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Dynamics of Stars and Linear Chains Dissolved in a Polymer Melt

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ABSTRACT: We derive the mobility and the relaxation time of stars (with g arms of Z monomers each) or long linear Z-mers embedded in a homopolymer melt of linear chains of N monomers, using a dissipation approach recently proposed by de Gennes.[20] For *stars*, we expect three main regimes depending on Z, N, and N_e, the number of monomers between entanglements. These regimes correspond to different relaxation mechanisms: (1) arm retraction; (2) "Rouse-like" or "Stokes-like" constraint release, in which the stars relax by reptation of surrounding N-mers; (3) Stokes–Einstein regime, in which the stars, ideal or swollen, move like compact spheres in a viscous solvent. For *linear chains*, a critical value N_c ($N_c = N_e^{5/3}$) separates two behaviors: for $N > N_c$, we recover two regimes, reptation and Stokes–Einstein, as predicted long ago by Daoud and de Gennes; For $N < N_c$, an extra Rouse-like constraint release regime shows up between the two mentioned above. This may explain experimental results showing that tube renewal processes are important for stars and also for linear chains.

I. Introduction

The reptation theory[1] provides a simple qualitative description of the dynamics of entangled polymer melts and solutions of linear monodisperse polymers. The terminal relaxation time (reptation time) of a chain of Z monomers in a melt is given by

$$T_{\mathrm{rep}} \cong \tau Z^3/N_e \qquad (1)$$

where τ is a microscopic jump time (on the scale of one monomer) and N_e is the number of monomers between entanglements (here and in the following, we identify the "monomer" with a Kuhn segment, and we ignore numerical prefactors). For a linear chain, the diffusion coefficient D is related to the terminal time T_{ter} by

$$D \cong R_g^{\,2}/T_{\mathrm{ter}} \qquad (2)$$

For a reptating ideal chain, this leads to

$$D_{\mathrm{rep}} \cong Za^2/T_{\mathrm{rep}} \cong D_0 N_e/Z^2 \qquad (3)$$

where a is the monomer size (Kuhn length) and D_0 is a microscopic diffusion coefficient a^2/τ.

The importance of constraint release processes (quoted CR in the following) due to the finite lifetime of the tube has been the subject of considerable work in the past,[2–10] and several models have been proposed. For monodisperse melts of linear chains, CR has been shown to affect dynamic properties quantitatively but not qualitatively.[7,8] For systems with a wide range of polydispersity or for branched polymers, the terminal time and diffusion coefficient can be qualitatively affected by CR.

The simplest situation in which constraint release is expected to qualitatively affect the dynamics is that of a long chain (of Z monomers) embedded in a "sea" of shorter entangled chains of N monomers ($Z > N > N_e$). This "bidisperse" melt has become the standard paradigm for discussing CR models.[2–8] The first of these models, proposed by Daoud–de Gennes (DG) and Klein[2,3] treats the tube itself as a Rouse chain, with elementary segments of the size of the tube diameter, and a jump time equal to the reptation time of the surrounding N chains. This leads to a terminal time for CR

$$T_{\mathrm{CR}}(\mathrm{DG}) \cong (\tau N^3/N_e)(Z/N_e)^2 = \tau N^3 Z^2/N_e^{\,3} \qquad (4)$$

and to a diffusion coefficient

$$D_{\mathrm{CR}}(\mathrm{DG}) \cong D_0 N_e^{\,3}/N^3 Z \qquad (5)$$

As pointed out by Daoud and de Gennes,[2] the test chain may also drag along all surrounding chains, in a manner similar to the Stokes or Zimm behavior encountered in low molecular weight solvents. In this regime, the Z chain is expected to behave hydrodynamically as a Stokes sphere. If the chain retains a random-coil conformation, this leads to a terminal time T_{IS} (where the subscript IS stands for "ideal Stokes"):

$$T_{\mathrm{IS}} \cong \eta R_g^{\,3}/kT \cong \tau Z^{3/2} N^3/N_e^{\,2} \qquad (6)$$

where η is the macroscopic velocity. Using (2), this leads to a diffusion coefficient:

$$D_{\mathrm{IS}} = D_0 N_e^{\,2}/N^3 Z^{1/2} \qquad (7)$$

Very large Z-mers are expected to adopt a swollen conformation

$$R_g \cong aN(Z/N^2)^{3/5} \cong a(Z^3/N)^{1/5}$$

and dynamically behave as a swollen Stokes sphere (SS), leading to

$$T_{\mathrm{SS}} \cong \eta R_g^{\,3}/kT \cong \tau(Z^3/N)^{3/5} N^3/N_e^{\,2} \cong \tau Z^{9/5} N^{12/5}/N_e^{\,2} \qquad (8)$$

and to a diffusion coefficient

$$D_{\mathrm{SS}} \cong D_0 N_e^{\,2}/N^{2.8} Z^{3/5} \qquad (9)$$

In the scaling theory,[2] the crossover between ideal and swollen conformation scales as $Z_{\mathrm{crossover}} \sim N^2$. It is worth

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mentioning here, however, that the prefactors involved in dynamic and static quantities may be very different (see e.g. ref 11), so that an approach at a scaling level, such as the one proposed here, is to be taken with particular caution when combining dynamic and static crossovers.

