

Static and dynamic contributions to anomalous chain dynamics in polymer blends

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Abstract.

By means of computer simulations, we investigate the relaxation of the Rouse modes in a simple bead-spring model for non-entangled polymer blends. Two different models are used for the fast component, namely fully-flexible and semiflexible chains. The latter, which incorporate intramolecular barriers with bending and torsion terms, are semiflexible in the meaning that static intrachain correlations are strongly non-gaussian at all length scales. The dynamic asymmetry in the blend is strongly enhanced by decreasing temperature, inducing confinement effects on the fast component. The dynamics of the Rouse modes show very different trends for the two models of the fast component. For the fully-flexible case, the relaxation times exhibit a progressive deviation from Rouse scaling on increasing the dynamic asymmetry. This anomalous effect has a dynamic origin. It is not related to particular static features of the Rouse modes, which indeed are identical to those of the fully-flexible homopolymer, and are not modified by the dynamic asymmetry in the blend. On the contrary, in the semiflexible case the relaxation times exhibit approximately the same scaling behaviour as the amplitudes of the modes. This suggests that the origin of the anomalous dynamic scaling for semiflexible chains confined in the blend is essentially of static nature. We discuss implications of these observations for the applicability of theoretical approaches to chain dynamics in polymer blends.

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1. Introduction

Miscible polymer blends exhibit dynamic disparity. By starting from two homopolymers with different mobilities, two separated segmental relaxations are still found in the blend state [1, 2]. When the two homopolymers exhibit very different glass transition temperatures, and the concentration of the fast component is low, the respective time scales in the blend can differ by orders of magnitude, leading to strong dynamic asymmetry [3]. This effect is enhanced on decreasing the temperature, and can be of even 12 decades for high dilution of poly(ethylene oxide) (PEO) in poly(methyl methacrylate) (PMMA) [4]. In conditions of strong dynamic asymmetry, the motion of the fast component is confined by the slowly relaxing matrix formed by the slow component. Unusual dynamic features arise for the fast component in this case. Neutron scattering experiments in the blend PEO/PMMA reveal decoupling between self-motions and intrachain collective relaxation for the PEO [5]. Atomistic simulations of the former system reveal logarithmic decays of the scattering functions probing the segmental relaxation of the PEO [6]. Moreover, the Rouse modes of the PEO chains exhibit anomalous behaviour [7] (see below). All these observations have also been found in simulations of a simple blend of bead-spring chains with strong dynamic asymmetry [8, 9, 10], suggesting that they are generic features of real blends.

The simple bead-spring chains of the blends investigated in Refs. [8, 9, 10] are fully-flexible. No intramolecular barriers are implemented. The chain length, N , in all the investigated cases is smaller than the entanglement value. In such conditions, the simulations for the homopolymer system are consistent with expectations from the Rouse model [11, 12, 13, 14, 15]. This is also the case for the slow component in the blend state [10]. However a rather different scenario is found for the fast component in the blend [10], which only shows Rouse dynamics for vanishing dynamic asymmetry. Increasing the latter (by decreasing temperature) induces a progressive deviation from Rouse-like behaviour for *dynamic* observables of the fast component. These include intrinsic non-exponentiality of the Rouse modes and anomalous scaling of the corresponding relaxation times, $\tau_p \sim p^{-x}$, where p is the mode index. On increasing the dynamic asymmetry the exponent increases from the Rouse prediction, $x = 2$, to values $x \lesssim 3.5$. The origin of these features is dynamic. Indeed the static amplitudes of the Rouse modes are not affected by blending, and show gaussian, Rouse-like, scaling as in the homopolymer state [10].

The mentioned dynamic crossover, on increasing the dynamic asymmetry, from $\tau_p \sim p^{-2}$ to $\tau_p \sim p^{-3.5}$ in the *non-entangled* fast component is strikingly similar to that observed for entangled homopolymers on increasing the mode wavelength, N/p , beyond the entanglement length [14, 16, 17]. The crossover for the fast component in the blend is observed even in the limit of short chains. Thus, it was concluded that this feature is entirely controlled by the dynamic asymmetry in the blend, and not by a characteristic entanglement length scale [10]. Related observations have been presented by simulations of short fully-flexible chains in matrixes of fixed obstacles [18, 19, 20, 21]. Rouse modes

were not analyzed but a crossover, similar to the observation in homopolymers on increasing N , was found. Thus, the diffusivities changed from $D \sim N^{-1}$ to $D \sim N^{-2}$ on increasing the concentration of obstacles. Concomitantly, the end-to-end relaxation time changed from $\tau_e \sim N^2$ to $\tau_e \sim N^3$. Again, these observations are not related to particular static intramolecular features or to characteristic entanglement length scales, but being entirely controlled by the concentration of obstacles [20, 21].

In summary, the former results of Refs. [10, 18, 19, 20, 21] reveal a crossover to entangled-like dynamic features in non-entangled chains. This crossover is not connected to particular static features of the intrachain correlations. It has a entirely dynamic origin, related to the strength of the confinement effects induced by the surrounding matrix. Theories based on generalized Langevin equations (GLE) introduce a memory kernel accounting for the slow relaxation of density fluctuations around the tagged chain [22]. The Rouse model, which neglects memory effects, arises from such theories in the limit of fast relaxation of the kernel [22, 23]. Memory effects are enhanced on increasing the chain length beyond the entanglement value, and the theory reproduces non-exponentiality and anomalous scaling of the Rouse modes in entangled homopolymers [23]. It has been suggested that GLE methods may also account for the analogous dynamic features exhibited by the non-entangled fast component in polymer blends [10], through the incorporation in the kernel of the memory effects induced by the matrix, formed by the slow component in the blend or by the fixed obstacles in the systems of Refs. [18, 19, 20, 21].

