

Heterogeneity of the Segmental Dynamics in Cylindrical and Spherical Phases of Diblock Copolymers

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We have performed simulations of a simple bead-spring model for cylindrical and spherical phases of diblock copolymers. We have analyzed in detail the dynamic heterogeneity of the structural α -relaxation of the component confined in the minority domains. In analogy with previous investigations on the lamellar phase of the same bead-spring model, the analysis reveals moderate gradients of mobility in the investigated temperature range, which qualitatively probes time scales up to 100 ns. Thus α -relaxation times measured at different distances from the domain center spread over less than one decade. The spatial extension of the gradients of mobility is apparently consistent with that previously observed in the lamellar phase of the same model. Gradients of mobility do not seem to be related to gradients of density within the domains, which are indeed absent. We have performed an analysis of self- and effective concentrations, a concept usually invoked to explain the α -relaxation in polymer mixtures and that has been recently adapted to the analysis of experimental data of diblock copolymers in ordered phases. The simulation results reveal a strong disagreement with the proposed empirical relation between self- and effective concentration, as well as with the Flory-Fox mixing rule for the dynamics. This suggests that the use of these relations may bias the analysis of experimental data.

I. INTRODUCTION

Diblock copolymers formed by two thermodynamically immiscible components can exhibit microphase separation in domains rich in one component and poor in the other. These domains can be spatially arranged in ordered periodic structures, leading to phases with, e.g., lamellar, cylinder, spherical or gyroid morphologies [1–4]. The transition from the disordered to the ordered state and between the different ordered phases can be easily tuned by varying control parameters as the temperature, chain length, or monomer fraction of each component.

The local segmental dynamics in ordered phases of diblock copolymers, i.e, the α -structural relaxation associated to the glass transition of each block, has been characterized in several works [5–12]. A general observation is that the average α -relaxation times of each block are close to those of the corresponding homopolymer. However the dynamic response in the diblock ordered phase exhibits a strong broadening in the low-frequency side (long times) in comparison with that of the corresponding homopolymer [6, 8, 10, 11]. This feature is often rationalized in terms of dynamic heterogeneity. A picture of gradients of mobility is usually invoked in the analysis of experimental data. This picture assumes that the α -dynamics of a given component is strongly perturbed in the interfacial region due to, e.g., specific interactions with the other component or changes in the local density. This perturbation propagates over the domain up to a certain distance from the interface. Beyond such distance the block monomers recover the α -dynamics of the corresponding homopolymer.

In a recent publication [13] we presented a detailed computational investigation of the α -structural relaxation in the lamellar phase of a simple bead-spring model for diblock copolymers. This investigation aimed to characterize the heterogeneity of the α -dynamics as a function of the distance to the lamellar interface. The analysis of the data revealed that gradients of mobility were mostly an interfacial effect. Thus, the observed gradients of mobility extended over a limited range of a few nanometers ($\lesssim 4$ nm) from the interface and beyond such distance the α -dynamics of the corresponding homopolymer was recovered [13].

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In this article we extend our previous investigation in the lamellar phase of the mentioned bead-spring model to the case of strongly segregated cylindrical and spherical phases. As in our previous work, the analysis of dynamic heterogeneities reveal moderate gradients of mobility, of about one time decade, in the investigated temperature range, which qualitatively probes relaxation time scales of up to hundreds nanoseconds. The spatial extension of the gradients of mobility is apparently consistent with that previously observed in the lamellar phase. Gradients of mobility do not seem to be related to gradients of density within the domains, which are indeed absent. This feature is also consistent with observations in the lamellar phase.

An additional result of this article is the characterization of the self- and effective concentrations at the copolymer interface. The self- and effective concentrations are concepts usually invoked to explain the α -relaxation of polymer mixtures [14–18]. In a recent work [19] Lund *et al.* investigated, by means of broadband dielectric spectroscopy, the α -relaxation of poly(isoprene) in the minority domains of the cylindrical mesophase of a poly(isoprene)/poly(dimethylsiloxane) block copolymer system. They proposed a modification of the original Lodge-McLeish relation between the self- and effective concentration [15], in order to characterize the interphase of ordered diblock copolymers. A Helfand-Tagami function [20–22] for the local density profile in the cylindrical domain was assumed, leaving the domain radius and interfacial width as *fit parameters*. These ingredients were used in combination with the Flory-Fox mixing rule for the dynamics [23], and a good description of the experimental spectra was achieved. Here we test both the modified Lodge-McLeish and Flory-Fox relations proposed in Ref. [19], by using the effective and self-concentrations directly computed from the simulations. We find a strong disagreement between the simulation results and the former relations, suggesting that their use might bias the experimental analysis of the dynamics in block copolymers. We show that indeed the dynamic correlators obtained from the simulations can be described by invoking all the assumptions made in the experimental analysis. However the analysis provides an estimation of the local density profiles (through the fit parameters mentioned above) that strongly differs from the real profiles directly obtained from the simulations.

The article is organized as follows. In Section II we describe the investigated model and give simulation details. In Sections III and IV we characterize density profiles and gradients of mobility respectively. In Section V we characterize effective and self-concentrations.

Conclusions are given in Section VI.

II. MODEL AND SIMULATION DETAILS

The diblock chains are modelled as strings of n connected beads, each block containing beads of a single species F ('fast') or S ('slow'). In the following the different simulated systems will be denoted as $Fn_F Sn_S$ (if $n_F < n_S$) or $Sn_S Fn_F$ (if $n_S < n_F$), where n_F and n_S are respectively the number of F- and S-beads per chain, and $n_F + n_S = n$. Each simulated system consists of N_{cha} identical chains. We use $N_{\text{cha}} = 1008$ and 1782 for the cylindrical and spherical mesophase respectively. We have simulated complementary systems of compositions $FxSy$ and $SxFy$, i.e, with exchanged identities of the core and matrix monomers. Thus we have simulated the systems F13S37 and S13F37 for the cylindrical case and the systems F7S47 and S7F47 for the spherical case.

The interaction between any two given monomers of the species $\alpha, \beta \in \{F, S\}$ is given by a shifted Lennard-Jones potential:

$$V_{\alpha\beta}^{\text{LJ}}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 + \frac{1}{4} \right], \quad (1)$$

for $r < r_c$ and $V_{\alpha\beta}^{\text{LJ}}(r) = 0$ for $r \geq r_c$. By using a cut-off distance $r_c = 2^{1/6}\sigma_{\alpha\beta}$, the potential is purely repulsive and has no local minima. Moreover potential and forces are continuous at r_c . If the two monomers are bonded to each other, they also interact through an additional finitely extensible nonlinear elastic potential (FENE) [24]:

$$V_{\alpha\beta}^{\text{FENE}}(r) = -\epsilon_{\alpha\beta} K_F R_0^2 \ln \left[1 - \left(\frac{r}{R_0 \sigma_{\alpha\beta}} \right)^2 \right], \quad (2)$$

with $K_F = 15$ and $R_0 = 1.5$. The sum of the potentials (1) and (2) gives an effective potential between connected monomers with a deep minimum at $r = 0.96\sigma_{\alpha\beta}$, which guarantees chain uncrossability [24]. We use identical monomer masses $m_F = m_S = m = 1$ and interaction diameters $\sigma_{FF} = \sigma_{SS} = \sigma_{FS} = \sigma = 1$. In order to obtain different mobilities for the two species, we use different values for the energy scale of the self-interaction, $\epsilon_{FF} = 0.35$ and $\epsilon_{SS} = 1$, which leads to faster dynamics for the F-component (see below). For the cross-interaction we use $\epsilon_{FS} = 9$. With this strong energetic penalty for the F-S interactions and the used compositions, the minority component of the systems F13S37 and S13F37 is

expected to form an hexagonal lattice of cylindrical domains. For the systems F7S47 and S7F47 a bcc lattice of spherical domains is expected.

The structural and dynamic properties of the simulated mesophases have been investigated as a function of temperature. The results for the minority component have been compared with those of homopolymer systems with the same chain length as the minority blocks. Accordingly, the simulated homopolymer systems are denoted as αx , with $\alpha \in \{\text{F}, \text{S}\}$ and $x \in \{7, 13\}$. We have simulated homopolymer systems of $N_{\text{cha}} = 1000$ and 500 chains for chain lengths of $x = 7$ and 13 respectively. In the following temperature T , pressure P , monomer number density ρ , time t , and distance will be given respectively in units of ϵ_{SS}/k_B (with k_B the Boltzmann constant), $\epsilon_{\text{SS}}\sigma^{-3}$, σ^{-3} , $\sigma(m/\epsilon_{\text{SS}})^{1/2}$, and σ . Simulation units can be qualitatively mapped to real units as 5-10 Å for distance and 1-10 ps for time (see the discussion in, e.g., Refs. [24, 25]). With these conversion factors our simulations cover a time scale of the order of 100 nanoseconds, and domain sizes of the order of tenths of nanometers (see below).

Periodic boundary conditions are applied to the simulation cell, which is cubic for the homopolymer systems as well as for the spherical phases. An orthoedric cell is used for the cylindrical phases (see below). A linked-cell method is implemented for reducing computational expense in the calculation of interparticle distances [26]. Equilibration runs are performed in the isothermal-isobaric (NPT) ensemble at external pressure $P_{\text{ex}} = 3.0$, by using the Nosé-Hoover algorithm [26]. A further equilibration run is performed at constant volume under periodic velocity scaling according to the target temperature. Finally, a run is performed in the microcanonical ensemble for production of configurations, from which we compute the static and dynamic observables presented below. Equations of motion are integrated in the Martyna's scheme [26, 27] for the NPT runs and in the velocity-Verlet scheme [26] for the other runs. We use typical integration time steps of $4 \times 10^{-3} \geq \delta t \geq \times 10^{-3}$ according to the investigated temperature, which covers the range $0.14 \leq T \leq 0.30$. The corresponding equilibrium densities cover the range $1.06 \geq \rho \geq 0.98$ and $1.00 \geq \rho \geq 0.92$ for respectively the F- and S-homopolymer. These are typical melt densities for similar bead-spring models of polymer systems [24].

Except for the case of very short chains and temperatures far above T_g , the spontaneous formation at melt densities of mesophases with well-defined order is unfeasible in simulations due the extremely long characteristic time scales for chain diffusion [28–31]. Instead, we

follow the usual procedure of generating the system in the ordered state before starting the equilibration run [29, 32–34]. For the cylindrical case we construct a 2d hexagonal lattice with $n = 12$ sites. For each site we define a cylinder, of diameter σ , perpendicular to the lattice. We graft N_{cha}/n diblock chains to the surface of each cylinder, with the end monomers of the minority blocks directly attached to the surface. The chains are generated by random growth up, with a constraint avoiding core overlap of new inserted monomers with those previously inserted. This is facilitated by constructing the system at a low density $\rho \sim 0.5$. We use an orthoedric simulation cell, of side lengths L_x , L_y and L_z . The z -axis is parallel to the cylinder axes. According to the hexagonal symmetry of the lattice, we fix the ratio $L_y/L_x = 2/\sqrt{3}$.

The generated system is taken as the initial configuration for the equilibration *NPT* run. Though the imposed external pressure $P_{\text{ex}} = 3.0$ leads the system to melt densities $\rho \sim 1$, the applied isotropic cell fluctuations cannot provide the correct interdomain spacing. Indeed they do not produce by themselves the required balance of the x , y and z -components of the virial pressure. For this we follow the method proposed by Schultz and co-workers [32] and perform an *NPT* run combining the standard isotropic fluctuations with periodic anisotropic rescaling. The volume of the cell is maintained at each anisotropic rescaling. Thus, the z -coordinate is rescaled by a factor $f = 1 \pm \xi$, with ξ some small positive number ($0 < \xi \ll 1$), and simultaneously the x, y -coordinates are rescaled by a common factor $f^{-1/2}$. We use $f = 1 + \xi$ when $\langle P_{x,y} \rangle' < \langle P_z \rangle'$ and $f = 1 - \xi$ when $\langle P_{x,y} \rangle' > \langle P_z \rangle'$. Here $\langle \dots \rangle'$ denotes average over a certain interval prior to a rescaling event. We initially use $\xi = 0.01$ and progressively decrease its value as the pressure balance $\langle P_x \rangle = \langle P_y \rangle = \langle P_z \rangle = P_{\text{ex}}$ is approached.

