Dynamics of Entangled Polymer Layers: The Effect of Fluctuations

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Dynamics of thin layers of entangled polymers is considered theoretically using a generalization of the reptation model. It is shown that monomer-monomer excluded volume interactions suppress long-range motion of polymer chains, giving rise to an exponential increase of the longest relaxation time and the viscosity η as the layer thickness is decreased. Explicit dependencies of $\ln \eta$ on concentration, molecular weight, and thickness are obtained.   [S0031-9007(98)05294-6]

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Rheology of high molecular weight polymers attracts considerable scientific attention [1,2]. Recent advances in the understanding of polymer dynamics on the molecular level are connected with the idea of entanglements [3], the tube model, and the reptation theory [4,5]. The latter was definitely successful in describing rheology of bulk entangled polymers, yet some basic relationships like molecular weight dependence of viscosity were not completely understood. This is even truer for confined polymer systems, like a concentrated polymer solution or a melt in a narrow slab between parallel solid plates. In some of the previous studies [6,7] the dynamical implications of confinement were attributed to the effect of thin "glassy" layers formed near the plates due to specific monomer-surface interactions.

In this Letter I show that the effect of confinement is important (leading in some cases to an exponential increase of viscosity) even with no specific monomer-surface interactions, i.e., for purely repulsive plates.

It is known [6,8] that equilibrium properties of polymer layers are nearly not affected by the surfaces at distances larger than the static correlation length ξ. Thus the static surface effect is negligible if the layer thickness $H \gg \xi$; this condition is assumed below (note that in a concentrated solution or a melt ξ is of order of the monomer size b). In this case polymer chains locally obey Gaussian statistics, and their global statistics can be deduced from the mirror-image principle. The same principle is valid also for dynamics within the Doi-Edwards reptation model [9]: Any distribution function in the layer can be obtained from the bulk distribution function by superimposing all (multiple) reflections from the surfaces. Therefore, the reptation theory predicts the same stress relaxation time in the layer ($H \gg \xi$) as in the bulk, i.e., no appreciable effect of confinement.

The Doi-Edwards theory does not take into account the effect of monomer-monomer interactions on the reptation dynamics. This effect was proved to be important [10,11] for bulk reptation dynamics of very long polymers, in the regime $N \gg N_e^3$, where $N_e \sim 50$ is the number of monomers per entanglement. Below I show that this effect is even more important for polymer layers.

Qualitative picture.—The shear viscosity of an entangled system is $\eta = G_e \tau_{\mathrm{dis}}$, where $G_e = k_B T(c/N_e)$ is the plateau elastic modulus of the entanglement network (here c is the monomer concentration), and τ_{dis} is the so-called disentanglement time. The reptation model [2] implies that each polymer chain is enveloped in a virtual tube due to entanglements with surrounding chains. The main large-scale chain motion is a reptation along the tube axis. The disentanglement time is then the time of reptation on a distance of order of the tube length, L: $\tau_{\mathrm{dis}} = \mathrm{const} \times L^2/D_0$, where D_0 is the curvilinear diffusion constant, $D_0 = 1/\zeta$, where ζ is the friction constant corresponding to the reptation motion, $\zeta \propto N$ (here $k_B T$ is the energy unit). Hence the main result of the reptation model, $\eta \propto \tau_{\mathrm{dis}} \propto N^3$, which is valid if monomers do not interact.

Let us now switch on monomer interactions, assuming that N is very large. Then the reptation (curvilinear diffusion along the tube) should be globally hindered by high potential barriers (U) due to interactions [10–12],

$$\eta \propto \tau_{\mathrm{dis}} \propto N^3 \exp(U). \qquad (1)$$

In order to estimate the typical barrier U let us consider a chain that is creeping out of the original tube. Suppose that g monomers have escaped out of the original tube, and hence occur in a new less favorable environment. The typical lateral size (in xy plane) of the escaped chain segment is $R(g) \sim b g^{1/2}$, so that the total volume available for the segment is $V(g) \sim H R^2(g) \sim b^2 H g$ [here I assume that $R(g) > H$]. Let us assume for a moment that only one chain is moving, while monomers of all other chains are fixed. Then g monomers that come into the region $V(g)$ increase monomer concentration there by $\delta c \sim g/V(g)$. The interaction energy in this region is thus increased by $U(g) = (v/2) \int \delta c^2 d^3 r \sim v \delta c^2 V(g) \sim v g/b^2 H$. There are two ways to relax this additional energy: (1) by deformation of the entanglement network, which results in a partial relaxation of the energy down to $U^*(g) = (v^*/v)U(g)$, and (2) by reptation motion of other chains. Here $v^* = v/(1 + c^2 v/K_e)$ is the renormalized interaction constant which takes into account that the entanglement network is soft;

$K_e = \nu G_e = \nu c/N_e$ is the longitudinal elastic modulus of the network, and ν is a numerical factor determined by the network structure.