As mentioned above, the simulations of Refs. [10, 18, 19, 20, 21] were performed for fully-flexible chains. In this article we briefly review the results of [10] and present new results for blends where the fast component is semiflexible, i.e., it has intramolecular barriers. These are introduced by implementing bending and torsion potentials. It is well-known that the presence of strong intramolecular barriers violates the Rouse assumption of gaussian behaviour for the static intrachain correlations. Indeed significant non-Rouse effects appear as chains become stiffer [24, 25, 26, 27, 28, 29]. In the same spirit as the Rouse model for fully-flexible chains, phenomenological models for semiflexible polymers usually model the interactions of the tagged chain with the surroundings by means of a friction term and random forces [30, 31]. As in the Rouse model for gaussian chains, the dynamics of the tagged chain is encoded in the assumed form of the intramolecular interactions (e.g., worm-like chains). Memory effects induced by slow density fluctuations of the surrounding matrix are neglected, and non-Rouse effects are of intramolecular origin. The latter is entirely related to static contributions and the amplitudes and relaxation times of the Rouse modes follow the same scaling behaviour [28].

The chains studied in this work are semiflexible in the meaning that they can be deformed but, unlike fully-flexible chains, the static intramolecular correlations are strongly non-gaussian within all the chain length scale. We investigate the effect of blending on the dynamic scenario observed for the semiflexible homopolymer, aiming to discriminate static and dynamic contributions to anomalous chain dynamics in

the blend. We find strong deviations from Rouse behaviour. However, as in the homopolymer state, the amplitudes and relaxation times of the Rouse modes follow almost the same scaling behaviour, i.e, in this case the origin of the anomalous, non-Rouse, features found for chain dynamics in the blend is essentially static. We conclude that memory effects induced by the slow matrix are not significant for semiflexible chains in blends, at least for the range of dynamic asymmetry investigated here, and when the chains are non-gaussian over all their length scale. Presumably, memory effects will become relevant in semiflexible chains which are long enough, at large length scales for which intramolecular static correlations recover gaussian statistics.

The paper is organized as follows. We describe the model and give simulation details in Section 2. Results for static and dynamic observables are presented in Section 3 and discussed in Section 4. Conclusions are given in Section 5.

2. Model and simulation details

We simulate a binary mixture of bead-spring chains. Monomers within a same chain are identical, i.e, of the same species (A or B). Each chain consists of $N = 21$ monomers, which is below the entanglement length [32]. All monomers have identical mass $m = 1$. Non-bonded interactions between monomers are given by the potential

$$V_{\alpha\beta}(r) = 4\epsilon[(\sigma_{\alpha\beta}/r)^{12} - 7c^{-12} + 6c^{-14}(r/\sigma_{\alpha\beta})^2], \quad (1)$$

with $\epsilon = 1$, $c = 1.15$ and $\alpha, \beta \in \{A, B\}$. Potential and forces are continuous at the cutoff $r_c = c\sigma_{\alpha\beta}$. With this cutoff the potential $V(r)$ has no local minima and is purely repulsive. The interaction diameters are $\sigma_{AA} = 1.6$, $\sigma_{AB} = 1.3$, and $\sigma_{BB} = 1$. Chain connectivity is introduced by a FENE potential [33],

$$V_{\alpha\alpha}^{\text{FENE}}(r) = -kR_0^2\epsilon \ln[1 - (R_0\sigma_{\alpha\alpha})^{-2}r^2], \quad (2)$$

between consecutive monomers, with $k = 15$ and $R_0 = 1.5$. Intramolecular barriers are implemented by means of the bending and torsional potentials proposed in Refs. [26, 34]. The bending potential V_B is defined as

$$V_B(\theta_i) = (\epsilon K_B/2)(\cos \theta_i - \cos \theta_0)^2, \quad (3)$$

where θ_i is the bending angle between consecutive monomers $i - 1$, i and $i + 1$. We use $\theta_0 = 109.5^\circ$ for the equilibrium bending angle [26, 34]. The torsional potential V_T is defined as

$$V_T(\theta_i, \theta_{i+1}, \phi_{i,i+1}) = \epsilon K_T \sin^3 \theta_i \sin^3 \theta_{i+1} \sum_{n=0}^3 a_n \cos^n \phi_{i,i+1}, \quad (4)$$

where $\phi_{i,i+1}$ is the dihedral angle between the two planes defined by the sets of monomers $(i - 1, i, i + 1)$ and $(i, i + 1, i + 2)$. Following Refs. [26, 34], we use the values $a_0 = 3.00$, $a_1 = -5.90$, $a_2 = 2.06$, and $a_3 = 10.95$. In all the investigated systems the A-chains are fully-flexible, i.e., $K_B = K_T = 0$. We investigate two models (I and II) for the B-chains. In the model I all the B-chains are fully-flexible. In the model II all the B-chains are semiflexible, with $K_B = 15$ and $K_T = 0.5$.

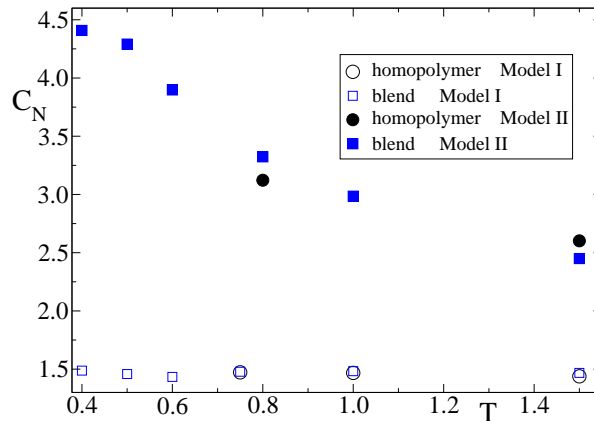


Figure 1. Temperature dependence of the characteristic ratio of the fully-flexible and semiflexible B-chains, both in the homopolymer and in the blend.

