# Dynamics of Entangled Polymer Solutions. II. Inclusion of Hydrodynamic Interactions

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ABSTRACT: We construct a scaling description for the stochastic motions of long, flexible chains in good solvents. (1) We reexamine the Edwards–Freed theory for the screening of hydrodynamic interactions, and show that the dynamical screening length is identical with the static correlation length $\xi$ introduced in connection with neutron experiments. (2) At long wavelengths $2\pi/\mathbf{k} > \xi$ we find viscous modes reminiscent of a gel with a cooperative diffusion coefficient $D_c \simeq k_BT/6\pi\eta_0\xi$ (where $T$ is the temperature, $\eta_0$ the solvent viscosity). $D_c$ should scale like $c^{3/4}$ where $c$ is the concentration. (3) There is a characteristic frequency $\Delta \simeq D_c/\xi^2$ ($\sim c^{2.25}$) separating a many-chain regime from a single-chain regime. For frequencies $\omega > \Delta$, or for $\mathbf{k}\xi > 1$, we find single-chain behavior with a characteristic frequency $\Delta\omega_{\mathbf{k}} \sim \mathbf{k}^3$. We also attempt to describe the disentanglement of one chain using the reptation concept suitably extended to polymer solutions. This leads to a relaxation time $T_r \sim M^3c^{3/2}$ and to a viscosity $\eta \sim M^3c^{3.75}$ (where $M$ is the molecular mass).

## I. The Concept of Dynamic Screening

In the first paper of this series[4] (hereafter referred to as I) we constructed a set of scaling laws for the motions of a set of Rouse chains,[5] including the effects of repulsive interactions between monomers and the effects of entanglements. One crucial point for the establishment of scaling laws (in the limit of high molecular mass $M \to \infty$) was the existence of a *single characteristic length* $\xi(c)$ defining the average distance between entanglement points at a monomer concentration $c$. The data on $\xi(c)$ for polystyrene in cyclohexane are discussed in ref 2. From this property we derived the existence of a *characteristic frequency* $\Delta(c)$, separating the high-frequency domain ($\omega > \Delta$), where single chain behavior is essential, from a lower frequency domain ($\omega < \Delta$), which is mostly dominated by a collective motion of the gel type.

The discussion in part I omitted the existence of hydrodynamic interactions between monomers. The origin of these interactions is classical:[6,7] each monomer when moving in the solvent under a force **f** creates a backflow velocity at distance **r** of the form[8]

$$\delta\mathbf{v} = \mathbf{G}\mathbf{f} = \frac{1}{6\pi\eta_0}\left\{\mathbf{f} + \frac{1}{4}\left[\frac{3(\mathbf{f}\cdot\mathbf{r})\mathbf{r}}{r^2}\right] - 1\right\}\frac{1}{r} + 0\left(\frac{1}{r^3}\right) \quad \text{(I.1)}$$

where $\eta_0$ is the solvent viscosity. The flow field $\delta\mathbf{v}$ reacts on the motion of other monomers, giving rise to a dynamic interaction between distant units.

Adding all the contributions $\delta v$, Debye and Bueche[9] arrived at a very simple picture for the motion of a single coil (under centrifugation or electrophoresis). They showed that inside the coil the overall velocity of the solvent **u** is essentially equal to the coil velocity $\dot{\mathbf{r}}$ and thus constant in space (no shear). Out of the coil there is the usual Stokes flow with shear. The coil thus behaves like a rigid sphere, except for a small shell, of thickness:

$$K_D^{-1} = \left(\frac{6rc^*}{B\eta_0}\right)^{1/2} \quad \text{(I.2)}$$

(where $c^*$ is the number of monomers/cm$^3$ in the coil, and $B$ the monomer mobility). Inside the thickness $K_D^{-1}$ there is a certain difference between **u** and $\dot{\mathbf{r}}$, and a certain shear. We may say that the shear flow is *screened out* from the coil, with a screening radius $K_D^{-1}$.

This picture applies for a single coil, i.e., for a monomer distribution which is very inhomogeneous in space. We shall mainly be concerned with the opposite limit, where many coils overlap; the medium with monomer concentration $c$ is then homogeneous, except for some small fluctuations. The problem of screening in such solutions has been attacked mainly by Edwards and Freed.[1] They showed that the medium screened out the backflow field in eq. I.1 adding a factor $e^{-Kr}$ where $K^{-1}$ is a concentration dependent screening length. Their calculation led to $K \sim c$. This raises a number of questions. (a) Why is there such a difference between the relation $K(c)$ and eq I.2 relating $K_D$ and $c^*$ for a single coil? (b) If the Edwards–Freed result for $K$ was strictly correct, we would have two characteristic lengths in a semidilute solution: $K^{-1}$ ($\sim c^{-1}$) and $\xi$ ($\sim c^{-3/4}$). This situation would be a catastrophe from the point of view of scaling theories; with two characteristic lengths, scaling can make no novel predictions.

