

## Statics and Dynamics of Polymeric Fractals

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Polymers of arbitrary fractal connectivity are considered. A Flory theory of chain swelling, with an  $n$ -body repulsion, gives a lower critical dimension equal to the spectral dimension,  $d_s$ , for any polymeric fractal with  $d_s < 2$ . The scaling form of the frequency-dependent complex viscosity of a monodisperse solution of polymeric fractals (at low or high concentration) is given in the absence of excluded-volume and entanglement effects.

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Recently, important progress has been made in the theoretical description of various physical processes (such as the diffusion of a particle) when these processes are constrained to take place on a fractal.<sup>1,2</sup> Central to this progress has been the introduction of an anomalous *spectral* or *fracton* dimension to describe the density of states of the generalized Laplacian operator.<sup>1</sup> In this paper these advances are exploited in the description of the static partition function and dynamical properties of a fractal itself. The excluded-volume problem is discussed at the Flory level: This turns out to be very simple. Some preliminary dynamical results, concerning the viscoelasticity of a solution of polymeric fractals, are also given.

The term "polymeric fractal" is here introduced to describe a class of fractals which are made of flexible polymer chain at short length scales, but have arbitrary self-similar connectivity at larger distances. Any such fractal has no inherent rigidity; its dynamics are diffusive and not vibrational. The formulation and results of this Letter allow discussion, within a single framework, of the statics and dynamics of a large range of physically interesting polymeric fractals, such as gelation clusters, branched polymers, and, perhaps, flexible types of fractal aggregates.<sup>3,4</sup>

*Formalism.*—The following treatment is an extension of the Alexander "wire" model of fractal connectivity.<sup>1</sup> Consider a hypercubic lattice  $S$  on which is inscribed an arbitrary (random or deterministic) connected lattice fractal  $\{s_i\}$ . This means that every site in the set  $\{s_i\}$  is adjacent to at least one other, and that the set is 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 be joined by a single bond, and define a set  $\{s\}$  which includes  $\{s_i\}$  and also coordinates  $s$  for all the points along each bond. Denote the fractal dimension<sup>5</sup> by  $d_{f0}$  and the mass, or total number of elements in  $\{s_i\}$ , by  $M$ ; then  $M \sim L^{d_{f0}}$ . A random

walk,  $s(t)$ , on the fractal obeys  $\langle [s(t) - s(0)]^2 \rangle \sim t^{2/d_{w0}}$ .

The spectral dimension,  $d_s$ , may be defined<sup>1</sup> by  $d_s = 2d_{f0}/d_{w0}$ . The spectral dimension is important because it is independent of the spatial configuration; it is an intrinsic parameter of the network connectivity.<sup>1</sup>

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  $\Omega_{ij}$  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  $L_0 \rightarrow \infty$  (this may require that  $m < 0$ ). For  $d_s < 2$ , the Einstein relation,<sup>6</sup>  $d_{w0} = d_{f0} + x_0$ , is obeyed and hence  $d_s = 2d_{f0}/(d_{f0} + x_0)$ .

Let us now replace 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 coordination 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. The above procedure defines the statistical connectivity of a polymeric network. The connectivity is characterized only by the spectral dimension  $d_s$ ; from now on  $d_{w0}$ ,  $d_{f0}$ , and  $x_0$  may be forgotten.

Now suppose we embed the polymeric network in a Euclidean 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  $R$  in Euclidean space is specified for every member of the set  $\{s\}$ . The resulting functional probability distribution,  $P[R(s)]$ , defines, statistically, a new random fractal,  $R(s)$ , which may be termed a "polymeric fractal." Note that the ensemble considered here is at constant network connectivity, rather than, say, constant fugacity for branch points.

*Statics.*—In general,  $R(s)$  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 purpose of defining  $d_w$  and  $x$ , these accidental contacts are *insulating*; a random walker cannot jump across at them. Subject to this definition, the spectral dimension is configuration invariant.<sup>1</sup>

The new  $d_f$  and  $x$  therefore obey  $d_s = 2d_f/d_w$ , where  $d_w = d_f + x$ ; hence

$$d_f = d_s x / (2 - d_s). \quad (1)$$

For the particular case of *ideal* phantom fractals (no excluded-volume forces) there is an *exact* correspondence between the resistance and spatial separation:  $\langle [R(s_i) - R(s_j)]^2 \rangle \sim \Omega_{ij}$ , and therefore

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

Note that this applies even in the presence of loops.

Equations (1) and (2) allow discussion of the excluded-volume problem for polymeric fractals generally at the Flory level.<sup>7</sup> Consider 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

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

The normal choice is, of course,  $n=2$ , but other values are sometimes appropriate. The usual minimization yields a swollen-fractal dimension  $d'_f$ , which may be expressed in terms of  $d_f$  or  $d_s$ :

$$\begin{aligned} d'_f &= d_f [(n-1)d + 2] / [2 + nd_f] \\ &= d_s [(n-1)d + 2] / [(n-1)d_s + 2]. \end{aligned} \quad (3)$$

The upper critical space dimension is easily found; it is

$$d_{uc} = nd_f / (n-1) = 2nd_s / [(n-1)(2-d_s)].$$

The lower critical space dimension,  $d_{lc}$ , in which  $d'_f = d$ , is

$$d_{lc} = 2d_f / (2 + d_f) = d_s \quad (4)$$

for all polymeric fractals, and independent of  $n$ . This is an interesting result<sup>8</sup>; an interpretation is given below.