In the following, temperature T , time t and distance are given respectively in units of ϵ/k_B (with k_B the Boltzmann constant), $\sigma_{BB}(m/\epsilon)^{1/2}$ and σ_{BB} . The blend composition is $x_B = N_B/(N_A + N_B)$, with N_α the total number of α -monomers in the system. All simulations are performed at fixed composition $x_B = 0.3$. Most of the simulated systems have 105 A-chains and 45 B-chains. At the lowest investigated temperatures we have used smaller systems of 49 A-chains and 21 B-chains. We have performed additional simulations for B-homopolymers of $N = 21$, with a system size ranging from 200 to 500 chains according to the simulated temperature. All the simulated systems have a packing fraction $\phi = [\pi/(6V)](N_A\sigma_{AA}^3 + N_B\sigma_{BB}^3) = 0.53$, with V the volume of the cubic simulation box. We implement periodic boundary conditions. Equations of motion are integrated in the velocity Verlet scheme [35], with a time step ranging from 10^{-4} to 4×10^{-3} according to the simulated temperature. After equilibration at each state point, the corresponding production run is performed in the microcanonical ensemble. The longest production runs are of about 400 million time steps. Averages are performed over up to four independent boxes, with 20 equispaced time origins per simulated box.

3. Results and discussion

3.1. Chain size and mean squared displacements

The selected values of the bending and torsion constants (K_B, K_T) considerably stretch the semiflexible B-chains in comparison with the fully-flexible case. This can be quantified by the characteristic ratio, $C_N = \langle R_e^2 \rangle / (N \langle b^2 \rangle)$, where $\langle R_e^2 \rangle$ and $\langle b^2 \rangle$ are respectively the average squared end-to-end radius and bond length of the B-chains. Figure 1 shows results of C_N for the fully-flexible and semiflexible B-chains. The fully-flexible B-chains exhibit an almost T -independent value $C_N \lesssim 1.5$, both in the homopolymer and in the blend. On the contrary, for the semiflexible B-chains decreasing temperature yields effectively higher intramolecular barriers. Thus, the chains become

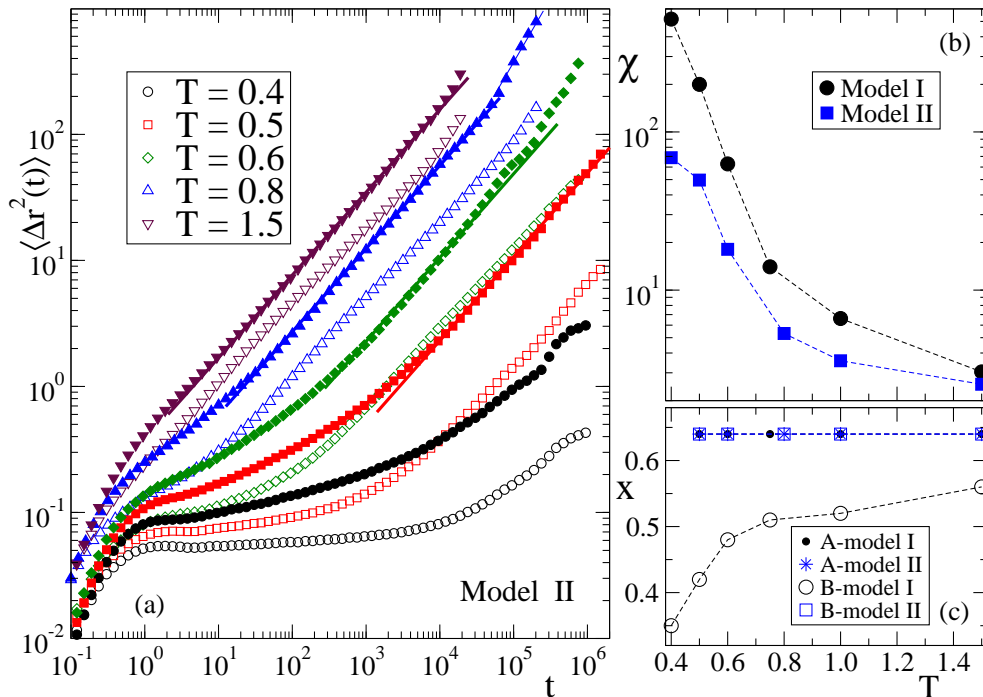


Figure 2. Panel (a): MSD in the model II at the different investigated temperatures. Empty and filled symbols correspond respectively to A- and B-monomers. Data sets with the same symbol code correspond to the same temperature. Thick straight lines indicate fits to power law behaviour $\langle \Delta r^2(t) \rangle \sim t^x$, with $x = 0.64$, over broad time windows. The thin line corresponds to the diffusive limit $\langle \Delta r^2(t) \rangle \sim t$. Panel (b): temperature dependence of the dynamic asymmetry (see text) for both models I and II. Panel (c): temperature dependence of the exponent x of the observed power law in the MSD (see above), for both models I and II.

stiffer, and C_N shows a strong increase on decreasing temperature. In the blend we find a variation of an 80 %, from $C_N = 2.45$ to $C_N = 4.40$, over the investigated T -range.

