Dynamics of Entangled Polymer Solutions.
I. The Rouse Model

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ABSTRACT: Recent advances on the static correlation properties of semidilute polymer solutions in good solvents, due to Des Cloiseaux, Daoud et al., etc, are extended here to time-dependent properties. In this first paper, we neglect all hydrodynamic interactions between monomers (Rouse model): this in incorrect, but pedagogically useful. We show that (a) there is a characteristic frequency Δ associated with the motions of chains between entanglement points (Δ is independent of the molecular mass M and varies with the concentration c like $c^{2.75}$ in the Rouse model); (b) at frequencies ω smaller than Δ (but larger than a certain relaxation rate $1/T_r$ for the total chain) a behavior reminiscent of polymer gels is expected; (c) at frequencies above Δ, or at wavelengths smaller than the correlation length, individual chain behavior is expected. We reexamine the single-chain modes in the presence of excluded volume effects, and propose a certain scaling behavior. A by-product of the discussion is an improved understanding of the success of the Flory calculation for excluded volume exponents. We also present a tentative calculation of the time T_r, using the reptation concept[4] plus a model of "tube reorganization" and obtain $T_r \sim N^3 c$ for the Rouse model. All our results are qualitative and lack precise numerical coefficients.

I. Introduction

The current understanding of entangled polymer solutions[1,2] (in good solvents) is based on the existence of a *correlation length* ξ (c) dependent on the concentration c ($\xi \sim c^{-3/4}$), but independent of the molecular mass M (Figure 1). The average number of contacts between different chains (per cm³) is proportional to $1/\xi^3$; thus ξ may be conceived as the distance between entanglement points. The osmotic pressure $\bar{\omega}$ is proportional to the number of contact points

$$\bar{\omega} \simeq k_B T / \xi^3 \sim c^{2.25} \tag{I.1}$$

(T is the temperature, k_B is Boltzmann's constant).[30] At distances $r > \xi$ the repulsive interactions between monomers are screened out by the other chains in the medium; thus on a scale $r > \xi$ the chain statistics are Gaussian. On the other hand, for $r < \xi$, each chain behaves as if it were alone, and shows strong excluded volume effects. All these properties have been checked by neutron experiments.[2]

It is a natural temptation to extend these views toward the *time-dependent* behavior of polymer solutions. A similar extension has been achieved during the past 10 years for critical phenomena: dynamical scaling laws have been proposed after static scaling,[5a] and more accurate versions of these dynamical laws have been produced later from renormalization group arguments.[5b] It has always been found that dynamical scaling is more delicate, and less universal, than static scaling. This will be particularly true for polymer solutions, where the effects of entanglements are extremely complex.[6] However, an analysis at the level of ref 5a will lead us to some possibly useful predictions.

The main theoretical reference on entanglements is a series of papers by Edwards and co-workers[7,8] with certain limitations. (a) Edwards thinks in terms of knots, or topological invariants, which are defined only for infinitely long chains; the most interesting dependences on chain length can be displayed only by truncating the final equations in a rather delicate manner. (b) Static correlations between chains are treated only by mean-field arguments, i.e., by a description of the Flory–Huggins type, which, as shown in ref 2, fails to give the correct exponents in quantities such as the correlation length.

The present work is very different in spirit, and attempts mainly (a) to define the dynamical modes in a few simple limiting cases; (b) to interpolate between these limits, making full use of the static scaling properties. The situations of interest are summarized on the diagram of Figure 2, where we plot in the abscissa the inverse correlation length $1/\xi$ (i.e., a quantity increasing with concentration like $c^{3/4}$) while the ordinate is the wave vector $\mathbf{k}$. The domain of interest to us is mainly the domain of "semidilute" solutions, where c is somewhat larger than the overlap concentration c^*

$$c^* \simeq N/R_F^3 \tag{I.2}$$

Here N is the polymerization index, and R_F (the "Flory radius") is the radius of an isolated coil in the presence of excluded volume effects.[7] We have $R_F \sim N^\nu$ (with $\nu \simeq \frac{3}{5}$ for three-dimensional systems) and thus $c^* \sim N^{-4/5}$. We find essentially three distinct regions in the plot of Figure 2, depending on the relative values of $\mathbf{k}^{-1}$, of the correlation length ξ and of the (concentration dependent) coil radius $R(c)$.

(A) For very long wavelengths ($kR < 1$) a macroscopic description can often be constructed; at frequencies ω which are low, but still higher than the relaxation rate $1/T_r$ of the entanglements, the solution is expected to behave like a gel. Two essential parameters come into play: the rigidity modulus E of the gel, and a friction constant describing the flow of solvent through the gel. We have already argued in ref 2 that the elastic modulus should scale like the osmotic pressure $\bar{\omega}$ (eq I.1)

$$E \simeq k_B T / \xi^3 \sim c^{2.25} \tag{I.3}$$

Since this proposal, various pieces of evidence have indeed confirmed that E behaves like c^x, where x is definitely larger than 2, and of order 2.30[10,11] We shall discuss the consequences of eq I.3 at some length in the following sections.