For long linear chains, the comparison between relations 1, 4, 6, and 8 shows that reptation dominates whenever $Z < N^2/N_e^{2/3}$ and $Z < N^3/N_e^2$. This leaves room for a very narrow range of constraint release ($N_e < N < N_e^{4/3}$ and $N^3/N_e^2 < Z < N_e^2$), so that this process was predicted to be of little importance for the terminal time and diffusion of linear melts.[2]

The static properties of stars have been studied in detail in ref 12. Here we restrict ourselves to stars with a small number g of arms (typically $g \leq 6$) of length Z each. Then, the interaction between arms remains small, and the conformation of the arms is expected to remain ideal for $Z < N^2$. The self-diffusion of large stars is much slower than that of linear chains. A star can move in a fixed matrix only by retraction of each arm, as was first pointed out by de Gennes.[13] This leads to exponentially long relaxation times[5,13,14]

$$T^*_{\text{self}} \cong \tau Z^2 \exp(\nu Z/N_e) \qquad (10)$$

where the values of the numerical constant ν and of the prefactor to the exponential are still the subjects of discussion. Note that, in contrast with linear chains, the renewal of the conformation of one arm corresponds to a typical displacement of the order of one tube diameter, $d = a\sqrt{N_e}$. Therefore, the diffusion coefficient is

$$D^*_{\text{self}} \cong d^2/T^*_{\text{self}} \cong D_0(N_e/Z^2) \exp(-\nu Z/N_e) \qquad (11)$$

The comparison of motions by constraint release (relation 4) and Stokes motion (relation 6) suggests that CR is faster than Stokes motion if $Z < N_e^2$. Arm retraction can dominate only for very small stars, $Z < Z^*_c$ where Z^*_c is of order N_e/ν within logarithmic corrections.

The early predictions recalled hereabove were not fully consistent with experiments. In particular, important regimes dominated by constraint release are encountered for both linear chains and stars.[6,15-19] Moreover, a quadratic dependence of the CR terminal time upon Z is generally observed, suggesting a Rouse-like behavior as in eq 4, but the exponent of N is systematically lower than predicted, around 2.5. Montfort et al.[6] and Klein[5] suggested that this discrepancy could arise from a correlation between the Rouse jumps of the tube and proposed to decrease the jump time (equated to the reptation time of the N-mers in the original theories[2,3]) by a factor f, corresponding to the number of entanglements along the Z chain released by a single neighboring N-mer reptation on its length. Then, the terminal time for CR becomes

$$T_{\text{CR}} \cong (Z/N_e)^2 \tau N^3/fN_e \cong \tau Z^2 N^3/fN_e^3 \qquad (12)$$

For f, Klein[5] proposed to choose the number of pairwise contacts between a Z-mer and an N-mer, $N^{1/2}$ (for the case $N < Z$), and found

$$T_{\text{CR}}(K) \cong \tau N^{2.5} Z^2/N_e^3 \qquad (13)$$

As far as the exponents of Z and N are concerned, this expression is in better agreement with experiments.[18]

In contrast, Montfort et al.[6,18] argued that the correlation between $N^{1/2}$ jumps yields and effective renormalization of the jump size by a factor $(N^{1/2}/N_e)$, leading to $f \sim N/N_e^2$, and kept the experimental exponent for the terminal time of the N-mers, $N^{3.4}$. This yields

$$T_{\text{CR}}(M) \sim \tau N^{2.4} Z^2/N_e \qquad (14)$$

(The exponent of N_e was not considered in ref 6.) As far as the exponents of Z and N are concerned, this expression is practically indistinguishable from relation 13. Note, however, that relation 14 would lead to a constraint release always slower than either self-reptation or Stokes, since $T_{\text{CR}}(M)/T_{\text{IS}} \cong N_e(Z/N)^{0.5}$. This is because it does not take into account a lower bound on f (which cannot be smaller than 1). Some extra information can be obtained by checking the dependence upon N_e (e.g. by dilution with polymers below N_e), as discussed in section V.

This brief summary suggests that the problem of constraint release is still not fully understood, even in the particularly simple case of a single "slow" chain immersed in faster ones.