In the spherical mesophases and in the homopolymers the three spatial directions are equivalent, and a standard *NPT* run (isotropic fluctuations) is performed. We generate the spherical mesophases in a similar manner as in the cylindrical case, by grafting the diblocks to spherical surfaces centered around the sites of a bcc lattice. The simulation cell contains $n_s = 2 \times 3^3 = 54$ lattice sites, with 33 chains associated to each site. It must be noted that by construction the cylindrical and spherical domains are initially monodisperse in the aggregation number $n_{\text{agg}} = N_{\text{cha}}/n_s$. We monitor the values of n_{agg} for the different domains [35] during the simulation. The monodispersity is maintained at low and intermediate temperatures in the time scale of the simulation. Only at the highest investigated temperatures

rare hopping events to neighboring domains have been observed (just one or two events in the whole simulation), i.e., the domains also remain essentially monodisperse. Thus, the statistical averages for the structural and dynamic properties presented in next sections are free of polydispersity effects, facilitating their physical interpretation.

It must be noted that the mesophases obtained after the ‘equilibration’ run are not expected to be the actual equilibrium ones, but metastable states in the simulation time scale. For instance, finite size effects induced by the periodic boundary conditions will likely modify the equilibrium domain spacing —despite having simulated large cells the used number of domains is small. Using larger cells would reduce such effects, but still would not solve an implicit drawback of the spherical mesophase. Namely, unless it coincides fortuitously, the used aggregation number $n_{\text{agg}} = 33$ for the spherical domains will not be the actual equilibrium one. Though we have also imposed specific values for the ‘aggregation numbers’ N_{cha}/n_s to the cylindrical domains, these have no major meaning because they become infinite by applying periodic boundary conditions along the cylinder axis. Thus, the constructed cylindrical system can approach the equilibrium domain size through (anisotropic) scaling of the cell. On the contrary the spherical system cannot approach it unless it starts from the correct aggregation number. A way to estimate this would be to construct cells with different values of n_{agg} , perform the equilibration runs as described above, and select the cell with the lowest energy. This would be computationally very demanding. Still, we believe that conclusions on the *qualitative* structural and dynamic features presented in next sections will not be modified by using the correct equilibrium aggregation number.

III. DENSITY PROFILES

As expected for the limit of strong segregation, the results displayed here and in the following for density profiles, effective and self-concentrations are almost temperature-independent. Therefore, for each phase the latter will be presented for a single temperature. Figs. 1 and 2 show two typical snapshots of the cylindrical and spherical phases, for the systems S13F37 and F7S47 respectively. We characterize local density profiles of the F- and S-components at both sides of the interface. For the cylindrical phases we quantify profiles in the direction normal to the cylinder axis. For this we introduce the quantity $\rho(r_{\perp}) = n(r_{\perp})/V(r_{\perp})$, with $n(r_{\perp})$ the number of monomers in a cylindrical shell of volume $V(r_{\perp})$, parallel to the cylin-

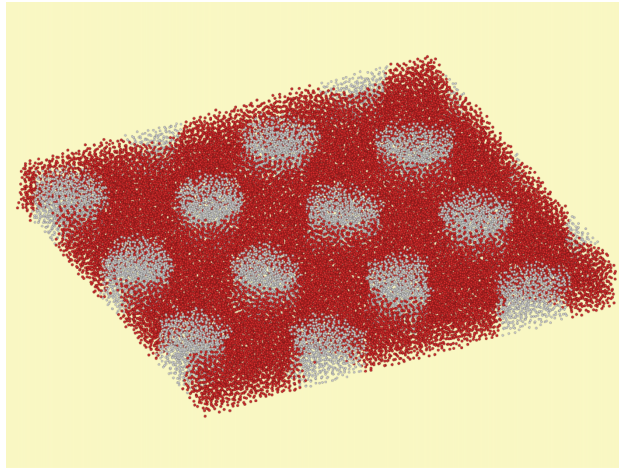


FIG. 1: Typical snapshot of the system S13F37 at $T = 0.15$. S- and F-beads are depicted in grey and red respectively. For the sake of clarity, the bead sizes are much smaller than the actual values of σ .

der axis and defined between the distances r_{\perp} and $r_{\perp} + \Delta$ normal to the axis. In a similar manner for the spherical phases we quantify radial profiles $\rho(r) = n(r)/V(r)$, with $n(r)$ the number of monomers in a spherical shell of volume $V(r)$, defined between the distances r and $r + \Delta$ from the center of the spherical domain. We use a bin size of $\Delta = 0.1\sigma$. Fig. 4 shows typical results ($T = 0.15$) of $\rho(r_{\perp})$ for F- and S-monomers in the cylindrical phase of the system F13S37. As expected for the strongly segregated regime, sharp boundaries are observed between the flat profiles characterizing the cylindrical domains and the matrix. By estimating the domain radius R_c as the crossing point between the profiles of both components, we find $R_c \sim 6\sigma$. The full-width of the interface, in which both profiles are significantly different from zero, is about 2σ . The bottom panel of Fig. 3 shows a detailed comparison of the local densities in the cylinders and matrix with the number densities ρ_{hom} of the respective homopolymers. Except for the interfacial region, this comparison reveals very small differences, below one per cent. Thus, the local densities in the inside of both the domains and the matrix are essentially identical to those of the homopolymer.

Fig. 4 displays similar results of $\rho(r)$ for the spherical phase of the system F7S47 at $T = 0.15$, and the corresponding comparison with the densities of the respective homopolymers. The domain radius is $R_c \sim 3.5\sigma$. As for the cylindrical case, the interface thickness is about 2σ . Again, very small differences are observed between the local densities in the inside of the domains and matrix and those of the respective homopolymers. This result found for both

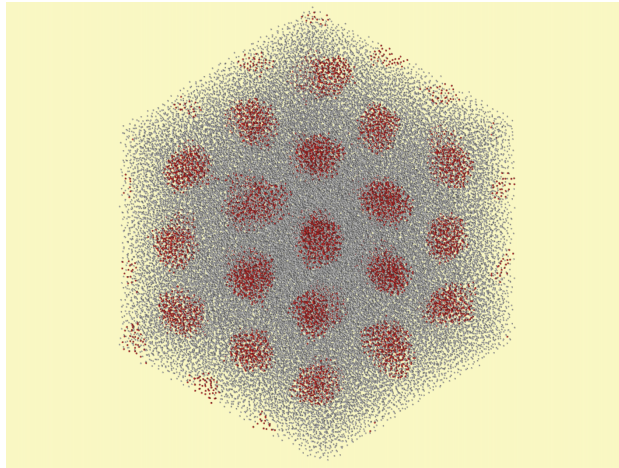


FIG. 2: As Fig. 1 for the system F7S47.

the cylindrical (F13S37) and spherical (F7S47) phase is also observed for the complementary compositions (S13F37 and S7F47), as well as for all the investigated temperatures. A similar analysis of local density profiles revealed the same qualitative features in lamellar phases [13] of the same bead-spring model investigated here (i.e, identical interactions given by Eqs. (1) and (2)). This suggests that this observation is a general feature of ordered mesophases, independent of their morphology.

Finally, it is worth mentioning that the density profiles can be very accurately described in terms of the Helfand-Tagami function predicted by self-consistent field theory [20–22],

$$\rho_{\alpha}(r) = \rho_0 + \frac{\rho_1}{1 + \exp[-2(R_c - r)/\sigma_c]}, \quad (3)$$

with R_c and σ_c the domain radius and interfacial width, respectively. The constants ρ_0 and ρ_1 are adjusted to match the amplitudes of the density profiles. Best fits to Eq. (3) are represented in Figs. 3a and 4a as thick solid lines.

IV. DYNAMIC HETEROGENEITY

Fig. 5 presents results for the temperature dependence of the mean squared displacement, $\langle \Delta s^2(t) \rangle$, of the F- and S-monomers in the two cylindrical phases F13S37 and S13F37. The corresponding results for the orientational correlator, $P(t)$, of F-F and S-S bonds are displayed in Fig. 6. The bond orientational correlator is defined as $P(t) = \langle \cos \theta(t) \rangle$, with $\theta(t)$ the angle between the orientations of the bond at $t = 0$ and at the considered t . For

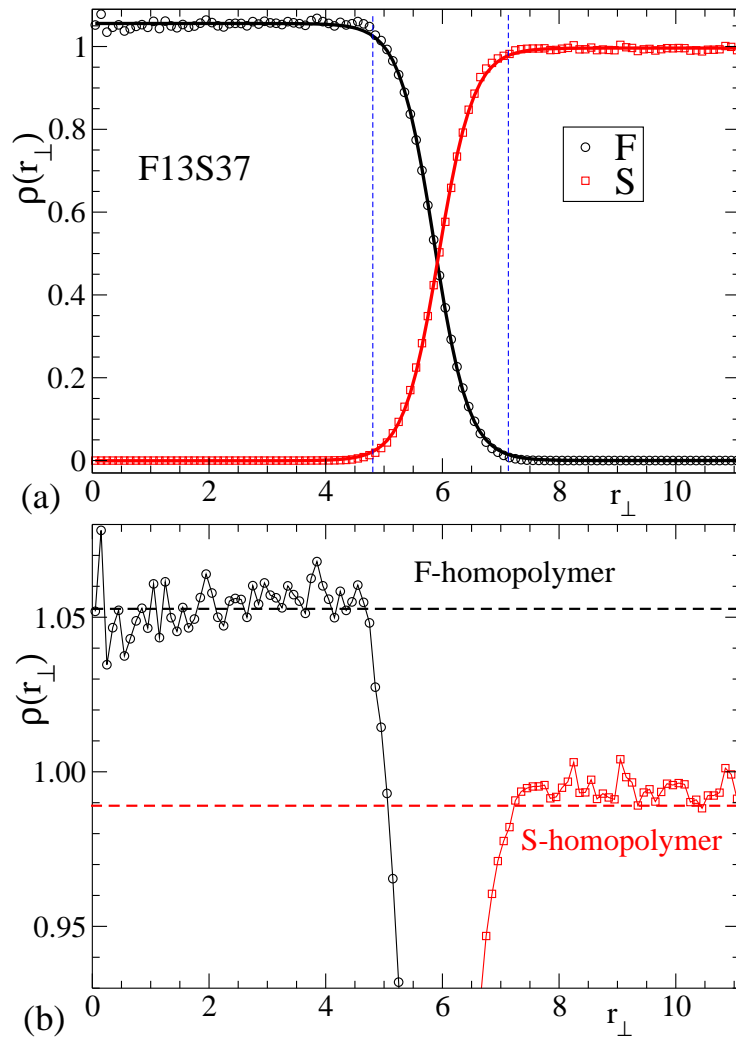


FIG. 3: (a): For both the F- and S-monomers in the system F13S37 at $T = 0.15$, density profiles $\rho(r_{\perp})$ perpendicular to the cylinder axis. Symbols are simulation data. Thick solid lines are best fits to Eq. (3). The vertical dashed lines indicate the approximate limits of the interfacial region. (b): Enhanced representation of data in (a), and comparison with the macroscopic densities of the respective homopolymers (horizontal dashed lines) at the same T . Thin solid lines are guides for the eyes.