(B) For wavelengths $2\pi/k$ which are shorter, but still larger than ξ ($1/R < \mathbf{k} < 1/\xi$), many features of the continuum analysis remain valid. In particular the longitudinal modes of the "gel" retain the same behavior, since the gel is a mesh of size $\xi < k^{-1}$. Certain other properties do change, however; in particular if we look at the slow motions of *one* labeled chain in the solution, we find a simple diffusion for $kR > 1$, but a more complicated motion for $kR < 1$. We shall analyze these motions in section IV in terms of the reptation concept,[4] suitably augmented to allow for motions of the surrounding "tube".[12]

(C) In the limit $k\xi \gg 1$ we must recover the dynamical response functions which are characteristic of a single
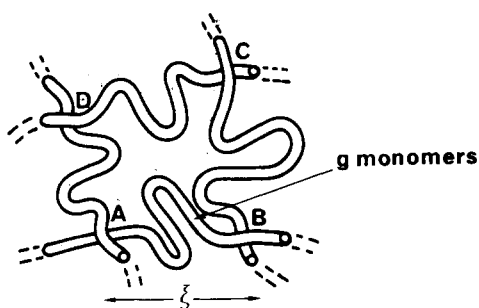
Figure 1. Qualitative picture of a semidilute polymer solution: A, B, C, . . . , are contact points between different chains. The average distance between neighboring contact points is ξ. The average number of monomers on an arc like AB is $g \sim \xi^{5/3} \sim (c^*/c)^{5/4}$.
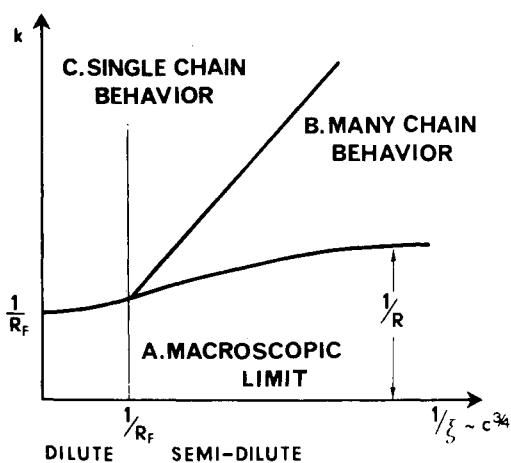
Figure 2. Different types of modes for polymer solutions. k is the wave vector of the mode, R is the coil radius.

chain. These response functions have been calculated in the past for ideal chains.[13,14a] But if we want to incorporate excluded volume effects in the calculation, we find a much more delicate problem. Two relevant proposals have been made: one in a brief paragraph of ref 14a, and one in a separate work.[14b] We have reexamined this question, and find both attempts inadequate, the basic point omitted being that the spring constants between beads must be renormalized when the chain is swollen. This point is nontrivial and will be discussed at some length in the next section.

As usual in flexible polymer dynamics, we can discuss semidilute solutions at two different levels of complexity: either we describe the local motions of each chain by a simple hopping process (the Rouse model[15]) or we include in our description the effects of hydrodynamic interactions between monomers (the Zimm model[16]). For physical predictions, we must use the Zimm model. However, it is somewhat simpler to start by a discussion of dynamical scaling for the unrealistic but simple Rouse model; the present paper (part I of the series) is restricted to this discussion.

Let us start with a brief description of the Rouse equations, following the simplified picture of ref 13 and 14. We consider first a single chain, with successive units 1, 2, . . . , N. The equation of motion for the nth unit is

$$\frac{\partial r_n}{\partial t} = B \left[\mathbf{f}_n + \frac{3k_BT}{\sigma^2}\frac{\partial^2 \mathbf{r}_n}{\partial n^2} + \varphi_n \right] \tag{I.4}$$

Here B is the mobility of one monomer. $\mathbf{f}_n$ is an external force. The second term in the bracket represents the elastic force due to neighboring units (σ^2 is the mean-square extension of one unit in a theta solvent). We are mainly inter-

ested in properties involving many monomers simultaneously, for which it is allowed, and convenient, to treat n as a continuous variable, hence the notation $\partial^2/\partial n^2$. Finally the force φ_n describes the repulsions between monomers (m) and (n) with ($m - n$) $\gg 1$, i.e., those repulsions which create the excluded volume effects. Fortunately, we shall not need to write down an explicit form of φ. One essential property of eq I.4 is the following: summing over the index n, we get an equation for the center of gravity $\bar{r}$

$$\frac{\partial}{\partial t}\bar{r} = \frac{1}{N}\sum_n \frac{\partial r_n}{\partial t} = \frac{B}{N}\sum_n f_n \tag{I.5}$$

since all the internal forces must add up to zero. Thus the overall mobility of a single chain is B/N. By Einstein's relation, the corresponding diffusion coefficient is

$$D_0 = Bk_BT/N \tag{I.6}$$

Note that D_0 is inversely proportional to the molecular mass, even when excluded volume effects are incorporated.

For a problem involving many chains, the monomer position should be labeled $\mathbf{r}_{ni}$, where i defines one particular chain. We can still write an equation of the form (I.4), provided that φ now includes interactions between chains. Again we shall avoid writing an explicit equation for φ, but start from situations where the motions are relatively simple.

II. Gel Behavior. Two-Fluid Model

Let us now consider a longitudinal mode of long wavelength, the polymer concentration $c(r)$ being slightly modulated in space and time

$$c(\mathbf{r}) = c + \delta c(rt) = c + \delta c_\mathbf{k}(t)e^{ikz} \tag{II.1}$$

where we have chosen (z) as the direction of propagation. We shall look for modes with an exponential decay $\delta c_\mathbf{k}(t) = \delta c_\mathbf{k}(0)e^{-t/\tau_\mathbf{k}}$ and we restrict our attention to the case

$$\tau_\mathbf{k} < T_r \tag{II.2}$$

where T_r is a relaxation time for complete disentanglement of one chain, to be discussed later. At first sight the condition in (II.2) may seem in conflict with the requirement of small k (which leads to large τ_k). However, we shall verify later than T_r is usually very large, and that we may have $\tau_\mathbf{k} \ll T_r$ while still keeping $kR \ll 1$. Our description is essentially a "two fluid" picture, with the solvent (concentration $c_s + \delta c_s$, velocity $\mathbf{u}$) and the solute (concentration $c + \delta c$, velocity $\dot{\mathbf{r}}$) as independent constituents.[31] If the displacement of the gel is $\mathbf{r}$ and is modulated as in eq II.1 there will be an elastic restoring force (per unit volume) on the gel

$$F_{el} = E\frac{\partial^2\mathbf{r}}{\partial z^2} = -E\mathbf{k}^2\mathbf{r} \tag{II.3}$$