Recently, de Gennes, Brochard-Wyart et al. proposed a rather different approach to the constraint release problem, based on the evaluation of the friction associated with a slow translational motion of the test chain.[20-22]

This dissipation approach is also used in refs 22 and 23 to derive the friction of one grafted chain immersed in a melt of longer chains and in ref 24 to derive the electrophoretic mobility of entangled polyelectrolytes. In section II, we generalize this approach to the friction of a Z-mer in a melt of N-mers, for both larger and smaller free chains, to derive the constraint release mobility μ_{CR}. Using the Einstein relation

$$D_{\text{CR}}/kT = \mu_{\text{CR}} = V/F_v \qquad (15)$$

(where F_ν is the frictional force associated with a velocity V), we then derive the diffusion coefficient D_{CR} and relaxation time T_{CR} of stars (section III) and of linear chains (section IV). Finally, we discuss in section V the physics underlying the discrepancies recalled in the first pages of this Introduction.

II. Constraint Release Friction of a *Z*-mer in *N*-mers

Following refs 20 and 21, we imagine in a thought experiment a Z-mer chain, the reptation of which is inhibited, moving at a constant and very small velocity V (as, for instance, in sedimentation). By "very small", we mean that enough time is left for all chains in the system to retain quasi-equilibrium conformations. In the absence of self-reptation, the motion of the Z-mer is made possible by the reptation of the N-mers. When an N-mer entangled with the Z-mer reptates at a distance of the order of its tube length, $L = d(N/N_e)$, it can release an entanglement with the Z-mer. The local displacement of the Z-mer permitted is only about one tube diameter d, however (Figure 1). Therefore, to allow a translation of the Z-mer at a velocity V, the surrounding chains must reptate at a faster velocity $VL/d = VN/N_e$. The dissipation per Z chain can be written[20,21]

$$T\mathring{S}_Z \cong n\zeta_1 N(VN/N_e)^2 \cong F_v V \qquad (16)$$

where ζ_1 is a monomer friction, F_v is the friction force on the Z-mer, and n is the number of free N chains which need to be displaced in order to allow a translation of the Z-mer. To evaluate n, it is convenient to divide the volume spanned by the Z-mer into cells of volume $a^3N_e^{3/2}$ (entanglement cells). We claim that n can be expressed as the number of entanglements felt by the Z-mer (i.e. the number of entanglement cells it visits, Z/N_e), divided by the number of entanglements simultaneously released by a single N-mer during its reptation, f. Combining this assumption with relations 15 and 16, one recovers relation 12. Our approach differs from the one proposed in ref 5 in the evaluation of f: we equate it to the number of entanglement cells shared by the Z-mer and the N-mer (this point will be commented on further in section V).

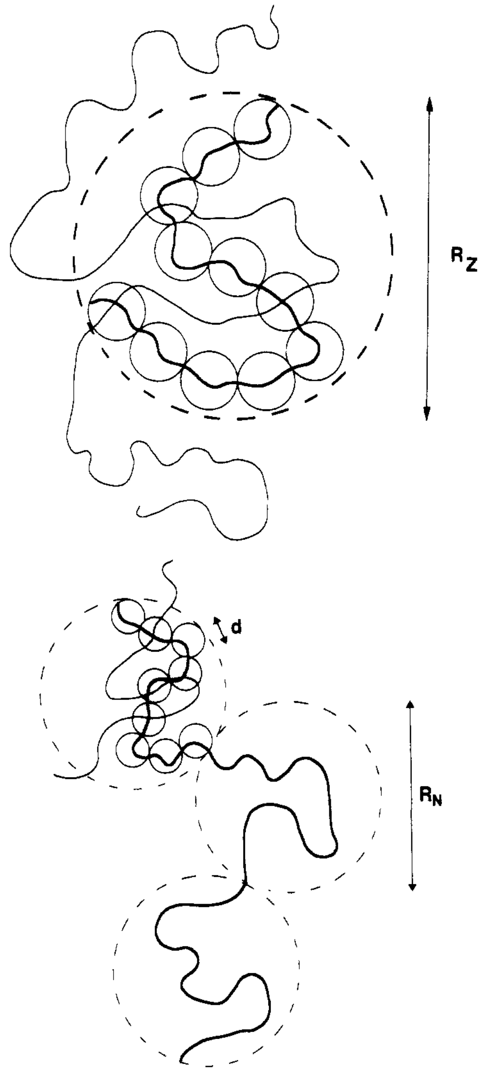

Figure 1. Schematic representation of constraint relase on a test chain (heavy line) by reptation of neighboring chains (thin line). Small circles represent the "blobs" of size d. Figure 1a (top) corresponds to $Z < N$ (the dotted circle corresponds to a sphere of radius $R_Z \cong aZ^{1/2}$), and Figure 1b (bottom) to $Z < N$ (the dotted circle corresponds to a sphere of radius $R_Z \cong aN^{1/2}$).

