Eur. Phys. J. B **1**, 87–94 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Dynamics of strongly entangled polymer systems: activated reptation

A.N. Semenov[1,a] and M. Rubinstein[2]

[1] Department of Applied Mathematics, University of Leeds, Leeds LS2 9JT, UK
[2] Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA

Received: 25 July 1997 / Accepted: 8 October 1997

Abstract. The effect of excluded-volume interactions on the reptation dynamics of long polymer chains is considered theoretically. It is shown that interactions give rise to an exponential increase of the reptation time, $\tau_{\mathrm{rep}} \sim \exp[(N/N^*)^{2/3}]$, if polymer chains are long enough: $N > N^* \sim N_{\mathrm{e}}^3$, where N_{e} is the number of monomers per entanglement. We propose a novel dynamical mechanism of activated reptation implying that neighboring chains exchange conformations of their terminal fragments. It is shown that the exchange mechanism is compatible with the equilibrium polymer chain statistics and that it provides a bridge between the previous theories.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 83.10.Nn Polymer dynamics – 83.20.Fk Reptation theories

1 Introduction

Polymer liquids show intriguing dynamical properties which are of considerable scientific and technological interest [1,2]. In particular, dynamics of linear homopolymers (in a way, the simplest system) attracted significant theoretical attention in recent years [2–5]. It was recognized that dynamics of melts (and solutions) of very high-molecular-weight polymers is strongly affected by the entanglements between polymer chains. The most successful theory that takes into account the effect of entanglements is based on the reptation model proposed by de Gennes [3] and further developed by Doi and Edwards [4,5]. The reptation theory assumes that motion of any chosen polymer chain is strongly restricted by the presence of surrounding polymers, which create a sort of a tube around the chosen chain, the tube diameter being $a = N_{\mathrm{e}}^{1/2} b$ with b, the monomer size, and N_{e}, the number of monomers per entanglement.

The main large-scale motion of a polymer chain is its reptation along the tube, which can be viewed as a random sequence of forward and backward displacements, *i.e.* one-dimensional diffusion along the tube axis. The reptation theory predicts N^3 scaling for both the viscosity η and the (longest) stress relaxation time τ_{stress} in the entangled regime $N > N_{\mathrm{e}}$ (here N is the number of monomers per chain). This is in reasonable agreement with the experimental data [1], which however show a bit stronger molecular-weight dependence of both quantities[1]: $\eta \propto \tau_{\mathrm{stress}} \propto N^{3.4}$.

The following rather academic question arises in this regard: what is the asymptotic dependence of η and τ_{stress} on molecular weight in the limit $N \to \infty$. It is this question that is considered in the present paper.

The problem received some attention in the past [6–12]. The main idea (also implemented in the present work) is that the reptation of extremely long polymers is additionally hindered by the excluded volume interactions coupled with the fluctuations of the entanglement network topology, or, in other words, by the fluctuations of the monomer molecular field. This conclusion was corroborated by the rigorous approach [8,9] treating fluctuations of molecular field as perturbations.

The effects of the excluded-volume interactions (which were completely neglected in the original reptation theory [4,5]) give rise to a strong slowing down of the reptation dynamics for $N > N^* \sim N_{\mathrm{e}}^3$ [8–11] (a slightly different crossover $N^* \sim N_{\mathrm{e}}^{11/4}$ was originally predicted by Deutsch [7]): in this region both the relaxation time and the viscosity grow exponentially with a power of N. The physical reasons for this behavior are discussed in the next section.

---

[a] e-mail: `A.Semenov@leeds.ac.uk`

[1] Note that a stronger than N^3 *apparent* dependence of viscosity in a limited, yet experimentally relevant, molecular-weight range has been predicted as the effect of tube-length fluctuation modes [13–15].

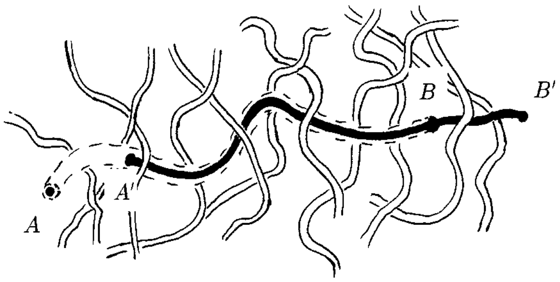


Fig. 1. The 'black' chain reptates out of the original tube AB creating a new tube section BB′.

2 Review of the existing theories

We first discuss the main concepts and the results of the original theory proposed by Deutsch [7]. Let us choose an arbitrary polymer chain in an entangled polymer melt (a 'black' chain in a melt of identical 'white' ones). On the time scales shorter than the reptation time $\tau_{\rm rep}$ (*i.e.* the time during which the chain moves along its tube a distance of order of the tube length[2]) the chain monomers are restricted to the tube region with diameter $a = N_{\rm e}^{1/2}b$ and length