In section II we reexamine the work of ref 1 using a very simplified language based on the "two fluid model" of part I. We show that the length $K^{-1}$ is in fact identical with $\xi$ when it is calculated in the presence of repulsive interactions (ref 1 was restricted to ideal chains). This then suggests that scaling theory can be applied fruitfully to the dynamics: the long wavelength modes ($\mathbf{k}\xi < 1$) are discussed in section II, and the short wavelength modes ($\mathbf{k}\xi > 1$) in section III. The problem of a single labeled chain moving among the others is attacked in section IV.

## II. The Two-Fluid Model ($\mathbf{k}\xi \ll 1$)

Following the approach of part I (section II) we describe our polymer solutions in terms of two velocities **u** (solvent) and $\dot{\mathbf{r}}$ (solute), and we write a set of coupled equations for them.

The acceleration equation for the solvent is

$$\rho\dot{\mathbf{u}} - \eta_0\nabla^2\mathbf{u} + \nabla p = c\tilde{B}^{-1}(\dot{\mathbf{r}} - \mathbf{u}) \quad \text{(II.1)}$$

where $\rho$ is the solvent density (practically equal to the total density for semidilute systems) $\eta_0$ the viscosity of pure solvent, $p$ the pressure, and $\tilde{B}$ an effective mobility per monomer, to be discussed later. For slow motions (far below acoustic frequencies) we have seen in part I that **u** and $\dot{\mathbf{r}}$ are related by a "condition of constant packing"

$$\operatorname{div}(\mathbf{u} + \epsilon\dot{\mathbf{r}}) = 0 \quad \text{(II.2)}$$

where $\epsilon$ is a small parameter, linear in the concentration $c$.

Finally we need an equation describing the behavior of the chains in the presence of perturbations: (i) the flow field **u**; (ii) the restoring forces due to gel elasticity, and discussed in part I; (iii) external forces **f** (as in electrophoresis or sedimentation).[24] The inclusion of this third contribution is not essential, but helps to follow the physics.

**(1) The Edwards–Freed Picture.** The calculation of ref

1 applied to noninteracting chains and included only contributions (i) and (iii). We shall summarize it briefly here: it is possible to define, and to calculate, the response of a single ideal chain to a prescribed system of flow fields and forces, and the result will be of the form[25]

$$\dot{\mathbf{r}}|_r = \int \mathbf{M}(\mathbf{r} - \mathbf{r}')[\tilde{B}\mathbf{f}(r') + \mathbf{U}(r')]\, \mathrm{d}\mathbf{r}' \qquad \text{(II.3)}$$

(where, for simplicity, we consider only the limit of *very low frequencies:* time independent **f** and **u**). The kernel **M** can be calculated from a specific model of chain dynamics such as the Zimm model.[7] The only properties of **M** which will be important for us are (a) the total integral must equal unity

$$\int \mathbf{M}(\mathbf{r})\, \mathrm{d}\mathbf{r} = 1 \qquad \text{(II.4)}$$

This is a reflection of Galilean invariance; if we add a constant velocity $v_0$ to the velocity field **u**, the chains must also increase their velocity by $v_0$ exactly.[26] (b) The range of the kernel (for non-interacting chains) must be equal to the chain radius R. In terms of Fourier transforms, for a mode of wave vector **k**, we have

$$\dot{\mathbf{r}} = \mathbf{M}(\mathbf{k})[\tilde{B}\mathbf{f} + \mathbf{u}] \qquad \text{(II.5)}$$

where

$$\mathbf{M}(\mathbf{k}) = \int \mathbf{M}(r) e^{i\mathbf{k}\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \qquad \text{(II.6)}$$

$$\mathbf{M}(\mathbf{k} = 0) = 1 \qquad \mathbf{M}(\mathbf{k} \gg 1/R) \rightarrow 0$$

Let us now insert eq II.5 into eq II.1 and consider specifically the problem of transverse modes (thus eliminating $\nabla p$). We have

$$\rho\dot{u} - \eta_0\nabla^2 u + c\tilde{B}^{-1}[1 - M(\mathbf{k})]u = cM(\mathbf{k})f \qquad \text{(II.7)}$$

Two limiting cases are important. (a) If $\mathbf{k}R < 1$, $1 - M(\mathbf{k}) = 0$ and we return to a standard hydrodynamic equation; in the low-frequency limit

$$-\eta_0\nabla^2 u = c\mathbf{f} \qquad \text{(transverse)} \qquad \text{(II.8)}$$

For a localized force **f** this gives rise to backflows decreasing like $1/r$; there is no screening. This is normal since the same equations must hold for small solute molecules ($R \rightarrow 0$) floating in a solvent; we expect no screening in this case.

