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Dynamics of Semidilute Polymer Solutions: Hydrodynamic Screening

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ABSTRACT: A study is made of the hydrodynamic screening effect on polymer solution dynamics in the semidilute regime. Starting from the time-dependent Ginzburg–Landau equations, the explicit crossover behavior of transport properties is calculated. Difficulties of existing theories are critically reviewed.

1. Introduction

A general theoretical framework for dynamics of non-dilute polymer solutions (without entanglement) has been offered by Freed and Edwards.¹ The important aspect of the Freed–Edwards theory is that the presence of many polymer chains leads to a screening of the hydrodynamic interaction between the monomers of a polymer chain. However, almost no quantitative results have been produced with regard to the overall concentration dependence of the screening effect. This is especially true when the effect of the complicated interplay of the self-avoiding and hydrodynamic interactions is considered. Subsequently, Edwards and Muthukumar^{2,3} devised a semiphenomenological framework to study good solutions. Later, Freed⁴ proposed a supposedly more tractable version of the Edwards–Freed theory, but still almost no nontrivial quantitative results have been given. Furthermore, the above-mentioned models are not fully acceptable to statistical physicists, as the model describe the chains and the solvent at different levels of description; the chains at the kinetic level and the solvent at the hydrodynamic level.

We have proposed a new stochastic model,⁵ which seems to offer a promising starting point for studying the crossover behavior of various dynamical quantities. Preliminary renormalization-group (RG) studies have been carried out on this model,⁶ although these calculations cannot incorporate the hydrodynamic screening effect due to the approximations employed. In addition, the model yields the coupled integral equations for the effective polymer viscosity and monomer mobility;⁵ however, the derivation is not a strict RG treatment. The formulas for viscosity and mobility happen to agree with those given by the Edwards–Freed theory. This, however, is not surprising because these formulas are sufficiently robust.

The same coupled equations have been explored by Edwards, Muthukumar, and others.^{1–3} However, their treatment has met considerable difficulties, perhaps because their treatment of equilibrium quantities in these equations is not reliable. For example, the approach used by Muthukumar and Edwards² does not give any natural overlapping parameter (see section 3) to be the most important parameter in the semidilute solution regime, so that their result is at variance with the general conclusions of the model they adopt and with experimental results.⁷ This criticism is equally applicable to a theory of relaxation times,³ which incorrectly identifies crucial parameters but fortuitously agrees with experiment. We fully analyze these coupled equations in this paper; the asymptotic results have already been published by one of the present authors.⁵

In section 2 we first describe our kinetic model equations and recapitulate the set of coupled equations. We present a derivation of those equations in the Appendix in the spirit of mode-coupling theory.⁸ From these equations formulas for the solution viscosity and the hydrodynamic screening length are derived. In section 3 asymptotic results are derived. In section IV we proceed to solve the coupled equations explicitly. We obtain the crossover behavior (i.e., the overlap-parameter dependence) of the hydrodynamic screening length and the polymer viscosity with the aid of the known renormalization-group theoretical results⁹ for semidilute solutions. The last section, 4, is a discussion and summary.

2. Model and General Results

In order to understand the nature of hydrodynamic screening effects, one needs a dynamical description of semidilute polymer solutions. We use a stochastic model⁵

which is a many-chain version of the one used for dilute polymer solutions to calculate both time-dependent and transport properties.^{10,11} In the dilute limit the model gives the conventional Oseen tensor description of the hydrodynamic interaction to the lowest nontrivial order in the ϵ -expansion.¹²

The model we consider is the following time-dependent Ginzburg-Landau equations¹³ in appropriate units:

$$\frac{\partial}{\partial t} \mathbf{c}_j(\tau, t) = -\zeta_0^{-1} \frac{\delta H[\mathbf{c}]}{\delta \mathbf{c}_j(\tau, t)} + \lambda_0 \int d\mathbf{r} \mathbf{v}(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{c}_j(\tau, t)) + \theta_j(\tau, t) \quad (2.1)$$

$$\frac{\partial}{\partial t} \mathbf{v}(\mathbf{r}, t) = \mathcal{T} \cdot \left[\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) - \lambda_0 \sum_{j=1}^n \int_0^n d\tau \frac{\delta H[\mathbf{c}]}{\delta \mathbf{c}_j(\tau, t)} \delta(\mathbf{r} - \mathbf{c}_j(\tau, t)) + \mathbf{f}(\mathbf{r}, t) \right] \quad (2.2)$$

One of the basic dynamical variables in the model is the position vector, $\mathbf{c}_j(\tau, t)$, of the monomer at the contour variable τ ($0 \leq \tau \leq N$) of the j th chain ($j = 1, \dots, n$). Although the polydispersity can be easily taken care of, we consider the monodisperse case for simplicity. The conserved field coupled to \mathbf{c}_j is the transverse part of the solvent velocity field, $\mathbf{v}(\mathbf{r}, t)$, at space-time point (\mathbf{r}, t) ; the velocity field is taken to satisfy the incompressibility condition $\nabla \cdot \mathbf{v} = 0$. Accordingly, the tensor operator \mathcal{T} selects the transverse part of the vector it is applied to and has a Fourier transfer given by $\mathcal{T}_{\alpha\beta} = \delta_{\alpha\beta} - k_\alpha k_\beta / k^2$. In eq 2.1 and 2.2, ζ_0 denotes the bare friction coefficient per segment of the chain, and λ_0 stands for the strength of the hydrodynamic coupling, η_0 being the bare solvent viscosity. The Gaussian stochastic noises, θ_j and \mathbf{f} , are governed by autocorrelation functions

$$\langle \theta_j(\tau, t) \theta_l(\tau', t') \rangle = \mathbf{I} \delta_{jl} 2\zeta_0^{-1} \delta(\tau - \tau') \delta(t - t') \quad (2.3a)$$

$$\langle \mathbf{f}(\mathbf{r}, t) \mathbf{f}(\mathbf{r}', t') \rangle = -\mathbf{I} \nabla^2 2\eta_0 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (2.3b)$$

