Macromolecules 1987, *20*, 2587–2599

alent to rotation of the entire chain, i.e. excitation of the rotational mode.

It should be noted that this simple kinetics scheme does not explain the maximum in the excitation time course of the birefringence (Figure 4).

Conclusions

In this work we have measured the amplitudes and decay times of the first three decay modes as a function of pulse duration and strength, showing that the magnitudes of the various decay modes are pulse width and field strength dependent. The field strength dependence is evident even under conditions where a modified form of the Kerr law is obeyed. Our experimental observations are consistent with those of Diekmann et al.,[17] Stellwagen,[18] and our previous work.[1] We have suggested possible pictures of the orientation mechanism of DNA in an electric field. Our hope is that these or similar pictures will give rise to a semiquantitative theory that can successfully explain the relatively complex behavior of flexible DNAs, both in an electric field and after the field is removed.

Acknowledgment. This work was supported through NSF Grant CHE85 11178 and NIH Grant 2 R01 GM 22517 to R.P. and through NIH Grant 2 R01 GM 31674 to D.E. This work was also supported by the NSF MRL program through the Center for Materials Research at Stanford University. R.J.L. was supported by the NIH Medical Scientist Training Program at the Stanford University School of Medicine. D.E. is the recipient of a NIH Research Career Development Award. We appreciate the helpful comments of the reviewers.

References and Notes

(1) Lewis, R. J.; Pecora, R.; Eden, D. *Macromolecules* **1986**, *19*, 134.
(2) Roitman, D. B.; Zimm, B. H. *J. Chem. Phys.* **1984**, *81*, 6333.
(3) Roitman, D. B.; Zimm, B. H. *J. Chem. Phys.* **1984**, *81*, 6348.
(4) Roitman, D. B. *J. Chem. Phys.* **1984**, *81*, 6356.
(5) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(6) Zimm, B. H.; Roe, G. M.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*, 279.
(7) Lewis, R. J.; Pecora, R. *Macromolecules* **1986**, *19*, 2074.
(8) Nagasaka, K.; Yamakawa, H. *J. Chem. Phys.* **1985**, *83*, 6480.
(9) Lewis, R. J.; Huang, J. H.; Pecora, R. *Macromolecules* **1985**, *18*, 1530.
(10) Provencher, S. W. *Biophys. J.* **1976**, *16*, 27.
(11) Provencher, S. W. *J. Chem. Phys.* **1976**, *64*, 2772.
(12) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. *J. Chem. Phys.* **1979**, *69*, 4273.
(13) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(14) Provencher, S. W. *CONTIN User's Manual*; European Molecular Biology Laboratory Technical Report EMBL-DA02, Heidelberg, 1980.
(15) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.
(16) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.
(17) Diekmann, S.; Hillen, W.; Morgeneyer, B.; Wells, R. D.; Porschke, D. *Biophys. Chem.* **1982**, *15*, 263.
(18) Stellwagen, N. C. *Biopolymers* **1981**, *20*, 399.
(19) Hagerman, P. J.; Zimm, B. H. *Biopolymers* **1981**, *20*, 1481.
(20) Hagerman, P. J. *Biopolymers* **1981**, *20*, 1503.
(21) Benoit, H. *Ann. Phys. (Paris)* **1951**, *6*, 561.
(22) Mandelkern, M.; Elias, J. G.; Eden, D.; Crothers, D. M. *J. Mol. Biol.* **1981**, *152*, 153.
(23) Gebhard, M. S.; Haleem, M.; Eden, D. *Biophys. J.* **1986**, *49*, 300a.
(24) Porschke, D. *Biophys. Chem.* **1985**, *22*, 237.
(25) Porschke, D. *Annu. Rev. Phys. Chem.* **1985**, *36*, 159.
(26) Elias, J. G.; Eden, D. *Macromolecules* **1981**, *14*, 410.
(27) Hogan, M.; Dattagupta, N.; Crothers, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 195.
(28) Rau, D. C.; Charney, E. *Biophys. Chem.* **1983**, *17*, 35.
(29) Diekmann, S.; Hillen, W.; Jung, M.; Wells, R. D.; Porschke, D. *Biophys. Chem.* **1982**, *15*, 157.
(30) Marion, C.; Perrot, B.; Roux, B.; Bernengo, J. C. *Makromol. Chem.* **1984**, *185*, 1665.
(31) Rau, D. C.; Charney, E. *Biophys. Chem.* **1981**, *14*, 1.
(32) Morita, A.; Watanabe, H. *Macromolecules* **1984**, *17*, 1545.
(33) Meyer, P. I.; Vaughan, W. E. *Biophys. Chem.* **1980**, *12*, 329.
(34) Mandel, M..; Odijk, T. *Annu. Rev. Phys. Chem.* **1984**, *35*, 75.
(35) Balasubramanian, D.; Charney, E. *J. Phys. Chem.* **1981**, *85*, 1943.
(36) Yamaoka, K.; Matsuda, K. *Macromolecules* **1980**, *13*, 1558.
(37) Yoshioka, K. *J. Chem. Phys.* **1983**, *79*, 3482.
(38) Sokerov, S.; Weill, G. *Biophys. Chem.* **1979**, *10*, 161.
(39) Yamaoka, K.; Matsuda, K. *J. Phys. Chem.* **1985**, *89*, 2779.
(40) Tinoco, Jr., I.; Yamaoka, K. *J. Phys. Chem.* **1959**, *63*, 423.
(41) Stellwagen, N. C. *Biophys. Chem.* **1982**, *15*, 311.
(42) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
(43) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(44) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
(45) van Dijk, W.; von der Touw, F.; Mandel, M. *Macromolecules* **1981**, *14*, 792.
(46) Watanabe, H.; Morita, A. *Adv. Chem. Phys.* **1984**, *56*, 255.
(47) Watanabe, H.; Morita, A. *J. Phys. Chem.* **1985**, *89*, 1787.
(48) Morita, A.; Watanabe, H. *J. Phys. Chem.* **1985**, *89*, 5755.
(49) Rau, D. C.; Bloomfield, V. A. *Biopolymers* **1979**, *18*, 2783.
(50) Fixman, M. *J. Chem. Phys.* **1981**, *75*, 4040.
(51) Fixman, M.; Jagannathan, S. *J. Chem. Phys.* **1981**, *75*, 4048.
(52) Pollak, M.; Glick, H. A. *Biopolymers* **1977**, *16*, 1007.
(53) Diekmann, S.; Porschke, D. *Biophys. Chem.* **1982**, *16*, 261.

Tracer Diffusion in Polymeric Mixtures

Walter Hess

Fakultät für Physik, Universität Konstanz, 7750 Konstanz, West Germany, and Max-Planck-Institut für Polymerforschung, 6500 Mainz, West Germany.

Received January 29, 1987

ABSTRACT: In the framework of a microscopic many-body theory the tracer diffusion coefficient is calculated for a system of interacting chains with different lengths. The important argument, which replaces the phenomenological tube concept and allows a concrete solution of the problem, is the translational invariance of the interaction potential for curvilinear displacements of the segments. In a self-consistent way we obtain a reptation transition, where at a critical strength of interaction the lateral motion of the segments freezes in. In the long-chain limit the tracer diffusion coefficient can be decomposed as $D_t = D_{rep} + D_{cr}$, where D_{rep} is the reptation and D_{cr} the constraint release mechanism. Whereas our result for D_{rep} is in agreement with the phenomenological theories, we obtain a much stronger constraint release contribution. For the special case of a monodisperse solution, the constraint release mechanism gives the same contribution to D_t as the reptation mechanism itself.

1. Introduction

Polymeric liquids are distinct from other kinds of liquids, consisting of smaller molecules, because of their spectacular rheological and viscoelastic properties. If a sudden force is exerted on a polymeric liquid, it responds elastically like a rubber. Only if the force acts over a sufficiently long span of time, the polymeric liquid starts to flow. This behavior may be characterized by the dynamic elastic moduli, for example, by the time-dependent shear modulus $G(t)$. Initially one observes[1] a monotonous decay of $G(t)$. But then, if the molecular weight of the system is sufficiently large, an elastic plateau develops, where $G(t)$ remains nearly constant over a considerable period of time. Finally, $G(t)$ continues to decay monotonically. This latter period corresponds to the observed slow flow of the material. The extent of the intermediate elastic plateau depends on the molecular weight of the molecules. Below a certain critical molecular weight the elastic plateau is not observed. Here $G(t)$ relaxes monotonically at all times. The most important material property of any liquid is the shear viscosity. Since formally the shear viscosity can be written as the time integral of $G(t)$, it is obvious that above the critical molecular weight, when the elastic plateau in $G(t)$ appears, a strong increase in the shear viscosity takes place.

Since the molecular configuration of a rubber has the form of a network, it was suggested to explain the unusual elastic behavior of high molecular weight polymeric liquids also by a networklike structure. In contrast to a rubber, the net points here are not permanent junctions, but only temporary topological entanglements. Nevertheless, since the unwinding of the topological entanglement affords the motion of a major part of a polymeric chain, the lifetime of such a temporary net point can be very long for large macromolecules. This explains why viscous flow sets in only after such a long time. Despite the success in explaining qualitatively the observed rheological and viscoelastic phenomena, a major drawback of the early network theories[2] was their inability to provide an expression for the lifetime of an entanglement. This quantity entered these theories only as an empirical parameter. Obviously, in order to calculate the entanglement lifetime, first we have to understand how a polymer moves in such a temporary network structure.

In 1967 Edwards[3] suggested that the motion of a polymer in a temporary network might be similar to the motion of a chain in a tube. In this model, the tube summarizes the restrictions on lateral motion of the segments of a test chain. A few years later de Gennes[4-6] concretized the model by defining the dynamical behavior of a chain under the tube constraint. Since the motion of a chain in a tube may be viewed as a snakelike motion, he created the word reptation for its characterization. A major result of this theory was a prediction for the self-diffusion coefficient of a reptating polymer,[4] $D_s \sim M^{-2}$, M being the molecular weight. Since in a dilute good-solvent system $D_s \sim M^{-0.6}$, this result means a strong reduction of chain mobility for an entangled system. Especially, for the semidilute concentration regime, de Gennes also derived the concentration dependence of D_s[6] as $D_s \sim c^{-7/4}M^{-2}$. Both the prediction for the molecular weight dependence and the prediction for the concentration dependence have since been verified. The reptation theory and the tube model also have been worked out by a number of authors and further experiments have been performed to test the result.

Doi and Edwards[7] proposed the model of a "primitive chain", which is allowed to diffuse only curvilinearly and which can change its configuration only at the ends. A seemingly different approach was introduced by Curtiss and Bird.[8] They start from a phase space kinetic theory for polymeric liquids.[9] But then, as in the works before, the theory is simplified to a single-chain description in which, instead of the tube constraint, an anisotropic friction tensor simulates the influence of interchain interactions. By adjusting the components of this friction tensor, lateral motions of the segments can be suppressed, compared to curvilinear motion. One cannot avoid the impression that, in the extreme case where the lateral friction coefficient is much larger than the curvilinear one, this approach is equivalent to the reptation model, although the mathematical structure of this theory is completely different.

A major drawback of the Curtiss–Bird theory is its inability to calculate this anisotropic single-segment friction coefficient in a self-consistent way. A self-consistent extension of the original reptation model was worked out by Klein[10] and Daoud and de Gennes.[11] Since in reality all polymers around the considered test polymer are also in motion and since the tube is constructed to represent the influence of these polymers, one should allow for fluctuations of the form of the tube. This is called the tube renewal or constraint release mechanism. If the constraint release mechanism is related to rate of motion of single chains and it is assumed that the influence of reptation and constraint release on the motion of the test chain can be simply superimposed, a self-consistent description is obtained.[10] This theory obtains a transition from unconstrained motion to constrained motion with increasing chain length, similar to a thermodynamic phase transition. In the long-chain limit the reptation result is recovered. A more quantitative formulation of this theory was given by Graessley.[12]

So far only the reptation result for the self-diffusion coefficient, as given above, was verified experimentally in a wholly convincing manner. For the shear viscosity and other dynamic quantities there are still unexplained discrepancies between theory and experiment. If we ask for the origin of this discrepancy, two possibilities are at hand. The first is that although the reptation picture is basically correct, the mean field theories presented so far are too simplified to account for the complicated correlations in a system of interacting random chains. The other possibility is that the reptation concept itself is too naive and the impressive prediction of the self-diffusion coefficient a mere accident. Such questions can only be answered if we go beyond the reptation theory, or reptation-like theories, and develop a microscopic theory, where neither assumptions about the structure nor about the mode of motion are made from the beginning. The hindrance of the motion of a chain should be related to the law of interaction between the chains in a self-consistent way. This certainly is a difficult program, but in its persuit we have the guidance of the reptation model. Only if reptation can be defined in a microscopic way should it emerge as a consequence of a property of the interaction potential, which is specific for systems of long chains. The result is that this specific property of the interaction potential, which substitutes the tube model and allows a solution of the many-body problem, is the translational invariance of the potential against curvilinear displacements of the segments. This translational invariance is strictly true only for infinitely long chains, with constant segment density along the chains. The true situation of chains with finite but large length and small curvilinear segment density fluctuations might then be treated as a small disturbance of the translational invariance.

