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Universal trend of the non-exponential Rouse mode relaxation in polymer systems:

A theoretical interpretation based on a generalized Langevin equation

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We show that the universal behavior of the Rouse-modes relaxation in polymer systems –which has been recently reported from experimental data [S. Arrese-Igor et al., Phys. Rev. Lett. **113**, 078302 (2014)]– can be quantitatively explained in the framework of a theoretical approach based on: (i) a generalized Langevin equation formalism and (ii) a memory function which takes into account the coupling between intra-chain dynamics and collective dynamics. This approach opens the way of generalizing the magnitudes probing chain dynamics in polymer systems.

Large-scale motions of macromolecular chains are unique dynamic processes of melts of polymer systems, which drive the viscoelastic properties of such materials. The theoretical description of chain dynamics is usually carried out in terms of the so-called Rouse modes and the Rouse-modes correlation functions[1]. If we consider a macromolecular chain composed by N beads of equal mass, the Rouse mode $\vec{X}_p(t)$ of index $p = 1, ..., N-1$ is defined as $\vec{X}_p(t) = \sum_{j=1}^{N} \vec{r}_j(t)\cos[(j-1/2)p\pi/N]$ with $\vec{r}_j$ being the vector giving the position of the j-bead in the chain. The wavelength of this mode is given by N/p. On the other hand, the Rouse-mode correlator $C_{p,q}(t)$ is defined in the usual way as $C_{p,q}(t) = \langle \vec{X}_p(t)\vec{X}_q(0)\rangle$. The Rouse model is nowadays the accepted theoretical framework for chain dynamics of unentangled polymers and also for the short-time regime (times shorter than the so-called entanglement time) of entangled polymers. This model fully neglects spatial and time correlations of the stochastic forces[1]. These approximations yield, respectively, orthogonality of the Rouse modes ($C_{p,q}(t) \equiv 0$ for $p \neq q$) and exponential relaxation of $C_p(t) = \langle \vec{X}_p(t)\vec{X}_p(0)\rangle$. As consequence, the magnitudes probing chain dynamics as, for instance, the correlation function of the chain end-to-end vector or the neutron scattering functions are constructed in terms of exponential Rouse mode correlators $C_p(t)$[1]. However, molecular dynamics simulations use to show deviations from the exponential behavior of $C_p(t)$, even in the long wavelength (N/p) limit ($p \to 1$) where local intrachain potentials and chain stiffness obviously do not play any role[2–5]. These deviations are of particular relevance in the case of the so-called dynamically asymmetric polymer blends, when the chain dynamics of the fast component is monitored in the presence of the slow component ('matrix')[3,5]. In a recent work[6] the relaxation of the $C_{p=1}(t)$ was experimentally isolated and observed for the first time by means of the thermally stimulated depolarization current (TSDC) technique in different unentangled polymer systems, including homopolymers and blends (see Ref.[6] for information about the molecular mass). It was shown that $C_{p=1}(t)$ deviates from the exponential behavior in all systems as soon as the characteristic time of the relevant density fluctuations in the system (τ_α) approaches the relaxation time of $C_{p=1}(t)$ ($\tau_{p=1}$). The deviations from the exponential behavior were quantified in the usual way, by fitting $C_{p=1}(t)$ by means of a stretched exponential function $C_{p=1}(t) \propto \exp[-(t/\tau_{p=1})^\beta]$ with $\beta < 1$. The obtained values of β for the different systems and the different temperatures showed a 'universal' trend when they were represented as a function of the ratio ($\tau_{p=1}/\tau_\alpha$). These data are reproduced here in Fig. 1. We remind that, as it was discussed in Ref.[6], the range of $\log(\tau_{p=1}/\tau_\alpha) \leq 0$ is only accessible in the case of asymmetric polymer blends where $\tau_{p=1}$ corresponds to the fast component in the blend and τ_α to the slow component (matrix). Obviously this range is not accessible in the case of a pure polymer where τ_α can never be longer than $\tau_{p=1}$. In this communication we show that this 'universal' behavior can be quantitatively explained (see Fig. 1) in terms of a theoretical approach based on the generalized Langevin equation (GLE) formalism and a memory function which takes into account at microscopic level the effect of the coupling between the collective dynamics of the system ('matrix') and the dynamics of the tagged chain ('probe') for unentangled polymer systems.

In Ref.[7] Schweizer proposed an approximated GLE treatment for a tagged chain in a polymer melt, which included the approximation of isotropy. In the framework of this simplified formalism, an integro-differential equation for the time evolution of the Rouse correlator $C_p(t)$ can be obtained[7]:

$$\frac{dC_p(t)}{dt} + \frac{1}{\xi_0}\int_0^t dt' \Gamma_p(t-t') \frac{dC_p(t')}{dt'} = -\frac{C_p(t)}{\tau_p^0} \ . \qquad (1)$$

ξ_0 and τ_p^0 are respectively the 'bare' constant friction coefficient and the relaxation time of the p-Rouse correlator corresponding to pure Rouse behavior (exponential decay of $C_p(t)$).