This must be balanced by a friction force proportional to the difference of velocities of the two fluids

$$F_{el} + \Phi(\mathbf{u} - \dot{\mathbf{r}}) = 0 \tag{II.4}$$

where Φ is a friction coefficient. We shall now show that for longitudinal modes, the solvent velocity $\mathbf{u}$ is negligible. The argument, already quoted in ref 17, is based on the conservation laws for solvent and solute molecules: they read

$$\frac{\partial}{\partial t}\delta c_s = -\text{div}\,(c_s\mathbf{u}) \simeq -c_s\,\text{div}\,\mathbf{u}$$

$$\frac{\partial}{\partial t}\delta c = -\text{div}\,(c\dot{\mathbf{r}}) \simeq -c\,\text{div}\,\dot{\mathbf{r}} \tag{II.5}$$

We are interested only in the slow modes (excluding the normal acoustic waves). Thus the mechanical pressure p is kept constant. We may always write

$$\delta p = \alpha_s \delta c_s + \alpha \delta c \qquad (\text{II}.6)$$

where α_s and α are two thermodynamic coefficients of comparable magnitude.[32] Setting $\delta p = 0$ and using (II.5) one finds

$$\text{div}\,(\mathbf{u}\alpha_s c_s + \dot{\mathbf{r}}\alpha c) = 0 \qquad (\text{II}.7)$$

We shall call eq II.7 the "packing condition", since it expresses that any piling up of solute (δc) must be accompanied by a drop in solvent concentration δc_s. Restricting our attention to longitudinal modes, the div operator may be removed and we get

$$\mathbf{u} = -\frac{\alpha}{\alpha_s}\frac{c}{c_s}\dot{\mathbf{r}} = -\epsilon\dot{\mathbf{r}} \qquad (\text{II}.8)$$

Since $\alpha/\alpha_s \sim 1$ and $c/c_s \ll 1$ (semidilute regime) we see that $\epsilon \ll 1$; for longitudinal modes the solvent motions can be completely omitted.

Dropping $\mathbf{u}$ in eq II.4 we arrive at a simple relaxation law

$$\dot{\mathbf{r}} = -\frac{1}{\tau_k}\mathbf{r}$$
$$\frac{1}{\tau_k} = \frac{E}{\Phi}\mathbf{k}^2 \qquad (\text{II}.9)$$

This form is already familiar in the physics of gels with permanent cross-links[18,19] and has been checked on such gels by inelastic light scattering.[19,20]

Let us now discuss the coefficient

$$E/\Phi = D_c \qquad (\text{II}.10)$$

which we might call the *cooperative diffusion coefficient* of the gel. Our estimate for E is given in eq I.3. For Φ, in the Rouse model, we expect that as in eq II.2 the monomer frictions are additive, thus

$$\Phi = cB^{-1} \qquad (\text{II}.11)$$

$$D_c \simeq \frac{k_B T B}{c\xi^3} \qquad (\text{II}.12)$$

$$D_c \sim c^{1.25} \qquad (\text{II}.13)$$

The above results are specific for three dimensions. However, we know from the physics of phase transitions that it is most instructive to write down the scaling results for an arbitrary dimensionality d. We then have from ref 2

$$\xi \sim c^{-\nu/(\nu d-1)} \qquad (\text{II}.14)$$

and thus

$$E \sim \xi^{-d} \sim c^{-\nu d/(\nu d-1)}$$
$$\Phi \sim c^{-1} \qquad (\text{II}.15)$$
$$D_c \sim c^{1/(\nu d-1)}$$

where ν is always the Flory exponent for the excluded volume, and depends on d

$$\nu = 3/(d+2) \qquad (d \leqslant 4) \qquad (\text{II}.16)$$

The main interest of eq II.15 appears in connection with the crossover between semidilute and dilute regimes. In the dilute limit the longitudinal fluctuations relax by diffusion of individual coils; for a wave vector k we have $1/\tau_k = D_0\mathbf{k}^2$ where D_0 has been defined in eq I.6 and scales like N^{-1}. At the crossover point ($c = c^*$) we see from (II.15) that

$$D_c \sim c^{*\,1/(\nu d-1)} \sim N^{-1} \qquad (\text{II}.17)$$

where we used the definition of c^* (eq I.2) generalized to d dimensions, namely $c^* \sim N^{1-\nu d}$. Equation II.17 shows that D_c and D_0 match smoothly at the crossover.

A more formal description of the crossover would have been the following; assume that at all concentrations, and for suitably small k, there is a longitudinal mode with relaxation rate $1/\tau_k = D(c)\mathbf{k}^2$. The scaling assumption is then

$$D(c) = D_0 f(c/c^*) \qquad (\text{II}.18)$$

where f is independent of chain length and $f(0) = 1$. If we further assume that (a) $f(x)$ behaves as a power of x (say x^m) for large x, (b) that in this regime $D(c) = D_c$ is independent of chain length, then we must have

$$D_c \sim \frac{1}{N}(c^*)^{-m}c^m \sim N^{-1+m(\nu d-1)}c^m \sim c^m$$

from which the value in (II.15) of m follows.

This discussion is a good example of our approach. It is possible to describe dynamical scaling in terms of formal assumptions such as (II.18), but they are not very illuminating. Whenever possible, we prefer to start from concrete physical models, and ultimately check that the crossover properties are correct.

