Entangled-like Chain Dynamics in Non-entangled Polymer Blends with Large Dynamic Asymmetry

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(Dated: February 1, 2008)

We discuss simulations of a simple model for polymer blends in the framework of the Rouse model. At odds with standard predictions, large dynamic asymmetry between the two components induces strong non-exponentiality of the Rouse modes for the fast component. Despite chains being much shorter than the entanglement length, it also induces dynamic features resembling a crossover to entangled-like chain dynamics. This unusual behavior is associated to strong memory effects which break down the assumption of time uncorrelation of the external forces acting on the tagged chain.

PACS numbers: 83.10.Rs, 83.10.Kn, 83.80.Tc

Polymer blends are systems of wide technological interest whose rheological properties can be tuned by varying the mixture composition. They are dynamically heterogeneous: starting from two homopolymers with different mobilities, two separated segmental relaxations are still observed in the blend state. In the usual scenario the two components display qualitatively similar dynamic features in the blend. A rather different scenario arises, for low concentration of the fast component, if the two homopolymers exhibit very different glass transition temperatures [1, 2]. In this case the two components exhibit strong dynamic immiscibility, with a large separation (dynamic asymmetry) in their respective relaxation times. The latter can be of even 12 decades for high dilution of poly(ethylene oxide) (PEO) in poly(methyl methacrylate) (PMMA) [1].

In such conditions the motion of the fast component seems to be strongly confined by the slowly relaxing matrix formed by the slow component. We have recently performed a computational investigation of the structural α-relaxation in a simple bead-spring model for polymer blends [3]. The introduction of size disparity between the monomers of the two components induces a large time scale separation at low concentrations of the fast component, which displays unusual dynamic features, as logarithmic relaxation for density correlators, or dynamic decoupling between self-motions and intrachain collective relaxation. These unusual observations are supported by recent fully atomistic simulations [2] and neutron scattering experiments [4] on the real blend PEO/PMMA.

In this Letter we show that anomalous dynamic features induced by confinement on the fast component extend to large scales. By analyzing relaxation of the chain degrees of freedom within the framework of the Rouse model [5] novel features are observed for the behavior of the chain normal modes of the fast component. We simulate short chains (4 ≤ N ≤ 21 monomers) corresponding to the non-entangled case in the homopolymer state (the entanglement length \( 2N_c \) is \( N_c = 35 \) monomers). This choice allows us to compare results between the blend and homopolymer states for chain lengths for which the homopolymer case shows reasonable agreement with predictions of the Rouse model [6, 7]. We test the two basic predictions: orthogonality and exponentiality of the Rouse modes. Simulations show that orthogonality is a reasonable approximation for both components, as well as exponentiality in the case of the slow one. However, large deviations from exponentiality are found for the fast component in the blend. We observe a striking crossover, by increasing the dynamic asymmetry in the blend, to a regime resembling scaling features characteristic of entangled-like chain dynamics, despite the used chain length being much shorter than \( N_c \). Anomalous scaling is found even in the short-chain limit. We associate the mentioned anomalous features for the Rouse modes of the fast component to strong memory effects, which are induced by the slow nature of the confining matrix, and break the Rouse assumption of time uncorrelation of the external forces acting on the tagged chain.

The model introduces a mixture A/B of bead-spring chains with the same number of monomers, \( N \). The monomer mass is \( m = 1 \). Monomers within a same chain are identical (of the same species A or B). We simulate systems with \( N = 4, 7, 10, 15, \) and 21. The monomer-monomer interaction potential is \( V_{\alpha\beta}(r) = 4\epsilon[\alpha^{12} - 6\epsilon^{10} + c^{-14} (r/\sigma_{\alpha\beta})^2] \), where \( \epsilon = 1, \) c = 1.15 and \( \alpha, \beta \in \{A, B\} \). Potential and forces are continuous at the cutoff \( r_c = \sigma_{\alpha\beta} \). The interaction diameters are \( \sigma_{BB} = 1, \sigma_{AA} = 1.6 \sigma_{BB}, \) and \( \sigma_{AB} = 1.3 \sigma_{BB} \).