\mathbf{I} being the unit tensor. The dynamical model defined by (2.1)–(2.3) ensures that the system relaxes to an equilibrium state with a probability distribution proportional to $\exp[-H[\mathbf{c}] - (1/2) \int d\mathbf{r} v^2]$. The free energy functional, $H[\mathbf{c}]$, associated with polymer chains of configuration $\{\mathbf{c}\}$ is chosen to be the following many-chain version of the Edwards Hamiltonian:¹⁴

$$H[\mathbf{c}] = \frac{1}{2} \sum_j \int d\tau \left(\frac{d\mathbf{c}_j(\tau)}{d\tau} \right)^2 + \frac{u_0}{2} \sum_{j,l} \int d\tau d\tau' \delta[\mathbf{c}_j(\tau) - \mathbf{c}_l(\tau')] \quad (2.4)$$

Here u_0 represents the strength of the repulsive excluded-volume interaction. It will be assumed that in the double integral we always have a microscopic cutoff to eliminate both the self-interaction of monomers and the multiple interactions of pairs of monomers. Notice that the Hamiltonian (2.4) is legitimate only if the monomer number density is infinitesimally small; i.e., we can use this Hamiltonian only for semidilute solutions.¹⁰

This model is an internally consistent kinetic-level description; not only the chains but also the solvent velocity field must obey Langevin-type equations. One might hold the opinion that the pure hydrodynamic description may be in the same universality class as our Langevin equations. However, we know^{12,15} that this is true only at most to order $\epsilon = 4 - d$, d being the spatial dimensionality. Hence

even in the sense of minimal models,^{10,16} the hydrodynamic fluctuations must be taken care of. This implies that the deterministic relation between the solvent velocity field and the monomer velocity in any form (i.e., not only the condition used by Edwards and Freed,¹ $\partial_t \mathbf{c}(\tau, t) = \mathbf{v}[\mathbf{c}(\tau, t), t]$, but also others, say the slippery boundary condition) is incompatible with the kinetic-level description of polymer solution dynamics.

It has been shown elsewhere⁵ that when the multiple scattering method¹ is incorporated to solve the above model, one arrives at the following coupled equations for the wave-vector dependent (renormalized) monomer mobility, $\zeta^{-1}(q)$, and viscosity, $\eta(\mathbf{k})$:

$$\zeta^{-1}(q) = \zeta_0^{-1} + \frac{d-1}{d} \lambda_0^2 \int_{\mathbf{k}} \frac{S_1(\mathbf{k}, q)}{\eta(\mathbf{k})} \quad (2.5)$$

$$\eta(\mathbf{k}) = \eta_0 k^2 + \rho \lambda_0^2 \int_q \frac{S_1(\mathbf{k}, q)}{\zeta^{-1}(q)} \quad kR_G \geq 1 \quad (2.6a)$$

$$\eta(\mathbf{k}) = (\eta_0 + \delta\eta) k^2 \quad kR_G \ll 1 \quad (2.6b)$$

with

$$\delta\eta = -\frac{\rho}{2d} \lambda_0^2 \int_q \frac{\Phi(q)}{\zeta^{-1}(q)} \quad (2.7)$$

where \mathbf{k} and q are conjugate momenta to \mathbf{r} (or \mathbf{c}_j) and τ , respectively, and $\int_{\mathbf{k}} \equiv (2\pi)^{-d} \int d\mathbf{k}$, $\int_q \equiv (2\pi)^{-1} \int dq$. Here $\rho \equiv nN/V$ is the monomer density and R_G the gyration radius of a chain; $\Phi(q)$ and $S_1(\mathbf{k}, q)$ are Fourier transforms of the static correlation functions $\langle |\mathbf{c}_j(\tau) - \mathbf{c}_j(\tau')|^2 \rangle$ and $V \langle \delta[\mathbf{r} - \mathbf{c}_j(\tau)] \delta[\mathbf{r}' - \mathbf{c}_j(\tau')] \rangle$, respectively, V being the volume of the system. It is also possible to derive the above coupled set of equations, (2.5) and (2.6), in the spirit of the mode-coupling theory.⁸ This alternative derivation, which is more transparent than the multiple-scattering method, is presented in the Appendix.

Since the kinetic coefficient $\zeta(q)$ is expected¹⁷ to vary more slowly with q than the correlation function S_1 , eq 2.6a may be replaced by

$$\eta(k) = \eta_0 k^2 + \rho \lambda_0^2 \zeta \quad \zeta \equiv \zeta(0) \quad (2.8)$$

The hydrodynamic screening length, κ^{-1} , is then defined by

$$\kappa^2 = \rho \lambda_0^2 \zeta / \eta_0 \quad (2.9)$$

Noting that the region $kR_G \gg 1$ dominates the integral in (2.5), we find that κ is the solution to the equation

$$\kappa^{-2} = \frac{d-1}{cd} \int_{\mathbf{k}} \frac{S_1(\mathbf{k})}{k^2 + \kappa^2} \quad (2.10)$$

where $c \equiv \rho/N$ is the polymer density. Here we have neglected the bare part in (2.5); this is permissible in the semidilute regime where the mode-coupling contribution dominates the background part. The function $S_1(\mathbf{k}) \equiv S_1(\mathbf{k}, 0)$ is just the scattering function of a test chain;

$$N^2 S_1(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \langle m_1(\mathbf{r}) m_1(0) \rangle \quad (2.11)$$

where $m_1(\mathbf{r}) = \int d\tau \delta[\mathbf{r} - \mathbf{c}_j(\tau)]$. Similarly, eq 2.7 may be reduced to

$$\delta\eta = -\frac{\rho \lambda_0^2}{2\pi d} \zeta \int_{q_0}^{\infty} dq \Phi(q) \quad (2.12)$$