In a recent paper[13] we have shown how this symmetry property of the interaction potential of long chains can be used for the derivation of a microscopic expression for the self-diffusion coefficient in monodisperse semidilute solutions. This theory is not a rigorous one, but the necessary approximations never violate the self-consistency of the theory. No ad hoc assumptions about the existence or strength of constraints on the motion of the test chain are made. But, to zero order in the effects which disturb the translational invariance of the interaction potential, a transition in the dynamical behavior is obtained at a critical strength of interaction. Beyond this "critical point" lateral motion is frozen in, due to the blocking by other chains. Now the chains can only move in a curvilinear manner, and for this mode of motion we might rightfully use the name reptation. To first order in the end effects, which disturb the translational invariance of the interaction potential, a slow lateral motion is still possible. This might be identified as the constraint release or tube renewal mechanism of the phenomenological theories.[10-12] For the molecular weight and concentration dependence of the self-diffusion coefficient a complete agreement with de Gennes' result was obtained.

Since the constraint release mechanism is sensitive to the molecular weight of the test chain as well as of the other chains, the matrix chains, much attention has been devoted in recent years to mixtures, consisting of a relatively small amount of labeled polymers, the tracer polymers, with a different molecular weight than the unlabeled polymers, the matrix. By choosing the ratio of the molecular weights, one expects that one can adjust the relative influence of the reptation and the constraint release mechanism on the tracer diffusion coefficient. But, whereas the experimental results for the self-diffusion coefficient are in excellent agreement with the reptation theory, the results for the tracer diffusion coefficient, as a function of tracer and matrix molecular weight, are for the most part in disagreement with the corresponding theoretical predictions. Therefore it is a natural and simple extension of the theory, presented in ref 13, to apply it to this situation and to see whether a better agreement with the experimental observations can be obtained. A short and very simplified version of these results has been published already.[14]

Since this approach to polymer dynamics is new and unconventional, I will also give a better definition of curvilinear and lateral motion. This paper is organized in the following way. In section II a rigorous relation between the tracer diffusion coefficient and a generalized friction function is obtained. This generalized friction function describes the effects of interactions between matrix chains and the tracer chain on the center-of-mass (com) motion of the tracer. We simplify the expression for this function by a number of approximations. Finally it is written as the product of com propagators of the tracer and the matrix chains. In section III we discuss the above-mentioned translational invariance of the interaction potential in terms of curvilinear displacements and those degrees of freedom which describe the geometrical form fluctuations of the chain as a whole. We show how the time evolution operator can be separated if coupling between these two sets of degrees of freedom is neglected. We calculate the com propagators to lowest order in this coupling and obtain a set of algebraic equations for the tracer diffusion coefficient in a mixture with arbitrary molecular weight distribution. In section IV we solve these equations for the special case of one tracer, with polymerization index n_t, in a matrix, all matrix chains having the same polymerization index n_p.

We derive explicit results for certain limiting cases and also present numerical evaluations for general values of n_t and n_p. In section V we dicuss our results in comparison with experimental results and the results of the other theoretical approaches.

2. Center-of-Mass Diffusion Coefficient in Polydisperse Solutions

The microscopic theory for the self-diffusion coefficient in monodisperse solutions was based on a Fokker–Planck equation for the phase space distribution function of N interacting continuous chains, each of length L.[13] The extension to a polydisperse solution of chemically equivalent polymers is straightforward, if we only attribute to each chain its own mean length L_i^0. The indices i denote the chains in the system, $1 \leq i \leq N$. The Fokker–Planck operator takes the form

$$\hat{\Omega} = \sum_{i=1}^{N} \frac{l}{l_0} \int_0^{L_i^0} \mathrm{d}s_i \left[-\mathbf{v}(s_i) \frac{\delta}{\delta \mathbf{r}(s_i)} - \frac{1}{m}(\mathbf{F}(s_i) + \mathbf{E}(s_i)) \cdot \frac{\delta}{\delta \mathbf{v}(s_i)} + \frac{\zeta(c)}{m} \frac{\delta}{\delta \mathbf{v}(s_i)} \cdot \left(\frac{k_B T}{m} \frac{\delta}{\delta \mathbf{v}(s_i)} + \mathbf{v}(s_i) \right) \right] \tag{2.1}$$

Here s_i is a parameter which runs along the contour of chain i, $\mathbf{r}(s_i)$ and $\mathbf{v}(s_i)$ are the coordinate and velocity of the chain at s_i. l_0 is the mean distance between neighboring segments and m is the mass of a segment in the corresponding discrete chain model. Writing $\hat{\Omega}$ as in eq 2.1, we have assumed that the effects of solvent friction can be approximated by a single segment friction coefficient $\zeta(c)$. This does not mean that hydrodynamic interaction effects are completely neglected, but they are incorporated in the spirit of an effective medium theory in the form of a concentration dependence of this single segment friction coefficient. This should be a reasonable ansatz as long as we are interested in phenomena which take place over a length scale much larger than the range of hydrodynamic interaction. A further concentration dependence of $\zeta(c)$ arises because of free volume effects at higher concentrations.[15] Thus solvent friction effects are treated in eq 2.1 in a rather phenomenological manner. But it is the basic assumption of this work that reptation phenomena in entangled solutions are finally due to excluded-volume interactions that guarantees the uncrossability of two chains. $\mathbf{F}(s_i)$ and $\mathbf{E}(s_i)$ are the two kinds of forces which act on the element s_i of chain i. $\mathbf{E}(s_i)$ is the elastic force in the backbone of a polymer,

$$\mathbf{E}(s_i) = 3\frac{\mathrm{d}^2\mathbf{r}(s_i)}{\mathrm{d}s_i^2} \tag{2.2}$$

$\mathbf{F}(s_i)$ is the excluded-volume force. The short-ranged excluded-volume potential is conveniently approximated by a pseudopotential[26]

$$U^{\mathrm{ev}} = {}^1\!/_2 k_B T \upsilon_0 \sum_{i,j=1}^{N} 1/l_0^2 \int_0^{L_i^0} \mathrm{d}s_i \int_0^{L_j^0} \mathrm{d}s_j \, \delta(\mathbf{r}(s_i) - \mathbf{r}(s_j)) \tag{2.3}$$

$\upsilon_0(T)$ is the excluded-volume parameter. In using the ansatz (2.3), we assume that a coarse graining has been performed, which averages over coordinate fluctuations on the scale of the range of the true interaction potential. It will be useful to consider also the Fourier representation of U^{ev},

$$U^{\mathrm{ev}} = \frac{1}{2} k_B T \sum_{i,j=1}^{N} \frac{1}{l_0^2} \int_0^{L_i^0} \mathrm{d}s_i \int_0^{L_j^0} \mathrm{d}s_j \, \frac{\upsilon_0}{(2\pi)^3} \int' \mathrm{d}^3 q \; e^{-i\mathbf{q}\cdot(\mathbf{r}(s_i)-\mathbf{r}(s_j))} \tag{2.4}$$

$\int' \mathrm{d}^3 q$ means that the range of integration is restricted to Fourier vectors $q \leq q_c$, and $q_c \sim \upsilon_0^{-1/3}$ is fixed by the condition $\nu_0/(2\pi)^3 \int' \mathrm{d}^3 q = 1$.

Such a simplified ansatz breaks down close to the Θ-temperature, since $\upsilon_0(\Theta) = 0$. In principle, it would be no problem to work with a more detailed expression for the interaction potential, simply by writing $u(\mathbf{q})$ instead of k_BTv_0 in eq 2.4. The actual difficulty, which is presented by the Θ-state, is that here three-segment correlations are essential, whereas in our further treatment we always want to assume that three-segment correlations are negligible, compared with two-segment correlations. Therefore the theory which is developed here is meant to be used for good-solvent systems only.

By means of a projection operator formalism one derives the following result for the center-of-mass diffusion coefficient of polymer i in terms of a generalized friction function,

$$D_i \equiv \frac{1}{3}\int_0^\infty \mathrm{d}t\ \langle v_i e^{\hat{\Omega}t} v_i\rangle = \frac{k_BT}{n_i} \Big/ [\zeta(c) + \Delta\zeta_i] \quad (2.5)$$

and

$$\Delta\zeta_i = \frac{1}{3n_ik_BT}\int_0^\infty \mathrm{d}t\ \langle F_i e^{\hat{\Omega}\hat{Q}_it} F_i\rangle \quad (2.6)$$

Here n_i is the polymerization index of polymer i, $n_i = L_i^0/l_0$, $\hat{Q}_i = 1 - \hat{P}_i$, and $\hat{P}_i$ projects an arbitrary phase space variable onto the com velocity of polymer i,

$$\mathbf{v}_i = \frac{1}{L_i^0}\int_0^{L_i^0} \mathrm{d}s_i\ \mathbf{v}(s_i) \quad (2.7)$$

$\mathbf{F}_i$ is the total interaction force on i,

$$\mathbf{F}_i = \frac{1}{l_0}\int_0^{L_i^0} \mathrm{d}s_i\ \mathbf{F}(s_i) \quad (2.8)$$

Using the excluded-volume potential, eq 2.4, we obtain

$$\mathbf{F}_i = k_BT\frac{v_0}{(2\pi)^3}\int' \mathrm{d}^3q\ i\mathbf{q}c_i(\mathbf{q})\sum_{j\neq i} c_j(-\mathbf{q}) \quad (2.9)$$

where $c_i(\mathbf{q})$ denotes the Fourier transform of the segment distribution of polymer i,

$$c_i(\mathbf{q}) = \frac{1}{l_0}\int_0^{L_i^0} \mathrm{d}s_i\ e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)} \quad (2.10)$$

The results (2.5) and (2.6) are simple extensions of the results that were obtained for the monodisperse case, using now only the Fokker–Planck operator (2.1) with an individual length for each polymer, instead of the corresponding operator used in ref 13, where all polymers were assumed to have the same length. If we insert eq 2.9, the friction coefficient $\Delta\zeta_i$, which results from interactions of polymer i with all other polymers, takes the form of a time integral over a dynamic four-point correlation function of the segment distribution fluctuations,

$$\Delta\zeta_i = -\frac{k_BT}{3n_i}\int_0^\infty \mathrm{d}t\ \frac{v_0^2}{(2\pi)^6}\int' \mathrm{d}^3q\int' \mathrm{d}^3q'\ \mathbf{q}\cdot \mathbf{q}'\sum_{\substack{j\neq i\\ k\neq i}} \langle c_i(\mathbf{q})c_j(-\mathbf{q})e^{\hat{\Omega}\hat{Q}_it}c_i(\mathbf{q}')c_k(-\mathbf{q}')\rangle \quad (2.11)$$

