Notes

Stress Relaxation in Polymer Melts and Solutions: Bridging between the Breathing and Reptation Regimes

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Received December 19, 1994
Revised Manuscript Received May 9, 1995

The dynamics of a single chain in polymer melts and semidilute solutions has been described mainly within the context of the de Gennes's[1] and Doi–Edwards'[2] (DE) reptation model. The original reptation model has been concerned with the late stage dynamics (*i.e.*, diffusion and stress relaxation) and builds on a Rouse-type curvilinear diffusion coefficient of a chain segment. The Rouse motion of the chain subject to the tube constraints is thus envisaged to promote the diffusion of loop "defects" (extending out of the tube contour), thereby enabling the whole chain to reptate along its contour. For polymer melts the model has been extended to shorter times t where two new regimes were found:[2,3] (i) $t < \tau_e$, where τ_e is the entanglement time, in which the chain moves by free Rouse motion and (ii) and intermediate "breathing" regime $\tau_e < t < \tau_R$ (with τ_R denoting the Rouse time), where a chain segment (n) follows anomalous Rouse diffusion *along* the tube, $\langle \Delta l_n^2 \rangle \sim t^{1/2}$ (with l_n denoting the segment position along the tube), so that $\langle \Delta r_n^2 \rangle \sim t^{1/4}$ in real space. As a result, the contour length fluctuates; however, the chain does not experience yet a truly reptative motion. These extensions to short times have been partially confirmed by molecular dynamics simulations.[4]

A similar effect related to these contour length fluctuations has been suggested for the stress relaxation function.[5,6] According to the DE model, stress is relaxed when the chain ends pass (for the first time) through an entanglement point. Since we consider times during which the displacement $\langle |\Delta l_n(t)| \rangle$ remains negligible relative to the contour length L, the fraction of the original tube which has not yet been reached by the chain ends at time t must have the form $1 - \beta \langle \Delta l_n(t)^2 \rangle^{1/2}/L$, where β is a numerical constant, resulting from the first passage time nature of this problem. It follows that the stress relaxation function in the breathing regime, $G_b(t)$ (with the plateau modulus normalized to unity), obeys

$$G_b(t) \simeq 1 - \alpha \left(\frac{N_e}{N}\right)^{1/2} \left(\frac{t}{\tau_R}\right)^{1/4} \tag{1}$$

where N_e is the entanglement index (number of "monomers" between two consecutive entanglement points), and α is another numerical constant (combining β and the numerical constant coming from $\langle \Delta l_n(t)^2 \rangle$). At even shorter times, times shorter than the entanglement time τ_e, stress relaxes by free Rouse motion.

We note in passing that, although the DE model has by now become widely accepted, it is still under debate from the theoretical viewpoint.[7] There is also an apparent discrepancy between the DE model and the experimental observation regarding the (zero-frequency) shear viscosity η: the model predicts $\eta \sim N^3$ for large N, while the experiment yields[7] $\eta \sim N^{3.4\pm0.2}$. This apparent discrepancy has been recently resolved, however, by O'Connor and Ball[8] using the extended DE model, which includes both the breathing and reptation relaxation regimes. By considering also tube renewal effects, they obtain a wide intermediate regime for η *vs* N which explains much of the experimental data. This strongly hints for the correctness of the DE approach, which we subsequently use.

In this short paper we derive a unified expression for the stress relaxation function for the time regime $t > \tau_e$, which encompasses both breathing and reptation regimes. Our approach is based on a precise knowledge of the curvilinear diffusion process of the chain end segments. The latter may be described in terms of a *time-dependent* diffusion coefficient $D(t)$ via a generalized diffusion equation for the probability density $P(x,t)$

$$\frac{\partial P}{\partial t} = \int_0^t \mathrm{d}t'\, D(t-t') \frac{\partial^2 P(t')}{\partial x^2} \tag{2}$$

Equivalently, $D(z)$—the Laplace transform of $D(t)$—is expressed, within linear response theory, in terms of the (one-dimensional, curvilinear) mean-square displacement (MSD) as[9]

$$D(z) = \frac{z^2}{2} \int_0^\infty e^{-zt} \langle (\Delta x(t))^2 \rangle \tag{3}$$

