

Dynamics of fractal sol-gel polymeric clusters

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The dynamics of flexible polymeric fractals in solutions is discussed using a linearization self-consistent approximation. When hydrodynamic interaction is not screened (Zimm model) we find that the mean square displacement $\langle \Delta(t)^2 \rangle$ of a monomer is anomalously increasing with time, $\langle \Delta(t)^2 \rangle \mathcal{D} \sim t^\alpha$ with a universal exponent $\alpha = 2/d$ in d dimensions, independent of the fractal (d_f) and spectral dimensions. The viscoelastic modulus behaves as $G(\omega) \sim (i\omega)^u$, with $u = d_f/d$. When hydrodynamics is screened (Rouse model) we find $\alpha = 2/(2 + d_f)$ and $u = d_f/(2 + d_f)$. We conclude that measurements of $\alpha = 2/d$ indicate unambiguously that the Zimm model is applicable and thus should be correlated with $u = d_f/d$ in rheology measurements. [S1063-651X(98)51109-9]

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Polymers in solution form a variety of self-similar structures. For example, a linear polymer molecule forms a coil with a radius of gyration $R_g \sim N^\nu$ where N is the number of monomers and the exponent ν depends on the solvent quality [1,2]. Sol-gel systems present another example of self-similarity [1,3-5]. They consist of polymers or aggregates randomly cross-linked to form network clusters embedded in the solvent. Gelation occurs when an infinite cluster percolates through the whole system [1,6]. The dynamic properties of these systems are of great theoretical and practical interest. Commonly measured quantities are the dynamic structure factor $S(q,t)$ (measured by light scattering), which is sensitive to the local monomer diffusion, and the macroscopic viscoelastic modulus $G(\omega)$ that is measured in rheology experiments.

The dynamics of linear polymers in dilute solution has been studied in several classical works [1,2]. The dynamics of sol-gel systems has also attracted a lot of experimental and theoretical attention [4,5,7,8] and relatively good understanding has been achieved. Some measurements of $S(q,t)$ [7,8], which could be associated with the dynamics of internal modes, have remained unsatisfactorily explained, however. A similar situation exists for measurements of $G(\omega)$ [7]. In this Rapid Communication we present a theoretical framework for self-similar, flexible polymers, encompassing both linear and branched polymers, that may help to clarify these measurements. Some of our results have been previously derived, but the approach we use is simpler than those available and allows straightforward calculations of other observables within the same framework.

We consider a fractal manifold of a noninteger dimension D [9,10]. Special integer values describe linear polymers with $D=1$ and membranes with $D=2$. Branched polymers forming a gel are described by D in the range $1 < D < 2$ because of the internal cross-linking [4]. Thus, the number of monomers within a manifold "radius" l (i.e., the chemical or minimal length defined in Ref. [6]) is $n \sim l^D$. When the manifold is embedded in a d -dimensional Euclidean space, it may crumple so that the mass n (i.e., the number of points, or "monomers," that belong to the fractal) within a radius r scales as $n \sim r^{d_f}$, where d_f is the *fractal dimension* (also known as the Hausdorff or self-similarity dimension) d_f

$\leq d$. Below we shall frequently use the gyration exponent ν (or the chemical length exponent $D_{\min} = 1/\nu$ used in Ref. [6]), which describes, *via* the scaling $r \sim l^\nu$, how the D -dimensional manifold is crumpled in the d -dimensional space. Using the relation between n and l , we have $r \sim n^{\nu/D}$, which implies $D = \nu d_f$ [10].

Because our fractals are flexible, their *configuration* in the solvent is fluctuating in time, even though their topology is fixed. Thus, the monomers can move in the embedding solvent by these configuration fluctuations. One of our objectives is to calculate the resulting mean square displacement (MSD) of a monomer (of the fractal) in the Euclidean space. This should be *distinguished* from the diffusion of a particle *on* a "frozen" fractal. The latter also leads to anomalous diffusion in the embedding space due to the self-similarity [11,12], but this will only serve us for defining various dynamic exponents.

The diffusion *on* a fractal can be described in the manifold space by $l^2(t) \sim t^{2/d_{wo}}$ with $d_{wo} \geq 2$. In real space this translates to $r^2(t) \sim t^{2/d_w}$, with $d_w = d_{wo}/\nu$. The probability of the random walker returning to the origin at time t is then $P_o(t) \sim r(t)^{-d_f} \sim l(t)^{-D}$, which scales as $P_o(t) \sim t^{-d_s/2}$, where $d_s = 2d_f/d_w = 2D/d_{wo}$ is the *spectral dimension* [11]. Since $\nu \leq 1$ and $d_{wo} \geq 2$ we have $d_s \leq D \leq d_f \leq d$. We note that for Euclidean manifolds [9] $d_s = D$ ($d_{wo} = 2$), but our approach will *not* be limited for this special case.