$$L = \frac{N}{N_{\rm e}}a\cdot$$

At equilibrium the conformations and the topological state (*i.e.* mutual entanglements) of the white chains in the vicinity of the tube are adjusted to the presence of the black chain. This makes the home tube attractive for the black chain: when the chain tries to reptate out, it enters a 'virgin' region (creates a new section of the tube at its 'head') which is not yet adjusted to the black chain; it also leaves an adjusted tube region at its 'tail' (Fig. 1). The new tube region can not easily accommodate the 'head' section of the reptating chain because of the entanglements: the entanglement network becomes locally stretched in this region. Note that entanglements cannot relax on the time-scales much shorter than the reptation time $\tau_{\rm rep}$ since their life-time is of the order of this reptation time $\tau_{\rm rep}$. Therefore it appears that the effective free energy of the system increases as the black chain reptates out of its home tube, the increase being $\Delta F \simeq g\Delta\mu$, where g is the number of monomers that reptate out, and $\Delta\mu$ is the difference between monomer chemical potentials in the 'virgin' region (μ_1) and in the home tube (μ_0): $\Delta\mu = \mu_1 - \mu_0 > 0$. The value of $\Delta\mu$ is determined by the structure of the entanglement network as discussed in Section 3 below. It is virtually independent of the chain length, N. Therefore the black chain has to overcome a large potential barrier, $U = N\Delta\mu$, in order to completely escape out of the home tube, *i.e.* the black chain is virtually trapped (localized) in the tube.

Thus the reptation motion turns out to be an activation process [7], so that, in particular, the reptation time is exponentially large: $\tau_{\rm rep} \propto \exp(U/k_{\rm B}T)$. However a different way to estimate the activation energy was suggested in reference [7]. Note that the average distance between the chain ends is

$$S \sim (Nv)^{1/3}$$

where v is the monomer volume. It was assumed [7] that the additional (activation) energy of the system can relax as soon as the spatial size of the escaped portion of the black chain, $r(g)$, becomes of the order of S. Taking into account that polymer chains obey Gaussian statistics in a melt state, $r(g) \sim bg^{1/2}$, we get the critical number of monomers in the escaped fragment:

$$g \sim G \equiv N^{2/3}$$

where we also assumed that $v \sim b^3$. Hence the activation barrier $U_{\rm a} \sim G\Delta\mu = N^{2/3}\Delta\mu$. The reptation process is then considered as a random sequence of jumps with size of order S. Each jump implies that a new portion of the tube containing $\sim G$ black monomers is created near one of the chain ends. The jump time τ_1 is determined by the activation energy $U_{\rm a}$: $\tau_1 \propto \exp\left(U_{\rm a}/k_{\rm B}T\right)$. The activation energy $U_{\rm a}$ is assumed to relax after each jump.

Unfortunately, the assumption of reference [7], mentioned above, does not seem to be correct. The relaxation of energy $U_{\rm a}$ implies the relaxation of the entanglement network structure in the vicinity of the 'new' tube part (around the head fragment, G). The only possible way to relax this structure is by a tube renewal process [16] which takes longer than the reptation time, $\tau_{\rm rep}$. Obviously $\tau_{\rm rep}$ must be much larger than τ_1, the time during which typically $G \sim N^{2/3}$ monomers reptate out of the original (home) tube: during the reptation time $\tau_{\rm rep}$ the chain must vacate the whole home tube. Therefore a noticeable relaxation of energy $U_{\rm a}$ during time τ_1 is impossible.

The original theory [7] does not describe what happens on the time-scales $t > \tau_1$. The dynamical picture was elaborated in more detail in the paper [12]. The suggested dynamical mechanism can be summarized as follows: On time scales $t > \tau_1$ the spatial displacement of the black chain end, $r(g)$, is larger than S, so that there are few ends of the other chains in the region $r^3(g)$, explored by the black end. Some of these surrounding chains also reptate along their tubes leaving empty traces which are attractive for the black chain. The latter thus follow one of the empty traces, *i.e.* reptates along the home tube of another chain until an intersection with another empty trace, where the black chain has a choice of directions. The effective energy of the black chain thus does not increase any more: the only unfavorable part of its tube of length $\sim G$ was created at the earlier stage, $t < \tau_1$. However, the problem here is that more and more reptating chains become simultaneously involved in the process, each additional chain increasing the *total* free energy by $\sim U_{\rm a}$ (as its head must find a way through the unfavorable 'virgin' environment at the initial stage). Therefore the activation barrier must be actually much higher than $U_{\rm a}$.

A different treatment of the activated reptation was suggested in references [8,9]. The new idea was to take

---

[2] Note that the reptation theory predicts that reptation time $\tau_{\rm rep}$ is of the order of the stress relaxation time $\tau_{\rm stress}$.

into account the randomness of the entanglement network, *i.e.* the fact that the molecular field μ_1 is random, $\mu_1(\mathbf{r})$, rather than completely uniform. The average field $\langle\mu_1\rangle$ is higher than μ_0: the virgin environment is *on average* less favorable than that of the home tube. On the other hand fluctuations of the molecular field make this environment more attractive for the black chain: the chain tends to move along the regions of lower μ_1 (valleys) avoiding the elevations (mountains). The *effective* monomer potential felt by the black chain outside its home tube, μ_1, is thus smaller than the average value $\langle\mu_1\rangle$. It was argued that this fluctuation effect cancels the difference between the home tube and the virgin environment, *i.e.* that $\Delta\mu = \mu_1 - \mu_0 = 0$. This statement was corroborated by the perturbation analysis which shows that $\Delta\mu = \mu_1 - \mu_0$ does vanish to the second order in the molecular field fluctuations [8,9]. This picture leads to the barrier which is due to the fluctuations of the molecular field rather than the permanent difference between the molecular field near the home tube and far from it. The resultant barrier, U_a, is thus proportional to $\sqrt{G}$ rather than G: $U_\mathrm{a} \propto \sqrt{G} \sim N^{1/3}$, *i.e.* the effective $\Delta\mu$ is proportional to $1/\sqrt{G}$. It is important that this smaller energy barrier U_a can relax much faster than the reptation time: it can certainly relax during time τ_1[3]. This makes the dynamical picture considered in references [7,12] self-consistent. Unfortunately the height of the activation barrier U_a was underestimated in references [8,9]. A careful analysis shows that $\Delta\mu$ can not possibly vanish if higher-order effects of the molecular field fluctuations are taken into account, as was noted in reference [12] ($\Delta\mu$ is estimated in the next section).

