

Self-Diffusion and Reptation in Semidilute Polymer Solutions

W. Hess

Fakultät für Physik, Universität Konstanz, 7750 Konstanz, West Germany.
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ABSTRACT: In a microscopic and self-consistent way the existence of a reptation transition in the center-of-mass diffusion of flexible polymers in semidilute solutions is shown. The transition takes place at a critical value of the entanglement parameter $\psi(c,n)$, which is defined in terms of the mean interaction energy of a polymer and proportional to its number of entanglements (c is the mean segment concentration and n is the number of segments of a polymer). A general result for the self-diffusion coefficient D_s is derived, which determines D_s in terms of $\psi(c,n)$ and a single-segment friction coefficient. For short polymers the formula yields a Rouse-like expression, $D_s \sim n^{-1}$; for long polymers de Gennes' reptation result, $D_s \sim n^{-2}c^{-1.75}$, is recovered. The crossover between both limiting laws is quite extended, in contrast to the assumptions of scaling theories.

I. Introduction

Interacting polymer chains are one of the most fascinating and challenging many-body problems in statistical physics. A polymer in solution takes the form of a random coil. At even moderate concentrations the coils start to interpenetrate, and the chains become entangled. Since the backbones of the polymers cannot intersect each other, the entanglements produce strong topological restrictions on the mobility of the polymers. Experimentally the most striking and important effect is a sudden increase in the dependence of the shear viscosity on molecular weight. Whereas for "short" polymers the viscosity is proportional to M , there exists a critical molecular weight, above which $\eta_s \sim M^{3.4}$. Closely related to that phenomenon is the observation that the time-dependent elastic modulus shows an extended elastic plateau above M_c .^{1,2} The cause of these and other drastic changes in the dynamic behavior of concentrated polymeric liquids has been vividly discussed.^{1,2} The most fruitful concept has been de Gennes' reptation model.³ The basic idea is that the entanglements between a chain and its neighbors prevent any large-scale motions perpendicular to its local direction. Therefore, the chains can only "reptate" in a snakelike motion parallel to their own curve. The obstacles that the other chains offer to a certain test chain may summarily be described as a tube in which the test chain is engaged and which it can leave only at the ends. Using simple scaling arguments, de Gennes has made a large number of predictions for the static and dynamic properties of entangled polymeric liquids.⁴ These have been important stimuli for experimental research. In general, the experimental results have shown a convincing verification of the scaling predictions.⁴

A second important impetus in the development of the reptation theory was given by Doi and Edwards in a series of papers⁵ in which they develop the model of a "primitive chain", which only at its ends has complete freedom of motion. The interior segments can only diffuse longitudinally along the line of the chain. Therefore this model has built in the reptation idea from the beginning. Since it is mathematically well-defined, the primitive chain model can be used to calculate various dynamical properties in detail.

The establishment of the reptation theory has stimulated a tremendous number of works:⁶ theoretical ones, which have refined the model, computer simulations in order to test the details of its predictions,⁷ and experiments, which were interpreted in terms of the reptation model. But a microscopic foundation of the model, which really derives the existence of the reptative motion of the chains as a consequence of the repulsive interactions from first principles, is still lacking. This is the theme which

we try to undertake in this paper. We concentrate on the center-of-mass motion of the polymers, since this is a question that is central to the understanding of the reptation model. We find that the established picture for the reptation process becomes fully justified and that the transition to the reptating state is well-defined. Especially for the strongly entangled state we can reproduce de Gennes' result⁵ for the self-diffusion coefficient, $D_s \sim n^{-2}c^{-7/4}$. Here n is the number of segments of a polymer, $c = nN/V$, the mean segment concentration, N is the number of polymers, and V is the volume.

The starting point of our work is a Fokker-Planck equation for the phase-space distribution of polymer segments. Thus the treatment is not fully microscopic, since the solvent is treated as a continuous background that is assumed to be in local equilibrium with the degrees of freedom of the polymer segments. But the Fokker-Planck equation itself is microscopically well-defined, since it has been derived from the Liouville equation for a two-component system of solvent molecules and Brownian particles by projection operator techniques.^{9,10} In our case the polymer segments play the role of Brownian particles. The Fokker-Planck equation reads

$$\frac{\partial}{\partial t}P(\Gamma,t) = \hat{\Omega}(\Gamma)P(\Gamma,t) \quad (1.1)$$

$$\hat{\Omega}(\Gamma) = -\sum_{i=1}^N \sum_{\alpha=1}^n \left(\frac{\mathbf{p}_\alpha^i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_\alpha^i} + \mathbf{F}_\alpha^i \cdot \frac{\partial}{\partial \mathbf{p}_\alpha^i} \right) + \sum_{i,j=1}^N \sum_{\alpha,\beta=1}^n \frac{\partial}{\partial \mathbf{p}_\alpha^i} \cdot \zeta_{\alpha\beta}^{ij} \left(k_B T \frac{\partial}{\partial \mathbf{p}_\beta^j} + \frac{\mathbf{p}_\beta^j}{m} \right)$$

Γ denotes the set of momenta and coordinates of all segments, $\{\mathbf{p}_\alpha^i, \mathbf{r}_\alpha^i\}$, and $P(\Gamma,t)$ is the phase-space distribution function for all polymer segments. The Greek indices number the segments of one polymer, $\alpha = 1, \dots, n$, and the Latin indices number the polymer in the system, $i = 1, \dots, N$. \mathbf{F}_α^i is the total force on segment (α,i)

$$\mathbf{F}_\alpha^i = - \frac{\partial}{\partial \mathbf{r}_\alpha^i} U(\Gamma) \quad (1.2)$$

where $U(\Gamma)$ is the total potential energy. $\zeta_{\alpha\beta}^{ij}$ is a two-segment friction tensor. It describes the friction force that is exerted on segment (α,i) if segment (β,j) moves with velocity \mathbf{p}_β^j/m , m being the mass of a segment. The friction tensor $\zeta_{\alpha\beta}^{ij}$ depends in principle on the coordinates of all segments, $\zeta_{\alpha\beta}^{ij} = \zeta_{\alpha\beta}^{ij}(\{\mathbf{r}\})$. It is related to the more familiar mobility tensors of the Kirkwood theory by the matrix equation

$$\sum_{k=1}^N \sum_{\gamma=1}^n \zeta_{\alpha\gamma}^{ik} \cdot \mu_{\gamma\beta}^{kj} = \delta_{\alpha\beta} \delta_{ij} \mathbf{1} \quad (1.3)$$

The use of the Fokker-Planck equation (1.1) is relatively unfamiliar in polymer theory, where usually the Kirkwood equation serves as a starting point. But for systems of strongly interacting particles the Kirkwood equation should be considered with caution. The Kirkwood equation, or generalized Smoluchowski equation, can be derived^{9,11-13} from the Fokker-Planck equation (1.1) under the assumption that solvent friction is the dominating relaxation process. But, especially for entangled solutions, the dominating relaxation processes are due to interactions among the polymers. The condition by which the diffusion equation has been derived then becomes invalid. If we consider the extreme case of highly concentrated solutions or polymeric melts, solvent friction becomes negligible or vanishes, respectively. This is correctly described by the Fokker-Planck equation (1.1), which for $\zeta_{\alpha\beta}^{ij} \rightarrow 0$ goes over into the Liouville equation for the one-component system of polymers alone. A transport theory based on the Fokker-Planck equation has been developed previously for colloidal solutions,¹⁴ where long-range electrostatic forces also lead to strong interaction effects in the viscoelastic and diffusion properties. There are only minor differences in the formal structure of the transport equations between colloidal systems and polymeric solutions.

These formal transport equations are derived in the next section. In section III we will show how the generalized transport functions are connected with the self-diffusion coefficient and related functions, like the mean-square displacement and the velocity autocorrelation function of the center of mass of a polymer. In section IV we will calculate the time-dependent generalized friction function in an approximation that is suitable for semidilute solutions. We will find that it can be related to a curvilinear response function and to a response function for motions which are locally perpendicular to the line of the polymer. These response functions are calculated in section V. It is found that the curvilinear response function describes the motion of a free Rouse chain, whereas the perpendicular degrees of freedom freeze in at a critical concentration or chain length. Above that transition only curvilinear motion is possible. In section VI we finally calculate the self-diffusion coefficient for the whole range of entanglement strength.

II. Correlation Function Formalism

The basic quantity in which we are interested is the self-diffusion coefficient of a polymer chain, D_s . We will obtain D_s as a time integral of the velocity autocorrelation function. But it will prove to be useful if we first derive results for the autocorrelation function of segment density fluctuations of one test chain (say, $i = 1$).

$$F(\mathbf{q}, t) = \frac{1}{n} \langle c^1(\mathbf{q}) e^{\hat{n}t} c^1(-\mathbf{q}) \rangle \quad (2.1)$$

$$c^i(\mathbf{q}) = \sum_{\alpha=1}^n e^{-i\mathbf{q} \cdot \mathbf{r}_\alpha^i} \quad (2.2)$$

The equilibrium average is defined as

$$\langle \dots \rangle \equiv \int d\Gamma \dots P_0(\Gamma) \quad (2.3)$$

$P_0(\Gamma)$ is the equilibrium distribution

$$P_0(\Gamma) = Z^{-1} \exp[-\beta(U(\Gamma) + \sum_{i=1}^N \sum_{\alpha=1}^n (\mathbf{p}_\alpha^i)^2 / 2m)] \quad (2.4)$$

and $\beta = (k_B T)^{-1}$. If the average (2.3) is performed over an operator, that operator acts also on $P_0(\Gamma)$. $F(\mathbf{q}, t)$ may be considered as a dynamic generalization of the form factor of a polymer, since

$$\begin{aligned} F(\mathbf{q}, 0) &= \frac{1}{n} \langle c^1(\mathbf{q}) c^1(-\mathbf{q}) \rangle \\ &= \frac{1}{n} \sum_{\alpha, \beta} \langle e^{-i\mathbf{q} \cdot (\mathbf{r}_\alpha^1 - \mathbf{r}_\beta^1)} \rangle \equiv F(\mathbf{q}) \end{aligned} \quad (2.5)$$

is just the form factor.

