

## Entangledlike Chain Dynamics in Nonentangled Polymer Blends with Large Dynamic Asymmetry

Angel J. Moreno<sup>1</sup> and Juan Colmenero<sup>1,2,3</sup>

<sup>1</sup>*Centro de Física de Materiales (CSIC-UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain*

<sup>2</sup>*Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain*

<sup>3</sup>*Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain*

(Received 22 August 2007; revised manuscript received 16 January 2008; published 28 March 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 nonexponentiality 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 entangledlike chain dynamics. This unusual behavior is associated with strong memory effects which break down the assumption of time uncorrelation of the external forces acting on the tagged chain.

DOI: [10.1103/PhysRevLett.100.126001](https://doi.org/10.1103/PhysRevLett.100.126001)

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  $\alpha$  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 ( $4 \leq N \leq 21$  monomers) corresponding to the non-entangled case in the homopolymer state (the entangle-

ment length [6] is  $N_e \sim 35$  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 [6–9]. 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 entangledlike chain dynamics, despite the used chain length being much shorter than  $N_e$ . 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  $V_{\alpha\beta}(r) = 4\epsilon[(\sigma_{\alpha\beta}/r)^{12} - 7c^{-12} + 6c^{-14}(r/\sigma_{\alpha\beta})^2]$ , where  $\epsilon = 1$ ,  $c = 1.15$ , and  $\alpha, \beta \in \{A, B\}$ . Potential and forces are continuous at the cutoff  $r_c = c\sigma_{\alpha\beta}$ . 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 finitely extensible nonlinear elastic (FENE) potential [6,7],  $V_{\alpha\alpha}^{\text{FENE}}(r) = -kR_0^2\epsilon \ln[1 - (R_0\sigma_{\alpha\alpha})^{-2}r^2]$ , 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  $\alpha$  monomers. The total number of monomers is typically 2000–3000. We use  $x_B = 0.3$  and

a packing fraction  $\phi = 0.53$  [3]. 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  $800 \times 10^6$  time steps.

Monomer size disparity induces strong dynamic asymmetry between the two components by decreasing  $T$  [3]. We define the “dynamic asymmetry,”  $\chi = \tau_{AA}/\tau_{BB}$ , with  $\tau_{\alpha\alpha}$  the relaxation time of the normalized density-density correlator  $F_{\alpha\alpha}(q, t)$  for  $\alpha$ - $\alpha$  pairs [3], evaluated at the wave vector  $q$  for the maximum of the static structure factor [3]. Thus,  $\tau_{\alpha\alpha}$  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 [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  $p = 1, \dots, N-1$  are defined as  $\mathbf{X}_p(t) = N^{-1} \sum_{j=1}^N \mathbf{r}_j(t) \cos[(j-1/2)p\pi/N]$ , and follow the equations of motion  $2N\zeta \dot{\mathbf{X}}_p = -k_p \mathbf{X}_p + \mathbf{g}_p$ , with  $k_p = 24Nk_B T b^{-2} \sin^2[p\pi/2N]$ . The external force for the  $p$ th mode is  $\mathbf{g}_p(t) = 2 \sum_{j=1}^N \mathbf{f}_j(t) \cos[(j-1/2)p\pi/N]$ . Integration of the equations of motion yields  $\langle \mathbf{X}_p(t) \cdot \mathbf{X}_q(0) \rangle = (2N\zeta)^{-2} \int_{-\infty}^t dt' e^{-(t-t')/\tau_p} \times \int_{-\infty}^0 dt'' e^{t''/\tau_q} \langle \mathbf{g}_p(t') \mathbf{g}_q(t'') \rangle$  for the correlators of the Rouse modes. The relaxation times are given by  $\tau_p = (b^2 \zeta / 12k_B T) \sin^{-2}[p\pi/2N]$ . The Rouse model fully neglects spatial and time correlation of the stochastic forces, i.e.,  $\langle \mathbf{g}_p(t') \mathbf{g}_q(t'') \rangle = 12N\zeta k_B T \delta_{pq} \delta(t' - t'')$ . The former two approximations yield, respectively, orthogonality and exponential relaxation of the Rouse correlators, leading to the expression  $\langle \mathbf{X}_p(t) \cdot \mathbf{X}_q(0) \rangle = (b^2/8N) \times \sin^{-2}[p\pi/2N] \delta_{pq} \exp[-t/\tau_p]$ . 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 [5]. By using the mentioned approximations, one obtains  $D_{c.m.} = (N\zeta)^{-1} k_B T$  for the diffusivity of the chain center-of-mass [5]. By introducing this result in  $\tau_p$  (see above) we find the scaling relation for the Rouse relaxation times:

