Dynamics of Concentrated Polymer Systems

Part 1.—Brownian Motion in the Equilibrium State

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In this series of papers, the dynamics of polymers in melts and concentrated solutions are discussed with the eventual aim of constructing the rheological constitutive equation. The basic ideas are introduced in this paper. A mathematical model chain which describes the motion of the polymer in the fully entangled state is presented and its Brownian motion in equilibrium is studied. The model chain, called the primitive chain, shows much qualitatively different behaviour from that of the Rouse chain used in dilute solution theory.

1. INTRODUCTION

The flow properties of polymer melts and concentrated solutions are very unusual and complicated. Though being basically liquids, they behave like an elastic solid under some conditions, and show a range of curious flow behaviours in various circumstances. These flow properties have significance for the industrial application of polymers, and have motivated a new field of science, their rheology.

The rheology of polymeric liquids has been intensively studied for several decades both experimentally and theoretically. Extensive experimental studies have demonstrated the various basic distinctions of these polymeric liquids from the usual Newtonian liquids, and accumulated a large amount of systematic data. On the theoretical side, advances have been made mainly in phenomenological theories, which have clarified the interrelations between various phenomena and shown the universal aspects of the polymeric liquids. A recent comprehensive survey of this rapidly developing field is given in the textbook by Bird *et al.*[1]

These studies showed that in polymeric liquids the stress response is a non-linear function of the past history of deformation. Such a relation is called the constitutive equation and is a basic starting point of every application of polymer rheology.

The purpose of this series of papers (1 to 3) is to present the constitutive equation based on a molecular model. This final aim is achieved in Part 3. To that end the molecular motion of polymers in the condensed state is discussed in Parts 1 and 2. In this first paper, we present a simple mathematical model which describes the Brownian motion of polymers in equilibrium. In Part 2, this model is extended to the non-equilibrium case.

The major factor governing the overall molecular motion of polymer in a dense system is the effect of entanglements *i.e.*, chains cannot pass through each other. Since the mathematical formulation of the entanglement effect has already been given,[2] it is desirable to construct the theory starting from a fundamental model of the polymer chain, *e.g.*, the Rouse model. However, this approach encounters an extremely difficult mathematical problem. Therefore here, instead of starting from

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this first principle, we start by constructing a model chain which reasonably describes the molecular motion in the dense system, using plausible physical arguments. This model chain, called the primitive chain, has a definite mathematical character and, once established, can be used to discuss various dynamical phenomena of entangled chains. In this sense the model chain is expected to play a role similar to the Rouse
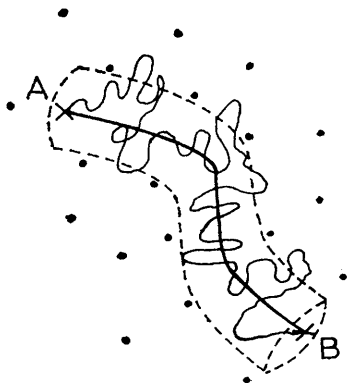

FIG. 1.—Chain segment AB in dense rubber. The points A and B denote the cross-linked points, and the dots represent other chains which, in this drawing, are assumed to be perpendicular to the paper. Due to entanglements the chain is confined to the tube-like region denoted by the broken line. The bold line shows the primitive path.

chain which has been applied widely in dilute solution theory. Though our major interest is in rheological properties, other interesting features, such as diffusion and chain conformation are discussed where appropriate in Parts 1 and 2.

The original idea of the primitive chain was presented by Edwards [3] in the theory of rubber elasticity. In dense rubber, even if the cross-linking points are dilute, the
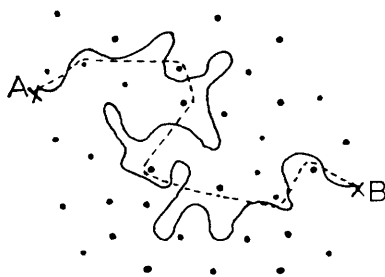

FIG. 2.—Another version of fig. 1. The full line is the real chain segment and the dotted line the primitive path.

chains cannot move freely because they cannot pass through each other. This constraint effectively confines each chain inside a tube-like region (fig. 1). The centre line of such a tube-like region was called the primitive path,[4] and can be regarded as the shortest curve which has the same topology as the real chain relative to the other polymer molecules (see fig. 2). The primitive path is shorter than the real chain and, given a primitive path, the real chain is conceived as wriggling around it.

When the rubber is deformed, the primitive path is deformed, and the entropy associated with the wriggling motion also changes. One result is that, for large deformations, the system has a rubber elasticity much larger than that predicted by conventional rubber elasticity theory.

