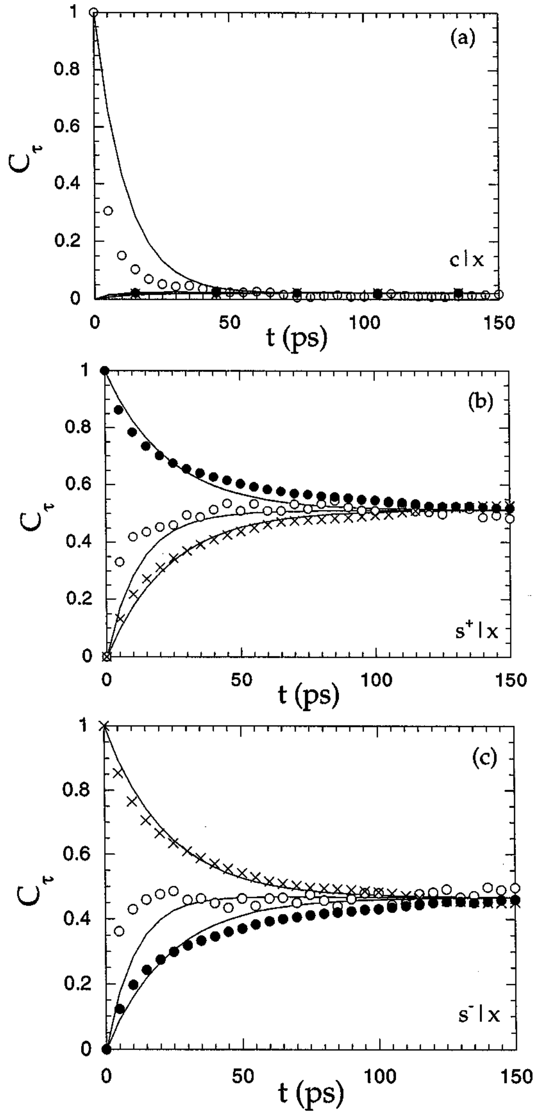

FIG. 1. First-order time-delayed transition probabilities for the CH–CH$_2$ bond in *trans*-PBD at 425 K; (a) $C_\tau(c|x)$, (b) $C_\tau(s^+|x)$. (c) $C_\tau(s^-|x)$, $x=c$, s^+, and s^-, evaluated by the DRIS approach (solid curves) and MD simulation [points plotted as (○), (●), (×) for c, s^+ and s^-, respectively].

have also been studied, the DRIS formalism yields a poor estimation of the transition rates from the simulation. As the temperature and the mobility of the segments decreases, it becomes very difficult to make a correct estimation of the initial decays of the curves from which the rate is calculated, or even to observe in some cases any initial decay in the curves, using data from a MD trajectory of length 1 ns.

C. Correlation functions

Local dynamics of polymer chains are probed by many spectroscopic techniques;[15,16] time-resolved fluorescence anisotropy, nuclear magnetic resonance, electron spin resonance, etc. For the interpretation of experimental results for polymers with different local structures, often simple functional forms for the correlation functions are used. Thus, in theoretical and simulation studies, it is of great interest to study the local relaxation phenomenon in terms of correlation functions. In the simulation study[3] of *cis*- and *trans*-PBDs, many different types of conformational and orientational correlation functions were calculated. In this section, we assess the ability of the DRIS model to reproduce some of the correlation functions.

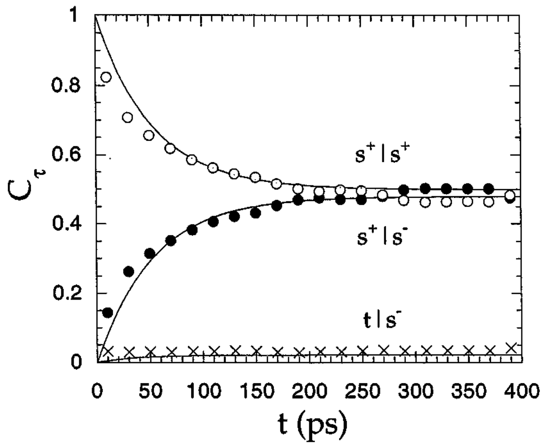

FIG. 2. First-order time-delayed transition probabilities for the CH–CH$_2$ bond in *cis*-PBD at 425 K; the curves are results from DRIS approach and the points depict MD simulation results.