So far the result given in eq 2.5 and 2.11 is rigorous on the basis of our model, defined in eq 2.1–2.4. The dynamic four-point correlation function in eq 2.11 can more explicitly also be written as

$$\langle 4\rangle = \sum_{s_i,s_i'=1}^{n_i}\sum_{s_j=1}^{n_j}\sum_{s_k=1}^{n_k} \langle e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)}e^{i\mathbf{q}\cdot\mathbf{r}(s_j)}e^{\hat{\Omega}\hat{Q}_it}e^{i\mathbf{q}\cdot\mathbf{r}(s_i')}e^{-i\mathbf{q}\cdot\mathbf{r}(s_k)} \times \exp[-i(\mathbf{q}' + \mathbf{q})(\mathbf{r}(s_i') - \mathbf{r}(s_k))]\rangle \quad (2.12)$$

where for the moment we went back to a discrete chain model. This expression describes a correlation between segments s_i and s_j of chains i and j at time t, correlated to the fact that at time 0 there was a contact between segments s_i' and s_k of chains i and k. The fact that s_i' and s_k are in contact at $t = 0$ has to be seen together with the q' integral in (2.11), which gives a contribution only for $\mathbf{r}(s_i') = \mathbf{r}(s_k)$. Let us now assume that this correlation at time t is only due to that contact at $t = 0$ that subsequently has been transmitted from the segments in contact to other segments of the same chains. Neglecting therefore the possibility of additional contacts at intermediate times and more complicated correlations between many chains, we simply factor the four-point correlation function as

$$\langle 4\rangle \simeq \delta_{jk}\sum_{s_i,s_i'=1}^{n_i}\sum_{s_j,s_j'=1}^{n_j} \langle e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)}e^{\hat{\Omega}t}e^{i\mathbf{q}\cdot\mathbf{r}(s_i')}\rangle \times \langle e^{i\mathbf{q}\cdot\mathbf{r}(s_j)}e^{\hat{\Omega}t}e^{-i\mathbf{q}\cdot\mathbf{r}(s_j')}\rangle\langle \exp[-i(\mathbf{q}' - \mathbf{q})(\mathbf{r}(s_i') - \mathbf{r}(s_j'))]\rangle \quad (2.13)$$

Note that for the factored time correlation function the full time evolution operator $\exp(\hat{\Omega}t)$ can be used instead of the reduced one, $\exp(\hat{\Omega}\hat{Q}_it)$. Now the q′ integration in (2.11) can be performed, to lowest order in q_c^{-1},

$$k_BT\frac{v_0}{(2\pi)^3}\int' \mathrm{d}^3q'\ \mathbf{q}\cdot\mathbf{q}'\langle \exp[-i(\mathbf{q}' + \mathbf{q})(\mathbf{r}(s_i') - \mathbf{r}(s_j'))]\rangle = -q^2k_BTv_0\langle \delta(\mathbf{r}(s_i') - \mathbf{r}(s_j'))\rangle \quad (2.14)$$

which is just $-\mathbf{q}^2$ times the mean excluded-volume interaction between the segments s_i' and s_j'. Except for segments close to the ends of the chains, all segments will be statistically equivalent. Neglecting such end effects we may write

$$\varphi(c)/V = v_0k_BTl_0^2\langle \delta(\mathbf{r}(s_i') - \mathbf{r}(s_j'))\rangle \quad (2.15)$$

for any pair of segments. The quantity $\varphi(c)$ is the mean excluded-volume energy between two segments. In mean-field treatment one simply has $\varphi(c) = v_0k_BT$. In general $\varphi(c)$ depends on concentration, temperature, and other thermodynamic parameter of the system but not on the molecular weights of the polymers. Using now eq 2.13–2.15 in eq 2.11, we obtain

$$\Delta\zeta_i = \frac{\varphi(c)}{3n_iV}\frac{v_0}{(2\pi)^3}\int' \mathrm{d}^3q\ \mathbf{q}^2\int_0^\infty \mathrm{d}t\ S_i^{\mathrm{coh}}(\mathbf{q},t)\sum_{j\neq i} S_j^{\mathrm{coh}}(\mathbf{q},t) \quad (2.16)$$

where $S_i^{\mathrm{coh}}(\mathbf{q},t)$ is the single-chain coherent dynamic structure factor of chain i,

$$S_i^{\mathrm{coh}}(\mathbf{q},t) = \langle c_i(\mathbf{q})e^{\hat{\Omega}t}c_i(-\mathbf{q})\rangle \quad (2.17)$$

Since the upper limit of the q integral goes to infinity for small excluded volume, the integral will be dominated by the large q contributions. This can be seen by introducing a scaled integration variable $\kappa = \mathbf{q}/q_c$. Then

$$\lim_{v_0\to 0}\frac{v_0}{(2\pi)^3}\int' \mathrm{d}^3q\ \mathbf{q}^2S_i^{\mathrm{coh}}(\mathbf{q},t)S_j^{\mathrm{coh}}(\mathbf{q},t) = \int' \mathrm{d}^3\kappa\ \kappa^2\lim_{q_c\to\infty} S_i^{\mathrm{coh}}(q_c\kappa,t)S_j^{\mathrm{coh}}(q_c\kappa,t) \quad (2.18)$$

In the limit of large wavevectors, the single-chain dynamic structure factor goes over into the incoherent scattering function, since all the interference terms between different segments in $S_i^{\mathrm{coh}}(\mathbf{q},t)$ vanish in this limit. This can be shown explicitly for Gaussian chain models, but it can be expected that this relation is much more general and does not depend on a specific chain model. Then

$$\lim_{q_c\to\infty} S_i^{\mathrm{coh}}(q_c\kappa,t) = S_i^{\mathrm{inc}}(q_c\kappa,t) \quad (2.19)$$

where

$$S_i^{\mathrm{inc}}(\mathbf{q},t) = (1/l_0)\int_0^{L_i^0} \mathrm{d}s_i\ \langle e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)} e^{\hat{\Omega}t} e^{i\mathbf{q}\cdot\mathbf{r}(s_i)}\rangle \qquad (2.20)$$

Treating again all segments as statistically equivalent, we obtain

$$S_i^{\mathrm{inc}}(\mathbf{q},t) = n_i R_i^{1}(\mathbf{q},t) \qquad (2.21)$$

where $R_i^1(\mathbf{q},t)$ is the dynamic propagator for a single segment of the chain i. Now eq 2.16 becomes

$$\Delta\zeta_i = \frac{\varphi(c)}{3V}\frac{\upsilon_0}{(2\pi)^3}\int' \mathrm{d}^3q\ \mathbf{q}^2 \int_0^\infty \mathrm{d}t\ R_i^1(\mathbf{q},t)\sum_{j\neq i} n_j R_j^1(\mathbf{q},t) \qquad (2.22)$$

and we understand that this expression should be evaluated to lowest order in υ_0. The physical interpretation of this result is very clear: the friction which polymer i feels due to interaction with the other polymers results from the sum of excluded-volume interactions between the segments. Since excluded-volume interactions are extremely short ranged, the different contacts that a chain has are treated as uncorrelated. But since the segments in contact are connected with their neighboring segments, they cannot move independently from the rest of the chain. Therefore, after sufficiently long time, global chain properties will determine the single-segment propagators. It is this dependence of $\Delta\zeta_i$ on global chain properties that we are looking for. For sufficiently long times the displacement of a segment is determined by center-of-mass motion alone, thus we can write

$$R_i^1(\mathbf{q},t) = R_i^{\mathrm{cm}}(\mathbf{q},t) + \Delta R_i^1(\mathbf{q},t) \qquad (2.23)$$

$R_i^{\mathrm{cm}}(\mathbf{q},t)$ is the com propagator of chain i,

$$R_i^{\mathrm{cm}}(\mathbf{q},t) = \langle e^{-i\mathbf{q}\cdot\mathbf{r}_i} e^{\hat{\Omega}t} e^{i\mathbf{q}\cdot\mathbf{r}_i}\rangle \qquad (2.24)$$

where $\mathbf{r}_i$ is the com coordinate of chain i,

$$\mathbf{r}_j = \frac{1}{L_i^0}\int_0^{L_i^0} \mathrm{d}s_i\ \mathbf{r}(s_i) \qquad (2.25)$$

and $\Delta R_i^1(\mathbf{q},t)$ is a function which is characterized by internal relaxation processes of the chain. The com propagator depends strongly on the molecular weight of a chain. In the long-chain limit, $R_i^{\mathrm{cm}}(\mathbf{q},t) \to 1$ for $n_i \to \infty$, and the corresponding contribution to the friction coefficient $\Delta\zeta$ becomes singular in this limit, since then the time integral in eq 2.22 diverges. In contrast, for noninteracting Gaussian chains one can show explicitly that internal relaxation processes become independent of molecular weight. Although this is a much more subtle point for a system of interacting chains, we will here assume that also in this case the contribution of $\Delta R_i(\mathbf{q},t)$ to the time integral in eq 2.22 behaves regularly in the long-chain limit. Then

$$\Delta\zeta_i = \Delta\zeta_i^{\mathrm{sin}} + \Delta\zeta_i^{\mathrm{reg}} \qquad (2.26)$$

$$\Delta\zeta_i^{\mathrm{sin}} = \frac{\varphi(c)}{3V}\frac{\upsilon_0}{(2\pi)^3}\int' \mathrm{d}^3q\ \mathbf{q}^2 \int_0^\infty \mathrm{d}t\ R_i^{\mathrm{cm}}(\mathbf{q},t)\sum_{j\neq i} n_j R_j^{\mathrm{cm}}(\mathbf{q},t) \qquad (2.27)$$

and $\Delta\zeta_i^{\mathrm{reg}}$ gives the rest of the terms, which result from the decomposition (2.23). In the following we will disregard the regular part of $\Delta\zeta_i$, setting $\Delta\zeta_i \simeq \Delta\zeta_i^{\mathrm{sin}}$, which becomes correct in the long-chain limit.

3. Separation of Curvilinear and Lateral Degrees of Freedom

In a previous paper[13] we have used the argument that the interaction between two polymers should not depend on curvilinear displacements of the segments. As a corollary, one can also say that the direction of interaction forces is always perpendicular to the local axes of the two chains at the point of contact. These statements are only true as long as we do not consider end effects and as long as we are allowed to describe a polymer in the framework of the usual two-parameter theory, as a structureless continuous chain. Then, if we would make a drawing of our system, we would simply draw a line for a polymer. In this picture, interaction between two polymers means that two lines meet somewhere. In three dimensions typically two lines meet transversely. Since for the short-ranged forces, which we assume in our model, their direction is parallel to the vector of closest distance between the two lines, it follows that the force direction is also transverse to both lines at the point where they meet.

These properties of the interaction between two polymer chains are of central importance for the method by which we will calculate the dynamic friction function, which we also want to suggest in a more general context as a suitable way for the treatment of the dynamical properties of entangled polymeric liquids. Therefore it seems worthwhile to consider the separation of curvilinear and of lateral displacements in detail. The way this was done in our previous paper was not entirely precise.

Let us first consider what we mean by curvilinear motion. Curvilinear motion means that a segment just follows the line that the polymer forms. Then, at any later time the position of a segment s_i will be at a place where some other segment of the same chain, lets say s_i', has been before,

$$\mathbf{r}(s_i,t+\tau) = \mathbf{r}(s_i',t) = \mathbf{r}_0 \qquad (3.1)$$

This equation, which is the basis of the Doi–Edwards theory,[7] defines curvilinear motion. We expand the equation for small τ and small $s_i - s_i'$,

$$\mathbf{r}(s_i,t) + \left.\frac{\mathrm{d}\mathbf{r}(s_i,t)}{\mathrm{d}t}\right|_{\mathrm{cl}}\tau + \ldots = \mathbf{r}(s_i,t) + \frac{\mathrm{d}\mathbf{r}(s_i,t)}{\mathrm{d}s_i}(s_i' - s_i) + \ldots \qquad (3.2)$$

or, for $\tau \to 0$,

$$\left.\frac{\mathrm{d}\mathbf{r}(s_i,t)}{\mathrm{d}t}\right|_{\mathrm{cl}} = \frac{\mathrm{d}\mathbf{r}(s_i,t)}{\mathrm{d}s_i}\frac{\mathrm{d}s_i}{\mathrm{d}t} \qquad (3.3)$$

Here $\mathrm{d}s_i/\mathrm{d}t$ is the change in the segment index seen by an external observer at $\mathbf{r}_0$. Now, if this observer interacts with that segment of the chain which is at $\mathbf{r}_0$, he will not care about the segment index, as long as the interaction law does not depend explicitely on it. Therefore the interaction will not be changed by curvilinear motion. Equation 3.3 also says, although this is also intuitively clear, that curvilinear motion goes in the direction of the local tangent vector of the chain. By introduction of the contour length of the chain as

$$l(s_i) = \int_0^{s_i} \mathrm{d}s_i' \left|\frac{\mathrm{d}\mathbf{r}(s_i')}{\mathrm{d}s_i'}\right| \qquad (3.4)$$

the local tangent vector is

$$\hat{\mathbf{t}}(s_i) = \frac{\mathrm{d}\mathbf{r}(s_i)}{\mathrm{d}l(s_i)} \qquad (3.5)$$