The tube constraint is quite an effective idea for taking into account the entanglement effect, and is naturally used for the system without cross-links. However, a complication arises in this case. In an unlinked system, the tube which surrounds the chain is no longer fixed in space, but is constantly renewed as the chain diffuses through the tube (fig. 3).

The dynamics of such a process were discussed by de Gennes.[5] He described the wriggling motion by a diffusion equation of a " defect gas ", and showed that this motion is very rapid. (Its longest relaxation time T_{eq}, called the equilibration time of the defect gas, is proportional to N_0^2, where N_0 is the degree of polymerization of the real chain.) He then argued that in a time scale $t \gtrsim T_{eq}$, the wriggling motion gives merely a fluctuation around the primitive path, and that, on average, the chain moves coherently with a certain diffusion constant, keeping its arc length constant.
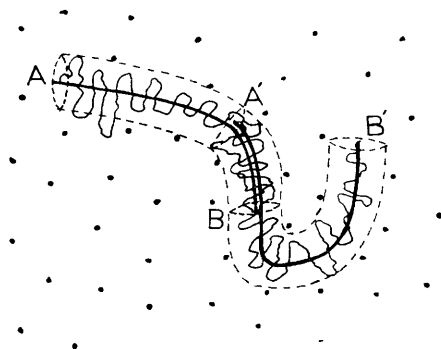

FIG. 3.—In uncross-linked systems if the chain AB moves to A'B', part of the tube (AA) is destroyed and a new part (BB) is created.

Since the diffusion is allowed to occur only along the primitive path, for the chain to change its conformation it has to disengage from the original tube. Based on this picture de Gennes calculated the effective diffusion constant of the centre of mass, and the time correlation function of the end-to-end vector.

The present theory is an extension of these theories. We call the centre line of the tube the primitive chain instead of the primitive path because the tube itself is moving with the chain and, when averaged over a time interval T_{eq}, the real chain coincides with the primitive chain. What we are going to do is to set up the dynamics of the primitive chain. For the equilibrium problems, which are dealt with in this paper, the basic picture is essentially the same as that of de Gennes. However, the idea is put more completely into mathematical terms, and various time correlation functions are calculated by a new method which yields new results in addition to those of de Gennes. This method will be used in Parts 2 and 3.

2. THE CAGE AND THE PRIMITIVE CHAIN

We try to construct the primitive chain model by imposing various assumptions, which will be denoted by (A), (B), etc.

The first and most important assumption is introduced to reduce the many-chain-problem to single-chain-problem (mean field approximation):

(A) In concentrated systems, each polymer chain moves independently in the mean field imposed by the other chains. The mean field is represented by a three dimensional field pattern (or cage). In this cage field, each polymer is confined in a tube-like region surrounding it. When the system is at rest, the cage is assumed to be fixed in space; when the system is macroscopically deformed, the cage also deforms in accordance with the deformation.

The detailed structure of the cage is not important (clearly it is random), but its mesh size is important and denoted by a. The step length of the primitive chain is given by a. For the time being, a may be thought as a mean intermolecular distance,[3, 6] or the correlation length ξ,[7] if the polymer is non-ideal. (A more detailed argument on the meaning of the cage is given in Part 2). In any case, a is a function of only the mass concentration ρ of polymers and independent of molecular weight M. Theories suggest

$$a \propto \rho^{-\alpha} M^0. \tag{2.1}$$

If a is identified with the correlation length, the mean field theory gives $\alpha = \frac{3}{5}$,[8] and the scaling theory $\alpha = \frac{3}{4}$,[9] but α can be obtained exactly from experiment.

An objection may be raised against the fixed cage assumption. The cage must fluctuate in time because it is made of other mobile chains. This fluctuation would be important for shorter chains or for lower concentrations (in which case the problem may be solved by a Rouse-like model in a certain viscoelastic medium).[12] However, for a highly concentrated state of long chains, it is unlikely that such fluctuation occurs on the scale of the radius of the polymer chain because such large fluctuation involves the distortion of many other chains. In such a situation it is more likely that the free movement of a chain is limited to a certain distance a, and that the large scale movement of the chain is attained by a sliding motion through the network of other entangled chains. The fixed cage model is a simple idealization of such a situation. It is not an assumption that the motion of other chains is frozen.

The primitive chain is a centre line of the tube in which the polymer is trapped. The real chain is wriggling around the primitive chain. This wriggling motion determines the basic statistical nature of the primitive chain. However, since the wriggling motion occurs rapidly ($t \lesssim T_{eq}$), and its magnitude is small (length $\lesssim a$), their effect can be represented by a few parameters; once these basic properties of the primitive chain are determined, the wriggling motion can be forgotten. (This situation is analogous to obtaining the hydrodynamic equations from the Boltzmann equation, in which case the effect of complicated collision processes is expressed by viscosity. Actually the interplay between the wriggling motion and the primitive chain motion is important in some cases, but it will not be described here.) The primitive chain is characterized by the following two properties.