Then the memory function $\Gamma_p(t)$ in Eq. 1 only contains the non-Rouse contributions, which are related to the correlation function of the intermolecular forces acting on the tagged polymer segment. In the long wavelength (N/p) limit $(p \to 1)$ and in the framework of a 'pseudo-Markov' approximation[7–9] the solution of Eq. 1 can be expressed as:

$$\phi_{p\to 1}(t) = \frac{C_{p\to 1}(t)}{C_{p\to 1}(0)} = \exp\left[-\frac{\xi_0}{\tau_p^0}\int_0^t \frac{dt'}{\xi_0 + \xi(t')}\right] , \tag{2}$$

where $\xi(t) = \int_0^t \Gamma_p(t')dt'$ is a time-dependent effective friction coefficient which does not depend on N. The validity of this non-rigorous approximation[10] in the framework of this work will be discussed at the end of this paper. On the other hand, we note that Eq. 2 is only a formal expression, which is a consequence of the approximations made but independent of the particular form of $\Gamma_p(t)$. Equations 1 and 2 define the formal framework of this work.

To solve Eq. 2 we would need to construct a microscopic model for the memory function $\Gamma_p(t)$ suitable for the problem we are considering. The starting point is the general expression of the memory matrix elements $\Gamma_{m,n}(t) \propto \langle \mathbf{F}_m^Q(0)\mathbf{F}_n^Q(t)\rangle$, which describes the dynamic correlation of the intermolecular forces acting on segments m, n of the tagged chain at times 0 and t. Here, the upper index Q indicates that the time evolution of these magnitudes is controlled by the so-called 'projected' dynamics, i. e., by the propagator e^{iQLt}, where L is a Liouvillian taking into account all interactions and determining the real dynamics through the propagator e^{iLt} (see, e. g.[7,12]). Based on different assumptions, Schweizer[7] proposed a general memory function that, in principle, captures the effect of collective dynamics of the matrix around the tagged chain:

$$\Gamma_p(t) = A\int_0^N d\lambda \cos\left(\frac{p\pi\lambda}{N}\right)\int_0^{\sigma^{-1}} dk k^4 \omega_\lambda^Q(k,t) S^Q(k,t) \ . \tag{3}$$

Here $\lambda = |m-n|$; $A \equiv k_B T\rho_m d^6 g^2(d)$, where k_B is the Boltzmann constant; ρ_m the matrix segmental number density; d is the segmental hard core diameter defining the chain thickness;

and $g(d)$ the radial intermolecular distribution function averaged over all segments and calculated at d. Moreover, σ is the statistical polymer segment length and N the number of statistical segments (beads) in the chain. On the other hand, $S^Q(k,t)$ is the 'projected' collective dynamic structure factor and $\omega_\lambda^Q(k,t)$ the 'projected' intrachain dynamic structure factor of the tagged chain. Here k is the momentum transfer (wavevector). Equation 3 reflects the fact that the above defined force time correlation function decays via both tagged polymer and collective matrix projected dynamical motions. This general equation is our starting point for evaluating $\Gamma_{p\to 1}(t)$. For intermediate wavevectors $R_g^{-1} << k << \sigma^{-1}$ (R_g being the radius of gyration of the polymer chain) and times $t < \tau_R$ (τ_R being the Rouse time), $\omega_\lambda^Q(k,t)$ can be approximately expressed[13] as $\omega_\lambda^Q(k,t) \approx \omega_\lambda^Q(k)\exp\left[-\frac{k^2}{6}\langle r^2(t)\rangle_Q\right]$, where $\langle r^2(t)\rangle_Q$ is the 'projected' mean squared displacement of a polymer segment and $\omega_\lambda^Q(k)$ for a Gaussian coil is given by $\omega_\lambda^Q(k) = \exp\left(-\frac{k^2\sigma^2}{6}\lambda\right)$. Taking into account that for $N >> 1$, $\int_0^N d\lambda\cos\left(\frac{p\pi\lambda}{N}\right)\exp\left(\frac{k^2\sigma^2}{6}\lambda\right) \simeq \frac{k^2\sigma^2/6}{(k^2\sigma^2/6)^2+(p\pi/N)^2}$, in the long wavelength (N/p) limit $(p\to 1)$ and in the k-range of interest, Eq. 3 can be simplified as:

$$\Gamma_{p\to 1}(t) = 6A\sigma^{-5}\int_0^1 d\bar{k}\bar{k}^2\exp\left[-\frac{\bar{k}^2}{6\sigma^2}\langle r^2(t)\rangle_Q\right]S^Q(\bar{k},t) \tag{4}$$