Here we have introduced the infrared cutoff, $q_0 \equiv \pi/N$, since the $q = 0$ mode is not coupled to the elastic force as seen in eq 2.7. Combining eq 2.9 and 2.12, we get

$$\delta\eta / \eta_0 = \kappa^2 R_G^2 / 2d \quad (2.13)$$

which simply relates the polymer viscosity to the hydrodynamic screening length through the gyration radius, R_G ,

$$R_G^2 = \frac{1}{2N^2} \int \int d\tau d\sigma \langle |\mathbf{c}_j(\tau) - \mathbf{c}_j(\sigma)|^2 \rangle \quad (2.14)$$

We should note that the approximation (2.12) is not reliable in the dilute limit. By properly keeping the q -dependence of ζ , we can recover the correct Rouse-Zimm dilute solution behavior. Another point to be mentioned is that the condition under which the expansion in (2.6b) is allowed is $kR_G \ll 1$, as may be inferred from (2.7) (see Appendix). Thus we get the solution viscosity for the range far outside the domain occupied by a single chain. On the other hand, if $kR_G \gg 1$, i.e., well inside of the single-chain territory, there is a hydrodynamic screening. In other words, we see $\kappa^2 \rightarrow 0$ if $kR_G \ll 1$, not if $k\xi \ll 1$, where ξ is the static correlation length, contrary to the claim by Edwards and Muthukumar.² The difference can be significant since R_G/ξ can be indefinitely large if we use long polymer chains. If the length scale R_G were not important, then at least in the large overlap limit, the description of polymer solution by the monomer density field should be reliable. However, as has been stressed in previous papers,^{10,6a} this is not the case. Thus ξ should not be the relevant length scale to determine whether the hydrodynamic screening is important or not. If we neglect the entanglements, the tracer diffusion constant is given by $N^{-1}\zeta^{-1}$. Thus the viscosity couples to the tracer diffusion constant as can be seen from (2.12). It is natural that R_G is the relevant length scale for tracer diffusion.

3. Asymptotic Results

The simplified formulas in the preceding section for viscosity and other quantities, (2.9), (2.10), and (2.13), give us the asymptotic concentration dependence.⁵

Since¹⁸ (ν is the excluded-volume exponent)

$$S_1(\mathbf{k}) \sim N^2(kN^\nu)^{-1/\nu} \quad (3.1)$$

(2.10) gives

$$\kappa \sim \rho^{\nu/(d\nu-1)} \quad (3.2)$$

where we have used the fact that the main contribution to the integral in (2.10) comes from k larger than $O(\kappa)$. With (3.2) and the static result¹⁸

$$R_G^2 \sim N\rho^{(1-2\nu)/(d\nu-1)} \quad (3.3)$$

(2.13) tells us that

$$\eta \sim \nu_0 N\rho^{1/(d\nu-1)} \quad (3.4)$$

From this and (2.9) we have for $D_t \equiv (N\zeta)^{-1}$

$$D_t^{-1} \sim N\rho^{[(d-2)\nu-1]/(d\nu-1)} \quad (3.5)$$

These results agree with those by the standard scaling argument.^{18,19} However, we must remember that in semidilute solution ρ is infinitesimally small, so that ρ is not a natural variable. As now we well know, for static quantities the good parameter is X (overlap parameter) which is proportional to $cN^{d\nu}$, c being the polymer number density. Since dimensionally the excluded-volume parameter and the translational friction coefficient behave identically, we conclude that there must be a dynamical counterpart of X also proportional to $cN^{d\nu}$, which is denoted by Y , the dynamical overlap parameter. In the nondraining self-avoiding limit X and Y are proportional (see (4.1) and (4.2) below). Hence everything should be written in terms of N and X in this asymptotic limit. Indeed, we have $R_G^2 \sim N^{2\nu}X^{(1-2\nu)/(d\nu-1)}$ and

$$\kappa \sim N^{-\nu}X^{\nu/(d\nu-1)} \quad (3.6)$$

$$\eta \sim X^{1/(d\nu-1)} \quad (3.7)$$

$$D_t \sim N^{(2-d)\nu}X^{1-2\nu/(d\nu-1)} \quad (3.8)$$

Equation 3.8 can be rewritten as

$$D_t \sim 1/\eta\xi \quad (3.9)$$

The relation (3.9) tells us that D_t can be obtained by the Stokes-Einstein relation: a blob of size ξ is moving through the solution of renormalized viscosity η . Hence for D_t the hydrodynamic screening is very important, in accordance with the point mentioned after eq 2.14.

4. Numerical Results

At the crudest level we can get transport coefficients once we can calculate the screening length κ^{-1} , i.e., if we can solve (2.10) we can calculate all the other quantities. Nakanishi and Ohta^{9a} have already given us $S_1(\mathbf{k})$ by a renormalization-group calculation.

We introduce the following scaled variables:

$$\begin{aligned} \mathbf{Q} &= \mathbf{k}(N/2) & \hat{\kappa} &= \kappa(N/2)^\nu \\ X &= 4cu^*(N/2)^{d\nu} & Y &= 4c\zeta^*(N/2)^{d\nu} \end{aligned} \quad (4.1)$$

Here u^* and ζ^* are fixed-point values associated with the coupling constants u_0 and $\lambda_0^2\zeta_0/\eta_0$, respectively; they are given by (see, e.g., ref 16)

$$u^* = \frac{\pi^2}{2}\epsilon + O(\epsilon^2) \quad \zeta^* = 2\pi^2\epsilon + O(\epsilon^2) \quad (4.2)$$

and $\nu = 1/2[1 + \epsilon/8 + O(\epsilon^2)]$.