(b) If $\mathbf{k}R > 1$, $M(\mathbf{k}) \rightarrow 0$, and from eq II.5 $\dot{\mathbf{r}}$ is much smaller than **u**; different regions of a single coil see flows of opposite sign, and the coil does not move. Thus we reach a situation reminiscent of the flow in porous, immobile media, which was the starting point of the Debye–Bueche paper.[9] We then have an equation for **u** of the form

$$\nabla^2 u - K^2 u = -\frac{cM}{\eta_0} f \qquad (kR > 1;\ \text{transverse}) \qquad \text{(II.9)}$$

This leads to backflows which decay like $e^{-Kr}/r$. There is a screening length

$$K^{-1} = (c/\tilde{B}\eta_0)^{1/2} \qquad \text{(II.10)}$$

This is similar in form to eq I.2. But we shall see that for semidilute solutions the effective monomer mobility $\tilde{B}$ is in fact concentration dependent; this will explain the difference between Edwards–Freed[1] and Debye–Bueche[9] for the dependence on $c$.

**(2) Self-Consistent Calculation of the Effective Monomer Mobility.** Let us now write down the explicit equation of motion for one chain including backflow, following the work of Zimm[7]

$$\dot{\mathbf{r}}_n = \mathbf{u}(r_n) + \sum_m \mathbf{G}(\mathbf{r}_m - \mathbf{r}_n) \cdot \left[\mathbf{f}(\mathbf{r}_m) + \frac{3k_\mathrm{B}T}{\sigma^2}\frac{\partial^2\mathbf{r}_m}{\partial m^2} + \varphi m\right] \qquad \text{(II.11)}$$

The first term represents the drift velocity. The sum for $n \approx m$ describes backflow effects due to ($m$) and acting on ($n$).[27] The bracket describes all the forces involved: external, elastic, and excluded volume effects.

The essential point, noted by Edwards–Freed, is that the backflow kernel $G$ must not be taken as the backflow in pure solvent (eq I.1) but must be self-consistently renormalized $G \rightarrow Ge^{-Kr}$. Then the sum $\Sigma_m$ involves only a finite number of monomers $h$, all those which are roughly within a distance $K^{-1}$ from $r_n$. Also, if we are interested in space variations which are slow ($\mathbf{k} \lesssim K$) we may replace $\mathbf{f}(\mathbf{r}_m)$ by $\mathbf{f}(\mathbf{r}_n)$ and take it out of the summation, etc. Thus we arrive at

$$\dot{\mathbf{r}}_n = \mathbf{u}(\mathbf{r}_n) + \tilde{B}\mathbf{f}(\mathbf{r}_n) + \tilde{B}\left[\frac{3k_\mathrm{B}T}{\sigma^2}\frac{\partial r_n}{\partial n^2} + \varphi n\right] \qquad \text{(II.12)}$$

i.e., at an equation of the Rouse form (see eq. I.4 of part I), but with a renormalized, concentration-dependent mobility:

$$\tilde{B} = \sum_m \langle G(\mathbf{r}_n - \mathbf{r}_m)\rangle \qquad \text{(II.13)}$$

$$= \frac{1}{6\pi\eta_0}\sum_{m \neq n}\left\langle \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} e^{-K(\mathbf{r}_n - \mathbf{r}_m)}\right\rangle \qquad \text{(II.14)}$$

where we have already averaged the kernel $G$ over angles. Note that in eq II.12 **f** and **u** enter only in the combination $\mathbf{u} + \tilde{\mathbf{B}}\mathbf{f}$, as postulated in eq II.3 (for $\mathbf{k} < K$). Let us now consider the explicit evaluation of (II.14), assuming for the moment that $K^{-1} < \xi$ so that the correlations between monomers ($n$) and ($m$) in eq I.14 correspond to a single chain with excluded volume. Then the number of terms $h$ in the sum is such that

$$h^\nu \sim K^{-1}$$

and each term brings a contribution to $\Sigma$ of order $K$. Thus we may write (for three-dimensional systems)

$$\tilde{B} \simeq hK/\eta_0 \qquad \text{(I.15)}$$

A more precise evaluation of the coefficient in (I.15) would require the knowledge of the static correlation functions between monomers in a coil with excluded volume, which is not available at present. As explained in ref 1 we find it useful to write scaling formulas like eq II.15 more generally for an arbitrary dimension $d$; then

$$G \sim \frac{1}{\eta_0 r^{d-2}} e^{-Kr}$$

and

$$\tilde{B} \simeq \frac{hK^{d-2}}{\eta_0} \sim K^{d-2-1/\nu} \qquad \text{(II.16)}$$