We shall discuss the limits $k_{\min}$ and $k_{\max}$ within which k must remain for the gel model to be valid. Let us start by the lower limit $k_{\min}$. We recall that our description holds only when the entanglements do not relax. Later in this section we shall estimate the relaxation time T_r, and find that $T_r \sim N^3 c$ in the Rouse model (eq IV.4). The wave vector $k_{\min}$ at which $\tau_k = T_r$ is then of order

$$\mathbf{k}_{\min}^2 \simeq \frac{1}{D_c T_r} \sim \frac{1}{c^{2.25}N^3} \qquad (d=3) \qquad (\text{II}.19)$$

Let us compare $\mathbf{k}_{\min}$ to $1/R(c)$ where $R(c)$ is the coil radius. It has been shown (both experimentally and theoretically) in ref 2 that

$$R^2(c) \sim Nc^{-1/4}. \qquad (\text{II}.20)$$

Thus

$$\mathbf{k}_{\min}^2 R^2 \sim c^{-2.5}N^{-2} \sim (c^*/c)^{2.5} \qquad (\text{II}.21)$$

Equation II.21 shows that in the semidilute regime ($c > c^*$) the wave vector $k_{\min}$ is significantly smaller than $1/R$.

Let us finally define the upper limit $\mathbf{k}_{\max}$; the continuum behavior is expected to hold whenever the wavelength is much larger than the mesh of the transient network shown on Figure 1, thus we expect $\mathbf{k}_{\max} \simeq 1/\xi$.

III. The Limit $k\xi > 1$ (Single-Chain Behavior)

(1) **Statement of the Problem.** The time-dependent correlations (relevant for neutron inelastic scattering) inside a single, ideal, Rouse chain have been calculated in ref 13. For a given wave vector $\mathbf{k}$ (much larger than the inverse coil radius $1/R$) one finds a frequency spectrum[33] depending only on one characteristic width $\Delta\omega_k$. This width varies rapidly with $\mathbf{k}$

$$\Delta\omega_k \sim BT\sigma^2\mathbf{k}^4 \qquad (\text{ideal chain}) \qquad (\text{III}.1)$$

Our problem here is to find (at least qualitatively) how eq III.1 must be modified when the chain is not ideal, but is placed in a good solvent where excluded volume effects become important. We shall proceed in two steps: first we consider the first distortion mode of the chain (with wavelength comparable to R); then in a second step we estimate $\Delta\omega_k$ for shorter wavelengths by a scaling procedure.

The first mode of a single coil may be depicted physically as a pulsation, where the coil alternatively swells and contracts; we must ascertain what is the elastic energy involved, and then balance the corresponding restoring force against viscous friction.

(2) Mean-Field Estimate for the Elastic Energy. A first attempt amounts to use of the Flory picture of the coil with repulsive interactions[9] leading to a free energy of the form

$$F(R) = k_B T \left[a_1 \frac{R^2}{\sigma^2 N} + a_2 \frac{N^2 v}{R^d} \right] \qquad \text{(III.2)}$$

The first term is the elastic energy for an ideal coil (of unperturbed radius $\sigma N^{1/2} = R_0$). The second term is the repulsive energy for N particles, each with excluded volume v, filling more or less uniformly a volume R^d. a_1 and a_2 are two numerical constants, which will not play a role in our discussion.[34] Minimization of F with respect to R leads to an equilibrium radius R_F given by

$$\frac{2a_1 R_F}{N \sigma^2} - \frac{d a_2 N^2 v}{R_F{}^{d+1}} = 0$$

$$R_F{}^{d+2} = \text{const} N^3 \sigma^2 v \qquad \text{(III.3)}$$

$$R_F \sim N^\nu \text{ with } \nu = 3/(d+2)$$

Here we are interested in small deviations from the equilibrium radius:

$$R = R_F + \delta R$$

$$F(R) - F(R_F) = \frac{1}{2} F''(R_F) \delta R^2 + \ldots = a_1(d+2)(T \delta R^2 / R_0{}^2)$$

$$F(R) - F(R_F) \simeq T \delta R^2 / R_0{}^2 \qquad \text{(III.4)}$$

Thus, in the mean-field theory of Flory, the spring constant of a swollen coil differs from the spring constant of an ideal coil only by a numerical coefficient; a_1 is changed into $a_1(d+2)$.

(3) Critique of the Mean-Field Theory. The mean-field theory is remarkably successful in predicting the exponent ν. However, it has been gradually recognized[21] that the free energy F of eq III.2 overestimates *both* the elastic and the repulsive energy by a large amount. Consider for instance the excluded volume term; Flory assumes that the probability p for two given monomers (n) and (m) [$|n - m| \gg 1$] to be in contact is of order $1/R^d \sim N^{-\nu d}$. But, at present, we have rigorous predictions for the correlation between ends (i.e., $n = 1$ and $m = N$). The result is quite different:[22]

$$P \sim 1/N^{\nu d + \gamma - 1} \qquad \text{(III.5)}$$

where γ is another critical exponent, related to the entropy of the swollen chain.[23,24] For $d = 3$, $\gamma \sim 1.2$ and thus the repulsive energy is overestimated in the mean-field theory by a factor $N^{0.2}$. However, we know that the *ratio* between elastic and repulsive energy is rather well estimated by Flory, since the value of ν is good for all $d = 1, 2, 3, 4$.[35] Thus we conclude that the elastic term in eq III.2 is also overestimated by something like $N^{0.2}$ (for $d = 3$). This conclusion can also be arrived at from a different starting point. Consider a swollen chain with an end-to-end vector $\mathbf{R}$. In the absence of external forces the average $\bar{\mathbf{R}}$ vanishes. But if we apply small forces $+\mathbf{f}$ at one end and $-\mathbf{f}$ at the other end, we obtain a finite thermal average

$$\bar{\mathbf{R}} = \chi \mathbf{f} \qquad \text{(III.6)}$$

We might call χ the susceptibility of the chain. In terms of χ the free energy of a chain with prescribed elongation $\bar{R}$ may be written

$$F(\bar{R}) - F(0) = \frac{1}{2\chi} \mathbf{R}^2 - \mathbf{R} \cdot \mathbf{f} \qquad \text{(III.7)}$$

(and minimization of (III.7) with respect to $\bar{R}$ brings us back to (III.6)). Thus we are essentially interested in the inverse susceptibility $1/\chi$.