We define a first projection operator \hat{P}_1 , which projects an arbitrary variable onto $c_1(\mathbf{q})$

$$\hat{P}_1 \equiv \dots c^1(-\mathbf{q}) \rangle (nF(\mathbf{q}))^{-1} \langle c^1(\mathbf{q}) \dots \quad (2.6)$$

\hat{P}_1 is idempotent and Hermitian. The same holds for $\hat{Q}_1 \equiv 1 - \hat{P}_1$. The time derivative of $F(\mathbf{q}, t)$ is

$$\begin{aligned} \dot{F}(\mathbf{q}, t) &= \frac{1}{n} \langle c^1(\mathbf{q}) \hat{\Omega} e^{\hat{n}t} c^1(-\mathbf{q}) \rangle \\ &= \frac{1}{n} \langle (-i\mathbf{q} \cdot \mathbf{j}^1(\mathbf{q})) e^{\hat{n}t} c^1(-\mathbf{q}) \rangle \end{aligned} \quad (2.7)$$

$\mathbf{j}^1(\mathbf{q})$ being the current fluctuations of the segments of the test polymer

$$\mathbf{j}^1(\mathbf{q}) = \sum_{\alpha=1}^n (\mathbf{p}_\alpha^1 / m) e^{-i\mathbf{q} \cdot \mathbf{r}_\alpha^1} \quad (2.8)$$

The time evolution operator is decomposed according to the operator identity

$$e^{\hat{n}t} = e^{\hat{n}\hat{Q}_1 t} + \int_0^t dt' e^{\hat{n}\hat{Q}_1(t-t')} \hat{\Omega} \hat{P}_1 e^{\hat{n}t'} \quad (2.9)$$

Then

$$\begin{aligned} \dot{F}(\mathbf{q}, t) &= \frac{1}{n} \langle (-i\mathbf{q} \cdot \mathbf{j}^1(\mathbf{q})) e^{\hat{n}\hat{Q}_1 t} c^1(-\mathbf{q}) \rangle + \int_0^t dt' \frac{1}{n} \langle (-i\mathbf{q} \cdot \mathbf{j}^1(\mathbf{q})) e^{\hat{n}\hat{Q}_1(t-t')} \hat{\Omega} c^1(-\mathbf{q}) \rangle F(\mathbf{q})^{-1} \frac{1}{n} \langle c^1(\mathbf{q}) e^{\hat{n}t'} c^1(-\mathbf{q}) \rangle \end{aligned} \quad (2.10)$$

The first term vanishes, since $\langle \mathbf{j}^1(\mathbf{q}) c^1(-\mathbf{q}) \rangle = 0$ and $\hat{Q}_1 c^1(\mathbf{q}) = 0$. We then define a generalized diffusion function

$$D(\mathbf{q}, t) = \frac{1}{nF(\mathbf{q})} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) e^{\hat{n}\hat{Q}_1 t} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \quad (2.11)$$

$\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$, and eq 2.10 takes the form of a generalized diffusion equation

$$\dot{F}(\mathbf{q}, t) = -q^2 \int_0^t dt' D(\mathbf{q}, t-t') F(\mathbf{q}, t') \quad (2.12)$$

In the long-wavelength limit, $D(\mathbf{q}, t)$ becomes the velocity autocorrelation function for the center-of-mass motion of the test polymer

$$D(0, t) = \frac{1}{3} \langle \mathbf{v}^1 \cdot e^{\hat{n}t} \mathbf{v}^1 \rangle \quad (2.13)$$

since in the limit $q \rightarrow 0$, $\hat{n}\hat{Q}_1 \rightarrow \hat{\Omega}$, and

$$\mathbf{v}^1 = \frac{1}{n} \sum_{\alpha=1}^n \mathbf{p}_\alpha^1 / m = \frac{1}{n} \mathbf{j}^1(0) \quad (2.14)$$

We derive then a memory equation for $D(\mathbf{q}, t)$ in the same way as has been done for $F(\mathbf{q}, t)$. The projection operator is

$$\hat{P}_2 \equiv \dots \sum_{i=1}^N \mathbf{j}^i(-\mathbf{q}) \rangle \cdot \frac{m}{nk_B T} \langle \mathbf{j}^i(\mathbf{q}) \dots \quad (2.15)$$

and $\hat{Q}_2 \equiv 1 - \hat{P}_2$. Then

$$\begin{aligned} \dot{D}(\mathbf{q}, t) &= \frac{1}{nF(\mathbf{q})} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{Q}_1 (\hat{P}_2 + \hat{Q}_2) e^{\hat{n}\hat{Q}_1 t} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \\ &= \frac{m\beta}{n^2 F(\mathbf{q})} \sum_{i=1}^N \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \mathbf{j}^i(-\mathbf{q}) \rangle \cdot \langle \mathbf{j}^i(\mathbf{q}) e^{\hat{n}\hat{Q}_1 t} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle + \frac{1}{nF(\mathbf{q})} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{Q}_2 e^{\hat{n}\hat{Q}_1 t} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \end{aligned} \quad (2.16)$$

Here $\hat{Q} \equiv \hat{Q}_1 \hat{Q}_2 = 1 - \hat{P}_1 - \hat{P}_2$.

For the second term in (2.16) we use an operator identity similar to eq 2.9 and obtain

$$\begin{aligned} \dot{D}(\mathbf{q}, t) = & \frac{m\beta}{n^2 F(\mathbf{q})} \sum_{i=1}^N \left\{ \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \mathbf{j}^i(-\mathbf{q}) \rangle \cdot \langle \mathbf{j}^i(\mathbf{q}) e^{\hat{\Omega} \hat{Q}_1 t} \hat{\mathbf{q}} \cdot \right. \\ & \mathbf{j}^1(-\mathbf{q}) \rangle + \int_0^t dt' \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{Q} e^{\hat{\Omega} \hat{Q}(t-t')} \hat{\Omega} \mathbf{j}^i(-\mathbf{q}) \rangle \cdot \langle \mathbf{j}^i(\mathbf{q}) e^{\hat{\Omega} \hat{Q}_1 t'} \hat{\mathbf{q}} \cdot \\ & \left. \mathbf{j}^1(-\mathbf{q}) \rangle \right\} + \frac{1}{n F(\mathbf{q})} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{Q} e^{\hat{\Omega} \hat{Q} t} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \quad (2.17) \end{aligned}$$

The last term vanishes again, since $\dots \hat{Q} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle = 0$.

Any correlation function containing the current fluctuations $\mathbf{j}^i(\mathbf{q})$ and $\mathbf{j}^1(-\mathbf{q})$, with $i \neq 1$, involves the probability of finding polymer i somewhere when polymer 1 is at a certain position, which is of $\mathcal{O}(1/V)$. In each of the two remaining terms in eq 2.17 are $N-1$ terms with products of such correlation functions. The sum of these terms is of $\mathcal{O}(N/V^2)$ and vanishes in the thermodynamic limit. Only the term with $i = 1$ survives. When the isotropy of the system is also used, we find

$$m \dot{D}(\mathbf{q}, t) = -\zeta^\infty(\mathbf{q}) D(\mathbf{q}, t) - \int_0^t dt' \Delta \zeta(\mathbf{q}, t-t') D(\mathbf{q}, t') \quad (2.18)$$

Here we have defined a wave vector dependent instantaneous friction coefficient,

$$\begin{aligned} \zeta^\infty(\mathbf{q}) = & -\frac{m^2}{n k_B T} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \\ = & \frac{1}{n} \sum_{\alpha, \beta=1}^N \langle \hat{\mathbf{q}} \cdot \zeta_{\alpha\beta}^{11} \cdot \hat{\mathbf{q}} \exp[-i\mathbf{q} \cdot (\mathbf{r}_\alpha^1 - \mathbf{r}_\beta^1)] \rangle \end{aligned} \quad (2.19)$$

which represents the friction forces of the solvent, averaged with the equilibrium distribution of segments. A second dynamic contribution to the friction acting on the test polymer stems from interactions between polymer segments and fluctuations in the solvent friction forces.