While the second channel can provide a complete relaxation, it works only if there are free ends of other chains inside the region $V(g)$, i.e., if $(c/N)V(g) > 1$, so that $g > g^* \sim N/cb^2H$. Therefore the effective barrier that a chain has to overcome in order to move along the tube on $g > g^*$ is

$$U \sim U^*(g^*) \sim \frac{\nu^* N}{cb^4 H^2} \sim \frac{\nu}{c^2 b^4} \frac{1}{H^2} \frac{N}{N_e}. \qquad (2)$$

The argument described above is analogous to that used for bulk 3D systems [11,12], where the activation energy $U \sim (N/N^*)^{2/3}$, $N^* = (cb^3)^4 N_e^3/\nu^3$ (the scaling $U \propto N^{2/3}$ was originally predicted in Ref. [13] using a different argument).

Note that in the melt case $cb^3 \sim 1$, and so $N^* \sim N_e^3$; i.e., N^* is extremely large. Let us consider the regime $N_e < N < N_e^3$ (the last inequality is valid for most polymers synthesized so far). Here the bulk activation energy is small; i.e., the classical Doi-Edwards picture is valid in the bulk. However, the effect of interactions might be strong for dynamics in a thin molten layer: $U \gg 1$ if $H \ll H^{**} = (1/cb^2)(\nu N/N_e)^{1/2}$. The effective curvilinear diffusion constant is exponentially small in the region $H < H^{**}$: $D \sim D_0 \exp(-U)$, and both the disentanglement time τ_{dis} and the viscosity are exponentially large; see Eqs. (1) and (2). The effect of interactions is enhanced as the layer thickness decreases. This conclusion is further supported by the perturbation analysis below using a new simple approach which is first applied to derive the bulk diffusion constant and relaxation time [11], and then to the confinement effect.

Perturbation analysis.—Let us consider one chain in its tube. It is convenient to rescale the curvilinear coordinate (along the tube) s, so that it measures the average number of links along the tube; with this definition $L \equiv N$. Then an instantaneous curvilinear velocity along the tube of any monomer of a given chain is $\dot{s} = \xi(t)$, where $\xi(t)$ is the random thermal noise, $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(t') \rangle = 2\delta(t - t')$, where $1/D_0$ is chosen as the time unit. These equations specify the Doi-Edwards reptation model. With interacting monomers the situation is different: a displacement of the chain along the tube might change the total interaction energy $F_{\text{int}} = (\nu/2)\int[c(\mathbf{r}) - c]^2 d^3r$, where $c(\mathbf{r})$ is the local monomer concentration, $\langle c(\mathbf{r}) \rangle = c$, and ν is the interaction parameter. This results in an effective force $f(t) = \nu[c(\mathbf{r}_0(t), t) - c(\mathbf{r}_N(t), t)]$ which drives the chain in the direction of lower concentration; here $\mathbf{r}_0(t)$ and $\mathbf{r}_N(t)$ are the spatial positions of the chain ends corresponding to $s = 0$ and $s = N$. Thus $\dot{s} = \xi(t) + f(t)$. The molecular drift velocity is zero on the average, $\langle f(t) \rangle = 0$. It is fluctuating in time like $\xi(t)$ does; however, the correlation time of $f(t)$ is large: It is determined by polymer dynamics. The drift force gives rise

to a renormalization of the effective diffusion constant which is defined as $D/D_0 = \int_0^\infty \langle \dot{s}(0)\dot{s}(t) \rangle dt = 1 + \Delta$, $\Delta = \int_0^\infty \langle f(0)f(t) \rangle dt + \int_{-\infty}^\infty \langle \xi(0)f(t) \rangle dt$. It is the renormalized diffusion constant that determines the macroscopic dynamical properties, in particular, the disentanglement time, $\tau_{\text{dis}} = \text{const } N^2/D$, and the viscosity.