temperatures $T \lesssim 0.22$ the mean squared displacements and bond correlators exhibit a plateau after the initial ballistic regime. The plateau extends over longer time scales as temperature decreases. This plateau corresponds to the caging regime, i.e., the temporary trapping of each particle by the surrounding ones, which is a universal feature of glass-forming liquids on approaching the glass transition temperature [36]. The plateau is followed

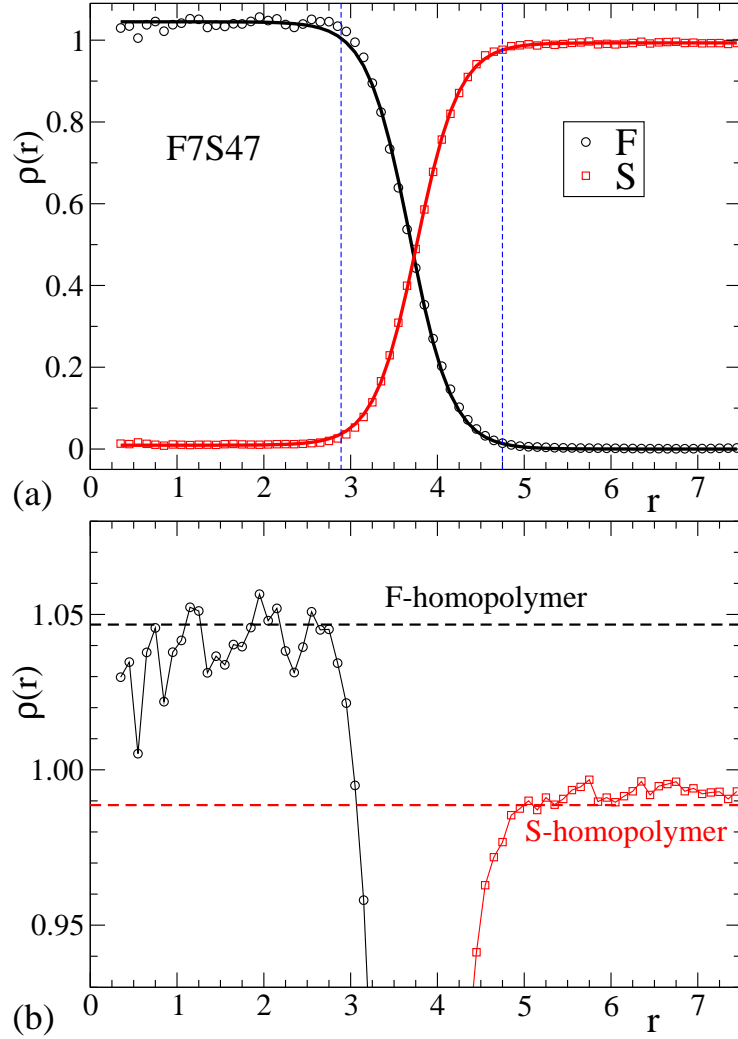


FIG. 4: (a): For both the F- and S-monomers in the system F7S47 at $T = 0.15$, radial density profiles $\rho(r)$. Symbols are simulation data. Thick solid lines are best fits to Eq. (3). The vertical dashed lines indicate the approximate limits of the interfacial region. (b): Enhanced representation of data in (a), and comparison with the macroscopic densities of the respective homopolymers (horizontal dashed lines) at the same T . Thin solid lines are guides for the eyes.

by an increase in $\langle \Delta s^2(t) \rangle$ and a decay in $P(t)$, which reflect the structural α -relaxation. Consistently with observations in the lamellar phase [13], a progressive dynamic separation between the F- and S-components is observed as temperature decreases. Estimating α -relaxation times τ as those for which $\langle \Delta s^2(\tau) \rangle = \sigma^2$ or $P(\tau) = e^{-1}$, we find a separation of about one decade in τ at the lowest investigated temperature $T = 0.14$. For comparison, we include the results of the corresponding homopolymer for the minority component. As

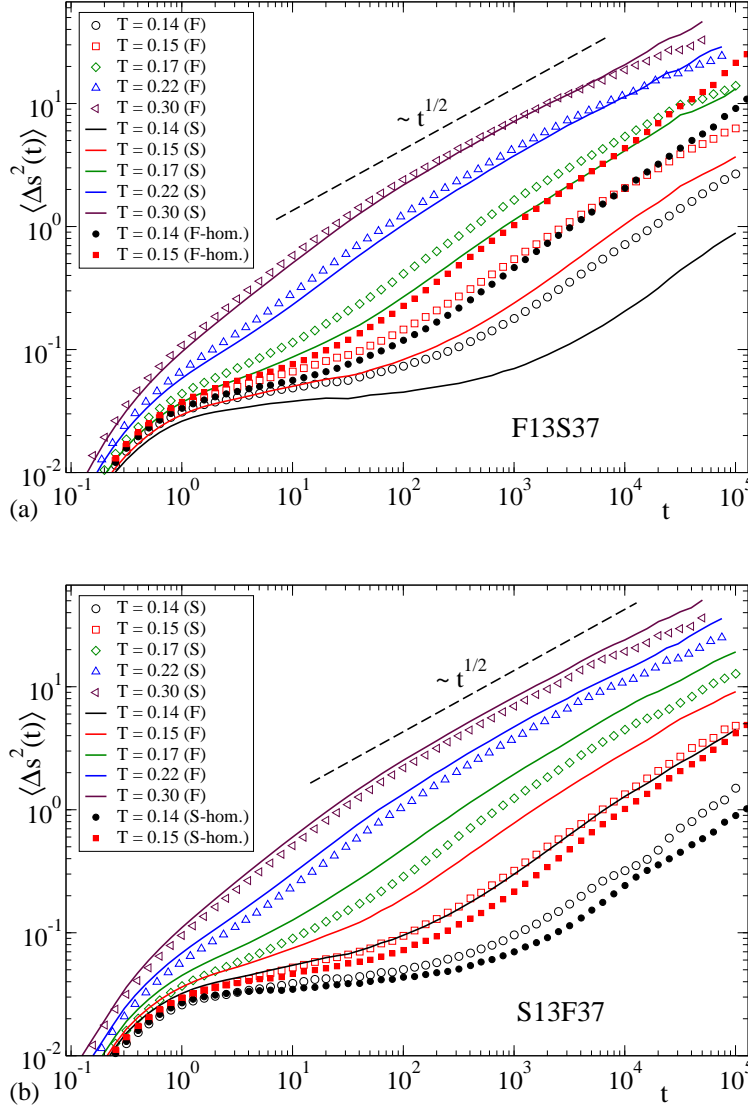


FIG. 5: Temperature dependence of the mean squared displacements of both species in the cylindrical phases F13S37 (a) and S13F37 (b). Data for the minority and majority species are represented by open symbols and solid lines respectively (see panels). Filled symbols are data for the homopolymers corresponding to the minority species. Rouse-like power-laws (dashed lines) are included for comparison.

expected the dynamics of the S-monomers in the cylindrical domains of the S13F37 system is sped up by their coupling to the fast F-matrix. Likewise the dynamics of the F-monomers in the counterpart F13S37 system is slowed down by the surrounding slow S-matrix. Dynamic differences between the confined minority component and its homopolymer counterpart are

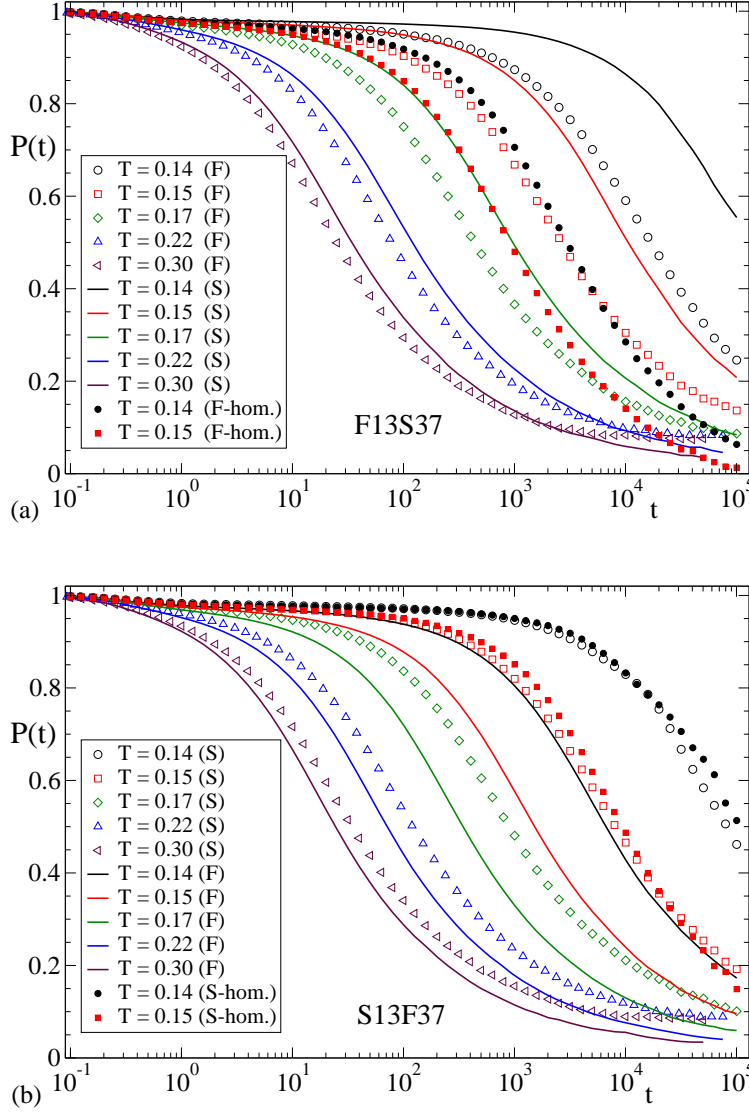


FIG. 6: Temperature dependence of the bond orientational correlators of both species in the cylindrical phases F13S37 (a) and S13F37 (b). Data for the minority and majority species are represented by open symbols and lines respectively (see panels). Filled symbols are data for the homopolymers corresponding to the minority species.

stronger when the matrix is intrinsically slower (F13S37 system) than when it is intrinsically faster (S13F37 system).