In the equilibrium state, the conformation of a primitive chain is a random walk, and its step length (or Kuhn's persistence length) will be of the order of a. Thus for simplicity we assume:

(B) The primitive chain is a freely jointed chain with step length a, and arc length L. The arc length L can be determined from the molecular property of the real chain as follows: the mean square end-to-end distance of the primitive chain is La, which must be equal to the mean square end-to-end distance $N_0 b^2$ of the real chain (b being the effective bond length of the real chain.) Hence

$$L = N_0 b^2 / a. \tag{2.2}$$

Each step in the primitive chain is called a primitive chain segment.   The number of primitive chain segments is denoted by N

$$N = L/a = N_0(b^2/a^2).$$ (2.3)

The second property determines the Brownian motion of the primitive chain.

(C) The primitive chain is moving randomly forward or backward only along itself.   Therefore every point on the primitive chain follows its neighbours.   Important exceptions are chain ends; when the chain moves forward, the " head " can choose its direction randomly and when the chain moves backward, the " tail " can choose random direction (fig. 4).   This random motion is characterized by another
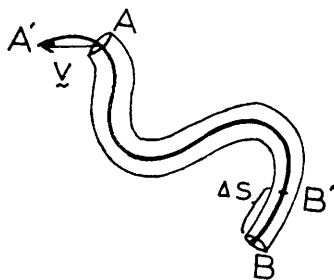

FIG. 4.—When the primitive chain moves forward, the "head" A can choose its direction randomly, and the rest of the primitive chain follows this motion, sliding by a constant arc length ΔS.

important parameter, the curvilinear diffusion constant D, defined by

$$D = \frac{\langle \Delta s^2 \rangle}{2\Delta t}$$ (2.4)

where Δs is the curvilinear length by which the primitive chain travels in a time interval Δt.   ($\Delta s \geqslant 0$ means that the primitive chain moves forward and $\Delta s < 0$ means backward).   The molecular weight dependence of D is determined by the following considerations.   If the real chain is pulled with constant velocity v_s inside the tube, it feels a frictional force ζv_s.   It is clear that the friction factor ζ is proportional to N_0, thus the Einstein's relation indicates

$$D = k_B T/\zeta \propto N_0^{-1},$$ (2.5)

where k_B denotes Boltzmann's constant. D also depends on the concentration, thus we write

$$D \propto \rho^{-\beta} M^{-1}.$$ (2.6)

The parameter β is not easy to estimate theoretically.   In the case of semi-dilute solution, however, the frictional force is mainly due to the relative motion between the polymer and solvent; therefore D will be independent of ρ and $\beta = 0$*.

3. THE LANGEVIN EQUATION

Having defined the primitive chain model, we now set up a basic equation describing the Brownian motion of the primitive chain.   It is desirable to write the Langevin equation in a differential form, but it turns out that this differential equation

* However, it has to be remembered that, in general, polymer concentration changes the free volume of the solvent molecule and changes the solvent viscosity.

produces many subtle and pathological problems related to the analyticity of the functions described by the Wiener measure. Therefore to be clear, we start from a discrete model, and write the Langevin equation as a difference equation.

We assume that the primitive chain is made of N points $R_1 \ldots R_N$ connected by bonds of constant length a, and that in a time interval Δt, the primitive chain hops exactly one step either forward or backward with equal probability. Clearly, this model gives the curvilinear diffusion constant

$$D = a^2/2\Delta t. \tag{3.1}$$

To describe this random process, we introduce a random variable $\xi(t)$, which takes the value 1 when the chain moves backward, or -1 when the chain moves forward. Then the Langevin equation is

$$R_n(t+\Delta t) = \frac{1+\xi(t)}{2}R_{n+1}(t)+\frac{1-\xi(t)}{2}R_{n-1}(t) \qquad (2 \leqslant n \leqslant N-1)$$

$$R_1(t+\Delta t) = \frac{1+\xi(t)}{2}R_2(t)+\frac{1-\xi(t)}{2}[R_1(t)+v(t)]$$

$$R_N(t+\Delta t) = \frac{1+\xi(t)}{2}[R_N(t)+v(t)]+\frac{1-\xi(t)}{2}R_{N-1}(t) \tag{3.2}$$

where $v(t)$ is a random vector of length a, specifying the new primitive chain segment chosen by the chain ends. The time t now takes the value of a multiple of Δt. Eqn (3.2) is merely a mathematical expression of the statement that if the chain moves backward [i.e., if $\xi(t) = 1$], $R_1(t) \ldots R_{N-1}(t)$ jumps to $R_2(t) \ldots R_N(t)$ and $R_N(t)$ jumps to $R_N(t)+v(t)$, etc.

