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Non-exponential Rouse correlators and generalized magnitudes probing chain dynamics

J. Colmenero [1]

Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, E-20018 San Sebastián, Spain

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ABSTRACT

Inspired by the generalized Langevin equation (GLE) formalism with some approximations, we have proposed a method to generalize the Rouse expression of the magnitudes probing chain dynamics, taking into account the non-exponential character of the Rouse mode correlators. In this way, generalized expressions for the incoherent neutron scattering function and for the End-to-End relaxation – which give rise in the frequency domain to the dielectric 'normal mode' relaxation – have been obtained. These magnitudes have been checked by means of fully atomistic molecular dynamics (MD) simulations corresponding to pure poly(ethylene oxide) (PEO) and to PEO in an asymmetric blend with poly(methyl methacrylate) (PMMA). Moreover, the results obtained also seem to give support to the unified scenario recently proposed for explaining the non-exponential relaxation of the long-wavelength Rouse modes in polymer systems in terms of the effect of density fluctuations (α-process) on chain dynamics.

1. Introduction

Chain dynamics dictate the viscoelastic properties of melts of polymer systems. Nowadays it is generally assumed that the Rouse model [1] provides a suitable description of chain dynamics of unentangled polymer melts, i.e., melts of chains of molecular weight lower than a certain limit ('entanglement mass'). The Rouse model can also be seen as a 'fixed point' of all theories of polymer dynamics in which linear connected objects are ideal and subjected to local dissipation. For instance, in the chain dynamics theories of entangled polymers based on the 'tube' concept [2,3], the Rouse model is a basic ingredient because chains move ideally (Rouse behavior) until they feel the effects of the confining tube.

In the framework of the Rouse model, a tagged chain is represented as a string of N beads of equal mass connected by harmonic springs of constant $3k_BT/\ell^2$, with ℓ the bond length and k_B the Boltzmann constant. The effective interaction experienced by the chain is given by a friction coefficient ξ and a set of stochastic forces $\vec{f}_j$. Excluded volume interactions are neglected. The chain normal (Rouse) mode $\vec{X}_p(t)$ of index $p = 1 \ldots N-1$ (wavelength N/p) is defined as $\vec{X}_p(t) = N^{-1}\sum_{j=1}^{N}\vec{r}_j(t)\cos\left[(j-1/2)p\pi/N\right]$, with $\vec{r}_j$ the vector giving the position of the j-bead in the chain. $\vec{X}_p(t)$ follows the equation of motion

$$2N\xi\frac{d\vec{X}_p(t)}{dt} = -K_p\vec{X}_p + \vec{g}_p \qquad (1)$$

with $K_p = 24Nk_BT\ell^{-2}\sin^2(p\pi/2N)$. The external force for the p-th mode is $\vec{g}_p = 2\sum_{j=1}^{N}\vec{f}_j(t)\cos\left[(j-1/2)p\pi/N\right]$.

The Rouse model fully neglects spatial and time correlations of the stochastic forces, i.e., $\left\langle\vec{g}_p(t')\vec{g}_q(t'')\right\rangle = 12N\xi k_BT\delta_{pq}\delta(t-t')$. The former two approximations yield, respectively, orthogonality of the Rouse modes and exponential relaxation of the Rouse correlators, leading to the expression for the correlation function of the p-mode, $C_p(t) = \left\langle\vec{X}_p(t)\vec{X}_p(0)\right\rangle$, $C_p(t) = \frac{\ell^2}{8N}\sin^{-2}\left(\frac{p\pi}{2N}\right)e^{-\frac{t}{\tau_p}}$ with the relaxation time given by $\tau_p = \frac{\ell^2\xi}{12k_BT}\sin^{-2}\left(\frac{p\pi}{2N}\right)$. Due to the effects of local potentials and chain stiffness at short length scales in real systems, Rouse model results are usually discussed in the long wavelength (N/p) limit. In this range $\sin^2\left(\frac{p\pi}{2N}\right)\approx\left(\frac{p\pi}{2N}\right)^2$.

Orthogonality of the Rouse modes and exponentiality of the Rouse correlators are the two main assumptions of the Rouse model and are the basis of the derivation of the magnitudes probing chain relaxations [3].

