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Brownian dynamics of self-similar macromolecules

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Résumé. — Nous présentons un travail théorique sur la dynamique d'une solution de « fractals polymériques ». Chaque fractal est une macromolécule obtenue par le pontage, avec une connectivité self-similaire, d'éléments constitués de chaînes polymères linéaires flexibles. L'hydrodynamique est décrite par l'approximation de Kirkwood avec écrantage (« milieu effectif »). Les fractals sont décrits par une théorie d'échelle utilisant le concept de dimension spectrale. Les spectres de relaxation obtenus à concentration faible ou élevée sont la généralisation des spectres classiques (de type Rouse ou Zimm) au cas de fractals polymériques quelconques. Une extension de la théorie de milieu effectif nous conduit à un modèle approché pour l'effet du volume exclu et de la polydispersité ; les enchevêtrements ne sont pas pris en compte. Dans le cas d'une distribution de masse moléculaire en loi de puissance (avec coupure aux grandes masses), nous trouvons qu'un régime d'« écrantage anomal » peut apparaître pour lequel le propagateur effectif est $G(k) \sim k^{-\alpha}$, avec $0 < \alpha < 2$. Généralement, un argument d'autocohérence détermine de façon univoque α , ainsi que l'exposant décrivant la divergence de la viscosité à fréquence nulle en fonction de la coupure aux grandes masses. Il y a cependant des exceptions remarquables, en particulier le modèle de percolation. Notre dérivation s'applique à un système trempé en cours de gélation, pour lequel nous calculons divers exposants dynamiques.

Abstract. — A theory is presented of the dynamics of a solution of flexible chain macromolecules of arbitrary self-similar connectivity (« polymeric fractals »). The methods used are a Kirkwood approximation/effective medium theory of hydrodynamics, and a scaling theory of fractal correlations based on the idea of the spectral dimension. The resulting relaxation spectra at high and low concentrations are the generalizations (to the case of arbitrary polymeric fractals) of the well-known Rouse-like and Zimm-like spectra for linear polymers. The effective medium theory is extended to include an approximate dynamical description of excluded volume effects (but not entanglements) and also to account for polydispersity. In the presence of a power-law mass distribution (with a high mass cutoff) an « anomalous screening » regime is possible in which the effective fluid propagator $G(k) \sim k^{-\alpha}$, with $0 < \alpha < 2$. In most cases, both α , and an exponent describing the divergence of the zero-frequency viscosity with the high mass cutoff, are determined uniquely by a self-consistency requirement. However, there are notable exceptions, including the percolation model. The theory is used to calculate various exponents describing the dynamical behaviour of a polymer sol-gel system close to its critical point.

1. Introduction.

In many processes of interest to polymer scientists, linear polymer molecules containing active chemical groups cross-link or associate irreversibly to form larger macromolecules of a more complex structure. The structure of these larger sol-molecules will typically depend on the nature of the association or gelation process. However, a prediction common to several models of such processes is that the new molecules exhibit fractal behaviour — that is, they show statistical invariance under dilatation about an internal point. (This prediction arises, for example, in the percolation model of sol formation [1, 2], and also in a variety of kinetic growth models which have been studied recently [3-5].)

The dilatation symmetry of a fractal manifests itself in various ways. For example, the mass M of a fractal is related to its linear size, R , by a power law

$$M \sim R^{d_f}$$

where d_f , the fractal dimension [6], describes also the power-law correlations of the internal monomer concentration $c(r)$:

$$\langle c(r) c(r') \rangle \sim |r - r'|^{d_f - d}.$$

In general though, it is important to realise that d_f contains only a limited amount of structural information. To see this, we should distinguish between the

following two ideas :

(a) the intrinsic self-similar connectivity of a given polymeric or molecular network, and

(b) the arrangement (possibly time-dependent) of this network in space.

Of these, d_f can tell us about (b), but not (a). For example, an ordinary linear polymer has $d_f = 2$ (in the ideal limit) or $d_f \simeq 5/3$ (in the limit of a swollen coil), but in either case, its internal connectivity remains strictly one dimensional. This is expressed more formally in the statement that the linear chain has a spectral dimension, d_s , equal to one. The spectral dimension (see Sect. 2) tells us about the connectivity of a fractal but not about its spatial arrangement. (Because d_s remains constant even when this arrangement is varying with time, it is very important in the description of dynamics.)

In contrast to the case of a linear chain, a fractal sol-molecule will typically contain a hierarchy of branches and/or loops on every lengthscale; its connectivity is not one dimensional. Instead, such a molecule is expected to have a spectral dimension $d_s > 1$. For example, sol molecules described by the percolation model have a value of d_s close to $4/3$. Other values in the range $1 < d_s < 2$ are predicted by models of kinetic gelation and aggregation-type cluster growth [3-5].

The purpose of the present paper is to extend where possible the existing formalism and results of polymer solution theory to the case of a solution of « polymeric fractals » with arbitrary values of d_s between $d_s = 1$ and $d_s = 2$. This can be accomplished at the level of a Flory theory of chain swelling and an effective medium theory [7-9] of hydrodynamics. The static formulation and the Flory theory (see Sect. 3), along with some of the main dynamical results of section 4 have been previously reported in a Letter [10]. Here we review and clarify some of the underlying scaling assumptions, and present the full dynamical formalism for the first time. New results are presented for an approximate dynamical description of excluded volume effects, and for the treatment of polydisperse systems, such as a real polymer sol.

The term « polymeric fractal » describes a class of fractals which are made of flexible polymer chain at short lengthscales, but have arbitrary self-similar connectivity at larger distances. This model is particularly suited to the description of macromolecules arising by disorderly cross-linking (gelation or aggregation) of flexible chain precursors, but can also be used to describe any other fractal which has no inherent rigidity and therefore has diffusive (rather than vibrational) dynamics.

The proposed extensions to existing polymer solution theories are carried out in this paper in several stages. Firstly, in section 2, several results concerning the definition of d_s and its relation to other exponents are reviewed. These results were first obtained in another, apparently unrelated, context — that of

determining how Laplacian transport processes (such as conduction or the diffusion of a particle) are modified when constrained to take place on a self-similar resistor network. To enable comparison with the existing literature, we first discuss these results in their original context. We then show in section 3 how they can be exploited in the description of the static configuration of an arbitrary polymeric fractal.

In section 4 a dynamical theory of polymeric fractals in solution is developed. This is then used to calculate the scaling form of the frequency-dependent viscosity of a monodisperse solution of arbitrary polymeric fractals, in the absence of excluded volume and entanglements. The methods used are an effective medium (EM) theory of hydrodynamics, and a scaling theory of fractal correlations involving d_s . The resulting relaxation spectra are generalizations of the well known Rouse-like and Zimm-like spectra [11, 12] for linear polymers.

The dynamical theory is possible because the generalized Laplacian operator, defined in a manner suggested by the conductivity problem on a fractal network, may also be used to describe the thermodynamic force on a polymeric fractal (in the limit of ideal phantom chains). This allows one to write down a Rouse-type Langevin equation for a flexible macromolecule of arbitrary d_s . Somewhat more surprisingly, one can go further and obtain (to within numerical factors) a full hydrodynamic theory at the effective medium level.

In section 5, the effective medium theory is generalized to include an approximate description of excluded volume effects, based on a rescaling procedure for the eigenvalues of the Laplacian operator on the fractal. In section 6 the results are discussed in the light of the dynamical scaling hypothesis of de Gennes. In section 7, polydispersity effects are incorporated and discussed. The case of power law polydispersity turns out to be interesting; for some values of the polydispersity exponent, it appears that the self-consistency requirement of effective-medium theory does not uniquely determine the fluid response. Applications of the theory are given to the modelling of a polymeric sol/gel system close to its critical point, and comparison is made with existing theories and experimental results for the static limit.

Throughout the paper, the emphasis is on calculating the viscoelastic properties of a solution of polymeric fractals. However, the formalism presented allows one to study explicitly the internal relaxation modes and dynamical correlation functions of a typical single macromolecule. (The influence of neighbouring molecules is described, on average, by the effective medium.) By studying these dynamics, it may be possible to gain a better understanding of irreversible cross-linking processes such as gelation.

1.1 THE PROBLEM OF ENTANGLEMENTS. — A remaining drawback of the work described in this paper is the neglect of entanglement effects at high densities. The

averaging procedure adopted in EM theory does not honour topological constraints, and in any case a fuller hydrodynamic treatment [13] would require more information about the fractal correlations than can be obtained from a scaling picture. However, although entanglements should dominate at high enough molecular weights and densities, there is, for linear chains, a fairly well-defined molecular weight below which they can satisfactorily be ignored [12]. One might expect such a regime for other polymeric fractals also. Indeed, one can speculate that, whilst linear chains can form long-lasting entanglements at concentrations just above the overlap threshold, the topological interaction between more complicated molecules may, in some cases, remain relatively harmless up to much higher densities (see Fig. 1).

One can also argue that the effects of entanglements in the vicinity of the overlap threshold may be decreased by the excluded volume repulsion between neighbouring molecules. Furthermore, polydispersity reduces the effects of entanglements, because an entanglement between a large molecule and a smaller one will resolve on a timescale short compared with the diffusive relaxation time of the larger. In view of these remarks, it seems worthwhile to give a first treatment of the problem in which entanglements are neglected, whilst of course bearing in mind that this approximation is not expected to be a very good one, except in the dilute regime.

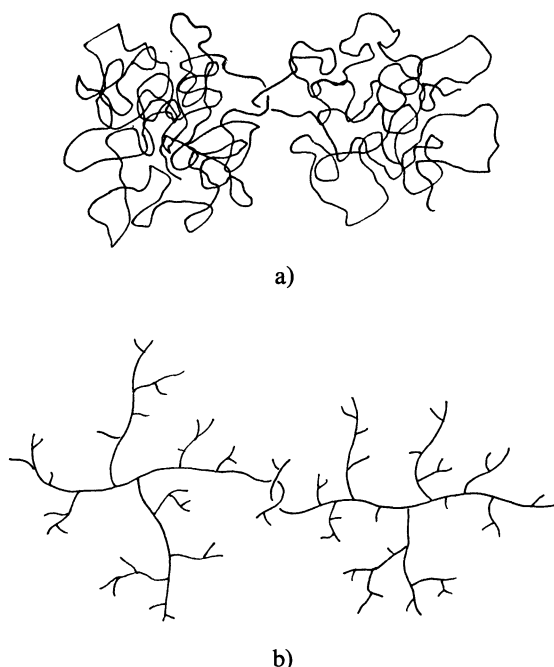


Fig. 1. — (a) An enduring entanglement between linear chains near C^* . (b) For these branched molecules, most entanglements form between side-limbs and can therefore resolve themselves on a shorter timescale than the overall chain relaxation.

In fact, even at densities so high that entanglements must dominate completely, it seems unlikely that a theoretical treatment of their effects could be developed without first understanding the underlying Rouse-Zimm dynamics. Thus the work of this paper may possibly form the starting point for a more complete theory, just as, in the case of linear chains, the Rouse equation (when combined with the tube concept) can be used as a starting point for understanding the theories of reptation [14, 15]. Reptation itself, for polymers which are branched and/or contain loops on every lengthscale, is likely to be extremely slow; even simple star-branched molecules have much reduced mobility when compared with linear chains [15]. Thus, the most likely dynamics for, say, fractal sol-molecules under melt conditions (obtained by quenching the gelation process before completion and evaporating off the solvent) could be simply a Rouse-like motion with a greatly enhanced local friction. Such a motion would result if the only available relaxation was by constraint release [15], as might apply in the presence of an (effectively infinite) hierarchy of reptation-suppressing branch points. If this supposition were to prove correct, the basic results of this paper for the Rouse-like dynamics at high density would remain applicable, but the enhanced friction would lead to a new concentration dependence for the relaxation times. Obviously, in the absence of definitive experimental information, the above remarks must be viewed as highly speculative.