Let us now insert this form into eq I.10 for $K$. We obtain

$$c = \eta_0 K^2 B \sim K^{(\nu d-1)/\nu} \qquad \text{(II.17)}$$

This is to be compared with the equation relating the correlation length $\xi$ to the concentration, discussed in ref 2

$$\xi = c^{-\nu/\nu d-1} \qquad \text{(II.18)}$$

We see that $K\xi \sim 1$; *the static and the dynamic correlation lengths are identical.*[28] At low concentrations ($c \rightarrow c^*$) the hydrodynamic interactions are not screened ($K^{-1} \rightarrow R_\mathrm{F}$). At high concentrations they are totally screened out; $K^{-1}$ becomes comparable to the monomer size $\sigma$.

It is important however to realize that screening is *progressively* established with increasing concentrations; it is thus not possible to neglect backflow effects in semidilute solutions; the calculations of part I, based on a pure Rouse model, do not give the correct exponents for the various physical observables as a function of concentration.

From a physical standpoint, it is again useful to consider one polymer chain in the solution as built up of "blobs" of size $\xi = K^{-1}$, each with a number of monomers $h = g \sim \xi^{1/\nu}$. Successive blobs are independent statically and dynamically. The mobility of one blob is

$$B_b = \tilde{B}/g \tag{II.19}$$

Using (I.15) and $K\xi \simeq 1$, one finds that for $d = 3$ this may also be written as

$$B_b \simeq 1/6\pi\eta_0\xi \qquad (d = 3) \tag{II.20}$$

The latter form is more transparent, since it would correspond to an impenetrable sphere of radius $\xi$. (The numerical coefficient in the formula has no fundamental justification.)

**(3) Inclusion of the Gel Elasticity.** The Edwards–Freed calculation ignored all interactions betweeen chains. When these interactions are taken into account, the picture must be modified; in particular the response kernel $M$ of eq II.3 is completely altered. The radius $R$ of the chains, which played an essential role in the kernel $M$, becomes unimportant since for most practical frequencies the system behaves like a gel, of mesh size $\xi$ much smaller than $R$. If we apply a force $\mathbf{f}$ at one point in the gel, there will be an elastic response in terms of displacements (not velocities) spreading very far from the source. On the other hand, if we write down a relation between the friction force and the elastic force, this relation can now be taken as local, since the size $\xi$ of the unit cell in the network is much smaller than the wavelength. We are thus led to replace eq (II.3) by a balance of forces, as in part I:

$$c\tilde{B}^{-1}(\dot{\mathbf{r}} - \mathbf{u}) = -E\mathbf{k}^2\mathbf{r} \tag{II.21}$$

In principle we should distinguish between a transverse elastic modulus $E_t$ and a longitudinal modulus $E_l$, but, for the scaling considerations of interest here, this distinction is irrelevant:

$$E_l \simeq E_t \simeq k_BT/\xi^d \tag{II.22}$$

The discussion of *longitudinal modes* based on eq II.21 and II.2 follows paper I exactly, the bare mobility $B$ being replaced by the self-consistent mobility $\tilde{B}$. We find modes with a relaxation rate

$$1/\tau_{\mathbf{k}} = D_c\mathbf{k}^2 \tag{II.23}$$

where the cooperative diffusion coefficient $D_c$ is given by

$$D_c = E\tilde{B}/c \simeq E/\eta_0\xi^2 \tag{II.24}$$

or, in terms of the blob mobility $B_b$

$$D_c \simeq \frac{EB_bg}{c} \simeq \frac{k_BT}{c\xi^d}gB_b \simeq k_BTB_b \tag{II.25}$$

(since the number of monomers per blob is $g \simeq c\xi^d$; see ref 2). Using eq II.20 this leads to

$$D_c \sim \xi^{-1} \sim c^{3/4} \text{ for } d = 3 \tag{II.26}$$

The relaxation eq II.4 and the scaling properties (eq II.24, 25, 26) for $D_c$ could be checked in principle by laser light scattering, as has been done on cross-linked gels.[10,11]

The discussion of *transverse modes* is slightly different and will be reserved for a later paper.