Thus the existing approaches do not provide a consistent picture of polymer motion on time-scales larger than τ_1. The questions remaining to be answered are: What is the mechanism of polymer motion on these time-scales? How many chains must be involved in an elementary activation process (jump)? What is the effective activation energy? These questions are answered in the following sections.

3 The novel mechanism of the activated reptation

3.1 Reptation through a random medium

When g monomers at the head of the black chain 'leak out' of the home tube, they enter a random entanglement network, which is frozen on time-scales smaller than the reptation time, $t < \tau_\mathrm{rep}$. The random network structure implies that its stress is random: $\sigma_\mathrm{e} = \sigma_\mathrm{e}(\mathbf{r})$. At equilibrium the average stress is zero. By virtue of the melt incompressibility, the incoming black fragment causes additional deformation of the network, $\Delta\epsilon$. The excess elastic free energy $F(g)$ is proportional to the local stress. Hence $F(g)$ fluctuates as the head fragment moves from a more stressed to a less stressed region. A typical value of the excess elastic free energy is

$$F(g) = \int \sigma_\mathrm{e}(\mathbf{r})\Delta\epsilon(\mathbf{r})\mathrm{d}^3 r = \bar{\sigma}_\mathrm{e} \int \Delta\epsilon(\mathbf{r})\mathrm{d}^3 r = \bar{\sigma}_\mathrm{e} g v$$

where gv is the intrinsic volume of the fragment, and $\bar{\sigma}_\mathrm{e}$ is the network stress averaged over the volume $V(g)$ explored by the fragment[4]. The elastic energy corresponding to a particular $\bar{\sigma}_\mathrm{e}$ can be estimated as $W(\bar{\sigma}_\mathrm{e}) \sim V\frac{\bar{\sigma}_\mathrm{e}^2}{K_\mathrm{e}}$, where $V = V(g)$ is the relevant volume, and K_e is the longitudinal elastic modulus of the entanglement network. It is natural to expect that K_e is of the order of the shear elastic modulus, $K_\mathrm{e} \sim \frac{k_\mathrm{B}T}{vN_\mathrm{e}}$. Fluctuations of the stress must obey the Boltzmann statistics since the system is at equilibrium. Therefore $W(\bar{\sigma}_\mathrm{e}) \sim k_\mathrm{B}T$, *i.e.* $\delta\bar{\sigma}_\mathrm{e} \sim (k_\mathrm{B}TK_\mathrm{e}/V)^{1/2}$. Taking into account that the volume explored by the fragment $V \sim r(g)^3 \sim b^3 g^{3/2}$, we get the typical fluctuation of the free energy of the fragment:

$$\delta F(g) \sim gv\delta\bar{\sigma}_\mathrm{e} \sim \frac{g^{1/4}}{{N_\mathrm{e}}^{1/2}} k_\mathrm{B}T \sim (g/g^*)^{1/4} k_\mathrm{B}T$$

where $g^* \approx N_\mathrm{e}^2$ and we also took into account that $v \sim b^3$.

If the segment is short $g \ll g^*$ then the effect of the random field is weak: $\delta F \ll k_\mathrm{B}T$, so that the penetrating segment of the chain explores the whole volume $V(g)$ determined by its Gaussian size. In the opposite regime, $g \gg g^*$, the segment's conformation is localized in the regions of lower molecular field (lower frozen stress). In this case the segment can be considered as a sequence of localization blobs, g^*, each blob being virtually trapped in a favorable region. The free energy per one localization blob is of order of $-k_\mathrm{B}T$. The total free energy of penetration is then $F(g) \simeq -k_\mathrm{B}T\nu\frac{g}{g^*}$, where the reduction factor ν (smaller than unity) takes into account that the favorable network regions, where the blobs, g^*, tend to be localized, do not always form a continuous sequence: sometimes they are separated by less favorable regions. On the other hand the home (equilibrium) tube is a *continuous* sequence of the favorable regions, *i.e.* the free energy of the segment in its home tube is $F_0(g) \simeq -\frac{g}{g^*}k_\mathrm{B}T$. Therefore the effective difference of the chemical potentials is

$$\Delta\mu = \frac{F(g) - F_0(g)}{g} \sim \frac{k_\mathrm{B}T}{g^*} = \frac{k_\mathrm{B}T}{N_\mathrm{e}^2}\,\cdot \tag{1}$$

The same result can be obtained by considering a chain fragment that follows a trace of another chain, *i.e.* a vacated tube. Deutsch [7] demonstrated that the fragment

---

[3] The following relaxation mechanism is possible: Consider a white chain W with one end in the region S^3 explored by the head of the black chain B during τ_1. The typical number of intersections between the head G-segment of chain B and a similar segment of chain W is $n \sim G^{1/2}$ (this is the number of contacts between two Gaussian coils of G monomers). During the time τ_1 the W chain can reptate 'inside' its tube on a distance $\sim G$ thus removing $n \sim G^{1/2}$ contacts with the B chain. The effective energy of the B chain would then decrease by $\Delta F \sim nk_\mathrm{B}T$, leading to a considerable relaxation of the energy barrier U_a since $\Delta F \sim U_\mathrm{a}$.