$$\begin{aligned} \Delta \zeta(\mathbf{q}, t) = & -\frac{m^2}{n k_B T} \langle \hat{\mathbf{q}} \cdot \mathbf{j}^1(\mathbf{q}) \hat{\Omega} \hat{Q} e^{\hat{\Omega} \hat{Q} t} \hat{\Omega} \hat{\mathbf{q}} \cdot \mathbf{j}^1(-\mathbf{q}) \rangle \\ = & \frac{1}{3n k_B T} \langle (\mathbf{f}^1(\mathbf{q}) + \mathbf{h}^1(\mathbf{q})) \cdot e^{\hat{\Omega} \hat{Q} t} (\mathbf{f}^1(-\mathbf{q}) - \mathbf{h}^1(-\mathbf{q})) \rangle \end{aligned} \quad (2.20)$$

$$\mathbf{f}^1(\mathbf{q}) = \sum_{\alpha=1}^n \left[\frac{\mathbf{p}_\alpha^1}{m} (-i\mathbf{q} \cdot \mathbf{p}_\alpha^1) + \mathbf{F}_\alpha^1 + i\mathbf{q} \frac{k_B T}{F(\mathbf{q})} \right] e^{-i\mathbf{q} \cdot \mathbf{r}_\alpha^1} \quad (2.21)$$

$$\begin{aligned} \mathbf{h}^1(\mathbf{q}) = & \sum_{i=1}^N \sum_{\alpha, \beta=1}^n \left[(\zeta_{\alpha\beta}^{1i} \cdot \mathbf{p}_\beta^i / m) e^{-i\mathbf{q} \cdot \mathbf{r}_\alpha^1} - \langle \zeta_{\alpha\beta}^{1i} e^{-i\mathbf{q} \cdot (\mathbf{r}_\alpha^1 - \mathbf{r}_\beta^i)} \rangle \cdot \mathbf{j}^i(\mathbf{q}) \right] \end{aligned} \quad (2.22)$$

The projection operator method is a formal way to obtain closed equations for correlation functions, here the generalized diffusion function $D(\mathbf{q}, t)$. The same purpose could also have been achieved by using a different projector, namely the operator $\hat{P}_2 \equiv \dots \mathbf{j}^1(-\mathbf{q}) \rangle (m/n k_B T) \cdot \langle \mathbf{j}^1(\mathbf{q}) \dots$, instead of \hat{P}_2 , as defined in eq 2.15. \hat{P}_2 projects on a much larger space of variables, compared to \hat{P}_2 ; therefore, the space of orthogonal variables is smaller, compared to the space that is orthogonal to $\mathbf{j}^1(\mathbf{q})$ alone. The different projection operators produce different equations for $D(\mathbf{q}, t)$, but since both ways are mathematically equivalent, both equations contain the same information. But for the equation (2.17), which results from using \hat{P}_2 , we can use the additional argument of the thermodynamic limit. In the thermodynamic limit all individual correlations be-

tween segments of different polymers vanish.

In contrast, if working with the projector \hat{P}_2 , it is hard to see how to introduce the argument of the thermodynamic limit, since then these correlations between different polymers do not show up explicitly but are hidden in the generalized friction function. The result is that the generalized friction forces $\mathbf{h}^1(\mathbf{q})$, eq 2.22, contain less correlation and are therefore simpler quantities and more amenable to approximations, compared to the corresponding generalized forces, which would have been obtained by using the projector \hat{P}_2 .

In the long-wavelength limit the two generalized random forces take especially simple forms,

$$\mathbf{f}^1(0) = \sum_{\alpha=1}^n \mathbf{F}_\alpha^1 = \sum_{i=2}^N \sum_{\alpha, \beta=1}^n \mathbf{F}_{\alpha\beta}^{1i} \equiv \mathbf{F}^1 \quad (2.23)$$

is the total interaction force on the test polymer. Intramolecular forces drop out, since $\sum_{\alpha, \beta=1}^n \mathbf{F}_{\alpha\beta}^{11} = 0$.

$$\mathbf{h}^1(0) = \sum_{i=1}^N \sum_{\alpha, \beta=1}^n [\zeta_{\alpha\beta}^{1i} \cdot \mathbf{p}_\beta^i / m - \langle \zeta_{\alpha\beta}^{1i} \rangle \cdot \mathbf{v}^i] \quad (2.24)$$

is the difference between the total friction force acting on the test polymer and a mean friction. The latter would result if each segment has the same velocity as the center of mass of its chain and if the friction tensors $\zeta_{\alpha\beta}^{1i}$ are averaged with the equilibrium segment distribution. A frequently used approximation for hydrodynamic interaction is the preaveraging approximation, which from the beginning replaces the configuration-dependent hydrodynamic interaction tensors by their equilibrium averages. Then

$$\mathbf{h}^1(0) = \sum_{i=1}^N \sum_{\alpha, \beta=1}^n \langle \zeta_{\alpha\beta}^{1i} \rangle \cdot (\mathbf{p}_\beta^i / m - \mathbf{v}^i) \quad (2.25)$$

is indeed proportional to the deviation of segment velocities from the center-of-mass velocity. For very long chains the great majority of the segments are statistically equivalent, only the segments near the ends having distinct statistical properties. In the long-chain limit such end effects will be negligible. Therefore, for long chains $\sum_{\alpha=1}^n \langle \zeta_{\alpha\beta}^{1i} \rangle$ will depend only weakly on the index β .

$$\sum_{\alpha=1}^n \langle \zeta_{\alpha\beta}^{1i} \rangle \simeq 1/n \sum_{\alpha, \beta=1}^n \langle \zeta_{\alpha\beta}^{1i} \rangle$$

This assumption would become true if we assume periodic boundary conditions. Therefore, we can expect that for long chains $\mathbf{h}^1(0)$ should be a very small quantity, since

$$\mathbf{h}^1(0) \simeq \sum_{i=1}^N (1/n \sum_{\alpha, \beta=1}^n \langle \zeta_{\alpha\beta}^{1i} \rangle) \sum_{\beta=1}^n (\mathbf{p}_\beta^i / m - \mathbf{v}^i) = 0$$

Thus we may neglect $\mathbf{h}^1(0)$ for preaveraged hydrodynamic interaction in the long-chain limit. For concentrated solutions it is found, in contrast, that hydrodynamic interaction is strongly screened and may be approximated by an effective (concentration-dependent) single segment friction coefficient, $\zeta_{\alpha\beta}^{ij} \rightarrow \zeta(c) \delta_{\alpha\beta} \delta_{ij}$. It follows immediately then that $\mathbf{h}^1(\mathbf{q}) = 0$ for all values of \mathbf{q} .

A formal solution of eq 2.12 and 2.18 can be obtained by Laplace transformation. Denoting Laplace transformed functions by a tilde

$$\tilde{F}(\mathbf{q}, z) = \frac{F(\mathbf{q})}{z + \tilde{D}(\mathbf{q}, z) \mathbf{q}^2} \quad (2.26)$$

and

$$\tilde{D}(\mathbf{q}, z) = \frac{k_B T / F(\mathbf{q})}{mz + \zeta^\infty(\mathbf{q}) + \Delta \tilde{\zeta}(\mathbf{q}, z)} \quad (2.27)$$

The set of equations (2.26) and (2.27) describes the complete spectrum of the segment fluctuations of a polymer chain, including high-frequency oscillations. In polymer dynamics mostly one is only interested in the low-frequency diffusive branch of excitations. One may then safely neglect the acceleration term in eq 2.27 and write

$$\tilde{D}(\mathbf{q}, z) = \frac{k_B T / F(\mathbf{q})}{\zeta^\infty(\mathbf{q}) + \Delta\tilde{\zeta}(\mathbf{q}, z)} \quad (2.28)$$

The frequency dispersion in $\Delta\tilde{\zeta}(\mathbf{q}, z)$ cannot be neglected, since it will show up that the dynamic friction function relaxes by spatial diffusion on the same frequency scale as $\tilde{F}(\mathbf{q}, z)$.

III. Center-of-Mass Diffusion

The self-diffusion coefficient of a polymer may be defined either in terms of the long-time limit of the mean-square displacement of its center of mass

$$D_s = \lim_{t \rightarrow \infty} \left[\frac{1}{6t} \langle (\mathbf{r}^1(t) - \mathbf{r}^1(0))^2 \rangle \right] \\ \mathbf{r}^1 = \frac{1}{n} \sum_{\alpha=1}^n \mathbf{r}_\alpha^1 \quad (3.1)$$

or by the Kubo formula, as the time integral over the velocity autocorrelation function.

$$D_s = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}^1(t) \cdot \mathbf{v}^1(0) \rangle \quad (3.2)$$

Both formulations are equivalent, since

$$\langle (\mathbf{r}^1(t) - \mathbf{r}^1(0))^2 \rangle = \int_0^t dt' \int_0^{t'} dt'' \langle \mathbf{v}^1(t') \cdot \mathbf{v}^1(t'') \rangle \\ = \int_0^t dt' (t - t') \langle \mathbf{v}^1(t') \cdot \mathbf{v}^1(0) \rangle \quad (3.3)$$

According to eq 2.13, the center-of-mass velocity autocorrelation function is just the long-wavelength limit of the generalized diffusion function. Therefore

$$D_s = \int_0^\infty dt D(0, t) = \tilde{D}(0, 0) \quad (3.4)$$

Equation 2.27 then yields the result (since $F(0) = n$)

$$D_s = \frac{k_B T}{n \left(\zeta_{\text{RZ}}(c, n) + \int_0^\infty dt \Delta\zeta(0, t) \right)} \quad (3.5)$$

where $\zeta_{\text{RZ}}(c, n)$ can be considered as a generalized Rouse-Zimm friction coefficient

$$\zeta_{\text{RZ}}(c, n) = \frac{1}{n} \sum_{\alpha, \beta=1}^n \langle \hat{\mathbf{q}} \cdot \zeta_{\alpha\beta}^{11} \cdot \hat{\mathbf{q}} \rangle \quad (3.6)$$