Figs. 7 and 8 shows results for the mean squared displacements and bond correlators in the spherical phases F7S47 and S7F47. We find the same qualitative trends observed in Figs. 5 and 6 for the cylindrical phases. Having said this, dynamic differences between

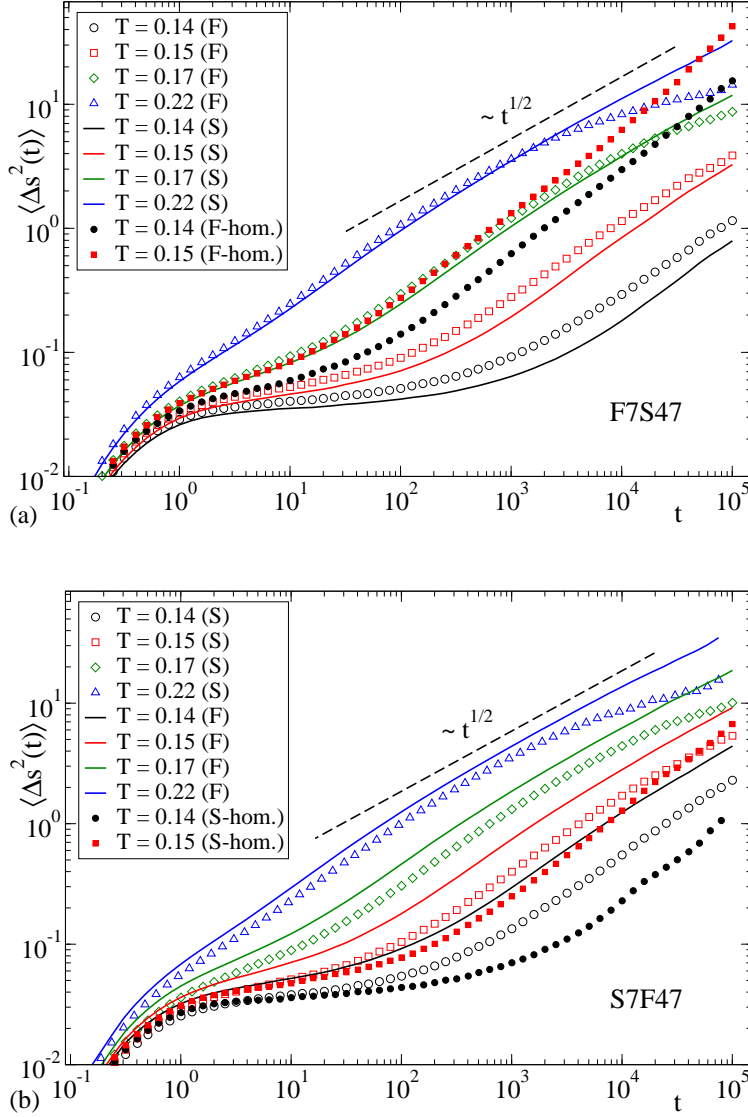


FIG. 7: As Fig. 5 for the spherical phases F7S47 (a) and S7F47 (b).

the minority component and its homopolymer counterpart are more pronounced than in the cylindrical phases. This feature is tentatively related to the smaller radius of the spherical domains in the simulated systems (see above), leading to a larger number of interfacial monomers than in the cylindrical phase, and therefore to a stronger perturbation of the intrinsic homopolymer dynamics. This question will be discussed later by analyzing gradients of mobility within the domains.

At times beyond the α -relaxation scale apparent Rouse-like behavior $\langle \Delta s^2(t) \rangle \sim t^{1/2}$ is found. This feature is a direct consequence of the chain connectivity and a universal

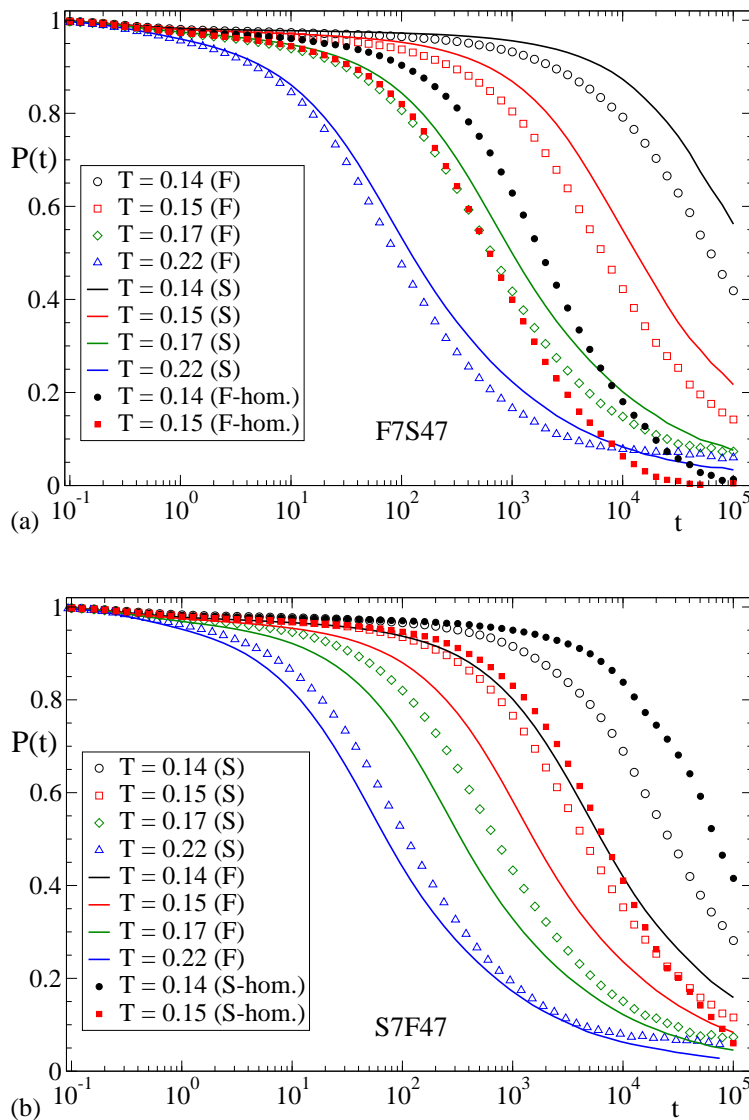


FIG. 8: As Fig. 6 for the spherical phases F7S47 (a) and S7F47 (b).

feature of polymer melts [37]. Strongly entangled polymer melts exhibit further sublinear regimes at longer times, that are commonly understood in the framework of the reptation model [37], before reaching the diffusive regime ($\langle \Delta s^2(t) \rangle \sim t$) at late times. Having said this, reptation effects are minor for the weakly entangled chains of length $n \sim 50$ here investigated. Indeed this chain length is comparable to the estimated entanglement length ($n_e \sim 35$) in flexible bead-spring melts [24]. Presumably the saturation of $\langle \Delta s^2(t) \rangle$ observed after the Rouse regime in Figs. 5 and 7 is mostly related to the presence of the interface, more than to intrinsic features of chain dynamics. Thus, the attachment of the blocks to

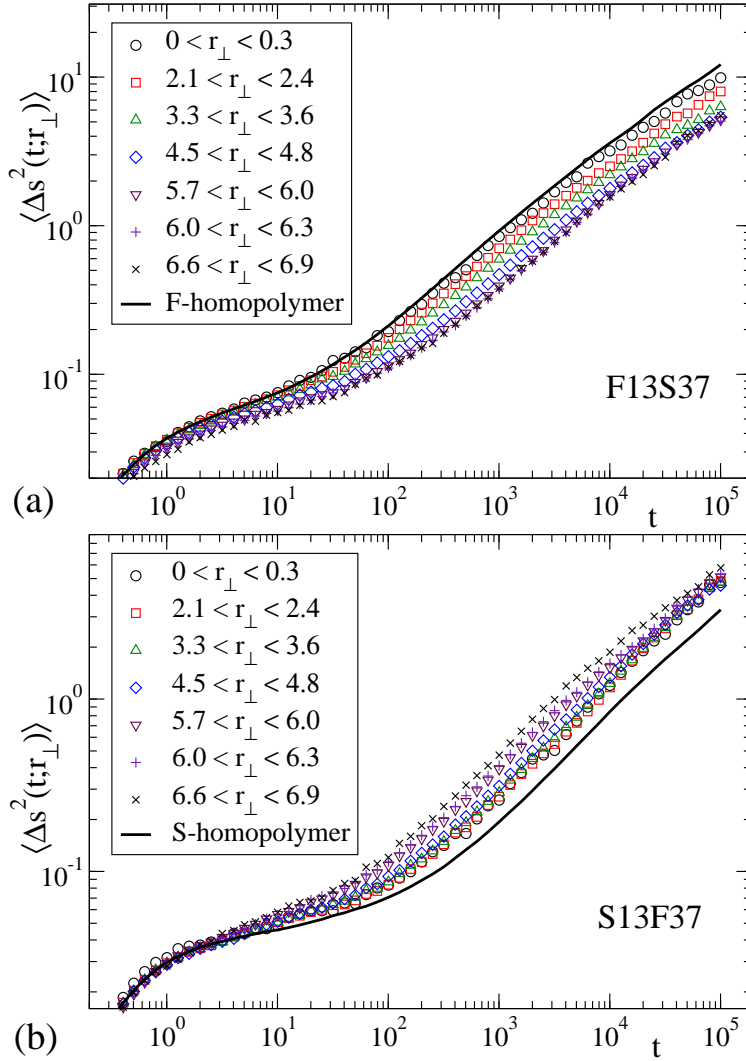


FIG. 9: Symbols: mean squared displacements for different shells in the cylindrical domains at $T = 0.15$. Panel (a) shows data for the F-monomers in the F13S37 system. Panel (b) shows data for the S-monomers in the S13F37 system. Data for the F- and S-homopolymers (lines) are included for comparison in (a) and (b) respectively.

the interface creates and extremely large effective barrier for perpendicular diffusion. The observed saturation will persist over time scales far beyond the simulation window, prior to the final crossover to diffusion.

As mentioned in the Introduction, the segmental relaxation of each component of the diblock system is expected to exhibit dynamic heterogeneity in the ordered mesophases. We may characterize this dynamic heterogeneity as a function of the distance of the monomer

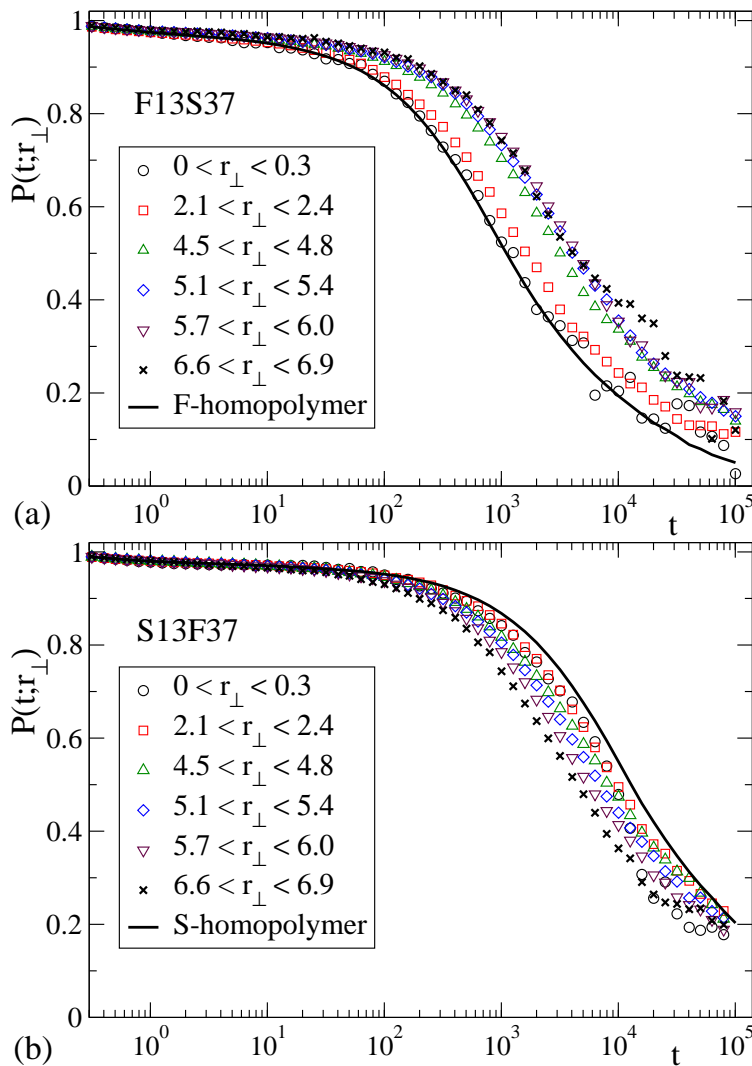


FIG. 10: Symbols: bond orientational correlators for different shells in the cylindrical domains at $T = 0.15$. Panel (a) shows data for the F-F bonds in the F13S37 system. Panel (b) shows data for the S-S bonds in the S13F37 system. Data for the F- and S-homopolymers (lines) are included for comparison in (a) and (b) respectively.

to the centers of the domains. Following the same procedure as in Ref. [13], we divide the cylindrical and spherical domains in (cylindrical or spherical) shells of thickness $\delta = 0.3$ and compute shell-dependent mean squared displacements and bond correlators. Thus, for a given shell $r_{\min} < r < r_{\min} + \delta$, the quantity $\langle \Delta s^2(t; r) \rangle$ is computed only over the monomers that are initially (i.e., at $t = 0$) located in the shell. Likewise the bond correlators $P(t; r)$ are computed only for the bonds whose centers are within the specific shell at $t = 0$.