[4] For simplicity we neglect here the tensorial character of the stress.

is attracted to the trace and is adsorbed on it. Using the arguments similar to those presented above one can show that the adsorption energy per monomer is exactly $\Delta\mu$ (Eq. (1)). Note that the adsorption energy obtained by Deutsch is a bit different: his $\Delta\mu$ is proportional to $N_e^{-11/6}$. The reason for the difference in the exponents is that the scaling result for adsorption from a good solvent was used in [7]. The result of reference [7] becomes identical to equation (1) when corrected for the Gaussian statistics of chains in a melt.

When the reptating fragment interacts with a trace, it follows it with the precision of order of the localization blob size:

$$\Lambda \approx b\,(g^*)^{1/2} \approx bN_e. \tag{2}$$

The same localization length was obtained in reference [12]; the same scale was also derived earlier [8,9] using the perturbation approach.

3.2 Fluctuations of tube length

Let us consider again the ‘black’ chain which must be trapped for a long time in its home tube (as discussed above). Naturally, the total tube length occupied by the chain does not remain constant, but rather fluctuates. The equilibrium fluctuations were originally considered by Doi [13]: the excess free energy corresponding to $\Delta L = L - \bar{L}$, where $\bar{L}$ is the average tube length, is

$$E(\Delta L) \approx \frac{k_\mathrm{B}T}{2}\frac{(\Delta L)^2}{Nb^2}\,. \tag{3}$$

Therefore the amplitude of the typical fluctuations is $\Delta L \approx bN^{1/2}$.

The equilibrium result, equation (3), is not relevant, however, to the tube length fluctuations for a *given* chain while it is trapped in the corresponding home tube. An increase of the total tube length implies that a number (g) of head monomers has created a new tube part (ΔL_h) in the unfavorable (‘virgin’) environment. Therefore the free energy increases by $E(\Delta L_\mathrm{h}) \sim k_\mathrm{B}Tg/g^*$. If, on the contrary, the tube length decreases by ΔL_h, then the same number of head monomers vacate the head part of the home tube moving inside it. The corresponding free energy increase is the same as in the previous case since g black monomers moved into the home tube which is already occupied by other black monomers. Taking into account that $\Delta L_\mathrm{h} = a\frac{g}{N_e}$ we thus get

$$E(\Delta L_\mathrm{h}) \sim \frac{|g|}{g^*}k_\mathrm{B}T \sim \frac{k_\mathrm{B}T}{bN_e^{3/2}}\,|\Delta L_\mathrm{h}| \tag{4}$$

if $|g| > g^*$, *i.e.* if $|\Delta L_\mathrm{h}| > bN_e^{3/2}$.

The typical fluctuation is $\Delta L_\mathrm{h} \sim bN_e^{3/2}$; it is independent of N and is much smaller than the equilibrium fluctuation $b\sqrt{N}$ if N is large enough, $N \gg N_e^3$. The last statement is not a contradiction: the fluctuation ΔL_h in equation (4) is the difference between the current tube length and the home tube length L_h while the chain is trapped near a given home tube. On the other hand L_h varies from *chain to chain* fluctuating around the equilibrium average $\bar{L}$. Therefore the total fluctuation is $\Delta L = \Delta L_\mathrm{h} + (L_\mathrm{h} - \bar{L})$ and for large $N \gg N_e^3$ the total fluctuation is dominated by the second term, $L_\mathrm{h} - \bar{L}$.

3.3 Activated reptation with tube-length fluctuations

We suggest the following mechanism of polymer dynamics for ultra-long chains with

$$N \gg N^* \equiv N_e^3. \tag{5}$$

Consider a chain 1, and mark its ends as e1 and e2. Let us denote the end of another chain (chain 0), which is the neighbor of the end e1, by e0 (Fig. 2). The distance between e1 and e0 is of the order of

$$S \sim bN^{1/3}$$

(see Sect. 2), *i.e.* much smaller than the chain size $bN^{1/2}$. The two chains (1 and 0) are then likely to have close encounters, *i.e.* some of their monomers are closer to each other than the attraction distance (the localization length) Λ, equation (2). The typical number of monomers n_1 from the end e1 to the first close encounter I is of order of $G \approx N^{2/3}$. The same is true for the number of monomers n_0 between e0 and I:

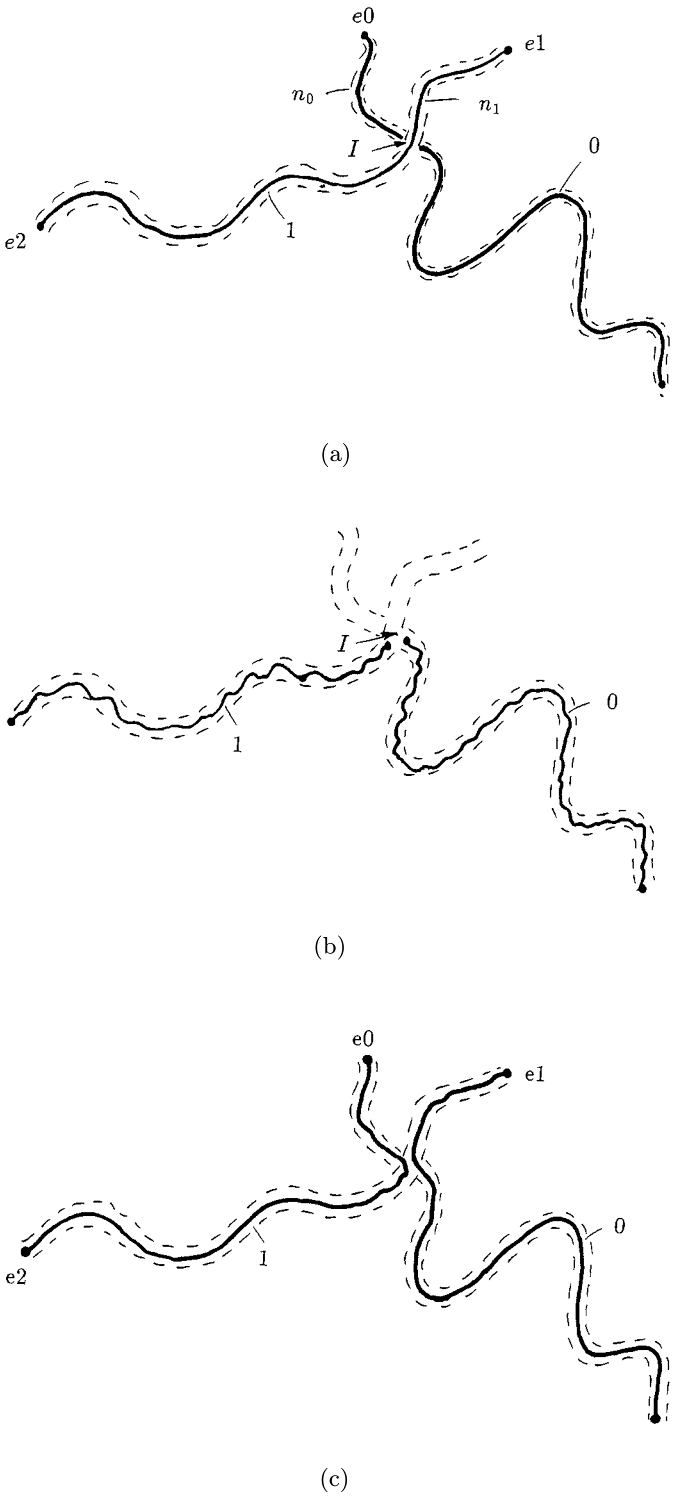
$$n_0 \sim n_1 \sim G \sim N^{2/3}.$$

Note that here we assume that $G \gg g^* = N_e^2$ (see Eq. (5)). If both chains simultaneously compress inside their home tubes vacating the intersection (close encounter) region (see Fig. 2b), then during the reverse process they will have a choice to return to their original home tubes, or to exchange the fragments I−e1 and I−e0 (see Fig. 2c). In the latter case the conformations of both chains would change. The activation energy for this process is $E_1 \approx k_\mathrm{B}T\frac{n_0+n_1}{g^*}$. The tube lengths of the chains also change as a result of the exchange process. For example, if $n_1 > n_0$, then the chain 1 would have to occupy a shorter tube of length smaller than the equilibrium one by $a\frac{(n_1-n_0)}{N_e}$. Thus the free energy of the final state is higher than the initial free energy by

$$\Delta E \approx k_\mathrm{B}T\frac{n_1 - n_0}{g^*}\cdot$$

As for the other chain 0, it enjoys being in a tube longer than it needs by the same length $a\frac{(n_1-n_0)}{N_e}$; thus this chain can freely move along the new tube to some extent.

The system now has to find a way to relax the additional energy ΔE since the free energy at the end of an elementary activation step must be equal to the initial free energy (otherwise the total activation energy would increase after each step up to infinity). One possibility for the compressed chain 1 to relax is to do an exchange of its terminal tube section n_2 near its other end e2 with chain 2 having one of its ends, marked as e3, in the vicinity of



(a)

(b)

(c)

Fig. 2. The tail exchange mechanism of the activated reptation. (a) Two chains "0" and "1" with neighboring ends e0 and e1 intersect at the point I. The terminal tube parts I − e0 and I−e1 contain n_0 and n_1 segments respectively. (b) Both chains are compressed so that the terminal parts of their tubes are vacated. (c) The chains decompress following new terminal paths.