The dynamic friction function in the long-wavelength limit is

$$\Delta\zeta(0, t) = \frac{1}{3nk_B T} \langle (\mathbf{F}^1 + \mathbf{h}^1(0)) \cdot e^{\hat{\mathbf{q}} \cdot \hat{\mathbf{q}} t} (\mathbf{F}^1 - \mathbf{h}^1(0)) \rangle \quad (3.7)$$

According to our discussion before, the hydrodynamic fluctuations $\mathbf{h}^1(0)$ can be considered as small, especially in concentrated solutions, and may be neglected, compared to the interaction forces \mathbf{F}^1 . We then have an especially simple decomposition of the phenomena that contribute to the friction of a polymer: the solvent friction as a static instantaneous process, since the dynamic modes of the solvent are considered as fast compared to the time scale of polymer diffusion, and a dynamic friction force due to interactions of the test polymer with other polymers. The calculation of this dynamic friction effect is the main

theme of the paper. But it is instructive to consider here also the result for the dilute limit. The forces between different polymers then vanish, and

$$D_s = \left[k_B T / n \left[\zeta_{\text{RZ}}(0, n) - \frac{1}{3k_B T n} \int_0^\infty dt \langle \mathbf{h}^1(0) e^{\hat{\mathbf{q}} \cdot \hat{\mathbf{q}} t} \mathbf{h}^1(0) \rangle \right] \right]^{-1} \quad (3.8)$$

is the rigorous result (on the basis of the Fokker-Planck equation 1.1) for the dilute limit. Here friction on the center of mass is entirely caused by solvent friction: first, by the mean-field friction term $\zeta_{\text{RZ}}(0, n)$ and second, by fluctuations in the friction force due to fluctuations in the segment and in the momentum distribution. If hydrodynamic interaction is neglected, $\zeta_{\alpha\beta}^{ij} \rightarrow \zeta_0 \delta_{\alpha\beta} \delta_{ij}$, where ζ_0 is the unrenormalized single-segment friction coefficient, we obtain the Rouse result, $D_s = k_B T / n \zeta_0$. In contrast, if only the fluctuating forces $\mathbf{h}^1(0)$ are neglected, assuming preaveraged hydrodynamic interaction and statistical equivalence of segments in the long-chain limit, we have

$$D_s = \frac{k_B T}{n \zeta_{\text{RZ}}(0, n)} = \frac{k_B T}{\sum_{\alpha, \beta=1}^n \langle \hat{\mathbf{q}} \cdot \zeta_{\alpha\beta}^{11} \cdot \hat{\mathbf{q}} \rangle} \quad (3.9)$$

which is in agreement with the corresponding result of the Kirkwood theory.¹⁵ Especially if the Oseen tensor is used for hydrodynamic interaction and for Gaussian chain statistics, one obtains $\zeta_{\text{RZ}}(0, n) \sim n^{1/2}$; therefore $D_s \sim n^{-(1/2)}$.

In the long-wavelength limit the polymer segment fluctuations decay much slower, compared to the velocity fluctuations. If we formally take the hydrodynamic limit ($\lim_{q \rightarrow 0} \lim_{t \rightarrow \infty}$, but $\mathbf{q}^2 t = \text{const}$) of the generalized diffusion eq 2.12, we obtain the ordinary diffusion equation

$$\dot{F}(\mathbf{q}, t) = -D_s \mathbf{q}^2 F(\mathbf{q}, t) \quad (3.10)$$

with the solution

$$F(\mathbf{q}, t) = e^{-D_s \mathbf{q}^2 t} F(\mathbf{q}) \quad (3.11)$$

Since D_s describes the motion of the center-of-mass coordinates, we have verified that the long-wavelength segment fluctuations of the test polymer evolve for long times according to its center-of-mass motion.

$$\lim_{\substack{q \rightarrow 0 \\ q^2 t = \text{const}}} \lim_{t \rightarrow \infty} F(\mathbf{q}, t) = n \exp[-6 \mathbf{q}^2 \langle (\mathbf{r}^1(t) - \mathbf{r}^1(0))^2 \rangle] \quad (3.12)$$

IV. Dynamic Friction Function in the Semidilute Regime

For concentrated solutions it has been observed that hydrodynamic interaction effects become negligible.^{1,2} This occurs even at concentrations well below the concentration above which entanglement effects become decisive. Theoretically this is understood as a screening effect, due to a scattering of the solvent modes which transmit hydrodynamic interaction.^{16,17} If we focus only on larger length scale effects, compared to the screening length, we may incorporate the screened hydrodynamic interaction in terms of a concentration-dependent effective single-segment friction coefficient. The actual concentration dependence of the screening length, and therefore of the effective friction coefficient, has been under dispute, but it is quite clear that no unique answer can be expected. The strength of the screening mechanism will depend on the correlations in the segment distribution.

For entangled solutions, de Gennes obtained⁸ $\zeta(c) \sim c^{1/2}$. But the actual concentration dependence of $\zeta(c)$ is not an essential point in this paper. Only if we compare the

general result in section VI with de Gennes' result will we need the explicit concentration dependence of $\zeta(c)$. If we therefore set

$$\zeta_{\alpha\beta}^{ij} = \zeta(c)\delta_{\alpha\beta}\delta_{ij}1 \quad (4.1)$$

the long-wavelength dynamic friction function is simply the force correlation function

$$\Delta\zeta(0,t) = \frac{1}{3nk_B T} \langle \mathbf{F}^1 \cdot e^{\hat{\mathbf{Q}}t} \mathbf{F}^1 \rangle \quad (4.2)$$

So far our approach has been fairly general and may apply to stiff or flexible chains, polyelectrolytes or uncharged polymers, linear as well as star polymers, etc. Now we restrict our treatment to linear flexible polymers with short-ranged interactions only. It will also be of advantage for the following discussion if we use the model of a continuous chain, $\mathbf{r}_\alpha^i \rightarrow \mathbf{r}^i(s)$, where s is a continuous variable that runs along the contour of the chain, $0 \leq s \leq L$. L is the contour length of the chain, $L = ln$, where l is the mean distance of two neighboring segments in the discrete chain model. The standard form of the potential energy for this model is¹⁸

$$U(\Gamma) = \frac{3}{2l} \sum_i \int_0^L ds \left(\frac{\partial \mathbf{r}^i(s)}{\partial s} \right)^2 + \frac{1}{2l^2} \sum_{i,j=1}^N \int_0^L ds \int_0^L ds' u(\mathbf{r}^i(s) - \mathbf{r}^j(s')) \quad (4.3)$$

The first term in $U(\Gamma)$ describes the elastic energy of the polymer chains in harmonic approximation. The second term represents excluded-volume forces, which prevent an intersection of the lines of two chains or a self-intersection of a chain. This second term in $U(\Gamma)$ is most important at higher concentrations, since it represents the entanglements between the chains and is responsible for the transition to a reptative state of motion in concentrated polymeric liquids, as we will see. The short-ranged excluded-volume force is conveniently approximated as a δ -function

$$u(\mathbf{r}^i(s) - \mathbf{r}^j(s')) = k_B T v_0 \delta(\mathbf{r}^i(s) - \mathbf{r}^j(s')) = k_B T v_0 \frac{1}{(2\pi)^3} \int^{q_c} d^3 q \exp(-i\mathbf{q}(\mathbf{r}^i(s) - \mathbf{r}^j(s'))) \quad (4.4)$$

where for the second equality we have used the Fourier representation. $v_0(T)$ is the excluded-volume parameter, which is closely related to the second virial coefficient. The upper integration limit q_c reminds us that this approximation is restricted to Fourier modes $\lesssim v_0^{-1/3}$.

The use of a δ -function for the pseudopotential (4.4) has always to be considered as an idealization of a potential with a very short but finite range. Writing the excluded volume as $v_0 = (4\pi/3)a^3$, we may express the δ -function as the limit of a step function, $\delta(\mathbf{r}) = \lim_{a \rightarrow 0} [1/v_0 \theta(a - |\mathbf{r}|)]$, and the excluded-volume potential is $u(\mathbf{r}) = k_B T \theta(a - |\mathbf{r}|)$, when a is smaller than any other length of the problem. The upper integration limit is then fixed by the condition

$$u(0)/k_B T = v_0/(2\pi)^3 \int^{q_c} d^3 q = 1$$

The interaction potential is now

$$U(\Gamma) = \frac{3}{2l} \sum_{i=1}^N \int_0^L ds \left(\frac{\partial \mathbf{r}^i(s)}{\partial s} \right)^2 + \frac{1}{2} k_B T \sum_{i,j=1}^N \frac{v_0}{(2\pi)^3} \int^{q_c} d^3 q c^i(\mathbf{q}) c^j(-\mathbf{q}) \quad (4.5)$$

Since only intermolecular interactions enter the expression

for $\Delta\zeta(0,t)$, we obtain from eq 4.5a

$$\Delta\zeta(0,t) = -\frac{k_B T}{3n} \sum_{i,j=2}^N \frac{v_0^2}{(2\pi)^6} \int^{q_c} d^3 q \int^{q_c} d^3 q' \mathbf{q} \cdot \mathbf{q}' \langle c^1(\mathbf{q}) c^i(-\mathbf{q}) e^{\hat{\mathbf{Q}}t} c^1(\mathbf{q}') c^j(-\mathbf{q}') \rangle \quad (4.6)$$