A general thermodynamic theorem relates χ to the spontaneous fluctuations of $\mathbf{R}$:[25]

$$\chi = \langle R^2 \rangle / 3 k_B T \qquad \text{(III.8)}$$

where the symbol $\langle \rangle$ represents a thermal average in the absence of any external force $\mathbf{f}$. From the scaling properties of the excluded volume problem[23,24] we predict

$$\langle R^2 \rangle \sim N^{2\nu} \qquad \text{(III.9)}$$

Inserting (III.9) and (III.8) into (III.7) we see that the correct scaling form for the first term in eq III.2 is

$$F(\bar{R}) - F(0)|_{\text{elastic}} \sim N^{-2\nu} \bar{R}^2 \qquad \text{(III.10)}$$

The mean-field estimate of this term is too large by a factor $N^{2\nu - 1}$. The profound reason for the success of the Flory theory appears thus related to the fact that $2\nu - 1$ is nearly equal to $\gamma - 1$ or that $\gamma - 2\nu$ is very small.[36]

(4) The Fundamental Mode of a Swollen Coil. The above discussion shows that the spring constant of a swollen coil is not given by the mean-field estimate of (III.4) but rather by

$$F(R) - F(R_F) \simeq k_B T \frac{\delta R^2}{R_F{}^2} \qquad \text{(III.11)}$$

where R_p is the swollen radius. Knowing the restoring force involved, let us now estimate friction effects; if the time rate of change of $R = R_F + \delta R$ is $\delta \dot{R}$, the velocities of all beads in the expansion mode are of order $\delta \dot{R}$ and the overall dissipation rate is

$$T \dot{S} \simeq N B^{-1} (\delta \dot{R})^2 \qquad \text{(III.12)}$$

Equating this to the change of spring energy per unit time, we arrive at

$$N B^{-1} \delta \dot{R} \simeq -k_B T \frac{\delta R}{R_F{}^2} \qquad \text{(III.13)}$$

and thus at a relaxation rate for the fundamental mode of a single coil

$$\frac{1}{\theta_1} \simeq \frac{k_B T B}{N R_F{}^2} \qquad \text{(III.14)}$$

Thus θ_1 scales like $N^{1+2\nu}$, while for an ideal chain it scaled like N^2. Of course, since the Rouse model is an oversimplified idealization, we cannot compare (III.14) to experiments. But in paper II of this series we shall construct a similar formula including hydrodynamic interactions, and this (hopefully) will be meaningful.

(5) Characteristic Frequency for a Given k in a Single Chain. Returning now to the width $\Delta \omega_k$ of the dynamic structure factor for neutron or light scattering, at a given wave vector $\mathbf{k}$, we make the following assumption

$$\Delta \omega_k = (1/\theta_1) f_s(kR_F) \qquad (c \ll c^*) \qquad \text{(III.15)}$$

where $f_s(x)$ is a dimensionless function, which must have the following properties.

(a) For kR_F ($=x$) small, we must recover the macroscopic diffusion of the whole coil. This corresponds to

$$\Delta \omega_k \rightarrow D_0 k^2 \qquad (x \ll 1)$$

Thus $f_s (x \rightarrow 0) \rightarrow x^2$ and $D_0 \simeq R_F{}^2 / \theta_1$. Using eq III.14 for θ_1 it is possible to check that this definition of D_0 is consistent with (I.6). (b) For $x \sim 1$ we must have $\Delta \omega_k \sim 1/\theta_1$ and thus $f_s(1) \sim 1$. (c) For $x \gg 1$ we expect $f_s(x) \rightarrow x^p$, where p is some exponent, as yet unknown. In this limit the width $\Delta \omega_k$, which measures a local property, must become independent of N (i.e., of the total chain length)

$$\Delta \omega_k \rightarrow \frac{1}{\theta_1} R_F{}^p k^p \sim N^{-1-2\nu} N^{p\nu} k^p$$

Since $\Delta\omega_k$ is independent of N we must have

$$p = 2 + 1/\nu \qquad \text{(III.16)}$$

In particular, for $d = 3$, $\nu = \frac{3}{5}$ and $p = 3.66$ for the Rouse model.

(6) Longitudinal Modes in Semidilute Solutions. Returning now to region C of Figure 2, we expect eq III.16, for the spectral width $\Delta\omega_k$, to hold (in the Rouse model) provided that the chain portions which are probed are smaller than the correlation length ξ. The crossover between region B (gel-like) and region C (single chain) can be described in terms of another dimensionless scaling function f_m (m stands for many chain)

$$\Delta\omega_k = f_m(\mathbf{k}\xi)\Delta \qquad \text{(III.17)}$$

where Δ is a characteristic frequency, dependent on concentration. For frequencies smaller than Δ, we expect the pseudo-gel behavior. For frequencies larger than Δ, we shall have individual chain motions. This corresponds to the following requirements on the function f_m

(i) *For $\dot{x} \ll 1$* we must have $\Delta\omega_k \to D_c \mathbf{k}^2$, where D_c is given by eq II.10. This imposes $f(x) \to x^2$ and gives us an explicit formula for Δ

$$\Delta = D_c/\xi^2 \qquad \text{(III.18)}$$

The frequency Δ will play an important role in all our discussions. Note that $\Delta \sim c^{2.75}$ for $d = 3$.

(ii) *For $x \gg 1$* the width $\Delta\omega_k$ has to be independent of c (since it expresses a single-chain property), and proportional to $\mathbf{k}^p$, where p is the same exponent which was discussed in eq III.16. Thus we must have $f_m(x) \to x^p$ and also:

$$\frac{\Delta\omega_k}{\mathbf{k}^p} \simeq D_a \xi^{p-2} \sim c^{[1+(2-p)\nu]/(\nu d - 1)}$$

Since this is independent of c we must have $1 + (2 - p)\nu = 0$ in agreement with our earlier calculation of p (eq III.16).