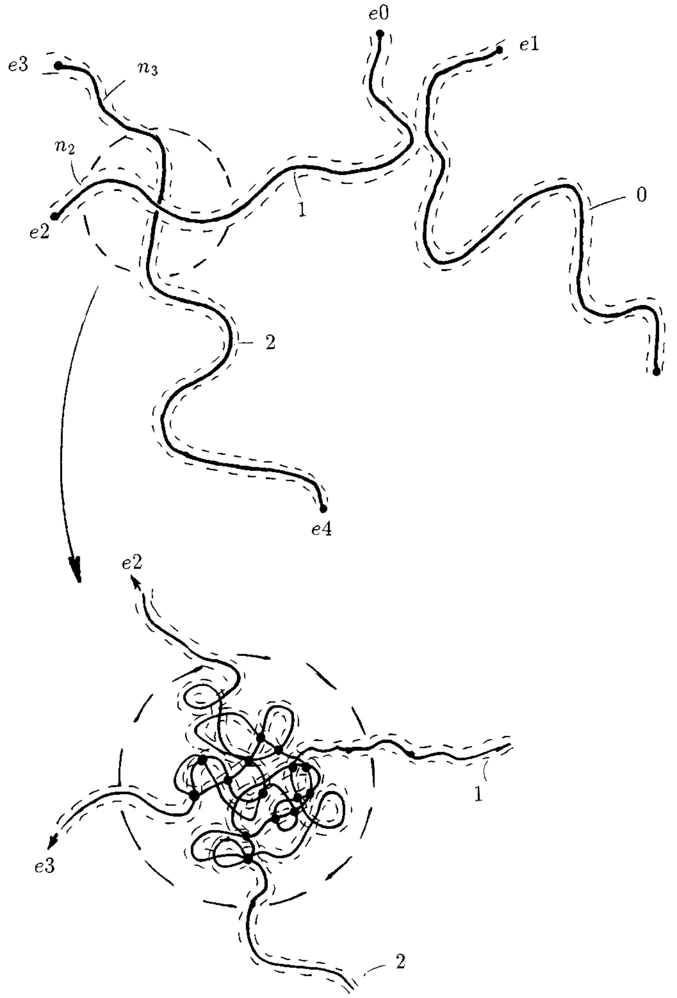


Fig. 3. The second end e2 of chain "1" is close to the end e3 of another chain "2" (e3−e4); the distance between the ends is of order of $S \sim (Nv)^{1/3}$. Inset at the bottom: close encounters between terminal fragments of chains "1" and "2" are marked by black circles; the typical number $\mathcal{N}$ of these encounters is proportional to S.

the end e2, *i.e.* to exchange n_2 to n_3 (see Fig. 3). A complete relaxation of chain 1 implies that its tube length returns to its equilibrium value after these two exchanges, *i.e.* that

$$|(n_3 - n_2) - (n_1 - n_0)| < g^*. \tag{6}$$

It is unlikely that this condition is satisfied for *the first* close encounter between the chains 1 and 2. Fortunately, any close encounter (intersection) between two Gaussian chains is typically supplemented by a large number of additional intersections. By a close encounter between two chains we mean that their monomers are getting within distance Λ of each other (see Eq. (2)). The typical number $\mathcal{N}$ of close encounters between n_2 and n_3 terminal fragments (see inset in Fig. 3) is of order $\mathcal{G}^{1/2}$, where

$$\mathcal{G} \sim G/g^* \sim N^{2/3}/N_{\mathrm{e}}^2 \tag{7}$$

is the typical number of localization blobs (g^*) per fragment ($n_2 \sim n_3 \sim G$). Thus if both chains simultaneously compress into their tubes by pulling in $\sim \mathcal{G}g^*$ monomers, there are $\mathcal{N} \sim \mathcal{G}^{1/2}$ close encounters between their home tubes vacated in the process. This pair of chains would have a choice of 2 different trajectories at each intersection during the reverse process, *i.e.* the total number of different trajectories is $2^{\mathcal{N}}$. Hence a choice of $2^{\mathcal{N}}$ different values of $(n_3 - n_2)/g^*$. These values are distributed within a limited range, since $|n_3 - n_2|$ can not exceed the total number of monomers $n_2 + n_3$ of both pulled-in chain sections, which is of order $G \sim N^{2/3}$. A continuous distribution of the values of $(n_3 - n_2)/g^*$ imply that any number within the specified range can be approximated by a value from this set with an exponentially small error since $2^{\mathcal{N}} \gg \mathcal{G} \sim \mathcal{N}^2$. Thus the condition 6 can be satisfied by choosing the appropriate trajectory if the difference $(n_1 - n_0)/g^*$ is not too large, which is normally the case (otherwise the chains would have to compress a bit more). The maximum activation energy at this stage, E_2, is still of order $\mathcal{G}k_\mathrm{B}T \approx k_\mathrm{B}TN^{2/3}/N_\mathrm{e}^2$.

The activation step is still not finished at this stage since the extra free energy was just transmitted from chain 1 (which is now relaxed) to chain 2 which is now compressed. However the process described above can continue: an exchange with another chain 3 can occur at the opposite end e4 of chain 2, and so on. Obviously the process should terminate as soon as chain 0 is involved again in the exchange: in this case all the tube lengths of all the involved chains return to their initial equilibrium values. In other words, the process (elementary activation step) is finished when a closed loop of exchanges is formed.

Let us estimate the number ω of exchanges in a typical shortest loop. Note that every next exchange occurs at the opposite end of the current compressed chain, *i.e.* the exchange region jumps every time by the chain end-to-end distance $R \sim bN^{1/2}$. At any stage the current (ith) chain has a choice of a few neighbors. By neighbors we mean chains with an end within distance $S \approx bN^{1/3}$ of the end of the i th chain to enable the exchange of tube sections, as described above. Let us consider a spherical region of radius $\sim R$ including the chains 0, 1, 2, and 3. Let us allow further exchanges only with those neighbors whose both ends are inside the region. There is still typically a choice of a few (say, 2) such neighbors suitable for an exchange at each stage. The number of different chains involved in the sequence of i exchanges thus grow as 2^i (of course, the base 2 is just an example). The total number of chains in the spherical region is of the order of $R^3/(Nv) \sim N^{1/2}$. Thus the loop of exchanges would close as soon as $2^i \sim N^{1/2}$ and chain 0 participates again so that the extra stress finally relaxes. Therefore the typical number of exchanges is $\omega = i \sim \ln N$.