Equation 4.6 relates the dynamic evolution of the friction function to the dynamics of products of concentration fluctuations. Remembering eq 4.4, we may also characterize this as the dynamic evolution of "contacts" between different polymers. Although these "contacts" influence the motion of the polymers severely, their number is small in semidilute solutions, compared to the number of segments of a chain, and they are randomly distributed. Thus the correlation between two polymers, which is caused by the excluded-volume forces, is only a local one, and we may assume that the overall motion of the polymers can still be treated as uncorrelated. We then factorize

$$\Delta\zeta(0,t) = -\frac{k_B T}{3n} \sum_{i,j=2}^N \frac{v_0^2}{(2\pi)^6} \int^{q_c} d^3 q \int^{q_c} d^3 q' \mathbf{q} \cdot \mathbf{q}' R(\mathbf{q},t)^2 \langle c^1(\mathbf{q}) c^i(-\mathbf{q}) c^1(\mathbf{q}') c^j(-\mathbf{q}') \rangle \quad (4.7)$$

The response function $R(\mathbf{q},t)$ is defined by

$$F(\mathbf{q},t) = R(\mathbf{q},t)F(\mathbf{q}) \quad (4.8)$$

The initial value in eq 4.7 is proportional to the term

$$k_B T \sum_{i,j=2}^N \frac{v_0}{(2\pi)^3} \int^{q_c} d^3 q' \mathbf{q} \cdot \mathbf{q}' \langle c^1(\mathbf{q}) c^i(-\mathbf{q}) c^1(\mathbf{q}') c^j(-\mathbf{q}') \rangle = \sum_{i=2}^N l^{-3} \int_0^L ds \int_0^L ds' ds'' \left\langle e^{-i\mathbf{q} \cdot \mathbf{r}^1(s)} e^{i\mathbf{q} \cdot \mathbf{r}^i(s')} i\mathbf{q} \cdot \left(\frac{\partial}{\partial \mathbf{r}^1(s'')} U(\Gamma) \right) \right\rangle \quad (4.9)$$

Since the equilibrium distribution function is $\sim \exp(-\beta U(\Gamma))$, the expression above vanishes from $s \neq s''$; therefore it is

$$\sum_{i=2}^N l^{-2} \int_0^L ds \int_0^L ds' \left\langle e^{-i\mathbf{q} \cdot \mathbf{r}^1(s)} e^{i\mathbf{q} \cdot \mathbf{r}^i(s')} i\mathbf{q} \cdot \left(\frac{\partial}{\partial \mathbf{r}^1(s)} U(\Gamma) \right) \right\rangle = k_B T \sum_{i,j=2}^N l^{-3} \int_0^L ds \int_0^L ds' ds'' \frac{v_0}{(2\pi)^3} \int^{q_c} d^3 q' \mathbf{q} \cdot \mathbf{q}' \langle e^{-i(\mathbf{q}+\mathbf{q}') \cdot \mathbf{r}(s)} e^{i\mathbf{q} \cdot \mathbf{r}^i(s')} e^{i\mathbf{q}' \cdot \mathbf{r}^j(s'')} \rangle$$

The expectation value above describes static correlations among two ($i = j$, $s' = s''$) or three segments. We assume that the system is sufficiently dilute, so that the three-segment correlations can be neglected. Equation 4.9 then becomes

$$\begin{aligned} &= k_B T \sum_{i=2}^N \frac{v_0}{(2\pi)^3} \int^{q_c} d^3 q' \mathbf{q} \cdot \mathbf{q}' \langle c^1(\mathbf{q} + \mathbf{q}') c^i(-\mathbf{q} - \mathbf{q}') \rangle \\ &= -q^2 k_B T \sum_{i=2}^N \frac{v_0}{(2\pi)^3} \int^{q_c} d^3 q' \langle c^1(\mathbf{q} + \mathbf{q}') c^i(-\mathbf{q} - \mathbf{q}') \rangle \quad (4.10) \\ &= -q^2 k_B T v_0 \sum_{i=2}^N \frac{1}{l^2} \int_0^L ds \int_0^L ds' \langle \delta(\mathbf{r}^1(s) - \mathbf{r}^i(s')) \rangle \end{aligned}$$

since $\langle c^1(\mathbf{q}) c^i(-\mathbf{q}) \rangle$ is an even function of \mathbf{q} .

The contribution in the free energy density, which stems from interactions among different chains, is

$$\begin{aligned} \Delta F &= \frac{1}{2V} \sum_{i,j=1}^N \frac{1}{l^2} \int_0^L ds \int_0^L ds' \langle u(\mathbf{r}^i(s) - \mathbf{r}^j(s')) \rangle \\ &= \frac{k_B T v_0}{2V} N \frac{1}{l^2} \int_0^L ds \int_0^L ds' \langle \delta(\mathbf{r}^1(s) - \mathbf{r}^2(s')) \rangle \quad (4.11) \end{aligned}$$

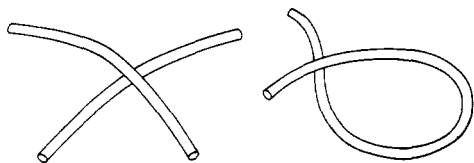


Figure 1. Inter- and intramolecular excluded-volume interaction of flexible cylinders.

when the statistical equivalence of the polymers is used. Using eq 4.9–4.11 in eq 4.7, we obtain

$$\Delta\zeta(0,t) = \frac{2}{3} \frac{\Delta F}{c} \frac{v_0}{(2\pi)^3} \int d^3q \mathbf{q}^2 R(\mathbf{q},t)^2 \quad (4.12)$$

The decisive point in the actual calculation of $\Delta\zeta(0,t)$ is the insight that excluded-volume forces are always orthogonal to the local tangent vectors of the two chains at the place of interaction. This can be easily seen if we visualize each polymer as a long flexible cylinder (Figure 1) and if we neglect interactions at the ends. We define now a local coordinate system, where one axis is parallel to the local tangent vector and the other two are arbitrary but orthogonal. The Fokker–Planck operator (1.1) is then decomposed as

$$\hat{\Omega}(\Gamma) = \hat{\Omega}_{\parallel}(\Gamma) + \hat{\Omega}_{\perp}(\Gamma) \quad (4.13)$$

$$\hat{\Omega}_{\parallel}(\Gamma) = \sum_{i=1}^N \frac{1}{l} \int_0^L ds \left\{ -\frac{\mathbf{p}_{\parallel}^i(s)}{m} \cdot \frac{\partial}{\partial \mathbf{r}_{\parallel}^i(s)} - \mathbf{F}_{\parallel}^i(s) \cdot \frac{\partial}{\partial \mathbf{p}_{\parallel}^i(s)} + \zeta(c) \frac{\partial}{\partial \mathbf{p}_{\parallel}^i(s)} \cdot \left(k_B T \frac{\partial}{\partial \mathbf{p}_{\parallel}^i(s)} + \mathbf{p}_{\parallel}^i(s)/m \right) \right\} \quad (4.14)$$

and $\hat{\Omega}_{\perp}(\Gamma)$ takes the corresponding form.

Here we have performed the continuum limit, and we neglect hydrodynamic interaction, eq 4.1. The parallel and the orthogonal vector components are defined as

$$\mathbf{x}_{\parallel}^i(s) = (\mathbf{x}^i(s) \cdot \mathbf{t}^i(s)) \mathbf{t}^i(s) \quad (4.14a)$$

$$\mathbf{x}_{\perp}^i(s) = \mathbf{x}^i(s) - \mathbf{x}_{\parallel}^i(s) \quad (4.14b)$$

$\mathbf{t}^i(s)$ is the local tangent unit vector

$$\mathbf{t}^i(s) = \frac{\partial \mathbf{r}^i(s)}{\partial s} \bigg/ \left| \frac{\partial \mathbf{r}^i(s)}{\partial s} \right| \quad (4.14c)$$

The essential simplification of the decomposition (4.13) arises since the force components $\mathbf{F}_{\parallel}^i(s)$ are only produced by the elastic forces in the chains. In the harmonic approximation (4.3) they depend only on the locally parallel coordinates of the chain, $\{\mathbf{r}_{\parallel}^i(s)\}$. Thus $\hat{\Omega}_{\parallel}(\Gamma) = \hat{\Omega}_{\parallel}(\Gamma_{\parallel})$ is the same operator as for a system of noninteracting Rouse chains. In contrast, $\mathbf{F}_{\perp}^i(s)$ contains, besides the corresponding elastic contribution, the excluded-volume force

$$-\frac{\partial}{\partial \mathbf{r}_{\perp}^i(s)} \sum_{k,l} \int_0^L ds \int_0^L ds' u(\mathbf{r}^k(s) - \mathbf{r}^l(s'))$$

The excluded-volume potential in principle depends both on the orthogonal and on the parallel coordinates. But the dependence on the parallel coordinates is very weak. Considering Figure 1, we see that a pure curvilinear motion of such a flexible cylinder does not change the interaction energy of the two cylinders. Only if one of the cylinders has moved so far by curvilinear motion that its end reaches the contact point will the curvilinear motion lead to a change in excluded-volume interaction. But that is a small effect, of $\mathcal{O}(1/n)$, and we assume now that $\mathbf{F}_{\perp}^i(s)$ depends only on the set of orthogonal coordinates, $\{\mathbf{r}_{\perp}^i(s)\}$. In that

approximation $\hat{\Omega}_{\parallel}(\Gamma_{\parallel})$ and $\hat{\Omega}_{\perp}(\Gamma)$ commute and

$$e^{\hat{\Omega}t} = e^{\hat{\Omega}_{\parallel}t} e^{\hat{\Omega}_{\perp}t} \quad (4.15)$$

The response function $R(\mathbf{q},t)$ then is simply a product of a curvilinear propagator and a lateral propagator

$$R(\mathbf{q},t) = R_{\parallel}(\mathbf{q},t) R_{\perp}(\mathbf{q},t) \quad (4.16)$$

where

$$\langle c^i(\mathbf{q}) e^{\hat{\Omega}_{\parallel}t} c^i(-\mathbf{q}) \rangle = R_{\parallel,\perp}(\mathbf{q},t) F(\mathbf{q}) \quad (4.17)$$

For the dynamic friction function we now obtain

$$\Delta\zeta(0,t) = \frac{2}{3} \frac{\Delta F}{c} \frac{v_0}{(2\pi)^3} \int d^3q \mathbf{q}^2 R_{\parallel}(\mathbf{q},t)^2 R_{\perp}(\mathbf{q},t)^2 \quad (4.18)$$

This result may be considered as a first-order term in an expansion with respect to the curvilinear propagator.