This completes our discussion of the longitudinal modes for the Rouse model. The transverse modes are not very significant in this model (since the whole description of viscosities is not correct) and we shall omit them. (A discussion of transverse modes with hydrodynamic interactions will be given in the second paper of this series.)

IV. Motions of One-Labeled Chain in the Solution

(1) Description of Entanglements in Terms of a Tube. We now focus our attention on the motion of one particular chain inside the transient network provided by the others. In principle, it would be possible to study these motions by inelastic neutron scattering using a few labeled (deuterated) chains mixed with a larger fraction of "normal" (hydrogen carrying) chains. In practice the motions to be discussed are usually too slow to be observed in this way. However, they retain a considerable theoretical interest, because they are largely controlled by entanglement effects. Two parameters of particular significance are[37] (i) the macroscopic self-diffusion of the labeled chain D_s and (ii) the renewal time T_r required for a complete change in the chain conformation and in the topological relations with its neighbors. It is plausible to expect that these two quantities are related by

$$D_s T_r = R^2(c) \qquad \text{(IV.1)}$$

where $R(c)$ is the coil radius given by eq II.20. Equation IV.1 expresses that there is a smooth crossover between the diffusion rate $D_s \mathbf{k}^2$ (at a wave vector k) and the renewal rate $1/T_r$, when $\mathbf{k} \sim 1/R$.

Some time ago we discussed a related but simpler prob-

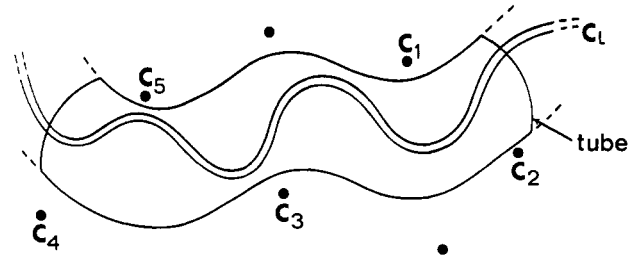**Figure 3.** One chain C_L trapped inside other chains C_1 C_2 C_3 ... For not too long times, C_L is essentially confined inside a tube of radius $\sim\xi$.

lem, where one (ideal) mobile chain "reptates" inside a fixed network.[4] The essential conclusion was that T_r scaled like N^3, and D_s like N^{-2}. Extensions of these results to the case of molten polymers (where all chains are mobile) have been constructed by Edwards and Grant[8] and by Doi.[27]

Our approach here will be different and only qualitative, but it does give some insight, and also allows for the concentration effects (on ξ and on the coil radius R) in a way which is consistent with the static scaling laws of the system.

Central to our picture is the motion of a tube (Γ) inside which the labeled chain is trapped (Figure 3). The diameter of the tube is the diameter of the pores in Figure 1; i.e., it is the correlation length ξ.[38] It is shown in ref 2 that the labeled chain can be visualized as a sequence of N/g noninteracting "blobs", each with g monomers and a size ξ. A similar picture applies to the tube itself; we may picture it as a Rouse chain, with N/g successive segments of length ξ. The total extended length of the tube is thus $L_t = (N/g)\xi$. We shall now investigate the long-time motions of the chain in the tube, and later the effects of tube deformation.

(2) Relaxation by Reptation. Let us first ignore the tube motions, as in the simple reptation problem of ref 4. Then for times t such that $\Delta^{-1} < t < T_r$, we can think of the chain as performing a one-dimensional random motion along Γ. The diffusion coefficient of the whole chain in this one-dimensional problem will be called D_t. For semidilute solutions (where friction on the solvent dominates) we expect $D_t \simeq D_0 \simeq kBTB/N$. This can be understood in terms of the associated tube mobility $\mu_t = D_t/k_BT$; if we pull a Rouse chain inside a tube of finite diameter ($\xi \gg \sigma$), filled mostly with solvent, $c \ll c_s$, with a certain force, we expect that the friction will be proportional to the number of beads whatever the shape of the tube.

Knowing D_t, we can estimate the time T_{rep} required for the chain to reptate on one tube length L_t; after such a time, the conformation is completely renewed. We have

$$T_{rep} \simeq L_t^2/D_t \sim \left(\frac{N\xi}{g}\right)^2 \frac{N}{Bk_BT} \qquad \text{(IV.2)}$$

Using the relation $\xi \sim g^\nu$ and the formula of (I.13) for ξ, this gives

$$T_{rep} \sim N^3 c^{2(1-\nu)/(\nu d - 1)} \qquad \text{(IV.3)}$$

If in this expression we insert the Flory value for ν (eq II.16) we find a remarkably simple result, independent of the dimensionality d.

$$T_{rep} \sim N^3 c \qquad \text{(IV.4)}$$

The time required do disentangle one chain increases very rapidly with molecular mass; it also increases, at fixed N, linearly with concentration.

(3) Relaxation by Tube Reorganization. The above discussion ignored the possibility of modifications occur-
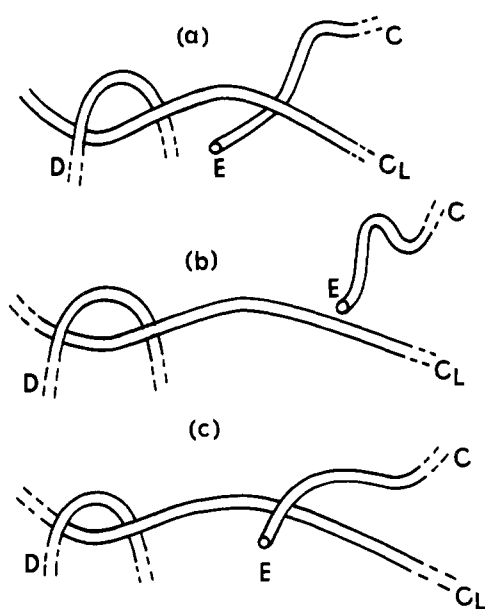
Figure 4. The fundamental process of tube renewal. The chain C_L is trapped by other chains: C, D, ... If the extremity E of chain C is close to C_L, C can shift from "below C_L" to "above C_L" in a short time.