1. Conformational correlation functions

(1) The torsional autocorrelation function (TACF) is defined for each dihedral angle, $\Phi(t)$, as

$$G_1(\tau)=\langle\cos[\Phi(\tau)-\Phi(0)]\rangle. \tag{10}$$

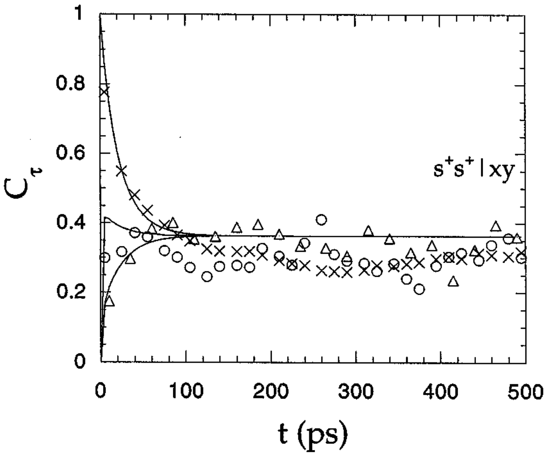

FIG. 3. Second-order transition probabilities for the CH–CH$_2$ bond pair at the two ends of the double bond in *trans*-PBD at 425 K. The curves depict the DRIS results, and the points depict MD simulation results, (×), (○), and (△) for s^+s^+, s^+c, and s^-c, respectively.

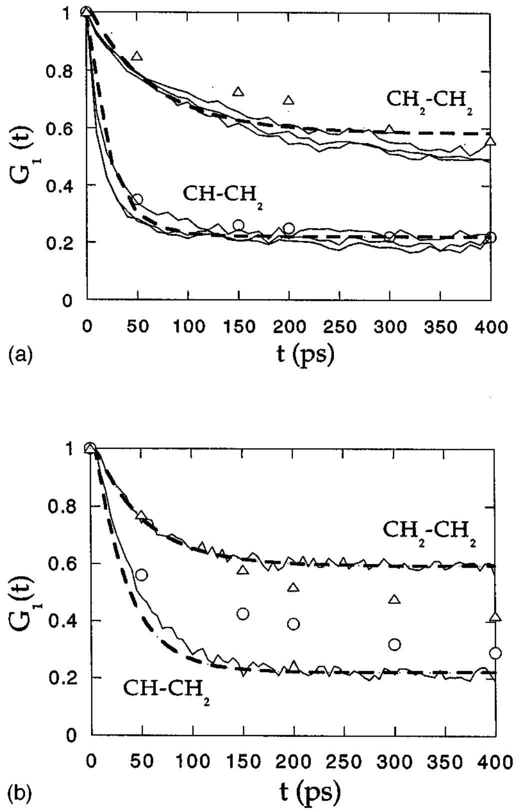

FIG. 4. (a) First-order torsional autocorrelation functions, $G_1(t)$, for CH–CH_2 and CH_2–CH_2 bonds of *trans*-PBD at 425 K. The thin solid curves depict the DRIS results obtained using approach (b) with first-, second-, and third-order time-delayed transition probabilities. The thick dashed curves are calculated from approach (a) by Eqs. (5), (7), (8), based on first order transitions. MD simulation results are depicted by circles and triangles for the respective correlation functions of CH–CH_2 and CH_2–CH_2 bonds (points are from Fig. 2, Ref. 3). (b) First-order torsional autocorrelation functions, $G_1(t)$, for the CH–CH_2 and CH_2–CH_2 bonds of *cis*-PBD at 425 K. The thick dashed curves and thin solid curves depict DRIS results of approaches (a) and (b), respectively, for first order transitions. MD simulation results are depicted by circles and triangles for the respective correlation functions of CH–CH_2 and CH_2–CH_2 bonds (points are from Fig. 2, Ref. 3).