2. Laplacian theory on fractals [16-19].

2.1 THE LAPLACIAN. — Our first purpose is to review some fundamental scaling ideas concerning the solution of the Laplace and Helmholtz equations on a fractal. The central point is that the scaling behaviour of several different physical quantities (related in one way or another to the Laplacian operator) can be described by the introduction of a single new parameter, namely, the spectral dimension [17]. The results will be stated in terms of the transport properties of self-similar resistor networks, but in subsequent sections we will translate these ideas into a description of polymeric fractals.

To define unambiguously the connectivity of a fractal, a short-length cutoff is required. A convenient representation of the connectivity is provided by the Alexander « wire » model [19], in which the fractal is viewed as consisting of a network of resistive wires of a suitable (self-similar) geometry. If two-fold coordinated junctions are included, the wire « bonds » can, without loss of generality, be taken of equal length. For the present, we restrict ourselves to the simplest (discrete) definition of the generalized Laplacian operator (which will be denoted by \mathcal{D}). We consider only the junction points between bonds (including those of two-fold co-ordination) and label these points by $s = s_i, s_j, s_k$, etc. Then for any function

$F(s)$, we define

$$\mathcal{D}F(s) \Big|_{s=s_i} = \sum_j (F(s_j) - F(s_i)) \quad (2.1)$$

where the sum extends only over points s_j which are joined to point s_i directly by a bond. \mathcal{D} has eigenvalues E and (real) eigenfunctions ψ_E defined by :

$$(\mathcal{D} + E) \psi_E(s) = 0. \quad (2.2)$$

The boundary condition at singly co-ordinated junction points is the vanishing of a (discretized) derivative of ψ_E .

The definition of \mathcal{D} is independent of how we arrange the network in space. However, it will be useful to describe the spatial correlations of the eigenfunctions. In order to do this, we suppose a position $\mathbf{R}(s)$ in space to be defined for every point s on the fractal. We can therefore change from arc co-ordinates, s , to spatial co-ordinates, \mathbf{r} , by defining

$$\psi_E(\mathbf{r}) = \sum_{s=s_i} \psi_E(s) \delta(\mathbf{R}(s) - \mathbf{r}). \quad (2.3)$$

It is important to realize that $\psi_E(\mathbf{r})$ exists only for spatial points \mathbf{r} which are on the fractal, and is therefore a highly singular function. Also, for a random (as opposed to deterministic [6]) fractal, $\mathbf{R}(s)$ is governed by a probability distribution; hence $\psi_E(\mathbf{r})$ is itself only defined as a statistical quantity. However, we will usually be interested in averaged products of the following type :

$$\langle \psi_E(\mathbf{r}) \psi_E(\mathbf{r}') \rangle = g(|\mathbf{r} - \mathbf{r}'|, E). \quad (2.4)$$

The average is taken over all pairs of points \mathbf{r}, \mathbf{r}' on the fractal at fixed scalar (i.e. angle-averaged) separation; this quantity is then further averaged over the distribution of $\mathbf{R}(s)$. Thus $g(r, E)$ is a smooth function for most cases of interest in this paper.

2.2 SPECTRAL DIMENSION. — The simple arguments of this section closely follow those of Alexander, Orbach [17], and Alexander [19]. We consider an arbitrary self-similar wire network of fractal dimension d_f and mass M ; its linear size, L , therefore obeys $L^{d_f} \sim M$. The aim is to find the scaling behaviour of the density of states, $N(E)$, of \mathcal{D} in terms of d_f and an exponent characterizing the diffusion of a particle on the fractal. The Green function for diffusion, $P(\mathbf{r}, \mathbf{r}', t)$, which is the probability that a diffusant particle, initially at the point \mathbf{r} , is found at the point \mathbf{r}' after a time interval t (where \mathbf{r} and \mathbf{r}' are points *on the fractal*) is given by

$$P(\mathbf{r}, \mathbf{r}', t) = \sum_E \psi_E(\mathbf{r}) \psi_E(\mathbf{r}') e^{-Et}. \quad (2.5)$$

This may be averaged to give a translation-invariant quantity, $P(r, t) = \langle P(\mathbf{0}, \mathbf{r}, t) \rangle$.

Because of dilatation symmetry, we expect $P(r, t)$ to be a homogeneous function of its arguments. Hence we write

$$P(r, t) = \xi_t^a f(r/\xi_t) \quad (2.6)$$

where a is (as yet) arbitrary, and ξ_t is a power of t :

$$\xi_t \sim t^{1/d_w}$$

(this notation will be clarified shortly). By conservation of probability,

$$\int d^{d_f} \mathbf{r} P(\mathbf{r}, \mathbf{r}', t) = 1$$

where the notation $\int d^{d_f} \mathbf{r}$ means a sum or integral over all points \mathbf{r} on the fractal. We suppose that an equivalent condition (see Sect. 2.4) is

$$\int r^{d_f-1} dr P(r, t) = \text{constant}. \quad (2.7)$$

Then dimensional analysis of condition (2.7) shows that $a = -d_f$.

Consider now the mean-square displacement of a diffusant particle at time t . Again factorizing the averages (see Sect. 2.4), we write this as

$$\langle r^2(t) \rangle \sim \int r^2 r^{d_f-1} dr P(r, t) \sim \xi_t^2.$$

Thus ξ_t is a « diffusion length ». Since $r(t)^{d_w} \sim t$, d_w is the fractal dimension of a random walk on the network (hence the notation in (2.6)). From (2.5), we can write the « diagonal » Green function, $P(\mathbf{0}, t)$, as

$$P(\mathbf{0}, t) = \left\langle \sum_E \psi_E(\mathbf{0}) \psi_E(\mathbf{0}) e^{-Et} \right\rangle.$$

We suppose this to be adequately represented by

$$P(\mathbf{0}, t) \sim \int N(E) dE e^{-Et} g(\mathbf{0}, E) \quad (2.8)$$

where $N(E)$ is a smoothed out density of states, and where, by the usual normalization requirement for the eigenfunctions,

$$g(\mathbf{0}, E) = \langle \psi_E(\mathbf{0}) \psi_E(\mathbf{0}) \rangle = M^{-1}.$$

But from (2.6), $P(\mathbf{0}, t) = \xi_t^{-d_f} \sim t^{-d_f/d_w}$. Combining these results, we find

$$t^{-d_f/d_w} \sim \int N(E) dE e^{-Et}.$$

It immediately follows that

$$N(E) \sim E^{d_w/2-1} \quad (2.9)$$

where the spectral dimension, d_s , so defined, obeys

$$d_s = 2 d_f/d_w. \tag{2.10}$$

This is the central scaling relation of Alexander and Orbach [17].

From the definition of $N(E)$ in (2.9) as a density of states, we deduce that d_s is an intrinsic parameter of the fractal connectivity, and is independent of the way in which the network is arranged in space. If as is often more convenient, one thinks in terms of a variable $q = E^{1/2}$, the density of states in q -space is given by q^{d_s-1} :

$$\sum_q () \rightarrow M \int d^q q (). \tag{2.11}$$

Thus d_s may be thought of as the anomalous (fractal) dimensionality of the set of allowed q -values.

2.3 AN EINSTEIN RELATION. — We now turn to another scaling law which relates d_w and d_f to the mean electrical resistance (allowing conduction only along the bonds) between two points on the fractal network. This will prove important because of a mapping between resistances and displacements in a polymer network.

Consider the average frequency-domain diffusion propagator $\bar{P}(r, \omega) = \langle \bar{P}(0, \mathbf{r}, \omega) \rangle$ where

$$\bar{P}(\mathbf{r}, \mathbf{r}', \omega) = \sum_E \frac{\psi_E(\mathbf{r}) \psi_E(\mathbf{r}')}{i\omega + E}. \tag{2.12}$$

Because of scale invariance, we can take $\bar{P}(r, \omega)$, like $P(r, t)$, to be a homogeneous function of its arguments. Thus

$$\bar{P}(r, \omega) \sim r^b f(r/\xi_\omega) \tag{2.13}$$

where ξ_ω is a power of ω . Subject to some assumptions about the treatment of averages (see Sect. 2.4), $\bar{P}(r, \omega)$ is, within a constant factor, the Fourier transform of $P(r, t)$. We deduce that

$$\xi_\omega \sim \omega^{-1/d_w}.$$

If we now apply the normalization condition (2.7) to the Green function in this form, we obtain

$$\int d\omega \int r^{d_f-1} dr e^{i\omega t} \bar{P}(r, \omega) = \text{const.}$$

which requires

$$d_w = d_f + b. \tag{2.14}$$

We now show that (for $b > 0$) the mean resistance, $\Omega(r)$, between points on the fractal separated by a distance r , scales as r^b . The proof is simple; suppose we inject a steady unit current into the fractal at point \mathbf{r}_1 and draw it off at \mathbf{r}_2 . Denoting the electrostatic potential by $V(\mathbf{r})$, we find, as a consequence of Kir-

choff's laws and definition (2.1).

$$\mathcal{D}V(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_1) - \delta(\mathbf{r} - \mathbf{r}_2).$$

The solution for $V(\mathbf{r})$ is then

$$V(\mathbf{r}) = \bar{P}(\mathbf{r}, \mathbf{r}_1, 0) - \bar{P}(\mathbf{r}, \mathbf{r}_2, 0).$$

The potential difference, and hence the resistance, Ω_{12} , between \mathbf{r}_1 and \mathbf{r}_2 is given by

$$\Omega_{12} \propto V(\mathbf{r}_1) - V(\mathbf{r}_2) = P_{21} - P_{22} - (P_{11} - P_{12})$$

in an obvious notation. Averaging gives

$$\begin{aligned} \Omega(|\mathbf{r}_1 - \mathbf{r}_2|) &\propto 2(\bar{P}(|\mathbf{r}_1 - \mathbf{r}_2|, 0) - \bar{P}(A, 0)) \sim \\ &\sim \text{sign}(b) \{ |\mathbf{r}_1 - \mathbf{r}_2|^b - A^b \} \end{aligned} \tag{2.15}$$

where A is a short cutoff.

Defining a resistance exponent, x , by

$$\Omega(r) = r^x \quad (r \gg A)$$

we see that $x = b$ (for $b > 0$) and $x = 0$ (for $b < 0$). We may therefore rewrite equation (2.14) as

$$d_w = d_f + x \quad (x > 0).$$

Since the value $b = 0$ corresponds to $d_s = 2$ (by substitution of $b = 0$ into (2.10) and (2.14)) an equivalent statement is

$$d_w = d_f + x \quad (d_s < 2). \tag{2.16}$$

For $d_s > 2$, b is negative, and $x = 0$. The scaling law (2.16) has been called an « Einstein relation » by some authors [20].