V. Curvilinear and Lateral Propagators

Equations for $R_{\parallel}(\mathbf{q},t)$ and $R_{\perp}(\mathbf{q},t)$ can be obtained in the same way as for $F(\mathbf{q},t)$ in section II. When $\hat{\Omega}_{\parallel,\perp}$ is substituted for $\hat{\Omega}$, the results for the Laplace-transformed functions are

$$\tilde{R}_{\parallel,\perp}(\mathbf{q},z) = \frac{1}{z + D_{\parallel,\perp}(\mathbf{q},z) \mathbf{q}^2} \quad (5.1)$$

$$\tilde{D}_{\parallel}(\mathbf{q},z) = \frac{1}{3} \frac{k_B T / F(\mathbf{q})}{\zeta(c) + \Delta\tilde{\zeta}_{\parallel}(\mathbf{q},z)} \quad (5.2a)$$

and

$$\tilde{D}_{\perp}(\mathbf{q},z) = \frac{2}{3} \frac{k_B T / F(\mathbf{q})}{\zeta(c) + \Delta\tilde{\zeta}_{\perp}(\mathbf{q},z)} \quad (5.2b)$$

Here we have neglected the acceleration term and assumed that hydrodynamic interaction is screened, eq 4.1.

Equations 5.1 and 5.2a are certainly not the simplest way to get a result for the curvilinear propagator. Since excluded-volume forces do not enter in $\mathbf{F}_{\parallel}^i(s)$, $\hat{\Omega}_{\parallel}(\Gamma)$ describes the evolution of a Rouse chain. This problem can be solved directly by normal mode expansion. Neglecting the acceleration terms, one just reproduces Pecora's solution¹⁹ of the Kirkwood equation or de Gennes' corresponding result from a continuous chain.²⁰

In the following we will neglect internal fluctuations of the chains, and we will assume that for our purpose the response functions can be approximated by the long-wavelength center-of-mass propagators. This will lead to a self-consistent calculation of the lateral propagator. Then

$$\tilde{R}_{\parallel,\perp}(\mathbf{q},z) = \frac{1}{z + \tilde{D}_{\parallel,\perp}(0,z) \mathbf{q}^2} \quad (5.3)$$

$$\tilde{D}_{\parallel}(0,z) = \frac{1/3 D_0}{1 + \Delta\tilde{\zeta}_{\parallel}(0,z) / \zeta(c)} \quad (5.4a)$$

$$\tilde{D}_{\perp}(0,z) = \frac{2/3 D_0}{1 + \Delta\tilde{\zeta}_{\perp}(0,z) / \zeta(c)} \quad (5.4b)$$

the effective Rouse diffusion coefficient is

$$D_0(c,n) = \frac{k_B T}{n\zeta(c)} \quad (5.5)$$

Since

$$\Delta\zeta_{\parallel}(0,t) = \frac{1}{3nk_B T} \frac{1}{l^2} \int_0^L ds \int_0^L ds' \times \langle \mathbf{F}_{\parallel}^1(s) \cdot e^{\hat{\Omega}_{\parallel}t} \mathbf{F}_{\parallel}^1(s') \rangle = 0 \quad (5.6)$$

the curvilinear center-of-mass propagator is

$$R_{\parallel}(\mathbf{q}, t) = \exp\left(-\frac{1}{3}D_0\mathbf{q}^2t\right) \quad (5.7)$$

For $\Delta\zeta_{\perp}(0, t)$ we use the same approximations as were obtained for $\Delta\zeta(0, t)$ in the last section. The only difference is that the time evolution of $\Delta\zeta_{\perp}(0, t)$ is independent of curvilinear motion. Then, following eq 4.18

$$\Delta\zeta_{\perp}(0, t) = \frac{2}{3} \frac{\Delta F}{c} \frac{v_0}{(2\pi)^3} \int^{q_c} d^3q \mathbf{q}^2 R_{\perp}(\mathbf{q}, t)^2 \quad (5.8)$$

Equation 5.8, together with eq 5.3 and 5.4b, yields a self-consistent description for the evolution of the lateral propagator: for short times also $R_{\perp}(\mathbf{q}, t)$ evolves as an unperturbed Rouse propagator. Scattering due to entanglements with other chains (represented by $\Delta F/c$ in $\Delta\zeta_{\perp}(0, t)$) then slows down the lateral diffusion of the chain. After a time over which many of such scattering processes have taken place, $R_{\perp}(\mathbf{q}, t)$ will be dominated by its hydrodynamic pole

$$R_{\perp}(\mathbf{q}, t) = e^{-D_{\perp}\mathbf{q}^2t} \quad (5.9)$$

$$D_{\perp} = \tilde{D}_{\perp}(0, 0) = \frac{\frac{2}{3}D_0}{1 + \tilde{\zeta}_{\perp}(0, 0)/\zeta(c)} \quad (5.10)$$

Instead of solving the equations for $R_{\perp}(\mathbf{q}, t)$ numerically, we approximate $R_{\perp}(\mathbf{q}, t)$ in eq 5.8 by the long-time result (5.9). Then

$$\Delta\tilde{\zeta}_{\perp}(0, 0) = \frac{1}{3} \frac{\Delta F}{c D_{\perp}} \frac{v_0}{(2\pi)^3} \int^{q_c} d^3q = \frac{1}{3} \frac{\Delta F}{c D_{\perp}} \quad (5.11)$$

Equations 5.10 and 5.11 yield two solutions for D_{\perp} :

$$D_{\perp} = 0 \quad (5.12a)$$

and

$$D_{\perp} = \frac{2}{3}D_0(1 - \psi(c, n)), \quad \text{for } \psi \leq 1 \quad (5.12b)$$

with

$$\psi(c, n) = n\Delta F/2k_B Tc \quad (5.13)$$

For $\psi \ll 1$ the expression (5.12b) is the correct physical solution for the perpendicular diffusion coefficient. But for $\psi \rightarrow 1$, that expression goes to zero, and for $\psi \geq 1$, D_{\perp} is always zero. This is the central result of our paper. We have obtained in a self-consistent way a transition to a state in which the degrees of freedom of the chain, which are orthogonal to its space curve, are frozen in. For $\psi(c, n) \geq 1$ only curvilinear motion is possible, and therefore we might name that the reptation transition.

A similar localization transition has been obtained for diffusion processes in a Lorentz gas by Götze, Leutheusser, and Yip.²¹ Here a single hard-sphere particle moves in a random matrix of fixed scatterings. There is a great formal similarity in the dynamic equations for the propagators and diffusion functions if one compares our results with the corresponding results for the Lorentz gas. The vanishing of D_{\perp} in the reptating phase means that the mean-square displacement perpendicular to the chain becomes finite, which may be also expressed as $\tilde{D}(0, z) = zd^2$, defining a localization length d , which is infinite in the nonreptating phase. The response function then is $\tilde{R}_{\perp}(\mathbf{q}, z) = 1/z(1 + \mathbf{q}^2d^2)$; therefore, $R_{\perp}(\mathbf{q}, t) = 1/(1 + \mathbf{q}^2d^2)$ for $t \geq 0$. When that result is inserted in the dynamic friction function (5.8), the self-consistent equation for d becomes

$$1 = \frac{4}{3}\psi(c, n)v_0d^{-3} \frac{1}{(2\pi)^3} \int^{q_c} d^3x x^2(1 + x^2)^{-2} \quad (5.14)$$

The solution may be expressed as $d = v_0^{1/3}y(\psi)$. Therefore,

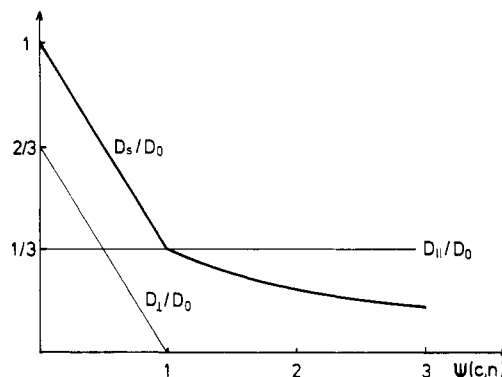


Figure 2. Self-diffusion, curvilinear, and lateral diffusion coefficients as a function of the entanglement parameter $\psi(c, n)$. $D_0 = k_B T/n\zeta(c)$ is the effective Rouse diffusion coefficient.