Here, the angle bracket represents averaging over all time origins and over all the bonds of the same type along the chain.

Figure 4(a) shows first-order TACFs, $G_1(t)$, for CH_2–CH_2 and CH–CH_2 bonds in *trans*-PBD, calculated by both approaches (a) and (b) of DRIS. First-order interdependence in the former, and first- to third-order interdependence in the latter, of conformational transitions have been considered. The curves calculated by approach (b) display some noise, due to the MC sampling, but the curves by approach (a) are smooth because a purely analytical expression is used. The equilibrium values of TACFs, $G_1(\infty)$, calculated from Eq. (8), are 0.58 and 0.22 for CH_2–CH_2 and CH–CH_2 bonds, respectively. In both cases, kinetic units of different sizes (different chain lengths) yield the same results. The TACFs of the two approaches of DRIS and MD simulation results are in satisfactory agreement, although they do not capture the very fast (~0.1 ps) delay of $G_1(\tau)$ to 0.98 or 0.94, for CH_2–CH_2 and CH–CH_2, respectively, because the DRIS model ignores librational oscillation with a rotational isomeric state. It should be noted here that the first-order kinetics is a major factor controlling the conformational relaxation, and perturbation due to effects of short range bond interdependence is inconsequential. Thus, it is implied that long range interdependence would be also unimportant. Furthermore, TACFs ascribed to the bonds of the same type situated in different places along the chain basically give the same relaxation.

Figure 4(b) displays TACF curves for CH–CH_2 and CH_2–CH_2 bonds of *cis*-PBD at 425 K, calculated from both approaches (a) and (b) for first-order bond interdependence. $G_1(\infty)$ is 0.59 for the CH_2–CH_2 bond, and 0.22 for the CH–CH_2 bond. The DRIS model gives a somewhat faster relaxation for the CH–CH_2 bond, and slower relaxation for the CH_2–CH_2 bond, than does the MD simulation.

(ii) The torsional cross-correlation function (TCCF) between a pair of bonds is described as

$$G_c(j,\tau)=\langle\sin[\phi_i(\tau)-\phi_i(0)]\sin[\phi_{i+j}(\tau)-\phi_{i+j}(0)]\rangle, \tag{11}$$

where j represents the jth-neighbor bonds. This definition of the correlation function provides direct information on relative torsional directions for a pair of bond. TCCFs calculated both by simulations and DRIS [both approaches (a) and (b)] are depicted in Figs. 5(a)–5(b) for CH–CH_2 bonds using $j=0,2,-2$. The fragment is CH_2–CH=CH–CH_2 when $j=2$, and CH–CH_2–CH_2–CH when $j=-2$. For $j=0$, the agreement is quite good for both *cis*- and *trans*-PBDs. $G_c(j,\infty)$ is 0.34 for the former and 0.39 for the latter. The cross correlations, $j=\pm 2$, are weak in the DRIS analysis, as is also the case in the MD simulation. However, definite cross-correlations are observed in the MD simulation at ~50–100 ps for $j=-2$ for *cis*-PBD and at $j=2$ for *trans*-PBD.

The absence of the cross correlations in the DRIS analysis sheds light on their origin in the MD simulation. In the DRIS analysis, three discrete values (one for each rotational isomeric state) are used for ϕ at each CH–CH_2 bond. Librations about one of these discrete ϕ are ignored in the DRIS analysis. Instead the DRIS analysis focuses only on the larger changes in ϕ that arise from the transition from one rotational isomeric state to the another. If the cross correlations observed in the MD simulation arise from counter rotations, or corotations, within the potential energy wells that define the rotational isomeric states, they will not appear in the cross-correlation functions obtained by DRIS analysis, although they will appear in the direct analysis of the MD simulation, where the range for ϕ is continuous. We conclude that the cross correlations observed in the MD simulation are dominated by correlations in librational motions within the potential well. The influence of librational motion within a rotational isomeric state is also evident for $j=0$ at very short times (see Fig. 6 of Ref. 3), but on the time scale of 20+ ps emphasized here in Fig. 5, the influence of the transitions between rotational isomeric states makes the dominant contribution to $G_c(0,\tau)$.