It is also interesting to note that Eq. (3) is valid for a repulsion  $c^n$ , for all  $n > 1$ , not just integer values ( $c$  is the internal monomer concentration). Because  $c$  is small, the most efficient possible repulsion comes from a low power of  $c$ . The limiting case is therefore  $n \rightarrow 1$  from above (or, equivalently, an interaction of the form  $c \log c$ ). Inserting this into Eq. (3) gives, for all space dimensions,  $d'_f = d_s$ .

This suggests, as does Eq. (4), that there is a strong inhibition against a value  $d'_f < d_s$ . These results may be explained by the following argument (which is based in part on the discussion given by Alexander *et al.*<sup>8</sup>).

For any fractal, a relation  $d_f < d_s$  implies that  $d_w < 2$ . Therefore a random walk on the fractal makes *faster* progress than it would in free space, or on a straight line. Such progress is only possible if the motion includes long-range hops in space. This can be arranged in principle, because the time taken to diffuse down a polymeric strand is independent of the length to which it is stretched. Hops can occur, if (and only if) some sites which are adjacent in  $S$  are separated by large distances in  $R(s)$ . But since these hops must occur on all length scales, the corresponding free-energy penalty from stretching the polymer strands is extremely large; at least some of the bonds must be stretched to lengths comparable with  $L'$  itself. If one tries to embed an infinite fractal in a Euclidean space of dimension  $d < d_s$ , it will, by a similar argument, cause the mean square<sup>9</sup> bond length to be unbounded, with a correspondingly infinite elastic penalty. We have, in effect, a bound,  $d'_f \geq d_s$ , which is saturated in the limit of extreme repulsion ( $n \rightarrow 1$ ) and at the lower critical dimension.

When we look beyond Flory theory, new questions arise; for example, does the *exact* value of  $d'_f$  depend only on  $d_s$ , or are other details important?<sup>9</sup> Also, for a network containing loops, *topological* constraints (noncrossing of polymer strands) have effects separate from those of excluded volume.<sup>3</sup>

Finally, there follow some remarks about the case of  $d_s \geq 2$ . From Eq. (1), as  $d_s \rightarrow 2$ ,  $d_f \rightarrow \infty$ ; the structure is collapsed in all dimensions. For  $d_s > 2$ , the resistance of the network is dominated by local contributions, and the Einstein relation,  $d_w = d_f + x$ , ceases to apply: Instead  $x_0 = x = 0$ . Hence for an ideal Gaussian network,  $\langle [R(s_i) - R(s_j)]^2 \rangle \sim \Omega_{ij} = \text{const}$ , for all pairs  $(s_i, s_j)$ . Thus as  $M$  increases,  $L$  saturates, and the density diverges. The likely effect of excluded volume would be to limit the divergent density to a constant (i.e., close-packed) value. For  $d_s = 2$ , there will in general be logarithmic effects.

*Dynamics.*—A dynamical theory is possible because the generalized Laplacian operator,<sup>1</sup>  $\nabla_s^2$ , controls the thermodynamic force on a member in the ensemble  $P[R(s)]$  appropriate to ideal phantom fractals (i.e., with excluded-volume and entanglement effects ignored).

For example, the Rouse equation<sup>3</sup> for an arbitrary polymeric network, undergoing diffusive

motion in the presence of a local friction,  $\nu$ , is

$$[\nu \partial / \partial t - (k_B T / l) \nabla_s^2] R(s) = \text{random force.} \quad (5)$$

(Here  $l$  is a steplength; from now on  $k_B T / l$  is set equal to unity.) The spectral dimension,  $d_s$ , is therefore the dimensionality of a generalized "Rouse-mode"  $q$  space. One can now obtain, for this simple dynamical model, a stress-relaxation spectrum, which is most simply expressed as a frequency-dependent viscosity increment,  $\eta(\omega)$ :

$$\eta(\omega) = \sum_q \frac{1}{i\omega\nu + q^2} \sim \int \frac{N(q) dq}{i\omega\nu + q^2}. \quad (6)$$

The density of states has the form<sup>1</sup>  $N(q) \sim q^{d_s-1}$ . For linear chains,  $d_s=1$ , and (6) then reduces to the ordinary Rouse spectrum.<sup>10</sup>

In fact, one can go beyond (5) to construct a full hydrodynamic theory of polymeric fractals in solution. Here I outline the scope of the theory and present the main results; a fuller discussion will appear elsewhere.<sup>11</sup>

The treatment rests on the following scaling assumption concerning the eigenfunctions,  $\psi_q(r)$ , and eigenvalues,  $q^2$ , of the Laplacian operator on the fractal:

$$\langle \psi_q(r) \psi_q(r') \rangle \sim M^{-1} f(|r-r'|/\xi(q)), \quad (7)$$

where  $r$  and  $r'$  label arbitrary points on the fractal,  $f(0)=1$ , and  $\xi(q)$  is a length which scales as a power of  $q$ .