2.4 SOME REMARKS. — The Alexander-Orbach relation (2.10) and the Einstein relation (2.16) show that for a given d_f , the exponents d_w , d_s , and x are all fixed by choosing any one of them. Since d_s is independent of spatial configuration, it is sensible to think of it alone as the fundamental new parameter. Before proceeding to the next section, it is worth clarifying one assumption which has been made, and another which has not been used yet but which will be needed later.

(a) In a number of places above, averages have been factorized under integration :

$$\int \langle AB \rangle dr \propto \int \langle A \rangle \langle B \rangle dr. \tag{2.17}$$

In equation (2.7), for example, « A » denotes a singular function of \mathbf{r} , describing the precise arrangement of the fractal in space (so $A dr = d^{d_f} \mathbf{r}$) and « B » is the Green function. The dimensionless factor, $f(r/\xi_t)$, in (2.6) is assumed to make the resulting integral converge, thereby allowing its behaviour to be determined by dimensional analysis.

To see how this assumption sometimes needs more careful attention, we consider the example of an ideal polymer chain ($d_s = 1$, $d_t = 2$) for which (recalling that conduction is defined to occur only along the bonds)

$$\Omega(r) \sim \int_0^M s^{1-d/2} \exp(-r^2/2s) ds.$$

For $d < 4$, and $r \ll L (= M^{1/2})$, $\Omega(r)$ varies like $M^{2-d/2}$ (rather than as any power of r). This is as a result of the large fluctuations present in the ensemble. However we can still define a resistance exponent, x , by

$$\langle \Omega_{12}^m \rangle^{1/m} \sim r_{12}^x \quad (2.18)$$

where $m < 0$ is chosen so as to make the average independent of M . We find, not surprisingly, that $x = 2$. It is also simple to show that d_w exists and is 4. Hence (2.10) holds, and (2.16) is also correct so long as $\Omega(|\mathbf{r}_1 - \mathbf{r}_2|)$ is interpreted as being defined by (2.18). Note that $\bar{P}(r, \omega)$ must be subjected to a similar redefinition before it can be written in the homogeneous form (2.13).

This example suggests that results (2.10) and (2.16) should still apply even when a simple factoring of averages as in (2.17) leads formally to cutoff- or mass-dependent integrals ⁽¹⁾.

(b) So far we have not assumed a particular scaling form for the correlation function $g(r, E) = \langle \psi_E(\mathbf{0}) \psi_E(\mathbf{r}) \rangle$. However in all cases of interest, it seems very probable that this may be written

$$g(r, E) \sim M^{-1} f(r/\xi_E) \quad (2.19)$$

where ξ_E is a power of E , and $f(0) = 1$. The factor M^{-1} arises from equation (2.4) which also precludes any power law prefactor in (2.19). If by analogy with

⁽¹⁾ A heuristic justification is as follows : Suppose we know, on physical grounds, that the integral on the left in (2.17) exists. For our results to be meaningful, the scaling behaviour must be independent of the precise way in which the averages are taken. We can therefore use an approximation of the form

$$\int \langle AB \rangle dr \sim \int \langle A^n \rangle^{1/n} \langle B^m \rangle^{1/m} dr$$

with equal validity for any values of n , m , for which the right-hand side exists (and is independent of M); the answer should be the same for all such values. If the integral does not exist for the case $n = m = 1$ (as it was assumed to do in sections 2.2, 2.3) it is sensible to choose other values for which it does. The only change to the previous results is that certain exponents must be redefined by equations like (2.18).

(2.8), we write (for r nonzero)

$$P(r, t) \sim \int N(E) dE e^{-Et} g(r, E) \quad (2.20)$$

then the form (2.19) is indeed implied, with

$$\xi_E \sim E^{-1/d_w}. \quad (2.21)$$

Equations (2.19-2.21) will be assumed in sections 4 and 5.

3. Physics of polymeric fractals : statics.

3.1 CO-ORDINATE SYSTEMS FOR FRACTAL POLYMERS [10].

— Here and in section 4, the idea of spectral dimension is used to discuss the physics of polymeric macromolecules of arbitrary self-similar connectivity. To start with, we concentrate on the distribution of static configurations for such a molecule in the absence of excluded volume. Excluded volume effects are then treated at the level of Flory theory.

Throughout, we will be interested in the behaviour of an ensemble of self-similar molecules at constant connectivity distribution (CCD). This is an extension of the configuration ensemble for a single specified polymer network; the essential requirement is that d_s is well-defined and invariant as an ensemble property. This is not the case in an ensemble of, say, branched polymers at fixed loop fugacity, where the distribution of network topologies, and hence d_s , varies with the interaction parameters (including, for example, the value of d).

The CCD ensemble is the appropriate one with which to examine the swelling behaviour of, for example, a branched polymer when the solvent quality is varied after the polymer has been made. It therefore complements the fixed fugacity ensemble, with which one can examine the behaviour as a function of the conditions prevailing when the network was formed. In general one expects the CCD results to be different from those at fixed fugacity; however the differences are not detectable at the level of Flory theory. If, as assumed in this paper, our fractal macromolecules form irreversibly (i.e., the lifetime of an association or cross-link is much greater than experimental timescales), then the CCD ensemble is the one appropriate for the study of dynamics.

We will require a set of co-ordinates with which to describe the configuration of a random fractal macromolecule. At the most fundamental level, these co-ordinates have already been introduced in section 2.1 : they are merely the labels $s = s_i, s_j, s_k$. Although this definition is in fact sufficient for the work of subsequent sections, it is rather abstract; it provides, for example, no concept of a distance function in the space of network co-ordinates.

To help get a more intuitive picture of what is going on, we can imagine « laying out » an arbitrary fractal network, say for simplicity on a discrete

lattice, in such a way that its connectivity is clearly defined. We can then specify a mapping between points on this network, and the positions in space of points on a macromolecule of the same connectivity. By taking this step, the new co-ordinates emerge more clearly as the natural generalization of the single arc parameter, s , with which an ordinary linear polymer is described by a curve $\mathbf{R}(s)$.

Consider, then, a lattice S of arbitrary dimensionality on which is inscribed some arbitrary connected « lattice-fractal » $\{s_i\}$. That is, we take every site in the set $\{s_i\}$ to be adjacent to at least one other, and the set to be self-similar on any length-scale much larger than a lattice spacing and much smaller than its linear size, L_0 , in S -space. Let every adjacent pair of sites be joined by a single bond, and define a set $\{s\}$ which includes $\{s_i\}$ and also co-ordinates, s , for all the points along each bond. We denote the fractal dimension in S -space by d_{f0} and the mass, or total number of elements in $\{s_i\}$, by M ; then $M \sim L_0^{d_{f0}}$.

Suppose a co-ordinate $s(t)$, describing the position in S -space, at time t , of a particle executing a random walk on the network, obeys

$$\langle |s(t) - s(0)|^2 \rangle \sim t^{2/d_{w0}}.$$

Then the spectral dimension, d_s , is defined by equation (2.10) :

$$d_s = 2 d_{f0}/d_{w0}. \quad (3.1)$$

Note that $d_s \geq 1$, because the set s_i is connected. For the moment, we insist that $d_s < 2$. The resistance exponent, x_0 , is defined by

$$\langle \Omega_{ij}^m \rangle \sim |s_i - s_j|^{mx_0}.$$

Here Ω_{ij}^m is the resistance between sites s_i and s_j , allowing conduction only along the bonds; m is chosen so that the moment exists as $L_0 \rightarrow \infty$. For $d_s < 2$, the Einstein relation (Eq. (2.16)) is obeyed :

$$d_{w0} = d_{f0} + x_0 \quad (3.2)$$

and hence

$$d_s = 2 d_{f0}/(d_{f0} + x_0). \quad (3.3)$$

We now imagine replacing every bond in the fractal by an identical section of ideal phantom polymer chain; the « occupied » sites $\{s_i\}$ are chain ends, connectors, or cross-links according to co-ordination number (1, 2, or > 2 , respectively). Note that even a single bond corresponds to a long, flexible piece of polymer — there is no rigidity in the structure. This procedure generates, in an intuitively direct way, a polymeric macromolecule of some chosen connectivity (or ensemble of connectivities), together with a natural (inbuilt) set of co-ordinate labels, $\{s\}$. The values of d_{w0} , d_{f0} , and x_0 depend on how we

chose to lay out the network in S -space; the connectivity is characterized by the spectral dimension, d_s , which does not.

Next we embed the macromolecule in a Euclidian space of dimension d , and consider it in an appropriate thermal ensemble (in the presence of excluded volume forces, if required). For each member of the ensemble, a position \mathbf{R} in Euclidian space is specified for every member of the set $\{s\}$. The resulting functional probability distribution, $P[\mathbf{R}(s)]$, describes a new random fractal, $\mathbf{R}(s)$, which can be called a « polymeric fractal ». Formally, we should consider $P[\mathbf{R}(s)]$ as conditional on a distribution, $P[\{s_i\}]$, for the network itself. However, at the level of scaling arguments, we need consider only one network of a « typical » character.

3.2 IDEAL CHAIN DIMENSIONS AND THE FLORY THEORY.

— In general, $\mathbf{R}(s)$ will have a new size, L , and new exponents d_f , d_w , and x . There will usually be new contacts (multiple-points) which are not cross-linked. For the purposes of defining d_w and x , it is important to remember that these accidental contacts are insulating, a random walker cannot jump across at them. Subject to this definition, the spectral dimension is configuration invariant. The new d_f and x therefore obey $d_s = 2 d_f/d_w$, where $d_w = d_f + x$; hence

$$d_f = d_s x/(2 - d_s). \quad (3.4)$$

We first consider the « ideal » behaviour, i.e. that in the absence of any excluded volume forces. In this case there is an exact relation between resistance and separation :

$$\langle (\mathbf{R}(s_i) - \mathbf{R}(s_j))^2 \rangle \sim \Omega_{ij}, \quad (3.5)$$

and therefore

$$x = 2 \quad (\text{for ideal phantoms}). \quad (3.6)$$

Results (3.5) and (3.6), which are obvious for trees, also apply when loops are present, in the ideal phantom limit. The reason is simply the well-known correspondence between a Gaussian polymer network and a network of « thermal springs » (see Eq. (4.8) below). Equation (3.6) is therefore an identity characterizing the ideal state. The « Gaussian » fractal dimension, d_{fg} , is thus given by

$$d_{fg} = 2 d_s(2 - d_s). \quad (3.7)$$

This result is of central importance. For example, it allows one to construct a Flory theory of excluded volume for arbitrary polymeric fractals. Suppose we take a fractal of some d_s and « ideal » size L . The Flory free energy in the presence of an n -body repulsion is given as a function of the swollen size, L' , by

$$F(L') = (L'/L)^2 + M^n L'^{(1-n)d}. \quad (3.8)$$

The normal choice of n is, of course, $n = 2$. Minimization now yields a swollen fractal dimension, d'_f , which may be expressed in terms of d_s as :

$$d'_f = d_s[(n-1)d + 2]/[(n-1)d_s + 2], \quad (3.9)$$

a result which has been discussed elsewhere [10].