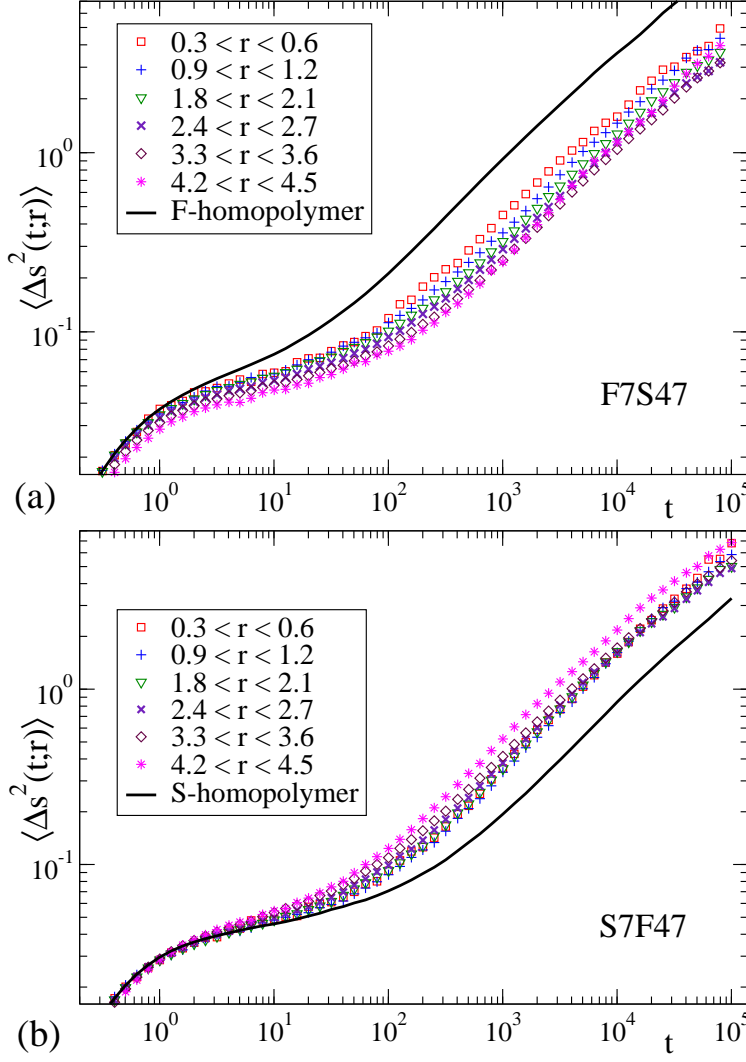


FIG. 11: As Fig. 9 for the spherical phases F7S47 (a) and S7F47 (b).

Fig. 9 shows results, at $T = 0.15$, for the shell-dependent mean squared displacements of the minority component in the cylindrical phases F13S37 and S13F37. Fig. 10 shows, for $T = 0.15$, the shell-dependent bond correlators of the minority component in the former cylindrical phases. The corresponding results for shell-dependent mean squared displacements and bond correlators in the spherical phases (F7S47 and S7F47) are shown in Figs. 11 and 12. A moderate dispersion, over about one decade, is observed in the relaxation times at the lowest investigated temperature. The relaxation of the minority F-monomers and F-F bonds initially located in the center of the domains is faster than the relaxation of those initially located in the interfacial region and in direct contact with the slow S-matrix (for the

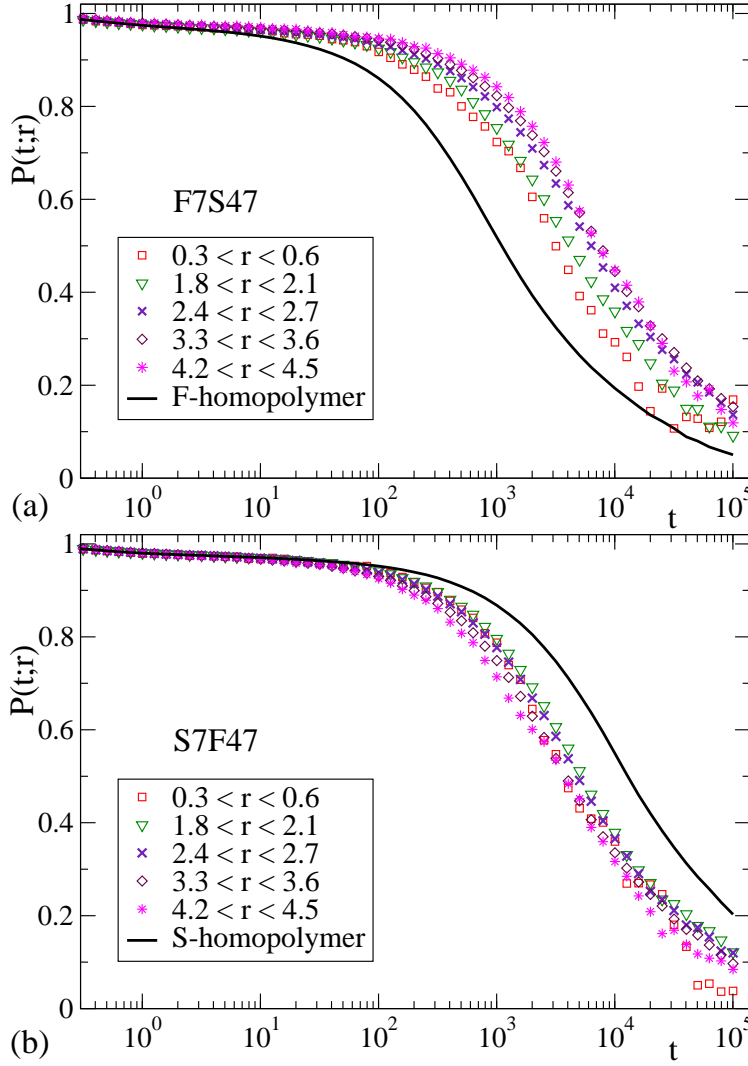


FIG. 12: As Fig. 10 for the spherical phases F7S47 (a) and S7F47 (b).

represented cases, the interfacial region begins at $r_{\perp} \lesssim 5$ in the F13S37 system and $r \lesssim 3$ in the F7S47 system, see Figs. 3 and 4). The opposite effect is observed when the minority component is the slow one. Thus, S-monomers and S-S bonds initially located in the center of the domains show a slower relaxation than those initially located in the interfacial region, i.e, in direct contact with the fast F-matrix.

These features are analogous to those observed in simulations of lamellar phases [13], suggesting that they are independent of the morphology of the domains. In Ref. [13] it was shown that relaxation in the lamellar domains approached that of the corresponding homopolymer as the distance to the interface increased. Namely, for distances beyond about

$d \approx 4$ the relaxation was indistinguishable from that of the corresponding homopolymer. Results presented here for the cylindrical and spherical phases (Figs. 9 to 12) seem to be, at least partially, consistent with the result found in lamellar phases. In the cylindrical phase (Figs. 9 and 10) the homopolymer dynamics is nearly recovered at the center of the domain ($r_{\perp} \rightarrow 0$). Indeed the interfacial region — i.e., the decay of the density profile of the minority component — starts at a distance $r \approx d \approx 4$ from the domain center, and at smaller distances the local density is within statistics the same as in the corresponding homopolymer (see Fig. 3). A different result is found in the spherical phases. Though we still find the former trends with increasing distance to the interface, the relaxation of the corresponding homopolymer is not recovered in the center of the spherical domains. Results in Figs. 11 and 12 show that, for $T = 0.15$, relaxation in the center of the spherical domains differs from that in the corresponding homopolymer by up to one decade. Tentatively this feature may be understood by the fact that the interfacial region begins at a distance $r \approx 3$ (see Fig. 4), smaller than the characteristic distance $d \approx 4$ associated to the gradient of mobility. More demanding simulations of longer chains, in order to obtain domain radii larger than d , would be necessary to recover the homopolymer dynamics in the domain center.

V. EFFECTIVE AND SELF-CONCENTRATION

The concept of effective and self-concentration is usually invoked in theoretical frameworks for explaining the behavior of the α -relaxation in polymer blends [14–18]. Even being miscible systems, two different α -relaxation times are usually found, each of them corresponding to the dynamics of each component modified by blending. This behavior is the so-called ‘dynamic heterogeneity’ of the α -relaxation in polymer blends. In the framework of the self-concentration ideas the presence of two α -relaxation processes in the blend is a direct consequence of the chain connectivity. More precisely, because of the chain connectivity the local concentration in a given volume, relevant for the α -process, around a segment of one of the blend components will be different from the average concentration of the blend.

Given a blend of F- and S-chains, the macroscopic concentrations of each species are given by $\Phi_{\alpha} = N_{\alpha}/(N_{\alpha} + N_{\beta})$, with N_{α} the total number of α -monomers in the system and $\alpha \in \{F, S\}$. Let us define the effective concentration, $\Phi_{\alpha}^{\text{eff}}(R)$, as the average concentration of α -monomers within an sphere of radius R around a given (‘tagged’) α -monomer, i.e., $\Phi_{\alpha}^{\text{eff}}(R) =$

$\langle N_\alpha(R)/[N_F(R) + N_S(R)] \rangle$, with $N_\alpha(R)$ the number of α -monomers within the sphere. In the following we will refer to R as the ‘observation radius’. Provided that the observation radius is sufficiently small (a few Kuhn lengths or less), the effective concentration $\Phi_\alpha^{\text{eff}}(R)$ will be higher than the macroscopic concentration Φ_α . This is a direct consequence of the chain connectivity. Since the tagged α -monomer is connected to an α -chain, the observation sphere will contain an excess of α -monomers over the macroscopic concentration Φ_α .

The self-concentration is defined as $\Phi_\alpha^{\text{self}}(R) = \langle N_\alpha^{\text{intra}}(R)/[N_F(R) + N_S(R)] \rangle$, with $N_\alpha^{\text{intra}}(R)$ the number of α -monomers belonging to the chain of the tagged α -monomer and contained in the observation sphere of radius R . Lodge and McLeish proposed a simple linear relation between the effective and self-concentration [15]:

$$\Phi_\alpha^{\text{eff}}(R) = \Phi_\alpha^{\text{self}}(R) + [1 - \Phi_\alpha^{\text{self}}(R)]\Phi_\alpha. \quad (4)$$

Since obviously $\Phi_\alpha^{\text{self}}(R \rightarrow \infty) = 0$ and $\Phi_\alpha^{\text{self}}(R \rightarrow 0) = 1$, the Lodge-McLeish formula leads to the expected limits $\Phi_\alpha^{\text{eff}}(R \rightarrow \infty) = \Phi_\alpha$ and $\Phi_\alpha^{\text{eff}}(R \rightarrow 0) = 1$.