Then (2.10) reads

$$\hat{\kappa}^{-2} = \frac{8}{3}Y^{-1} \int_0^\infty dQ \frac{Q^2}{Q^2 + \hat{\kappa}^2} I(Q;X) \quad (4.3)$$

where $I(Q;X) \equiv S_1(\mathbf{k})$, whose expression can be found in the paper by Nakanishi and Ohta.^{9a} We adopt the exponentiated form which gives the correct asymptotic behavior to $O(\epsilon)$ and then $\epsilon = 1$. If we are truly faithful to the original idea of mode-coupling theory, we should use the correct $I(Q;X)$ instead of the $O(\epsilon)$ counterpart. We can expect that by augmenting $I(Q;X)$ to give correct exponents we can get a very reliable $I(Q;X)$ (at least in the dilute solution limit this has been verified empirically). However, here we use the form given in the paper by Nakanishi and Ohta (for simplicity). In this connection, the following point should be emphasized. Namely, it is exactly this use of the rigorous expression for $S_1(\mathbf{k})$ [hence its correct scaling limit (3.1)] that distinguishes our treatment of the coupled integral equations from that of the Freed-Edwards theory; in this way the static interchain correlation is taken into account, whereas in the Freed-Edwards treatment interchain correlations are totally neglected.

Equation 4.3 has been solved numerically for $\hat{\kappa}$, and the result is illustrated in Figure 1. It should be remarked that even in the absence of the excluded-volume interactions, there still exists the hydrodynamic screening. The upper curve in the figure corresponds to such a Gaussian-chain solution, where the abscissa should be interpreted as $Y/4$. In this case eq 4.3 reduces to

$$Y = \frac{16}{3} \left[-\pi^{1/2} + \frac{\pi}{2}(\hat{\kappa} + \hat{\kappa}^{-1}) - \frac{\pi}{2\hat{\kappa}} e^{\hat{\kappa}^2} \operatorname{erfc}(\hat{\kappa}) \right] \quad (4.4)$$

with $\operatorname{erfc}(x) \equiv (2/\pi^{1/2}) \int_x^\infty dt e^{-t^2}$, since

$$I(Q;0) = 2(Q^{-2} - Q^{-4} + e^{-Q^2}Q^{-4}) \quad (4.5)$$

Figure 1 clearly shows the gradually increasing magnitude of the screening length as X is increased. However, this

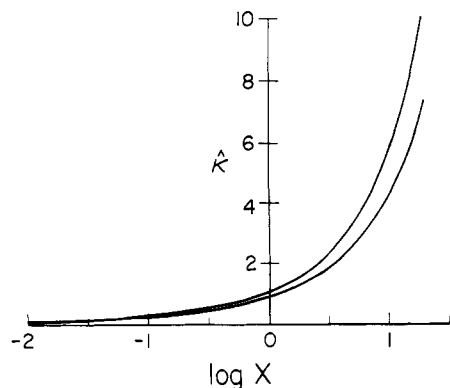


Figure 1. Inverse of the reduced hydrodynamic screening length, $\hat{\kappa}$, as function of the overlap parameter X . The upper curve represents the polymer solution when no excluded-volume interaction is present. To obtain these curves, eq 4.3 has been solved setting $\epsilon = 4 - d = 1$.

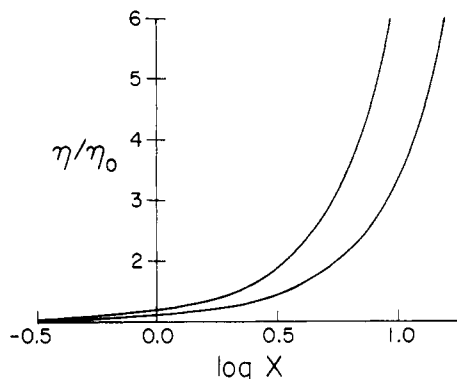


Figure 2. Reduced viscosity η/η_0 versus X . The curves are labeled as in Figure 1.

behavior should not be confused with the so-called incomplete hydrodynamic screening proposed by Binder et al.²⁰ The latter refers to the residual hydrodynamic interaction at infinite distance.

With the screening length thus obtained, the polymer viscosity can readily be found from the relation (2.13). Here, too, we adopt the renormalization-group theoretical expression for R_G .^{9b} The result is shown in Figure 2, where the upper curve represents the Gaussian chain case ($\eta/\eta_0 = 1 + \hat{\kappa}^2/6$).

5. Discussion

We have given the full overlap-parameter dependence of the viscosity and the hydrodynamic screening and also their asymptotic behavior. Admittedly, our present formulation contains several uncontrollable approximations. However, since our results agree asymptotically with the predictions by scaling arguments without entanglement, we should regard that at least a certain amount of truth about the model has been captured by the present approach.

In the approaches by Edwards, Freed, Muthukumar, and others, the solvent is described hydrodynamically. Therefore, in their models, motions with widely separated spatial and temporal scales are coupled. Our starting model does not contain such an internal self-contradiction. Ideally, we would like to write everything in terms of the monomer density field and the solvent (or solution) velocity field as has been done by Kapral et al.²¹ long ago. However, this approach is highly unlikely to be successful. The reason is quite simple: the crucial feature of polymer solutions is that polymers are stringlike, connected objects, but there is absolutely no way to describe this connectedness by an over-coarse-grained variable such as the

monomer density (see also the last paragraph of section 2).