Finally, we consider the problem of a polymeric fractal with $d_s \geq 2$. As d_s approaches 2 from below, d'_{fg} diverges but d'_f tends to a finite limit. Thus the Flory theory gives a definite prediction for d'_f in the case of a membrane ($d_s = 2$). Naively, for $d_s > 2$, one might remark that d'_f in (3.9) above still exists. However, the Einstein relation in the form (3.2) which was used to derive (3.9) no longer applies, and so the Flory formula (3.9) becomes meaningless for $d_s > 2$. In the absence of excluded volume, equations (3.5) and (2.15-2.16) in fact predict that for $d_s > 2$

$$\langle (\mathbf{R}(s_i) - \mathbf{R}(s_j))^2 \rangle \sim \Omega_{ij} \sim \Lambda^b \quad (\text{all } i, j)$$

where Λ^b can be identified with the mean-square length of a *single* polymeric « bond ». Thus the radius of the ideal molecule should saturate as its mass increases. The most probable effect of an excluded volume interaction in such a case is to replace the saturating radius with a saturating density (i.e., to give $d'_f = d$).

4. Dynamics of polymeric fractals.

4.1 A ROUSE MODEL. — The simplest dynamical theory of a linear polymer is provided by the Rouse model [1, 11, 12]. We are now in a position to generalize this model to the case of polymeric fractals with $1 < d_s < 2$. First, though, we assemble some of the results of previous sections which are needed here. Recall the definition (2.1) of \mathcal{D} on $\{s_i\}$. An alternative, continuous, definition of \mathcal{D} is possible on $\{s\}$:

$$\mathcal{D} = \partial/\partial s \kappa \partial/\partial s \quad (4.1)$$

where $\partial/\partial s$ is a local gradient along a bond and κ represents a « connectivity operator ». Using this form of \mathcal{D} we can define the eigenfunctions $\psi_E(s)$ everywhere on $\{s\}$. In continuous notation, the co-ordinate transformation (2.3) becomes

$$\psi_E(\mathbf{r}) = \int d^{d_{ro} s} \psi_E(s) \delta(\mathbf{R}(s) - \mathbf{r}) \quad (4.2)$$

where $\int d^{d_{ro} s}$ means an integral over s in $\{s\}$.

A further assumption which will be required is that discussed in section 2.4 :

$$\langle \psi_E(\mathbf{0}) \psi_E(\mathbf{r}) \rangle = g(r, E) = M^{-1} f(r/\xi_E) \quad (2.19)$$

where we recall

$$\xi_E = E^{-1/d_w}. \quad (2.21)$$

Recall also that for ideal phantoms, from (2.10), (2.16) and (3.7),

$$d_s = 2 d_f/d_w \quad \text{where} \quad d_w = d_f + 2. \quad (4.3)$$

We will also need to use the results that $\psi_0(\mathbf{r}) = M^{-1/2}$ and (for $E > 0$)

$$\int d^{d_r} \mathbf{r} \psi_E(\mathbf{r}) = 0 \quad (4.4)$$

which follows by orthogonality.

These definitions and scaling relations are important in the context of polymer dynamics because the operator \mathcal{D} controls the thermodynamic force on a member $\mathbf{R}(s)$ in the thermal ensemble, $P[\mathbf{R}(s)]$, appropriate to ideal phantom fractals. The spectral dimension, d_s , determines the density of states in q -space and in this particular problem the q -space is simply *Rouse-mode space*.

To see this, we expand $\mathbf{R}(s)$ in terms of the eigenfunctions, ψ_E :

$$\mathbf{R}(s) = \sum_E \psi_E(s) \mathbf{R}_E.$$

Then, for $P[\mathbf{R}(s)]$, postulate (see below) :

$$P[\mathbf{R}(s)] \propto \exp\left(\int d^{d_{ro} s} \mathbf{R}(s) \mathcal{D}\mathbf{R}(s)\right) \propto \exp\left(-\sum_E |\mathbf{R}_E|^2 E\right). \quad (4.5)$$

The thermodynamic force is therefore

$$-\frac{\delta}{\delta[\mathbf{R}(s)]} \{\ln P[\mathbf{R}(s)]\} = \mathcal{D}\mathbf{R}(s). \quad (4.6)$$

(The units in (4.5) and (4.6) are chosen to absorb various factors ⁽²⁾.)

To write equations (4.5) and (4.6) in the order given above is perhaps a little misleading. In fact equation (4.6) may more conveniently be derived directly — e.g. from the « bead-spring » model. If one places beads at the intersections $\{s_i\}$, the resulting

⁽²⁾ A factor of $1/l$ (where l is a short cutoff length) which one might expect to find in the exponential in (4.5) has been eliminated by taking the Brownian limit [34]; this amounts to an adsorption of l into the measure of s , with a corresponding redefinition of M . Since we can only hope to find results to within arbitrary numerical factors, this is permitted. In (4.6) a factor $k_B T$ is set equal to unity; again, since we cannot calculate prefactors, this does not lose generality. The temperature dependence of the resulting viscosity spectra is obtainable by time-temperature superposition (see Refs. [11, 12]).

force on any given bead s_i is given by

$$F(s_i) = \sum_j [\mathbf{R}(s_j) - \mathbf{R}(s_i)] = \mathcal{D}\mathbf{R}(s) |_{s=s_i}. \quad (4.7)$$

But the correspondence between a network of springs (with mean length zero) and a network of ideal phantom polymer chains is an exact one, in the following sense :

$$\int P[\mathbf{R}(s)] \delta(\mathbf{R}(s_i) - \mathbf{R}(s_j) - \mathbf{r}) \equiv (2\pi\Omega_{ij})^{-d/2} e^{-r^2/2\Omega_{ij}} \quad (4.8)$$

(with similar expressions for higher point functions). It is this that allows us to deduce the form of P given in equation (4.5), and also allows us to write $x = 2$ (Eq. (3.6)) as a rigorous result.

Using (4.6), we finally make contact with the dynamical motion, $\mathbf{R}(s, t)$ of the polymeric fractal. For a simple linear chain, the simplest possible Langevin equation is the Rouse equation [1, 11, 12]

$$(\partial/\partial t - \mu\partial^2/\partial s^2) \mathbf{R}(s, t) = \text{random force}. \quad (4.9)$$

Here μ is a phenomenological mobility coefficient. For an arbitrary polymeric fractal this becomes simply

$$(\partial/\partial t - \mu\mathcal{D}) \mathbf{R}(s, t) = \text{random force} \quad (4.10)$$

which can of course be thought of as coming directly from (4.7) in the bead spring model. The corresponding relaxation spectrum for the increment of viscosity, $\delta\eta(\omega)$, contributed by such a fractal would be (setting $\mu = 1$)

$$\delta\eta(\omega) = \sum_{E>0} \frac{1}{i\omega + E}. \quad (4.11)$$

However, this may be written

$$\delta\eta(\omega) \sim \int_{E_0} \frac{N(E) dE}{i\omega + E} \quad (4.12)$$

where $N(E) = ME^{d_s/2-1}$. Note that because of equation (2.21), the lowest nonzero eigenvalue, E_0 , is given by

$$E_0 = L^{-d_w}. \quad (4.13)$$

As an alternative to (4.12) one can use q (the generalized Rouse-mode index) as the variable and write

$$\delta\eta(\omega) \sim M \int_{L^{-d_w/2}} \frac{q^{d_s-1} dq}{i\omega + q^2}. \quad (4.14)$$

But d_s and d_w are related by equation (4.3). Substituting in (4.14) and setting $\omega = 0$, we see that the zero frequency viscosity, $\delta\eta(0)$, is proportional to

$$ML^{-(d_s-2)d_w/2} = ML^2.$$

Also, by taking the opposite limit, we find that

$$\delta\eta(\omega) \sim (i\omega)^{d_s/2-1}$$

is the asymptote at high frequency.

In fact, for the hydrodynamic theory, described in the next two sections, there is no need for a phenomenological equation such as (4.10); when hydrodynamic interactions are properly treated the frictional drag arises through coupling to the solvent and is not required in the « bare » dynamical equations (unless one wishes to model internal friction effects at very high frequency (3)). Nonetheless, as is well known in the case of linear polymers, the Rouse-like spectrum (4.14) does occur at high concentrations (as a result of hydrodynamic screening) but with a concentration-dependent friction coefficient. At low concentrations hydrodynamics dominates and the spectrum is different.

These remarks apply when $d < d_f + 2$. For higher values of d , the hydrodynamic interaction between different points on the fractal is short-range divergent and (4.14) will result at all concentrations. The mobility, μ , is then dependent on a short cutoff and not on concentration. (For $d = d_f + 2$ there are liable to be logarithmic corrections.)

4.2 POLYMERIC FRACTALS IN SOLUTION. — The formalism introduced here is based on that of Freed and Edwards for solutions of linear polymers [7-9], but is kept to a simpler level. We start initially with a dilute solution theory, and then, in the next section, introduce the effective medium approximation for higher concentrations. The original effective medium theory, and the multiple-scattering analysis by which it was derived, have subsequently been developed to a high level of sophistication by Freed and co-workers [7, 21-24]. Here though, because the whole treatment rests on a scaling description of network correlations (in which all numerical factors are unspecified) it is appropriate to start with the simplest formulation able to give us the right qualitative behaviour.

The model considered is that of a system of completely flexible (see Note (3)), ideal phantom polymeric fractals, coupled to an incompressible thermal fluid by a no-slip (Stokes) boundary condition. The Reynolds number is taken to be low, and for simplicity, the effects of inertia (that of the fluid, and that of the

(3) An internal « hopping » dynamics (see Refs. [7-9]) can be incorporated into the effective medium theory without difficulty, by the replacement

$$\mathcal{D} \rightarrow \mathcal{D} + i\omega\tau$$

in the polymer dynamical equation. This gives a finite real viscosity at high frequency; (4.34) becomes

$$\Sigma(\mathbf{k}, \omega) \propto n\eta \sum_{E>0} \frac{(i\omega\tau + E) \langle \psi_E \psi_E \rangle_{\mathbf{k}}}{i\omega\eta + (i\omega\tau + E) \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle}.$$

suspended fractals) are ignored. These are standard approximations in polymer solution theory. In order to expose the structure of the theory, d is left unspecified (but we in fact require $d > 2$). For simplicity also, a monodisperse solution is studied, but in section 7 the results will be extended to cover an arbitrary molecular weight distribution.

The first aim is to use a Kirkwood-Riseman or pre-averaging approximation to express the viscosity increment of a dilute solution of fractal molecules in terms of the static correlation functions, $g(r, E)$, introduced in section 2.1. We consider initially the response of the fluid (in the absence of any molecules) to an applied force, \mathbf{F} . The velocity response, \mathbf{u} , is given by

$$\mathbf{u}(\mathbf{r}) = \int d^d \mathbf{r}' \mathbf{G}_0(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{F}(\mathbf{r}')$$

or, in a more abstract notation

$$\mathbf{u} = \mathbf{G}_0 \cdot \mathbf{F} \quad (4.15)$$

where \mathbf{r} integrals are incorporated into the dot. The « bare » Green function, \mathbf{G}_0 , is given in Fourier transform by

$$\mathbf{G}_0(\mathbf{k}) = (\eta k^2)^{-1} (\mathbf{1} - \mathbf{k}\mathbf{k}/k^2) \quad (4.16)$$

or in real space by

$$\mathbf{G}_0(\mathbf{r}) \propto \eta^{-1} r^{2-d} (\mathbf{1} + \mathbf{r}\mathbf{r}/r^2). \quad (4.17)$$

There is no frequency dependence in \mathbf{G}_0 because fluid inertia is neglected; the transverse (Oseen) projection operator, $\mathbf{1} - \mathbf{k}\mathbf{k}/k^2$, accounts for the fact that the fluid is incompressible.