Eqn (3.2) is not easy to solve, (though not impossible, a complete analysis will be published later) because the random variable $\xi(t)$ appears as a coefficient of the unknown variable $R_i(t)$. However, various time correlations of practical interest can be calculated easily without the full solution of eqn (3.2). The method is described in the next section.

4. DIFFUSION PROPERTIES

DIFFUSION OF CENTRE OF MASS

We first discuss the diffusion of the centre of mass of the primitive chain. The position of the centre of mass $R_G(t)$ is given by

$$_G(t) = \frac{1}{N} \sum_{n=1}^{N} R_n(t). \tag{4.1}$$

From eqn (4.1) and (3.2), we get

$$R_G(t+\Delta t)-R_G(t) = \frac{1}{N}\xi(t)V(t)+\frac{1}{2N}v(t) \tag{4.2}$$

where $V(t) = R_N(t)-R_1(t)$ is the end-to-end vector. Hence, the "velocity correlation function" of $R_G(t)$ is

$$\langle [R_G(t+\Delta t)-R_G(t)] \cdot [R_G(t'+\Delta t)-R_G(t')]\rangle$$

$$= \frac{1}{N^2}\langle \xi(t)\xi(t')V(t) \cdot V(t')\rangle+\frac{1}{4N^2}\langle v(t) \cdot v(t')\rangle+$$

$$\frac{1}{2N^2}[\langle \xi(t)V(t) \cdot v(t')\rangle+\langle \xi(t')V(t') \cdot v(t)\rangle]. \tag{4.3}$$

Now for $t \neq t'$ the first term $\langle \xi(t) \, \xi(t') \, V(t) \, V(t') \rangle$ vanishes because if $t > t'$, the average over $\xi(t)$, which is independent of the present state and past history, gives zero, and if $t < t'$, the average over $\xi(t')$ gives zero. Hence

$$\langle \xi(t) \, \xi(t') \, V(t) \, V(t') \rangle = \delta_{tt'} \langle V(t)^2 \rangle = \delta_{tt'} N a^2. \tag{4.4}$$

By the similar argument, the averages of the second and the third terms in eqn (4.3) are proved to give $\delta_{tt'} a^2$ and 0 respectively. Hence

$$\langle [R_G(t+\Delta t) - R_G(t)] \cdot [R_G(t'+\Delta t) - R_G(t')] \rangle = \delta_{tt'} \left(\frac{a^2}{N} + \frac{a^2}{4N^2} \right). \tag{4.5}$$

The second term is neglected for $N \gg 1$. Thus we get

$$\langle [R_G(t) - R_G(0)]^2 \rangle = \sum_{t,t'} \frac{a^2}{N} \delta_{tt'}$$

$$= \frac{a^2}{N} \frac{t}{\Delta t}. \tag{4.6}$$

Using eqn (3.1), we get

$$\langle [R_G(t) - R_G(0)]^2 \rangle = \frac{2}{N} Dt. \tag{4.7}$$

Eqn (4.5) and (4.7) mean that the motion of the centre of mass obeys the Fick's law, with diffusion constant

$$D_G = \frac{D}{3N}. \tag{4.8}$$

That the diffusion of the centre of mass obeys Fick's law is not a trivial result. To see this, let us imagine a hypothetical case that a polymer chain is trapped in an
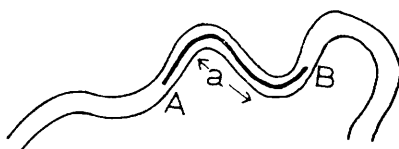

FIG. 5.—Illustration of the hypothetical case: a primitive chain AB is trapped inside an infinitely long tube, and undergoing Brownian motion. The tube itself is a random walk of step length a.

infinitely long tube of random conformation (fig. 5). In this case, the mean-square-displacement of the nth point is given by

$$\langle [R_n(t) - R_n(0)]^2 \rangle = a \langle |\sigma(t)| \rangle \tag{4.9}$$

where $\sigma(t)$ is the curvilinear distance by which the chain has moved in a time interval t. Since the distribution of σ is gaussian;

$$P(\sigma, t) = (4\pi Dt)^{-\frac{1}{2}} \exp \left(-\frac{\sigma^2}{4Dt} \right)$$

eqn (4.9) is evaluated as

$$\langle [R_n(t) - R_n(0)]^2 \rangle = \int_{-\infty}^{\infty} d\sigma \, a |\sigma| P(\sigma, t) = 2a \sqrt{\frac{Dt}{\pi}}. \tag{4.10}$$

Therefore if $a\sqrt{Dt} \gg La^2$,

$$\langle [R_G(t) - R_G(0)]^2 \rangle \simeq \langle [R_n(t) - R_n(0)]^2 \rangle \propto \sqrt{t} \tag{4.11}$$

and in this case the motion of the centre of mass is not at all the Fickian diffusion.