All the existing theories, including ours, start from dynamical equations for polymers (suspended particles) and solvent (surrounding fluid). They then try to decouple these equations, and from the resulting dressed equations for the solvent and the polymer chains one extracts transport coefficients. If the solute density is infinitesimally small, as in the case of semidilute polymer solutions, this procedure may be legitimate. In the present paper, we at least tentatively stick to this opinion. However, if the solute density becomes larger, the above procedure fails to be correct. Consider for argument's sake the extreme situation where the solute density is very large. For example, absorb a tiny amount of a solvent to a polymer melt. Can we correctly obtain the experimentally measurable viscosity of the melt from the motion of solvent molecules perturbed by polymers? It is quite unlikely. If we write down the Kubo formula for the solution viscosity, it is easy to realize that there are many terms not taken into account by the above naive procedure. Thus we must conclude that our present formula is at best applicable only up to the semidilute solutions. This is the reason why we have never mentioned the concentration dependence but the overlap-parameter dependence.

Unfortunately, there are only a few experimental results that are obtained in the semidilute regime. This is because the constraint that the monomer number density be infinitesimally small must be seriously respected. In our judgement, the Cannell group, the Noda-Nagasawa group, and the Léger group have published relevant experimental data so far. Cannell et al.²² measured the cooperative diffusion constant, D_{coop} , which was compared successfully with a renormalization-group calculation.^{6a} Even in the present scheme D_{coop} can be obtained and the result²³ also agrees with their data. Léger's group²⁴ has given extensive experimental data for the self-diffusion constant. If we naively identify our $(N\zeta)^{-1}$ with the self-diffusion constant, D_t , its molecular-weight (M) dependence $D_t \sim M^{-1}$ is definitely at variance with the experimental result $D_t \sim M^{-2}$. In fact, if one properly takes into account the renormalization effect due to the entanglements, the resultant dressed quantity can reproduce the behavior observed by the Léger group. This demonstration based upon our coupled equations (2.5)–(2.7) is given elsewhere.²³

The Noda-Nagasawa group²⁵ has measured the solution viscosity over wide ranges of c/c^* , where c^* is the overlap threshold concentration (so that c/c^* is proportional to our X or Y). As is shown in Figure 3, our result agrees with their data for X up to $X \sim 5$. However, there is no way to fit the data to our theoretical curve for $X \gtrsim 10$. They claim that for very large molecular weight samples the region $c/c^* \gtrsim 10$ is beyond the semidilute regime, and that η behaves there according to the 3.4-power law, as in the melt. Notice that this observation is quite different from the behavior of the static properties (e.g., the osmotic pressure) and of the cooperative diffusion constant. For these we have one regime (i.e., the semidilute regime) for all X . Presumably, the most important effect that has been left out in our theory is that of the entanglement. It is likely that once the overlap parameter is positive, chains start to entangle even if the monomer density is zero. The parameter X may be roughly interpreted as the number of chains overlapping with a specific chain. The probability of making entanglements between two overlapping chains which govern the global motion of chains should be independent of the molecular weight (at least asymptotically). This is because chains are more or less self-

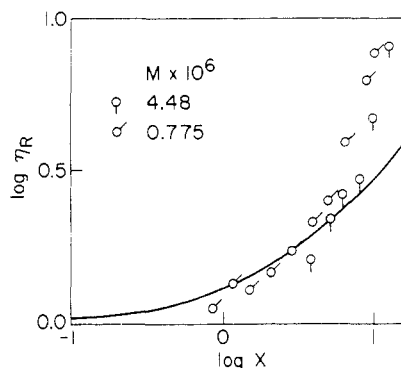


Figure 3. Reduced polymer viscosity η_R versus X ; $\eta_R = (\eta - \eta_0)/\eta_0 c[\eta]$ where c is the polymer concentration and $[\eta]$ is the intrinsic viscosity. Open circles are experimental results for polystyrene in toluene due to Nagasawa et al.,^{25b} M denoting the molecular weight. We have adjusted the unknown proportional constant between X and c/c^* , where c^* is the critical concentration of chain overlapping.

similar objects, so the relevant entanglements at the time scale of the chain relaxation must be the entanglements between appropriately coarse-grained chains (like primitive chains). Then the effect of the entanglement in the semidilute regime can also be described universally in terms of X . The experimental observations of the Noda-Nagasawa group seem to corroborate this assertion. Contrary to the claim of Noda et al., we therefore believe that what they regard as the entangled regime is still the semidilute regime. Including the entanglement effect into the theory should hence improve the present result.

The incompatibility of (3.7) with the generally accepted behavior of viscosity in the entangled regime might be ascribed to the insufficiency of the lengths of chains used in the experiment. If this is the case, as has been shown by the Noda-Nagasawa group, one will observe a behavior neither of the semidilute nor of the entangled asymptotic regime. Then there is a possibility that not the true entanglement but a mere increase of direct chain-chain friction, which has never been studied yet, can explain the discrepancy. This effect vanishes if the monomer density is strictly zero. Finally, in this connection, it should be mentioned that not every physical quantity is affected by the presence of entanglements. For static quantities, entanglements are obviously irrelevant. The entanglement effect is not crucial for the cooperative diffusion either, because it is a local relaxation of monomer density fluctuations which do not require any disentanglement or large-scale motion of each polymer chain.

In summary, we have given a kinetic-level description of semidilute polymer solutions starting from the time-dependent Ginzburg-Landau equations and calculated the overlap-parameter dependence of transport properties. Our calculation is the first one to give a full cross-over behavior of transport properties in the semidilute regime. Possible modifications and/or refinements of the theory toward the better agreement with experiments are indicated by critically reviewing the existing theories.

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Appendix. Mode-Coupling Theoretical Approach

In this appendix we derive the coupled equations (2.5) and (2.6) within a framework of mode-coupling theory

formalized by Kawasaki.⁸ His approach consists of two main steps. First, one expands all the quantities in terms of the mode-coupling parameter (λ_0 here) by iteratively solving the set of equations. Then, one calculates propagators to order λ_0^2 and imposes a self-consistency condition to partially sum higher order terms in λ_0 .