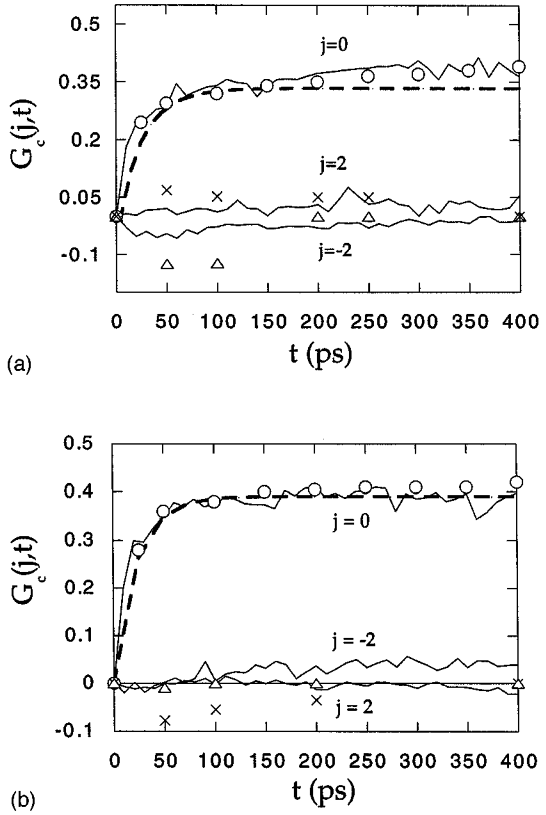

FIG. 5. Torsional cross-correlation functions, $G_c(j,t)$, for CH–CH$_2$ bonds using $j=0,\pm 2$ at 425 K by both approaches (a) (solid curve), and (b) (dashed curve). MD simulation results are depicted on the figure by the symbols, (○), (×), (Δ) for the respective functions of $j=0$, 2, and -2. (a) *cis*-PBD, with MD simulation results from Fig. 6 of Ref. 3. (b) *trans*-PBD, with MD simulation results from Fig. 7 of Ref. 3.

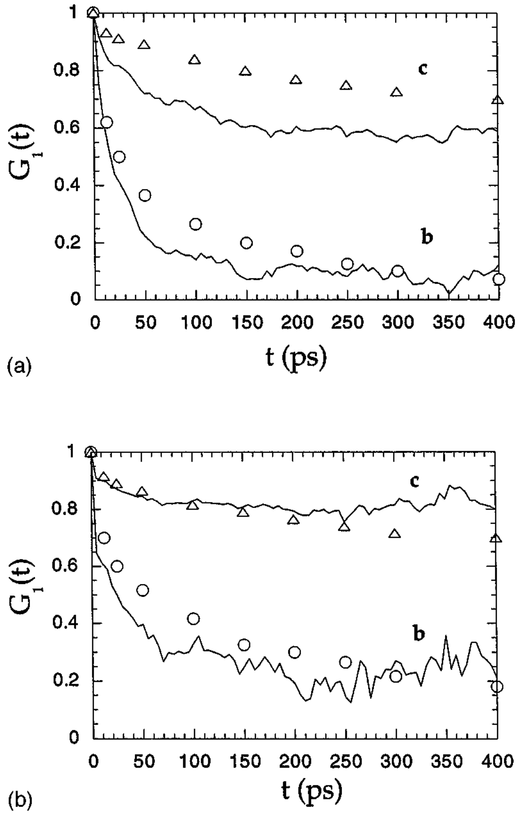

FIG. 6. First-order orientation autocorrelation functions $G_1(t)$ for out-of-plane **b** and chord vectors **c** defined at C_{sp2} at 425 K. MD simulation results are depicted by symbols (○) for the former, and (△) for the latter. The curves are obtained by applying the DRIS approach to a kinetic segment of four rotating bonds subject to third order conformational interdependence. (a) *cis*-PBD, with MD simulation results from Fig. 11 of Ref. 3. (b) *trans*-PBD, with MD simulation results from Fig. 12 of Ref. 3.