(i) For $Z < N$ (Figure 1a), f is obtained as the number of entanglement strands of the Z-mer (or, equivalently, the number of entanglement cells it occupies) Z/N_e, multiplied by ϕ_e, the relative fraction of entanglement cells in the Z-coil visited by one particular N-mer. $\phi_e = (Z/N_e)^{-1/2}$, so

$$f \cong Z/N_e\phi_e = (Z/N_e)^{1/2} \qquad (17)$$

and $n = Z/N_e f = (Z/N_e)^{1/2}$. Note that n is equal to unity for $Z = N_e$, as should be. This value of n could also be obtained more readily as the number of nonoverlapping Gaussian tubes of diameter d that can be fitted into the sphere of volume $R_g^3 = a^3Z^{3/2}$:

$$n \cong a^3Z^{3/2}/a^3ZN_e^{1/2} = (Z/N_e)^{1/2} \qquad (18)$$

Using relations 16 and 17 and the definition of ζ_1, one obtains

$$F_v \cong \eta_0 a(Z/N_e)^{1/2}N^3V/N_e^2 \cong \eta R_g(Z)V/N_e^{1/2} \qquad (19)$$

F_v is very similar to the Stokes friction on a sphere (within a numerical factor $N_e^{1/2}$), so we call this regime "Stokes-like constraint release" (SCR) in the following. From relations 15 and 19, one gets the diffusion coefficient

$$D_{\mathrm{SCR}} \cong D_0N_e^{2.5}/N^3Z^{1/2} \cong kTN_e^{1/2}/\eta R_0 \qquad (20)$$

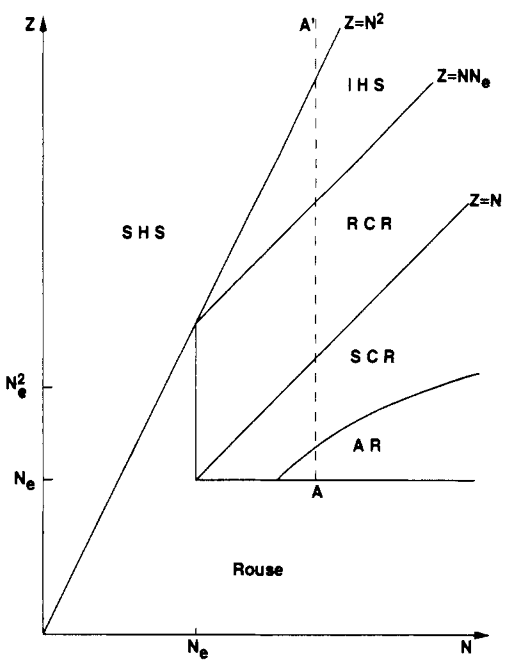

Figure 2. Diagram of the different relaxation regimes (terminal time) for a star with arms of length Z in a melt of N-mers. Key: SHS, swollen hydrodynamic Stokes; IHS, ideal hydrodynamic Stokes; RCR, Rouse constraint release; SCR, Stokes constraint release; AR, arm retraction.

and relation 2 provides the relaxation time:

$$T_{\mathrm{SCR}} = \tau N^3Z^{1.5}/N_e^{2.5} \qquad (21)$$

(note that this is identical to relation 12 with $f = (Z/N_e)^{1/2}$).

(ii) For $Z > N$ (Figure 1b), the N chains to consider (i.e. those able to interact with the Z-mer) are contained in a tube of diameter $N^{1/2}a$ surrounding the Z-mer. Equivalently, the Z-mer can be pictured as a sequence of Z/N "super-blobs" with N monomers. Each of these superblobs is entangled with N/N_e N-mers, leading to

$$n \cong f(Z/N) \cong (Z/N)(N/N_e)^{1/2} \qquad (22)$$

The resulting friction stems from relation 16:

$$F_v \cong \eta_0 aVZ(N/N_e)^{2.5} \cong \eta aVZ/N^{1/2}N_e^{1/2} \qquad (23)$$

Rather remarkably, this is (Z/N) times the friction of a Zimm "blob" containing N monomers (friction $\eta aVN^{1/2}/N_e^{1/2}$): the Z-mer behaves as a Rouse chain of Zimm blobs with N monomers.

This friction is linear in Z, so we call this regime "Rouse-like constraint release" (RCR). From relations 2, 15, and 23, one gets the diffusion coefficient

$$D_{\mathrm{RCR}} \cong D_0N_e^{2.5}N^{2.5}Z \qquad (24)$$

and the relaxation time:

$$T_{\mathrm{RCR}} \cong \tau N^{2.5}Z^2/N_e^{2.5} \qquad (25)$$

(note that this is identical to relation 12 with $f = (N/N_e)^{1/2}$).