This example shows the important role of the random vectors chosen at the chain ends: though their effect is of the order of $1/N$, it changes the stochastic behaviour completely.

The above example also demonstrates that one has to be careful about the statistical correlation. It is interesting to examine at which points the difference between eqn (4.7) and (4.11) appear in the argument used in deriving eqn (4.7). For the infinite tube, $v(t)$ is not independent of $\xi(t')$ (for $t > t'$), and the second and third terms of eqn (4.3) do not vanish. These terms turn out to cancel the first term, giving the $\sqrt{t}$ behaviour.

From eqn (2.1), (2.3), (2.5) and (4.8), it follows that

$$D_G \propto \frac{a^2}{N_0 b^2} D \propto M^{-2} \rho^{-2\alpha - \beta}. \tag{4.12}$$

The relation $D_G \propto M^{-2}$ was first predicted by de Gennes [5] and has been confirmed experimentally.[10] [Our argument is more comprehensive than that of de Gennes [5] since his argument, when applied to the above infinite tube case, does not predict the $\sqrt{t}$ behaviour of eqn (4.11).]

<center>DIFFUSION OF A MONOMER</center>

Let us now consider the mean square displacement of the nth point of the chain:

$$\langle [R_n(t) - R_n(0)]^2 \rangle.$$

This quantity is not easy to calculate by the probability method used by de Gennes,[5] but can be straightforwardly calculated by the following method. We define

$$f_{nm}(t) = \langle [R_n(t) - R_m(0)]^2 \rangle \tag{4.13}$$

and set up a set of equations for $f_{nm}(t)$. For the internal part, i.e., for $2 \leqslant n \leqslant N-1$, $R_n(t + \Delta t)$ must be either $R_{n+1}(t)$ or $R_{n-1}(t)$, hence

$$f_{nm}(t + \Delta t) = \tfrac{1}{2}[f_{n+1\ m}(t) + f_{n-1\ m}(t)] \qquad (2 \leqslant n \leqslant N-1). \tag{4.14}$$

For $n = 0$, $R_1(t + \Delta t)$ is either $R_2(t)$ or $R_1(t) + v(t)$, then

$$
\begin{aligned}
f_{1m}(t + \Delta t) &= \tfrac{1}{2} f_{2m}(t) + \tfrac{1}{2} \langle [R_1(t) + v(t) - R_m(0)]^2 \rangle \\
&= \tfrac{1}{2} f_{2m}(t) + \tfrac{1}{2} \{ \langle [R_1(t) - R_m(0)]^2 \rangle + 2 \langle [R_1(t) - R_m(0)] \cdot v(t) \rangle + \langle v(t)^2 \rangle \} \\
&= \tfrac{1}{2} [f_{2m}(t) + f_{1m}(t)] + \tfrac{1}{2} a^2.
\end{aligned}
\tag{4.15}
$$

Similarly,

$$f_{Nm}(t + \Delta t) = \tfrac{1}{2} [f_{Nm}(t) + f_{N-1\ m}(t)] + \tfrac{1}{2} a^2. \tag{4.16}$$

Thus $f_{nm}(t)$ is easily solved from the set of difference eqn (4.14)-(4.16), with the initial condition

$$f_{nm}(0) = a^2 |n - m|. \tag{4.17}$$

Though it is not difficult to solve this difference equation, the analysis becomes easier if the difference equation is rewritten into a differential equation. The translation

can be done by noting that eqn (4.14)-(4.16) are equivalent to the following equation for f_{nm} for $1 \leqslant n \leqslant N$

$$f_{nm}(t+\Delta t) = \tfrac{1}{2}[f_{n+1\,m}(t)+f_{n-1\,m}(t)] \qquad (1 \leqslant n \leqslant N) \tag{4.18}$$

with the definition of fictitious elements :

$$f_{0m} = f_{1m}+a^2$$
$$f_{N+1\,m} = f_{Nm}+a^2. \tag{4.19}$$

In the continuous limit, eqn (4.18) gives

$$\frac{\partial}{\partial t} f_{nm} = \frac{1}{2\Delta t} \frac{\partial^2}{\partial n^2} f_{nm}. \tag{4.20}$$