$$12ND_{c.m.}\tau_p = b^2 \sin^{-2}[p\pi/2N]. \quad (1)$$

In the following we test the former predictions in the bead-spring blend here investigated. We compute normalized Rouse correlators for the  $\alpha$  chains,  $\Phi_{pq}^\alpha(t) = \langle \mathbf{X}_p^\alpha(t) \cdot \mathbf{X}_q^\alpha(0) \rangle / [\langle X_p^\alpha(0) \rangle^2]$ . According to orthogonality  $\Phi_{pq}^\alpha(0) = \delta_{pq}$ . For both the  $A$  and  $B$  chains simulation data fulfill

$|\Phi_{pq}^\alpha(0)| < 0.1$  for all the cases  $p \neq q$  at all the temperatures, indicating that 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. More precisely, it is not affected by the observed confinement effects on the fast component. Now we test the exponentiality of the Rouse modes. Figure 1(a) 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 [10] to an empirical Kohlrausch-Williams-Watts (KWW) function,  $\propto \exp[-(t/\tau_p)^\beta]$ . Figures 1(b) and 1(c) show, for the  $A$  and  $B$  chains, respectively, 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  $T$ , nonexponentiality 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 [7], which even at very low  $T$  shows exponents  $\beta_p \geq 0.8$ . Hence, blending induces much stronger nonexponentiality for Rouse correlators.

In principle, nonexponentiality may be related to a distribution of intrinsically exponential processes originating from structural and/or dynamic heterogeneity. It is well

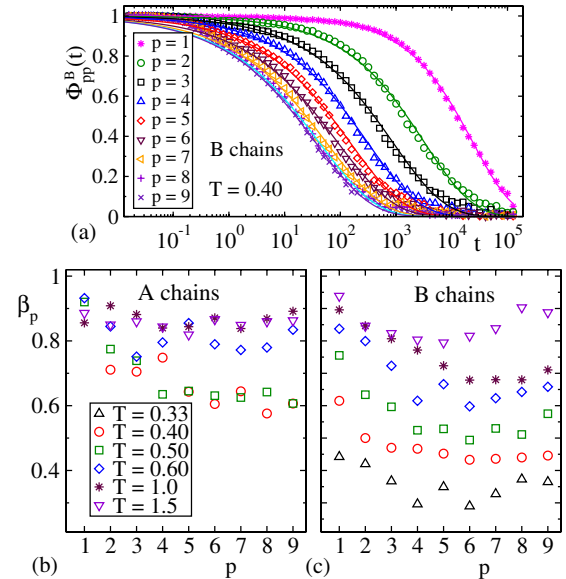


FIG. 1 (color online). (a) Symbols are correlators of the Rouse modes for the  $B$  chains, for  $N = 10$  at  $T = 0.40$ . Lines are fits to a KWW function. (b),(c) For, respectively, the  $A$  and  $B$  chains,  $p$  dependence of the stretching exponents, for  $N = 10$  at different temperatures. Symbol codes in (b) and (c) are identical.

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 nonexponential for the  $B$  ones. Since the relaxation times for the elementary processes would be  $\tau_p = \xi^{-1} \sin^{-2}(p\pi/2N)$  (see above), with  $\xi$  a  $p$ -independent factor, we can write  $\exp[-(t/\tau_p^K)^{\beta_p}] = \int d\xi G(\xi) \exp[-\xi t \sin^2(p\pi/2N)]$ , with  $\tilde{t} = t \sin^2(p\pi/2N)$  the “conjugated variable” of  $\xi$ . By defining  $\tilde{\tau} = \tau_p^K \sin^2(p\pi/2N)$ , we find  $\exp[-(\tilde{t}/\tilde{\tau})^{\beta_p}] = \int d\xi G(\xi) \times \exp[-\tilde{t}\xi]$ . Since the right side of this equation is  $p$ -independent, consistency requires the scaling condition  $\tau_p^K \propto \sin^{-2}(p\pi/2N)$ . Figure 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 nonentangled 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 nonexponentiality 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. 2(b)]. 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 nonexponential nature. Equation (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 regime  $\tau_p \sim (N/p)^{\chi \approx 3.5}$ . This crossover is concomitant with the onset of nonexponentiality of the Rouse modes. It must be stressed that this anomalous scaling behavior is not related to particular static features of the Rouse modes. Figure 2(c) 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  $\sim (N/p)^{2.2}$ , both for the  $A$  and  $B$  chains, in full analogy with observations for the homopolymer case [7,12]. Therefore, anomalous scaling in Fig. 2(b) is definitively a nontrivial dynamic effect.