We now discuss the resulting dynamic regimes for stars and linear chains in an N-mer solvent.

III. Dynamics of Stars in a Sea of N-mers

Comparing the diffusivities arising from arm retraction (relation 11), constraint release (relations 20 and 24), and Stokes (relations 7–9) types of motion, one obtains the diagram of regimes displayed in Figure 2. From relations 11 and 7, one can see that the diffusion coefficient varies exponentially with Z (relation 11) only in a narrow regime,

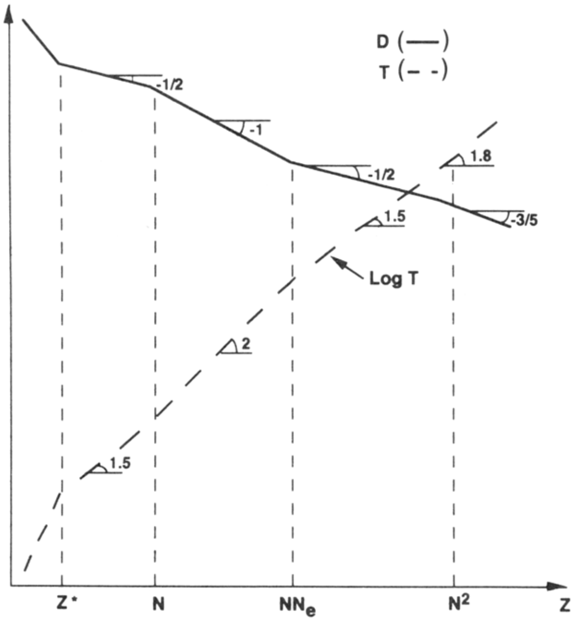

Figure 3. Evolution as a function of Z (following the dotted line AA′ in Figure 2), of the diffusion coefficient (full line) and terminal time (dotted line) for a star with arms of length Z in a melt of N-mers (log–log scale).

$Z < Z_c^*$, where Z_c^* is given by a transcendental equation: $Z_c^* \cong (N_e/\nu)\log(N^3/N_eZ_c^{*1.5})$. Note in particular, that Z_c^* increases only logarithmically with N: it will never exceed 5–10N_e for experimentally achievable situations.[25] For stars with longer arms ($Z > Z_c^*$), difusivity is controlled by constraint release. For $Z_c^* < Z < N$, we expect Stokes-like CR (relations 20 and 21), and for $N < Z < NN_e$, Rouse-like CR (relations 24 and 25). Finally, for $Z > NN_e$, the star drags "solvent" N-mers as a Stokes sphere, ideal if $Z < N^2$ (relations 6 and 7) and swollen if $Z > N^2$ (relations 8 and 9) (we always consider a small number of arms). The schematic evolution of the diffusion coefficient and terminal time with Z is represented in Figure 3 in log–log scale. Taking into account the fact that this is a simplified view ignoring crossover effects, the main conclusion of this diagram is that it is probably impossible to achieve experimentally a reasonably extended "pure" scaling regime. This may explain the large variety of experimental exponents proposed in the literature.

IV. Dynamics of a Linear *Z*-mer in a Sea of *N*-mers

Using the same method as in the previous section, we compare the diffusivities of reptation (relation 3), constraint release (relations 20–24), and Stokes (relations 7–9) types of motion to obtain the diagram of regimes displayed in Figure 4 (note that CR shows up only in the case $Z > N$). We call Z_c the crossover between reptation and Stokes,

$$Z_c \cong N^2/N_e^{2/3} \tag{26}$$

and Z_c' the crossover between reptation and Rouse CR (relation 24):

$$Z_c' \cong N^{5/2}/N_e^{3/2} \tag{27}$$

Comparing relations 26 and 27, it can be seen that, for

$$N_e < N < N_e^{5/3} \tag{28}$$

a regime exists in which constraint release dominates even for linear chains. This conclusion is one of our main results. It qualitatively agrees with earlier suggestions by Klein[5] and Montfort,[6] but it involves different scaling laws (compare relation 25 and relations 13 and 14) and is obtained by a very different approach.