In terms of the arc length variables $s = an$, $s' = am$, eqn (4.20) becomes

$$\frac{\partial}{\partial t} f(s, s'; t) = D \frac{\partial^2}{\partial s^2} f(s, s'; t) \tag{4.21}$$

and eqn (4.19) reduces to

$$\frac{\partial f}{\partial s} = -a \quad \text{at} \quad s = 0 \quad \text{and} \quad \frac{\partial f}{\partial s} = a \quad \text{at} \quad s = L. \tag{4.22}$$

The initial condition now becomes

$$f(s\,s'; t) = a|s-s'|. \tag{4.23}$$

Eqn (4.21)-(4.23) are easily solved by a standard method. (The introduction of an auxiliary function $h(ss'; t) \equiv f(s,s'; t)-a|s-s'|$ helps solving the problem). The result is

$$f(s, s'; t) = a|s-s'|+\frac{2Da}{L}t+ \sum_{p=1}^{\infty} \frac{4aL}{p^2\pi^2} \cos \frac{p\pi s}{L} \cos \frac{p\pi s'}{L}[1-\exp(-\lambda_p t)] \tag{4.24}$$

and

$$\langle[R(s, t)-R(s, 0)]^2\rangle = \frac{2a}{L}Dt+ \sum_{p=1}^{\infty} \frac{4aL}{p^2\pi^2} \cos^2\left(\frac{p\pi s}{L}\right)[1-\exp(-\lambda_p t)] \tag{4.25}$$

where

$$\lambda_p = p^2/T_d; \quad T_d = L^2/D\pi^2. \tag{4.26}$$

The longest relaxation time T_d was called the disengagement time by de Gennes.[5] By eqn (2.1), (2.2) and (2.6), the concentration and molecular weight dependence of T_d is given by

$$T_d \propto M^3 \rho^{2\alpha+\beta}. \tag{4.27}$$

It is easy to see that eqn (4.24) is an expected result : for $t \gg T_d$, the motion is determined by the motion of the centre of mass, and eqn (4.25) agrees with eqn (4.7) ; for $t \ll T_d$, the motion is the same as that of a chain in infinite tube [eqn (4.10)].

The time correlation function of the tangent vector of the primitive chain,

$$u(s, t) = \frac{\partial}{\partial s} R(s, t), \tag{4.28}$$

is easily calculated from eqn (4.24). Differentiating eqn (4.24) with respect to s and s', we get

$$\langle u(s, t) \cdot u(s', 0) \rangle = -\frac{1}{2} \frac{\partial^2}{\partial s \, \partial s'} f(s, s'; t)$$

$$= \delta(s-s') - \frac{2a}{L} \sum_{p=1}^{\infty} \sin\left(\frac{p\pi s}{L}\right) \sin\left(\frac{p\pi s'}{L}\right) [1 - \exp(-\lambda_r t)]$$

$$= \frac{2a}{L} \sum_{p=1}^{\infty} \sin\left(\frac{p\pi s}{L}\right) \sin\left(\frac{p\pi s'}{L}\right) \exp(-\lambda_p t) \qquad (4.29)$$

which is a result obtained by de Gennes.[5]

An interesting observation is that the results so far obtained, eqn (4.7), (4.24) and (4.29) are exactly the same as the Rouse chain if $D/3$ is replaced by the diffusion constant of a " bead " of the Rouse chain. Also it can be shown that the time correlation functions of quantities which are linear in $R(s, t)$ are the same as in the Rouse chain. Such a coincidence may be rather striking considering the basic difference between the Rouse chain and the primitive chain. However, this coincidence is not very profound. If we look at other time correlation functions, there is a significant difference between them. This is shown in the next example.

DYNAMIC STRUCTURE FACTOR

As the last example, we consider the dynamic structure factor. As in the case of neutron scattering, we introduce two structure factors;

$$S_{\text{incoh}}(k, t; n) = \langle \exp\{ik \cdot [R_n(t) - R_n(0)]\} \rangle$$

$$S_{\text{coh}}(k, t) = N^{-2} \sum_{n,m=1}^{N} \langle \exp\{ik \cdot [R_n(t) - R_m(0)]\} \rangle. \qquad (4.30)$$

At the present stage, it is not clear what sort of scattering source is used to measure these structure factors. (Note that the pertinent wavelength is in the region of $\lambda \lesssim 10^3\,\text{Å}$ and the energy exchange is very small $(1/\omega \gtrsim 1\,\text{s})$. A high resolution photon correlation technique may be a possible one.) Apart from these problems, calculation of these scattering functions is interesting because the result shows a qualitative difference from that of the Rouse chain.