These magnitudes (incoherent and coherent scattering functions, dielectric 'normal mode relaxation', etc.) are thereby constructed in terms of exponential Rouse mode correlators. For homopolymer melts this seems to be a rather good approximation in the high temperature range (with respect to the glass-transition temperature T_g) were most of the measurements of the chain dynamics are usually carried out and taking into account that the relevant modes are the slowest ones. However, significant deviations from the exponentiality of these mode relaxations have been recently reported in the low temperature range approaching T_g [4]. This range was accessible by using a thermo-stimulated depolarization current (TSDC) technique, which, on the

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E-mail address: juan.colmenero@ehu.es.

[1] Also at Donostia International Physics Center, Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain.

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other hand, allows isolating experimentally the dielectric response of the slowest Rouse mode ($p = 1$) relaxation. As usually, deviations from exponentiality were accounted for by using the well known stretched exponential function $C_p(t) \approx \exp\left[-(t/\hat{\tau}_p)^{\beta}\right]$. The β values characterizing these deviations resulted to be correlated with the ratio $\hat{\tau}_R/\tau_\alpha$ being $\hat{\tau}_R = \hat{\tau}_{p=1}$ and τ_α the characteristic relaxation time of the α-relaxation in the system. This process is a general feature of glass-forming systems and it is associated with the evolution of density fluctuations in the system at the inter-macromolecular scale (first maximum of the static structure factor $S(Q)$ in the case of polymers). In the high temperature range, τ_α uses to be well separated from that of the slowest chain mode relaxation (τ_R), thereby implying that the statistical independence of both processes could be taken as a good approximation. However, as soon as the temperature decreases approaching the T_g of the polymer melt, both processes approach each other, implying some kind of coupling between both. This would break the Rouse assumption of uncorrelation of the random forces acting on a polymer chain and would explain the non-exponential behavior of the Rouse mode relaxation. Although the possible coupling between chain dynamics and α-relaxation has been widely discussed in the literature concerning the problem of the different temperature dependence of both processes approaching T_g (see, e.g. [5–8]), the effect of local density fluctuations (α-relaxation) on the non-exponentiality of the Rouse mode correlators in homopolymers has started to be recognized only recently [4].

On the other hand, in the case of the chain dynamics of the fast component of asymmetric polymer blends, strong deviations from the exponential relaxation of the slowest Rouse modes are well documented [9–11]. Asymmetric blends are miscible polymer systems A/B where the two components display very different segmental mobility or T_gs. In this case, the deviations from the exponentiality of the Rouse mode relaxation also depend on temperature, being negligible at high temperature where the dynamic contrast between the two components vanishes. As soon as the temperature decreases, the α-relaxation of the slow component of the blend will slow down and its relaxation time will approach the characteristic times of the slowest Rouse mode relaxation of the fast component in the blend. This situation seems to be similar to that described above for homopolymer melts, being now the relevant density fluctuations those associated with the freezing of the slow component in the blend. In fact, based on experimental results of polyisoprene (PI) and PI in different blends, it has been reported [4] that the β values corresponding to the slowest ($p = 1$) Rouse mode of the fast component in a blend follow the same trend with respect to the ratio $\hat{\tau}_R/\tau_\alpha$ than those corresponding to the homopolymer case, being τ_α the characteristic time of the relevant density fluctuations in the system: the α-process for the homopolymer melt and the α-process of the slow component in the blend. We note that in the case of the asymmetric blends we can face situations where $\hat{\tau}_R/\tau_\alpha \leq 1$, something that would not be possible in the case of homopolymers. Thus, in general, we should expect stronger deviations from the exponentiality of $C_{p=1}(t)$ [called $C_R(t)$] – i.e., lower values of β – in the case of blends.

