

### Static and dynamic scattering from fractals

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A scaling form for the pair correlation function of random fractals is combined with the scaling form of the percolation distribution of cluster sizes to obtain expressions for the static structure factor  $S(q)$  and first cumulant  $K_1$  of the dynamic structure factor  $S(q,t)$  at the gel point. We find  $S(q) \sim q^{-\mu}$  and  $K_1 \sim q^3$  with  $\mu = D(3 - \tau)$ , where  $D$  is the fractal dimension and  $\tau$  is the exponent for the distribution of cluster sizes. Special forms are suggested for the scaling functions to obtain results for the nonscaling regime.

Three relations serve as equivalent definitions of the fractal dimension of the mass  $D$

$$M \sim R^D, \quad g(r) \sim 1/r^{d-D}, \quad r \ll R, \\ S_M(q) \sim 1/q^D, \quad q^{-1} \ll R. \tag{1}$$

Here  $R$  is the radius of gyration,  $M$  is the mass,  $g(r)$  is the pair correlation function,  $d$  is the dimensionality of space,  $S_M(q)$  is the static structure factor, and  $q$  is the momentum transfer. The intensity of scattering  $I(q)$  from a single fractal is related to  $S_M(q)$  through  $I(q) = BM^2 S_M(q)$ , where  $B$  is a constant which depends on instrument geometry, solvent-fractal contrast factors, and the nature of the incident radiation. This relation for  $I(q)$  is appealing because it provides a simple and direct method of measuring the fractal dimension of monodisperse systems. Indeed, recent x-ray and light scattering intensity measurements by Schaefer and Keefer<sup>1</sup> for silica gels and by Schaefer, Martin, Cannell, and Wiltzius<sup>2</sup> for colloidal aggregates have demonstrated such a scaling regime where  $I(q) \sim q^{-\mu}$  with  $\mu \sim 2.0$ . While it is tempting to identify  $\mu$  with the fractal dimension of the particles in these systems, fractals produced by gelation processes are especially polydisperse and the effect of the distribution of cluster sizes must be taken into account.

In this Brief Report we propose a simple scaling form for the pair correlation function of a random volume fractal and use the scaling form of the percolation distribution of cluster sizes to obtain a theory of static and dynamic scattering from gelling solutions. In all that follows it is assumed that the scattering measurements are made on quenched and diluted samples so that interparticle contributions to the scattering functions can be neglected.

While  $g(r)$  for an infinite fractal may be represented by a simple power law, a finite fractal has a natural length scale  $\lambda$  which can be introduced into  $g(r)$  through a crossover function  $f(x)$

$$g(r) = f(r/\lambda)/r^{d-D}. \tag{2}$$

For  $x \ll 1$ ,  $f(x) \sim 1$ , whereas for  $x \gg 1$ ,  $f(x)$  must decay faster than a power law. The normalization, radius of gyration, and structure factor are defined in terms of  $g(r)$

by

$$M = \int d^d r g(r), \tag{3}$$

$$R^2 = (1/2M) \int d^d r r^2 g(r), \tag{4}$$

$$S_M(q) = (1/M) \int d^d r e^{iq \cdot r} g(r). \tag{5}$$

It may be readily shown that  $M = f_{D-d} \lambda^D$  and  $R^2 = \lambda^2 f_{2+D-d} / 2f_{D-d}$ , where  $f_\alpha = \int f(s) s^\alpha d^d s$ , which gives the necessary fractal relation  $M \sim R^D$ . From (5), it is apparent that  $S_M(q)$  is a function of the variable  $q\lambda$  alone, that  $S_M(q)$  is normalized in the usual way [ $S_M(0) = 1$ ], and that the general small  $q$  expansion,  $S_M(q) = 1 - q^2 R^2/d + \dots$ , can be obtained from (5) using (3) and (4).