The calculation is done in almost the same way as in the previous section. We define

$$g_{nm}(t) = \langle \exp\{ik \cdot [R_n(t) - R_m(0)]\} \rangle \qquad (4.31)$$

and set up a set of difference equations for $g_{nm}(t)$. Clearly $g_{nm}(t)$ satisfies the same equation as eqn (4.14). The only difference is the boundary condition. Instead of eqn (4.19), we now have,

$$g_{0m}(t) = \langle \exp\{ik \cdot [R_1(t) + v(t) - R_m(0)]\} \rangle = g_{1m}(t) < \exp[ik \cdot v(t)] \rangle \qquad (4.32)$$

and

$$g_{N+1\ m}(t) = g_{Nm}(t) < \exp[ik \cdot v(t)] \rangle. \qquad (4.33)$$

For simplicity we assume $|kv(t)| \simeq ka \ll 1$, and

$$\langle \exp[ik \cdot v(t)] \rangle = 1 + i\langle k \cdot v(t) \rangle - \tfrac{1}{2}\langle [k \cdot v(t)]^2 \rangle + \dots$$

$$= -\tfrac{1}{6}k^2 a^2. \qquad (4.34)$$

Therefore the final set of differential equations for $g(s,s';t)$ becomes

$$\frac{\partial}{\partial t}g = D\frac{\partial^2}{\partial s^2}g$$

$$\frac{\partial g}{\partial s} = \kappa g \quad \text{at } s = 0 \quad \text{and} \quad \frac{\partial g}{\partial s} = -\kappa g \quad \text{at } s = L \tag{4.35}$$

where

$$\kappa = k^2 a/6.$$

The initial condition for g is

$$g(s,s';t=0) = \langle \exp\{i\mathbf{k}\cdot[R(s,0)-R(s',0)]\}\rangle = \exp(-\kappa|s-s'|). \tag{4.36}$$

The solution of the above equation is

$$g(s,s';t) = \sum_{p=1}^{\infty}\left\{\frac{2\mu}{\mu^2+\alpha_p^2+\mu}\cos\left[\frac{2\alpha_p}{L}\left(s-\frac{L}{2}\right)\right]\cos\left[\frac{2\alpha_p}{L}\left(s'-\frac{L}{2}\right)\right]\exp(-4Dt\alpha_p^2/L^2)+\right.$$

$$\left.\frac{2\mu}{\mu^2+\beta_p^2+\mu}\sin\left[\frac{2\beta_p}{L}\left(s-\frac{L}{2}\right)\right]\sin\left[\frac{2\beta_p}{L}\left(s'-\frac{L}{2}\right)\right]\exp(-4Dt\beta_p^2/L^2)\right\} \tag{4.37}$$

where

$$\mu = \tfrac{1}{12}k^2aL \tag{4.38}$$

and α_p and β_p are the solutions of the equation

$$\alpha_p\tan\alpha_p = \mu, \quad \beta_p\cot\beta_p = -\mu. \tag{4.39}$$

From eqn (4.37), we get

$$S_{\text{incoh}}(k,t;s) = \langle\exp\{i\mathbf{k}\cdot[R(s,t)-R(s,0)]\}\rangle$$

$$= \sum_{p=1}^{\infty}\left\{\frac{2\mu}{\mu^2+\alpha_p^2+\mu}\cos^2\left[\frac{2\alpha_p}{L}\left(s-\frac{L}{2}\right)\right]\exp(-4Dt\alpha_p^2/L^2)+\right.$$

$$\left.\frac{2\mu}{\mu^2+\beta_p^2+\mu}\sin^2\left[\frac{2\beta_p}{L}\left(s-\frac{L}{2}\right)\right]\exp(-4Dt\beta_p^2/L^2)\right\} \tag{4.40}$$

$$S_{\text{coh}}(k,t) = \frac{1}{L^2}\int_0^L ds\int_0^L ds'\,\langle\exp\{i\mathbf{k}\cdot[R(s,t)-R(s',0)]\}\rangle$$

$$= \sum_{p=1}^{\infty}\frac{2\mu}{\alpha_p^2(\mu^2+\alpha_p^2+\mu)}\sin^2\alpha_p\exp(-4Dt\alpha_p^2/L^2). \tag{4.41}$$

The expressions are simplified for two limiting cases, (i) $\mu \ll 1$, i.e., $k^2La \ll 1$. In this large wavelength limit, the scattering factor is determined only by the motion of the centre of mass and the dynamic structure factor reduces to

$$S_{\text{incoh}}(k,t,s) = S_{\text{coh}}(k,t) = \exp(-D_Gk^2t). \tag{4.42}$$

(ii) $\mu \gg 1$, i.e., $k^2La \gg 1$. In this case, α_p and β_p are approximated by

$$\alpha_p = (p-\tfrac{1}{2})\pi, \quad \beta_p = p\pi \quad (p = 1, 2, \ldots). \tag{4.43}$$