Let us calculate Δ by perturbations assuming that the interaction parameter ν is small. By definition the random noise $\xi(0)$ is independent of the system history at $t < 0$. Therefore $\langle \xi(0)f(t) \rangle = 0$ for $t < 0$. Let us now make use of the time, isotropy, i.e., of the fact that the system maps to itself under the transformation $t \to -t$. Obviously the transformation implies that $\dot{s}$ being a velocity must change its sign, whereas $f(t)$ being a force (which is in turn proportional to a concentration fluctuation) is invariant. Hence $\langle \dot{s}(t_1)f(t_2) \rangle = -\langle f(t_1)\dot{s}(t_2) \rangle$. Taking into account that $\dot{s}(t) = \xi(t) + f(t)$ we get the relation $\langle \xi(0)f(t) \rangle = -2\langle f(0)f(t) \rangle \Theta(t)$, where $\Theta(t)$ is the Heaviside function. Therefore

$$\Delta = -\int_0^\infty \langle f(0)f(t) \rangle dt, \qquad (3)$$

so that Δ is definitely negative.

The force $f(t) = \nu[\delta c(\mathbf{r}_0(t), t) - \delta c(\mathbf{r}_N(t), t)]$, where $\delta c(\mathbf{r}, t) = c(\mathbf{r}, t) - c$ is the concentration fluctuation. Hence, in order to proceed we need to know the correlation function of concentration fluctuations $S(r, t) = \langle \delta c(\mathbf{r}, t)\delta c(0, 0) \rangle$. This function was calculated in Refs. [10,11]; the result in the Fourier-Laplace representation is

$$S(q, p) = \frac{\nu^*}{p\nu^2}\left[1 + \frac{2c\nu^*}{N} \frac{2q^2 + \sqrt{p}}{\sqrt{p}\,(\sqrt{p} + q^2)^2}\right]^{-1}, \quad (4)$$

where $S(q, p) = \int_0^\infty S(r, t)e^{-i\mathbf{q}\cdot\mathbf{r} - pt} d^3r\, dt$. Note that monomer size $a \equiv b/\sqrt{6}$ is considered as unit length here. Equation (4) is valid in the relevant region $p\tilde{t} \sim 1$ which provides dominant contribution to Δ as given by Eq. (3), where $\tilde{t} = N/c\nu^* D_0$.

Neglecting correlations between $\delta c(\mathbf{r}_0)$ and $\delta c(\mathbf{r}_N)$, which is legitimate since the relevant correlation length is much smaller than the end-to-end distance, I rewrite Eq. (3) (taking into account that the system is macroscopically homogeneous) as

$$\Delta = -2\nu^2 \int_0^\infty dt \int d^3r\, S(r, t)P(r, t), \qquad (5)$$

where $P(r, t)$ is the probability density that a chain end is at point $\mathbf{r}$ at the moment t under the condition that it was at $\mathbf{r} = 0$ initially (at $t = 0$). The function $P(r, t)$ can be easily calculated using the reptation model described above. Since the aim is to calculate Δ in the main order, we can neglect the molecular field while considering $P(r, t)$. The result, which is valid in the relevant regime $t \sim \tilde{t} \ll \tau_{\text{dis}}$, is [11,14] $P(q, p) = 1/(q^2 + \sqrt{p})^2$, where $P(q, p) = \int P(r, t)e^{-i\mathbf{q}\cdot\mathbf{r} - pt} d^3r\, dt$. Thus we get after

some transformations (d = dimension of space)

$$\Delta = -2v^2 \int \frac{d^d q}{(2\pi)^d} \int_{-i\infty+0}^{i\infty+0} \frac{dp}{2\pi i} P(q,p) S(q,-p)$$

$$= -I_d (v^*)^{d/4}\left(\frac{N}{c}\right)^{(4-d)/4}, \qquad (6)$$

where

$$I_d = \frac{2^{1-3d/4}}{\pi^{d/2}\Gamma(d/2)\sin(\pi d/4)}$$

$$\times \int_0^\infty t^{d/2}(1+t^2)^{-2}(2t+1)^{d/4-1}(1+t)^{2-d/2}\,dt.$$

Equation (6) represents the main-order perturbation result which is supposed to be valid if $|\Delta| \ll 1$. In particular, for $d = 3$ the result is

$$\Delta \simeq -0.0779(v^*)^{3/4}\left(\frac{N}{c}\right)^{1/4} \simeq -\frac{1.14 v^{3/4}}{cb^3}\left(\frac{N}{N_e^3}\right)^{1/4}. \qquad (7)$$

In the last equation an explicit dependence on the statistical segment b is inserted; also v^* was approximated as

$$v^* \simeq v/cN_e, \qquad (8)$$

which is valid if $vc^2 \gg K_e$.