$\hat{\mathbf{t}}(s_i)$ is a unit vector, $|\hat{\mathbf{t}}(s_i)| = 1$. Then eq 3.3 can be written as

$$\begin{aligned}\left.\frac{\mathrm{d}\mathbf{r}(s_i,t)}{\mathrm{d}t}\right|_{\mathrm{cl}} &= \hat{\mathbf{t}}(s_i)\frac{\mathrm{d}l(s_i)}{\mathrm{d}s_i}\frac{\mathrm{d}s_i}{\mathrm{d}t} \\ &= \hat{\mathbf{t}}(s_i)\frac{\mathrm{d}l(s_i)}{\mathrm{d}t} \qquad (3.6)\end{aligned}$$

By eq 2.3, U^{ev} is a functional of the vectors $[\mathbf{r}(s_i), 0 \leqslant s_i \leqslant L_0]$. Taking eq 3.4 as a transformation law between parameters $l_i \equiv l(s_i)$ and s_i, we may also consider l_i as the independent parameter and describe the contour of the chain by $[\mathbf{r}(l_i), -L_{\mathrm{i}}^{\mathrm{a}} \leqslant l_i \leqslant L_i^{\mathrm{e}}]$. In order to treat the two ends of the chain on the same footing, we have shifted the origin of the contour length to the middle of the chain, $l(s_i/2) = 0$, $l(0) = -L_i^{\mathrm{a}}$ and $l(L_i^0) = L_i^{\mathrm{e}}$. The total contour length of chain i is $L_i = L_i^{\mathrm{a}} + L_i^{\mathrm{b}}$. The transformation between $\mathbf{r}(l_i)$ and $\mathbf{r}(s_i)$ can be written as

$$\mathbf{r}(l_i) = \int_0^{L_i^0} \mathrm{d}s_i\, \delta(s_i - s(l_i))\mathbf{r}(s_i) \tag{3.7}$$

and

$$\mathbf{r}(s_i) = \int_{-L_i^{\mathrm{a}}}^{L_i^{\mathrm{e}}} \mathrm{d}l_i\, \delta(l_i - l(s_i))\mathbf{r}(l_i) \tag{3.8}$$

which has to be supplemented by eq 3.4 and the corresponding back-transformation, to obtain $s(l_i)$. For our purpose it is sufficient to know that the back-transformation exists.

Whereas $\mathbf{r}(s_i)$ gives us the full information about the position of the physical chain elements, $\mathbf{r}(l_i)$ has lost the details of the distribution of segments along the contour of the chain. Therefore $\mathbf{r}(l_i)$ only characterizes the geometrical form of the chain. The curvilinear degrees of freedom are given by $l(s_i)$. If we now express the excluded-volume potential (2.3) by this new set of degrees of freedom, we obtain

$$U^{\mathrm{ev}} = \frac{1}{2}k_{\mathrm{B}}T \sum_{i,j=1} \frac{1}{l_0^2} \int_{-L_i^{\mathrm{a}}}^{L_i^{\mathrm{e}}} \mathrm{d}l_i \int_{-L_j^{\mathrm{a}}}^{L_j^{\mathrm{e}}} \mathrm{d}l_j\, v_0 \frac{\mathrm{d}s_i}{\mathrm{d}l_i} \frac{\mathrm{d}s_j}{\mathrm{d}l_j}\, \delta(\mathbf{r}(l_i) - \mathbf{r}(l_j)) \tag{3.9}$$

which now is a functional of $[\mathbf{r}(l_i), s(l_i), -L_i^{\mathrm{a}} \leqslant l_i \leqslant L_i^{\mathrm{e}}]$. The interesting point is that the law of distance depends only on the geometrical form fluctuations, but not on the curvilinear degrees of freedom. The latter enter the interaction law merely in the form of a renormalization of the excluded volume parameter, $v_0(\mathrm{d}s_i/\mathrm{d}l_i)$ $(\mathrm{d}s_j/\mathrm{d}l_j)$. Since l_0^{-1} $\mathrm{d}s(l_i)/\mathrm{d}l_i$ is just the curvilinear segment density at l_i, the physical meaning of this renormalization of the excluded-volume parameter is immediately clear: the effective strength of the interaction at a contact point has to be proportional to the local segment densities of both chains. A further dependence on curvilinear degrees of freedom is seen in the contour lengths of the end points of the chains, L_i^{a}, L_j^{a}, L_i^{e}, L_j^{e}. For finite chains this end dependence of U^{ev} will always be present, but the influence of curvilinear density fluctuations will be small, compared to the change in energy which is produced by a contact or a separation of two chains.

We assume now that fluctuations in the curvilinear segment density are small, compared to the equilibrium density, which is l_0^{-1}. Setting therefore $\mathrm{d}s_i/\mathrm{d}l_i = 1$ and, consistent with this approximation, $L_i^{\mathrm{a}} = L_i^{\mathrm{e}} = L_i^0/2$, we obtain

$$U^{\mathrm{ev}} = \frac{1}{2}v_0 k_{\mathrm{B}}T \sum_{i,j=1}^{N} \frac{1}{l_0^2} \int_{-L_i^0/2}^{L_i^0/2} \mathrm{d}l_i \int_{L_j^0/2}^{L_j^0/2} \mathrm{d}l_j\, \delta(\mathbf{r}(l_i) - \mathbf{r}(l_j)) \tag{3.10}$$

On a first view this looks the same as our starting expression, eq 2.3. The important difference is that the $\mathbf{r}(l_i)$ now has a different meaning, compared to $\mathbf{r}(s_i)$.

The second important quantity, which we have to consider with respect to a decomposition in curvilinear and geometrical form fluctuations, is the functional derivative $\delta/\delta\mathbf{r}(s_i)$. Multiplying with the tangent vector, we obtain the parallel component of the derivative as

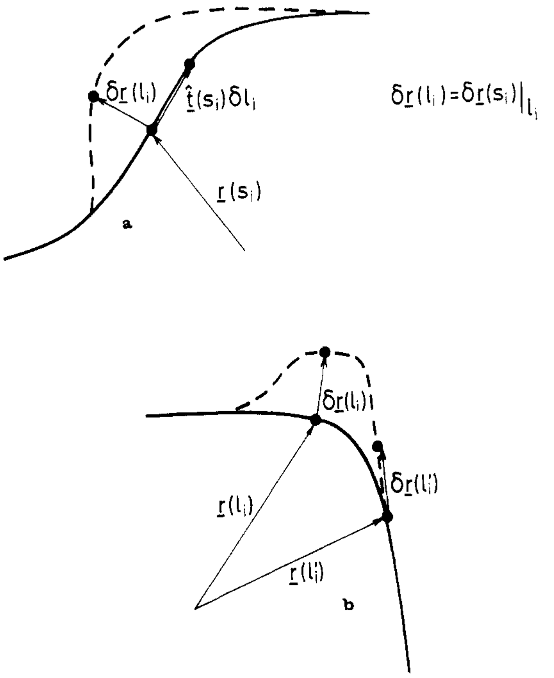

Figure 1. Curvilinear and lateral displacements.

$$\hat{\mathbf{t}}(s_i)\cdot\frac{\delta}{\delta\mathbf{r}(s_i)} = \frac{\mathrm{d}\mathbf{r}(s_i)}{\mathrm{d}l(s_i)}\frac{\delta}{\delta\mathbf{r}(s_i)} = \frac{\delta}{\delta l(s_i)} \tag{3.11}$$

It would be tempting to identify the lateral components of the functional derivative with the derivative with respect to $\mathbf{r}(l_i)$, which describes the geometric form of the chain. If we look at Figure 1a, we see indeed that a lateral displacement is always connected with a change of the form of the chain, and vice versa. Then one would obtain a simple decomposition

$$\frac{\delta}{\delta\mathbf{r}(s_i)} = \frac{\delta}{\delta\mathbf{r}(l_i)} + \hat{\mathbf{t}}(s_i)\frac{\delta}{\delta l(s_i)} \tag{3.12}$$

where, according to eq 3.11,

$$\frac{\delta}{\delta\mathbf{r}(l_i)} = (1 - \hat{\mathbf{t}}(s_i){:}\hat{\mathbf{t}}(s_i))\frac{\delta}{\delta\mathbf{r}(l_i)} \tag{3.13}$$

Unfortunately, the true decomposition is not as simple. Physically, the $\mathbf{r}(s_i)$ are the independent degrees of freedom of our system,

$$\delta\mathbf{r}(s_i)/\delta\mathbf{r}(s_j') = \delta(s_i - s_j') \tag{3.14}$$

and not the $l(s_i)$, $\mathbf{r}(l_i)$. If we now chose to treat the latter set of variables mathematically as independent quantities, we have to account for the physical coupling between these variables in our time evolution operator. Figure 1b illustrates the nature of this coupling: a lateral displacement of segment s_i, which does not change the contour length of that segment, produces a displacement in $\mathbf{r}(l_i)$. But it also changes automatically the contour length of all segments $s_i' > s_i$, and therefore also the position of the length element l_i', $\mathbf{r}(l_i')$, although the position of the segment s_i', $\mathbf{r}(s_i')$, is not changed. Comparing parts a and b of Figure 1, we see that this nonlocal coupling among the length elements is negligible if the curvature radius at s_i is large, compared with the displacement, i.e., if the curve is sufficiently smooth on that length scale. The complete form of the functional derivative is worked out in the Appendix. Here, in order to proceed, we simply assume that we consider the chains on an already coarse-grained length scale, on which this condition of smoothness is fulfilled. So we will use eq 3.12 for the decomposition of the functional derivative as an approximation, instead of the complete relation (A6).

In fact, analogous assumptions of smoothness also had to be introduced into the reptation models of de Gennes[4-6] and Curtiss and Bird.[8] Since it is our aim to give a self-consistent description of the dynamics in entangled polymeric liquids (although the concept of entanglements is never explicitely used), one might rightfully ask here whether by this assumption of smoothness we have now put into the theory that feature which we actually want to obtain as a result: reptation. But this is not the case. The essence of the reptation picture is a freezing in of lateral motion. In the phenomenological models this is accomplished by a tube,[4-6] by postulating curvilinear motion according to eq 3.1 from the beginning,[7] or by introducing an anisotropic effective friction coefficient for each segment, which hinders lateral motion more strongly than the curvilinear motion.[8] In the approach presented here, such concepts are not used, but the hinderence of lateral motion comes as a collective effect, due to the interaction between the chains. In a simple liquid increasing interaction effects would lead to a slowing down of all degrees of freedom, leading finally to a solidification. The reason why for a polymeric liquid only lateral motion is affected comes from the specific, highly anisotropic form of the interaction potential of two chains, as we have outlined before. Therefore, not the smoothness assumption, but only the interaction law between chains, will be responsible for reptative motion.