This is similar, though not identical in form, to the scaling assumptions discussed by Alexander *et al.*<sup>12</sup> By use of this assumption,<sup>13</sup> and mode-mode coupling, it is possible to extend the effective-medium theory of Freed and Edwards,<sup>14</sup> given originally to describe the frequency-dependent viscosity of solutions of linear polymers, to calculate (to within numerical factors) that of solutions of *arbitrary* polymeric fractals. The results of the formal theory involve all the equilibrium correlation functions,  $\langle \psi_q(r) \psi_q(r') \rangle$ , which are then rewritten in scaling form with use of (7).

At low concentrations, this treatment reduces to a generalized Kirkwood-Riseman<sup>3,15</sup> preaveraged hydrodynamic theory, while at high concentration the answers are modified (just as for linear chains<sup>14</sup>) by the effects of hydrodynamic screening. The results, given below, therefore constitute a generalization of the well-known<sup>10</sup> "Zimm-like" and "Rouse-like" viscoelastic spectra (for linear chains) to the case of arbitrary polymeric fractals. These results are for monodisperse solutions, but can easily be extended to allow discussion of, say, a (polymeric) sol-gel system near, but below, its gel

point. Effective-medium theory should be applicable whenever the *interfractal* correlations are not themselves critical.<sup>14</sup>

The results of the theory for the frequency-dependent viscosity increment,  $\delta\eta(\omega)$ , of a number density  $n$  of fractals of mass  $M$  ( $c = nM$ ) and linear size  $L$  in a solvent of viscosity  $\eta$ , are as follows:

(i) At low concentration, the motion of a given fractal is controlled by long-range hydrodynamics (with an interaction varying as  $q^{2(d-d_f-2)/d_w}$ ) and a Zimm-like<sup>10</sup> spectrum is obtained,

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

with a "hard-sphere"<sup>3</sup> asymptote at low frequency,  $\delta\eta \sim \eta n L^d$ , and, at high  $\omega$ , i.e.,  $\eta\omega \gg L^d$ ,

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

(ii) At high concentration, hydrodynamic interactions are screened, and effectively there is a (concentration-dependent) local friction. This results in a Rouse-like spectrum [cf. Eq. (6)],

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

where the hydrodynamic screening length,  $\xi_H$ , is given by  $\xi_H^{d_f-d} = c$ . The limiting forms are, as  $\omega \rightarrow 0$ ,  $\delta\eta \sim \eta c^{2/(d-d_f)} L^2$ , and, for  $\eta\omega \gg L^d$ ,

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

Because of Eqs. (1) and (2), these results may be expressed in terms of either  $d_s$  or  $d_f$  alone. The crossover between Zimm-like and Rouse-like behavior occurs when  $\xi_H \sim L$ . The above results apply for  $d$  values such that  $2 < d < d_f + 2$ . For  $d > d_f + 2$ , the hydrodynamic interaction is, in effect, short-range divergent and the Rouse spectrum (6) arises at all concentrations. At  $d = d_f + 2$  there are logarithmic corrections. The relations between high- and low-frequency asymptotes are, in both dilute and concentrated cases, consistent with the dynamical scaling hypothesis of de Gennes.<sup>16</sup> However, the effective-medium treatment provides more information about the structure of the relaxation spectra (for the ideal-phantom model) than can be obtained by dynamical scaling alone.

Obviously, the neglect of excluded volume and entanglement is a serious shortcoming of the above analysis. In fact, the theory is easily extended to cover "fractional" polymeric fractals,<sup>5,8</sup> which have an adjustable parameter that allows one to choose  $d_f$  (independent of  $d_s$ ) in order to simulate the ef-

fects of excluded volume. However, the use of this model for dynamics cannot easily be justified.

Unfortunately, also, it is not possible to incorporate entanglements into the theory at this level. Nonetheless it is hoped that the above generalizations of the Rouse and Zimm effective-medium dynamics might be useful in any future discussion of the subject, just as the standard Rouse equation is an essential ingredient in the reptation theories<sup>17</sup> which describe the dynamics of linear chains in the entangled regime.

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<sup>9</sup>F. Leyvraz (private communication) has made the following important observation: A requirement that all bonds have finite length (not just that the mean square length be finite) can in general lead to a stricter bound on  $d_f'$  than the one given here. This constraint is not, however, represented in any Gaussian model; if it were included, parameters other than  $d_s$  would have to become relevant in low  $d$ .

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<sup>13</sup>This assumption implies several (well-established) scaling relations which are also used.

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