These results coincide with those obtained in Ref. [11]. The effect of molecular field gives rise to a slowing down of the curvilinear diffusion, and hence to a longer disentanglement time, $\tau_{\rm dis} = \text{const} \times [N^2/D_0(1-|\Delta|)]$ and higher viscosity, $\eta = G_e \tau_{\rm dis} \propto N^3/(1-|\Delta|)$. The effect is strong if $N \gtrsim N_e^3$. The derivation of Eq. (7) is based on the pure reptation model; i.e., Rouse-like chain motion inside the tube (tube length fluctuations) [15] are neglected. An analysis shows that these fluctuations could give rise to a slight change (decrease) of the numerical prefactor; however, they do not affect any dependence of Δ on the parameters.

The effect of confinement.—The perturbation analysis of the previous section can also be performed for a confined polymer layer in essentially the same way. The only difference stems from the fact that the system is not homogeneous any more in the z direction normal to the layer, so that Eq. (5) should be rewritten in a more general form,

$$\Delta = -2v^2 \int_0^\infty dt \int d^3r\, d^3r'\, S(\mathbf{r},\mathbf{r}',t) P(\mathbf{r},\mathbf{r}',t), \qquad (9)$$

where $S(\mathbf{r},\mathbf{r}',t) = \langle \delta c(\mathbf{r},t)\delta c(\mathbf{r}',0)\rangle$ is the correlation function, and $P(\mathbf{r},\mathbf{r}',t)$ is the probability density that a given chain end was at the point $\mathbf{r}'$ at $t = 0$ and moved to the point $\mathbf{r}$ during time t. For a homogeneous (bulk) system these functions depend only on $\mathbf{r} - \mathbf{r}'$, e.g., $P(\mathbf{r},\mathbf{r}',t) = (1/V)P_b(\mathbf{r}-\mathbf{r}',t)$, where $P_b(\cdot)$ is the bulk probability density considered in the previous section, and V is the volume.

In the confined geometry any distribution function can be obtained as a superposition of the bulk distribution function and all its reflections at the film surfaces, $z = 0$

and $z = H$ (here H is the layer thickness),

$$P(\mathbf{r},\mathbf{r}',t) = \frac{1}{V}\sum_{n=-\infty}^{\infty}[P_b(\mathbf{r}-\mathbf{r}'+2Hn\mathbf{e}_z,t)$$
$$+ P_b(\mathbf{r}-\mathbf{r}'+(2z'+2Hn)\mathbf{e}_z,t)]$$

where $\mathbf{e}_z$ is the unit vector along the z axis, $z = \mathbf{e}_z\mathbf{r}$, $z' = \mathbf{e}_z\mathbf{r}'$. Similarly,

$$S(\mathbf{r},\mathbf{r}',t) = \sum_{n=-\infty}^{\infty}[S_b(\mathbf{r}-\mathbf{r}'+2Hn\mathbf{e}_z,t)$$
$$+ S_b(\mathbf{r}-\mathbf{r}'+(2z'+2Hn)\mathbf{e}_z,t)].$$

Inserting the last two equations in Eq. (9) I get instead of Eq. (6)

$$\Delta(H) = -\frac{2v^2}{H}\int \frac{dq_x\, dq_y}{(2\pi)^2}\sum_{q_z}\int_{-i\infty+0}^{i\infty+0}\frac{dp}{2\pi i}$$
$$\times P_b(\mathbf{q},p)S_b(\mathbf{q},-p),$$

where $q_z = \pi n/H$, $n = 0,1,2,\ldots$; $S_b(q,p)$ is defined by Eq. (4), and $P_b(q,p)$ is defined just above Eq. (6). After appropriate transformations

$$\Delta(H) = -\frac{\sqrt{2}}{\pi^2}\frac{1}{H}\left(\frac{v^*N}{c}\right)^{1/2} I[2^{3/4}H(cv^*/N)^{1/4}], \quad (10)$$

where $I(\alpha) \equiv \int_0^\infty \varphi[\alpha t^{1/2}(2t+1)^{1/4}/(1+t)^{1/2}][t(1+t)/(1+t^2)^2(2t+1)^{1/2}]\,dt$ and $\varphi(u) \equiv (\pi/4) + (u/2) + \arctan[e^{-u}\sin u/(1-e^{-u}\cos u)]$.