Hence,

$$S_{\text{incoh}}(k,t;s) = \sum_{p=1}^{\infty}\frac{8\mu}{4\mu^2+p^2\pi^2}\cos^2\left[\frac{p\pi}{L}\left(s-\frac{L}{2}\right)\right]\exp(-\lambda_pt) \tag{4.44}$$

where λ_p is given by eqn (4.25). Approximating $\cos^2[p\pi(s-\tfrac{1}{2}L)/L]$ by $\tfrac{1}{2}$, and replacing the sum over p by an integral, we get

$$S_{\text{incoh}}(k, t; s) = \exp(k^4 a^2 Dt/9)\,\text{erf}(k^2 a\sqrt{Dt}/3) \tag{4.45}$$

where

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x dy\,\exp(-y^2). \tag{4.46}$$

This expression is more easily obtained as follows; when $k^2 La \gg 1$, the primitive chain is assumed to be infinite, and $S_{\text{incoh}}(k, t; s)$ can be calculated from the infinite tube model of fig. 5;

$$S_{\text{incoh}}(k, t; s) = \int_{-\infty}^{\infty} d\sigma\,\exp\left(-\frac{k^2 a}{6}\sigma\right)P(\sigma; t) \tag{4.47}$$

which gives eqn (4.45). In the Rouse chain, $S_{\text{incoh}}(k, t; s)$ is given by de Gennes [11]

$$S_{\text{incoh}}^{(\text{Rouse})}(k, t; s) = \exp\{-k^2\langle[R(s, t)-R(s, 0)]^2\rangle\}$$

$$= \exp\left(-\frac{ak^2}{3}\sqrt{\frac{Dt}{\pi}}\right). \tag{4.48}$$

In contrast the asymptotic form of eqn (4.45) is

$$S_{\text{incoh}}(k, t; s) = \begin{cases} 1 - \dfrac{ak^2}{3}\sqrt{\dfrac{Dt}{\pi}} & t \ll \dfrac{a^2}{D}(ka)^{-4} \\[3mm] 1/6k^2 a\sqrt{Dt} & t \gg \dfrac{a^2}{D}(ka)^{-4}. \end{cases} \tag{4.49}$$

Therefore the decay in S_{incoh} of the primitive chain is much slower than that of the Rouse chain.

The difference appears more significantly in the coherent scattering factor. From eqn (4.41) and (4.43), we get

$$S_{\text{coh}}(kt) = \frac{96}{k^2 aL}\sum_{p\,\text{odd}}\frac{1}{p^2\pi^2}\exp(-\lambda_p t). \tag{4.50}$$

Note that the characteristic decay rate of $S_{\text{coh}}(k, t)$ is given by $1/T_d$, and strongly depends on the molecular weight. This is in sharp contrast to the Rouse chain. In the Rouse chain, the coherent scattering factor decays independently of the molecular weight, when $k^2 N_0 b^2 \gg 1$. This difference comes from the basic difference in the diffusion motion. In the Rouse chain, the decay of $S_{\text{coh}}(k, t)$ occurs at every point on the chain, whereas in the primitive chain, the decay occurs only at the chain ends as shown in fig. 6.

(a)   (b)

Fig. 6.—In the Rouse chain (a), the memory of $\rho_k = \Sigma_n \exp[i\mathbf{k}\cdot R_n(t)]$ is lost at every part of the chain, whereas in the primitive chain its memory is lost only at the chain ends. Therefore the decay of $\langle \rho_k(t)\rho_{-k}(0)\rangle$ is independent of molecular weight in the Rouse chain, whereas in the primitive chain it strongly depends on the molecular weight.

5. CONCLUSION

In this paper we have shown how the motion of polymer chains in concentrated systems is idealised and have presented a model chain called the primitive chain. The primitive chain is characterized by two parameters, the step length a and the diffusion constant D, both of which depend on concentration and the molecular weight. Its Brownian motion is described by a simple Langevin equation [eqn (3.2)]. The analysis of this Langevin equation indicates the following characteristic aspects of the Brownian motion of the primitive chain.

(i) The diffusion coefficient D_G of the centre of mass and the characteristic relaxation time T_d depend strongly on molecular weight and concentration as was first predicted by de Gennes.

(ii) The mean square displacement of a point on a primitive chain and the time correlation function of the tangent vector are exactly the same as in the Rouse chain *provided* D and a are appropriately interpreted.

(iii) The dynamic structure factors are qualitatively different from those of the Rouse chain. For the wave vector $1/a < |k| < 1/\sqrt{La}$, the incoherent scattering factor $S_{\text{incoh}}(k, t)$ decays slowly in time as $S_{\text{incoh}}(k, t) \propto 1/\sqrt{t}$ and the coherent scattering factor $S_{\text{coh}}(k, t)$ decays very much more slowly with a relaxation time T_d.

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