If we now calculate the interaction force on a segment, on the basis of eqs. (3.10) and (3.12), we obtain for the tangential component

$$\hat{\mathbf{t}}(s_i)\cdot\mathbf{F}(s_i) = -\frac{\delta U^{\mathrm{ev}}}{\delta l(s_i)} = -v_0 k_{\mathrm{B}} T[\delta(l(s_i) - L_i^0/2) - \delta(l(s_i) + L_i^0/2)]\sum_{j=1}^{N}\frac{1}{l_0}\int_{-L_j^0/2}^{L_j^0/2} \mathrm{d}l_j\, \delta(\mathbf{r}(l_i) - \mathbf{r}(l_j)) \quad (3.15)$$

The lateral component is

$$\mathbf{F}^{\perp}(l_i) = -\frac{\delta}{\delta \mathbf{r}(l_i)} U^{\mathrm{ev}} \quad (3.16)$$

The elastic force $\mathbf{E}(s_i)$ is readily expressed in $l(s_i)$ and $\mathbf{r}(l_i)$ as

$$\mathbf{E}(s_i) = 3\frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2}\hat{\mathbf{t}}(s_i) + 3\left(\frac{\mathrm{d}l(s_i)}{\mathrm{d}s_i}\right)^2 \frac{\mathrm{d}^2\mathbf{r}(l_i)}{\mathrm{d}l_i^2} \quad (3.17\mathrm{a})$$

Now, $\mathrm{d}^2\mathbf{r}(l_i)/\mathrm{d}l_i^2 = \mathrm{d}\hat{\mathbf{t}}(l_i)/\mathrm{d}l_i$, which is always normal to the tangent vector. The absolute value of $\mathrm{d}\hat{\mathbf{t}}(l_i)/\mathrm{d}l_i$ is just the inverse of the curvature radius. Therefore, in order to be consistent with our assumption of a locally smooth chain, we will neglect this second term in the elastic force and we keep only the first one, which describes the elasticity of the curvilinear fluctuations,

$$\mathbf{E}(s_i) = 3\frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2}\hat{\mathbf{t}}(s_i) \quad (3.17\mathrm{b})$$

After all these steps we can write the Fokker–Planck operator as the sum of a curvilinear term $\hat{\Omega}''$ and a term $\hat{\Omega}^{\perp}$, which describes the evolution of the topological structure of the system, irrespectively of the actual segment distribution along the chains.

$$\hat{\Omega} = \hat{\Omega}'' + \hat{\Omega}^{\perp} \quad (3.18)$$

These events, where the end of a chain interacts with another chain, should be seldom (of $\mathcal{O}(1/L_i^0)$) compared to interactions of inner segments of the same chain. Then the tangential component of the excluded-volume force will be negligible, and $\hat{\Omega}''$ describes the curvilinear motion of N independent Rouse chains,

$$\hat{\Omega}'' = \sum_{i=1}^{N}\frac{1}{l_0}\int_0^{L_i^0}\mathrm{d}s_i \left[-v''(s_i)\frac{\delta}{\delta l(s_i)} - \frac{3}{m}\frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2}\frac{\delta}{\delta v''(s_i)} + \frac{\zeta(c)}{m}\frac{\delta}{\delta v''(s_i)}\left(\frac{k_{\mathrm{B}}T}{m}\frac{\delta}{\delta v''(s_i)} + v''(s_i)\right)\right] \quad (3.19)$$

For $\hat{\Omega}^{\perp}$ we obtain

$$\hat{\Omega}^{\perp} = \sum_{i=1}^{N}\frac{1}{l_0}\int_{-L_i^0/2}^{L_i^0/2}\mathrm{d}l_i \left[-\mathbf{v}^{\perp}(l_i)\cdot\frac{\delta}{\delta\mathbf{r}(l_i)} - \frac{1}{m}\mathbf{F}^{\perp}(l_i)\cdot\frac{\delta}{\delta\mathbf{v}^{\perp}(l_i)} + \frac{\zeta(c)}{m}\frac{\delta}{\delta\mathbf{v}^{\perp}(s_i)}\cdot\left(\frac{k_{\mathrm{B}}T}{m}\frac{\delta}{\delta\mathbf{v}^{\perp}(s_i)} + \mathbf{v}^{\perp}(s_i)\right)\right] \quad (3.20)$$

Here we have also defined curvilinear and lateral velocities

$$v''(s_i) = \hat{\mathbf{t}}(s_i)\cdot\mathbf{v}(s_i) \quad (3.21\mathrm{a})$$

$$\mathbf{v}^{\perp}(s_i) = \mathbf{v}(s_i) - v''(s_i)\hat{\mathbf{t}}(s_i) \quad (3.21\mathrm{b})$$

and $\mathbf{v}^{\perp}(l_i)$ means $\mathbf{v}^{\perp}(l(s_i))$. Changing from s integration to l integration we have again, as for eq 3.10, assumed a preaveraging over curvilinear density fluctuations, setting $\mathrm{d}s_i/\mathrm{d}l_i = 1$.

$\hat{\Omega}''$ is completely independent of the topological structure of the system, and $\hat{\Omega}^{\perp}$ depends on the curvilinear degrees of freedom only by a dependence on the positions of the ends, since the l integrals should be understood as

$$\int_{-L_i^0/2}^{L_i^0/2}\mathrm{d}l_i \ldots \int_{-\infty}^{\infty}\mathrm{d}l_i\, \theta(l_i - l(s_i{=}0))\theta(l_i + l(L_i^0)) \ldots \quad (3.22)$$

All approximations which we have made so far, preaveraging over curvilinear density fluctuations in those terms which depend primarily on the geometrical form fluctuations of the chains, the assumption of local smoothness, etc., have been made because of mathematical convenience or necessity. We consider them as not essential for the physical problem. But neglecting now the end effects in $\hat{\Omega}^{\perp}$ is really at the heart of this theory. The idea is that in general the force autocorrelation function (2.6) will be dominated by interactions between inner segments of the chains and the relaxation of the function is largely determined by lateral motions of the segments, described as a fluctuation in $\mathbf{r}(l_i)$. But if lateral motion can freeze in, then this mechanism no longer exists and then a force between two chains can relax only if one of the chains has moved so far that one of its ends has reached the point of contact. In such a situation this small relaxation mechanism becomes the only one left. Therefore we are not allowed to neglect the dependence of the excluded-volume potential completely, but we have to retain it to the lowest order. This was the reason why we used the complete Fokker–Planck operator (2.1) for the derivation of eq 2.5 and 2.6. But now, in the spirit of an expansion with respect to end effects, we neglect such end effects in the time evolution operator. Then, for the use in expression 2.27 for $\Delta\zeta_i^{\mathrm{sin}}$, we calculate the com propagator as

$$R_i^{\mathrm{cm}}(\mathbf{q},t) = \langle e^{-i\mathbf{q}\cdot\mathbf{r}_i} e^{\hat{\Omega}'' t} e^{\hat{\Omega}^{\perp} t} e^{i\mathbf{q}\cdot\mathbf{r}_i}\rangle \quad (3.23)$$

It is not proposed that this formula should lead to an acceptable result for the com propagator per se.

Since in this expression only the curvilinear time evolution operator depends on curvilinear velocities, we can perform the average over $[v''(s_i)]$ separately. Asuming that the velocities relax to equilibrium much faster than the coordinates, we show[25] that

$$\langle e^{\hat{\Omega}''t}\rangle_{v''} = e^{\hat{\Omega}_{\mathrm{D}}''t} \tag{3.24}$$

Here $\hat{\Omega}_{\mathrm{D}}''$ is the diffusion operator for a one-dimensional chain,

$$\hat{\Omega}_{\mathrm{D}}'' = \frac{k_{\mathrm{B}}T}{\zeta(c)l_0}\sum_{i=1}^{N}\int_0^{L_i^0}\mathrm{d}s_i\,\frac{\delta}{\delta l(s_i)}\left(\frac{\delta}{\delta l(s_i)} - 3\beta\,\frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2}\right) \tag{3.25}$$

Let us consider first an expression like

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i}\,\hat{\Omega}_{\mathrm{D}}''...$$

where $\langle$ ... means an integration over all phase space variables, $\int \mathrm{d}\Gamma$... Using the fact that the integral over all internal forces of a chain vanishes,

$$\frac{3}{l_0}\int_0^{L_i^0}\mathrm{d}s_i\,\mathbf{iq}\cdot\hat{\mathbf{t}}(s_i)\,\frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2} = i\mathbf{q}\cdot\frac{1}{l_0}\int_0^{L_i^0}\mathrm{d}s_i\,\mathbf{E}(s_i) = 0 \tag{3.26}$$

we obtain easily

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i}\hat{\Omega}_{\mathrm{D}}''... = D_i''\langle\frac{3}{L_i^0}\int_0^{L_i^0}\mathrm{d}s_i\,(\hat{\mathbf{t}}(s_i)\cdot\mathbf{q})^2 e^{-i\mathbf{q}\cdot\mathbf{r}_i}... \tag{3.27}$$

If we perform a preaveraging over the tangent vectors in the first term, we obtain

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i}\hat{\Omega}_{\mathrm{D}}''... \simeq D_i''\mathbf{q}^2\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i}... \tag{3.28}$$

where

$$D_i'' = \frac{1}{3}\frac{k_{\mathrm{B}}T}{n_i\zeta(c)} \tag{3.29}$$

is the com diffusion coefficient of a one-dimensional Rouse chain. Now the com propagator can be factorized in a curvilinear term and in a term that describes the evolution of $R_i^{\mathrm{cm}}(\mathbf{q},t)$ under the action of the lateral operator alone,

$$R_i^{\mathrm{cm}}(\mathbf{q},t) = e^{-D_i''\mathbf{q}^2 t}\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i}e^{\hat{\Omega}^{\perp}t}e^{i\mathbf{q}\cdot\mathbf{r}_i}\rangle \tag{3.30}$$

The second factor in eq 3.30 has the same formal structure as the complete propagator itself, the only difference being that here only the lateral component of the Fokker–Planck operator appears, instead of the full operator, (2.1). The calculation of this lateral propagator can therefore proceed in exactly the same manner as the calculation of the full propagator. For sufficiently long times the motion becomes diffusive. Then

$$R_i^{\mathrm{cm}}(\mathbf{q},t) = e^{-D_i''\mathbf{q}^2 t}e^{-D_i^{\perp}\mathbf{q}^2 t} \tag{3.31}$$

where

$$D_i^{\perp} = \tfrac{1}{3}\int_0^{\infty}\mathrm{d}t\,\langle \mathbf{v}_i\cdot e^{\hat{\Omega}^{\perp}t}\mathbf{v}_i^{\perp}\rangle \tag{3.32}$$

and $\mathbf{v}_i^{\perp}$ is the lateral com velocity of chain i,

$$\mathbf{v}_i^{\perp} = \frac{1}{L_i^0}\int_0^{L_i^0}\mathrm{d}s_i\,\mathbf{v}^{\perp}(s_i) \tag{3.33}$$

The approximative result for the com propagator, eq 3.31, seems to suggest that the com diffusion can be written as the sum of independent contributions from curvilinear diffusion and lateral diffusion. Again it is important to stress that this assumption is too crude in general, since it would amount to a complete neglect of the coupling between curvilinear and lateral motion. Especially in the reptating state this is not justified, as will be shown later on. Instead of this, the form (3.31) is only used for the calculation of the friction coefficient $\Delta\zeta_i$, eq 2.27. Performing now the time and the $\mathbf{q}$ integration in eq 2.27 and using eq 2.5 we obtain

$$D_i = k_{\mathrm{B}}T\Big/\left(n_i\zeta(c) + \frac{\varphi(c)}{3V}\sum_{j\neq i}\frac{n_i n_j}{D_i'' + D_j'' + D_i^{\perp} + D_j^{\perp}}\right) \tag{3.34}$$

where D_i'' is given by eq 3.29.

Due to the formal similarity in the definitions of D_i, eq 2.5, and $D_i^{\perp}$, eq 3.32, we obtain a result for $D_i^{\perp}$ by simply following the steps which have led us to eq 3.34. The only differences arise because the lateral velocity autocorrelation function is completely independent of curvilinear dynamics, and the degrees of freedom are reduced, thus

$$\langle \mathbf{v}_i^{\perp}\cdot\mathbf{v}_i^{\perp}\rangle = 2\frac{k_{\mathrm{B}}T}{n_i m} \tag{3.35}$$

Then we obtain a self-consistent set of algebraic equations for the $D_i^{\perp}$,

$$D_i^{\perp} = \frac{2}{3}k_{\mathrm{B}}T\Big/\left(n_i\zeta(c) + \frac{\varphi(c)}{3V}\sum_{j\neq i}\frac{n_i n_j}{D_i^{\perp} + D_j^{\perp}}\right) \tag{3.36}$$

The solution of these equations, together with eq 3.29, allows for the determination of the com diffusion coefficients by eq 3.34. The parameters, which determine the solution, are the concentration-dependent single-segment friction coefficient $\zeta(c)$, the concentration-dependent interaction strength $\varphi(c)$, and distribution of polymerization indices $\{n_i\}$. In general, a solution of eq 3.36 will only be obtained numerically. But for the special case of one tracer polymer, with polymerization index n_{t}, in a matrix of other polymers of the same kind, but with polymerization index n_{p}, we can obtain an analytic solution and discuss the result in detail.