Let us first consider the equation of motion for chains. Equation (2.1) reads

$$\partial_t \mathbf{c}_j(\tau, t) = \zeta_0^{-1} \partial_\tau^2 \mathbf{c}_j(\tau, t) + \lambda_0 \int d\mathbf{r} \tilde{\mathbf{v}}(\mathbf{r}, t) \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] + \theta_j(\tau, t) \quad (\text{A.1})$$

with $\tilde{\mathbf{v}}(\mathbf{r}, t) = \mathbf{v}(\mathbf{r}, t) - (u_0/\lambda_0 \zeta_0) \nabla m(\mathbf{r}, t)$ where $m(\mathbf{r}, t) \equiv \sum_j \int d\tau \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)]$ is the monomer density. We imagine that $\tilde{\mathbf{v}}$ is a given field and transform (A.1) into an integral form,

$$\mathbf{c}_j(\tau, t) = \int dt' d\tau' \mathbf{G}_0(t - t'; \tau, \tau') \theta_j(\tau', t') + \lambda_0 \int dt' d\tau' \mathbf{G}_0(t - t'; \tau, \tau') \tilde{\mathbf{v}}[\mathbf{c}_j(\tau', t'), t'] \quad (\text{A.2})$$

where the polymer Green function, \mathbf{G}_0 , is defined by

$$(\partial_t - \zeta_0^{-1} \partial_\tau^2) \mathbf{G}_0(t - t'; \tau, \tau') = \delta(\tau - \tau') \delta(t - t'), \quad t \geq t'$$

with a suitable boundary condition. Symbolically, we can write (A.2) as ($\mathbf{c} \equiv \mathbf{c}_j$)

$$\mathbf{c}(\tau, t) = \mathbf{G}_0 \cdot \theta + \lambda_0 \mathbf{G}_0 \cdot \tilde{\mathbf{v}}(\mathbf{c}) = \mathbf{c}_0 + \lambda_0 \mathbf{c}_1 + \lambda_0^2 \mathbf{c}_2 + \dots$$

where $\mathbf{c}_0 = \mathbf{G}_0 \cdot \theta$, $\mathbf{c}_1 = \mathbf{G}_0 \cdot \tilde{\mathbf{v}}(\mathbf{c}_0)$, etc. This must be inserted into the equation for the transverse component of the velocity field, (2.2). It is then rewritten as

$$\partial_t \mathbf{v}(\mathbf{r}, t) = \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) + \lambda_0 \mathcal{T} \cdot \langle \mathbf{e}(\mathbf{r}, t) \rangle + \mathbf{f}'(\mathbf{r}, t) \quad (\text{A.3})$$

with a new fluctuating force, $\mathbf{f}' \equiv \mathbf{f} + \lambda_0 \mathcal{T} \cdot (\mathbf{e} - \langle \mathbf{e} \rangle)$, $\mathbf{e}(\mathbf{r}, t)$ being the elastic-force density defined by

$$\mathbf{e}(\mathbf{r}, t) = \sum_j \int d\tau \partial_\tau^2 \mathbf{c}_j(\tau, t) \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)]$$

In (A.3) the average $\langle \dots \rangle$ is taken over the random force θ_j . We then obtain, to leading order in λ_0 ,

$$\mathcal{T} \cdot \langle \mathbf{e}(\mathbf{r}, t) \rangle = \lambda_0 c \int d\mathbf{r}' dt' d\tau d\tau' [\partial_\tau^2 \mathbf{G}_0(t - t'; \tau, \tau')] S_1^0(\mathbf{r} - \mathbf{r}', \tau, \tau', t - t') \mathbf{v}(\mathbf{r}', t') \quad (\text{A.4})$$

where $S_1^0(\mathbf{r} - \mathbf{r}', \tau, \tau', t - t') \equiv V \langle \delta[\mathbf{r} - \mathbf{c}_0(\tau, t)] \delta[\mathbf{r}' - \mathbf{c}_0(\tau', t')] \rangle$ and $c \equiv n/V$ is the polymer chain density, V being the system volume. In (A.4) the self-avoiding interaction does not contribute due to the presence of the projection \mathcal{T} . After Fourier transforming we arrive at the following equations for \mathbf{v} :

$$\partial_t \mathbf{v}(\mathbf{k}, t) = - \int_{\mathbf{k}'} \int_{\omega} e^{-i\mathbf{k} \cdot \mathbf{r} - i\omega t} \eta(\mathbf{k}, \omega) \mathbf{v}(\mathbf{k}', \omega) + \mathbf{f}'(\mathbf{k}, t)$$

with

$$\eta(\mathbf{k}, \omega) = \eta_0 k^2 + \lambda_0^2 \rho \int_q \int_{\omega'} q^2 \mathbf{G}_0(-q, \omega - \omega') S_1^0(\mathbf{k}, q, \omega') \quad (\text{A.5})$$

Here $\rho \equiv cN$ is the monomer density, and $\int_{\mathbf{k}} \equiv (2\pi)^{-d} \int d^d \mathbf{k}$ etc., d being the spatial dimensionality. We neglect the chain end effect throughout and have thus introduced the momentum, q , conjugate to the contour variable τ . We see that the result (A.5) replaces the bare hydrodynamic transport coefficient $\eta_0 k^2$ by a k - and ω -dependent object.