## III. Individual Chain Motions

**(1) The Characteristic Width $\Delta\omega_{\mathbf{k}}$ for a Wave Vector k.** We now focus our attention on the short-wavelength behavior ($\mathbf{k}\xi > 1$). We shall mainly consider the characteristic width $\Delta\omega_{\mathbf{k}}$ which would be observed in neutron inelastic scattering at a wave vector $\mathbf{k}$.[29] These widths are usually very small, but with the present high resolution techniques, they may be amenable to measurement. To make things quite definite we shall consider the width for *coherent* scattering (but the incoherent width will in fact be qualitatively similar).

For $\mathbf{k}\xi > 1$ we expect that $\Delta\omega_{\mathbf{k}}$ will become identical with the width measured (with the same $\mathbf{k}$) for one isolated chain. For ideal chains (with hydrodynamic interactions) this width has been calculated in ref (13). The result was of the form

$$\Delta\omega_{\mathbf{k}} \sim \mathbf{k}^3 \qquad (d = 3) \tag{III.1}$$

We shall argue that eq III.1 is *not modified* qualitatively when excluded volume effects are incorporated in the theory. This conclusion disagrees with an earlier proposal (at the end of ref 13). It also disagrees with a later proposal by other authors.[14] As explained in part I, the novel feature of the present analysis is a renormalization of the spring constants in the molecule, which comes in the power laws.

**(2) The Lowest Mode of a Zimm Coil.** We begin by a discussion of the first relaxation mode for a single coil, incorporating excluded volume effects. Later, by a scaling argument, we shall proceed to the evaluation of the width $\Delta\omega_{\mathbf{k}}$ at "large" $\mathbf{k}$. Similar arguments have been given in detail in part I, and our presentation here will be rather brief.

We consider a single coil and represent it in the dumbbell model of Peterlin;[15] i.e., we consider only the end-to-end vector $\mathbf{R}$. The restoring force on $\mathbf{R}$ is of the form

$$F_{el} \simeq -k_BT\frac{\mathbf{R}}{R_F^2} \tag{III.2}$$

where $R_F$ is the Flory radius, including the effects of excluded volume. (The justification of (III.2) is given at length in part I.) The friction force is of the form

$$F_{fr} \simeq -\dot{\mathbf{R}}6\pi\eta_0R_F \qquad (d = 3) \tag{III.3}$$

In eq III.3 we have used the Stokes friction coefficient for *translation* of the coil. The motion considered here is different (*distortion*), but the coefficient remains qualitatively unchanged for the lowest mode. (The factor $6\pi$ is not meaningful.)

Balancing the two forces we get a relaxation equation for $\mathbf{R}$:

$$\dot{\mathbf{R}} = -\mathbf{R}/\theta_1$$

$$1/\theta_1 \simeq k_BT/6\pi\eta_0R_F^3 \tag{III.4}$$

The reader may check directly that for an ideal coil ($R_F \to R_0 \sim N^{1/2}$) this agrees qualitatively with the formulas of Zimm.[7]

**(3) Scaling Formula for $\Delta\omega_{\mathbf{k}}$.** Following the approach of part I, we postulate the following form for the neutron width $\Delta\omega_{\mathbf{k}}$ due to a single coil

$$\Delta\omega_{\mathbf{k}} = \frac{1}{\theta_1}f_S(kR_F) \tag{III.5}$$

with the following limits for the dimensionless function $f_S$: (a) *for* $x \ll 1$, $f_S = x^2$, and $\Delta\omega_{\mathbf{k}} = D_0\mathbf{k}^2$ where

$$D_0 = k_BT/6\pi\eta R_F \qquad \text{(single coil)} \tag{III.6}$$

(this agrees of course with the Stokes formula and Einstein's relation between diffusion and mobility); (b) for $x \sim 1$, $f_S \sim 1$, in agreement with (III.4); (c) for $x \gg 1$, we must reach a $\Delta\omega_{\mathbf{k}}$ which is independent of the molecular mass of the chain. This can be satisfied only if $f \sim x^3$ giving

$$\Delta\omega_{\mathbf{k}} \simeq \frac{k_BT}{6\pi\eta_0}\mathbf{k}^3 \qquad (d = 3) \tag{III.7}$$

More generally for an arbitrary dimensionality $d$ we would have a friction coefficient proportional to $R_F{}^{d-2}$ in eq III.3 and $\Delta\omega_{\mathbf{k}} \sim \mathbf{k}^d$. The exponent is always independent of the presence, or absence, of excluded volume effects!