The dynamic structure factor,  $S_M(q,t)$ , is proportional to the autocorrelation function of the scattered field,<sup>3</sup>  $\langle E(q,0)E(q,t) \rangle$ . For a monodisperse collection of rigid, spherical particles,  $S_M(q,t)$  is just the exponential time decay  $e^{-q^2 D t} S_M(q)$ , where  $D$ , the translational diffusion constant, is inversely proportional to  $R$ . If the particles are nonspherical, rotational effects will contribute to the scattering, causing  $S_M(q,t)$  to become quite complex. Still, explicit calculations<sup>3</sup> for optically isotropic rods are of the form

$$S_M(q,t) = e^{-q^2 D t} H(qR; \theta t), \tag{6}$$

where  $\theta$ , the rotational diffusion constant, is inversely proportional to  $R^3$ . This  $R^3$  dependence of  $\theta$  is quite general, and has been explicitly demonstrated for oblate and prolate spheres, and flexible macromolecules.<sup>4</sup> The dynamic structure factor of flexible fractals (linear and branched polymers) is complicated by shape changing modes, known as "configurational" diffusion. Again explicit calculations<sup>3</sup> indicate

$$S_M(q,t) = e^{-q^2 D t} H(qR; \phi t). \tag{7}$$

In the Kirkwood approximation to the hydrodynamics<sup>5</sup>  $\phi = kT/\eta_s R^3$ , where  $\eta_s$  is the solvent viscosity. The initial decay of (6) and (7) is conveniently expressed by the first cumulant,<sup>3</sup>  $K_{1M}$

$$K_{1M} = - \left. \frac{d \ln S_M(q,t)}{dt} \right|_{t=0} = Dq^2 + A_\Omega(qR) \Omega, \tag{8}$$

where  $\Omega = \theta, \phi$ . The amplitude function  $A_\Omega(qR)$  vanishes like  $q^4$  for  $qR \ll 1$  (in this regime, translational diffusion dominates and  $K_1 \sim q^2$ ) and is a monotonically increasing function of  $qR$ . Scaling arguments<sup>5</sup> show that for  $qR \gg 1$ ,  $A_\phi(x) \sim x^3$ , so for flexible polymers at large  $q$ ,  $K_1 \sim q^3$ . No such scaling behavior is observed for rotational amplitude  $A_\theta(x)$ .

A polydisperse sample may be characterized by the distribution function  $N(M) = V(M)/c\nu$ , where  $V(M)$  is the number of particles of molecular weight  $M$  in the scattering volume  $\nu$ , and  $c$  is the mass concentration per unit volume. The distribution is normalized such that  $\sum MN(M) = 1$ . The scaling theory of percolation clusters<sup>6</sup> gives

$$N(M) = M^{-\tau} h(\epsilon M^\sigma), \quad (9)$$

where  $\epsilon = p - p_c$ ,  $p$  is the conversion (fraction of filled sites), and  $p_c$  is the conversion at the gel point. The exponents  $\tau$  and  $\sigma$  are related to critical exponents through

the following relations:

$$\left( \sum N(M) \right)_{\text{sing}} \sim |\epsilon|^{2-\alpha}, \quad (10)$$

$$\left( \sum MN(M) \right)_{\text{sing}} \sim \begin{cases} \epsilon^\beta, & p > p_c \\ 0, & p < p_c \end{cases} \quad (11)$$

$$\left( \sum M^2 N(M) \right)_{\text{sing}} \sim |\epsilon|^{-\gamma}, \quad (12)$$

where the subscript sing denotes the nonanalytic part of the sum. Substitution of (9) into these relations gives  $2 - \alpha = (\tau - 1)/\sigma$ ,  $\beta = (\tau - 2)/\sigma$ , and  $-\gamma = (\tau - 3)/\sigma$ . Elimination of  $\tau$  and  $\sigma$  gives the well-known relation of critical theory,  $2 - \alpha = \gamma + 2\beta$ . Equation (11) requires that the nonanalytic part of  $\sum MN(M)$  vanishes beneath the gel point. Physically this means that the gel fraction is zero beneath the gel point; mathematically it amounts to the constraint<sup>6</sup>  $\int z^{-\beta} h'(-z) dz = 0$  on the scaling function  $h(z)$ .

The total scattered intensity from a polydisperse fractal sample is expressed as an integration of the static structure factor (5) over the distribution of sizes (9). Using (2) for  $g(r)$  gives

$$I(q) = Bc\nu M_w S(q) = Bc\nu \int d^d r (e^{iq \cdot r} / r^{d-D}) \int dM f(r/M^{1/D}) M^{1-\tau} h(\epsilon M^\sigma), \quad (13)$$

where

$$S(q) = \int M^2 N(M) S_M(q) dM / M_w$$

and  $M_w = \int M^2 N(M) dM$ . At the gel point  $\epsilon = 0$  and

$$I(q) \sim q^{-\mu}, \quad (14)$$

where  $\mu = D(3 - \tau)$ . For percolation clusters, accepted values of  $\tau$  and  $D$  are 2.2 and 2.5, respectively,<sup>6,7</sup> so the intensity is seen to vary as  $q^{-2}$  near the gel point, giving an exponent quite different from the fractal dimension. In two dimensions the effect is much smaller; here  $\tau \sim 2.05$ ,  $D \sim 1.89$ , and  $\mu \sim 1.80$ .

In a similar fashion the polydispersity-smear dynamic intensity factor  $I(q, t)$  may be written

$$I(q, t) = Bc\nu \int M^2 N(M) S_M(q, t) dM \quad (15)$$

with first cumulant

$$K_1 = I(q, 0)^{-1} \int M^2 N(M) S_M(q) \times [Dq^2 + A_\Omega(qR)\Omega] dM \quad (16)$$

Using  $D \sim R^{-1}$  (Stokes-Einstein diffusion) and  $\Omega \sim R^{-3}$  (valid for rotational and configurational diffusion) gives the highly universal gel point scaling results

$$I(q, t) \sim q^{-\mu} f(q^3 t) \quad (17)$$

and

$$K_1 \sim q^3 \quad (18)$$

It is interesting to note that translational, rotational, and configurational degrees of freedom all contribute a term of order  $q^3$  to  $K_1$  at the gel point. Further, while the function  $f(q^3 t)$  will be highly nonexponential, the first cumulant exhibits the same  $q$  dependence as the fully exponential time decay of  $S(q, t)$  in fluids at thermodynamic critical or conso-

lute points.<sup>8,9</sup> Physically this  $q^3$  dependence is due to large, slow-moving fractals contributing relatively more to the scattering at small  $q$ . Thus a power-law distribution of cluster sizes modifies the scaling exponent of  $S(q)$  from the single fractal value and gives a first cumulant which has a universal  $q^3$  dependence similar to that found in critical phenomena experiments on fluids.

These gel point results are valid beneath the gel point if attention is restricted to the "Porod" regime, where  $qR_z \gg 1$ . Here  $R_z$  is the  $z$ -averaged radius, defined by

$$R_z^2 = M_w^{-1} \int M^2 N(M) R^2 dM \sim \epsilon^{-2\gamma/\mu} \quad (19)$$

In the "Guinier" regime, where  $qR_z \ll 1$ , the structure factor and the first cumulant becomes insensitive to the fractal nature of the solutions. In this small  $q$  limit, the intensity depends on  $R_z$  alone through

$$I(q) = Bc\nu M_w (1 - q^2 R_z^2 / d + \dots)$$

and the first cumulant becomes  $q^2$  dependent, so  $K_1/q^2 = D_z$ , where  $D_z$  is the  $z$ -averaged diffusion coefficient.

In the "crossover" regime, where  $qR_z \sim 1$ , the structure factor and first cumulant become sensitive to the details of the nonuniversal functions  $f(r/\lambda)$  and  $h(z)$ . The scaling function  $f(r/\lambda)$  may be given by a detailed model, as in the case of linear polymers,<sup>5</sup> or may be chosen for mathematical convenience. An example of the latter is  $f(x) = e^{-x}$  for  $d = 3$  and  $D = 2$ , which gives the Ornstein-Zernike form,<sup>10</sup>  $S_M(q) = (1 - q^2 R^2 / 3)^{-1}$ . To simplify calculations, we assume the following special form for  $f(x)$ :

$$f(x) = e^{-x^2} \quad (20)$$

The results of Monte Carlo simulations led Leath<sup>11</sup> to propose  $h(z) = \exp[-b(z - z_{\text{max}})^2]$ . We simplify this somewhat by using the asymptotic form of this function

$$h(z) = e^{-bz^2} \quad (21)$$

This gives the scaling singularity correctly and corrections for nonzero  $z_{\max}$  may be calculated systematically. Furthermore, we limit the present calculation to  $d=3$  and assume  $\sigma \sim 1/D$ , which is approximately true for three dimensions, where  $\nu=0.84$  and  $\sigma\nu=1/D$ . Substituting (20) and (21) into (13) then gives

$$I(q) = \pi Bc\nu D \Gamma(D/2) G(0) (1 + 2q^2 R_z^2 / \mu D)^{-\mu/2}, \quad (22)$$

where

$$G(x) = (8R_z^2 / \mu D)^{\mu/2 - x} \Gamma(\mu/2 - x) F(\mu/2 - x, 3/2 - D/2; 3/2; (2q^2 R_z^2 / \mu D) / (1 + 2q^2 R_z^2 / \mu D)),$$

$F$  is the hypergeometric function,  $\Gamma$  is the gamma function, and  $\mu = D(3 - \tau)$ . By construction, for small  $q$  this function reduces to the proper Guinier expansion. In the Porod regime, where  $qR_z \gg 1$ , the hypergeometric function becomes a simple  $q$ -independent constant,  $F(\mu/2, 3/2 - D/2; 3/2; 1)$  and (22) reduces to the scaling result  $I(q) \sim q^{-\mu}$ . It is interesting to note that for  $D=3$ , the particles are not fractal ( $g(r) = f(r/\lambda)$ ) yet the power-law distribution of sizes gives power law behavior for the intensity. In fact, this nonfractal particle calculation can be shown to be equivalent to an earlier droplet model calculation which gives the Fisher-modified Ornstein-Zernike form<sup>12</sup> for  $I(q)$ .

For rigid particles which are roughly spherically symmetric, the first cumulant may be calculated in a similar fashion to find

$$K_1 = D_0 G(1/2) q^2 (1 + q^2 R_z^2 / \mu D)^{1/2} / G(0). \quad (23)$$

Here  $D_0$  is the  $M_w$  independent prefactor for the  $z$ -averaged diffusion coefficient (observed in the  $q=0$  limit). Equation (23) exhibits the  $K_1 \sim q^3$  dependence in the Porod regime, and the expected  $K_1 \sim q^2$  dependence in the Guinier regime. Again, this behavior is quite similar to that found for the first cumulant of correlation functions near thermodynamic critical or consolute points. In fact, in the limit that  $\mu=2$ ,  $D=3$ , and  $d=3$ ,  $K_1$  is identical to the Perl and Ferrel result for the time decay rate of correlation functions near the critical point, and gives a good fit to experimental data.<sup>9</sup> However, this choice of parameters in the "dynamic droplet" model does not satisfy the scaling conditions on the distribution of sizes and thus the present calculation represents an improved version of this droplet model.

In the beginning of this article, the fractal dimension of a single particle was introduced through relations involving the radius, mass, pair correlation function, and structure factor. For a polydisperse system the exponent  $\mu$  may be considered a fractal dimension if the mass and radius are defined as  $M_w$  and  $R_z$ , respectively. Then

$$M_w \sim R_z^\mu, \quad g(r) \sim 1/r^{d-\mu}, \quad r \ll R_z, \\ S(q) \sim 1/q^\mu, \quad q^{-1} \ll R_z.$$

It is the polydispersity-smeared fractal dimension which is of practical interest to the experimentalist. To extract  $D$  from the measured exponent  $\mu$  will require a separate determination of the exponent  $\tau$ —an experimentally difficult prospect.

For percolation clusters near the critical point,  $D$  is thought (as we have assumed) to be  $1/\sigma\nu \sim 2.5$ , where the correlation length,  $R_z$ , scales like  $\epsilon^{-\nu}$ . Using  $3 - \tau = \gamma\sigma$  gives  $\mu = \gamma/\nu = 2 - \eta$ . This polydispersity-smeared fractal dimension is in agreement with the effective dimensionality proposed by Stanley,<sup>13</sup> and Stanley, Birgneau, Reynolds, and Nicoll,<sup>14</sup> and later by Daoud, Family, and Jannink,<sup>15</sup> and demonstrates the relevance of this effective dimensionality to experimental work. Stanley has pointed out that in  $1 < d < 6$ ,  $\gamma/\nu$  is very nearly 2, and for  $d \geq 6$ ,  $\gamma/\nu$  is identically 2.

In conclusion, the principal results of this paper are the scaling forms for the structure factor and first cumulant of power-law polydisperse fractal systems. These are directly obtained from (13) and (16). We see that the structure factor is a function of the product  $qR_z$  alone,  $S(q) = F_1(qR_z)$ , and the first cumulant is of the form  $K_1 = q^2 D_z F_2(qR_z)$ , where  $F_1$  and  $F_2$  are functions which scale like  $q^\mu$  and  $q^3$ , respectively, for  $qR_z \gg 1$ . This  $q^3$  dependence of the first cumulant could be valuable in the interpretation of experimental data; if the first cumulant does not scale like  $q^3$  on length scales smaller than the correlation range then the system must not be power-law polydisperse, and any growth mechanism which predicts a power law for the polydispersity must be ruled out.

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