(Using eq 2 to evaluate $D(z)$ in eq 3 leads to an identity.) The curvilinear MSD of an arbitrary segment has been calculated by Doi and Edwards.[2] Using their expression for the chain end segments (replacing N by N/N_e and the monomer length b by the real-space entanglement length a), we obtain explicitly

$$D(z) = D_R + \frac{2(N/N_e)a^2}{3\pi^2 \tau_R} \sum_{p=1}^{\infty} \left[1 + \frac{p^2}{z\tau_R}\right]^{-1} \tag{4}$$

where D_R is the (long time, $z = 0$) Rouse diffusion constant. (Similar, but essentially numerical, approaches have been described by O'Connor and Ball[8] and by Ketzmerick and Ottinger.[10] A time-dependent diffusion coefficient was also introduced in this context by des Cloizeaux.[11] However, he did not use a memory kernel in the diffusion equation, as in eq 2, so that his approach is less accurate than ours in this respect.)

Consider now the stress relaxation function. According to the DE reptation model, it is proportional to the (time-dependent) survival probability of a particle diffusing between two absorbing walls, starting with uniform initial conditions. Given $D(z)$, we can now proceed to calculate this survival probability. Laplace transforming eq 2 ($t \rightarrow z$) and solving—in Laplace space—for the survival probability $\Psi(z)$ (as in the standard reptation theory), we obtain

$$\Psi(z) = \frac{8}{\pi^2} \sum_{p,\mathrm{odd}} p^{-2}\left[z + \frac{p^2\pi^2}{L^2} D(z)\right]^{-1} \tag{5}$$

Here L is the box size and is set equal to the contour length, thereby obeying the equality

$$L = (N/N_e)a \tag{6}$$

(Note that in semidilute solutions $a \simeq \xi$, the blob size.[1]) Equations 5 and 4 give a unified expression for the survival probability, and so for the stress relaxation function (since $G(t) \propto \Psi(t)$), that smoothly interpolates between the breathing and reptation regimes. (The complex modulus $G^*(\omega)$ is obtained under the substitution $G^*(\omega) = i\omega\Psi(i\omega)$.)

We now consider the short-time (or large z) behavior of these equations where $D(z) \ll zL^2$, which encompasses both breathing and short-time reptation. Equation 5 may be rewritten as

$$\Psi(z) = \frac{1}{z}\left\{1 - \frac{8}{L^2}\frac{D(z)}{z} \sum_{p,\mathrm{odd}} \left[1 + \frac{p^2\pi^2}{L^2}\frac{D(z)}{z}\right]^{-1}\right\} \tag{7}$$

Transforming the sum to an integral and performing the integration, we obtain

$$\Psi(z) \simeq \frac{1}{z}\left[1 - \frac{2}{L}\left(\frac{D(z)}{z}\right)^{1/2}\right] \tag{8}$$

Considering now the breathing regime. For $z\tau_R \gg 1$ we may convert the sum in eq 4 to an integral, which is evaluated to yield

$$D(z) \simeq \frac{1}{3\pi}\frac{N}{N_e}a^2\left(\frac{z}{\tau_R}\right)^{1/2} \tag{9}$$

Upon substitution of eq 9 into eq 8 (using also eq 6), we find

$$\Psi(z) \simeq \frac{1}{z} - \frac{2}{(3\pi)^{1/2}}\left(\frac{N_e}{N}\right)^{1/2}\frac{1}{z^{5/4}\tau_R^{1/4}} \tag{10}$$

This result is already very useful for obtaining the viscoelastic spectra. Inverting the Laplace transform, we obtain in the time domain

$$\Psi(t) \simeq 1 - \alpha\left(\frac{N_e}{N}\right)^{1/2}\left(\frac{t}{\tau_R}\right)^{1/4} \tag{11}$$

with

$$\alpha = \frac{2}{(3\pi)^{1/2}\Gamma(5/4)} \simeq 0.72 \tag{12}$$

(This is in fact the first analytic evaluation of the value of α.) The decay form of eq 11 has been previously suggested[5] and may be understood by looking at the MSD for the chain ends, as explained above.

For $\tau_R \ll t \ll \tau_d$ we may use $D(z) = D_R$ in eq 8, and in the time domain we obtain the well-known short-time reptation result

$$\Psi(t) \simeq 1 - 4\left(\frac{t}{\pi^3\tau_d}\right)^{1/2} \tag{13}$$

where $\tau_d = L^2/(D_R\pi^2)$ is the reptation time.[2] Equations 5 and 4 are thus seen to bridge smoothly between the breathing and reptation regimes. They can be useful in the numerical evaluation of the complex modulus $G^*(\omega)$, *e.g.*, as was done for "living" polymer systems.[12]

References and Notes

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MA946311+