the localization length is of the order of the excluded volume, and we can set $d = 0$ since we are only interested in the behavior on a much larger length scale. Our final result for the lateral propagator is

$$R_{\perp}(\mathbf{q}, t) = \exp\left(-\frac{2}{3}D_0(1 - \psi(c, n))\mathbf{q}^2t\right) \quad \text{for } 0 \leq \psi \leq 1$$

$$= 1 \quad \text{for } 1 \leq \psi \quad (5.15)$$

VI. Self-Diffusion Coefficient in the Semidilute Concentration Regime

The self-diffusion coefficient cannot be obtained by a simple linear superposition of the curvilinear and the lateral motion. This would mean a total neglect of the coupling of both modes. Although this coupling is small, it becomes essential after the reptation transition. We have to go back to the original result for D_s , eq 3.5, and we use the expression 4.18 for the dynamic friction function, which allows for the coupling between lateral and curvilinear diffusion, to first order in $R_{\perp}(\mathbf{q}, t)^2$. Again we neglect here short-wavelength internal fluctuations and the details of the initial relaxation process, assuming that the segment distribution follows adiabatically the center-of-mass propagators 5.7 and 5.15. Then

$$D_s = \frac{D_0}{1 + D_0 \frac{n}{k_B T} \Delta\tilde{\zeta}(0, 0)} \quad (6.1)$$

and the time integral of the friction function 4.18 is

$$\Delta\tilde{\zeta}(0, 0) = \frac{\Delta F}{3c} / (D_{\parallel} + D_{\perp}) \quad (6.2)$$

which yields

$$D_s = \frac{D_0}{1 + \frac{2}{3}\psi(c, n) \frac{D_0}{D_{\parallel} + D_{\perp}}}$$

$$= D_0(c, n) \left(1 - \frac{2}{3}\psi(c, n)\right) = D_{\parallel} + D_{\perp} \quad \text{for } 0 \leq \psi \leq 1$$

$$= \frac{D_0(c, n)}{1 + 2\psi(c, n)} \quad \text{for } 1 \leq \psi \quad (6.3)$$

The behavior of D_s , D_{\perp} , and D_{\parallel} as a function of the entanglement parameter $\psi(c, n)$ is shown in Figure 2. Both the lateral and the self-diffusion coefficient show a critical transition for $\psi(c, n) = 1$, where the slopes of the curves change discontinuously. But, whereas lateral diffusion is totally suppressed in the reptation phase, there is still a finite mobility of the center of mass. The result (6.3)

describes the self-diffusion coefficient over the whole range of the entanglement parameter $\psi(c,n)$. For small ψ we have Rouse-like behavior $D_s = k_B T / n \zeta(c)$; for large ψ we recover de Gennes' reptation result $D_s = k_B T / (2n \zeta(c)) \psi(c,n) \sim n^{-2}$. We have by now used suggestively the name entanglement parameter for the quantity $\psi(c,n)$. From the definition of ψ , eq 5.13, ψ is just one-half of the mean interaction energy of one polymer, in units of $k_B T$. If we now ask for the specific concentration dependence of $\psi(c,n)$, we need an expression for the free energy density. de Cloizeaux²² has shown that for semidilute solutions in the limit of long chains the osmotic pressure is $\sim c^{9/4}$. From the relation between the osmotic pressure and the free energy density follows $\Delta F \sim c^{9/4}$.²³ We obtain then

$$\psi(c,n) = K(T) n c^{5/4} \quad (6.4)$$

where $K(T)$ is an undetermined parameter. In contrast, de Gennes⁴ has obtained from scaling arguments that the mean number of segments between two entanglements, $g(c)$, decreases with concentration as $c^{-5/4}$. Thus we may also write

$$\psi(c,n) = \tilde{K}(T) n / g(c) \quad (6.5)$$

Using this argument, we find that $\psi(c,n)$ is just proportional to the mean number of entanglements of one chain polymer, $n/g(c)$. Another so far undetermined parameter in our result (6.3) is the effective friction coefficient of a segment. Here de Gennes⁷ has shown for strongly entangled solutions that $\zeta(c) \sim c^{1/2}$.

Using this and eq 6.4, we obtain

$$D_s \sim n^{-2} c^{-7/4} \quad \text{for } n/g(c) \gg 1 \quad (6.6)$$

which was first derived by de Gennes.⁷

Unfortunately, the mean number of segments between two entanglements, $g(c)$, cannot be directly measured. Another way to reexpress the entanglement parameter $\psi(c,n)$ in terms of experimentally observable quantities is to write

$$\psi(c,n) = n/n_c = M/M_c \quad (6.7)$$

where n_c or M_c are respectively the critical segment number and the critical molecular weight, at which the reptation transition is observed. Since we found that this transition takes place for $\psi(c,n) = 1$, our result for n_c is

$$n_c = 2k_B T c / \Delta F \quad (6.8)$$

D_s may then be expressed as

$$\begin{aligned} D_s &= \frac{k_B T}{n \zeta(c)} \left(1 - \frac{2}{3} n/n_c \right) & \text{for } n \leq n_c \\ &= \frac{k_B T}{n \zeta(c)} \frac{1}{1 + 2n/n_c} & \text{for } n \geq n_c \end{aligned} \quad (6.9)$$

Figure 3 shows a double-logarithmic plot of D_s , normalized to $k_B T / n_c \zeta(c)$, as a function of n/n_c . The broken lines indicate the asymptotic behavior for small n and for large n . Scaling theories would locate the reptation transition at the point of intersection of the two limiting laws. It is interesting to note that this point is smaller by approximately a factor of $1/2$ than the cusp point (arrow), where the reptation transition actually takes place.

VII. Summary

In this work we have derived a general formula for the self-diffusion coefficient of polymeric liquids, starting from a Fokker-Planck equation for the phase-space distribution function of polymer segments and using the rigorous projection operator method. The range of validity of this result, eq 3.5, in principle extends from dilute solutions

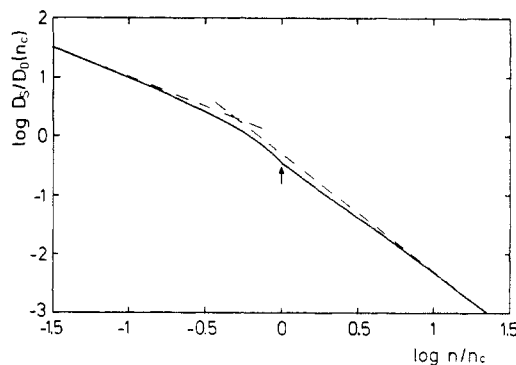


Figure 3. Self-diffusion coefficient D_s , normalized to $D_0(n_c) = k_B T / n_c \zeta(c)$, as a function of chain length. The arrow indicates the reptation transition at $n = n_c$.

over semidilute and concentrated solutions up to polymeric melts. In order to obtain a more explicit result, we have to supplement the general theory with a detailed expression for hydrodynamic interaction and we have to calculate the dynamic friction function defined in eq 2.20. For dilute solutions we recover then the result of the Kirkwood theory, eq 3.9. But our main emphasis lies in a calculation of the self-diffusion coefficient for the semidilute concentration regime and in a microscopic and self-consistent foundation of the reptation mechanism as the only possible mode of large-scale motions in semidilute and higher concentrated polymer liquids.

This is accomplished by the introduction of a local coordinate system, where one axis is parallel to the local direction of the polymeric chain and the other two are perpendicular. Since the direction of short-ranged interaction between polymers is always perpendicular to the local chain axis and since the interaction potential depends only weakly on curvilinear motion, the coupling of both sets of coordinates is small. To zero order in that coupling it is possible to write the center-of-mass propagator as a product of a curvilinear and a lateral propagator. The curvilinear propagator is found to describe the motion of a one-dimensional Rouse chain. For the lateral propagator we derive a self-consistent set of equations and we find that there exists a critical strength of interaction for a chain at which lateral motion becomes completely blocked. Above that critical interaction, which is proportional to the length of the polymers, only curvilinear motion, i.e., reptation, is possible.

Here one has to say a word of caution. In the way of deriving that result we have neglected the coupling between center-of-mass motion and internal fluctuations in the segment distribution of the chains. We do not believe that the basic features of the mechanism that lead to the reptating state would be seriously affected if such internal fluctuations would be taken into account. But it is likely that the sharpness of the reptation transition, which we found in eq 5.12, is an artifact of that approximation.

The dynamic friction function for center-of-mass motion is then calculated to first order in the coupling between curvilinear and lateral diffusion. The resulting equation (6.3) for the self-diffusion coefficient determines D_s in terms of two parameters. $\zeta(c)$ is the concentration-dependent single-segment friction coefficient, and $\psi(c,n) = n \Delta F(c) / 2ck_B T$, which we named the entanglement parameter, is one-half of the mean interaction energy per polymer, in units of $k_B T$. For small chain lengths $\psi(c,n) \ll 1$, and we obtain a Rouse-like diffusion, $D_s \sim n^{-1}$. But for large chain length at sufficiently high concentrations, when $\psi(c,n) \gg 1$, we find $D_s \sim n^{-2}$. This behavior can be considered as typical for reptation and has been obtained

earlier by de Gennes,^{3,8} and by an extension of de Gennes' reptation theory, by Schaefer, Joanny, and Pincus.²⁴ A main virtue of our microscopic approach is that it produces not only these limiting laws but also a result which is valid for arbitrary chain lengths and concentrations, provided that the assumption of screened hydrodynamic interaction on the one side and the model of a flexible cylinder on the other side can be justified. Figure 3 illustrates the dependence of D_s on chain length. Both branches of the D_s function merge in the form of a slight cusp, which locates the reptation transition. We find a remarkable wide crossover regime between both asymptotic laws, in contrast to the sharp crossover that is usually assumed by scaling theories.