The overall activation energy can be estimated as

$$U_\mathrm{a} \sim \max_i (E_i) + \omega k_\mathrm{B}T \tag{8}$$

where E_i is the activation barrier for the ith exchange, $E_i \sim \mathcal{G}k_\mathrm{B}T$. The second term, $\omega k_\mathrm{B}T$, takes into account that the exchanges are not random, but rather at any stage i a particular neighbor is chosen in order to create the shortest loop. Obviously the second term in equation (8) is negligible in comparison with the first one, so that[5]

$$U_\mathrm{a} \approx \mathcal{G}k_\mathrm{B}T \approx k_\mathrm{B}TN^{2/3}/N_\mathrm{e}^2. \tag{9}$$

Thus the elementary activation step is the loop of $\omega \sim \ln N$ exchanges between terminal sections of the chain trajectories. The time of one activation step is

$$\tau_1 \propto \exp(U_\mathrm{a}/k_\mathrm{B}T) \simeq \exp\left(\mathrm{const}\, N^{2/3}/N_\mathrm{e}^2\right) \tag{10}$$

where we have ignored the pre-exponential factors. This result is similar to that obtained by Deutsch [7], except that $N_\mathrm{e}^{11/6}$ is replaced by N_e^2 in equation (10).

During the elementary step the chain 1 (and all other chains involved in the loop) moves along the tube by a distance of order $aN^{2/3}/N_\mathrm{e}$ in a random direction (*i.e.* backward or forward). The overall reptation time τ_rep by definition corresponds to the displacement along the tube on a distance of order of the total tube length, *i.e.* $L = aN/N_\mathrm{e}$. Therefore

$$\tau_\mathrm{rep} \sim \left(\frac{N/N_\mathrm{e}}{N^{2/3}/N_\mathrm{e}}\right)^2 \tau_1 \sim N^{2/3}\tau_1. \tag{11}$$

4 Discussion and conclusions

In this paper we have demonstrated that the large-scale motion of entangled polymer chains is significantly slowed down by the excluded-volume interactions if the chains are long enough: $N > N^* = N_\mathrm{e}^3$. In this case the polymer reptation motion can be considered as a sequence of activation steps. During each step the chain end moves in space by the distance of order $S \sim bN^{1/3}$, which is comparable with the distance between neighboring chain ends. The typical time of one step, τ_1, is exponentially long, see equation (10). This time, τ_1, determines both the viscosity $\eta \propto \tau_\mathrm{stress} \propto \tau_1$ and the macromolecular diffusion constant $D \propto 1/\tau_1$.

The presented theoretical picture is similar to that proposed by Deutsch [6,7]. The main new points are:

(1) The activation barrier, U_a, is treated more accurately. The result, equations (9), is now in agreement with the prediction based on the exact perturbation approach [8,9] that a significant slowing down of the dynamics starts at $N \sim N^* = N_\mathrm{e}^3$, *i.e.* in the region where the present theory predicts a barrier of order $k_\mathrm{B}T$.

(2) A new dynamical mechanism of activated reptation is proposed, namely, the tail exchange mechanism, which implies that at each step two or more chains exchange the tail parts of their tubes. It is explicitly shown that this mechanism is compatible with the equilibrium

---

[5] A more careful analysis taking into account fluctuations of E_i leads to the following estimate: $U_\mathrm{a} \sim (\ln\omega)^{2/3}\mathcal{G}k_\mathrm{B}T$. However the additional $(\ln\omega)^{2/3} \simeq (\ln\ln N)^{2/3}$ is always of order unity, unless N is astronomically large.

polymer statistics, and in particular does not imply any accumulation of the free energy. The tail exchange mechanism replaces the dynamical picture of Deutsch [7,12] which implies that at each step the leading chain part has to penetrate through unfavorable regions leading to the free energy accumulation.

We also proposed that each activation step is actually a closed loop of exchanges between different chains leading to a complete relaxation of the activation energy. The qualitative idea of the cooperative reptation along closed cycles involving many chains was suggested earlier [17]. Pakula [18] proposed a model for numerical simulation of reptation dynamics in dense polymer systems which is based on the same idea of closed loops.

Any activation step implies that some chains temporarily occupy the tubes which are a bit too short (or too long) for them. The corresponding *defects* can be characterized by the difference between the current tube length and the equilibrium tube length, $\Delta L = L - \bar{L}$. The dynamics can be also interpreted in terms of these defects: in particular the loop of exchanges can be considered as a sequence of jumps of a $+\Delta L$ defect from one chain to another until it annihilates with a $-\Delta L$ defect created by the initial exchange. It is possible that the real polymer dynamics is even more complicated. For example a defect once created by a thermal fluctuation might then 'diffuse' from chain to chain until it meets another one of the opposite sign. The defect might also split into two parts, $\Delta L = \Delta L_1 + \Delta L_2$, at some point. Two new defects could then either combine back to create the priming one, or diffuse apart. When a defect jumps onto a chosen chain, and then further to its neighbor, the chain makes a reptation step. This dynamical picture, although formally different from the one presented in the previous section, implies the same scaling for the activation barrier, which must still be defined by equation (9).