4. Diffusion of a Tracer Polymer in a Matrix with Different Molecular Weight

We consider now a system, consisting of a solvent, one single polymer, the tracer, and N other polymers, which form the matrix. Both kinds of polymers are of the same species and differ only in their molecular weight. The molecular weights are characterized by the polymerization indices, n_{t} for the tracer and n_{p} for the matrix. If N is sufficient large, the influence of the tracer polymer on the properties of the matrix can be neglected and the com diffusion coefficient of the matrix polymers is just the same as for a system where all the polymers have the same molecular weight n_{p}. Then

$$\begin{aligned} D_{\mathrm{p}}^{\perp} &= \frac{2}{3}\frac{k_{\mathrm{B}}T}{n_{\mathrm{p}}\zeta(c)}(1 - n_{\mathrm{p}}/n_{\mathrm{c}}) \qquad \text{for } n_{\mathrm{p}} \leqslant n_{\mathrm{c}} \\ &= 0 \qquad \text{for } n_{\mathrm{p}} \geqslant n_{\mathrm{c}} \end{aligned} \tag{4.1}$$

Here n_{c} is the critical polymerization index, where according to eq 3.39 the lateral motion of the matrix polymers freezes in,

$$n_{\mathrm{c}}^{-1} = \frac{1}{4}\frac{\varphi(c)\,c}{k_{\mathrm{B}}T} = \frac{1}{2}\frac{\Delta F(c)}{c k_{\mathrm{B}}T} \tag{4.2}$$

$\Delta F(c)$ is the excluded volume contribution to the free energy density,

$$\Delta F = \langle U^{\mathrm{ev}}\rangle/V = \tfrac{1}{2}\varphi(c)c^2 \tag{4.3}$$

and c is the concentration of matrix segments, $c = Nn_{\mathrm{p}}/V$ According to eq 4.2 and 4.3 the critical polymerization index n_{c} is just 2 times the ratio betwen $k_{\mathrm{B}}T$ and the mean interaction energy per chain. For the special case of a tracer polymer in a matrix eq 3.36 becomes

$$D_t^{\perp} = \frac{{}^2\!/_3 k_B T}{n_t[\zeta(c) + {}^1\!/_3\varphi(c)c/(D_t^{\perp} + D_p^{\perp})]} \qquad (4.4)$$

or

$$D_t^{\perp}\left(D_t^{\perp} + D_p^{\perp} + \frac{4}{3}\frac{k_B T}{n_c\zeta(c)}\right) = \frac{2}{3}\frac{k_B T}{n_t\zeta(c)}(D_t^{\perp} + D_p^{\perp}) \qquad (4.5)$$

For $n_p \geq n_c$ ($D_p^{\perp} = 0$), the solution is

$$\begin{aligned} D_t^{\perp} &= \frac{2}{3}\frac{k_B T}{n_t\zeta(c)}(1 - 2n_t/n_c) \qquad \text{for } n_t \leq {}^1\!/_2 n_c \\ &= 0 \qquad \text{for } n_t \geq {}^1\!/_2 n_c \end{aligned} \qquad (4.6)$$

We interprete the vanishing of the lateral diffusion coefficient as a transition to a dynamical state in which the com of a polymer can move only by curvilinear motion, that is, reptation. An interesting feature of the result above is that in a matrix of sufficiently long polymers, which are already in a reptating state, the reptation transition of the tracer polymer takes place at a polymerization index which is only half of the critical polymerization index of the matrix. In the conventional tube model the reptation transition corresponds to the formation of a tube. For the matrix this is a cooperative process, involving the dynamics of pairs of polymers. But for the tracer, if the lateral motion of matrix polymers is already frozen in, lateral friction can only relax by lateral motion of the tracer itself. Therefore, given a certain polymerization index n, the hindrance of the lateral motion of a polymer in a laterally frozen in matrix is larger, compared to the case where all polymers have the same polymerization index. For $n_p \leq n_c$ ($D_p^{\perp}$ the solution of eq 4.5 is

$$D_t^{\perp} = \frac{2}{3}\frac{k_B T}{n_t\zeta(c)}\frac{1}{2}\left[1 - \frac{n_t}{n_c} - \frac{n_t}{n_p} + \left(\left(1 - \frac{n_t}{n_c} - \frac{n_t}{n_p}\right)^2 + 4\left(\frac{n_t}{n_p} - \frac{n_t}{n_c}\right)\right)^{1/2}\right] \qquad (4.7)$$

In this case no reptation transition of the tracer polymer is obtained. The actual tracer diffusion coefficient is, from eq 3.34,

$$D_t = \frac{k_B T}{n_t\left(\zeta(c) + \frac{4}{3}\frac{k_B T/n_c}{D_t'' + D_t^{\perp} + D_p'' + D_p^{\perp}}\right)} \qquad (4.8)$$

Then, using eq 4.1 and 4.6, we obtain for the case $n_p \geq n_c$

$$\begin{aligned} D_t &= \frac{k_B T}{n_t\zeta(c)}\left(1 - \frac{n_t}{n_c}\frac{4}{3 + n_t/n_p}\right) \qquad \text{for } n_t \leq {}^1\!/_2 n_c \\ &= \frac{k_B T}{n_t\zeta(c)}\frac{1}{1 + \frac{n_t}{n_c}\frac{4}{1 + n_t/n_p}} \qquad \text{for } n_t \geq {}^1\!/_2 n_c \end{aligned} \qquad (4.9)$$

The result for D_t in the case $n_p \leq n_c$ is too lengthy to be written in a closed form. It can be obtained by inserting eq 4.1 and 4.7 and the expressions for the $D_{t,p}''$, eq 3.29, into eq 4.8.

We observe the existence of three different dynamic regimes: (a) $n_p < n_c$, the lateral motion of both tracer and matrix are only hindered by interaction; (b) $n_p \geq n_c$, $n_t < n_c/2$, the lateral motion of the matrix is frozen in, but the lateral motion of the tracer is only hindered; (c) $n_p \geq n_c$, $n_t \geq n_c/2$, the lateral motion of both tracer and matrix are frozen in. This is also shown in the form of a dynamic phase diagram in Figure 2. We should keep in mind here that if we talk about "laterally frozen motion", this only is true up to the approximation, in which end effects are neglected. If a polymer interacts by its end segment with a second polymer, then a small curvilinear displacement of the first polymer will remove the hindrance to the second polymer, and a small local lateral motion in this second polymer can take place. Such processes are neglected in the self-consistent calculation of $D_t^{\perp}$ and $D_p^{\perp}$, but they are taken into account in the calculation of the true diffusion coefficient D_t, as a perturbation.

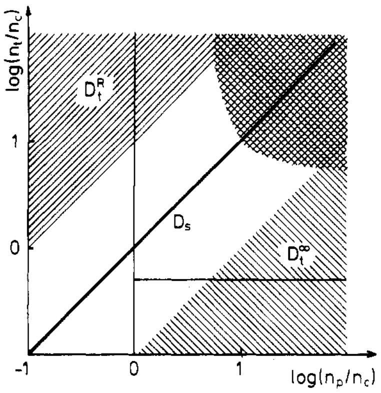

Figure 2. "Dynamic phase diagram" for the tracer diffusion coefficient.

Four cases now are of special interest: a long tracer polymer in a matrix of much shorter polymers, $n_t \gg n_p$; a tracer polymer which is much smaller than the matrix polymers, $n_t \ll n_p$; both kinds of polymers much larger than the critical polymerization index, n_t and $n_p \gg n_c$; and a tracer with the same length as the matrix polymers, $n_t = n_p = n$. This last case is just self-diffusion of a polymer in an unimodal solution and has been treated before.[13] The result is

$$\begin{aligned} D_s &= \frac{k_B T}{n\zeta(c)}\left(1 - \frac{2}{3}\frac{n}{n_c}\right) \qquad \text{for } n \leq n_c \\ &= \frac{k_B T}{n\zeta(c)}\frac{1}{1 + 2n/n_c} \qquad \text{for } n \geq n_c \end{aligned} \qquad (4.10)$$

(i) $n_t \gg n_p$: Rouse-Like Behavior. For $n_p \leq n_c$ we observe that $D_p'' + D_p^{\perp} \gg D_t'' + D_t^{\perp}$. Then, using also eq 4.1, we can simplify eq 4.8. For $n_p \geq n_c$ we use directly eq 4.9. From both formulas we find that D_t can be written in form of a Rouse-like diffusion coefficient,

$$D_t^R = \frac{k_B T}{n_t\zeta_{\text{eff}}(c,n_p)} \qquad (4.11)$$

where the effective friction coefficient depends only on concentration and polymerization index of the matrix, but not on n_t,

$$\begin{aligned} \zeta_{\text{eff}}(c,n_p) &= \zeta(c)\left(1 + \frac{\frac{4}{3}\frac{n_p}{n_c}}{1 - \frac{2}{3}\frac{n_p}{n_c}}\right) \qquad \text{for } n_p \leq n_c \\ &= \zeta(c)\left(1 + 4\frac{n_p}{n_c}\right) \qquad \text{for } n_p \geq n_c \end{aligned} \qquad (4.12)$$

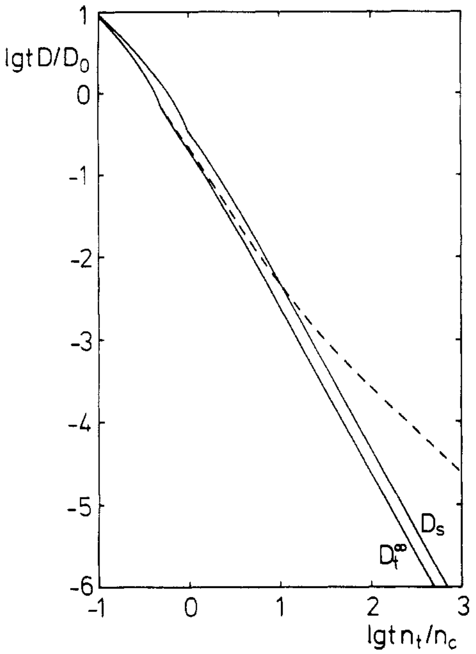

Figure 3. Comparison of the self-diffusion coefficient D_s ($n_t = n_p$), the tracer diffusion coefficient in frozen matrix $D_t^\infty(n_p=\infty)$ and the tracer diffusion coefficient D_t for a matrix with $n_p = 10n_c$ (broken line).

(ii) $n_p \gg n_t$: Diffusion in a Frozen Matrix. Since here $D_p'' \ll D_t''$ and $D_p^\perp \ll D_t^\perp$, we obtain in this limit

$$\begin{aligned} D_t^\infty &= \frac{k_BT}{n_t\zeta(c)}\left(1 - \frac{4}{3}\frac{n_t}{n_c}\right) && \text{for } n_t \leq \tfrac{1}{2}n_c \\ &= \frac{k_BT}{n_t\zeta(c)}\frac{1}{1 + 4\dfrac{n_t}{n_c}} && \text{for } n_t \geq \tfrac{1}{2}n_c \end{aligned} \qquad (4.13)$$

It is interesting to compare D_t^∞ with the self-diffusion coefficient D_s, eq 4.10. Both diffusion coefficients are shown in Figure 3. We observe that in the frozen matrix the effect of interactions is just twice as large as in the case where both interaction partners have the same mobility. Therefore, for given n_t/n_c, D_s is always larger than D_t^∞. Also, the reptation transition takes place already at a polymerization index $n_t = n_c/2$, compared to the case of self-diffusion, where the transition is just at n_c.