Lund and co-workers extended the idea of self-concentration to account for the α -relaxation within the minority domains of ordered phases of diblock copolymers [19]. In analogy with Eq. (4), the effective and self-concentration at a given distance r from the domain center are assumed to follow the linear relation:

$$\Phi_\alpha^{\text{eff}}(r; R) = \Phi_\alpha^{\text{self}}(r; R) + [1 - \Phi_\alpha^{\text{self}}(r; R)]\rho_\alpha^N(r). \quad (5)$$

Again, the former quantities are defined within an observation sphere of radius R . The quantity $\rho_\alpha^N(r)$ is defined in similar way as the local density profile of α -monomers discussed above (Figs. 3 and 4). Namely the profile $\rho_\alpha^N(r)$ is not normalized by the volume $V(r)$ of the shell, but by the total number of particles $N(r)$ in that volume, i.e., $\rho_\alpha^N(r) = n_\alpha(r)/N(r)$. For the cylindrical phase r must be again understood as the distance r_\perp normal to the cylinder axis (see above), whereas for the spherical phase r is the distance to the center of the spherical domain. For computing the quantities $\Phi_\alpha^{\text{eff}}(r; R)$ and $\Phi_\alpha^{\text{self}}(r; R)$ directly from the simulation data, we construct spheres of radius R around each of the (tagged) α -monomers contained in (cylindrical or spherical) shells defined within the interval $(r, r + \Delta)$, with $\Delta = 0.1\sigma$. These are the shells previously used for obtaining the density profiles $\rho_\alpha(r)$ (see above). In analogy with the former definitions, the effective and self-concentrations are

respectively obtained as

$$\Phi_{\alpha}^{\text{eff}}(r; R) = \left\langle \frac{N_{\alpha}(r; R)}{N_{\text{F}}(r; R) + N_{\text{S}}(r; R)} \right\rangle \quad (6)$$

and

$$\Phi_{\alpha}^{\text{self}}(r; R) = \left\langle \frac{N_{\alpha}^{\text{intra}}(r; R)}{N_{\text{F}}(r; R) + N_{\text{S}}(r; R)} \right\rangle. \quad (7)$$

The quantity $N_{\alpha}(r; R)$ is the total number of α -monomers within an observation sphere of radius R around a tagged α -monomer located in the shell $(r, r + \Delta)$. The quantity $N_{\alpha}^{\text{intra}}(r; R)$ accounts only for the α -monomers belonging to the same chain of the tagged α -monomer. Averages in Eqs. (6) and (7) are performed over all the shells $(r, r + \Delta)$ in the simulation cell (one shell per domain), all the tagged α -monomers contained in such shells, and over typically 100 independent configurations of the simulation cell.

Obviously, the values of the effective and self-concentrations depend on the selected value of the observation radius R . The analysis of experimental data based on the Lodge-McLeish formula is usually performed by using the Kuhn length [37], l_{K} , as the relevant dynamic length scale [15, 17]. For the bead-spring model investigated here one finds [24] a Kuhn length $l_{\text{K}} \approx 1.5\sigma$. Still, in the following we do not limit the discussion of simulation results to the specific case $R = l_{\text{K}}$ and present data for a broad range of observation radii.

Fig. 13 shows self-concentrations directly computed from the simulations at $T = 0.14$ and for several observation radii. Data correspond to self-concentrations of the minority F-component in the cylindrical phase F13S37 and in the spherical phase F7S47. As expected, $\Phi_{\alpha}^{\text{self}}(r; R)$ decreases by increasing the observation radius R , and tends to be position independent for large R . Because of the soft character of the Lennard-Jones potential [Eq. (1)] some monomer interpenetration is possible for $r \lesssim \sigma$. Therefore, there is a non-negligible probability of finding more monomers than the tagged one, including monomers of other chains, within an observation radius of $R = 1.0$. This feature explains the observed result $\Phi_{\alpha}^{\text{self}}(r; R = 1.0) \lesssim 1$, which would be impossible for hard-sphere interactions.

For relevant length scales $1.0 < R < 4.0$, the self-concentration shows a non-monotonous dependence on the distance to the domain center, with a maximum close to the innermost part of the interfacial region (see Fig. 13), except in the case $R = 1.1$ (see discussion below). This maximum reflects a certain degree of segregation of each chain from its neighbors in that region, resulting in a higher self-concentration. The self-concentration decays smoothly along the interface as the distance from the domain center increases. This range of distances

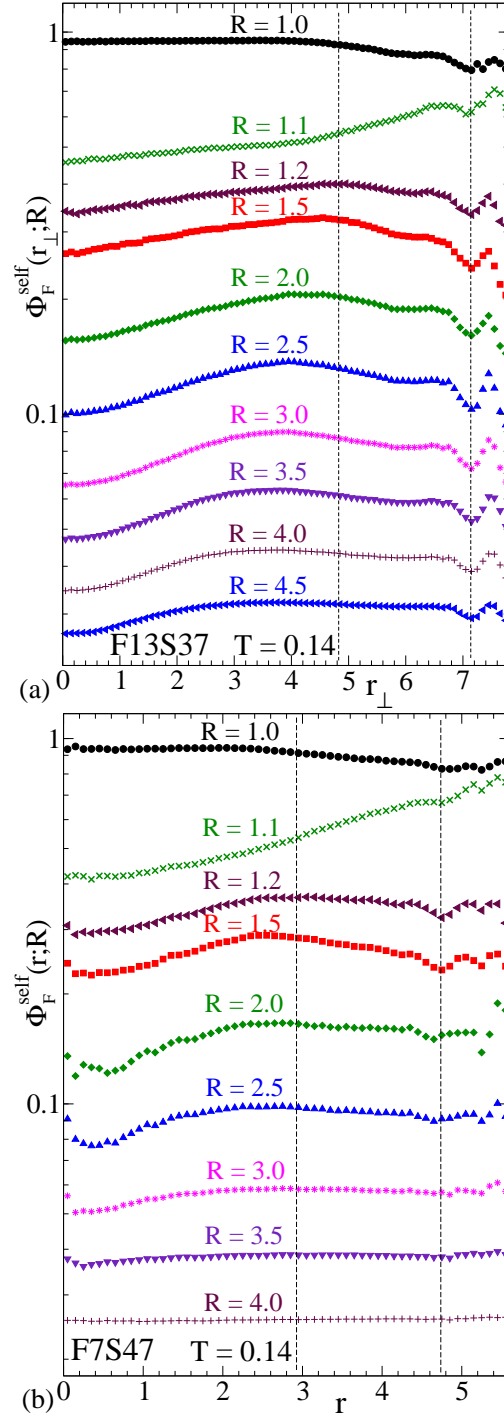


FIG. 13: Self-concentration (note the logarithmic scale) of the F-monomers at $T = 0.14$ in the cylindrical phase F13S37 (a) and in the spherical phase F7S47 (b). Different data sets correspond to different observation radii R (see legends). The dashed lines in both panels indicate the approximate limits of the interfacial region (see also Figs. 3 and 4).

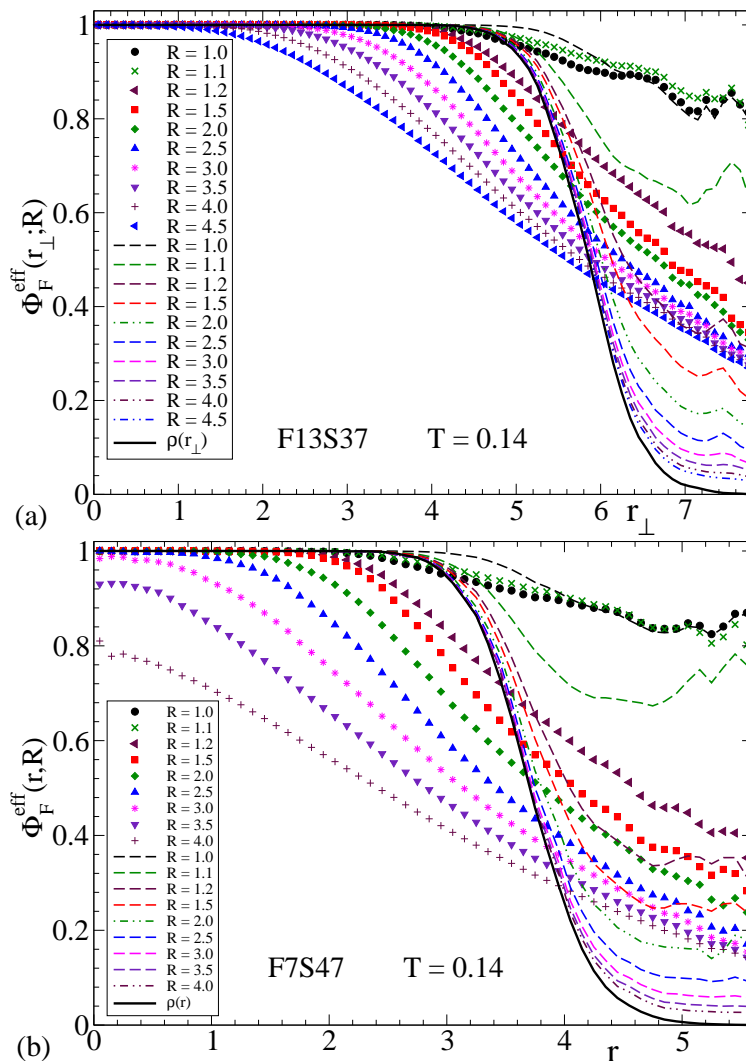


FIG. 14: Effective concentration, as a function of the distance to the domain center, of F-monomers at $T = 0.14$ in the cylindrical phase of the system F13S37 (a) and in the spherical phase of the system F7S47 (b). Symbols are results directly computed from the simulations through Eq. (6). Dashed lines are obtained by using Eq. (5) (see text for details). Same colors for symbols and lines correspond to a same observation radius R (see legend). The thick solid lines are the local density profiles $\rho_F^N(r)$ of the F-monomers (see text).

is progressively probed by minority monomers at the junction point of the two blocks. Since a fraction of their neighbors in the same chain belongs to the other species, the self-concentration shows an ultimate decay. In strongly segregated phases as those investigated here the minority monomers are rarely found far beyond the interfacial region. For this

reason their self-concentration in that region has poor statistics (see data at long r in Fig. 13).

The self-concentration for the specific case $R = 1.1$ shows a rather different behavior from that found for the other observation radii. Namely $\Phi_\alpha^{\text{self}}(r; R = 1.1)$ does not exhibit a maximum at the innermost neighborhood of the interface, but a sharp increase at long r . By analyzing the intramolecular radial distribution function $g(r)$ of the minority component (not shown), we find a main peak at $r \lesssim 1.0$, corresponding to the typical bond distance, and a weak secondary peak at $r \approx 1.1$. This secondary peak is not found in the $g(r)$ of the corresponding homopolymer, and reflects bond stretching in the interfacial region. Thus the observation radius $R = 1.1$ probes this feature, resulting in a sharp increase of the self-concentration by crossing the interface.

Fig. 14 shows, for the former systems and at the same $T = 0.14$, results for the effective concentration of the F-monomers. The symbols are data directly computed from the simulations by using Eq. (6). The dashed lines are the theoretical expectations from the generalized Lodge-McLeish formula, by inserting in the right-hand side of Eq. (5) the self-concentrations (Fig. 13) and density profiles $\rho_\alpha^N(r)$ directly obtained from the simulations. A good agreement is found only in the limit case $R = 1.0$, for which the effective and self-concentration are essentially identical. The simulations reveal a clear breakdown of Eq. (5) for any relevant length scale $R > 1.0$, including the usual assumption $R = l_K$ ($R = 1.5$ in this system [24]). The actual effective concentrations obtained from the simulations exhibit a much more stretched decay than those predicted by the modified Lodge-McLeish relation.