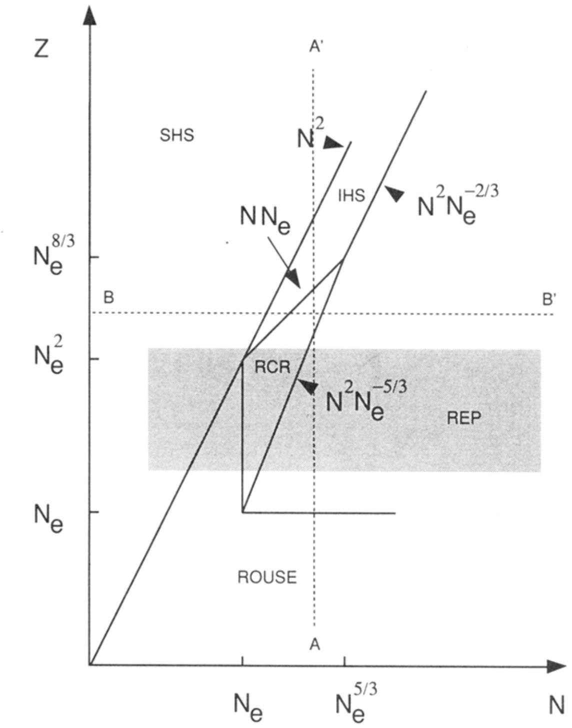

Figure 4. Diagram of the different relaxation regimes (terminal time) for a Z-mer in a melt of N-mers. Key: SHS, swollen hydrodynamic Stokes; IHS, ideal hydrodynamic Stokes; RCR, Rouse constraint release; REP, Reptation. The shaded area corresponds to the range in which the experiments presented in Figure 7 are performed (see section V for details).

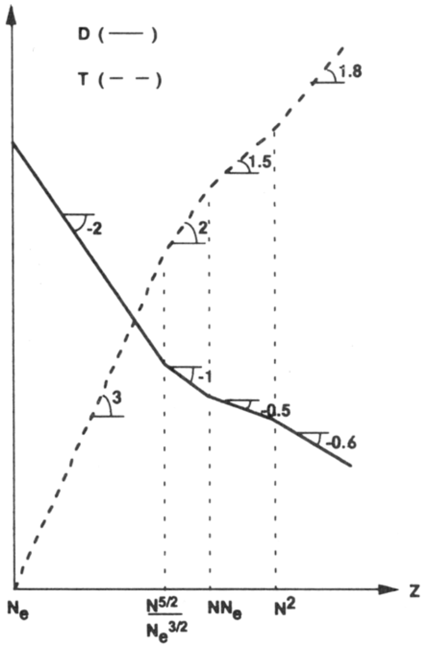

Figure 5. Evolution as a function of Z (following the dotted line AA′ in Figure 4), of the diffusion coefficient (full line) and terminal time (dotted line) for a Z-mer in a melt of N-mers (log–log scale).

The diagram of regimes is displayed in Figure 4, and the typical evolution of the diffusion coefficient and of the terminal time versus Z is presented in Figure 5. When relation 28 is verified, one expects the following sequence of migration mechanisms: self-reptation, Rouse-like constraint release, ideal Stokes, and swollen Stokes. The crossover between Rouse-like constraint release and ideal

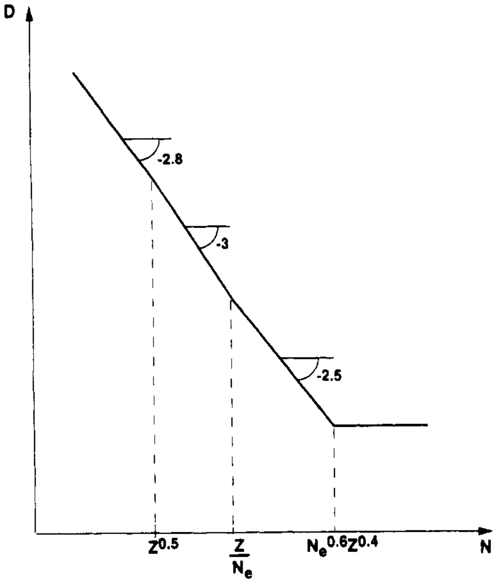

Figure 6. Evolution as a function of N (following the dotted line BB′ in Figure 4), of the diffusion coefficient for a Z-mer in a melt of N-mers (log–log scale).

Stokes arises for

$$Z_c'' \cong NN_e \tag{29}$$

As for stars, there is no single power law describing the general behavior of bidisperse melts. This conclusion is also valid for the evolution of the diffusion coefficient of the Z-mer with N, plotted in Figure 6.

V. Discussion

We have shown that the same expression for the CR terminal time is obtained by using a fluctuation approach based on a random Rouse tube or calculating the dissipation for a displacement at vanishing velocity and by applying the fluctuation–dissipation theorem (relation 15). The discrepancies between earlier predictions based on the Rouse tube approach[2,5,6] and on a "dissipation" approach[20–22] arose from implicit different evaluations of the correlation between constraint release events (factor f: note in particular that relation 25 is recovered when relation 22 is combined with relation 12). The first CR theories[2,3] simply ignored this correlation. Relations 18 and 22 introduced here assume that entanglements are highly cooperative in melts, i.e. that removing any one of the $N_e^{1/2}$ chains traversing an entanglement cell destroys the corresponding entanglement constraint. As mentioned in section II, this leads to a satisfying crossover at $Z = N_e$. This choice is also consistent with recent entanglement theories, which also assume cooperative entanglements.[26,27] Relation 13, proposed earlier by Klein,[5] implicitly associating one entanglement with each pairwise contact between monomers, overestimates the factor f (note in particular that it leads to $f > 1$ for $N = N_e$).