Let us now return to (2.2). This can be rewritten in terms of the fluid Green's function defined by

$$(\partial_t - \eta_0 \nabla^2) \mathbf{F}_0(\mathbf{r} - \mathbf{r}', t - t') = \mathcal{T} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad t \geq t'$$

as

$$\mathbf{v}(\mathbf{r}, t) = -\lambda_0 \sum_j \int d\mathbf{r}' d\tau' dt' \mathbf{F}_0(\mathbf{r} - \mathbf{r}', t - t') \cdot \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_j(\tau', t')} \delta[\mathbf{r}' - \mathbf{c}_j(\tau', t')] + \tilde{\mathbf{f}}'$$

with $\tilde{\mathbf{f}}' \equiv \mathbf{F}_0 \cdot \mathbf{f}$. When inserted back into (2.1), this leads to

$$\partial_t \mathbf{c}_j(\tau, t) = -\zeta_0^{-1} \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_j(\tau, t)} + \lambda_0^2 \sum_l \int d\mathbf{r} d\mathbf{r}' d\tau' dt' \mathbf{F}_0(\mathbf{r} - \mathbf{r}', t - t') \cdot \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_l(\tau', t')} \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] \delta[\mathbf{r}' - \mathbf{c}_l(\tau', t')] + \theta'_j(\tau, t) \quad (\text{A.6})$$

where $\theta'_j = \theta_j + \lambda_0 \int d\mathbf{r} \tilde{\mathbf{f}}'(\mathbf{r}, t) \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)]$. At this point, we neglect the interchain correlations. Then we may put, in (A.6),

$$\sum_l [\delta H / \delta \mathbf{c}_l(\tau', t')] \delta[\mathbf{r}' - \mathbf{c}_l(\tau', t')] \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] = [\delta H / \delta \mathbf{c}_j(\tau', t')] \delta[\mathbf{r}' - \mathbf{c}_j(\tau', t')] \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] = \langle \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] \delta[\mathbf{r}' - \mathbf{c}_j(\tau', t')] \rangle \delta H / \delta \mathbf{c}_j(\tau', t')$$

where in the last step we have also introduced a preaveraging approximation in accord with (A.2). In the connection note that $\langle \delta H / \delta \mathbf{c}_j(\tau, t) \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] \rangle = 0$. Thus (A.6) is cast into the form

$$\partial_t \mathbf{c}_j(\tau, t) = -\zeta_0^{-1} \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_j(\tau, t)} - \lambda_0^2 V^{-1} \int d\mathbf{r} d\mathbf{r}' d\tau' dt' \mathbf{F}_0(\mathbf{r} - \mathbf{r}', t - t') \cdot S_1(\mathbf{r} - \mathbf{r}', \tau, \tau', t - t') \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_j(\tau', t')} + \theta'_j(\tau, t)$$

where

$$S_1(\mathbf{r} - \mathbf{r}', \tau, \tau', t - t') \equiv V \langle \delta[\mathbf{r} - \mathbf{c}_j(\tau, t)] \delta[\mathbf{r}' - \mathbf{c}_j(\tau', t')] \rangle$$

In Fourier transforms,

$$\partial_t \mathbf{c}_j(\tau, t) = -\int_q \int_{\omega} e^{-iq\tau - i\omega t} \zeta^{-1}(q, \omega) \cdot \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}(q, \omega)} + \theta'_j(\tau, t)$$

$$\zeta^{-1}(q, \omega) = \mathbf{I} \zeta_0^{-1} + \lambda_0^2 \int_{\mathbf{k}} \int_{\omega'} \mathbf{F}_0(-\mathbf{k}, \omega - \omega') S_1(\mathbf{k}, q, \omega') \quad (\text{A.7})$$

It is now evident that the nonlinear couplings in the kinetic equations (2.1) and (2.2) give rise to an additional contribution to the transport coefficients. The dressed transport coefficients, $\eta(\mathbf{k}, \omega)$ and $\zeta(q, \omega)$ are those relevant to macroscopic measurements.

The lowest order calculations, (A.5) and (A.7), can be improved by making the calculation self-consistent. That is, proceeding in the spirit of the mode-coupling formalism, we replace the free propagators by the dressed ones; namely,

$$\mathbf{G}_0^{-1}(q, \omega) \mathbf{I} = (-i\omega + \zeta_0^{-1} q^2) \mathbf{I} \rightarrow -i\omega \mathbf{I} + \zeta^{-1}(q, \omega) q^2$$

$$\mathbf{T}_0^{-1}(\mathbf{k}, \omega) = (-i\omega + \eta_0 k^2) \mathbf{I} \rightarrow -i\omega \mathbf{I} + \eta(\mathbf{k}, \omega)$$

and accordingly $S_1^0 \rightarrow S_1$, where \mathbf{T}_0 is defined via $\mathbf{F}_0(\mathbf{k}, \omega) \equiv \mathbf{T}_k \cdot \mathbf{T}_0(\mathbf{k}, \omega)$. This finally results in the coupled set of equations for ζ and η

$$\zeta^{-1}(q, \omega) = \zeta_0^{-1} + \frac{d-1}{d} \lambda_0^2 \int_{\mathbf{k}} \int_{\omega'} \frac{S_1(\mathbf{k}, q, \omega')}{-i(\omega - \omega') + \eta(-\mathbf{k}, \omega - \omega')} \quad (\text{A.8})$$

$$\eta(\mathbf{k}, \omega) = \eta_0 k^2 + \rho \lambda_0^2 \int_q \int_{\omega'} \frac{q^2 S_1(\mathbf{k}, q, \omega')}{-i(\omega - \omega') + q^2 \zeta^{-1}(-q, \omega - \omega')} \quad (\text{A.9})$$

Here spatial isotropy has been assumed, hence ζ and η are now scalars.

To derive the above, we have used, besides standard approximations in the mode-coupling framework, an approximation that the interchain correlations are negligible. Unfortunately, this approximation may not be reliable in the semidilute regime. In this connection see the discussion on the entanglement effect in section 5.