Chain connectivity is introduced by a FENE potential \( V^{FENE}_{\alpha\alpha}(r) = -kR_0^2 \ln[1-(R_0\sigma_{\alpha\alpha})^{-2}r^2] \), between consecutive monomers, with \( k = 15 \) and \( R_0 = 1.5 \). The blend composition is \( x_B = N_B/(N_A + N_B) \), with \( N_{\alpha} \) the number of α-monomers. The total number of
monomers is typically 2000-3000. We use \( x_B = 0.3 \) and a packing fraction \( \phi = 0.53 \). Temperature \( T \), distance, and time \( t \) are measured, respectively, in units of \( \epsilon/k_B \), \( \sigma_{BB} \), and \( \sigma_{BB}(m/\epsilon)^{1/2} \). Equilibrium simulations are performed in the microcanonical ensemble, with 20-40 independent runs for statistical averages. The longest production runs extend to \( t \approx 4 \times 10^6 \), corresponding to about 800 million time steps.

Monomer size disparity induces strong dynamic asymmetry between the two components by decreasing \( T \) \cite{2}. We define the ‘dynamic asymmetry’, \( \chi = \tau_{AA}/\tau_{BB} \), with \( \tau_{AA} \) the relaxation time of the normalized density-density correlator \( F_{\alpha\alpha}(q,t) \) for \( \alpha\alpha \) pairs \cite{5}, evaluated at the wavevector \( q \) for the maximum of the static structure factor \cite{3}. Thus, \( \tau_{AA} \) is in the time scale of the structural \( \alpha \)-relaxation. By using the definition \( F_{\alpha\alpha}(q,\tau_{\alpha\alpha}) = 0.3 \), \( \chi \) increases, from about 4 at \( T = 1.5 \), more than three decades by decreasing \( T \).

Now we summarize the main predictions of the Rouse model \cite{5}. A tagged chain is represented as a string of beads of equal mass connected by harmonic springs of constant \( 3k_B T/b^2 \), with \( b \) the bond length. The effective interaction experienced by the chain is given by a friction coefficient \( \zeta \) and a set of stochastic forces \( \mathbf{f}_j \). Excluded volume interactions are neglected. The chain normal (Rouse) modes of index \( p = 1, \ldots, N - 1 \) are defined as \( \mathbf{X}_p(t) = N^{-1} \sum_{j=1}^{N} r_j(t) \cos[jp\pi/N] \), and follow the equations of motion \( 2N\zeta \ddot{\mathbf{X}}_p = -k_p \mathbf{X}_p + \mathbf{g}_p \), with \( k_p = 24Nk_B Tb^{-2}\sin^2[p\pi/2N] \). The external force for the \( p \)-th-mode is \( \mathbf{g}_p(t) = 2 \sum_{j=1}^{N} f_j(t) \cos[jp\pi/N] \). Integration of the equations of motion yields \( \langle \mathbf{X}_p(t) \cdot \mathbf{X}_q(0) \rangle = (2N\zeta)^{-1} \int_{-\infty}^{t} dt e^{-(t-t')/\tau_p} \int_{-\infty}^{0} dt' e^{t'/\tau_p} \langle \mathbf{g}_p(t') \mathbf{g}_q(t''') \rangle \) for the correlators of the Rouse modes. The relaxation times are given by \( \tau_p = (b^2\zeta/12k_B T)\sin^2[p\pi/2N] \).

At this point no assumption has been made about the nature of the forces \( \mathbf{f}_j \). The Rouse model fully neglects spatial and time correlation of the stochastic forces, i.e., \( \langle \mathbf{g}_p(t') \mathbf{g}_q(t'') \rangle = 12Nk_B T\delta_{p,q}(t' - t'') \). The former two approximations yield respectively orthogonality and exponential relaxation of the Rouse correlators, leading to the expression \( \langle \mathbf{X}_p(t) \cdot \mathbf{X}_q(0) \rangle = (b^2\zeta/8N)\sin^2[p\pi/2N]\delta_{pq} \exp[-t/\tau_p] \).