Experimentally, a regime with $T_{CR} \sim Z^2N^{2.5}$ is indeed commonly observed for linear Z-mers in N-mers.[15,18] Cassagnau et al. recently proposed an experimental evaluation of the dependence of T_{CR} on N_e, based on a comparison between several polymers.[18] Their data seem best fitted by the power law

$$T_{CR} \propto Z^{2\pm0.2}N^{2.4\pm0.1}N_e^{-2.0\pm0.3} \tag{30}$$

in rather good agreement with relation 25.

Finally, we propose in Figure 7 a comparison of the theory to a rather extensive study of the tracer diffusion coefficient of polystyrene chains in bimodal melts, performed by Green et al. using forward-recoil spectrometry.[28] The theoretical curves are built as follows.

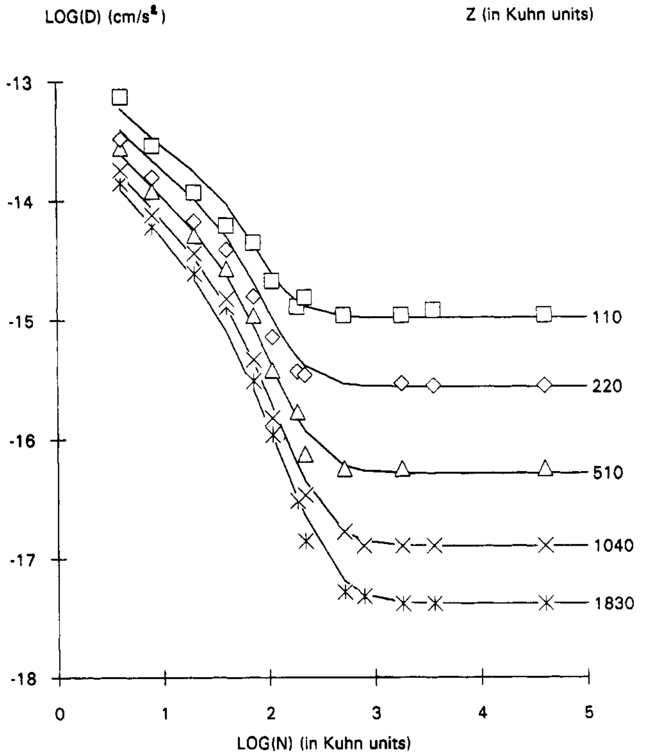

Figure 7. Comparison of the experimental (symbols) and theoretical (lines) values of the tracer diffusion coefficient of a Z-mer in a melt of N-mers (data from ref 28).

Using standard data,[29] we evaluate the molecular weight between entanglements $M_e \cong 18\,000$, the Kuhn length $a \cong 1.5$ nm, and the molecular weight per Kuhn length $M_{\mathrm{Kuhn}} \cong 500$, leading to $N_e \cong 36$ (in Kuhn units). The microscopic diffusion coefficient D_0 appearing in relation 3 is evaluated as $D_0 \cong 3.9 \times 10^{-13}$ cm s^{-2}, directly from the high molecular weight data ($M = 915\,000$ and $P = 20\,000\,000$ in ref 28, i.e. $Z \cong 1830$ and $N \cong 40\,000$), where reptation is expected to be the only significant relaxation process. This is the only adjustable parameter used in the fit. The diffusion coefficient corresponding to constraint release is evaluated from relation 24, using the prefactor α_{CR} proposed by Graessley,[7]

$$\alpha_{CR} \cong (48/25)z(12/\pi^2)^{z-1} \cong 8.5$$

and the value $z \cong 3$:[7,31]

$$D_{RCR} \cong 8.5D_0N_e^{2.5}/N^{2.5}Z \tag{31}$$

Since the processes of reptation and constraint release are expected to occur simultaneously, a good approximation of the diffusion coefficient in the entangled regime is

$$D_{ent} \cong D_{rep} + D_{RCR} \tag{32}$$

A significant part of the data in ref 28 corresponds to the unentangled regime of the matrix, where relation 32 breaks down. In this regime, it should be replaced by Rouse–Zimm relaxation. The Rouse diffusion coefficient is obtained from the relation (see e.g. relation 6.21 in ref 30)