(iii) n_p, $n_t \gg n_c$: Reptation and Constraint Release. From eq 4.9 we obtain in this limit

$$D_t = \frac{1}{4}\frac{k_BT}{n_t\zeta(c)}\left(\frac{n_c}{n_t} + \frac{n_c}{n_p}\right) \qquad (4.14)$$

The first term corresponds to diffusion in a frozen matrix, eq 4.13, in the limit $n_t \gg n_c$. This is the situation for which the tube model was meant originally, therefore we may identify this term as diffusion by reptation,

$$D_{\text{rep}} \equiv D_t^\infty(n_t \rightarrow \infty) = \frac{1}{4}\frac{k_BT}{n_t\zeta(c)}\frac{n_c}{n_t} \qquad (4.15)$$

The second term obviously is Rouse-like, it is also obtained from eq 4.12 in the limit $n_p \gg n_c$. If we trace back the origin of this contribution to the dynamic friction function, eq 2.27, we see that it is due to a relaxation of interaction forces by curvilinear diffusion of matrix polymers. This mechanism has been incorporated in the phenomenological tube model under the name constraint release diffusion, and, therefore, in our treatment we may call

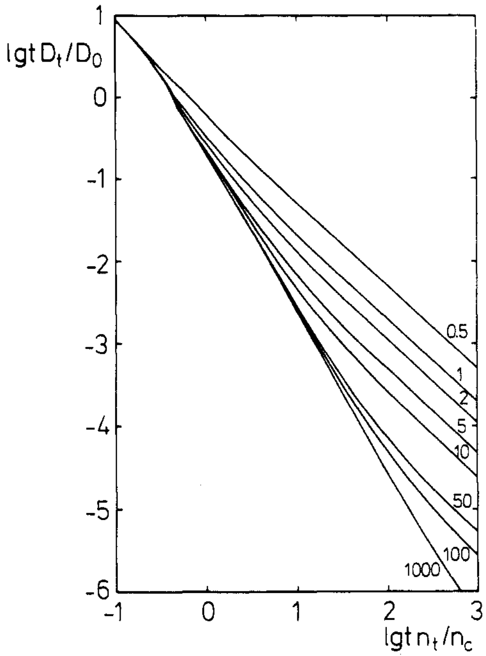

Figure 4. D_t as a function of the tracer polymerization index n_t, for various values of the matrix polymerization index in units of the critical polymerization index.

$$D_{\text{cr}} = \frac{1}{4}\frac{k_BT}{n_t\zeta(c)}\frac{n_c}{n_p} \qquad (4.16)$$

the constraint release diffusion coefficient. Then eq 4.14 is expressed as

$$D_t = D_{\text{rep}} + D_{\text{cr}} \qquad (4.17)$$

or

$$D_t = D_{\text{rep}}[1 + (n_t/n_p)] \qquad (4.18)$$

But this result for the constraint release mechanism is in marked contrast to the results of the tube model.[10-12] We will discuss these theoretical results, as well as experimental results, in the next section, but one important point should be outlined already here. For the case of self-diffusion, $n_t = n_p$, eq 4.18 gives

$$D_s = 2D_{\text{rep}} = 2D_t^\infty \qquad (4.19)$$

for $n_t/n_c \gg 1$. In the phenomenological tube model the results for the constraint release mechanism predict that constraint release should become unimportant in the long-chain limit, therefore $D_s = D_{\text{rep}} = D_t^\infty$ for $n_t/n_c \gg 1$!

In contrast, the result of our theory here states that the constraint release mechanism is always important for the self-diffusion coefficient and contributes just as much as reptation of the test chain alone. It is interesting to note that originally de Gennes expressed the opinion that "reptation inside the tube and reorganization of the tube give comparable contributions to the relaxation of entanglements".[5]

So far we have discussed our results for D_t, eq 4.8 and 4.9, only for some idealized asymptotic cases. But experiments are always performed at finite values of the molecular weight. Therefore, in order to gain insight in the general behavior of the tracer diffusion coefficient as a function of the polymerization indices of tracer and matrix, we present in Figures 4 and 5 numerical evaluations of eq 4.8 and 4.9. Figure 4 shows D_t at fixed values of n_p as a function of n_t. This corresponds to vertical paths through the "phase diagram", Figure 2. All the curves in Figure 4 show the same qualitative behavior. We observe two Rouse regimes, where $D_t \sim n_t^{-1}$, for small n_t and again for large n_t. In the first Rouse regime, friction is due to the solvent; in the second Rouse regime the friction on a long tracer polymer is dominated by interactions with the shorter matrix polymers. The crossover between both Rouse regimes is rather smooth for the examples where the matrix polymerization index is smaller or of the order of the critical polymerization index. If n_p is sufficiently large compared to n_c, then the crossover between the two Rouse regimes might be interpreted as an extended power law regime on its own. One would expect here to observe a typical reptation behavior. Surprisingly, even for the curve with $n_p = 100n_c$, the apparent power law exponent is not -2, but more like -1.8. One has to go to an extremely high matrix polymerization index ($n_t \simeq 1000n_c$) in order to find the reptation prediction $D_t \sim n_t^{-2}$.

Another example, which shows the discrepancy between the idealized idea of tracer diffusion in a frozen matrix and the real situation, where tracer polymers diffuse in an entangled matrix, is given in Figure 3. The broken curve shows D_t for $n_p = 10n_c$. Although the lateral motion of the matrix is completely frozen in, agreement with the D_t^∞ curve is observed only for the uninteresting regime $n_t < n_c/2$.

In Figure 5 we finally show D_t for fixed values of n_t, as a function of n_p, corresponding to horizontal paths through Figure 2. For small n_p, D_t is independent of n_p. At large n_p, again a plateau is reached, where D_t is independent of n_p. In between, for $n_p = n_c$, we observe the reptation transition in the form of a cusp. Again, for the curves with sufficiently large n_t, D_t seems to follow a power law for $n_p > n_c$, before it crosses over to the large n_p plateau. From our discussion of asymptotic limits, eq 4.12 in this case, we would expect a power law exponent of -1. But even for the curve with $n_t = 100n_c$ one rather extracts an apparent exponent of $\simeq -0.9$. Again, as in Figure 4, we find agreement with the idealized asymptotic calculation only when the tracer molecular weight is much larger than the critical molecular weight, for $n_t \simeq 1000n_c$.

5. Discussion

The most striking difference between the results, presented in the last section and the corresponding results of the phenomenological reptation theories, is the relative importance of the constraint release, or tube renewal mechanism, as compared to the reptation of the tracer polymer itself. Whereas originally de Gennes postulated that constraint release should contribute to the tracer diffusion coefficient as $D_{cr} \sim n_c/(n_t n_p)$, later on Klein[10] and Daoud and de Gennes[11] concluded that the rate of the constraint release mechanism should be much weaker and its contribution to the diffusion coefficient only of the form

$$D_{cr} \sim n_c^3/(n_t n_p^3) \qquad (5.1a)$$

Recently, Klein[16] corrected this prediction by taking into consideration correlations between the constraints, which hinder the lateral motion of the tracer polymer. This leads to a slight enhancement of the constraint release mechanism and D_{cr} is changed to

$$D_{cr} \sim n_c^{2.5}/(n_t n_p^{2.5}) \qquad (5.1b)$$

Our own result, eq 4.16, which was obtained without making any assumptions about entanglement densities or rates of constraint release processes, now actually comes back to de Gennes' original prediction. The significance of the difference between the result (4.16) on the one hand and (5.1a) or (5.1b) on the other hand can be seen best in Figures 3 and 5.

If the results of the tube model would be true, then for $n_t \gg n_c$ the self-diffusion coefficient D_s should be the same as the diffusion coefficient of a tracer in a matrix with infinite molecular weight, D_t^∞. In contrast, our result says $D_s = 2D_t^\infty$, if $n_t \gg n_t \gg n_c$. Even at the largest molecular weights, self-diffusion is always faster than the diffusion of a tracer in an immobile matrix. According to eq 5.1a and 5.1b, with increasing molecular weight of the matrix, constraint release processes should become unimportant when $n_p > n_c$. Then the large molecular weight plateaus would be reached for all curves in Figure 5 at the same molecular weight, slightly above n_c. But, according to our result, the crossover occurs for each curve at a different molecular weight, when $n_p \simeq n_t$.

So far, besides an early work of Klein,[17] only one detailed experimental study[18,19] of tracer diffusion in melts found agreement with the established model on the constraint release mechanism, eq 5.1a or 5.1b, respectively. Both versions for D_{cr} give an excellent fit to these experiments, the difference between both theoretical results being so small that from the experiments no could not decide which one is the better one. Although this experimental test of the reptation theory looks very convincing, the results have been questioned by McKenna,[20] who noticed that the data, if evaluated for the special case of self-diffusion ($n_t = n_p$), are not consistent with the experimentally observed n^{-2} dependence of the self-diffusion coefficient in the same range of molecular weights.

All other measurements of the tracer diffusion coefficient, in melts[21,22] as well as in semidilute solutions,[23] clearly indicate a much stronger influence of the constraint release mechanism and are qualitatively in good agreement with our own result, eq 4.16. In melts, Smith et al.[21] measured D_t as a function of the matrix molecular weight, for different values of the tracer diffusion coefficient. For $n_p > n_c$, they find that the dependence of D_t on n_p increases when the tracer polymer becomes longer. If the data are fitted to a power law, $D_t \sim n_p^{-x}$, the apparent exponent x is a function of n_t and increases with increasing n_t. For the longest tracer an experimental value $x \simeq 0.93$ is obtained. This is in agreement with our Figure 5, which shows that the asymptotic result, $x = 1$, is in fact only obtained for very large values of n_t. In contrast, the phenomenological reptation model would suggest that no dependence on matrix molecular weight should be observed at all, for $n_p > n_c$. Unfortunately the experiments were restricted to the case $n_p < n_t$, so that the extent of the constraint release (or tube renewal) regime could not be determined. Smith et al. also show D_t as a function of the tracer molecular weight, for different values of the matrix molecular weight. Also this figure (Figure 5 in ref 21) is qualitatively similar to our Figure 4, insofar as for $n_p > n_c$ no simple power law dependence is seen, but the slope of log D_t versus log n_t decreases continuously as n_p increases. Finally, for the largest value of n_p, $D_t \sim n_t^{-1.9}$ for large n_t is obtained. Again, this is in agreement with our finding that the asymptotic exponent, -2, is obtained only when $n_p \gg n_c$. Also the case of self-diffusion is considered and the results are in good agreement with $D_s \sim n^{-2}$. It was also noticed that the result for D_s appears to be a combination of both a motion of the tracer and motion of the surrounding matrix.

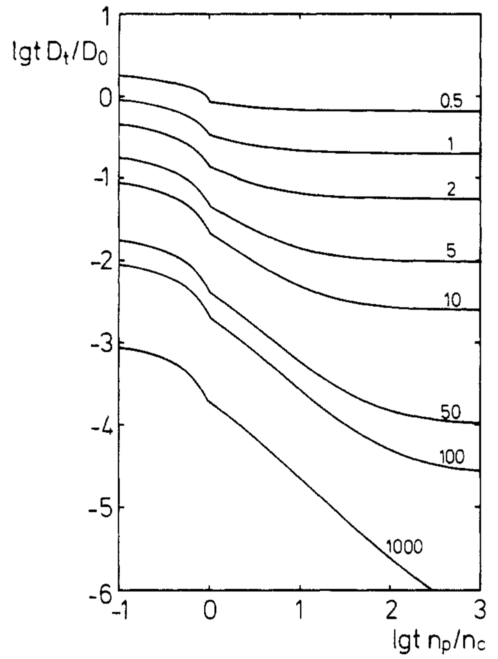

Figure 5. D_t as a function of n_p, for various values of n_t/n_c.

In another study, Antonietti et al.[22] have measured the tracer diffusion coefficient in melts consisting of linear polymers but also the diffusion of a linear tracer in a cross-linked matrix. Since in a cross-linked matrix constraint release is not possible, it is tempting to identify the tracer diffusion coefficient in the cross-linked matrix with D_t^{∞}, the hypothetical diffusion coefficient of a tracer in a frozen matrix. Indeed, it is found that the tracer diffusion coefficient in the linear matrix approaches the value for the cross-linked matrix, in the limit of a large molecular weight of the linear matrix. But again, in contrast to the expectations from the reptation model, it is found that a matrix influence on D_t is observable for matrix molecular weights well beyond the critical molecular weight. The dependence of D_t on the matrix molecular weight roughly can be described as $D_t \sim n_p^{-1}$ for $n_p < n_t$. At $n_t \simeq n_p$ the n_p dependence becomes weaker and finally seems to approach a constant value, D_t^{∞}. For all samples it is found that the self-diffusion coefficient is larger than the asymptotic tracer diffusion coefficient, $D_s > D_t^{\infty}$. All these results show that the constraint release mechanism is important for high molecular weight samples and only becomes negligible when the matrix molecular weight is much larger than the tracer molecular weight. Antonietti et al. also observe that the onset of reptative motion takes place for relatively short tracer polymers, provided that the molecular weight of the matrix is larger than the critical one! The estimates, given in the paper, agree well with our condition for the "reptative state" region in Figure 2: $n_p \geqslant n_c$ and $n_t \geqslant {}^1/_2 n_c$.