In contrast to the chain-length dependence, it is not possible to give a unique answer to the question of concentration dependence of D_s in the entanglement-dominated regime. de Gennes' result is $D_s \sim n^{-2}c^{-7/4}$, but Schaefer, Joanny, and Pincus²⁴ claim that de Gennes' result applies only to a limited concentration regime, which they call the semidilute good solvent regime. They predict the existence of a semidilute marginal regime at higher concentrations, where $D_s \sim n^{-2}c^{-2.5}$, and a semidilute θ regime at still higher concentrations, where $D_s \sim n^{-2}c^{-3}$. All these results are based on specific assumptions concerning the interrelationship of certain correlation lengths. Our result is $D_s \sim n^{-2}(\zeta(c)\Delta F(c)/c)^{-1}$, and in order to give a more explicit result we have to rely on theories that yield the concentration dependence of the single-segment friction coefficient and the free energy density $\Delta F(c)$. This has been done only for the good solvent regime, and we obtain indeed $D_s \sim n^{-2}c^{-7/4}$. At concentrations below the reptation transition, in the Rouse-like regime, the result would be $D_s \sim n^{-1}c^{-1/2}$ if we assume still that $\zeta(c) \sim c^{1/2}$.

Following the publication of de Gennes' reptation theory, a number of experiments, using mainly the forced Rayleigh scattering and the pulsed field gradient NMR methods, have been undertaken in order to verify his results.²⁵⁻²⁹ In general there has been a convincing agreement for the concentration dependence as well as for the molecular weight dependence. A very beautiful verification of the $c^{-7/4}$ law in the semidilute regime has been obtained by Wang, Lowry, and Wu.³⁰ The results cover nearly two decades of concentration and extend also in the low-concentration regime. Here the results are in good agreement with a Rouse-like concentration dependence, $D_s \sim c^{-1/2}$. Some experiments^{27,28} have found a different molecular weight dependence, $D_s \sim n^{-1.4}$ (ref 27) or $D_s \sim n^{-1.6}$ (ref 28), intermediate between the Rouse-like behavior and the reptation behavior. One possible explanation is offered from our finding that the transition between these two regimes is not so abrupt, as has been assumed by the scaling theories, but is a rather smooth crossover. If we would draw straight lines in Figure 3 with slopes -1.4 or -1.6 , they would agree quite well with the actual curve in the crossover region, over a considerable range of n/n_c . Recent experiments by Callaghan and Pinder²⁸ were also able to verify the predictions concerning the existence of a semidilute θ regime in the high-concentration regime. At small concentration their results agree with de Gennes' theory. But no evidence for the existence of an intermediate marginal regime could be obtained.

A serious approximation in this work concerns the way hydrodynamic interaction is treated in the form of a concentration-dependent effective single-segment friction coefficient. This rests on the assumption that hydrodynamic interaction is completely screened on a length scale of the order of the average distance between two entan-

gements. This is certainly a rather crude assumption for a microscopic theory, since in reality the screening of hydrodynamic interaction will be a gradual process. Moreover, recent neutron-scattering experiments³¹ have revealed that under certain conditions there exists a residual long-ranging hydrodynamic interaction even in semidilute or concentrated solutions. A more explicit treatment of hydrodynamic interaction would be desirable, but then it would spoil the arguments which allow us to treat the coupling between curvilinear and lateral propagator as small. The basic assumption of this work is that the mechanism which causes the reptational motion is the excluded volume interaction and that hydrodynamic effects will only influence the finer details of this mechanism.

The opposite point of view was taken by Edwards,³² who derived a generalized diffusion equation for the distribution function of a test polymer, neglecting completely the direct interactions between polymers but taking into account the full hydrodynamic interaction. The generalized diffusion function is a function of the distribution of all other polymers in the system, and it was shown that this function becomes zero when two polymer segments are at the same place, which takes into account the fact that the lines of two polymers cannot cross each other. But so far a solution of this equation has not been given and no explicit result about the onset of reptation or of the form of the self-diffusion coefficient or of other transport parameters was obtained. One should also recall that the entanglement and reptation effects in polymeric melts are certainly not due to hydrodynamic interactions but result from short-ranged direct interactions between the polymer segments.

Many experimental studies of self-diffusion in semidilute or concentrated polymeric liquids are performed on mixtures or on polymers diffusing in a network. The extension of the theory given here to such situations is a trivial matter. The results will be presented in a separate publication.

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Semidilute Solutions of Star Branched Polystyrene: A Light and Neutron Scattering Study

Klaus Huber, Siegfried Bantle,[†] Walther Burchard,* and Lewis J. Fetters[‡]

*Institute of Macromolecular Chemistry, University of Freiburg, D-7800 Freiburg, FRG.
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ABSTRACT: Small-angle neutron scattering (SANS) and static and dynamic light scattering have been carried out with a 12-arm polystyrene star in toluene at 20 °C in a concentration range up to 16%, which corresponds to a value of $c/c^* \approx 8$, with $c^* = 1/[\eta]$ being the coil overlap concentration. Behavior similar to flexible linear chains is observed, with some characteristic differences: (i) a more sudden transition from the dilute behavior to a transient network is found, with $M_{app} \rightarrow \infty$ and a slow motion of diffusion with $D_{slow} \rightarrow 0$; (ii) around the gel formation concentration the complementary SANS measurements in the high- q region display a liquidlike structure factor. The results in the semidilute regime were found to depend on the time of centrifugation, which was applied for optical clarification. This observation is in agreement with older findings by Dautzenberg and Koberstein et al. with linear polystyrene in good solvents and indicates a metastable state of the semidilute solution.

Introduction

Solutions of macromolecules at higher concentrations have been the subject of research for a long time. The solution properties were found to be significantly different from those in the dilute regime, but a satisfactory theory for this regime was lacking. In 1975 des Cloizeaux¹ and later de Gennes² introduced a new concept by which a semidilute solution is supposed to be separated rather sharply from the regime of dilute solution. This conception has been cast more precisely in the form of a "phase diagram" by Adam and Delsanti.⁴ The point of crossover in this diagram is determined by the coil overlap concentration c^* , which is affected by the geometric size of the individual molecules. There are different alternatives for defining this geometric size. According to de Gennes, one can assume with certainty

$$c^* \sim M/\bar{R}^3 \quad (1)$$

Furthermore, by the Fox-Flory relationship³ the intrinsic viscosity is related to \bar{R}^3/M as

$$[\eta] \approx \phi \bar{R}^3/M \quad (2)$$

Thus it may be useful to set

$$c^* = 1/[\eta] \quad (3)$$

a suggestion first made by Utracki and Simha.²¹ In these equations \bar{R} is the root of the mean square end-to-end distance of a coil in a good solvent and the symbol \sim means here and in the rest of the text "proportional to".

For concentrations sufficiently larger than c^* , a transient network of entangled chains is assumed, and, consequently, all measurable quantities must become independent of the chain length of the individual molecules. This demand

leads to a number of simple relationships that in the recent past have been the subject of extensive examination.

In the past, linear chains, in particular polystyrene (PS),^{4-9,32} have been the most extensively studied subjects of static and dynamic light scattering (LS) measurements. The scope of research has been extended recently to other flexible and semiflexible linear chains⁸⁻¹⁷ in good solvents. In some previous papers,¹⁵⁻¹⁷ the necessity of static LS in combination with dynamic LS experiments has been demonstrated. Here we report results obtained with a 12-arm-star branched PS in a concentration range up to $c = 16\%$, which corresponds to $c \approx 8c^*$. The purpose of this study is to investigate the influence of branching on semidilute solutions.

In the following, we first review briefly the main statements of the scaling theory for semidilute solutions. Scaling laws are strictly valid only in the limit of $c \gg c^*$ and do not make any predictions about the crossover region. Experiments, on the other hand, often have to be carried out near this region, and it appears, therefore, of interest to study this particular regime in order to get a deeper insight into real semidilute solutions.

Predicted Properties in Semidilute Solutions

Osmotic Pressure. The demand of the molecular weight independence of the properties at $c \gg c^*$ led des Cloizeaux to a relationship for the osmotic pressure that reads

$$\Pi/RT = (c/M)f(c\bar{R}^3/M) = (c/M)f(c/c^*) = (c/M)(c/c^*)^m \quad (4)$$

This relationship is based on the impenetrable sphere approximation for the second virial coefficient

$$A_2 \sim \bar{R}^3/M^2 \quad (5)$$

For linear chains in very good solvents des Cloizeaux¹ finds $m = 5/4$, which follows from the condition $\Pi \sim M^0$ and from

[†] Institute Laue-Langevin, Grenoble, France. Present address: Sandoz AG, Basel, Switzerland.

[‡] Present address: Corporate Research—Science Laboratories, Exxon Research and Engineering Co., Annandale, NJ 08801.