$$D_{Rouse} = 3ZD_{rep}/N_e \tag{33}$$

Finally, the Zimm diffusion coefficient is evaluated as

$$D_{Zimm} \cong 0.2kT/\eta_N R_Z \cong 21.6D_0/ca^2NR_Z$$

where we made use of relations 4.84 and 7.33 in ref 30. η is the Rouse viscosity of the embedding melt of N-mers and c is the number concentration of Kuhn segments in the melt. For a melt of polystyrene, $ca^3 \cong 4$, so

$$D_{\mathrm{Zimm}} \cong 5.4 D_0 a / N R_Z \tag{34}$$

R_Z, the end-to-end distance of the tracer chain, is ideal,

$$R_Z = a Z^{1/2} \tag{35}$$

for $Z < Z_s$, and swollen,

$$R_Z = K a (Z^3/N)^{1/5} \tag{36}$$

for $Z > Z_s$, where

$$Z_s(N) \cong N^2/K^{10} \tag{37}$$

Relation 35 is accurate, but to our knowledge, the prefactor K in relation 36 has received little theoretical interest. Using independent data, we were able to get an estimate for it, $K \cong 0.68$.[32] Then, relation 37 indicates that all data in ref 28 belong to the "ideal regime", or very close to it. Therefore, swelling can be ignored, and

$$D_{\mathrm{Zimm}} \cong 5.4 D_0 a / N R_Z \tag{38}$$

is a good approximation for the data considered. Finally, we use an approximate relation to interpolate between the entangled and nonentangled regimes:

$$D \cong (D_{\mathrm{ent}} D_{\mathrm{unent}}) / (D_{\mathrm{ent}} + D_{\mathrm{unent}}) \tag{39}$$

where $D_{\mathrm{unent}} = D_{\mathrm{Rouse}} + D_{\mathrm{Zimm}}$.

The theoretical evaluation provided by relation 39, represented by the continuous lines in Figure 7, is in very good agreement with the data, considering the number of approximations involved in the evaluation of prefactors and the use of one single adjustable parameter for all curves.

In summary, for *stars*, we predict a broad domain in which the dominant relaxation process is constraint release. For $Z_c^* < Z < N$, the stars apparently behave like Stokes spheres ($D \sim N^{-3} Z^{-1/2}$, or terminal time $T \sim N^3 Z^{3/2}$), but the diffusion coefficient is increased and the terminal time is decreased by a factor $N_e^{1/2}$. For $N < Z < NN_e$, aZ^{-1} dependence of the diffusion coefficient (Z^2 dependence of the terminal time), characteristic of Rouse chains, is obtained, but the N dependence is not trivial.

For *linear chains*, the theory predicts a rather small domain dominated by Rouse-like constraint release, i.e. with a Z^2 dependence of the terminal time. This "Rouse-like constraint release" regime, limited by

$$N^{5/2} N_e^{-3/2} < Z < N N_e$$

disappears when $Z > N_e^{8/3}$ or $N > N_e^{5/3}$. At first sight, it may seem strange that a regime valid in such a limited range of molecular weights would be so universally observed in experiments. This is because it is very difficult to have N-mers that are well entangled (which requires $N \geq 10$) and altogether satisfy $Z > NN_e$. The domain of validity of Rouse-like constraint release is small, but it is the easiest to reach experimentally. Note that the diffusion coefficient and terminal time in this regime are easily evaluated by considering that the Z-mer behaves as a Rouse sequence of Zimm blobs with N monomers.

The approach to constraint release proposed here provides new predictions for the terminal time and diffusion coefficient, which are in good agreement with available experimental data. It also provides some new insight into the still intriguing problem of the nature of entanglement interactions. Further investigations would be interesting, in particular to check the crossovers between different relaxation regimes. Since the present theory ignores numerical prefactors of order unity, a more detailed model taking into account molecular parameters may be necessary for a quantitative comparison with experiments. Another way to check more critically constraint release models is to put more constraints on the system. This will be done in a following paper, in which the same bidisperse polymer melt is confined between impenetrable walls.

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(32) To evaluate K, we consider a solution of polystyrene in a monomolecular solvent with a similar chemical structure (e.g. ethylbenzene or toluene). The intrinsic viscosity of a chain with arbitrary molecular weight (chosen in the middle of the range spanned by the experiments, e.g. 255 000), is obtained using the interpolation Mark–Houwink–Sakurada formula.[29] This yields $[\eta] \cong 80$ cm^3 g^{-1}). An end-to-end distance of 58.3 nm is then obtained using the relation[33] $[\eta] \cong 2.5 R_Z^3 N_A / 6\sqrt{6} M_w$. Comparing with the ideal end-to-end distance 33.8 nm, one gets a crossover from ideal to swollen behavior around $Z \cong 2$. The monomolecular solvents considered here, with molecular weights around 100, correspond roughly to "polymers" with $Z \cong 0.2$. Putting these values in the scaling relation 36 lead to the value of K.
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