Figure 2a shows results for the mean squared displacement (MSD) of both species A and B in the model II, at all the investigated temperatures. After the initial ballistic regime, a plateau arises for both components at $T < 1.5$, and extends over longer time scales on decreasing temperature. This reflects the usual caging regime observed in glass-forming systems when approaching a glass transition. In analogy with previous observations for the model I [8, 9], there is a progressive separation, on decreasing T , of the time scales of the A- and B-monomers. We quantify the dynamic asymmetry in the blend as the ratio $\chi = \tau_A/\tau_B$, where τ_α is the time at which the MSD reaches the value $\langle \Delta r_\alpha^2(\tau_\alpha) \rangle = 0.45$. This roughly corresponds to the time scale of the structural α -relaxation (segmental relaxation). Figure 2b shows the T -dependence of the dynamic asymmetry, both for models I and II. In both cases the dynamic asymmetry becomes stronger on decreasing T . However, this effect is less pronounced in the model II, which shows a lower χ than the model I at the same temperature, blend composition and packing fraction. This is not surprising since the only difference between both models

is the strength of the intramolecular barriers in the B-chains. Thus, dynamics of the B-monomers in the semiflexible homopolymer are strongly slowed down respect to the fully-flexible case [29, 34, 36, 37], and blending with the same A-homopolymer leads to a weaker dynamic asymmetry in the model II.

For times longer than τ_α , the MSD of both species exhibits subdiffusive behaviour over several time decades, prior to the final crossover to diffusive behaviour at much longer times. The subdiffusive regime can be described by an effective power law $\langle \Delta r^2(t) \rangle \sim t^x$, with $x < 1$. This is a consequence of chain connectivity and a characteristic feature of polymer systems. In the case of fully-flexible homopolymers it reflects Rouse dynamics. Figure 2c shows the temperature dependence of the x -exponents for the two species in both models I and II. Within statistics, the (fully-flexible) A-chains show the same temperature independent exponent, $x \approx 0.64$, in both models. This is also the value observed for the fully-flexible A- and B-homopolymers (not shown), and can be easily understood in terms of Rouse dynamics. The value $x \approx 0.64$ is higher than the Rouse exponent $x = 0.5$, which is the effective value predicted by the Rouse model in the limit $N \rightarrow \infty$ [11]. Thus, the former difference is mostly due to the finite size, $N = 21$, of the chains [13]. We obtain a similar, almost T -independent, exponent $x \sim 0.64$ for the semiflexible B-homopolymer. This coincidence is probably fortuitous, since the x -value for the semiflexible homopolymer cannot be assigned to Rouse dynamics, which does not incorporate semiflexibility.

Concerning the exponents for the B-chains *in the blend* they exhibit a rather different behaviour in the models I and II (see Figure 2c). In the model I, the exponent x decreases monotonically, taking values much smaller than the T -independent value $x = 0.64$ found for the fully-flexible B-homopolymer.

This trend reflects the breakdown of the Rouse model for the fully-flexible B-chains in the blend, as discussed in [10]. This breakdown is also reflected in the anomalous scaling observed for the relaxation times of the Rouse modes on decreasing T (see below). The lowest investigated temperature in the model II at which x can be solved is $T = 0.5$. The dynamic asymmetry at this T is the same that in the model I at $T \gtrsim 0.6$, for which x has decreased by about a 15% from its value at $T = 1.5$. On the contrary, in the model II it remains, within statistics, constant with a value $x \sim 0.64$, as observed for the semiflexible B-homopolymer (see above).

3.2. Rouse modes

The latter observations suggest that, unlike for fully-flexible polymers, scaling properties for chain dynamics in semiflexible polymers may be unaltered by blending. We confirm this point by analyzing the relaxation of the internal chain degrees of freedom. This can be quantified by computing the correlators of the Rouse modes. The latter are defined as [11]

$$\mathbf{X}_p(t) = N^{-1} \sum_{j=1}^N \mathbf{r}_j(t) \cos[(j - 1/2)p\pi/N], \quad (5)$$

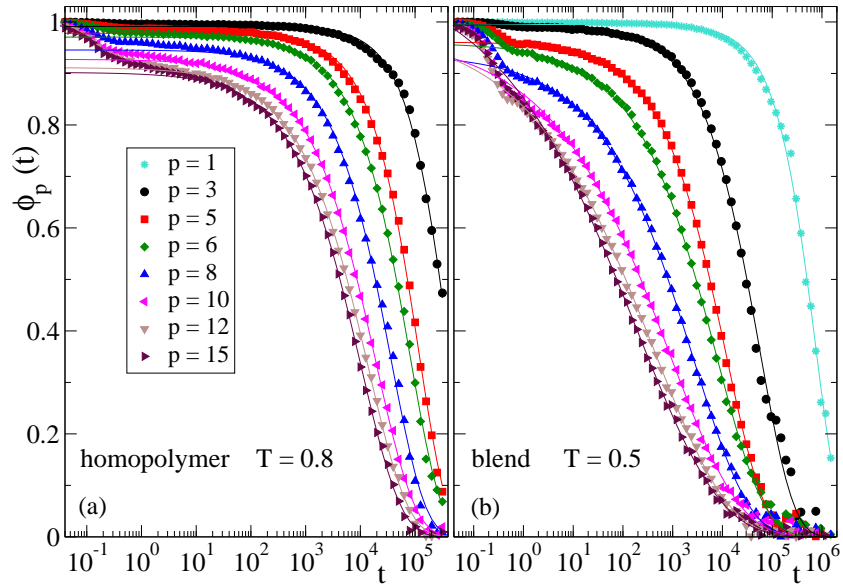


Figure 3. Symbols: Rouse correlators for semiflexible B-chains in the homopolymer state (a) and in the blend (b), at respectively $T = 0.8$ and $T = 0.5$. Lines are fits to stretched exponentials (see text).