We start by generalizing the Zimm model for linear self-avoiding polymers [2] to arbitrary *flexible* fractals. The internal coordinate of a monomer will be described, even if just symbolically, by the "vector" \vec{l} . The vector $\vec{R}(\vec{l})$ will denote the position of this monomer in the d -dimensional embedding space. The free energy of the manifold is described by a generalized Edwards "spring and bead" Hamiltonian ($k_B = 1$ in our units) [9]

$$H[\{\vec{R}(\vec{l})\}] = \frac{T}{b^D} \int d^D l (\nabla_D \vec{R}(\vec{l}))^2 + \nu \int d^D l \int d^D l' \delta^d(\vec{R}(\vec{l}) - \vec{R}(\vec{l}')), \quad (1)$$

where b is the bead linear size and ν is the excluded volume

parameter. The self-avoidance, described by the second term, makes an exact treatment of the dynamics impossible, but it becomes tractable in the so-called linearization approximation that we now describe.

We shall make use of the orthogonal set of eigenstates $\Psi_E(\vec{l})$ of the Laplacian in the manifold space [11,4,6], which is defined as the continuum limit of a finite nearest-neighbor difference operator, $\nabla_D^2 \phi(\vec{l}) \equiv b^{-2D/d_s} \sum_{\vec{l}' \in \vec{l}} [\phi(\vec{l}') - \phi(\vec{l})]$. (These eigenstates have been studied extensively in the context of vibrations [6].) Thus,

$$\nabla_D^2 \Psi_E(\vec{l}) = -E \Psi_E(\vec{l}), \quad (2)$$

where $\int d^D l \Psi_E^*(\vec{l}) \Psi_{E'}(\vec{l}) = L^D \delta_{E,E'}$, with L as the fractal chemical size, and $\Psi_E^*(\vec{l}) = \Psi_E(-\vec{l})$. This allows us to construct an *effective Hamiltonian* H_{eff} that is Gaussian and diagonal in the manifold eigenstate space

$$H_{\text{eff}} = \frac{1}{2} T \sum_E \frac{\vec{R}(E)^2}{\langle |\vec{R}(E)|^2 \rangle}, \quad (3)$$

where $\vec{R}(\vec{l}) = \sum_E \vec{R}_E \Psi_E(\vec{l})$. The mean value $\langle |\vec{R}(E)|^2 \rangle$ will be determined self-consistently from knowing the real space correlation function

$$\begin{aligned} \langle (\vec{R}(\vec{l}) - \vec{R}(\vec{l}'))^2 \rangle &= 2 \int dE N(E) \langle |\vec{R}(E)|^2 \rangle \\ &\times (1 - g_E(|\vec{l} - \vec{l}'|)), \end{aligned} \quad (4)$$

where $N(E) \sim E^{d_s/2-1}$ is the density of eigenstates Ψ_E [11] and $g_E(|\vec{l} - \vec{l}'|) = \langle \Psi_E(\vec{l}) \Psi_E^*(\vec{l}') \rangle_{\text{dis}}$ is a disorder ensemble average eigenstate correlator. Requiring that the Ψ_E 's also be eigenstates of the translation operator on the fractal implies that $\Psi_E(\vec{l}) \Psi_E(-\vec{l}') = \Psi_E(0) \Psi_E(\vec{l} - \vec{l}')$, which leads to $\Psi_E(0) = 1$ and

$$g_E(l) = \langle \Psi_E(\vec{l}) \rangle_{\text{dis}} \equiv \bar{\Psi}_E(l), \quad (5)$$

where $\bar{\Psi}_E(l)$ is the disorder ensemble averaged eigenstate. Following the general considerations described in Refs. [4] and [11], the latter should have the following scaling form:

$$\bar{\Psi}_E(l) = f(E^{d_s/2D} l). \quad (6)$$

(Note that the dimensions of E are $[E] = [l]^{-2D/d_s}$.) This also agrees (using $r \sim l^\nu$) with the suggested *real space* ‘‘superlocalization’’ form [6]

$$\bar{\Psi}_E(r) \sim \exp[-\text{const}(rE^{1/d_w})^{1/\nu}]. \quad (7)$$

Equation (4) must be equal to $\sim b^{2-2\nu} |\vec{l} - \vec{l}'|^{2\nu}$, which implies that

$$\langle |\vec{R}(E)|^2 \rangle \approx b^{2-2\nu} E^{-2/d_w - d_s/2}. \quad (8)$$