Now suppose we introduce a single polymeric fractal, $\mathbf{R}(s)$, coupled to the solvent *via* the no-slip boundary condition

$$\dot{\mathbf{R}}(s) = \mathbf{u}(\mathbf{R}(s))$$

which may be written as

$$\dot{\mathbf{R}}(s) = \int d^d \mathbf{r} \delta(\mathbf{R}(s) - \mathbf{r}) \mathbf{u}(\mathbf{r}) \quad (4.18)$$

or, in terms of the functions $\psi_E(\mathbf{r})$,

$$\dot{\mathbf{R}}_E = \psi_E \cdot \mathbf{u}. \quad (4.19)$$

Rather than consider the Brownian motion of the fractal explicitly [7-9], we now simply balance the thermodynamic and solvent forces on it at every point. The effect of this is to introduce an extra reaction force on the fluid, $\sigma(\mathbf{r})$, where

$$\begin{aligned} \sigma(\mathbf{r}) &= \int d^d r_s \delta(\mathbf{R}(s) - \mathbf{r}) \mathcal{D}\mathbf{R}(s) \\ &= \sum_E \psi_E \mathcal{D}\mathbf{R}_E = - \sum_E \psi_E E \mathbf{R}_E. \end{aligned} \quad (4.20)$$

If we include this extra force in (4.16), the response \mathbf{u} becomes

$$\mathbf{u} = \mathbf{G}_0 \cdot \mathbf{F} + \mathbf{G}_0 \cdot \sum_E \psi_E \mathcal{D}\mathbf{R}_E. \quad (4.21)$$

Now multiplying both sides by $\psi_{E'}$ and using (4.19) gives

$$\dot{\mathbf{R}}_{E'} = \psi_{E'} \cdot \mathbf{G}_0 \cdot \mathbf{F} + \psi_{E'} \cdot \mathbf{G}_0 \cdot \sum_E \psi_E \mathcal{D}\mathbf{R}_E. \quad (4.22)$$

This can now be averaged over configuration to obtain

$$\dot{\mathbf{R}}_E = \psi_E \cdot \mathbf{G}_0 \cdot \mathbf{F} + \langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle \mathcal{D}\mathbf{R}_E \quad (4.23)$$

where off-diagonal couplings (i.e., $\langle \psi_{E'} \cdot \mathbf{G}_0 \cdot \psi_E \rangle$ for $E \neq E'$) have been neglected. We now introduce a Green function, \mathcal{G}_E , to describe the (pre-averaged) fractal dynamics. This is defined by

$$(i\omega - \langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle \mathcal{D}) \mathcal{G}_E = \mathbf{1} \quad (4.24)$$

where, after averaging, $\langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle$ is isotropic (scalar) so we have, using (4.20) and (4.24) in (4.21),

$$\mathbf{R}_E = \mathcal{G}_E \psi_E \cdot \mathbf{G}_0 \cdot \mathbf{F}. \quad (4.25)$$

By substituting (4.25) in (4.21), and then averaging, we see that the ensemble average response, $\langle \mathbf{u} \rangle$, to the applied force \mathbf{F} is given by

$$\langle \mathbf{u} \rangle = \mathbf{G}_0 \cdot \mathbf{F} + \left\langle \mathbf{G}_0 \cdot \sum_E \psi_E \mathcal{D}\mathcal{G}_E \psi_E \cdot \mathbf{G}_0 \cdot \mathbf{F} \right\rangle \quad (4.26)$$

or

$$\langle \mathbf{u} \rangle = [\mathbf{G}_0 - \mathbf{G}_0 \cdot \langle \mathbf{T} \rangle \cdot \mathbf{G}_0] \cdot \mathbf{F} \quad (4.27)$$

where

$$\begin{aligned} \langle \mathbf{T}(\mathbf{r}, \mathbf{r}') \rangle &= - \mathbf{1} \sum_E \langle \psi_E(\mathbf{r}) \mathcal{D}\mathcal{G}_E \psi_E(\mathbf{r}') \rangle \\ &= \mathbf{1} \sum_E \frac{E \langle \psi_E(\mathbf{r}) \psi_E(\mathbf{r}') \rangle}{i\omega + \langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle E}. \end{aligned} \quad (4.28)$$

The central steps in obtaining this result are the pre-averaging, and the neglect of off-diagonal coupling, in (4.23) and (4.24).

Suppose now we have a number density n of fractals in dilute solution. If the concentration is low, we may treat the scattering kernels, \mathbf{T} , from different fractals as uncorrelated. Then (4.27) becomes

$$\begin{aligned} \langle \mathbf{u} \rangle &= [\mathbf{G}_0 - n \mathbf{G}_0 \cdot \langle \mathbf{T} \rangle \cdot \mathbf{G}_0 + \\ &+ n^2 \mathbf{G}_0 \cdot \langle \mathbf{T} \rangle \cdot \mathbf{G}_0 \cdot \langle \mathbf{T} \rangle \cdot \mathbf{G}_0 - \dots] \cdot \mathbf{F} \end{aligned} \quad (4.29)$$

or $\langle \mathbf{u} \rangle = \mathbf{G} \cdot \mathbf{F}$, where the effective fluid Green function \mathbf{G} obeys

$$\mathbf{G}^{-1}(\mathbf{k}, \omega) = \mathbf{G}_0^{-1}(\mathbf{k}) + n \langle \mathbf{T}(\mathbf{k}, \omega) \rangle. \quad (4.30)$$

Comparison with (4.16) and (4.17) shows that this describes a fluid of viscosity $\eta'(\omega) = \eta + \delta\eta(\omega)$, where

$$\begin{aligned} \delta\eta(\omega) &= k^{-2} n \langle \mathbf{T}(\mathbf{k}, \omega) \rangle \\ &= k^{-2} n \sum_E \frac{E \langle \psi_E \psi_E \rangle_k}{i\omega + \langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle E} \end{aligned} \quad (4.31)$$

with

$$\langle \psi_E \psi_E \rangle_k = \left\langle \int d^d \mathbf{r} d^d \mathbf{r}' \psi_E(\mathbf{r}) \psi_E(\mathbf{r}') e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \right\rangle$$

and

$$\begin{aligned} \langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle &= \\ &= \left\langle \int d^d \mathbf{r} d^d \mathbf{r}' \psi_E(\mathbf{r}) \psi_E(\mathbf{r}') \mathbf{G}_0(\mathbf{r} - \mathbf{r}') \right\rangle. \end{aligned}$$

Rather than evaluate (4.31) immediately, we first see how it is modified at higher concentration.

4.3 EFFECTIVE MEDIUM THEORY. — The dilute solution theory may now be extended to high concentration by incorporating the effects of hydrodynamic screening in a self-consistent approximation scheme. Suppose we have a solution of (ideal phantom) polymeric fractals of mass M and linear size L at number-density n . The monomer concentration, c , is defined by $c = nM$.

We expect the generalization of (4.30) at arbitrary c to be

$$\mathbf{G}^{-1}(\mathbf{k}, \omega) = \mathbf{G}_0^{-1}(\mathbf{k}) + \Sigma(\mathbf{k}, \omega). \quad (4.32)$$

The idea of effective medium theory is to suppose that $\mathbf{G}(\mathbf{k})$ describes a medium which has enhanced viscosity, $\eta + \delta\eta(\omega)$, at low k , but which may have screening properties,

$$\Sigma \sim \text{const.} \sim \eta \xi_H^{-2}$$

at high k . A single typical macromolecule is thought of as embedded in this medium and the contribution it makes to $\Sigma(\mathbf{k}, \omega)$ is calculated. By adding up the contributions from all the fractals, one can work out Σ self-consistently.

The presence of screening can be understood as follows. At very short distances, the real-space hydrodynamic propagator, $\mathbf{G}(\mathbf{r})$ must have its unperturbed value

$$\mathbf{G}(\mathbf{r}) \sim \mathbf{G}_0(\mathbf{r}) \sim \eta^{-1} r^{2-d} \quad (d > 2).$$

This is because a sufficiently small volume almost always has no polymer in it. However, at very large distances, there must be a response appropriate to the macroscopic solution behaviour :

$$\mathbf{G}(\mathbf{r}) \sim \eta'^{-1} r^{2-d}.$$

If, as one expects in concentrated systems, $\eta' \gg \eta$, then these behaviours are incompatible unless $\mathbf{G}(\mathbf{r})$ falls dramatically at intermediate r . A reasonable guess is the form

$$\mathbf{G}(\mathbf{r}) \sim \eta^{-1} r^{2-d} e^{-r/\xi_H}$$

and (less obviously) this turns out to be self-consistent for a monodisperse solution. (Note that in the presence of polydispersity this need not be the case; see Sect. 7.) The screening form only applies at intermediate lengthscales; there is no constant part to Σ as $k \rightarrow 0$. This is obvious if the solution is to be a liquid (i.e., to obey the Stokes equation) on a macroscopic lengthscale.

The formal adoption of the EM approximation is very simple; we merely replace \mathbf{G}_0 by \mathbf{G} in the defining equation (4.24) of \mathcal{G}_E :

$$(i\omega - \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \mathcal{D}) \mathcal{G}_E = 1.$$

Each macromolecule is now coupled to the final, effective, medium. The dilute limit ($\mathbf{G} \rightarrow \mathbf{G}_0$) is included as a special case.

The effective dynamical equation for $\mathbf{R}(s)$ is now

$$(\partial/\partial t + \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle E) \mathbf{R}_E = \psi_E \cdot \mathbf{G} \cdot \mathbf{F} \quad (4.33)$$

where, for equilibrium to be maintained, \mathbf{F} must include a thermal (random) component. Equation (4.33) is the starting point for any discussion of the dynamics of entropic fractals in solution. In the calculation of the viscosity, however, one wishes to eliminate the motion of the fractals to obtain the average response of the macroscopic medium. This may be done in an identical manner to that described in section 4.2. The resulting expression for $\Sigma(\mathbf{k}, \omega)$ is

$$\Sigma(\mathbf{k}, \omega) = n \sum_{E>0} \frac{E \langle \psi_E \psi_E \rangle_k}{i\omega + \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle E}. \quad (4.34)$$

The various formulae collected in section 4.1 permit evaluation of this expression (to within numerical factors) at high and low k , and for both dilute and concentrated regimes.

4.4 RESULTS FOR THE DYNAMICS. — First note some relevant properties of the integrals in (4.34). For k large,

$$\langle \psi_E \psi_E \rangle_k \sim \int d^d \mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} g(r, E) \sim k^{-d} f(k\xi_E).$$

For k small, we expand

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r})^2 \dots,$$

so

$$\langle \psi_E \psi_E \rangle_k \sim \int d^{d_f} \mathbf{r} k^2 r^2 g(r, E) \sim k^2 \xi_E^{d_f+2}.$$

(The constant term vanishes by (4.4) and the k term by symmetry.) For a hydrodynamic screening length ξ_H ,

$$\begin{aligned} \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle &\sim \eta^{-1} M \int e^{-r/\xi_H} g(r, E) r^{2-d} d^{d_f} \mathbf{r} \simeq \\ &\simeq \eta^{-1} [\inf(\xi_E, \xi_H)]^{d_f+2-d} \end{aligned} \quad (4.35)$$

where the right-hand side requires $d < d_f + 2$ to be convergent near $r = 0$. Using these relations, the following results may be obtained; they may easily be checked for self-consistency. Detailed discussion is postponed to section 6.