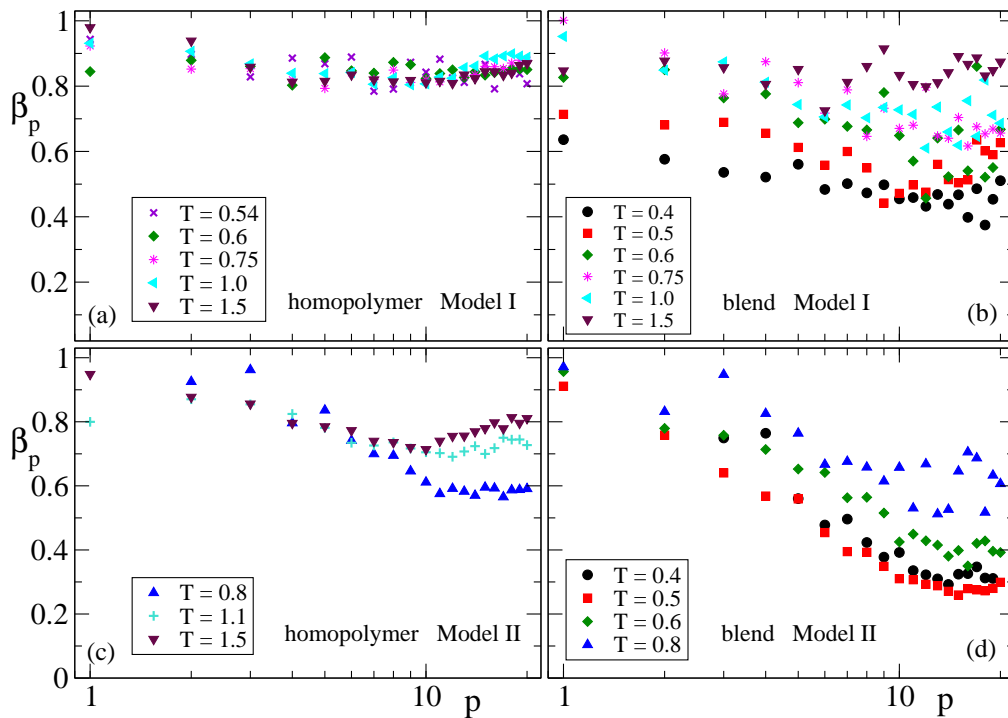


Figure 4. T - and p -dependence of the stretching exponents of the Rouse correlators for the B-chains (see text). The data in the left panels correspond to the fully-flexible (a) and semiflexible (c) B-homopolymer. The data in the right panels correspond to B-chains in the blend, for the models I (b) and II (d). The p -axis is represented in logarithmic scale for comparison with Figures 5 and 6.

where \mathbf{r}_j denotes the position of the j th-monomer of the tagged chain, and $0 \leq p \leq N-1$ is the mode index. The wavelength of each p -mode is given by N/p . Therefore, smaller p -values probe relaxation at larger length scales. The normalized Rouse correlators are defined as $\Phi_p(t) = \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle / \langle X_p^2(0) \rangle$. According to the Rouse model [11], the correlators decay exponentially $\Phi_p(t) = \exp(-t/\tau_p)$, and the relaxation times scale as $\tau_p \sim (N/p)^2$. This is also the scaling behaviour of the static amplitudes of the modes, $\langle X_p^2(0) \rangle \sim (N/p)^2$, which follows from the assumed gaussian model for the static intrachain correlations [11]. In summary, according to the Rouse model $\tau_p \sim \langle X_p^2(0) \rangle \sim (N/p)^2$.

Figure 3 shows results of $\Phi_p(t)$ for semiflexible B-chains in the homopolymer state and in the blend (model II) at two selected low temperatures. The first decay, at short times, to the plateau reflects the onset of the caging regime already observed in the MSD. The second decay at long times reflects the relaxation of the corresponding p -mode. We analyze the latter by fitting the decay to a stretched exponential or Kohlrausch-Williams-Watts (KWW) function $\Phi_p(t) = A_p \exp[-(t/\tau_p)^{\beta_p}]$, with $A_p, \beta_p < 1$. The KWW time τ_p provides an estimation of the relaxation time of the p -mode. Figure 4 shows, at several temperatures, the stretching exponents β_p for the fully-flexible and semiflexible B-chains, both in the homopolymer and in the blend. The general trend displayed by the four panels is that stretching is enhanced both by the presence of intramolecular barriers and by blending. The data for the fully-flexible B-homopolymer (Figure 4a) are roughly T -independent and take values close to Rouse-like exponential behaviour $\beta_p = 1$ (see above). This is in agreement with observations in similar fully-flexible models [13]. A rather different behaviour is observed for the fully-flexible B-chains in the blend (Figure 4b). Exponential behaviour is only approached at high temperatures, in the limit of vanishing dynamic asymmetry. On decreasing temperature and increasing the dynamic asymmetry, the correlators exhibit stronger stretching, reaching values of even $\beta_p \sim 0.4$.

In principle, the observed 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, at least formally, expressed as a sum of pure exponential functions weighted by an adequate distribution G , though the latter does not necessarily have a physical meaning. Hence, we express the KWW function for the p th-mode as $\int d\tau_p^0 G(\tau_p^0) \exp[-t/\tau_p^0]$, where the distributed values τ_p^0 are the relaxation times of the different exponential Rouse modes. According to the Rouse model, these follow the p -scaling $\tau_p^0 = \xi \langle X_p^2(0) \rangle$, where the prefactor ξ is proportional to the p -independent friction constant [11]. Thus, if the observed stretching in the Rouse correlators essentially arises from a distribution of exponential Rouse-like processes, this reflects a distribution of friction terms $g(\xi)$. By simple mathematical transformation it is found [10] that the KWW time τ_p must follow the same scaling behaviour as the distributed Rouse times τ_p^0 , i.e., $\tau_p \sim \langle X_p^2(0) \rangle$. Therefore, if this condition is fulfilled, stretching essentially arises from a distribution of exponential Rouse-like processes. Otherwise, though distribution effects can also be present, strong deviations from the