In the regime $H \gg H^*$, $H^* = (N/cv^*)^{1/4} \simeq a(NN_e/v)^{1/4}$, Eq. (10) agrees with Eq. (7); i.e., the bulk behavior is recovered: $\Delta(H) \simeq \Delta(\infty)$. The dynamical effect of interactions becomes more pronounced for thinner films: $|\Delta| \simeq 0.834(1/cb^2H)(vN/N_e)^{1/2}$ for $H \ll H^*$; i.e., the correction is increasing as H is decreased [the approximation, Eq. (8), is used here].

The perturbation approach is valid as long as $|\Delta| \lesssim 1$. This condition can be rewritten as $H < H^{**} \sim (1/cb^2)(vN/N_e)^{1/2}$. Note that we get exactly the same crossover thickness (H^{**}) as in the second section; i.e., the activated reptation sets in as soon as perturbation expansion fails.

It is interesting to consider now the H dependence of the viscosity. Let us consider the melt case, $cb^3 \sim 1$, and the region $N_e < N < N_e^3$; the last inequality ensures that $H^{**} < H^*$. The reduced viscosity normalized by the bulk value, $\eta(H)/\eta(\infty) \simeq \tau_{\rm dis}(H)/\tau_{\rm dis}(\infty)$, is nearly equal to $[1+\Delta(\infty)]/[1+\Delta(H)]$ if $H \gg H^{**}$, and is roughly $\exp(U)$ if $H \ll H^{**}$. Thus using Eqs. (10), (2), and (1) we get

$$\ln\left(\frac{\eta(H)}{\eta(\infty)}\right) = \begin{cases} 0.417\,\frac{1}{cb^2H}\left(\frac{vN}{N_e}\right)^{1/2}, & H \gg H^*, \\[2mm] 0.834\,\frac{1}{cb^2H}\left(\frac{vN}{N_e}\right)^{1/2}, & H^* \gg H \gg H^{**}, \\[2mm] \text{const}\,\frac{1}{c^2b^4H^2}\frac{vN}{N_e}, & H^{**} \gg H \gg \xi, \end{cases}$$

$$(11)$$

where const ~ 1 is a numerical factor and $\xi \sim b/\sqrt{cv} \sim b$. Note a smooth crossover between the second and the third regimes.

In the most interesting regime $H \ll H^{**}$ the large-scale motions of polymer chains (on the distance of order of chain size or larger) are virtually frozen: The relevant time τ_{dis} is exponentially long as a result of excluded-volume interactions. However, short-scale monomer motions on a distance of order of the tube diameter, $N_e^{1/2} b$, are not suppressed by interactions and are fast. In this regard, the situation reminds one of a liquid near its α glass transition temperature. Note, however, that in the case of a polymer layer considered here the temperature is fixed, and its role is played by the layer thickness H: $\ln \eta \propto \frac{1}{H^2}$. The lowest H compatible with essentially homogeneous (liquid) structure of the system is of order of the static correlation length $\xi \sim b$. For $H \sim \xi$ the system is virtually two dimensional, and the stress relaxation time is proportional to the extremely large factor $\exp(\mathrm{const} \times N/N_e)$.

So far it was assumed that N_e does not depend on H. This assumption is surely reasonable if H is larger than the entanglement size (tube diameter): $H > N_e^{1/2} b$. For thinner layers N_e could depend on H; however, no dramatic variation is expected.

In summary, I predict a glasslike slowing down of long-range motions in thin confined layers of melted or dissolved polymers. The effect is attributed to excluded volume interactions between monomers rather than to surface-monomer interaction. An experimental verification of the predicted shear viscosity behavior might be complicated by wall slip [16–18]. This complication could be avoided either by special surface treatment [17] or by preparing a polymer layer on a liquid substrate. In the latter case the shear gradient should be applied parallel rather than perpendicular to the film. Another possibility is to measure polymer self-diffusion parallel to the film: The corresponding diffusion constant is not affected by the wall slip and is predicted to scale as $1/\tau_{\mathrm{dis}}$. The self-diffusion can also be probed in computer simulations.

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