where $\bar{k}$ is a dimensionless integration variable defined as $\bar{k} = k\sigma$. This equation for the memory function is still ill-defined because, as it has been mentioned, it contains 'projected' dynamic magnitudes instead of real ones. Thereby, in order to further evaluate Eq. 4, we need to postulate a plausible (and mathematically tractable) approximation for these magnitudes. To do that, first of all we will follow the essence of the so-called renormalization Rouse model (RRM), which was proposed by Schweizer[7] and later extended by Fatkullin and coworkers (see, e. e., the review[14]). In that framework, the matrix polymer motions are considered to be unaffected on relatively large length scales by the projection operation and thereby they follow their 'real' dynamics. Thus, $S^{Q}(\bar{k},t)$ in Eq. 4 should be replaced by the actual collective dynamic structure factor $S(\bar{k},t)$. On the other hand, in the first formulation of Schweizer, it was assumed that the 'projected' mean squared displacement of the probe segment $\langle r^2(t)\rangle_Q$ evolves following the actual Rouse behavior. Later, Fatkullin and coworkers introduced the concept of n-RRM, in which $\langle r^2(t)\rangle_Q$ is replaced by the actual mean squared displacement obtained in the $(n-1)$-RRM. As it is widely discussed in[14], there are some technical limitations how far one can go with this, in principle, iteration strategy. This fact limits in practice the renormalization procedure to $n \in [1,2,3]$. In any case, it is worthy of remark that, as it is recognized in[14], 'the renormalization procedure in general is nothing more than a heuristic way of closure the equations of motion' –a general and extremely difficult problem for systems with strong interactions. Then, the use of a renormalization ansatz with a given value of n, should be considered as a type of modeling, which, at the end, is only justified at phenomenological level, i. e., by the success of describing experimental findings. Schweizer[7] and Fatkullin and coworkers[14] applied this formalism trying to understand from a microscopic point of view the effect of entanglements in the long-time behavior of chain dynamics of high-molecular weight polymers –a problem different from that we are discussing here. In such an application, they assumed the same 'projected' dynamics for both, intra-chain motions of the probe and collective dynamics of the matrix. This approximation seems to be not suitable, at least for the problem discussed in this work (see, e. g.,[15] for a general critical discussion of such a procedure). Then, here, keeping in mind the essence of the RRM, we will also replace the 'projected' collective dynamics by the actual one but without the approximation above mentioned. Instead of we will use the ansatz recently proposed for describing the collective dynamics at 'intermediate length scales' [i. e., k-values lower than that at the first maximum of $S(k)$] of glasses[16] and polymers[17,18]. We note that in the case of polyisobutylene (PIB)[17,18], this ansatz was able to describe not only neutron scattering data ($k \gtrsim 0.2$ Å^{-1}), but also light scattering results ($k \sim 10^{-3}$ Å^{-1}). In the case of polymers and in the k-range of interest here ($R_g^{-1} < k < \sigma^{-1}$) the collective dynamic structure factor $S(k,t)$ in the framework of this ansatz can be approximated by $S(k,t) \simeq S(0)\exp[-(t/\tau_c)^{0.5}]$ where the collective time, τ_c, results to be approximately k-independent and given by $\tau_c = (M_L/K_{bulk})\tau_\alpha$[16–18]. Here K_{bulk} is the bulk modulus and M_L the longitudinal elastic modulus. The time τ_α is an *alpha* (structural) relaxation time corresponding to a $k \approx 0$ correlation function. In Refs.[17,18] it has been shown that this time can be identified with the α-relaxation time associated to a dielectric or viscoelastic response. We note that the time τ_α used in ref.[6] for calculating the ratio $\tau_{p=1}/\tau_\alpha$ (see Fig. 1) was just the α-dielectric time. On the other hand, the factor M_L/K_{bulk} should be of the order of 1 for most unentangled polymer melts. Here, following the work reported in Ref.[18] for PIB, we will assume $\tau_c \approx 2\tau_\alpha$. Then, in Eq. 4 $S^Q(\bar{k},t)$ will be approximated by $S^Q(\bar{k},t) \simeq S(0)\exp\{-[t/(2\tau_\alpha)]^{0.5}\}$. As τ_α is $\bar{k}$-independent, Eq. 4 can be written as:

$$\Gamma_{p\to1}(t) = 6A\sigma^{-5}S(0)\exp\left[-\left(\frac{t}{2\tau_\alpha}\right)^{0.5}\right]\int_0^1 d\bar{k}\bar{k}^2\exp\left[-\frac{\bar{k}^2}{6\sigma^2}\langle r^2(t)\rangle_Q\right]. \qquad (5)$$

Now, concerning $\langle r^2(t)\rangle_Q$, we can first consider what we will call the static limit, i. e., the range where τ_α is very large and thereby $S(\bar{k},t) \approx S(0)$. In Fig. 1, this limit corresponds to the lower values of $\log(\tau_{p=1}/\tau_\alpha)$ where the β-values corresponding to $\phi_{p\to1}(t)$ are of the order of 0.4. For the static limit, the time dependence of Eq. 5 only enters via $\langle r^2(t)\rangle_Q$. Then this is formally equivalent to the situation described by Schweizer[7] and Fatkullin and coworkers[14] in the framework of the n-RRM approach above mentioned. Therefore we will calculate $\Gamma_{p\to1}(t)$ in the static limit ($\Gamma^s_{p\to1}$) by the n-RRM methods but in the framework of our approximations. $\Gamma^{nRR}_{p\to 1}(t)$ can be expressed (see Supplemental Material) as:

$$\Gamma^{nRR}_{p\to 1}(t) \simeq C\left[\frac{\tau^{(n-1)RR}_{p=1}}{t}\right]^{(3/4)^n} \tag{6}$$