As it has been mentioned above, in the framework of the Rouse model the non-exponentiality of the Rouse mode correlators will directly affect the magnitudes probing chain dynamics because these magnitudes are written in terms of such correlators. We have also to take into account that in the tube-reptation theories for well entangled polymers, chain dynamics at times $t < \tau_e$ – where τ_e is the so-called entanglement time – is also described in terms of the Rouse model, thereby being affected as well by the non-exponential behavior of Rouse correlators. Moreover, in the case of the End-to-End correlation function, the mathematical expression is formally the same in the framework of both, Rouse and reptation theories. With these ideas in mind, in a recent paper [12] we have generalized the Rouse expressions for the mean squared displacement of a polymer segment $\langle r_s^2(t)\rangle$ and that of the center of mass of the chain $\langle R_{CM}^2(t)\rangle$, by considering the non-exponential character of the Rouse mode relaxation. Starting from these expressions and taking into account the Gaussian approximation, we have also proposed equations for the corresponding incoherent scattering functions $F_{self}^{s}(Q,t)$ and $F_{self}^{CM}(Q,t)$. The results obtained were checked by using molecular dynamics (MD) simulations data of poly(ethylene oxide) (PEO) in asymmetric blends with poly(methyl methacrylate) (PMMA). In the present work, after briefly summarizing the main approximations used to generalize the Rouse expressions for $\langle r_s^2(t)\rangle$ and $\langle R_{CM}^2(t)\rangle$, we will extend this approach to the case of the End-to-End correlation function. Finally, we will apply the results obtained to MD-simulation data of both, bulk PEO and PEO in PEO/PMMA blends.

2. A simple approach inspired by the GLE formalism

As it has been commented in the Introduction section, the exponential nature of the relaxation of the Rouse modes arises as a consequence of neglecting time correlations of the random forces acting on a polymer segment. In a general formulation (generalized Langevin equation, GLE, formalism) for the time evolution of the Rouse mode correlators, the correlation between the random forces can be introduced within a memory kernel in the Langevin equation. This term effectively produces an extra friction non-local in time and thereby a non-exponential decay of the mode relaxation. The standard Rouse behavior and the corresponding constant friction are recovered when the memory function decays to zero at very short times in comparison to those characteristic of the mode relaxation. In the framework of a simplified GLE formalism [13], we can write an integro differential equation for the time evolution of a Rouse correlator, $C_p(t) = \left\langle \vec{X}_p(t)\vec{X}_p(0)\right\rangle$

$$\frac{dC_p(t)}{dt} + \frac{1}{\xi_o}\int_0^t dt'\,\Gamma(t-t')\,\frac{dC_p(t')}{dt'} = -\frac{C_p(t)}{\tau_p^o}. \tag{2}$$

We note that in order to arrive to Eq. (2), the fast decaying 'Rouse contribution' has been extracted from the general memory function of the GLE formalism [13,14]. In this way, the memory function $\Gamma(t)$ in Eq. (2) only contains the non-Rouse contribution. As consequence of this partition, ξ_o and τ_p^o in Eq. (2) are respectively the 'bare' constant friction coefficient connected with the fast local motions and the relaxation time of the Rouse correlator corresponding to pure Rouse behavior. Moreover, as it was described in ref. [12], we considered two additional approximations. First, $\Gamma(t)$ was assumed to be independent of the length scale (wavelength of the mode, N/p) due to the fact that we were interested in the long wavelength (N/p) limit. Moreover, based on the arguments widely discussed in ref. [12], a second step was to consider a 'pseudo-Marcovian' approximation and to replace the convolution integral of Eq. (2) by a time local product. As it was discussed in ref. [12], this strong approximation would be justified under the assumption that in the long wavelength (N/p) limit, $\Gamma(t)$ decays faster than $C_p(t)$. This is equivalent to say that $\Gamma(t = \hat{\tau}_p) \approx 0$, where $\hat{\tau}_p$ is the relaxation time of $C_p(t)$ (see below). In ref. [12], this assumption was numerically checked by means of MD-simulations of PEO/PMMA system, also considered in this work. It was obtained that $\Gamma(t = \hat{\tau}_p) \approx 0$ for the range $N/p \geq 10$ (see Fig. 7 in ref. [12]), i.e., the relevant long wavelength range considered here (see Section 5).

In the framework of the above-described approximations and defining a time dependent effective friction coefficient as $\xi(t) = \int_0^t dt'\Gamma(t')$ the solution of Eq. (2) can be expressed as

$$\varphi_p(t) = \frac{C_p(t)}{C_p(0)} = \exp\left[-\frac{\xi_o}{\tau_p^o}\int_0^t \frac{dt'}{\xi_o + \xi(t')}\right]. \tag{3}$$

To proceed further with Eq. (3) we have two possibilities. The first, and more rigorous one, would be to construct a microscopic theory for