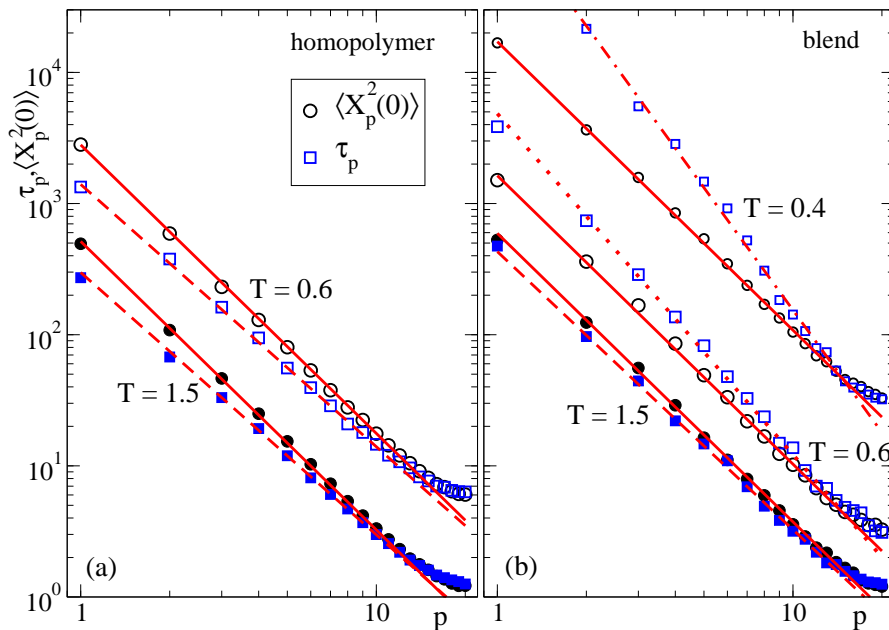


Figure 5. Squares and circles are respectively the relaxation times τ_p and the static amplitudes $\langle X_p^2(0) \rangle$ of the Rouse correlators for the fully-flexible B-chains. Panel (a): data for the fully-flexible B-homopolymer at $T = 0.6$ (empty symbols) and $T = 1.5$ (filled symbols). Panel (b): data for the fully-flexible B-chains in the blend, at $T = 0.4$ (small empty symbols), $T = 0.6$ (big empty symbols) and $T = 1.5$ (filled symbols). Units in the vertical axis are arbitrary. Each data set has been rescaled by a factor to facilitate comparison of τ_p and $\langle X_p^2(0) \rangle$ at common T . Solid lines in both panels are power laws with $x = 2.2$. Dashed lines are power laws with $x = 2.0$ in panel (a) and $x = 2.1$ in panel (b). The dotted ($T = 0.6$) and dashed-dotted ($T = 0.4$) lines in panel (b) are power laws with respectively $x = 2.7$ and $x = 3.3$.

scaling $\tau_p \sim \langle X_p^2(0) \rangle$ are the signature of a strong intrinsic non-exponential character of the mode relaxation [38].

Figure 5 shows results for the p -dependence of τ_p for the fully-flexible B-chains in the homopolymer and in the blend (Model I). The selected temperatures cover all the investigated range. We also include the amplitudes of the modes $\langle X_p^2(0) \rangle$, and rescale the data sets by arbitrary factors to facilitate comparison between dynamic and static quantities at the different temperatures. In agreement with similar fully-flexible models [13], relaxation times for the homopolymer are consistent with Rouse scaling, $\tau_p \sim p^{-2}$, and therefore the Rouse modes are essentially exponential. The observed dynamic Rouse scaling is consistent with the static scaling displayed by the amplitudes of the modes, $\langle X_p^2(0) \rangle \sim p^{-2.2}$, again in agreement with previous works [13] and very close to the ideal gaussian behaviour $\langle X_p^2(0) \rangle \sim p^{-2}$ expected within the Rouse model [11]. Thus, Rouse relaxation times and amplitudes for the homopolymer are roughly proportional, $\tau_p \sim \langle X_p^2(0) \rangle$.

The static scaling $\langle X_p^2(0) \rangle \sim p^{-2.2}$ observed in the fully-flexible B-homopolymer is not altered by blending at any investigated temperature (Figure 5b). On the contrary,

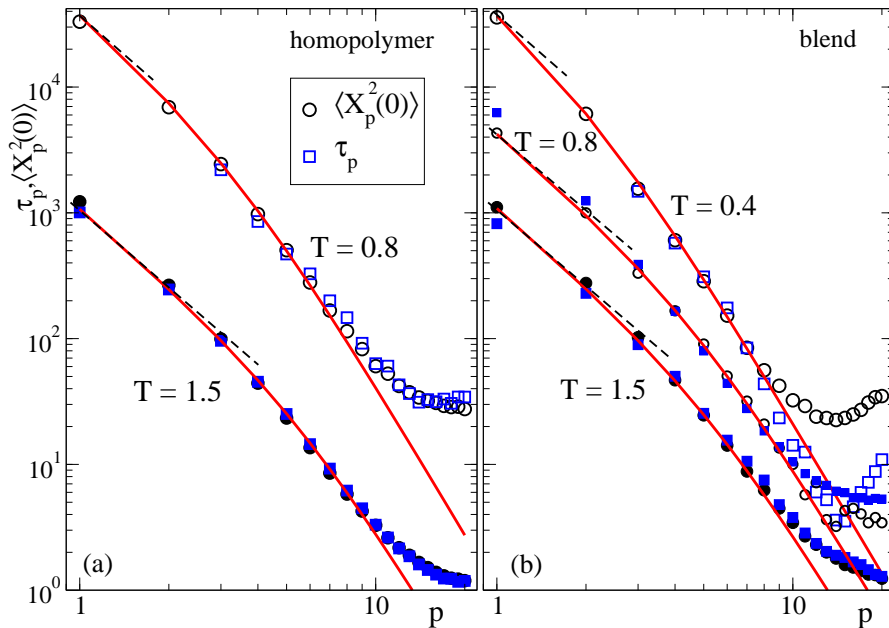


Figure 6. Squares and circles are respectively the relaxation times τ_p and the static amplitudes $\langle X_p^2(0) \rangle$ of the Rouse correlators for the semiflexible B-chains. Panel (a): data for the semiflexible B-homopolymer at $T = 0.8$ (empty symbols) and $T = 1.5$ (filled symbols). Panel (b): data for the semiflexible B-chains in the blend, at $T = 0.4$ (big empty symbols), $T = 0.8$ (small empty symbols) and $T = 1.5$ (filled symbols). Units in the vertical axis are arbitrary. Each data set has been rescaled by a factor to facilitate comparison of τ_p and $\langle X_p^2(0) \rangle$ at common T . Solid lines in both panels are fits to the Equation (6). Dashed lines represent Rouse-like behaviour $\tau_p, \langle X_p^2(0) \rangle \sim p^{-2}$.

dynamic Rouse scaling is observed in the blend only at high temperature. On decreasing temperature and increasing the dynamic asymmetry, a progressive deviation from the relation $\tau_p \sim \langle X_p^2(0) \rangle$ is observed. We describe the behaviour of the relaxation times by an effective power law $\tau_p \sim p^{-x}$, with x increasing on decreasing temperature, up to $x = 3.3$ for $T = 0.4$. Thus, dynamic asymmetry in the blend leads to an intrinsic strongly non-exponential character of the Rouse modes for the fully-flexible B-chains. Intrinsic non-exponentiality and the observed anomalous scaling for the relaxation times are not related to particular static features of the modes, which indeed are not affected by blending. The origin of the stretching of the Rouse correlators for the semiflexible B-chains [see panels (c) and (d) of Figure 4] will be discussed below.

Figure 6 shows results of τ_p and $\langle X_p^2(0) \rangle$ for the semiflexible B-chains in the homopolymer and in the blend (Model II), at temperatures covering all the investigated range. In analogy with the representation of Figure 5, we rescale the different data sets to facilitate comparison between times and amplitudes. This procedure yields a nice overlap of the latter for the B-homopolymer, and as in the fully-flexible case, the data follow the approximate relation $\tau_p \sim \langle X_p^2(0) \rangle$. This is also the case for the semiflexible B-chains in the blend at high T . The relation $\tau_p \sim \langle X_p^2(0) \rangle$ is also maintained at the lowest $T = 0.4$ except for modes $p > 9$, corresponding to small wavelengths $N/p \lesssim 2.3$.

However, it is noteworthy that the static data of Figure 6 follow a rather different p -dependence from the gaussian behaviour $\langle X_p^2(0) \rangle \sim p^{-2}$, which is only approached in the limit $p \rightarrow 1$ at high T . This confirms the non-gaussian character of the semiflexible chains within all their length scale (see Introduction). Obviously, also the p -dependence of the times is very different from the scaling $\tau_p \sim p^{-2}$ predicted by the Rouse model.

We discuss the behaviour of τ_p and $\langle X_p^2(0) \rangle$ in terms of the framework proposed by Harnau and co-workers [31, 39, 40]. In this approach, the equations of motion for the tagged chain are derived from the Hamiltonian of the worm-like chain model [41]. This leads to modified Rouse equations of motion, which include intrachain bending forces not present in the original Rouse model for fully-flexible chains. As in the original Rouse model, chain dynamics is encoded in the intramolecular interactions, and the interactions of the tagged chain with the surroundings are again modelled in terms of a friction term and random forces [31, 39, 40]. Solution of the equations of motion leads to a modified p -dependence of the amplitudes and relaxation times of the Rouse modes, but as in the original Rouse model, $\langle X_p^2(0) \rangle$ and τ_p are proportional. The obtained relation is

$$\tau_p \sim \langle X_p^2(0) \rangle \sim \left[p^2 + \frac{\pi^2 l^2}{N^2 \langle b \rangle^2 p^4} \right]^{-1}, \quad (6)$$

where l is the persistence length of the chain. Recent simulation results by Steinhäuser and co-workers [27, 28] on semiflexible homopolymers are in good agreement with Equation (6). On this basis, we use it for describing the data sets of Figure 6. Instead of using different definitions of the persistence length proposed in the literature (see e.g., Ref. [42]) as input, we just obtain l as a fit parameter. At each temperature, this is forced to be identical for $\langle X_p^2(0) \rangle$ and τ_p , to be consistent with the relation $\tau_p \sim \langle X_p^2(0) \rangle$. The obtained values of the persistence length change from $l \sim 1.2$ at high temperatures to $l \sim 3$ at the lowest investigated T in the blend. Equation (6) provides a good description of the data of Figure 6 in the region $p < 9$, both for the B-homopolymer and for the B-chains in the blend. The behaviour at smaller wavelengths cannot be captured. Presumably this is mostly due to the influence of the torsional terms. The latter are not accounted for within the approach of Refs. [31, 39, 40] based on the worm-like model for the intramolecular interactions, which only includes bending terms.