These results suggest that the use of Eq. (5) might bias the experimental analysis of the α -relaxation in block copolymers [38, 39], and in particular the so-obtained values characterizing structural properties relevant for the segmental dynamics. In Ref. [19] a block copolymer system of poly(isoprene)/poly(dimethylsiloxane) was investigated in its cylindrical mesophase. The α -relaxation of poly(isoprene) confined in the cylindrical domains was analyzed in terms of a model based on self- and effective concentrations following the scheme described above. The temperature dependence of the α -times at different distances to the domain center was assumed to follow a Vogel-Fulcher-Tamman (VFT) law,

$$\tau(r) = \tau_\infty \exp[E/(T - T_0(r))], \quad (8)$$

with $T_0(r)$ the VFT temperature at distance r . Eqs. (5) and (8) were combined with the empirical Flory-Fox mixing rule. This provides the VFT temperature of a component in a

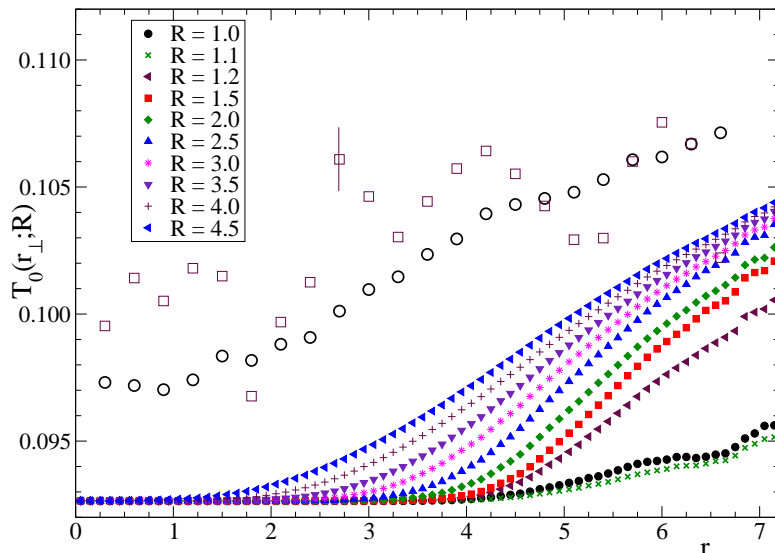


FIG. 15: VFT temperatures, as a function of the distance to the domain center, for the relaxation times of the F-F bonds in the cylindrical phase of the system F13S37. Large empty symbols are obtained by fitting the relaxation times directly obtained from the simulations (see text), with all free parameters (squares) or by fixing τ_∞ and E to the values of the F-homopolymer (circles). A typical error bar is included. Small symbols are obtained by using the Flory-Fox equation (9) with the effective concentrations directly obtained from the simulations (see Fig. 14a). The respective observation radii are given in the legend.

polymer mixture as an interpolation between the VFT temperatures of the two homopolymers, according to the concentration of each component [23]. In Ref. [19] the Flory-Fox equation was adapted to the case of ordered block copolymers. According to the scheme proposed there, the Flory-Fox equation for the minority F-component reads

$$\frac{1}{T_0(r; R)} = \frac{\Phi_{\text{F}}^{\text{eff}}(r; R)}{T_0^{\text{F}}} + \frac{1 - \Phi_{\text{F}}^{\text{eff}}(r; R)}{T_0^{\text{S}}}, \quad (9)$$

with T_0^{F} and T_0^{S} the VFT temperatures of the F- and S-homopolymers respectively, and $\Phi_{\text{F}}^{\text{eff}}(r; R)$ the effective concentration of the F-component in the diblock system. We have quantified the relaxation times τ of the F- and S-homopolymer as the times for which the respective bond orientational correlators decay to $P(\tau) = e^{-1}$. By fitting the values of τ obtained at the different temperatures to an VFT law we find $T_0^{\text{F}} = 0.093$ and $T_0^{\text{S}} = 0.11$ for the F- and S-homopolymer respectively. The latter and the effective concentrations

obtained from the simulation (symbols in Fig. 14a) are the inputs in Eq. (9), which provides the theoretical estimation of the VFT temperature along the F-domains. Since the effective concentrations are different for each observation radius R , different profiles for $T_0(r; R)$ are found. These theoretical profiles are displayed in Fig. 15 (small symbols) and compared with the real profile (large empty symbols). The real profile is obtained by determining the relaxation times of the shell-dependent orientational correlators $P(t; r)$ directly obtained from the simulations at the different temperatures (e.g., data sets in Fig. 10a), and fitting such times to the VFT Eq. (8). We have applied two fitting procedures. In the first one, the three parameters (T_0 , E and τ_∞) are free. The so-obtained values for T_0 are displayed in Fig. 15 as empty squares. In the second procedure — following assumptions of the experimental analysis in Ref. [19] — T_0 is the only free parameter, whereas the others are fixed to the values of the F-homopolymer ($E = 0.30$ and $\tau_\infty = 9.7$). The values of T_0 obtained by this second procedure are displayed as empty circles in Fig. 15. As expected, these show a much lower dispersion than the values obtained from fully free fits. Anyway, in both cases there is a full disagreement with the theoretical profiles. The discrepancy between simulation and theoretical results is reduced by increasing the observation radius R for the effective concentration, but strong differences persist even for unrealistic values as $R \sim 4\sigma$ — at this point we remind that R is assumed to be a relevant length scale for the segmental relaxation, i.e, it should be comparable to the Kuhn length $l_K \approx 1.5\sigma$ [24]. A full disagreement between simulation and theoretical profiles for the VFT temperatures is also found in the other investigated systems (not shown), independently of the specific geometry of the mesophase.

The results in Figs. 14 and 15 demonstrate that the modified Lodge-McLeish relation (Eq. (5)) and Flory-Fox mixing rule (Eq. (9)) are clearly incompatible with the simulation results. This is apparently in contradiction with the analysis presented in Ref. [19], which implemented the former relations and provided a good description of the experimental spectra. This was achieved even by assuming a fixed value of the self-concentration in the cylindrical domain (see below), which is also in clear disagreement with the trends observed in Fig. 13. Having said this, it must be noted that the density profile intervening in Eq. (5) was not directly accessed in Ref. [19]. Instead, it was modelled by the Helfand-Tagami function of Eq. (3), leaving R_c and σ_c as the *fit parameters* which provided the best description of the experimental spectra. The results discussed in this section suggest that the values obtained

for such parameters are biased by incorrect assumptions made in the experimental analysis, as the use of the modified Lodge-McLeish and Flory-Fox relations.

Now we clarify this point by performing a ‘blind analysis’ of the segmental dynamics within the same scheme of Ref. [19], i.e, by making assumptions on self-concentrations and density profiles instead of using the inputs from the simulations. We illustrate the procedure for the representative case of the system F13S37. In Ref. [19] the self-concentration of poly(isoprene) was assumed to take a fixed value $\phi^{\text{self}} = 0.45$, independently of the position within the domain and identical to the value of the homopolymer [15]. The latter was estimated by assuming $R = l_K$. For the system here investigated $l_K \approx 1.5\sigma$ [24], and accordingly we use $\Phi_{\text{F}}^{\text{self}} = 0.30$ in Eq. (5) as a reasonable value (similar values did not change the qualitative results discussed below). We construct density profiles $\rho_{\text{F}}^N(r)$ for different values of R_c and σ_c by using the Helfand-Tagami function, Eq. (3). For this we fix $\rho_0 = 0$ and $\rho_1 = 1 + \exp[-2R_c/\sigma_c]$, in order to fulfill the condition $\rho_{\text{F}}^N(r=0) = 1$ (indeed S-monomers were never found in the center of the domain). The so-obtained profiles $\rho_{\text{F}}^N(r)$ are inserted in Eq. (5), which together with Eq. (9) provides different theoretical profiles for $T_0(r)$. In general, the agreement between the real and theoretical profiles $T_0(r)$ is improved by increasing the width σ_c and decreasing the domain radius R_c in the Helfand-Tagami function for the theoretical density profile. The top panel of Fig. 16 shows results for fixed $\sigma_c = 2$ and different values of R_c . The real profile for $T_0(r)$ is qualitatively approached only for the smallest used value $R_c = 2$. For smaller values of σ_c the comparison (not shown) with the real $T_0(r)$ worsens and not even a qualitative agreement is found. Fig. 16b shows a comparison between the real density profile $\rho_{\text{F}}^N(r)$ and the Helfand-Tagami function for the former values $R_c = \sigma_c = 2$. This figure clearly illustrates how the improvement of the description of the real $T_0(r)$ is obtained at the expense of introducing a theoretical density profile that strongly differs from the real one.

Following the experimental analysis, the theoretical $T_0(r)$ is used to construct the theoretical profile $\tau(r)$ for the relaxation times according to Eq. (8), with the additional experimental assumption of using the values of the F-homopolymer for τ_∞ and E . We construct the theoretical function for the global orientational correlator as the weighted-average of the shell-dependent bond correlators, $P(t) = \sum_r \rho_{\text{F}}^N(r)P(t; r) / \sum_r \rho_{\text{F}}^N(r)$. In this expression we use for $\rho_{\text{F}}^N(r)$ the Helfand-Tagami function with $R_c = \sigma_c = 2$, which as discussed above, provides the best description of the real $T_0(r)$ in Fig. 16a. In analogy with the ex-

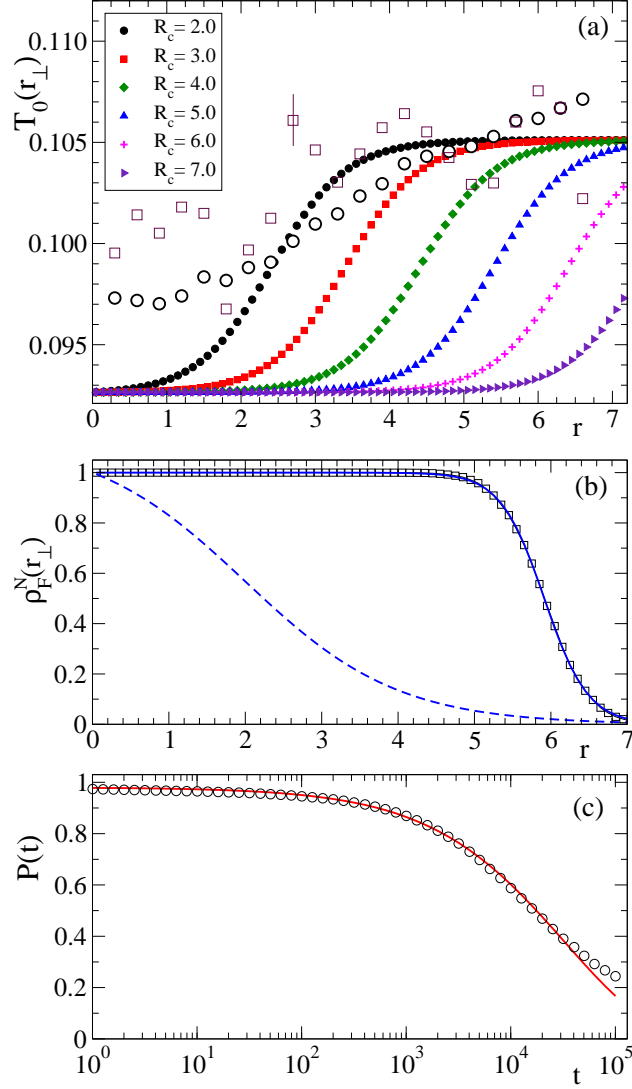


FIG. 16: Panel (a): VFT temperatures, as a function of the distance to the domain center, for the relaxation times of the F-F bonds in the cylindrical phase of the system F13S37. Large empty symbols are obtained by directly fitting the simulation results (see text), with all free parameters (squares) or by fixing τ_∞ and E to the values of the F-homopolymer (circles). A typical error bar is included. Small symbols are theoretical predictions by fixing $\Phi_F^{\text{self}} = 0.30$ and using a Helfand-Tagami function for the density profiles (see text), with fixed $\sigma_c = 2.0$ and different values of R_c (see legend). Panel (b): Density profiles $\rho_F^N(r)$ at $T = 0.14$ in the cylindrical phase of the system F13S37. The symbols are simulation data. The solid line is a best fit to a Helfand-Tagami function ($R_c = 5.9$ and $\sigma_c = 0.57$). The dashed line is obtained with $R_c = \sigma_c = 2$. Panel (c): Global orientational correlator $P(t)$ for the F-F bonds at $T = 0.14$ in the cylindrical phase of the system F13S37. Symbols are simulation results. The solid line is the theoretical prediction (see text) with $\Phi_F^{\text{self}} = 0.30$, and $R_c = \sigma_c = 2$.

perimental analysis of Ref. [19], we assume a Kohlrausch-Williams-Watts (KWW) function $P(t; r) \sim \exp[-(t/\tau(r))^\beta]$ for the shell-dependent bond correlators, with β the same stretching exponent as in the F-homopolymer at the same T [40, 41]. In the KWW function we use the theoretical α -times $\tau(r)$, obtained as described above. Fig. 16c shows a comparison between the theoretical global correlator $P(t)$ obtained by the former procedure and the simulation results. A good agreement is found, despite many of the assumptions and ingredients used to construct the theoretical $P(t)$ being incorrect. This agreement has been achieved by using as *input* of the model a density profile that strongly differs from the real one. This point, together with the fact that the experimental analysis of Ref. [19] provides the density profile as an *outcome* from the fitting procedure, suggests that the latter is strongly biased by the assumptions made on the Lodge-McLeish and Flory-Fox equations.