Figure 5. Tube deformation: a region of size ξ moves over distances ξ with a jump frequency Δ. Note that this process is associated with a change of topology only if an event of the type shown on Figure 4 takes place within the chains.
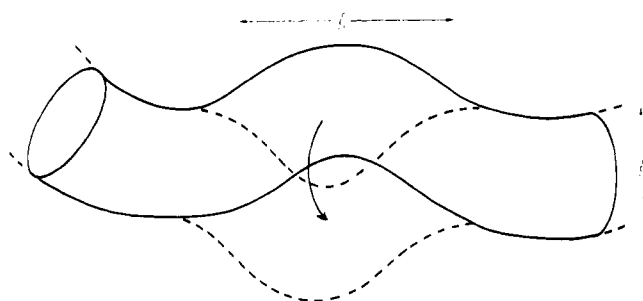
ring in the topology of the tube. We shall now estimate these modifications, and show that they do not qualitatively alter the relaxation rate. There are two types of tube motion. (i) Large-scale displacements, carrying around all chains. These displacements do not modify the local entanglements. (ii) A real contribution to tube renewal is shown on Figure 4. This occurs only when one of the chains C which constrain the motions of the labeled chain C_L has an extremity E lying close to C_L (i.e., lying in the tube region). Then, in a short time, the chain C may commute for instance from a situation "below C_L" to a situation "above C_L" (Figure 4c). If we do not draw the chains, but only a tube surrounding C_L, the above process must be described as a local jump of the type shown on Figure 5. The jumping unit is of length ξ, and has necessarily the characteristic jump frequency Δ introduced in eq II.41. However, only a small fraction f_E of the jumps may correspond to class (ii), namely those for which a chain extremity E is near Γ; considering only those jumps, we are led to a characteristic frequency $f_E\Delta < \Delta$.

The fraction f_E is the average number of chain ends E contained in a volume ξ^d. The concentration of end points is $2c/N$ (since each chain has two ends) and we may write

$$f_E \simeq \frac{2c}{N} \xi^d \simeq \frac{c}{N} \xi^d \simeq \frac{g}{N} \qquad \text{(IV.5)}$$

Following Edwards and Grant[8] we shall now picture the tube itself as a Rouse chain, the size of the fundamental unit being ξ. Successive units are separated by distances $>\xi$ and have their interactions screened out; Γ is ideal. The number of units on Γ is N/g. The lowest relaxation mode of the Γ chain can be called the *rate for tube reorganization* $1/\theta_\Gamma$. From the work of Rouse[15] we know that $1/\theta_\Gamma$ must be proportional to the jump frequency $(f_E\Delta)$ and to the inverse square of the number of beads N/g. Thus

$$1/\theta_\Gamma \simeq f_E\Delta(g/N)^2$$

$$\simeq \frac{c\xi^d}{N} \frac{D_c}{\xi^2} \left(\frac{g}{N}\right)^2 \qquad \text{(IV.6)}$$

$$\simeq BE\xi^d \frac{g^2}{N^3\xi^2}$$

where we have used the definitions of Δ (eq III.18) and D_c (eq II.12). Finally using eq I.3 or II.15 for E we get

$$\frac{1}{\theta_\Gamma} \simeq \frac{Bk_BT}{\xi^2} \frac{g^2}{N^3} \qquad \text{(IV.7)}$$

Comparing to eq IV.2 we see that $\theta_\Gamma \sim T_{\text{rep}}$; reptation inside the tube and reorganization of the tube give comparable contributions to the relaxation of entanglements. The total rate is

$$\frac{1}{T_r} \simeq \frac{1}{T_{\text{rep}}} + \frac{1}{\theta_\Gamma} \simeq \frac{1}{T_{\text{rep}}} \qquad \text{(IV.8)}$$

This qualitative resemblance between T_{rep} and T_r provides some justification for the work of Doi[27] on viscosities of melts, where reptation was the only process taken into account. Similar conclusions have been reached by Edwards and Grant.[8]

V. Conclusions

(1) Inelastic Scattering of Neutrons. Let us first summarize the principal results of this analysis, using the language of neutron scattering, since this technique measures some comparatively simple correlation functions.

(a) Coherent scattering probes the fluctuations $\delta c(\mathbf{r}t)$ of the concentration and measures a "dynamic form factor":

$$S_{\text{coh}}(\mathbf{k}\omega) = \frac{1}{2\pi} \int dt e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})} \langle \delta c(0,0)\delta c(\mathbf{r}t)\rangle \qquad \text{(V.1)}$$

For a given wave vector $\mathbf{k}$ and for $\omega > 1/T_r$ we expect a scaling form for S_{coh}:

$$S_{\text{coh}}(\mathbf{k}\omega) = S(\mathbf{k})\Delta\omega\mathbf{k}^{-1} \Psi_{\text{coh}}(\omega/\Delta\omega_{\mathbf{k}}) \qquad \text{(V.2)}$$

where $S(\mathbf{k})$ is the static form factor (discussed in ref 2) and $\Psi(x)$ is a dimensionless function (normalized by $\int \Psi \, dx = 1$). The crucial parameter is the frequency scale $\Delta\omega_{\mathbf{k}}$, and is described by eq III.17. For $\mathbf{k}\xi > 1$, $\Delta\omega_{\mathbf{k}}$ increases like $\mathbf{k}^{2+1/\nu}$. For $\mathbf{k}\xi < 1$, $\Delta\omega_{\mathbf{k}} \sim D_c k^2$ where D_c is a collective diffusion coefficient characteristic of a quasigel behavior [eq II.12]. But for $\mathbf{k}\xi < 1$, the width $\Delta\omega_{\mathbf{k}}$ is probably too small to be seen in practice by neutron experiments.