**(4) Crossover at k$\xi$ = 1 for the Many-Chain Problem.** The crossover between the continuum gel picture ($\mathbf{k}\xi < 1$) and the individual chain picture ($\mathbf{k}\xi > 1$) may be described (as in part I) by a scaling law of the form

$$\Delta\omega_{\mathbf{k}} = \Delta f_m(\mathbf{k}\xi) \qquad \text{(III.8)}$$

where the *characteristic frequency* $\Delta$ is given explicitly (for $d = 3$) by

$$\Delta = \frac{k_B T}{6\pi\eta_0\xi^3} \sim \xi^{-3} \sim c^{2.25} \qquad \text{(III.9)}$$

We may think of $\Delta$ as being the fundamental Zimm relaxation rate of one "blob". The dimensionless function $f_m$ has the following limits: (a) for $x \to 0$, $f_m(x) \to x^2$, in agreement with (II.23 and II.25); (b) for $x \gg 1$, $f_m(x) \to x^3$ in agreement with (III.7). The smooth crossover which is thus obtained demonstrates a certain consistency between the two-fluid model and the one-chain picture.

## IV. Motions of One-Labeled Chain

Our description of the motions of one particular chain at long times is based (as in part I) on the reptation concept,[3] and on the complementary notion of *tube reorganization.* Since the physical principles have been given in I we shall derive the results in a more direct way, based only on a reptation assumption, plus scaling. Let us consider for instance the *renewal time* $T_r$ (i.e., the time for a complete change in the topological relation of one chain with its neighbors) as a function of $N$ and $c$.

(a) The analysis of part I, as well as the work of Edwards and Grant,[16] gives a renewal time for concentrated solutions, in the Rouse model, proportional to $N^3$. We know that hydrodynamic interactions are totally screened out in concentrated solutions; thus the result of part I remains correct in this limit

$$T_r(N, c \gg c^*) \sim N^3 \text{ (at fixed } c\text{)} \qquad \text{(IV.1)}$$

(b) For low concentrations ($c < c^*$), $T_r$ must become comparable with the relaxation time $\theta_1$ associated with the first mode of one single coil; $\theta_1$ is given by eq III.4 for $d = 3$, and is more generally of the form

$$\begin{gathered} \theta_1 \sim R_F{}^d \sim N^{\nu d} \\ T_r(c \ll c^*) \sim N^{\nu d} \end{gathered} \qquad \text{(IV.2)}$$

(c) For all concentrations we assume a scaling law of the form

$$T_r = \theta_1 \varphi(c/c^*) \qquad \text{(IV.3)}$$

where the dimensionless function $\varphi$ has the following features

$$\varphi(0) = 1$$

$$\varphi(x \gg 1) = x^m$$

When compared with (IV.1) the latter condition requires that

$$N^{\nu d}(c/c^*)^m \simeq c^m\, N^{\nu d + m(\nu d - 1)}$$

be proportional to $N^3$. Thus

$$m = \frac{3 - \nu d}{\nu d - 1} \qquad \text{(IV.4)}$$

In particular for $d = 3$ ($\nu = 3/5$) this gives $m = 1.5$ and

$$T_r \simeq \frac{6\pi\eta_0 R_F{}^3}{k_B T}\left(\frac{c}{c^*}\right)^{1.5} \qquad \left(c_S > c > c^*\right) \qquad \text{(IV.5)}$$

The concentration dependence is thus notably different from what we had in the Rouse model ($T_r \sim c$). Knowing $T_r$ we can also make a prediction for the *self-diffusion coefficient* of one chain.

$$D_S \simeq \frac{R^2(c)}{T_r} \sim N^{-2}c^{-1.75} \qquad (d = 3)$$

Finally we expect a viscosity $\eta$ proportional to the elastic modulus $E$ (eq II.22) and to $T_r$, namely

$$\eta \simeq ET_r \simeq \eta_0 \left(\frac{R_F}{\xi}\right)^3 \left(\frac{c}{c^*}\right)^{1.5}$$

$$\eta \simeq \eta_0 \left(\frac{c}{c^*}\right)^{3.75} \sim c^{3.75}N^3 \qquad \text{(IV.6)}$$

We shall discuss these results in section V.