VI. CONCLUSIONS

We have presented a detailed characterization of several static and dynamic properties in a generic bead-spring model for cylindrical and spherical phases of diblock copolymers, This complements results previously obtained [13] for the lamellar phase of the same bead-spring model. We have characterized the dynamic heterogeneity of the structural α -relaxation of the component confined in the minority domains. Consistently with previous investigations in the lamellar phase [13] the analysis reveals moderate gradients of mobility in the investigated temperature range, which qualitatively probes time scales up to 100 ns. The estimated spatial extension of the gradients of mobility (a few nanometers) is also consistent with that observed in the lamellar phase. Gradients of mobility do not seem to be related to gradients of density within the domains, which are indeed absent.

We have performed a detailed analysis of effective and self-concentrations, a concept usually invoked to explain the α -relaxation of polymer mixtures and that has been recently adapted to analyze experimental data of diblock copolymers in ordered phases. The analysis of effective and self-concentrations directly computed from the simulations reveals a strong disagreement with the modified forms of both the Lodge-McLeish relation and the Flory-Fox mixing rule, which have been recently proposed for ordered block copolymers [19]. This suggests that their use may strongly bias the experimental analysis of the α -relaxation in block copolymers, in particular providing incorrect estimations of the local density profiles.

VII. ACKNOWLEDGEMENTS

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- [1] Bates, F.S.; Fredrickson, G.H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
 - [2] Matsen, M.W.; Bates, F.S. *Macromolecules* **1996**, *29*, 1091.
 - [3] Hamley, I.W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, UK, 1998.
 - [4] Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*; Wiley-IEEE: Hoboken, NJ, 2003.
 - [5] Alig, I.; Floudas, G.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 5004.
 - [6] Kyritsis, A.; Pissis, P.; Mai, S.-M.; Booth, C. *Macromolecules* **2000**, *33*, 4581.
 - [7] Zhukov, S.; Geppert, S.; Stühn, B.; Staneva, R.; Ivanova, R.; Gronski, W. *Macromolecules* **2002**, *35*, 8521.
 - [8] Lorthioir, C.; Alegría, A.; Colmenero, J.; Deloche, B. *Macromolecules* **2004**, *37*, 7808.
 - [9] Encinar, M.; Guzmán, E.; Prolongo, M. G.; Rubio, R. G.; Sandoval, C.; González-Nilo, F.; Gargallo, L.; Radić, D. *Polymer* **2008**, *49*, 5650.
 - [10] Mok, M. M.; Masser, K. A.; Runt, J.; Torkelson, J. M. *Macromolecules* **2010**, *43*, 5740.
 - [11] Sanz, A.; Nogales, A.; Ezquerro, T. A. *Soft Matter* **2011**, *7*, 6477.
 - [12] del Valle-Carrandi, L.; Alegría, A.; Arbe, A.; Colmenero, J. *Macromolecules* **2012**, *45*, 491.
 - [13] Slimani, M.Z.; Moreno, A.J., Colmenero, J. *Macromolecules* **2011**, *44*, 6952.
 - [14] Chung, G.C.; Kornfield, J.A.; Smith, S.D. *Macromolecules* **1994**, *27*, 964.
 - [15] Lodge, T.P.; McLeish, T.C.B. *Macromolecules* **2000**, *33*, 5278.
 - [16] He, Y.; Lutz, T.R.; Ediger, M.D. *J. Chem. Phys.* **2003**, *119*, 9956.
 - [17] Colmenero, J.; Arbe, A. *Soft Matter* **2007**, *3*, 1474.
 - [18] Cangialosi D.; Schwartz, G.A.; Alegría, A.; Colmenero, J. *J. Chem. Phys.* **2005**, *123*, 144908.
 - [19] Lund, R.; Willner, L.; Alegría, A.; Colmenero, J.; Richter, D. *Macromolecules* **2008**, *41*, 511.
 - [20] Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.
 - [21] Helfand, E.; Wasserman, Z. R. . *Macromolecules* **1978**, *11*, 960.

- [22] Helfand, E.; Wasserman, Z. R. . *Macromolecules* **1980**, *13*, 994.
- [23] Strobl, G. *The Physics of Polymers*; Springer-Verlag: Berlin, 2007.
- [24] Kremer, K.; Grest, G.S.; *J. Chem. Phys.* **1990**, *92*, 5057.
- [25] Baschnagel, J.; Varnik, F. *J. Phys.: Condens. Matter* **2005**, *17*, R851.
- [26] Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press (Elsevier): San Diego, 1996.
- [27] Martyna, G.J.; Tuckerman, M.E.; Tobias, D.J.; Klein, M.L. *Mol. Phys.* **1996**, *87*, 1117.
- [28] Hoffmann, A.; Sommer, J.U.; Blumen, A. *J. Chem. Phys.* **1997**, *106*, 6709.
- [29] Murat, M.; Grest, G.S.; Kremer, K. *Macromolecules* **1999**, *32*, 595.
- [30] Anderson, J.A.; Lorenz, C.D.; Travesset, A. *J. Chem. Phys.* **2008**, *128*, 184906.
- [31] Moreno, A.J.; Colmenero, J. *Macromolecules* **2009**, *42*, 8543.
- [32] Schultz, A.J.; Hall, C.K.; Genzer, J. *J. Chem. Phys.* **2004**, *120*, 2049.
- [33] Loison, C.; Mareschal, M.; Kremer, K.; Schmid, F. *J. Chem. Phys.* **2003**, *119*, 13138.
- [34] Grest, G.S.; Lacasse, M.D.; Kremer, K.; Gupta, A.M. *J. Chem. Phys.* **1996**, *105*, 10583.
- [35] The aggregation numbers of the cylindrical and spherical domains were determined by a standard cluster analysis. Thus, two monomers of the minority blocks were assigned to a same domain ('cluster') if their mutual distance was smaller than 1.5σ , which corresponds to the first minimum of the interchain radial distribution function. In the case of the cylindrical domains, which are obviously infinite by application of periodic boundary conditions, the 'aggregation number' must be understood as the value within the simulation cell.
- [36] Binder, K.; Kob, W. *Glassy Materials and Disordered Solids*; World Scientific: Singapore, 2005.
- [37] Doi, M.; Edwards, S.F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, UK, 1986.
- [38] Actually, it has been argued that the Lodge-McLeish relation is not valid even for the case of disordered polymer blends. Liu *et al.* performed simulations of a mixture of *identical* polymers, in which both components just differ by random labelling [39]. This is an ideal system to test the Lodge-McLeish relation, which implicitly assumes that deviations between the effective and the macroscopic concentration just originate from self-concentration effects, neglecting any additional contributions from microsegregation related to the strength of the cross-interactions. Though this assumption is clearly fulfilled in the system of Ref. [39], the

analysis presented in that work showed a clear disagreement with the Lodge-McLeish relation, i.e, with the functional relation between effective and self-concentration proposed by the *ansatz* of Eq. (4). Liu *et al.* proposed an alternative empirical relation [39], which provided a good description of the simulation results. In a similar manner as done with the Lodge-McLeish relation, we have adapted Liu and co-workers' relation to the case of ordered diblock copolymers. However this does not improve the comparison presented in Fig. 14, and leads again to a strong disagreement with simulation results.

- [39] Liu, W.; Bedrov, D.; Kumar, S.K.; Veytsman, B.; Colby, R.H. *Phys. Rev. Lett.* **2009**, *103*, 037801.
- [40] In Ref. [19] the dynamic response was analyzed in the frequency domain. Havriliak-Negami (HN) functions were assumed for the shell-dependent correlators —HN functions in the frequency domain can be related to KWW functions in the time domain [41]. The shape parameters of the HN functions were assumed to be identical to those of the homopolymer.
- [41] Alvarez, F.; Alegría, A.; Colmenero, J. *Phys. Rev. B* **1991**, *44*, 7306.

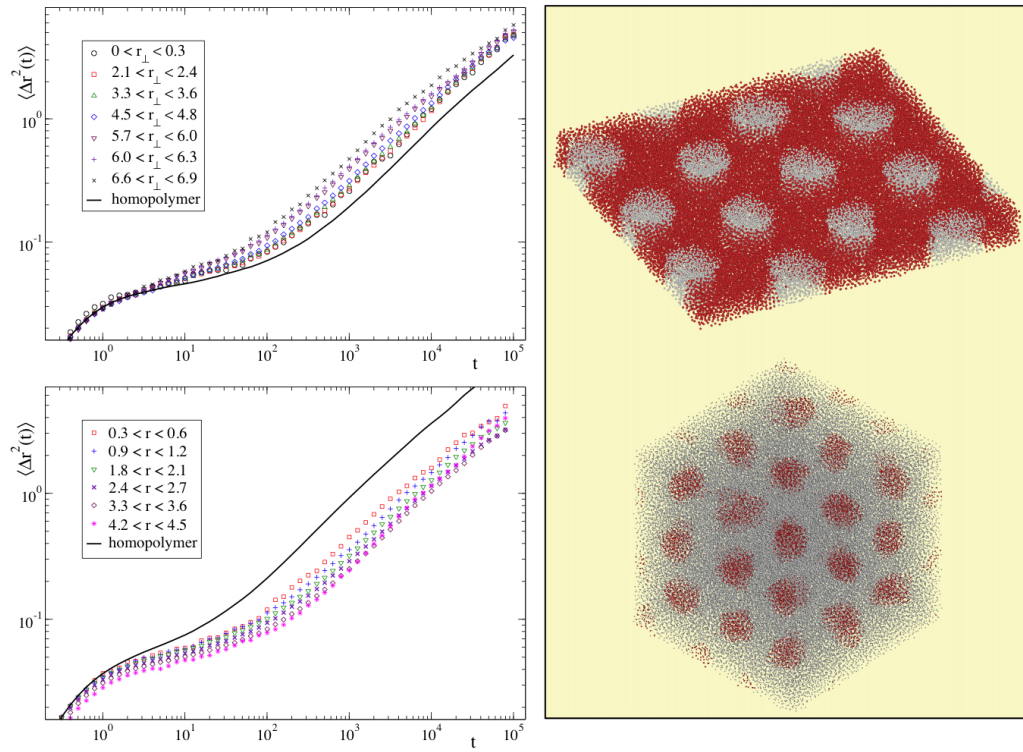


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Heterogeneity of the Segmental Dynamics in Cylindrical and Spherical Phases of Diblock Copolymers

Mohammed Zakaria Slimani, Angel J. Moreno and Juan Colmenero