2. Orientational correlation functions

To examine the reorientation anisotropy at a position on the chain backbone, an out-of-plane vector and a chord vector have been defined as

$$\mathbf{b}_i=\frac{\mathbf{l}_i\times\mathbf{l}_{i+1}}{|\mathbf{l}_i\times\mathbf{l}_{i+1}|}, \tag{12}$$

$$\mathbf{c}_i=\frac{\mathbf{l}_i+\mathbf{l}_{i+1}}{|\mathbf{l}_i+\mathbf{l}_{i+1}|}. \tag{13}$$

Here $\mathbf{l}_i$ is the vector affixed to the ith bond. Vectors $\mathbf{b}_i$ and $\mathbf{c}_i$ are defined at C_{sp3} and C_{sp2} atoms. These represent the local motions perpendicular and parallel to the chain axis, respectively. Figures 6(a) and 6(b) depict the first-order orientational correlation functions, $G_1(t)$, of **b** and **c**, respectively, for *trans*-PBD predicted by DRIS [approach (b)] and the simulation results previously reported in Ref. 3. The agreement between the simulation and the DRIS results is qualitatively satisfactory, being least acceptable for **c** at C_{sp2}. The very important point to note here is that, the DRIS results very much depend on the size of the kinetic unit considered. In contrast with the conformational correlations, the effect of the specific intermolecular and intramolecular interactions on the orientational correlations is important. The entire cooperative response to external perturbations may or may not be incorporated by only considering transition rates up to third order. Motions causing large amplitude swings of the chain segments surrounding a rotating bond in the DRIS model may not provide an accurate representation of the MD simulation. However, the torsional rotations are certainly localized along the chain by the random fluctuations of the environment. The kinetic segment considered here consists of four rotating bonds subject to third-order conformational transitions. The anisotropy in the calculation with the DRIS model results essentially from intramolecular effects (because the DRIS model uses only a single chain), but the perturbation caused by intermolecular effects is incorporated indirectly into the DRIS model via the transition rates which were deduced from the MD simulation, where intermolecular interactions are present.

The Brownian dynamics studies of Weber and Helfand[17] and DRIS studies of Bahar *et al.*[7] for polyethylenelike isolated chains show the anisotropy of local motions arising from intramolecular effects. On the other hand, as shown by the recent MD simulations of Roe,[18] the anisotropy in bulk systems results from intermolecular effects, considering that a polymer chain is to be confined to within a pipe. From those arguments, it is implied that the perturbations arising from intermolecular interactions appear in the intramolecular cooperative motions of the bonds which are extracted from an atomistic simulation trajectory. The higher the order of the interdependence, the more accurate are the transition rates employed in transition rate matrix, and hence the better is the agreement between the theory and the simulation. However, with the MD simulations that have been utilized here, it has not been statistically possible to go higher than third order interdependency in the conformation rotations.

V. CONCLUSION

DRIS formalism has been useful in gaining an understanding of the basic features of the local dynamics that arise exclusively from jumps between isomeric states in the amorphous state at bulk density. The constraints imposed by the environmental effects and the cooperativity resulting from the neighbors of the chains is of great importance, but it is incorporated only in an indirect manner via the transition rates, based on first-, second-, and third-order interdependent conformational statistics deduced from MD simulation trajectories for fully atomistic amorphous systems at bulk density. The calculations revealed that the time evolution of the rotational isomeric states, and the prediction of the torsional autocorrelation functions via the DRIS model is in reasonable agreement with the simulations. The latter is independent of the order of transitions. There is no end effect in the relaxation of any torsional bond. Cross-correlation functions are not reproduced as well by the DRIS model, presumably because they are dominated by torsional librations within rotational isomeric states. The anisotropic character of segmental motions is captured by some vector correlation functions, but it is dependent on the selection of the kinetic segment to implement into the DRIS formalism. Incorporation of information from a computationally intensive MD simulation into the much more efficient DRIS model provides an attractive means for extending the time scale for the theoretical analysis of the dynamics for amorphous chains at bulk density.

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