## V. Conclusions

It appears possible to construct a self-consistent set of scaling laws for semidilute polymer solutions. The underlying physical picture is a chain with $N/g$ entanglement points. According to ref 2 we must have[30]

$$N/g = (c/c^*)^{1.25} \qquad (d = 3) \qquad \text{(V.1)}$$

The chain portions between successive entanglement points have been called "blobs" in the present text. Each blob has $\sim g$ monomers and a size $\xi$, and behaves like a smaller coil, with excluded volume effects and complete hydrodynamic interactions. The fundamental stretching mode of one blob has a characteristic frequency $\Delta$ given in eq III.9. Between different blobs of a single chain we find that all interactions (static or dynamic) are screened out; thus on a certain large scale we have ideal chains with an internal dynamics of the Rouse type, plus entanglement constraints.

How can we compare this picture with experiments? (1) For relatively short wavelengths and high frequencies, *neutron inelastic scattering* may be a useful probe; the corresponding scaling formulas have been given in section III. (2) At "longer wavelengths" ($\mathbf{k}\xi < 1$) but frequencies $\omega$ well above $1/T_r$, the "pseudo-gel" modes of section II should be observable by *inelastic scattering of light.* The essential test here would be to measure the concentration dependence of the cooperative diffusion coefficient $D_c$ (eq II.26).

(3) Low-frequency mechanical measurements determine *the elastic modulus $E$ (eq II.22), the relaxation time $T_r$* (eq IV.5), and the viscosity $\eta$ (eq IV.6). Recent results on $E$ seem to suggest a rather good agreement with the scaling law exponent.[17,18] The situation with respect to $T_r$ and $\eta$ is much worse. Experimentally,[19] both these quantities appear to scale like $N^{3.3}$ or $N^{3.4}$ rather than like $N^3$. It was hoped at one time[16] that this difference could be explained as a critical exponent effect. But we have shown here that a consistent application of the static scaling laws, with nontrivial exponents, does not seem to improve the situation. In fact, since reptation by itself gives an $N^3$ law, any other relaxation process superimposed on it could only make $T_r$ shorter, i.e., decrease the exponent rather than increase it. Thus there remains a serious problem concerning the dependence on molecular mass of the viscoelastic parameters. This may be due to some fundamental flaw in the reptation model, but the work of ref 16 based on a very different approach also gives the $N^3$ law. On the other hand the shift between $M^3$ and $M^{3.4}$ may reflect some spurious complications, such as (i) the presence of a few branched polymers

in any batch of high molecular mass,[20] and (ii) segregation of terminal groups. Segregation is extremely frequent in polymer mixtures. If the terminal groups of each chain tended to behave like a foreign species, they might tend to form some sort of micellar aggregates, and all the viscoelastic properties of the medium could be strongly altered.[31]

Let us now consider the opposite view, and assume that even for strictly unbranched chains, without any spurious end effects, the viscosity $\eta$ does vary like $N^a$ where $a$ is larger than 3. We should then abandon the discussion of section IV. However, we could still construct a scaling law to predict the *concentration* dependence of $\eta$. This amounts to postulating a viscosity $\eta(N, c)$ of the form

$$\eta = \eta_0(c/c^*)^b \qquad (c_S > c > c^*) \tag{V.2}$$

Since $c^*$ is proportional to $N^{1-\nu d}$, this gives

$$\eta \sim c^b N^{b(\nu d - 1)}$$

and thus we must have

$$a = b(\nu d - 1) \tag{V.3}$$

even if the "reptation + reorganisation" model is not valid. In the usual case of three dimensions eq V.3 gives $b = 5/4a$. In section IV we had $a = 3$ and $b = 3.75$. The data do give a high exponent, but with rather scattered values (19) (roughly between $c^3$ and $c^4$).

(4) Acoustic and ultrasonic measurements[23] allow us to measure the behavior at frequencies below $\Delta$ (where the shear modulus $E(\omega)$ is predominantly real and of order $E$) and above $\Delta$. In the latter case we probe the motions inside one blob, and expect a series of modes

$$\begin{aligned} 1/\tau_p &\simeq \Delta p^{3\nu} \qquad p = 1, 2, 3, \ldots \; (d = 3) \\ &\simeq \Delta p^{1.75} \end{aligned} \tag{V.4}$$

Equation V.4 may be derived from eq III.1 by a scaling argument; with a wave vector $\mathbf{k}$ we probe regions of size $\mathbf{k}^{-1}$ containing a number $n$ of monomers such that $n^\nu = \mathbf{k}^{-1}$. The mode index $p$ is of order $g/n$ where $g$ is the total number of monomers in the blob.

The result in (V.2) is not very different from the Rouse model with ideal chains ($1/\tau p \sim p^2$) which has often been used as a reference.[23] However, from careful plots of ultrasonic data taken in the semidilute regime, it may be hoped that the frequency $\Delta$, separating two regimes, may be extracted, and that its dependence on concentration can be tested.