(i) For k large, $\Sigma(\mathbf{k}, \omega) \sim \eta \xi_H^{-2}$, where the hydrodynamic screening length, ξ_H , is given by

$$\xi_H^{d_f-d} \propto c. \quad (4.36)$$

This expression is self-consistent at high c (i.e., for $\xi_H \ll L$).

(ii) For $\xi_H \gg L$, the suspension is dilute. The viscosity increment

$$\delta \eta(\omega) = \lim_{k \rightarrow 0} [k^{-2} \Sigma(k, \omega)]$$

is given by

$$\delta \eta(\omega) \sim n \eta \sum_{E > 0} \frac{\xi_E^{d_f+2} E}{i\omega \eta + \xi_E^{d_f+2-d} E}. \quad (4.37)$$

This may conveniently be rewritten as a q -integral :

$$\delta \eta(\omega) \sim c \eta a \int_{L^{-d_w/2}} \frac{q^{d_a-1} dq}{i\omega \eta + b q^{2d/(d_f+2)}} \quad (4.38)$$

with a and b unknown numerical factors (which are from now on suppressed) and where (4.13) has been used to fix the lower limit. (Note that because of scaling relations (4.3), there is only one free variable amongst d_f , d_w and d_s .) This is a generalization of the well-known Zimm spectrum (with dominant hydrodynamic interaction) for the linear chain. The limiting behaviour for $\omega = 0$ is

$$\delta \eta(0) \sim \eta n L^d \quad (4.39)$$

and for high frequencies, i.e. $\eta \omega \gg L^{-d}$,

$$\delta \eta(\omega) \sim \eta c (i\omega \eta)^{d_f/d-1}. \quad (4.40)$$

(iii) For $\xi_H \ll L$, the hydrodynamics are screened. In this limit,

$$\delta \eta(\omega) \sim n \eta \sum_{E > 0} \frac{\xi_E^{d_f+2} E}{i\omega \eta + \xi_H^{d_f+2-d} E} \quad (4.41)$$

which may be rewritten using the scaling relations as

$$\delta \eta(\omega) \sim c \eta \int_{L^{-d_w/2}} \frac{q^{d_a-1} dq}{i\omega \eta + c^{1+2/(d_f-d)} q^2}. \quad (4.42)$$

This is the generalization of the Rouse-like spectrum to arbitrary polymeric fractals. The limiting forms are as follows :

$$\delta \eta(0) \sim \eta c^{2/(d-d_f)} L^2 \quad (4.43)$$

and for high ω ,

$$\delta \eta(\omega) \sim \eta c^{-2d/[(d_f+2)(d_f-d)]} (i\omega \eta)^{-2/(d_f+2)}. \quad (4.44)$$

Above we have concentrated on calculating the effective medium propagator, \mathbf{G} . Having done this, we may substitute (4.35) and (4.36) in (4.33). We then find that the effective Langevin equation (4.33), for the fractal dynamics, has the following behaviour :

At low c , the hydrodynamic coupling,

$$\langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle,$$

is given by

$$\langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle \sim \xi_E^{d_f+2-d} \sim E^{d/d_w-1}$$

and so (4.33) becomes

$$(\partial/\partial t + E^{d/d_w}) \mathbf{R}_E = \psi_E \cdot \mathbf{G}_0 \cdot \mathbf{F} \quad (4.45)$$

which is a generalized Zimm equation. At high c , the coupling is a constant :

$$\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \sim \xi_H^{d_f+2-d} \sim c^{1+2/(d_f-d)}.$$

This form arises because, in the presence of screening the effective hydrodynamic interaction is a local friction. Hence (4.33) reduces to

$$(\partial/\partial t + \mu(c) E) \mathbf{R}_E = \psi_E \cdot \mathbf{G} \cdot \mathbf{F} \quad (4.46)$$

which is a form of the Rouse equation (cf. Eq. (4.10)), but with a concentration-dependent mobility,

$$\mu(c) = c^{1+2/(d_f-d)}.$$

At intermediate c there is, as E increases, a crossover (at $\xi_E = \xi_H$) from Rouse-like to Zimm-like coupling.

The Brownian dynamics of a single macromolecule may be studied directly *via* the effective Langevin equations (4.45) and (4.46), or alternatively through the functional diffusion equation

$$\left[\frac{\partial}{\partial t} - \sum_E \frac{\partial}{\partial \mathbf{R}_E} \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \left(\frac{\partial}{\partial \mathbf{R}_E} + E \mathbf{R}_E \right) \right] \times \\ \times P[\{\mathbf{R}_E\}] = 0$$

to which they are equivalent.

5. Modelling excluded volume.

In this section we consider a method for the modelling of excluded volume effects within a dynamical theory. This is useful because excluded volume effects for polymeric fractals are likely to be even more important than they are for linear chains. For example, for any polymeric fractal with $d_s > 1$, it is impossible (in three dimensions) to eliminate the effects of excluded volume by varying the temperature. This is because, if a temperature is chosen at which two-body effects vanish, a three-body repulsion is generally still present, and for $d_s > 1$, this term is relevant in three dimensions. (For linear chains, it is marginal, as is well known [1].) Also, it is improbable that all excluded volume effects are screened at high densities [25], especially in the presence of extreme polydispersity as expected in a polymer sol.

Unfortunately, a full dynamical excluded volume calculation is not practical, even for a simple linear polymer [23, 26], and we are therefore obliged to make some further approximations.

We start by considering a linear chain, $\mathbf{R}(s)$, with the usual Wiener entropy

$$-\int (\partial\mathbf{R}/\partial s)^2 ds = -\sum_q |\mathbf{R}_q|^2 q^2. \quad (5.1)$$

This fractal has $d_f = 2$. If (5.1) is replaced by

$$-\sum_q |\mathbf{R}_q|^2 q^\alpha \quad (5.2)$$

the fractal dimension can be varied by altering α : $d_f = 2/(\alpha - 1)$. This allows one to fit d_f to simulate the effects of self-avoidance [22].

In principle, one should not assume that this quadratic form will generate the same dynamics as the true free energy, which is represented by

$$-\sum_q |\mathbf{R}_q|^2 q^2 - b \iint ds ds' \times \delta\left(\sum_q \mathbf{R}_q \cos qs - \sum_{q'} \mathbf{R}_{q'} \cos q' s'\right). \quad (5.3)$$

This is not quadratic (or even diagonal) in R_q . Nonetheless, if one considers a single q -mode, and integrates out all the remaining degrees of freedom in (5.3), then the form (5.2) is recovered [23, 27] (this is a consequence of the central limit theorem). Hence the use of (5.2) (or (5.4) below) to generate the Brownian dynamics corresponds to a natural extension of the pre-averaging approximation, in which the Langevin equation for a single q -mode is brought into a manageable form by averaging over all the remaining

polymer co-ordinates. We now extend this approximation to the case of polymeric fractals with $d_s > 1$.

First, the model free-energy (5.2) is generalized, by writing :

$$P[\mathbf{R}(s)] \propto \exp\left(-\sum_E |\mathbf{R}_E|^2 E^{\gamma+1}\right). \quad (5.4)$$

The ideal limit is now represented by $\gamma = 0$. The resulting d_f may be calculated by expanding $R(s)$ in the eigenfunction $\psi_E(s)$, with use of (2.19) or an equivalent assumption. One obtains

$$d_f = \frac{2 d_s}{2(\gamma + 1) - d_s}; \quad d_w = \frac{4}{2(\gamma + 1) - d_s}. \quad (5.5)$$

This allows a choice of γ to fit the appropriate swollen d_f , calculated by, for example, the Flory theory of section 3.

The corresponding modifications to the effective medium theory are straightforward : the eigenvalues E in the summand of (4.34) are replaced by the rescaled values, $E^{\gamma+1}$, and the correlation products, $g(r, E)$, calculated using the new values of d_f and d_w . One obtains the following results (with use of the appropriate scaling laws).

(i) The screening length is that appropriate to the new d_f :

$$\xi_H^{d_f-d} \propto c. \quad (5.6)$$

(ii) In the dilute regime (i.e., $\xi_H \gg L$) the viscosity increment is given by

$$\delta\eta(\omega) \sim \eta c \int_{L^{-d_w/2}} \frac{q^{d_s-1} dq}{i\omega\eta + q^{2d/d_w}} \quad (5.7)$$

which has the same limiting behaviour as given in equations (4.39), (4.40), except that the value of d_f is that given by equation (5.5) above.

(iii) In the screened regime ($\xi_H \ll L$), the viscosity increment is given by

$$\delta\eta(\omega) \sim \eta c \int_{L^{-d_w/2}} \frac{q^{d_s-1} dq}{i\omega\eta + \xi_H^{d_f+2-d} q^{2(\gamma+1)}} \quad (5.8)$$

which has high and low frequency limits given by equations (4.43), (4.44), again subject to the use of the new d_f in these equations.

In general, the screening of excluded volume at high c means that the relevant values of d_f to be used in equations (5.7) and (5.8), at low and high concentrations respectively, will be different. This fact has various consequences for the concentration depen-

dence of $\delta\eta(\omega)$ in the overlapped regime. These effects may be explored using the idea of blobs⁽⁴⁾.

The model free-energy (5.4) results in the effective dynamical equation (analogous to Eq. (4.33))

$$(i\omega + \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle E^{(d_r+2)/d_w}) \mathbf{R}_E = \psi_E \cdot \mathbf{G} \cdot \mathbf{F} \quad (5.9)$$

which, as mentioned above, in fact describes the motion of \mathbf{R}_E after all other degrees of freedom have been averaged away.

6. Discussion of dynamics.

The results of section 4 and 5 are now discussed, with reference to the dynamical scaling hypothesis of de Gennes [1, 28]. We consider first the dilute limit, with $\omega = 0$. The result (4.39)

$$\delta\eta(0) \sim \eta n L^d$$

which was obtained for both the ideal and excluded volume cases, can be interpreted, as for linear polymers, in terms of the usual Kirkwood model. The macromolecule effectively immobilizes a volume L^d of solvent, which gives a Stokes-Einstein viscosity increment L^d . For the case of a linear chain in a good solvent, some authors [29] have argued for a different « dynamical exponent » in three dimensions (i.e., $\delta\eta \sim L^z$, where $z \neq 3$), though this is disputed [30].

⁽⁴⁾ In the semidilute regime, the hydrodynamic and static screening lengths are comparable, and given by the blob size [1], ξ_b :

$$\xi_H \sim \xi_b \sim c^{1/(d_{rc} - d)}$$

where d_{rd} is the value of d_r as $c \rightarrow 0$. Hence the linear size of the fractal, L , is given by

$$L \sim M^{1/d_{rc}} \xi_b^{1 - d_{rd}/d_{rc}}$$

where d_{rc} is the value of d_r as $c \rightarrow \infty$. Apart from these changes, we expect (5.8) to apply with

$$d_r = d_{rc} = 2 d_s / (2(\gamma + 1) - d_s) \quad \text{and} \quad d_w = d_{wc} = 2 d_{rc} / d_s.$$

The results for limiting cases are

$$\delta\eta(0) \sim \eta M^{2/d_{rc}} c^p$$

where $p = [d_{rc}(d_{rd} - d_{rc}) - 2 d_{rd}] [d_{rc}(d_{rd} - d)]^{-1}$,

and for ω large, but not so large to probe inside a blob,

$$\delta\eta(\omega) \sim \eta(i\omega\eta)^{-2/(d_{rc}+2)} c^{p'}$$

where

$$p' = [(d_{rc} + 2)(d_{rd} - d_{rc}) - 2 d] [(d_{rc} + 2)(d_{rd} - d)]^{-1}.$$

The results, which are given only for completeness, are unlikely to be observable in practice because of entanglement effects.