One more complication arises from the fact that the system is not completely homogeneous. The current barrier U_i which determines the time of each elementary step (by a distance $\sim S$) strongly depends on the local environment of the 'active' chain end (*i.e.* the end which is going to make an exchange with another chain): the larger is the distance of its end to the closest end of the neighboring chains, the higher is the barrier. When the chain reptates along the tube its energy passes over different barriers U_i because of fluctuations of the local concentration of surrounding chain ends. The typical fluctuation is large $\delta U_i \sim U_i \sim \mathcal{G} k_{\mathrm{B}} T \gg k_{\mathrm{B}} T$. It is the largest barrier $U_{\mathrm{a}} = \max_i U_i$ that determines the overall reptation time since the chain must overcome all the barriers in order to considerably change its conformation. The number of different barriers is nearly equal to the number of G-blobs per chain, $n_G = N/G \sim N^{1/3}$ (this number is also equal to the number of neighboring chain ends in the vicinity of the given tube). The typical largest barrier $U_{\mathrm{a}} = \max_i U_i$ among $N^{1/3}$ barriers the chain must go over in order to reptate out of its tube can be estimated as follows.

Each individual barrier is proportional to the number of g^*-blobs per tail chain fragment with Gaussian size equal to the distance S_i to the nearest chain end: $U_i \sim k_{\mathrm{B}} T S_i^2/(b^2 g^*)$. Therefore the probability $P(u)$ that the barrier U_i exceeds an arbitrary level $k_{\mathrm{B}} T u$ ($u \gg \mathcal{G}$) is roughly equal to the probability that the distance to the nearest end S_i is larger than $s = b\sqrt{g^* u} = \Lambda\sqrt{u} = bN_{\mathrm{e}}\sqrt{u}$, *i.e.* that a spherical region of radius s (around the current tube part) is free of polymer chain ends. The latter probability is[6] $P = \exp\left(-c_{\mathrm{e}} V(s)\right)$, where $V(s) \sim s^3$ is the volume of the spherical region, and $c_{\mathrm{e}} = 2/(Nv) \sim 1/(Nb^3)$ is the average concentration of chain ends. Hence

$$P(u) \sim \exp\left(-\mathrm{const}\ (u/\mathcal{G})^{3/2}\right)$$

where $\mathcal{G} = N^{2/3}/N_{\mathrm{e}}^2$ is defined in equation (9). Obviously the typical maximum barrier $U_{\mathrm{a}} = \max_i U_i$, $i = 1, 2 \ldots n_G$, is roughly determined by the condition $P(U_{\mathrm{a}}) \sim 1/n_G$ (here we assume that the barriers U_i are distributed independently), *i.e.*

$$\frac{U_{\mathrm{a}}}{k_{\mathrm{B}} T} \sim \mathcal{G}(\ln n_G)^{2/3} \sim \left(\frac{N}{N^*} \ln N\right)^{2/3} \cdot \qquad (12)$$

Equation (12) differs from the previously obtained equation (9) by a logarithmic factor $(\ln N)^{2/3}$ which is hardly important as its molecular weight dependence is very weak.

Finally we note that the activated reptation dynamics is reminiscent of the dynamics near a glass transition. However we should consider N dependence of the dynamical quantities instead of temperature dependence (*i.e.* $1/N$ instead of $T - T_{\mathrm{g}}$). In particular, the idea of closed cycles of cooperative elementary motions (the cycles increase in size near glass transition) was also considered with regards to the glass transition dynamics [19,20].

This work was supported by NSF through the grants DMR-9409787 and DMR-9696081 and by the Eastman Kodak Company. A partial support of the EPSRC grant GR/L37694 and of NATO's Scientific Affairs Division in the framework of the Science for Stability Programme is also acknowledged.

References

1. J.D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
2. W.W. Graessley, Adv. Polym. Sci. **16**, 1 (1974).
3. P.G. de Gennes, J. Chem. Phys. **55**, 572 (1971).
4. M. Doi, S.F. Edwards, J. Chem. Soc. Farad. II **74**, 1789 (1978).
5. M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
6. J.M. Deutsch, Phys. Rev. Lett. **54**, 56 (1985).
7. J.M. Deutsch, J. Phys. France **48**, 141 (1987).
8. A.N. Semenov, Sov. Phys. JETP **69**, 107 (1989).
9. A.N. Semenov, Physica A **171**, 517 (1991).

---

[6] Fluctuations of the number of chain ends in a given region are governed by the Poisson distribution since the ends almost do not interact with each other.

10. A.N. Semenov, in *Theoretical Challenges in the Dynamics of Complex Fluids*, edited by P. McLeish, NATO ASI Ser. E **339** (Kluwer, Dordrecht, 1997).
11. A.N. Semenov, Phys. Rev. Lett., submitted.
12. M. Rubinstein, S.P. Obukhov, Phys. Rev. Lett. **71**, 1856 (1993).
13. M. Doi, J. Polym. Sci. B **21**, 667 (1983).
14. J. des Cloizeaux, J. Phys. France **45**, L17 (1984).
15. M. Rubinstein, Phys. Rev. Lett. **59**, 1946 (1987).
16. P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
17. M. Rubinstein, S.P. Obukhov (unpublished).
18. S. Geyler, T. Pakula, J. Reiter, J. Chem. Phys. **92**, 2676 (1990).
19. S.F. Edwards, T. Vilgis, Phys. Scr. T **13** 7 (1986).
20. S. Obukhov, D. Kobzev, D. Perchak, M. Rubinstein, J. Phys. I France **7**, 563 (1997).