with $C = (3/2)9^{(3/4)}\pi^{(11/4)}AS(0)\sigma^{-5}N^{-3/2}$ and $n \in [1,2,3]$. In this expression, $\tau^{(n-1)RR}_{p=1}$ means the characteristic time corresponding to $p = 1$ (i. e., the Rouse time) for the $(n-1)$-RRM. We note that $\Gamma^{nRR}_{p\to 1}(t)$ is an inverse power law of time $\Gamma^{nRR}_{p\to 1}(t) \propto (1/t)^{\beta}$ with $\beta = (3/4)^n$. For such a case, we know[7–9] that the solution of Eq. 2 for $t >> t_c$ (t_c being a crossover time defined by the condition $\xi(t_c) \sim \xi_0$) is a stretched exponential function $\phi_{p\to 1} = \exp[-(t/\tau_{p=1})^{\beta}]$. As in the static limit $\beta \sim 0.4$ (see Fig. 1), it seems that the suitable n-RRM memory function for modeling such a limit should be that corresponding to n=3, $\Gamma^{3RR}_{p\to 1}(t)$ (β=27/64~0.42). Then we will consider that in the static limit $\Gamma^{s}_{p\to 1}(t) \equiv \Gamma^{3RR}_{p\to 1}(t)$. According to Eq. 6, the characteristic time that enters in $\Gamma^{3RR}_{p\to 1}(t)$ is $\tau^{2RR}_{p=1}$. This time can be expressed in terms of $\tau^{0}_{p=1}$ (see Supplemental Material) as $\tau^{2RR}_{p=1} = \tau^{0}_{p=1}(3/7)^{16/9}a^{7/3}$, where a is a structural parameter given by $a = (9^{3/4}\pi^{3/4}\Psi N^{1/2}/4)^{4/3}$. Here Ψ is a dimensionless parameter defined as $\Psi \equiv 6\rho_m d^6\sigma^{-3}g^2(d)S(0)$, which –according to numerical RISM calculations for Gaussian chains with $d = \sigma$[19]– results to be $\Psi \sim 0.72$. Then, taking into account Eq. 6 for $n = 3$, $\Gamma^{s}_{p\to 1}(t) \equiv \Gamma^{3RR}_{p\to}(t)$ can be written as: $\Gamma^{s}_{p\to 1} \simeq b(\tau^0_s t^{-1})^{27/64}$ where $b = (3/7)^{3/4}Ca^{63/64}N^{27/32}$ and $\tau^0_s \equiv \tau^0_{p=1}N^{-2}$ is the shortest time corresponding to pure Rouse behavior of the tagged chain (τ^0_s is usually known as the 'segmental time'). Now, according to Eq. 5 the memory function for the general case would be $\Gamma_{p\to 1}(t) \simeq \exp\{-[t/(2\tau_\alpha)]^{0.5}\}\Gamma^{s}_{p\to 1}(t)$ which can be written as

$$\Gamma_{p\to 1}(t) \simeq b\left(\frac{\tau^0_s}{t}\right)^{27/64}\exp\left[-\left(\frac{t}{2\tau_\alpha}\right)^{0.5}\right] \tag{7}$$

Taking into account the N-dependence of C and a, it can be shown that b results to be

N-independent. Thereby, $\Gamma_{p\to 1}(t)$ only depends –apart from structural parameters– on two relaxation times: τ_s^0 and τ_α. We note in passing that, although τ_s^0 is in some way a local (segmental) time, it corresponds by definition to pure Rouse behavior. Then, its temperature (T) dependence is determined by the same intermoleculaer interactions (friction) driving $\tau_{p=1}^0(T)$. This is not necessarily the case of $\tau_\alpha(T)$, where local intra-chain potentials can also play a role. Moreover, for the case of dynamically asymmetric blends, τ_s^0 corresponds to the chain dynamics of the fast component and τ_α to the collective dynamics of the slow component (matrix). Now, by using $\Gamma_{p\to 1}(t)$ given by Eq. 7 in Eq. 2 we can finally calculate $\phi_{p\to 1}(t)$ in the time range $t >> t_c$. It is straightforward to show that in this range Eq. 2 can be approximated by

$$\phi_{p\to 1}(t) \simeq \exp\left[-\Xi \int_0^t \frac{dt'}{\tilde{\xi}(t')}\right]. \tag{8}$$

with $\Xi \approx 3\pi^{-7/4}\Psi^{-7/3}N^{-2}$ and

$$\tilde{\xi}(t) = \int_0^t dt' \left(\frac{\tau_s^0}{t'}\right)^{27/64} \exp\left[-\left(\frac{t'}{2\tau_\alpha}\right)^{0.5}\right]. \tag{9}$$

Equations 8 and 9 allow numerically computing $\phi_{p\to 1}(t)$ for a generic case. This can be defined for instance by the following values of the parameters involved in Ξ and $\tilde{\xi}(t)$: τ_s^0=3.75×10^{-2} ns; τ_α ranging from 1.2×10^{-3} ns to 5×10^{8} ns; N=20; and Ψ=0.72 (see above). Some representative results obtained for $\phi_{p\to 1}(t)$ are displayed in Fig. 2. This figure also includes the fitting curves obtained by fitting $\phi_{p\to 1}(t)$ by a stretched exponential function $\phi_{p\to 1}(t)) = \exp[-(t/(\tau_{p=1})^\beta]$ as it was done for the experimental data of $\phi_{p\to 1}(t)$ reported in[6]. Figure 2 shows that, for fixed N, the shape and the time scale of $\phi_{p\to 1}(t)$ depend on the values of τ_α with respect to that of τ_s^0.