However, the Kirkwood approximation (using static correlation functions) results inevitably in the form given here, in which the relaxation time for the first internal modes of the macromolecule remain proportional to the hard-sphere relaxation time for rotational diffusion.

The corresponding high frequency behaviour (4.40) is, in both the ideal and the excluded volume cases, consistent with de Gennes' dynamical scaling hypothesis [28], which was originally given for linear chains, but is general. The idea may be summarized as follows. Express the zero frequency viscosity by

$$\delta\eta(0) \sim n\tau$$

where τ is a relaxation time. Now argue that, for high ω ,

$$\delta\eta(\omega) \sim \delta\eta(0) (i\omega\tau)^a.$$

At high ω the dynamical response is limited to length-scales small compared with L ; the viscosity should therefore depend only on the total amount of polymer present, c (not on n or M separately). Hence

$$n\tau^{a+1} \sim c^b.$$

Inserting $\tau \sim L^d$, one obtains

$$n(M^{d/d_r})^{a+1} \sim (nM)^b.$$

Therefore $b = 1$ and $a + 1 = d_r/d$, so

$$\delta\eta(\omega) \sim c\eta(i\omega\eta)^{d_r/d - 1}$$

which is our result (4.40). Thus if we had assumed the Kirkwood form (4.39), then the high frequency asymptote could have been obtained by dynamical scaling. In the overlapped regime, a dynamical-scaling interpretation of the behaviour is not quite so simple. Certainly equation (4.36), for ξ_H , may be obtained quite directly : suppose that $\xi_H(c) = c^a$, and require $\xi_H = L$ when the fractals just overlap, i.e., when $nL^d = 1$. The result is equation (4.36). However, to get from this to the low frequency viscosity, equation (4.43), requires a lengthier argument. Having got (4.43), one can then proceed to the high frequency asymptote (4.44) by using dynamical scaling.

It is, of course, not surprising that our results, both for the ideal case, and also for the excluded volume model discussed in section 6, obey de Gennes' hypothesis. Dynamical scaling can hardly fail with a quadratic free energy, such as (5.4). The results do not, unfortunately, help us decide whether dynamical scaling would work with a more realistic free energy like (5.3).

If we include internal hopping effects (see Note⁽³⁾), the asymptotes at high frequency are altered. Dynamical scaling then breaks down (because the hopping time defines a new scale). The ideas of de Gennes are also harder to apply at intermediate concentration (when there is a crossover in the mode structure

from Rouse-like to Zimm-like behaviour at $\xi_H = \xi_E$, and in the presence of power-law polydispersity (as discussed in Sect. 7). It is important to notice that dynamical scaling does not, in any case, completely describe the relaxation spectrum at intermediate frequency. The spectrum is characterized not just by its asymptotes, but by at least one further parameter, which will in general depend on the model (and approximations) that one uses. In the ideal chain case (and also in the excluded volume model, if Flory theory is used) this parameter is simply the spectral dimension.

7. Applications to polymer sols.

7.1 POLYDISPERSITY. — The results of section 5 may be formally extended to account for polydispersity in a straightforward manner. For an arbitrary number density $n(M)$ of molecules of mass M , one obtains

$$\mathbf{G}^{-1}(\mathbf{k}, \omega) = \mathbf{G}_0^{-1}(\mathbf{k}) + \Sigma(\mathbf{k}, \omega) \quad (7.1)$$

where

$$\Sigma(\mathbf{k}, \omega) \sim \eta \int n(M) MF(M) dM \quad (7.2)$$

with

$$F(M) = \int_{M^{-2/d_s}} dE E^{d_s/2-1} \times \left[\frac{k^{-d_s} f(k\xi_E) E^{(d_s+2)/d_w}}{i\omega \eta + \left(\eta \int^{\xi_E} d^d \mathbf{r} \mathbf{G}(\mathbf{r}) \right) E^{(d_s+2)/d_w}} \right]$$

Here $\mathbf{G}(\mathbf{r})$ is the Fourier transform of $\mathbf{G}(\mathbf{k}, 0)$; $\xi_E = E^{-1/d_w}$; and the adjustable parameter γ has been eliminated using equations (5.5). The function $f(x)$ has the following asymptotes :

$$f(x) \sim x^{d_s+2} \text{ as } x \rightarrow 0$$

$$f(x) \rightarrow 0 \text{ as } x \rightarrow \infty .$$

The pair of self-consistent equations (7.1), (7.2) may now be studied for various forms of $n(M)$. In cases where $n(M)$ is centred about some well-defined average value \bar{M} , it is self-consistent to put (at $k \gg \bar{M}^{-1/d_s}$)

$$\Sigma \sim \eta \xi_H^{-2} \quad (7.3)$$

with the screening length, ξ_H , given by

$$\xi_H^{d_s-d} \propto c = \int n(M) M dM . \quad (7.4)$$

However, a very different (scale invariant) form of $\Sigma(k)$ can arise in a polymer sol, when $n(M)$ is a power law. This behaviour will be described in section 7.3; first we discuss the simpler case of a diluted sol.

7.2 QUENCHED POLYMER SOLS AT INFINITE DILUTION. — The self-consistent equations (7.1), (7.2) become simple at infinite dilution when screening is absent. In a quenched sol, or in the sol-component extracted from a gel, one expects $n(M)$ to be a power law of the form

$$n(M) = M^{-\tau} f(M/M_{\max}, M_{\min}/M) ,$$

where $f(0, 0) = 1$ and where M_{\max} and M_{\min} represent respectively the large and small-scale cutoffs in the size distribution.

At infinite dilution, the molecules are characterized by some fractal dimension d_{fd} which is not necessarily equal to the value d_{fc} (say) which applies at high concentration. The zero-frequency viscosity, as calculated from (7.2) by retaining only power laws and ignoring all prefactors, is given for various regimes of d , d_{fd} , and τ , in table I.

In the percolation model, $\tau \simeq 2.18$ and $d_{fd} \simeq 2.0$ (an approximation which may be obtained by setting $d_s = 4/3$ [17] in Eq. (3.9)). These values indicate a divergence of the intrinsic viscosity with the largest cluster size

$$[\eta] \sim M_{\max}^{\gamma} ,$$

where $\gamma_{\text{perc}} = 1 - \tau + d/d_{fd} \simeq 0.32$, a result obtained previously by Daoud, Family and Jannink [31]. This corresponds to

$$[\eta] \sim M_w^{0.37} ,$$

where $M_w = M_{\max}^{3-\tau}$ is the weight-average molecular weight. The experimental data, reviewed by Stauffer *et al.* in reference [2], appear to indicate that in fact $[\eta] \sim M_w^{0.17}$. Of course, there is no compelling reason to suppose that the percolation model describes real gelation in the laboratory, so this discrepancy is not alarming.

The Kirkwood predictions for the intrinsic viscosity contain no information about the internal modes of motion of the macromolecules, and indeed should apply equally to the case of rigid fractals, such as non-polymeric colloidal aggregates. A more sensitive test of the dynamical theories for flexible molecules is to measure the viscosity of a diluted polymer sol at high frequency. One expects a law of the form

$$|\delta \eta(\omega)| \sim \omega^{-q} \quad (7.5)$$

where, for $d_{fd} + 2 > d$ and $d_{fd}(\tau - 1) - d < 0$ (see Table I),

$$q = d_{fd}(1 - \tau)/d + 1 . \quad (7.6)$$

Inserting the values of τ and d_{fd} for the percolation model gives in three dimensions, $q_{\text{perc}} = 0.21$.

Note that, in contrast to the monodisperse case, it is impossible to calculate the phase in (7.5). For any molecule of finite size, one can show (cf. Eq. (4.40))

Table I. — Exponents x , y , z and q , describing properties of a polymer sol at infinite dilution for different regimes of d_f ($d_f = d_{fd}$), d and τ . $[\eta] \sim M_{\min}^x M_{\max}^y$; $\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \sim E^{-z}$; $\delta\eta(\omega) \sim \omega^{-q}$.

	$d_f + 2 < d$			$d_f + 2 > d$			
	$d_f(\tau - 2) > 2$	$d_f(\tau - 2) < 2$		$d_f(\tau - 1) > d$		$d_f(\tau - 1) < d$	
	$\tau > 2$	$\tau > 2$	$\tau < 2$	$\tau > 2$	$\tau < 2$	$\tau > 2$	$\tau < 2$
x	$2 - \tau + 2/d_f$	0	0	$1 - \tau + d/d_f$		0	
y	0	$2 - \tau + 2/d_f$	$2/d_f$	0	$\tau - 2$	$1 - \tau + d/d_f$	$d/d_f - 1$
z	0			$(d_f + 2 - d)/d_w$			
q	0	$d_f[2 - \tau + 2/d_f]/[2 + d_f]$		0		$d_f(1 - \tau)/d + 1$	

that the contribution to $\delta\eta(\omega)$ is of the form

$$\delta\eta(\omega) \sim \eta(i\omega\eta)^{d_f/d-1} \quad (7.7)$$

and one might expect this to give correctly the phase of $\delta\eta(\omega)$ at high enough frequency. However, at any fixed ω , there is an additional (real) contribution from clusters that are so small that their longest relaxation time is much less than ω^{-1} . These two contributions to the viscosity both scale as ω^{-q} , and so the phase cannot be determined. Nonetheless, the Zimm-like asymptote (7.7) could perhaps be observed at high ω if all clusters less than a certain (large) size were removed from the system. It should also describe, in principle, the high frequency response of a system just above its gel-point from which the sol-fraction has been entirely removed. In these circumstances there is no screening of hydrodynamics or excluded volume for the remaining gel component, and (7.7) should apply at frequencies high enough to probe distances shorter than the correlation (connectivity) length.

7.3 POLYMER SOLS AT HIGH CONCENTRATION. — At high concentrations, when the fractal dimension $d_f = d_{fc}$, the effective medium theory predicts a rich variety of behaviour for different values of the parameters d , d_{fc} and τ . The self-consistent evaluation of $\mathbf{G}(\mathbf{k}, 0)$ (within numerical factors) is tedious but mathematically straightforward, except when $d_{fc}(\tau - 1) = d$, a special case which is considered in more detail below. The results of the effective medium theory are summarized in table II, where for simplicity we have restricted attention to the case of $\tau > 2$, and have taken the total monomer concentration, $c = \int n(M) dM$, to be fixed.

In regime (1), the hydrodynamic self-interaction

$$\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \sim \int^{\xi_E} d^d \mathbf{r} \mathbf{G}(\mathbf{r})$$

is short-range divergent and hence independent of E .

Table II. — Exponents x' , y' , α , z' , and q' describing properties of a concentrated sol for different regimes of d_{fc} , d and τ ($\tau > 2$; $d_f = d_{fc}$). $\eta(0) \sim M_{\min}^x M_{\max}^y$; $G^{-1}(k, 0) \sim k^\alpha$ for $k \gg M_{\max}^{-1/d_f}$; $\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \sim E^{-z'}$; $\eta'(\omega) \sim \omega^{-q'}$.