The Langevin equations of motion in the creeping flow approximation are [2]

$$\frac{d\vec{R}(\vec{l})}{dt} = - \int d^D l' \mathbf{L}(\vec{R}_{ll'}) \cdot \frac{\delta H_{\text{eff}}}{\delta \vec{R}(\vec{l}')} + \vec{f}(t, \vec{l}), \quad (9)$$

where $\vec{R}_{ll'} = \vec{R}(\vec{l}) - \vec{R}(\vec{l}')$ and $\vec{f}(t, \vec{l})$ is thermal white noise. Here $\mathbf{L}(\vec{r})$ is the Oseen tensor describing the hydrodynamic interaction between different beads [13], which in d dimensions is given by $\mathbf{L}(\vec{r}) \propto (\hat{\mathbf{r}}\hat{\mathbf{r}} + \mathbf{1})/\eta r^{d-2}$, where η is the solvent viscosity. (Note that the viscosity dimensions are $[\eta] = [l]^{2-d}[M]/[t]$.) We now perform the preaveraging approximation [2], where \mathbf{L} is replaced by its equilibrium average. Assuming that the probability distribution of $\vec{R}_{ll'}$ depends only on $\vec{R}_{ll'}/\langle |\vec{R}_{ll'}| \rangle$ [consistent with the effective Hamiltonian in Eq. (3), which takes this distribution to be Gaussian] we have $\langle \mathbf{L}(\vec{R}_{ll'}) \rangle_{\text{eq}} = \Lambda(\langle \vec{R}_{ll'} \rangle) \mathbf{1}$, where $\Lambda(r) \sim 1/\eta r^{d-2}$. Therefore, Eq. (9) becomes linear and in the manifold eigenstate space it is

$$\frac{d\vec{R}(E)}{dt} = -\omega(E) \vec{R}(E) + \vec{f}(E, t), \quad (10)$$

where

$$\omega(E) = \frac{T\Lambda(E)}{\langle |\vec{R}(E)|^2 \rangle}. \quad (11)$$

Here $\Lambda(E)$ is the manifold eigenstate transform of the hydrodynamic interaction kernel $\Lambda(R_{ll'})$ (averaged over fractal disorder)

$$\Lambda(E) \approx \frac{1}{\eta} \int \frac{d^D l \bar{\Psi}_E(l)}{\langle |\vec{R}(\vec{l}) - \vec{R}(0)|^{d-2} \rangle} \approx \frac{E^{(d-2)/d_w - d_s/2}}{\eta b^{(d-2)(1-\nu)}} \quad (12)$$

[where we made use of $D/(vd_w) = d_s/2$]. Consequently, the mode relaxation rate becomes

$$\omega(E) \approx \frac{TE^{d/d_w}}{\eta b^{d(1-\nu)}}. \quad (13)$$

Equations (8) and (13) are equivalent to the Zimm model results for linear polymers [2].

We are now able to calculate the time-dependent MSD of a single monomer (bead) in the form

$$\begin{aligned} \langle \Delta(t)^2 \rangle &\equiv \langle (\vec{R}(\vec{l}, t) - \vec{R}(\vec{l}, 0))^2 \rangle \\ &= 2 \int dE N(E) \langle |\vec{R}(E)|^2 \rangle (1 - e^{-\omega(E)t}). \end{aligned} \quad (14)$$

Using Eqs. (8) and (13) for $|\vec{R}(E)|^2$ and $\omega(E)$ we obtain (for times $\eta b^{d/d_w} T \ll t \ll \eta R_g^{d/d_w} T$, where R_g is the radius of gyration)

$$\langle \Delta(t)^2 \rangle \approx \left(\frac{T}{\eta} t \right)^{2/d} \quad (15)$$

(which has been previously obtained for linear polymers in $d=3$ Θ solvent [14]). It is seen that a monomer performs *anomalous subdiffusion* $\langle \Delta(t)^2 \rangle \sim t^\alpha$ (with $\alpha < 1$) in the em-

bedding space. This anomalous diffusion is essentially *identical* to that of linear polymers, and the anomalous exponent $\alpha=2/d$ is *independent* of all fractal characteristics (i.e., independent of the exponents d_s and d_f). This can be attributed to the long range hydrodynamic interaction that strongly couples the motion of monomers through the Euclidean space, even when they are distant in the fractal manifold space. As a consequence, the fractal characteristics may become irrelevant. This becomes more evident when we consider below the Rouse model. We note that $\alpha=2/d$ has also been recently derived for polymerized membranes by renormalization group [15]. It also agrees with the scaling hypothesis $\langle \Delta(t)^2 \rangle = R_g^2 f(t/\tau)$, with $\tau = \eta R_g^d / T$ [$f(x)$ is a scaling function], if we assume that for $t \ll \tau$ the result should not depend on R_g , which implies that $f(x) \sim x^{2/d}$ for $x \ll 1$.