To summarize, we propose a number of scaling laws for the dynamical behavior of semidilute polymer systems, depending on two parameters: concentration and molecular mass. (a) All properties which depend on concentration only appear as natural extensions of static scaling, and should be rather general. (b) All properties where the molecular mass appears explicitly (such as the long renewal time $T_r$, or the viscosity) are estimated here with one further assumption based on the reptation model; they are thus much more tentative.

**Note Added in Proof:** Recent photon beat studies by Adam and Delsanti on semidilute polystyrene solutions do show a cooperative diffusion coefficient $D_c$ increasing with concentration as predicted in eq II.6.

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## References and Notes

(1) K. Freed and S. F. Edwards, *J. Chem. Phys.*, **61,** 3626 (1974).
(2) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, C. Duplessix, C. Picot, and P. G. De Gennes, *Macromolecules*, **8,** 804 (1975).
(3) P. G. De Gennes, *J. Chem. Phys.*, **55,** 572 (1971).
(4) P. G. Gennes, *Macromolecules*, **9,** 587 (1976).
(5) P. E. Rouse, *J. Chem. Phys.*, **21,** 1272 (1953).
(6) J. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16,** 565 (1956).
(7) B. Zimm, *J. Chem. Phys.*, **24,** 269 (1956).
(8) L. Landau and I. Lifshitz, "Fluid mechanics", Pergamon Press, London, 1959, p 20.
(9) P. Debye and A. Bueche, *J. Chem. Phys.*, **16,** 573 (1948).
(10) T. Tanaka, L. Hocker, and G. Benedek, *J. Chem. Phys.*, **59,** 5151 (1973).
(11) J. P. Munch, S. Candau, R. Duplessix, C. Picot, J. Herz, and H. Benoit, *J. Polym. Sci.*, to be published.
(12) S. F. Edwards and A. C. Miller, to be published.
(13) E. Dubois Violette and P. G. De Gennes, *Physics* (*Long Island City, N.Y.*), **3,** 181 (1967).
(14) R. Silbey and J. M. Deutch, *J. Chem. Phys.*, **57,** 5010 (1972).
(15) A. Peterlin, *Pure Appl. Chem.*, **12,** 273 (1966); *Adv. Macromol. Chem.*, **1,** 225 (1968).
(16) S. F. Edwards and J. Grant, *J. Phys. A: Math., Nucl. Gen.*, **6,** 1169, 1186 (1973).
(17) G. Allen, private communication.
(18) W. Graessley, private communication.
(19) See the review by W. Graessley, *Adv. Polym. Sci.*, **16,** 000 (1974).
(20) For a recent discussion of reptation in branched systems, see P. G. De Gennes, *J. Phys.* (*Paris*), **36,** 1199 (1975).
(21) J. Francois and F. Candau, *Eur. Polym. J.*, **9,** 1355 (1973); J. Francois, F. Candau, and H. Benoit, *Polymer*, **15,** 618 (1974).
(22) J. Francois, F. Candau, and H. Benoit, *Polymer*, **15,** 626 (1974).
(23) J. D. Ferry, "Viscoelastic Properties of Polymers", Wiley, New York, N.Y., 1970.
(24) We define $\mathbf{f}$ as a force per monomer.
(25) The fact that $\mathbf{f}$ and $\mathbf{u}$ enter only through the combination $\tilde{B}\mathbf{f} + \mathbf{u}$ is true only for space variations which are slow compared with the screening length: we restrict our attention to this case.
(26) In eq 2.2 and 2.5 of ref 2 Galilean invariance is not maintained explicitly.
(27) There is also a term $n = m$ which corresponds to the Rouse contribution (eq I.4 of part I). But whenever $K^{-1} > \sigma$ (i.e., in semidilute solutions), this term is dominated by the sum $\Sigma_m \approx n$.
(28) Our argument assumed $K\xi \lesssim 1$. A separate argument can be constructed from the opposite limit, starting from $K\xi \gtrsim 1$, i.e., treating the chain between $(n)$ and $(m)$ as ideal with an adequate radius. The result is the same.
(29) A brief description of the spectra which are measured in the neutron experiments is given in section V of part I.
(30) Note that eq V.1 predicts a critical molecular mass for entanglements $M_c \sim c^{-1.25}$. The experimental situation for $M_c$ is rather complex; see ref 19.
(31) The anomalous behavior of the density[21] and of the refractive index[22] for solutions or melts with very high N might also reflect such associations.