	$d_f + 2 < d$			$d_f + 2 > d$	
	regime (1) $d_f(\tau - 2) > 2$	regime (2) $d_f(\tau - 2) < 2$	regime (3) $d_f(\tau - 1) > d$	regime (4) $d_f(\tau - 1) < d$	special case $d_f(\tau - 1) = d$
x'	$2 - \tau + 2/d_f$	0	$1 - \tau + d/d_f$	0	
y'	0	$2 - \tau + 2/d_f$	0	$2 - \tau + 2/d_f$	$1 - \tau + (2 + d - \alpha)/d_f$
α	2	$d_f(\tau - 2)$	2	$d_f(\tau - 2)$	$d - d_f \leq \alpha \leq 2$
z'	0		$(d_f + 2 - d)/d_w$	0	$(d_f + \alpha - d)/d_w$
q'	0	$d_f[2 - \tau + 2/d_f]/[2 + d_f]$	0	$d_f[2 - \tau + 2/d_f]/[2 + d_f]$	$(1 - \tau) d_f / (2 - \alpha + d) + 1$

(Note that $\xi_E = E^{-1/d_w}$, with $d_w = d_{wc} = 2 d_{fc}/d_s$.) Also, the viscosity is dominated by the *smallest* molecules. This means that $\mathbf{G}^{-1}(\mathbf{k}, 0)$ takes on its macroscopic value, $\eta'(0) k^2$ on all lengthscales longer than a short cutoff.

In regime (2), the hydrodynamic self-interaction remains local, but the viscosity is now dominated by the largest molecules. At some wavevector k , only those of a linear size larger than k^{-1} contribute to the response $\mathbf{G}^{-1}(\mathbf{k}, 0)$ and the result is an anomalous propagator $\mathbf{G}^{-1}(\mathbf{k}, 0) \sim k^{d_{fc}(\tau-2)}$ at intermediate lengths.

In regime (3) the hydrodynamic coupling $\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle$ is Zimm-like. However, the viscosity is dominated by the smallest clusters, and once again $\mathbf{G}^{-1}(\mathbf{k}, 0) \sim \eta'(0) k^2$ on all but the shortest lengths. This lack of variation in \mathbf{G} indicates that screening is absent, and that the Zimm-like coupling is indeed self-consistent.

A more interesting case is regime (4). In this regime (unlike (1) and (2)) the *bare* hydrodynamic interaction,

$$\langle \psi_E \cdot \mathbf{G}_0 \cdot \psi_E \rangle \sim \int^{\xi_E} d^d \mathbf{r} r^{2-d} \sim E^{-(d\tau+2-d)/d_w}$$

is non-local (i.e., Zimm-like). However, the largest clusters dominate the viscosity, and thus an anomalous power law decay, $G(r) \sim r^{\alpha-d}$, is possible. However, the self-consistent value of $\alpha = d_{fc}(\tau - 2)$ is such that the final, « screened » interaction

$$\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle \sim \int^{\xi_E} d^d \mathbf{r} r^{\alpha-d}$$

is now short cutoff-dependent, effectively local, and hence Rouse-like.

In a polymer sol in $d = 3$, one certainly has $d_{fc} + 2 > d$, and hence the relevant regimes in practice are (3) and (4). It is possible to distinguish between these in terms of the nature of the overlap between macromolecules. Suppose we consider a molecule of mass m_0 . The hard sphere volume fraction of all molecules bigger than m_0 is given by

$$V(m_0) \sim \int_{m_0}^{M_{\max}} M^{-\tau} M^{d/d_{fc}} dM.$$

For $d_{fc}(\tau - 1) > d$ (regime (3)) this is small, and we see that a chosen molecule has negligible overlap with any chains of a comparable or larger size. Instead, it is « quasidilute », i.e., entirely surrounded by molecules much smaller than itself, which can in some sense be viewed as part of the solvent. In contrast, for $d_{fc}(\tau - 1) < d$ (regime (4)) any given molecule is strongly overlapping with others of a size comparable with (or larger than) its own. The solution is « quasi-concentrated » in the sense that, even at very low (but fixed) c the largest molecules overlap strongly as $M_{\max} \rightarrow \infty$.

As the parameters of the problem are varied, we see that the exponent, y' , defined by

$$\eta'(0) \sim M_{\max}^{y'}$$

jumps discontinuously, from zero to a finite value, at the special point $d_{fc}(\tau - 1) = d$ which divides regime (3) from regime (4) :

$$\begin{aligned} y' &= 0 & (d_{fc}(\tau - 1) > d) \\ y' &= 2 + 2/d_{fc} - \tau & (d_{fc}(\tau - 1) < d). \end{aligned} \quad (7.8)$$

To discuss the behaviour at the discontinuity, we must examine more carefully the special case of $d_{fc}(\tau - 1) = d$. When this equality holds, the largest molecules remain near the overlap threshold as M_{\max} is increased : we can call this a « quasi-C* » regime. An example is provided by the percolation model, for which $d_{fc}(\tau - 1) = d$ (when $d < 6$), by hyperscaling [2]. Let us make the ansatz that the anomalous response, $G^{-1}(k, 0) \sim k^\alpha$, leads to a *non-local*, anomalous hydrodynamic coupling

$$\begin{aligned} \langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle &\sim \int^{\xi_E} d^d \mathbf{r} r^{\alpha-d} \sim \\ &\sim E^{-(d_{fc} + \alpha - d)/d_w} \quad (\alpha \neq 2) \end{aligned}$$

which is neither Rouse-like nor Zimm-like in character. For $d_{fc}(\tau - 1) \leq d$, this assumption leads to a selfconsistency requirement of the form

$$\begin{aligned} \mathbf{G}^{-1}(k, 0) \sim k^\alpha &\propto \left(\int_{k^{-d_{fc}}} M^{-\tau} M dM \right) \times \\ &\times \int^{k^{d_{fc}}} \frac{E^{d_n/2-1} dE k^{-d\tau}}{\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle} \\ &\sim k^{d_{fc}(\tau-2)} k^{d_{fc} + \alpha - d} \\ &\Rightarrow k^\alpha \propto k^\alpha k^{d_{fc}(\tau-1)-d}. \end{aligned} \quad (7.9)$$

In regime (4), this cannot be satisfied for any α , and so the ansatz is not self-consistent. (The alternative assumption, $\langle \psi_E \cdot \mathbf{G} \cdot \psi_E \rangle = \text{constant}$, leads in this regime to the self-consistent results shown in Table II.) However, when $d_{fc}(\tau - 1) = d$, (7.9) can be satisfied, but does not uniquely determine α . A closer investigation shows that any α obeying

$$d - d_{fc} \leq \alpha \leq 2$$

gives (to within indeterminate prefactors) a self-consistent solution. The corresponding exponent y , which is given by

$$y = 1 - \tau + (2 + d - \alpha)/d_{fc},$$

is therefore able to take any value satisfying

$$0 \leq y \leq 2 - \tau + 2/d_{fc},$$

i.e., any value on the step discontinuity described by

(7.8). (In fact there are liable to be logarithmic corrections at either end point.)

This result is rather surprising and hard to interpret. Two possible explanations are as follows :

(i) For $d_{fc}(\tau - 1) = d$, the monomer concentration, c , remains relevant as $M_{\max} \rightarrow \infty$. (This is not true in the quasilute regime (3) when, however large c , the largest clusters do not overlap, nor in regime (4), when, however small c , they do.) Thus, it is possible (but by no means obvious) that α and y' each take on a continuous range of values between those of the Zimm-like ($\alpha = 2$, $y = 0$) and Rouse-like ($\alpha = d - d_{fc}$, $y = 2 - \tau + 2/d_{fc}$) limits. The values could depend on c , or, even at fixed c , on higher order fluctuations about the mean (effective) medium.

(ii) Alternatively, it is possible that only the Zimm-like and Rouse-like results represent physically correct solutions, and that there is really a smooth crossover between these as c is increased. If so, the apparently continuous range of permissible exponents is an artifice of the approximations inherent in the effective medium theory. If this explanation is correct, then at high enough concentrations, $\alpha = d_{fc}(\tau - 2)$, and the « special » point at $d_{fc}(\tau - 1) = d$ then belongs properly in regime (4).

As in the case of a diluted sol, some of the zero-frequency results given in table II can be obtained more heuristically from hydrodynamic arguments [32, 33]. For the percolation model, it is also possible to obtain an estimate of y' using an heuristic analogy with a superconducting network at percolation [2, 33]. This leads to a value of $y' = 0.32$, which lies roughly mid-way between the Zimm-like ($y = 0$) and Rouse-like ($y = 0.62$) limits, (suggestive perhaps of explanation (i) above) and which appears to agree broadly with experiments [2].

Again, the true test of the *dynamical* theories lies in experiments at high frequency. Predictions for the modulus of the complex viscosity in this regime are given in table II. If the percolation model lies in fact in regime (4) at high c (i.e., if explanation (ii) above is the correct one) then we obtain

$$|\eta'(\omega)| \sim \omega^{-q'}$$

where

$$q'_{\text{perc}} = [d_{fc}(2 - \tau) + 2]/[d_{fc} + 2] \simeq 0.38.$$

As before, the phase cannot be determined, because of the contribution of very small clusters; however, if these can be selectively removed, the following asymptotic form (cf. Eq. (7.7)) should result in regimes (2) and (4) :

$$\eta'(\omega) \sim \eta(i\omega\eta)^{-2/(d_{fc} + 2)}. \quad (7.10)$$

7.4 CONCLUDING REMARKS ON SOLS. — In sections 7.2, 7.3 above, we have given several new predictions concerning the dynamical response of a polymer sol near its critical point. These predictions are amenable to experimental test; used in conjunction with the Flory theory of section 3 relating d_{fc} to $d_{f\phi}$, they provide various cross-relations between the high and low frequency response, both in the reaction bath and at infinite dilution, even when (for example) d_{fc} and τ cannot be measured separately. It is hoped that these predictions will stimulate new experiments on polymer sols at high frequency.

To test the dynamical theory further, it would be very useful to probe directly the Brownian relaxation of a labelled macromolecule; this could perhaps be accomplished in dynamic light- or neutron-scattering experiments. The results could be compared with various scattering and dynamical correlation functions, calculable (in principle) by substituting the self-consistent hydrodynamic coupling from tables I and II into the effective Langevin equation (5.9).

Finally, we discuss the effects of entanglements in polydisperse systems at high concentration. In general, polydispersity reduces the effects of entanglements; an extreme example is provided by the quasilute regime (3) in which there can be no entanglements between any two chains of comparable size. In regime (4), entanglements must presumably dominate as $M_{\max} \rightarrow \infty$; however, it may still be possible to detect a regime of Rouse-like motion at high frequencies and wavevectors. Even in the entangled regime, it is perhaps possible that the basic motion remains Rouse-like (see Sect. 1.1).

For the case of a « quasi-C* » solution, entanglements are in some sense marginal, and their effects on exponents like y' are difficult to quantify. Of course, although the percolation model obeys $d_{fc}(\tau - 1) = d$, it is not clear whether real gelation in the laboratory results in a « quasi-C* » system. It is possible, for example, that both d_{fc} and τ are, in real systems, strongly altered from their values in the percolation model by the effects of the Brownian relaxation of a growing sol-molecule. If so, the dynamical formulation of this paper may help provide the basis for more realistic models of gelation.

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