The Kirkwood-Riseman-type approximation²⁶ amounts to replacing (A.8) and (A.9) by

$$\zeta^{-1}(q) = \zeta_0^{-1} + \frac{d-1}{d} \lambda_0^2 \int_{\mathbf{k}} \frac{S_1(\mathbf{k}, q)}{\eta(\mathbf{k})} \quad (\text{A.10})$$

$$\eta(\mathbf{k}) = \eta_0 k^2 + \rho \lambda_0^2 \int_q \frac{S_1(\mathbf{k}, q)}{\zeta^{-1}(q)} \quad (\text{A.11})$$

where $\zeta^{-1}(q) \equiv \zeta^{-1}(q, \omega=0)$, $\eta(\mathbf{k}) \equiv \eta(\mathbf{k}, \omega=0)$, and $S_1(\mathbf{k}, q) \equiv S_1(\mathbf{k}, q, t=0)$. This approximation may be admissible in (A.10), but in (A.11) this is unjustified as there is no reason to believe that the memory effect can be neglected in the integral; thus in (A.11) this approximation should be regarded as merely a simplifying assumption.

One should pay attention to one subtle point in obtaining the polymer viscosity, $\delta\eta$. Namely, one must take the $k \rightarrow 0$ limit of (A.9) before the $\omega \rightarrow 0$ limit;²⁷ $\eta_0 + \delta\eta = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \eta(\mathbf{k}, \omega) / k^2$. Then one finds

$$\delta\eta = -\frac{\rho \lambda_0^2}{2d} \int_q \int_{\omega'} \frac{q^2 \Phi(\mathbf{q}, \omega')}{i\omega' + q^2 \zeta^{-1}(-\mathbf{q}, -\omega')} \quad (\text{A.12})$$

where $\Phi(\mathbf{q}, \omega)$ is the Fourier transform of $\Phi(\tau, \tau', t - t')$:

$$\Phi(\tau, \tau', t - t') \equiv \langle |\mathbf{c}_j(\tau, t) - \mathbf{c}_j(\tau', t)|^2 \rangle$$

In the same spirit as for (A.10) and/or (A.11), we find

$$\delta\eta = -\frac{\rho \lambda_0^2}{2d} \int_q \frac{\Phi(q)}{\zeta^{-1}(q)} \quad (\text{A.13})$$

with $\Phi(q) \equiv \Phi(q, t=0)$. One should keep in mind that (A.12) is obtained by taking the $k \rightarrow 0$ limit of (A.11). Hence the condition under which the expansion of $S_1(\mathbf{k}, q)$ around $k = 0$ is allowed is $k^2 \Phi(q) \sim k^2 R_G^2 \ll 1$, R_G being the gyration radius. However, this condition $k R_G \ll 1$ should be considered as obtained separately from the Markovian approximation that is used to get (A.11) or (2.6a). These remarks also explain why the Markovian approximation form (A.11) cannot be carried over to the region $k R_G < 1$.

The above results, (A.10), (A.11), and (A.13), are our starting equations (2.5) and (2.6) in the main text.

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- lhs and rhs of (A) are completely different. Hence, even in the linear c -dependence regime (A) is false. The main objective of this theory was to have a theory beyond this regime, but in the nonlinear c -dependence regime there is no way to equate Q and $cA\rho^{-\kappa}$. If we were to accept (A) there, we would have another bad contradiction, because (A) is not correct in any regime.
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The Ubiquity of Stretched-Exponential Forms in Polymer Dynamics[†]

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ABSTRACT: Literature results on the zero-shear viscosity η , rotational diffusion coefficient D_R , and sedimentation coefficient s of polymers in good, θ , and marginal solvents are reanalyzed in terms of the universal scaling equation $A = A_0 \exp(-ac^v)$, where A is a transport coefficient, c is the polymer concentration, and a and v are scaling constants. This equation gives reasonably good descriptions of almost all results on η , D_R , and s , a single pair of parameters (a, v) sufficing for results from all concentrations. There is apparently no qualitative change in transport behavior between the dilute ($c < c^*$) and semidilute ($c \gg c^*$) regimes.

Introduction

The entire modern (through early 1986) literature on polymer self-diffusion was recently reexamined,^{1,2} finding that the dependence of D_s on polymer concentration is described by a stretched exponential

$$D_s = D_0 \exp(-ac^v) \quad (1)$$

D_0 being the diffusion coefficient at infinite dilution. v and a are constants that differ from system to system but are independent of c , with no change between the meltlike, semidilute, and dilute concentration regimes. (Recent data of Lodge et al.³ reveals a change in D_0 at $c > 0$; the change correlates well with changes in R_g at the same concentrations⁴). The stretched-exponential form affords a description of polymer and protein self-diffusion which, while in good agreement with experiment, is at variance with some⁵⁻⁹ scaling-law descriptions for polymer solution dynamics.

A heuristic picture—the hydrodynamic scaling model—which predicts eq 1 was recently presented.² The model predicts how D_0 , v , and a depend on polymer mo-

lecular weight M , namely, $D_0 \approx M^{-1/2}$ and $a \approx M^1$, with $v = 1$ at small M and $v = 1/2$ at large M . Physically, a is determined by the strength of whole-chain-whole-chain hydrodynamic interactions, i.e., a increases with increases in chain size. v is determined by chain contraction. Unlike small chains, large chains shrink at high c , so v is not the same for big as for small polymers.

A major positive contribution of the reptation/scaling models of polymer dynamics is the idea that different transport properties are interrelated,⁵ so that fixing the c and M dependences of D_s constrains the c and M dependences of the zero-shear viscosity η , entanglement relaxation time T_R , rotational diffusion coefficient D_R , and sedimentation coefficient s . If η and D_s are determined by the same polymer motions, their c and M dependences should be related. It might appear incongruous that eq 1 describes D_s , while an incompatible scaling equation

$$A \approx c^x M^y \quad (2)$$

has been said⁵⁻⁹ to describe η , D_R , and s . This paper reexamines published studies on polymer transport, showing that the apparent incongruity is illusory. Experimental results on η , D_R , s , and D_s are consistent, a stretched exponential providing a good description for each of these parameters.

The next three sections review literature studies on viscosity, rotational diffusion, and sedimentation, com-

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