So far, all experiments that we have discussed, have been performed in melts. Strictly speaking, since our theory has been developed for semidilute solutions only, it might be questionable whether its results can be compared to experimental results obtained in melts. But on the other hand, it is our opinion that reptation, defined here as the freezing in of lateral motion, is basically determined by the topology of the system. Since this is the same in melts and in semidilute solutions, there should be not much difference in the behavior of both kinds of systems with respect to the essential reptation phenomena. Indeed, one finds that experiments of Kim et al.[23] on semidilute solutions fit well into the picture, which we have already obtained from the experiments of Smith et al.[21] and Antonietti et al.[22] Again it is found that D_t depends on the matrix molecular weight up to a n_p that is 3 or 5 times higher than n_t and well beyond n_c. A second important feature of the results is that for samples where the molecular weight of the tracer is the same, the onset molecular weight, where D_t makes a crossover to the asymptotic value D_t^{∞}, does not seem to change much with matrix concentration. Since the conventional reptation model locates this crossover at $n_p \simeq n_c$ and n_c is strongly concentration dependent, one would have expected such a concentration dependence of the crossover molecular weight. According to our theory the crossover takes place at $n_p \simeq n_t$, which is concentration independent. Also here it is observed that the self-diffusion coefficient is always larger than the asymptotic tracer diffusion coefficient, by a factor of 2–3. This compares well with our result $D_s = 2D_t^{\infty}$ in the long-chain limit.

In summary, one can say that the experiments, except those of Green et al.,[18,19] show that the constraint release process contributes significantly to the tracer diffusion coefficient, unless the matrix molecular weight is significantly higher than that of the tracer. Another difference between our results and the corresponding results of the phenomenological models is found in the limit of a very large tracer polymer, surrounded by smaller, but already entangled, matrix polymers. But here it is likely that the difference is explained by the different concentration regimes, for which the theories are made.

Phenomenologically, the motion of a long tracer polymer in a melt of much shorter, but nevertheless already entangled, matrix polymers has been treated[11] as Stokes–Einstein diffusion,

$$D_t^{\mathrm{SE}} \sim \frac{k_B T}{R_g \eta_p} \sim n_t^{-1/2} n_p^{-3} \qquad (5.2)$$

where $R_g \sim n_t^{1/2}$ is the gyration radius of the tracer molecule and $\eta_p \sim n_p^3$ is the shear viscosity of the entangled matrix. In contrast, our result for the same situation, eq 4.11, takes the form of Rouse-like diffusion. The technical reason for this result can be traced back to the way the dynamic four-point correlation function in eq 2.11 was treated. There we simply factorized this function into a product of single-chain dynamic structure factors, neglecting the possibility of collective modes in the matrix around the tracer polymer. It was suggested that this approximation should be appropriate for the semidilute regime, but for a melt the situation would be different.

One should also remember that we have assumed from the beginning a complete screening of the hydrodynamic interaction in the solvent. Again the reason is a technical one, since a long-ranged hydrodynamic interaction would not allow for the separation of curvilinear density fluctuations and topological form fluctuations in section III. But the consequence is that our result cannot be extended to the dilute limit, where the Zimm formula should be obtained.

So far we have concentrated the discussion of the results on the molecular weight dependence of the tracer diffusion coefficient, and we have not talked about concentration dependence. The reason is that molecular weight dependence is generally believed to be a much more universal property than concentration dependence. For example, the self-diffusion coefficient shows n^{-2} dependence in semidilute solutions as well as in melts. Obviously this behavior is only determined by the topological structure of both kinds of systems and not by the details of the interaction law. But the concentration dependence, and also the temperature dependence, will strongly depend on such details. In our theory, concentration dependence enters via the effective single-segment friction coefficient $\zeta(c)$ and the interaction parameter $\varphi(c)$, eq 2.15. Naturally, both parameters are also temperature dependent. A calculation of these parameters will only be possible for idealized situations. For semidilute solutions de Gennes obtained[6] $\zeta(c) \sim c^{1/2}$, and from des Cloizeaux' work[24] one obtains $\varphi(c) \sim c^{1/4}$ in the long-chain limit. But the samples of the experimentalists do seldomly correspond to such an asymptotic limit, and therefore one should not be surprised if one finds rather smooth curves for the concentration dependence, instead of well-characterized power laws. And, although molecular weight dependence seems to be more universal, our own results, as seen in Figures 3 and 4, indicate that, also with respect to molecular weight dependence, one has to be cautious. The crossover regimes are quite extended and might easily simulate a power-law exponent which is smaller than the one that would be expected according to the scaling theories. But all such discrepancies between experimental results and the results of the phenomenological tube or reptation model should not be interpreted as evidence against the reptation mechanism. It only shows that the mathematical realization of this reptation picture has been too simplified.

Acknowledgment. It is my pleasure to thank Professor Z. Akcasu for many helpful and stimulating discussions and for the efforts which he made to help me clarify some of the problems in this work. I also acknowledge interesting discussions with Prof. H. Sillescu on the experimental aspects. This work was supported by the Deutsche Forschungsgemeinschaft in the form of a Heisenberg Fellowship and by the Sonderforschungsbereich 30 Konstanz.

Appendix

Here we want to obtain the complete form of the functional derivative $\delta/\delta\mathbf{r}(s_i)$, expressed as a derivative with respect to $\mathbf{r}(l_i)$ and with respect to the contour length $l(s_i)$.

$$\frac{\delta}{\delta\mathbf{r}(s_i)} = \frac{1}{l_0}\int_0^{L_i^0} \mathrm{d}s_i' \frac{\delta l(s_i')}{\delta\mathbf{r}(s_i)} \frac{\delta}{\delta l(s_i')} + \frac{1}{l_0}\int_0^{L_i} \mathrm{d}l_i' \frac{\delta\mathbf{r}(l_i')}{\delta\mathbf{r}(s_i)} \cdot \frac{\delta}{\delta\mathbf{r}(l_i')} \tag{A1}$$

From eq 3.3 and 3.6 we obtain

$$\frac{\delta l(s_i')}{\delta\mathbf{r}(s_i)} = \hat{\mathbf{t}}(s_i) l_0 \delta(s_i' - s_i) - \left(\frac{\mathrm{d}}{\mathrm{d}s_i}\hat{\mathbf{t}}(s_i)\right) l_0 \theta(s_i' - s_i) \tag{A2}$$

and

$$\frac{\delta\mathbf{r}(l_i')}{\delta\mathbf{r}(s_i)} = l_0\delta(s_i - s(l_i'))\,\mathbf{1} - \int_0^{L_i^0} \mathrm{d}s_i' \left[\frac{\delta}{\delta\mathbf{r}(s_i)}\delta(s_i' - s(l_i'))\right] : \mathbf{r}(s_i') \tag{A3}$$

The derivative of the δ function in (A3) is

$$\frac{\delta}{\delta\mathbf{r}(s_i)}\delta(s_i' - s(l_i')) = -\frac{\mathrm{d}}{\mathrm{d}s_i'}\delta(s_i' - s(l_i'))\frac{\delta s(l_i')}{\delta\mathbf{r}(s_i)} = -\frac{\mathrm{d}}{\mathrm{d}s_i'}\delta(s_i' - s(l_i'))\frac{\mathrm{d}s(l_i')}{\mathrm{d}l_i'}\frac{\delta l_i'}{\delta\mathbf{r}(s_i)} \tag{A4}$$

Using now eq A2 we obtain

$$\frac{\delta\mathbf{r}(l_i')}{\delta\mathbf{r}(s_i)} = l_0\delta(s_i - s(l_i'))\,\mathbf{1} + l_0\int_0^{L_i^0}\mathrm{d}s_i'\,\mathbf{r}(s_i')\frac{\mathrm{d}}{\mathrm{d}s_i'}\delta(s_i' - s(l_i'))\frac{\mathrm{d}s(l_i')}{\mathrm{d}l_i'}\left[\hat{\mathbf{t}}(s_i)\delta(s(l_i') - s_i) - \left(\frac{\mathrm{d}}{\mathrm{d}s_i}\hat{\mathbf{t}}(s_i)\right)\times\theta(s(l_i') - s_i)\right] = l_0\delta(s_i - s(l_i'))(\mathbf{1} - \hat{\mathbf{t}}(s_i):\hat{\mathbf{t}}(s_i)) + l_0\left(\frac{\mathrm{d}}{\mathrm{d}s_i}\hat{\mathbf{t}}(s_i)\right):\hat{\mathbf{t}}(l_i')\theta(s(l_i') - s_i) \tag{A5}$$

With eq A5 and A2 the functional derivative $\delta/\delta\mathbf{r}(s_i)$ becomes

$$\frac{\delta}{\delta\mathbf{r}(s_i)} = \hat{\mathbf{t}}(s_i)\frac{\delta}{\delta l(s_i)} + [\mathbf{1} - \hat{\mathbf{t}}(s_i):\hat{\mathbf{t}}(s_i)]\frac{\mathrm{d}l(s_i)}{\mathrm{d}s_i}\left.\frac{\delta}{\delta\mathbf{r}(l_i)}\right|_{l_i=l(s_i)} + \left(\frac{\mathrm{d}\hat{\mathbf{t}}(s_i)}{\mathrm{d}s_i}\right)\left[\int_{l(s_i)}^{L_i}\mathrm{d}l_i'\,\hat{\mathbf{t}}(l_i')\cdot\frac{\delta}{\delta\mathbf{r}(l_i')} - \int_{s_i}^{L_i^0}\mathrm{d}s_i'\frac{\delta}{\delta l(s_i')}\right] \tag{A6}$$

It will also be valuable to know the derivative of $\mathbf{r}(s_i')$ with respect to the new degrees of freedom, $\mathbf{r}(l_i)$ and $l(s_i)$. These are

$$\frac{\delta\mathbf{r}(s_i')}{\delta l(s_i)} = \hat{\mathbf{t}}(l(s_i))\delta(s_i - s_i')l_0 \tag{A7}$$

and

$$\frac{\delta\mathbf{r}(s_i')}{\delta\mathbf{r}(l_i)} = \mathbf{1}\delta(l(s_i') - l_i)l_0 \tag{A8}$$

The nonlocal term in eq A6 reflects the fact that under the constraint of constant length, a variation in $\mathbf{r}(s_i)$ will also result in a displacement of $\mathbf{r}(l_i')$, for $l_i' > l(s_i)$. This nonlocal coupling is especially pronounced at points where the radius of curvature is small, i.e., where $\mathrm{d}\hat{\mathbf{t}}(s_i)/\mathrm{d}s_i$ is large.

References and Notes

(1) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(2) Graessley, W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(3) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(4) De Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(5) De Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(6) De Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(7) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 1789, 1802, 1818.
(8) Curtiss, C. F.; Bird, R. B. *J. Chem. Phys.* **1981**, *74*, 2016.
(9) Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, D. F. *Dynamics of Polymeric Liquids*, Wiley: New York, 1977; Vol. II.
(10) Klein, J. *Macromolecules* **1978**, *11*, 852.
(11) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(12) Graessley, W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(13) Hess, W. *Macromolecules* **1986**, *19*, 1395.
(14) Hess, W.; Frisch, H. *J. Polym. Sci., Polymer Lett.* **1986**, *21*, 209.
(15) Wesson, A. J.; Noh, J.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(16) Klein, J. *Macromolecules* **1986**, *19*, 105.
(17) Klein, J. *Philos, Mag. A* **1981**, *43*, 771.
(18) Green, P. F.; et al. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(19) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(20) McKenna, G. B. *Polym. Commun.* **1985**, *26*, 324.
(21) Smith, B. A.; Samulski, E. T.; Yu, L. P.; Winnik, M. A. *Macromolecules* **1985**, *18*, 1901.
(22) Antonietti, M.; Contandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(23) Kim, H.; et al. *Macromolecules* **1986**, *19*, 2737.
(24) des Cloizeaux, J. *J. Phys.* (*Les Ulis, Fr.*) **1975**, *36*, 281.
(25) Hess, W.; Klein, R. *Adv. Phys.* **1983**, *32*, 173.
(26) Doi, M.; Edwards, S. F. *The Theory of Polymeric Dynamics*; Clarendon Press: Oxford, 1986.