4. Discussion

As shown in the previous section, the results presented in Figures 5 and 6 for the B-homopolymers are consistent with the approximate relation $\tau_p \sim \langle X_p^2(0) \rangle$, the specific p -dependence being distinct for fully-flexible and semiflexible chains. The latter is Rouse-like for fully-flexible chains, $\tau_p \sim p^{-2}$, and is well described by Equation (6) for semiflexible chains. Since the relation $\tau_p \sim \langle X_p^2(0) \rangle$ is fulfilled, the anomalous (in the meaning of non-Rouse) scaling of the relaxation times for the semiflexible homopolymers is essentially of static origin. More specifically, it is a direct consequence of the non-gaussian nature of the static intramolecular correlations. This is also the case for the

semiflexible B-chains in the blend (Model II), for which $\tau_p \sim \langle X_p^2(0) \rangle$ is maintained, except for short wavelengths ($N/p \lesssim 2.3$, see Figure 6b) at low temperatures.

According to the approach of Refs. [31, 39, 40] for semiflexible chains, the Rouse correlators $\Phi_p(t)$ decay, as in the Rouse model, exponentially. Following the same argumentation as for the fully-flexible case (see Section 3), stretching in $\Phi_p(t)$ arises from a distribution of the predicted exponential processes if the KWW times fulfill the relation $\tau_p \sim \langle X_p^2(0) \rangle$. Otherwise non-exponentiality is intrinsic. Thus, from data in Figure 6, we conclude that non-exponentiality of the Rouse modes of the semiflexible chains is intrinsic only for short wavelengths, in the blend state and at low temperature.

As shown by the data in Figure 2b, the dynamic asymmetry ($\chi \approx 68$) at the lowest investigated $T = 0.4$ of the Model II, is slightly higher than that of the Model I at $T = 0.6$ ($\chi \approx 63$). Though the strength of the confinement is essentially the same in both cases, the origin of anomalous chain dynamics seems to be very different. As discussed above, this is of intramolecular and static nature for the semiflexible B-chains of Model II. On the contrary, the origin is essentially dynamic for the fully-flexible B-chains of Model I, as indicated by the clear breakdown of the relation $\tau_p \sim \langle X_p^2(0) \rangle$. As shown in Figure 5b, we find strongly non-Rouse scaling for the times, $\tau_p \sim p^{-x}$ with $x = 2.7$, considerably *larger* than the exponent $x = 2.2$, close to gaussian behaviour, found for the amplitudes. Note that for the homopolymer we find a, Rouse-like, dynamic exponent $x = 2.0$ similar but *smaller* than the static $x = 2.2$ (Figure 5a).

As mentioned in the Introduction, within the Rouse model memory effects, related to slow density fluctuations of the matrix around the tagged chain, are neglected. The interactions of the tagged (gaussian) chain with the surroundings are simply modelled by a friction term and random forces [11]. This Markovian approximation is also followed by the approach of Harnau and co-workers [31, 39, 40], which just incorporates bending forces in the Rouse equations of motion to account for chain stiffness. The predicted scaling behaviour [Equation (6)] is observed for the semiflexible B-homopolymer and is not significantly affected by blending with a slower matrix, suggesting that memory effects are not relevant and the Markovian approximation can still be applied in the blend. As discussed above, the observed stretching of the Rouse correlators for the semiflexible B-chains in the blend essentially reflects a distribution of elementary exponential processes. It remains to be understood, from a microscopic basis, why memory effects induced by the matrix are apparently much weaker than intramolecular effects induced by the presence of the barriers. On the contrary, memory effects are crucial in the case of the fully-flexible B-chains in the blend [10], for which predictions of the Rouse model are strongly violated, and non-exponentiality is intrinsic.

Finally, we want to make a last remark on the dynamics of the semiflexible chains in the blend. As discussed above, the semiflexible chains considered here are strongly non-gaussian within all chain length scales. If longer chains were considered, with the same torsional and bending contributions, the semiflexible character would be lost beyond some mode wavelength, and gaussian statistics would be recovered for intrachain static correlations at large length scales. We expect that in such length scales, as observed

for the fast fully-flexible chains in blends with strong dynamic asymmetry, anomalous dynamic scaling will arise for the Rouse modes, distinct from the static gaussian scaling, and memory effects will be relevant. In fact this seems to be the case for the results reported in Ref. [7] from atomistic simulations of the dynamically asymmetric blend PEO/PMMA. There the relaxation times τ_p of the Rouse mode correlators of the fast component (PEO) still exhibit anomalous, non-Rouse, p -scaling at large mode wavelenghts N/p for which gaussian behaviour, $\langle X_p^2(0) \rangle \sim (N/p)^2$, is recovered in the mode amplitudes (see Figure 11 in Ref. [7]). This would be the general expected behaviour in real blends with strong dynamic asymmetry.

5. Conclusions

We have performed simulations of a simple bead-spring model of non-entangled semiflexible chains blended with a slower component. Chain stiffness is introduced by implementing intramolecular barriers with bending and torsion terms. Extending previous investigations for fully-flexible chains, we investigate the effect of the dynamic asymmetry in the blend on the relaxation of the semiflexible chains. We find the same anomalous scaling behaviour for the relaxation times and the static amplitudes of the Rouse modes, in agreement with Markovian models which extend the Rouse equations by the introduction of bending forces. Thus, anomalous dynamic features for the semiflexible chains essentially have a static and intramolecular origin. This is very different from the case of fully-flexible chains in blends with similar dynamic asymmetry. For the latter anomalous dynamic scaling is strongly correlated with the dynamic asymmetry, and not to features of the static amplitudes, which indeed still follow gaussian scaling.

The former results suggest that memory effects induced by the surrounding slow matrix are not relevant for non-entangled semiflexible polymers, and Markovian models can still be applied. However, if the chains are long enough, we expect that the influence of the memory effects will be recovered at large length scales where intrachain static correlations recover gaussian statistics. Work in this direction is in progress.

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