We now turn to a discussion of two other familiar observables. First, consider the dynamic structure factor $S(q, t)$. Generalizing the Doi-Edwards calculation for linear polymers [14], this is first expressed as (using a $1/N$ normalization, where N is the number of monomers)

$$S(q, t) \approx \frac{1}{b^D} \int d^D l \exp \left[-\frac{1}{6} q^2 \langle (\vec{R}(\vec{l}, t) - \vec{R}(0, 0))^2 \rangle \right]. \quad (16)$$

The correlation function in the exponent can be written as a sum of a static part and dynamic parts,

$$\langle (\vec{R}(\vec{l}, t) - \vec{R}(0, 0))^2 \rangle = \langle (\vec{R}(\vec{l}) - \vec{R}(0))^2 \rangle + \langle \Delta(\vec{l}, t)^2 \rangle, \quad (17)$$

where

$$\langle \Delta(\vec{l}, t)^2 \rangle = 2 \int dE N(E) g_E(l) \langle |\vec{R}(E)|^2 \rangle (1 - e^{-\omega(E)t}), \quad (18)$$

which reduces to the MSD of Eq. (14) for $\vec{l}=0$. We can then show that for $\eta/q^d T \ll t \ll \eta R_g^d / T$ the *decay* of $S(q, t)$ is dominated by $\langle \Delta(0, t)^2 \rangle$, the MSD of a single monomer. Thus, this decay becomes nearly a *stretched exponential*

$$S(q, t) \approx S(q) e^{-\text{const}[(Tq^d/\eta)t]^{2/d}}, \quad (19)$$

where $S(q) \sim q^{-d_f}$ is the static structure factor. The stretching exponent $2/d$ is therefore *independent* of all fractal characteristics. Importantly, it has been shown that such an internal mode induced decay is not modified by gel point polydispersity [8].

Second, we consider the contribution of clusters to the shear viscoelastic modulus $G(\omega)$ of the solution, assuming monodispersity of cluster sizes. In the time domain it is given by $G(t) = (T/v_c) G_R(t)$, where v_c is the volume available per cluster and the intrinsic modulus [2] is (for $t \ll \eta R_g^d / T$)

$$G_R(t) = \int dE N(E) e^{-\omega(E)t} \approx \left(\frac{\eta R_g^d}{Tt} \right)^{d_f/d}. \quad (20)$$

In the frequency domain $G_R(\omega) \sim (i\omega)^{d_f/d}$. Thus, the viscoelastic spectrum is sensitive to d_f , even if not to d_s . This should be contrasted with the dynamics shown by the MSD

and $S(q, t)$. Note that $G_R(t)$ saturates to unity for $t \geq \eta R_g^d / T$, which implies that for the long tail size distribution at the gel point the time dependence of the macroscopic modulus will be modified [5].

Equation (20) agrees with previous results of Cates [4] and of Martin *et al.* [5] (for the single cluster contribution), who used different methods. Our approach has an important advantage over these studies. Unlike in the work of Martin *et al.*, it does not involve an *ad hoc* hypothesis for the scaling of the mode relaxation rates with the Euclidean space wave vector. Our derivation also appears much simpler than the comprehensive study of Cates—even if closely related to it—which involves effective medium theory as a means of obtaining the relaxation rate spectrum [Eq. (13)]. More importantly, the MSD [or $S(q, t)$] and $G(\omega)$ were obtained using the same manifold mode analysis. We shall elaborate on this point at the end.

So far we have considered self-similar structures with the hydrodynamic interaction influencing the dynamics. In dense systems hydrodynamic backflow effects may become screened above a certain length $\xi_H \sim \xi$ (ξ is the mesh size) and we recover the free draining limit described by the Rouse model [2,4]. This implies that the observed dynamics should cross over from Zimm-like at short times to Rouse-like at longer times. The effect of the intercluster excluded volume interaction on the cluster distribution on space, i.e., in the exponent ν (or d_f), is less evident. However, even if the actual value of ν in the regime $\xi \ll r \ll R_g$ is not known, we can still use it as a model parameter in our dynamic self-consistent theory and examine the consequences. This is expected to be a good approximation, as long as entanglements do not play a role. The effective bead size b should then be set to ξ_H but we shall continue to use the parameter b for clarity.

For the Rouse model we can still apply the formalism used above, except that now the friction is local, and is simply the Stokes drag on a single bead [2]. We thus use (instead of the Oseen tensor) $\mathbf{L} = \Lambda \mathbf{1}$ with $\Lambda \approx b^D \delta^D(\vec{l} - \vec{l}') / \eta b^{d-2}$. Accordingly, $\Lambda(E)$ is independent of E , and the relaxation rate becomes

$$\omega(E) \approx \frac{TE^{2/d_w + d_s/2}}{\eta b^{d-D-2\nu}}. \quad (21)$$

Using Eqs. (8) and (21) in Eq. (14), we now obtain

$$\langle \Delta(t)^2 \rangle \approx b^2 \left(\frac{T}{\eta b^d t} \right)^{2/(2+d_f)} \quad (22)$$

Thus, for the Rouse model the anomalous diffusion exponent is dependent on d_f . For the intrinsic viscoelastic modulus we obtain

$$G_R(t) \approx N \left(\frac{\eta b^d}{Tt} \right)^{d_f/(2+d_f)}, \quad (23)$$

where $N \approx (L/b)^D \approx (R_g/b)^{d_f}$ is the fractal ‘‘mass.’’ Hence, $G_R(\omega) \sim (i\omega)^{d_f/(2+d_f)}$. This agrees with the studies of Cates [4] and Martin *et al.* [5], while Eq. (22) agrees with other studies in the context of linear polymer [16] and polymerized membrane dynamics [15].

Our main results can be summarized in terms of the two exponents: one describes the MSD of a monomer and the dynamic structure factor, $\langle \Delta(t)^2 \rangle \sim t^\alpha$ and $S(q,t) \sim e^{-\text{const} \times t^\alpha}$, and the other describes the complex modulus $G(\omega) \sim \omega^u$. Focusing on three dimensions, we have found that $\alpha = 2/3$ for all fractals that are subject to hydrodynamic interaction (Zimm model), independent of d_f and d_s , yet $u = d_f/3$. This contrasts with the case of screened hydrodynamics (Rouse model) where both power laws depend on d_f , $\alpha = 2/(2 + d_f)$ (i.e., $\alpha < 2/3$) and $u = d_f/(2 + d_f)$. Thus, measuring an exponent $\alpha = 2/3$ can imply nothing about the fractal; however, it can quite unambiguously suggest that the Zimm model is applicable, which means that $G(\omega)$ should be described by $u = d_f/3$. Measurements of $\alpha > 2/3$ are excluded by both models.

It should be noted that attempting to deduce $G(\omega)$ from the MSD alone on the basis of the generalized Langevin equation [17], which implies $i\omega G(\omega) \sim 1/\langle \Delta^2 \rangle_\omega$ [$\langle \Delta^2 \rangle_\omega$ is the Fourier-Laplace transform of $\langle \Delta^2(t) \rangle$], fails completely. For example, from $\alpha = 2/3$ one would predict $u = 2/3$, which is only true if $d_f = 2$ (e.g., linear Gaussian chains). This simply suggests that the *macroscopic* and the *microscopic* viscosities are different, and has important consequences on the interpretation of “microrheology” experiments in which $G(\omega)$ is obtained in this way from MSD measurements.

Recent measurements of $G(\omega)$ on chemically cross-linked pre-gel clusters yield $u = 0.69 \pm 0.005$ [7]. From the light scattering studies on *diluted* samples one can infer a fractal dimension in the range $2.02 < d_f < 2.11$. The Zimm model, where $u = d_f/3$, then predicts $0.67 < u < 0.70$, in good agreement with the experimental value. We note, however, that measurements of $G(\omega)$ on diluted samples are required for a more reliable comparison. In addition, for the same system it was found from dynamic light scattering that $\alpha = 0.77 \pm 0.02$, which is left unexplained. One of the reasons for such a discrepancy, however, could be that the long time relaxation regime $\eta/q^d T \ll t$ has not been reached [18]. In such cases a numerical fit to the full decay profile [Eqs. (16)–(18)] could be useful.

We conclude that combined measurements of $S(q,t)$ (or real space measurements of the MSD) and of $G(\omega)$ can be a powerful tool for understanding the dynamics of fractals in solutions. Since we have obtained the normal mode relaxation times and amplitudes, we are able to calculate other dynamic observables of interest.

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