Exponentiality of the Rouse modes originates from the assumption of time uncorrelation of the stochastic forces

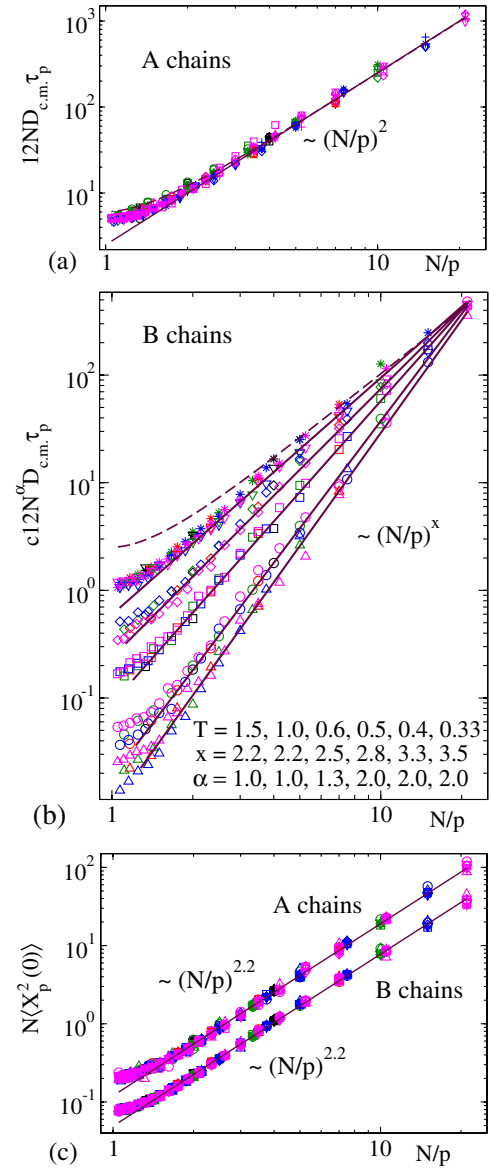


FIG. 2 (color online). (a),(b) Test of Rouse scaling for, respectively, the  $A$  and  $B$  chains. Identical symbols correspond to a same  $T$  (triangles,  $T = 0.33$ ; circles,  $T = 0.4$ ; squares,  $T = 0.5$ ; diamonds,  $T = 0.6$ ; crosses,  $T = 0.75$ ; stars,  $T = 1.0$ ; down triangles,  $T = 1.5$ ). Identical colors correspond to a same  $N$  (black,  $N = 4$ ; red,  $N = 7$ ; green,  $N = 10$ ; blue,  $N = 15$ ; magenta,  $N = 21$ ). Solid lines indicate power-law behavior  $\sim (N/p)^x$ . Dashed lines correspond to Eq. (1) corrected by a shift factor (see explanation in [7]). For clarity of presentation, data in (b) are rescaled by a  $T$ -dependent factor  $c$ . The latter drops about two decades from  $c \leq 1$  at  $T = 1.5$ . (c) Static Rouse modes (scaled by  $N$ ) for  $A$  and  $B$  chains. Lines indicate an effective power law  $\sim (N/p)^{2.2}$ . Color and symbol codes are as in (a) and (b).

(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

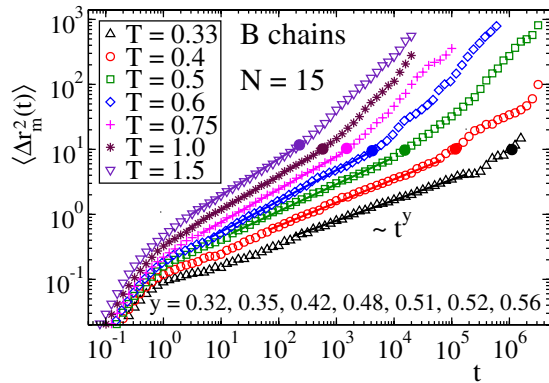


FIG. 3 (color online). Mean-squared displacement of middle monomers of the  $B$  chains, for  $N = 15$ . Lines indicate an effective power law  $\sim t^y$ . Filled circles mark the Rouse times  $\tau_1$ .

within a memory kernel in a generalized Langevin equation (GLE). Slow relaxation of the memory kernel induces strong nonexponentiality 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 well for simple nonentangled 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  $(N/p)^2 \rightarrow (N/p)^{x \approx 3.5}$  in entangled homopolymers [13]. The latter is in agreement with simulations [8,14–16] of homopolymers at fixed  $T$  by increasing the chain length beyond the entanglement value  $N_e \sim 35$ . A similar crossover is observed in the nonentangled 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  $\sim t^{y \approx 0.3}$  for the mean-squared displacement in the time interval prior to the Rouse time  $\tau_1$ . Figure 3 shows for  $N = 15$  a crossover, concomitant with that of Fig. 2(b), from Rouse-like scaling ( $\sim t^{y \approx 0.5}$ ) 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 entangledlike 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 with entanglement effects. They also open new possibilities for the application of GLE methods in complex polymer mixtures.

We acknowledge support from projects NMP3-CT-2004-502235 (SoftComp, EU), MAT2007-63681 (Spain), 2007-60I021 (CSIC, Spain), and IT-436-07 (GV, Spain).

- [1] T.R. Lutz *et al.*, *Macromolecules* **36**, 1724 (2003).
- [2] A.C. Genix *et al.*, *Phys. Rev. E* **72**, 031808 (2005).
- [3] A.J. Moreno and J. Colmenero, *J. Chem. Phys.* **124**, 184906 (2006); A.J. Moreno and J. Colmenero, *J. Phys. Condens. Matter* **19**, 466112 (2007).
- [4] K. Niedzwiedz *et al.*, *Phys. Rev. Lett.* **98**, 168301 (2007).
- [5] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University, Oxford, England, 1986).
- [6] K. Kremer and G.S. Grest, *J. Chem. Phys.* **92**, 5057 (1990).
- [7] C. Bennemann, J. Baschnagel, W. Paul, and K. Binder, *Comput. Theor. Polym. Sci.* **9**, 217 (1999).
- [8] J.S. Shaffer, *J. Chem. Phys.* **103**, 761 (1995).
- [9] T. Kreer *et al.*, *Macromolecules* **34**, 1105 (2001).
- [10] The selected fit interval begins at the inflection point prior to the plateau. Other possible choices [see, e.g., M. Aichele and J. Baschnagel, *Eur. Phys. J. E* **5**, 245 (2001)] yield only moderate variations  $|\Delta\beta_p| < 0.15$ . Hence, Fig. 1 unambiguously demonstrates the strongly stretched character of the Rouse correlators.
- [11] Similarly to Ref. [7], we use  $\Phi_{pp}(\tau_p) = 0.3$  instead of representing KWW times, whose values weakly depend on the selected fit interval. Having said that, trends and effective exponents in Fig. 2 are not affected within error bars by these particular choices.
- [12] Deviations from pure Rouse scaling,  $\sim (N/p)^2$ , for the static modes are related to the breakdown of Gaussian chain statistics at small length scales [7].
- [13] R. Kimmich and N. Fatkullin, *Polymer Chain Dynamics and NMR*, *Advances in Polymer Science* Vol. 170 (Springer, Berlin, 2004), pp. 1–113. The precise values of the effective exponents depend on the renormalization procedure.
- [14] K. Kremer, G.S. Grest, and I. Carmesin, *Phys. Rev. Lett.* **61**, 566 (1988).
- [15] J.T. Padding and W.J. Briels, *J. Chem. Phys.* **117**, 925 (2002).
- [16] As discussed in [8], some experimental results [D. Richter *et al.*, *Phys. Rev. Lett.* **71**, 4158 (1993)] in homopolymers suggest the realization of this crossover.
- [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  $D_{c.m.} \propto N^{-2}$ ) [5], it was already stressed for the entangled homopolymer [8] that reptation predicts a crossover in the  $N$  but not in the  $p$  scaling [5].