Orthogonality and exponentiality of the Rouse modes are the two main predictions of the Rouse model, and are the basis for the derivation of the correlators probing chain relaxation \cite{5}. By using the mentioned approximations, one obtains \( D_{CM} = (N\zeta)^{-1}k_B T \) for the diffusivity of the chain center-of-mass \cite{5}. By introducing this result in \( \tau_p \) (see above) we find the scaling relation for the Rouse relaxation times:

\[
12Nd_{CM}^{*}\tau_p = b^2\sin^2[p\pi/2N].
\] (1)

In the following we test the former predictions in the bead-spring blend here investigated. We compute normalized Rouse correlators for the \( \alpha \)-chains, \( \Phi_{pq}(t) = \langle \mathbf{X}_p(t) \cdot \mathbf{X}_q(0) \rangle / \langle \langle \mathbf{X}_p(0) \rangle^2 \rangle \). According to orthogonality \( \Phi_{pq}(0) = \delta_{pq} \). For both the \( \alpha \)- and \( \beta \)-chains simulation data fulfill \( |\Phi_{pq}(0)| < 0.1 \) for all the cases \( p \neq q \) at all the temperatures, indicating than deviations from orthogonality are small. Thus, we conclude that there are only weak spatial correlations between the external stochastic forces for the chains of both components, and Rouse modes as defined above are good normal modes. This prediction is not affected by blending, and in particular by the observed confinement effects on the fast component. Now we test the exponentiality of the Rouse modes. Fig. 11 shows results for normalized Rouse correlators of the B-chains for \( N = 10 \) at \( T = 0.40 \). The decay of \( \Phi_{pp}(t) \) from the plateau has been fitted to an empirical Kohlrausch-Williams-Watts (KWW) function, \( \propto \exp[-(t/t_p)^\beta_p] \). Figs. 11 and 11 show, for respectively the \( \alpha \)- and \( \beta \)-chains, the \( T \)- and \( p \)-dependence of the stretching exponent \( \beta_p \). According to the Rouse model relaxation of the Rouse correlators is purely exponential (\( \beta_p = 1 \)). Clear deviations from this prediction are observed by decreasing \( T \) (i.e., by increasing \( \chi \)). At a same \( T \), non-exponentiality is systematically more pronounced for the B-chains, which show \( \beta_p \)-values of even 0.3 at \( T = 0.33 \). Only at high temperature \( \Phi_{pp}(t) \) is approximately exponential (\( \beta_p \geq 0.8 \)) for both components. These features are rather different from observations in the homopolymer case \cite{5}, which even at very low \( T \) shows exponents
are rescaled by a factor $c_12N_dT_p^2$. The latter drops out of Eq. (1). Hence, blending induces much stronger non-exponentiality for Rouse correlators. In principle, non-exponentiality may be related to a distribution of intrinsically exponential processes originating from structural and/or dynamic heterogeneity. It is well-known that a KWW function can be formally expressed as a sum of pure exponential functions weighted by an adequate distribution $G$, though the latter does not necessarily have physical meaning. Hence, we express the KWW function for the $p$th-mode as $\exp[-(t/\tau_p^K)^{\beta_p}] = \int d\tau_p G(\tau_p) \exp[-t/\tau_p]$, where the distributed values $\tau_p$ are the relaxation times of the different exponential processes. Now we show that the latter is a good approximation for the A-chains but unphysical for the B-ones. In other words, the Rouse modes are basically exponential for the A-chains and strongly non-exponential for the B-ones. Since the relaxation times for the elementary processes would be $\tau_p = 0.3 \sin^{-2}(p\tau/2N)$ (see above), with $\xi$ a $p$-independent factor, we can write $\exp[-(t/\tau_p^K)^{\beta_p}] = \int d\xi G(\xi) \exp[-\xi t \sin^2(p\tau/2N)]$, with $\tilde{t} = t \sin^2(p\tau/2N)$ the ‘conjugated variable’ of $\xi$. By defining $\tilde{\tau} = \tau_p^K \sin^2(p\tau/2N)$, we find $\exp[-(\tilde{t}/\tilde{\tau})^{\beta_p}] = \int d\xi G(\xi) \exp[-\tilde{t}\xi]$. Since the right side of this equation is $p$-independent, consistency requires the scaling condition $\tau_p^K \sim \sin^{-2}(p\tau/2N)$. Fig. 2 shows a test of Eq. (1) — also in the long wavelength limit $\tau_p \sim (N/p)^2$ — for both components at the investigated values of $N$ and $T$. This comparison also provides a test of the mentioned scaling condition [11]. In agreement with observations for the non-entangled homopolymer case in similar bead-spring models [7] or in lattice models [9], data for the A-chains exhibit only small deviations, at small $N/p$. Therefore, exponentiality of the Rouse modes for the A-chains is actually a good approximation, and the observed non-exponentiality of the Rouse correlators basically originates from a distribution of elementary exponential processes. The apparently stronger distribution effects (stronger stretching), as compared to the homopolymer [7], might be related to structural and/or dynamic heterogeneities induced by blending.

The B-chains exhibit a clear breakdown of Rouse scaling (Fig. 2b). This result demonstrates that for the fast B-component, though distribution effects are (as for the slow A-component) presumably present, the Rouse modes are intrinsically, at low $T$, of strongly non-

\[ \beta_p \gtrsim 0.8. \]
exponential nature. Eq. (1) is approached only in the high \( T \) limit, where dynamic asymmetry (\( \chi \approx 4 \) at \( T = 1.5 \)) and confinement effects vanish. By decreasing \( T \) we find an ultimate scaling \( \tau_p \propto (N/p)^{2.35} \). This crossover is concomitant with the onset of non-exponentiality of the Rouse modes. It must be stressed that this anomalous scaling behavior is not related to particular static features of the Rouse modes. Fig. 2 shows, for all the investigated values of \( T \) and \( N \), results for the static Rouse modes, \( \langle [X_p(0)]^2 \rangle \). The latter display scaling behavior \( \propto (N/p)^{2.2} \), both for the A- and B-chains, in full analogy with observations for the homopolymer case \([13,12]\). Therefore, anomalous scaling in Fig. 2 is definitively a non-trivial dynamic effect.

Exponentiality of the Rouse modes originates from the assumption of time uncorrelation of the stochastic forces (see above). Results reported here evidence that the latter clearly breaks down for the fast component. Several theoretical approaches based on projector operator techniques incorporate density fluctuations around the tagged chain in a generalized Langevin equation (GLE). Slow relaxation of the memory kernel induces strong non-exponentiality of the Rouse modes \([13]\). The Rouse model (pure exponentiality) is recovered as a particular case for which density fluctuations around the tagged chain relax in a microscopic time scale \([13]\). This rough approximation seems to work reasonably for simple non-entangled homopolymers and for the slow component in the blend model here investigated, but it is clearly unrealistic for the fast component at low \( T \), which consists of chains diluted in a much slower host matrix.

The mentioned GLE methods, through approximations of the memory kernel within renormalized Rouse models, predict for \( \tau_p \) a crossover \( (N/p)^2 \rightarrow (N/p)^{2.35} \) in entangled homopolymers \([13,12]\). The latter is in agreement with simulations \([8,11,14,15,16]\) of homopolymers at fixed \( T \) by increasing the chain length beyond the entanglement value \( N_c \sim 35 \). A similar crossover is observed in the non-entangled blend model here investigated by increasing the dynamic asymmetry between the two components \([17]\). A further analogy in the fast B-component with predictions of GLE methods for entangled homopolymers \([13]\) is the observed anomalous scaling \( \propto t^{y=0.3} \) for the mean-squared displacement in the time interval prior to the Rouse time \( \tau_1 \). Fig. 4 shows for \( N = 15 \) a crossover, concomitant with that of Fig. 2, from Rouse-like scaling (\( \propto t^{y=0.5} \)) to an ultimate anomalous regime as the former. Similar results are obtained for the B-chains at the other investigated chain lengths. On the contrary, a \( T \)-independent exponent \( y \approx 0.6 \) is obtained for the slow A-component \([3]\), again in full analogy with the homopolymer case \([7]\).

Within GLE methods observation of the mentioned anomalous power laws is directly connected to slow relaxation of density fluctuations around the tagged chain \([13]\). The latter may be induced by entanglement, but data reported here for the fast component suggest that this is not a necessary ingredient. Analogies with entangled-like dynamics are indeed observed even for \( N = 4 \), provided that dynamic asymmetry in the blend is sufficiently strong. In summary, results presented here suggest a more general frame for chain relaxation features usually associated to entanglement effects. They also open new possibilities for the application of GLE methods in complex polymer mixtures.

We acknowledge support from NMP3-CT-2004-502235 (SoftComp, EU), MAT2007-63681 (Spain), and IT-436-07 (GV, Spain).

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[17] & Though confinement of the fast component in the blend may invoke the common tube picture and associated reptation dynamics (data at low \( T \) are even compatible with \( D_{\text{CM}} \propto N^{-2} \) \([8]\)), it was already stressed for the entangled homopolymer \([5]\) that reptation predicts a crossover in the \( N \)-but not in the \( p \)-scaling \([3]\).