(b) Incoherent scattering probes the position r_n of a single monomer at successive times and measures the quantity

$$S_{\text{inc}}(\mathbf{k}\omega) = \frac{1}{2\pi} \int dt e^{i\omega t} \langle e^{i\mathbf{k}\cdot(\mathbf{r}_n(t)-\mathbf{r}_n(0))}\rangle \qquad \text{(V.3)}$$

We could define a characteristic width $\Delta\omega_{\mathbf{k}}|_{\text{inc}}$ for incoherent scattering by an equation similar to (V.2). For $\mathbf{k}\xi > 1$, this is not qualitatively different from the coherent line width.

(2) Mechanical Relaxation. Mechanical measurements probe modes of very low wave vector ($k\xi \ll 1$) but span a very convenient range of frequencies ω.[30] Here the most interesting object is the complex, ω-dependent, shear modulus $E(\omega)$.

(a) At frequencies ω lower than the total disentanglement rate $1/T_r$ we have a purely fluid behavior $E(\omega) \to i\omega\eta$ with a viscosity η, which will be estimated below.

(b) At intermediate frequencies $1/T_r \ll \omega \ll \Delta$ we expect a rubberlike behavior, with a rigidity E (eq I.3).

(c) At high frequencies $\omega > \Delta$ we expect a complex E dominated by single-chain relaxation processes. Extending the discussion after eq III.14 we see that the mth mode of a swollen blob should have a relaxation rate $1/\theta_m \sim \Delta m^{-(1+2\nu)}$ (instead of m^{-2} for an ideal chain). This can be translated into a spectrum of relaxation times by the usual manipulations.[30]

The crossover between (b) and (c) is naturally smooth. The crossover between (a) and (b) should also be smooth, and this condition fixes the scaling behavior of the static viscosity η in the Rouse model:

$$\eta \simeq ET_r \sim N^3 c^{1+\nu d/(\nu d - 1)} \qquad \text{(V.4)}$$

where we have used eq IV.2 for T_r. In three dimensions $\eta \sim N^3 c^{3.25}$. Note that for $c = c^* \simeq N^{-4/5}$, this viscosity becomes $\eta \to N^{2/5} \sim c^* R_F^2$. This can be checked independently by a direct calculation for a single Rouse chain including swelling; thus all crossovers are smooth.

(3) Limitations Due to the Use of Specific Models. The scaling laws obviously fail when the size of the regions concerned becomes as small as a monomer unit; this imposes a limitation on k, and also on the concentration c; $\xi(c)$ must be much larger than the monomer size σ. Physically, when we go to high c values, the friction between monomers dominates over the friction between polymer and solvent; the behavior is then much less universal.

Assuming that c is not too large (semidilute regimes and that $k\sigma \ll 1$), we have to distinguish between two types of dynamic properties.

(a) All scaling laws which are independent of the molecular mass (i.e., which apply in the regions B and C of Figure 2) should hold quite strictly for an entangled system of *Rouse chains*. For instance the crossover at $\omega = \Delta$ (or $k = \xi^{-1}$) has a very general meaning. Of course, when, in the second paper of this series, we shall add hydrodynamic interactions, we shall see that the formulas for Δ (and the power laws above and below $\omega = \Delta$) are modified, but the existence of a crossover frequency Δ will be maintained.

(b) The equations which involve the molecular mass (or the polymerization index N) are much more tentative, since they are based on an extension of the reptation model; scaling by itself is not enough to predict the laws for the renewal time T_r or for the viscosity η.

Finally, it may also be useful to point out certain limitations in connection with the long wavelength modes ($k\xi < 1$) and their observation by light scattering. Our analysis assumed the elastic modulus E of the "pseudo-gel" to be real and independent of frequency in the range of interest ($\Delta \gg \omega \gg 1/T_r$). The mechanical data[6] do show a plateau in the real part $E'(\omega)$ and an imaginary part $E''(\omega)$ which is usually smaller than E' in the plateau region. But, to obtain a plateau while remaining in the semidilute regime requires a rather careful choice of concentrations, and a large molecular mass; basically we want $\Delta T_r \simeq (N/g)^3 \simeq (c/c^*)^{15/4}$ to be very large, while still maintaining a small c. If

ΔT_r is not large enough, the structure of $E(\omega)$ will be more complex and the spectrum of the scattered light at fixed k may become non-Lorentzian.

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(30) In all our equations the symbol $A \simeq B$ means $A = \text{const } B$ with a constant factor which is dimensionless and of order unity. The weaker symbol $A \sim B$ means A proportional to B (the dimensions of A and B being not necessarily the same).
(31) All our concentrations are measured in number of molecules per cm³.
(32) Since the modes of interest are very slow, it may be shown that α_s and α are essentially related to *isothermal* compressibilities.
(33) The detailed definition of the frequency spectrum $S(k\omega)$ is reproduced in section V.
(34) In eq III.2 the elastic term has been simplified, as allowed in the limit of strongly swollen coils ($\alpha = R/R_0 \gg 1$); this allows dropping of the term proportional to ($\log \alpha$) in the Flory calculation.
(35) For $d > 4$ the excluded volume effects become trivial.[23]
(36) The difference $\gamma - 2\nu$ is proportional to a small critical exponent η, first introduced by Fisher; see, for instance, ref 26 for a discussion of η in related phase transition problems.
(37) We do not include the viscosity in our list since the inclusion of hydrodynamic interactions is necessary to reach a consistent picture of this quantity. The viscosity for the Rouse model is briefly discussed in section V.
(38) Earlier discussions[28,29] on the tube diameter gave it proportional to $c^{-1/2}$. They were based on the mean-field estimate for ξ. We now know from ref 2 that $\xi \sim c^{-3/4}$.