From the fitting of the $\phi_{p\to 1}(t)$ curves of Fig. 2 (and others not shown in the figure) we have obtained the values of the two fitting parameters $\tau_{p=1}$ and β. Taking into account the values of the input parameter τ_α, we can now check whether our theoretical results reproduce the 'universal' trend of β as a function of $\tau_{p=1}/\tau_\alpha$ shown in Ref.[6] and reproduced here in Fig. 1. This figure shows that our theoretical curve (continuous line) almost quantitatively describes the 'universal' behavior' displayed by both experimental and simulated data. We note that changing the input parameters of the generic case (i. e., the values of τ_s^0, τ_α and N) we change the time scale and shape of $\phi_{p\to1}(t)$ but we always find the same curve of β as a function of $\tau_{p=1}/\tau_\alpha$ reproduced in Fig. 1. For instance, the behavior of the experimental data shown in Fig. 1 suggests that even for fixed τ_s^0 and τ_α, the β-value obtained should strongly depend on N because larger N-values would imply larger values of $\tau_{p=1}^0$ and $\tau_{p=1}$ and thereby larger values of $\tau_{p=1}/\tau_\alpha$ as well. This behavior is nicely reproduced by our theoretical approach. By means of Eqs. 8 and 9 we have calculated $\phi_{p\to1}(t)$, fixing the values of τ_s^0 and τ_α (τ_s^0=0.0375 ns; τ_α=1×10^3 ns) and changing the value of N in the range $5 \leq N \leq 200$. The obtained $\phi_{p\to1}(t)$ are shown in Fig. 3 together with the corresponding stretched exponential fitting curves. Not only the time scale ($\tau_{p=1}$) but also the shape (β) clearly depend on N. The values obtained for β are plotted in Fig. 1 as a function of the corresponding $\tau_{p=1}/\tau_\alpha$. These points nicely follow the theoretical curve above described. These results not only mean a robust test of our theoretical approach but they also indicate that the relevant parameter determining the value of β is the ratio $\tau_{p=1}/\tau_\alpha$ as it was suggested in Ref.[6]. In the limit of $(\tau_{p=1}/\tau_\alpha) << 1$ (only experimentally realizable in the case of dynamically asymmetric blends) the density fluctuations of the matrix (slow component) are frozen in the time scale $\tau_{p=1}$. Then a tagged chain of the fast component is moving in a frozen matrix. From the perspective of the memory function, this implies that in the relevant timescale for tagged chain dynamics, $\Gamma_{p=1}(t)$ reduces to an inverse power law function, $\Gamma_{p=1}(t) \propto t^{-27/64}$ and thereby $C_{p\to1}(t)$ becomes a stretched exponential function with β

= 27/64. As soon as the matrix density fluctuations start to relax in a shorter time scale (τ_α), the forces on the tagged chain relax faster as well and thereby $C_{p\to1}(t)$ is getting less and less non-exponential (β increases). In the limit $(\tau_{p=1}/\tau_\alpha)\ >>\ 1$, we recover the Rouse assumption of uncorrelation between forces and $C_{p\to1}(t)$ becomes purely exponential. It is noteworthy that the experimental behavior of β as a function of $(\tau_{p=1}/\tau_\alpha)$ shown in Fig. 1 is a universal trend, which contains –encoded in the relevant parameter $(\tau_{p=1}/\tau_\alpha)$– many different experimental situations (different polymers, temperature, blend composition, etc). The theoretical approach here proposed gives an explanation of this universal behavior in terms of the physical picture described above and captures the relevance of the parameter $(\tau_{p=1}/\tau_\alpha)$.

As it has been mentioned at the beginning, the theoretical approach proposed in his work involves the use of the so-called pseudo-Markov approximation for obtaining Eq. 2 from Eq. 1. Although this procedure cannot be considered as rigorous, the results included in the Supplemental Material (section III) show that it is a plausible approximation in the framework of our assumptions: (i) long wavelength (N/p) limit; (ii) $\Gamma_{p=1}(t)$ given by Eq. 7 and (iii) stretched exponential form for $C_{p\to1}(t)$. On the other hand, we can argue that the ansazt used (RRM with n=3) to model the so-called static limit $[(\tau_{p=1}/\tau_\alpha) << 1]$ is only based on phenomenological grounds. However, the question is that as far as to our knowledge, there is not any other model that can address the rich phenomenology found in this regime. This phenomenology is nowadays well-established thanks to the results obtained by exploring the dynamics of the so-called dynamically asymmetric polymer blends (see e. g.[3,5,6,20]) and references therein). In any case, we would like to emphasize that the essence of our approach is the physical mechanism mentioned above and not the particular model used to describe the static limit. For instance, if we use the 2-RRM instead of the 3-RRM, to fix the static limit we obtain a different value of β for this limit ($\beta \approx 0.56$) but qualitatively a similar $\beta(\tau_{p=1}/\tau_\alpha)$ behavior from this value towards 1 (see Fig. 1).

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can be written as $\phi_{p\to 1}(t) \simeq \exp[-\tilde{q}^2 \int_0^t F_{PM}(s)ds]$ ('PM' refers to 'Pseudo-Markov') which can be viewed as a Gaussian-like approximation of a general cumulant expansion (see, e. g., Ref.[11]) of $\phi_{p\to 1}(t) = \exp[-\tilde{q}^2 \int_0^t F(\tilde{q}, s)ds]$. This suggests that the 'pseudo-Markov' approximation should be formally equivalent to a Gaussian-like approximation, although we note that from a statistical mechanics perspective, such a Gaussian theory in the time domain would be different than the Mori-Zwanzing.

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FIGURE CAPTIONS

Figure 1: β-parameter corresponding to $\phi_{p\to1}(t)$ as function of $\tau_{p=1}/\tau_\alpha$. Symbols are data from Ref.[6]: (■) polyisoprene (PI), (⧫) polypropylene glycol (PPG), and (▼) polyethylene oxide (PEO) homopolymers; (⊠) PI in PI-polyvinylethylene blends, (⊞) PI in PI-polyterbutylstyrene blends, and (▲) PEO in PEO-poly(methyl methacrylate) blends. Continuous line is the theoretical curve for a generic case obtained in this work. The dotted points along the line correspond to calculations with τ_s^0 and τ_α fixed and N variable (see the text and Fig. 3). The dashed line also corresponds to this work but with a different approach for the memory function in the 'static' limit (see the text).

Figure 2: $\phi_{p\to1}(t)$ obtained by solving numerically Eqs. 8 and 9 for a generic case (see the text). The values of τ_α are indicated in the figure and follow the arrow. The value of τ_s^0 was 3.75×10^{-2} ns and N=20. The continuous lines are fitting curves by a stretched exponential function.

Figure 3: $\phi_{p\to1}(t)$ obtained by means of Eqs. 8 and 9 with fixed values of τ_s^0 (0.0375 ns) and τ_α (1×10^3 ns) and the different values of N indicated in the figure (they follow the arrow). The continuous lines are fitting curves by a stretched exponential function.

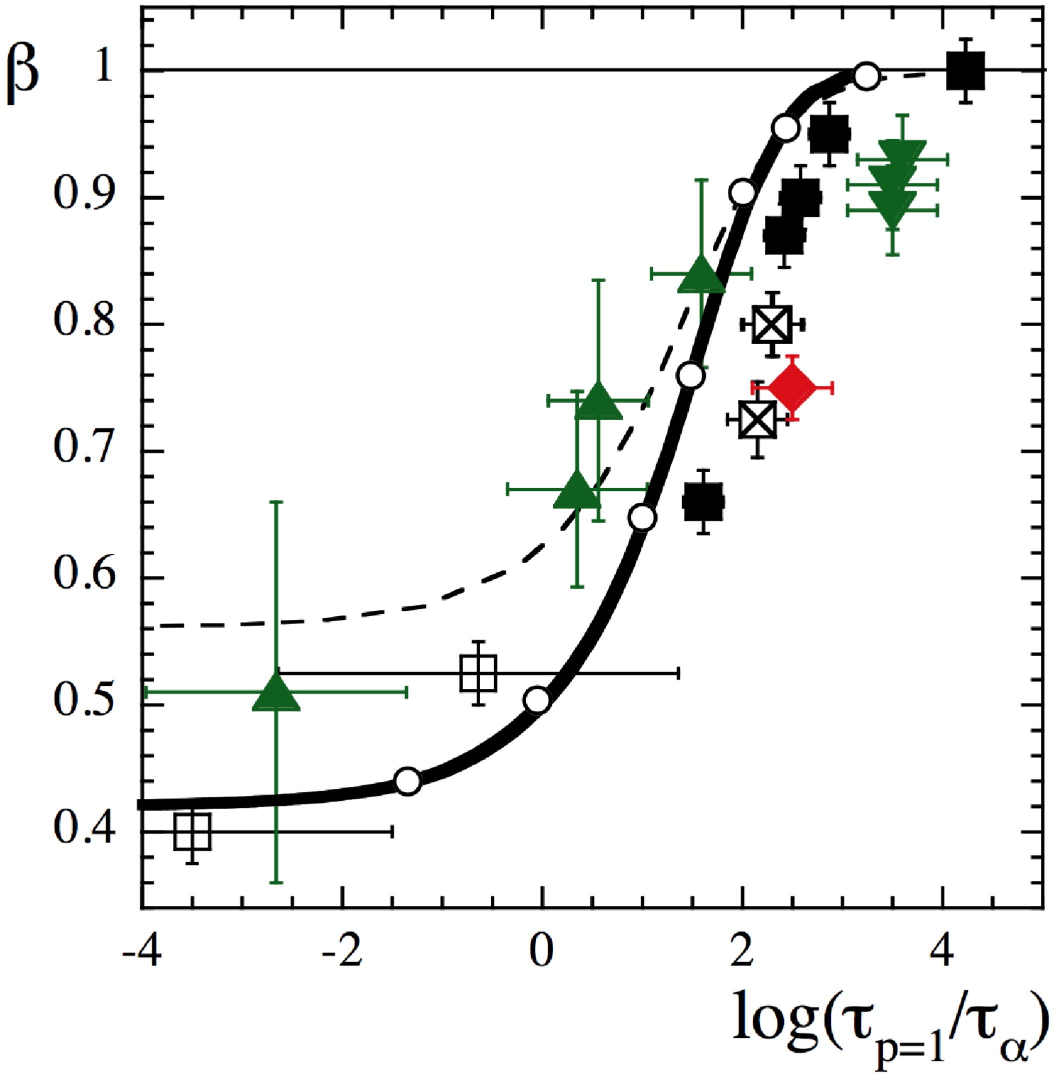

FIG. 1:

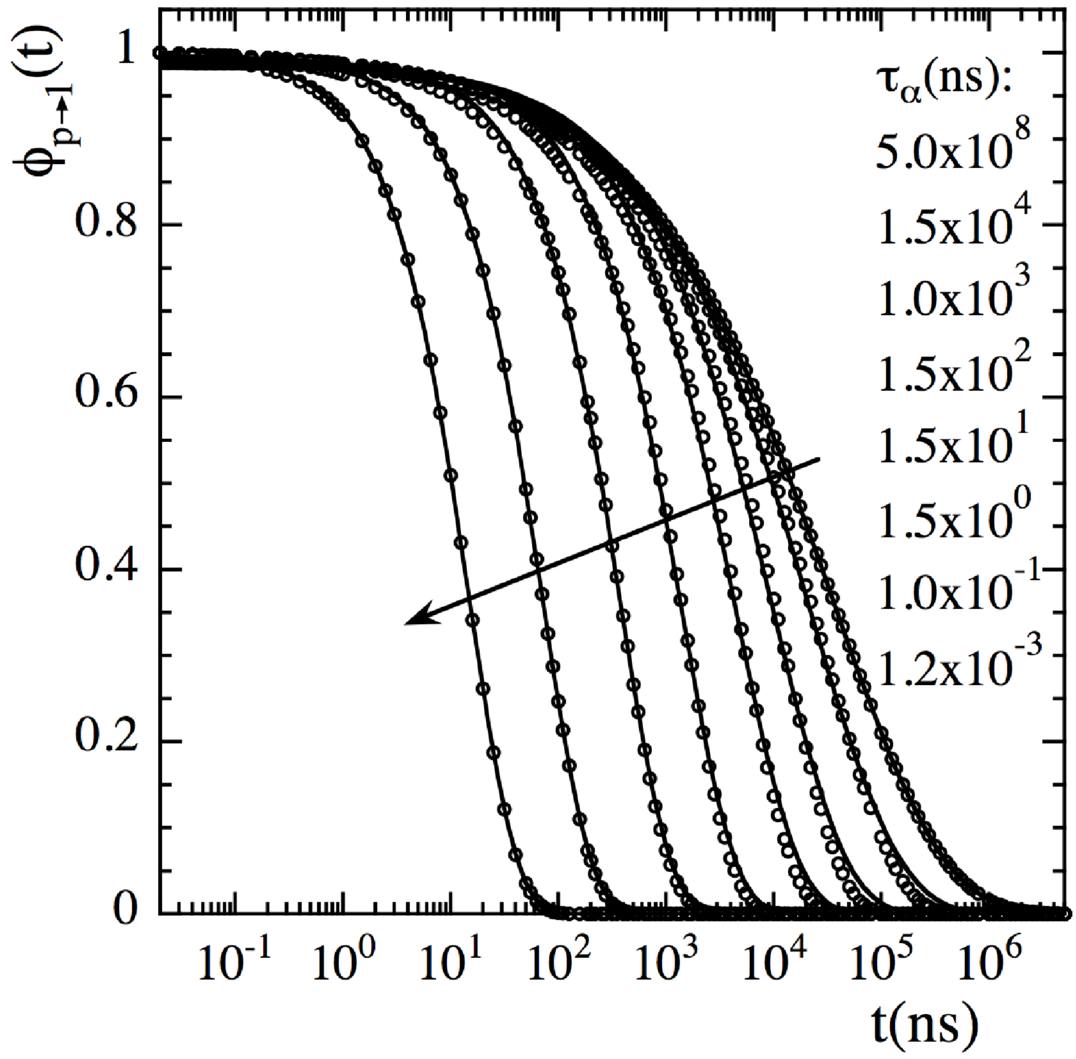
$\phi_{p\to 1}(t)$
1
0.8
0.6
0.4
0.2
0
τ_α(ns):
5.0×10^{8}
1.5×10^{4}
1.0×10^{3}
1.5×10^{2}
1.5×10^{1}
1.5×10^{0}
1.0×10^{-1}
1.2×10^{-3}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
t(ns)

FIG. 2:

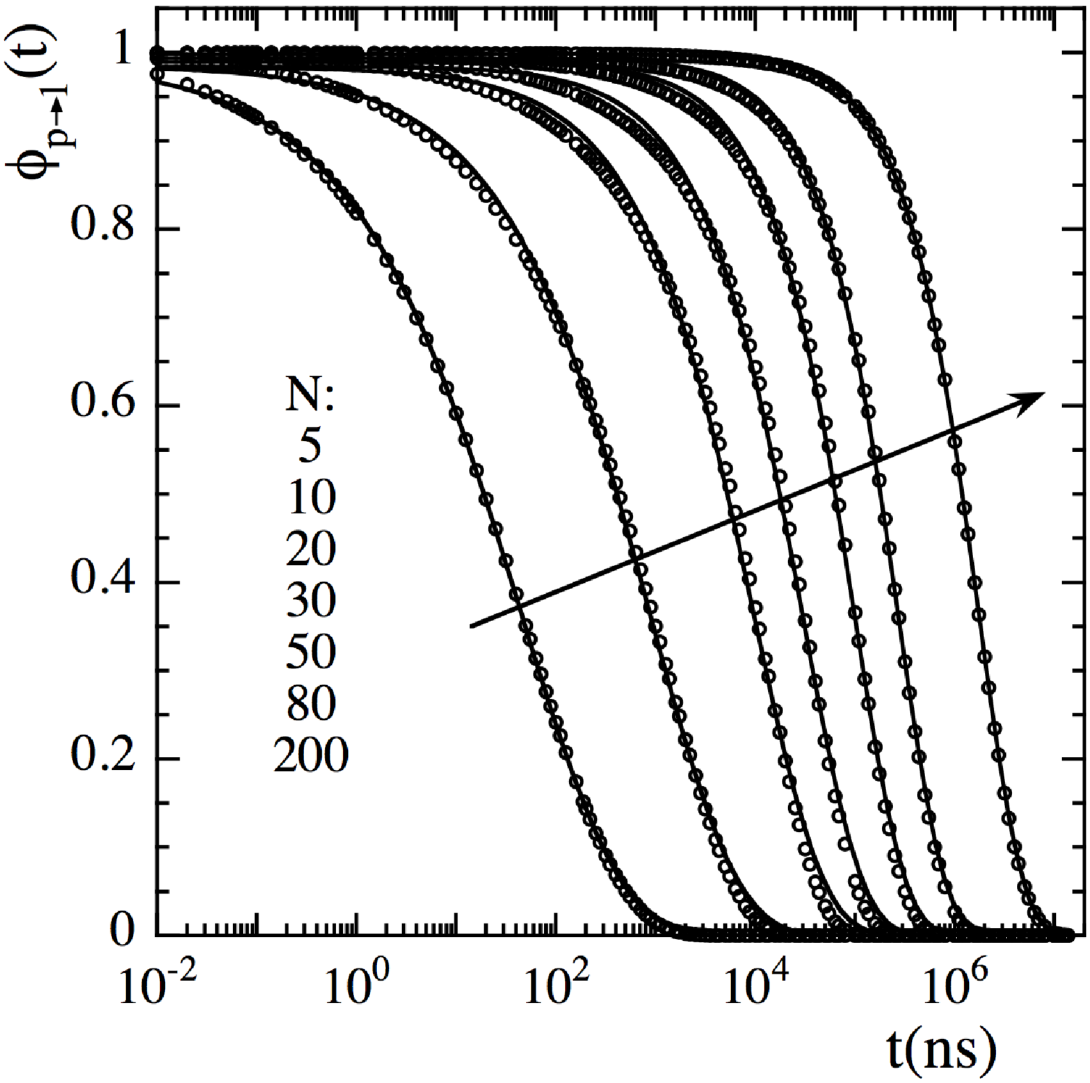
$\phi_{p\to 1}(t)$
1
0.8
0.6
0.4
0.2
0
10^{-2}
10^{0}
10^{2}
10^{4}
10^{6}
t(ns)
N:
5
10
20
30
50
80
200

FIG. 3:

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Universal trend of the non-exponential Rouse mode relaxation in polymer systems: A theoretical interpretation based on a generalized Langevin equation

J. Colmenero

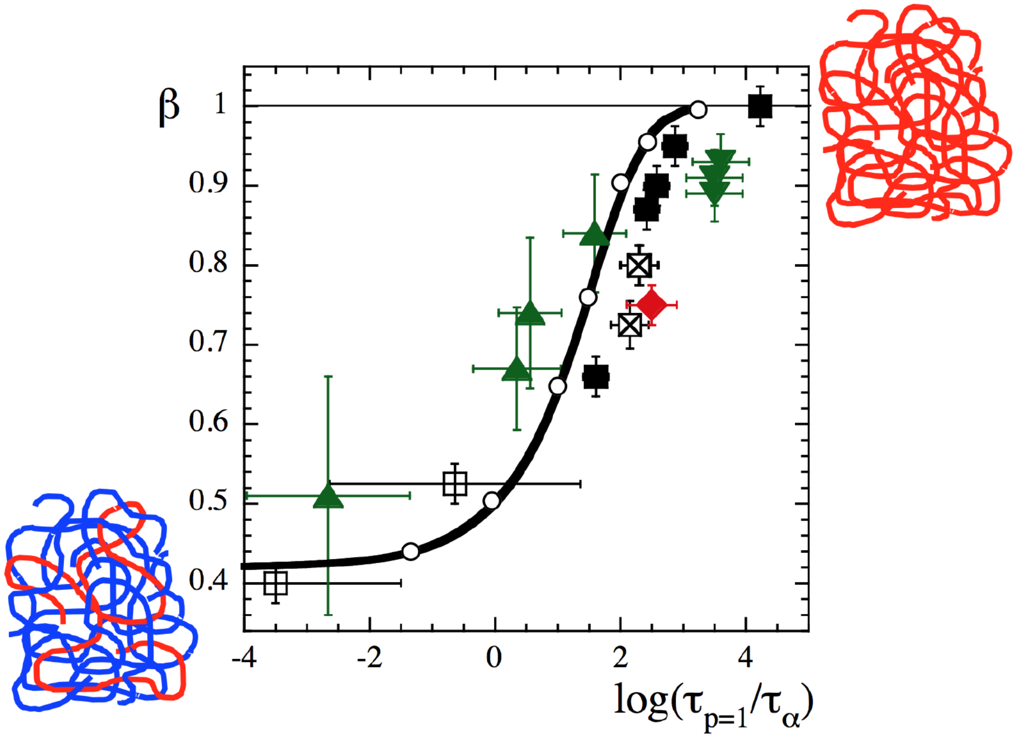

FIG. 4: