Second-Order Light Scattering and Local Anisotropy of Diffusion-Limited Aggregates and Bond-Percolation Clusters

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Though having similar fractal dimensionality ($D \approx 2.5$), diffusion-limited aggregates and bond-percolation clusters are shown to have quite different second-order light scattering (SOLS) behaviors. The SOLS intensities scale as power of the fractal mass, $I^{(2)} \propto N^x$, with x equal to ≈ 1.1 for diffusion-limited aggregates and ≈ 1.5 for bond-percolation clusters. This difference arises from the contribution of three- and four-body correlations. Thus it is suggested that SOLS can be used to reveal new structural information about fractals and to differentiate between them when they obey the same mass-size relations.

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During the past few years there has developed a great interest in fractal objects,[1] their study being invoked to understand various disorderly growth processes, the roughness of interfaces, transport in random (e.g., porous) media, flocculation, and gelation, and numerous other phenomena in colloid and materials sciences (see, for example, the papers collected in Refs. 2 and 3). Fractals[1] are scale-invariant structures and their properties are naturally described via scaling laws. These features bear a fundamental resemblance to critical phenomena, and it is now widely appreciated that a fractal is in general sufficiently complicated that it cannot be characterized by just a few exponents. Indeed it has been shown, for a wide variety of fractal systems and processes occurring on them, that infinite hierarchies of scaling indices and fractal dimensionalities are needed (see, for example, Mandelbrot,[4] Hentschel and Procaccia,[5] Halsey, Meakin, and Procaccia,[6] Halsey *et al.*,[7] de Arcangelis, Redner, and Coniglio,[8] and Meakin *et al.*[9]). The fractal dimensionality (D) defined in terms of the scaling of mass (number of particles or occupied sites) with a characteristic size (the radius of gyration, for example) is represented by only one point in this spectrum and therefore provides only one measure of the system properties. Accordingly, new probes which reveal further structural and dynamical information are highly desirable. In the present Letter we focus attention on the role of three- and four-body contributions to positional correlations in these systems.

First-order light scattering has been used extensively to determine the various particle sizes σ and correlation ranges ξ in simple liquids, polymers, and colloidal aggregates, etc.[10] Systematic analyses of the first-order intensity as a function of the magnitude of the wave vector $Q = (4\pi/\lambda)\sin\theta/2$ (here λ is the optical wave length and θ is the scattering angle) involve convolution of particle form factors $P(Q)$ and interference $S(Q)$; they depend sensitively on how Q^{-1} compares with σ and ξ. In the limit of small-angle scattering ($Q \to 0$), for example, we have $S(Q) \approx S(0)[-(Q^2/3)R_g^2]$ from which the radius of gyration R_g of a cluster is determined. For our present purposes, however, it suffices to note in general that the only *inter*particle correlations which enter are those associated with *two*-body effects:

$$I^{(1)} \propto S(Q) \propto \int d^3r [g(r) - 1] e^{-\mathbf{Q}\cdot\mathbf{r}}. \tag{1}$$

But the scaling behavior of the radial distribution function, $g(r)$, is determined by the same fractal dimensionality (D) which governs the dependence of particle number N on size R. That is, $N(R) \sim R^D$ implies

$$g(R) \sim R^{D-3}. \tag{2}$$

This scaling leads in turn to $S(Q) \sim (Q\sigma)^{-D}$ for intermediate wave numbers, i.e., $Q\sigma \ll 1$ and $Q\xi \gg 1$, where σ is the diameter of an individual scattering particle and ξ is the overall cluster size.[11,12] It follows from (1) and (2) that different kinds of fractals with a similar fractal dimensionality D cannot be distinguished by static-first-order intensities.

In *second*-order scattering, on the other hand, each electric field amplitude contributing to the detected signal involves polarization of *two* particles. We find that adding these amplitudes, squaring, and ensemble averaging then gives the observed intensity. Accordingly, two-, three-, *and* four-body correlation effects all contribute to

the static, second-order light scattering (SOLS). Furthermore, the SOLS includes a *de*polarized component, even though the system consists of isotropic particles. This arises to the extent that the *relative* positions involve a breaking of spherical symmetry. For this reason SOLS has been used widely to study local anisotropy and higher-order particle correlations in simple fluids,[13] polymers,[14] etc.

For self-similar objects such as fractals, a scaling law is expected for SOLS, e.g.,

$$I^{(2)} \sim N^{x}, \tag{3}$$

where the exponent x reflects the structural asymmetry and many-body correlations. Keyes *et al.*[15] have recently carried out an evaluation of x for bond-percolation clusters (BPC's) and have made some conjectures concerning its universality. In particular, they derive from scaling arguments a formula relating the exponent x to the fractal dimensionality D:

$$x = 4 - 6/D. \tag{4}$$

From numerical evaluation of $I^{(2)}$ for BPC's of increasing size, Keyes *et al.* found $x \approx 1.5$ and concluded that Eq. (4) is satisfied for this case ($D \approx 2.5$). Note, however, that if this relation were valid in general the N dependence of the SOLS would provide no structural information beyond that already known from $I^{(1)}$. In any case, we shall see below that Eq. (4) is violated for three-dimensional diffusion-limited aggregation[16] (DLA) clusters for which $x \approx 1.1$ even though the effective fractal dimensionality, D, is about 2.5[17] (at least for clusters of the size used in our work). This will be shown to arise from the different nature of the higher-order positional correlations in these two fractal objects.

Since the SOLS intensity involves the average square of the sum of doubly scattered waves, it is quadratic in the dipole propagator $\mathbf{F}(\mathbf{r}_{ij},\omega)$ which acts on a ω-varying polarization—induced by the incident field at the ith particle—to give the field at the jth particle.[18] More explicitly, in the long wavelength limit, we have $\mathbf{F}_{\omega\to 0} = \mathbf{T}$ where

$$\mathbf{T}(\mathbf{r}) = \frac{3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}}{r^{3}}, \tag{5}$$

the familiar (static) dipole tensor. Now, the first scattering process, involving the particle i, say, induces a dipole moment $\boldsymbol{\mu}_i$ proportional to the scalar polarizability α and the incident field amplitude E_0. This singly scattered wave has the form $\mathbf{T}(\mathbf{r}_{ji})\cdot(\boldsymbol{\mu}_i = \alpha\mathbf{E}_0)$ at each neighboring particle j. Summing over all j, and then over all i, we obtain the sum of doubly scattered waves at the detector. The squaring, and averaging over all many-particle configurations, then gives the second-order light-scattering intensity:

$$I^{(2)} \propto \left\langle \sum_{i,j}^{N} T_{xz}(\mathbf{r}_{ij}) \sum_{k,l}^{N} T_{xz}(\mathbf{r}_{kl}) \right\rangle. \tag{6}$$

In writing the above, i,j and k,l refer to the pairs of particles separated by $\mathbf{r}_{ij}$ and $\mathbf{r}_{kl}$, and the brackets denote as usual the appropriate ensemble average. In addition, we have expressed $I^{(2)}$ for a particular laboratory polarization geometry—*"VH"*[19]—in which the incoming beam lies in the xy plane, with the detector along the y axis. Note that $I^{(2)}$ is independent of scattering angle because we are working in the long wavelength limit. The incident and final linear polarization directions are z and x, so that only one space-fixed component (xz) of the T tensors enters. The *de*polarization in the SOLS arises from the fact that—even though, because of the scalar α, $\boldsymbol{\mu}_i = \alpha\mathbf{E}_0$ *is* necessarily parallel to $\mathbf{E}_0$—$\boldsymbol{\mu}_j = \alpha\mathbf{T}_{ji}\cdot\boldsymbol{\mu}_i$ is *not*, because of the anisotropy of the dipole tensor $\mathbf{T}$. Since the *first*-order scattering is strictly polarized, the much weaker second-order contributions are thus observed in the depolarization. Note also that the SOLS intensity scales as α^4, vs α^2 in the first-order case, whereas both $I^{(1)}$ and $I^{(2)}$ are linear in $|E_0|^2 = I_0$.

From Eqs. (5) and (6) it can be seen how the SOLS is sensitive to the structural *anisotropy* rather than just to the density of a cluster. In the case of a rigid rod, for example, the second-order intensity is proportional to N^2, and similarly for a uniform-density object in *two* dimensions (e.g., a rigid sheet, or disk). For three intersecting, perpendicular rods, however, the SOLS is greatly reduced because of greater cancellations in anisotropy. The same effect occurs to a most dramatic extent in a compact cubic lattice which of course has a much higher density and more fully developed spherical symmetry than the three-rod system. This "demise" of local anisotropy as the cubic lattice is "filled up" provided, in fact, a useful model for the decreasing (with density) SOLS intensity observed almost twenty years ago in the compressed rare-gas fluids.[20] Thus, even without the benefit of more detailed analyses, one must suspect the validity of relation (4).

We have evaluated numerically the SOLS, according to (6), for two types of fractals having similar fractal dimensionality: diffusion-limited aggregates[16] and bond-percolation clusters. For 300 lattice DLA's, with sizes up to $N = 1000$, the results for $\ln I^{(2)}$ vs $\ln N$ give a straight line with slope $x \approx 1.1$. To check the effect of the (cubic) lattice constraint, another 300 *off*-lattice DLA's[17] with the same sizes were also generated. Approximately the same N-scaling behavior for $I^{(2)}$ was observed, but with less fluctuation among the smaller clusters. The results for off-lattice DLA's are plotted in Fig. 1 by solid circles.

In order to compare the SOLS of DLA's with the results for BPC's reported in Ref. 15, the same rules were used to "grow" the BPC's and $I^{(2)}$ vs N again calculated. From the average of 32 clusters, with sizes up to $N = 1000$, we confirm that $x \approx 1.5$—see the solid circles in Fig. 2. We also checked the fractal dimensionalities D by computing the radii of gyration: We find $R_g \sim N^{D}$

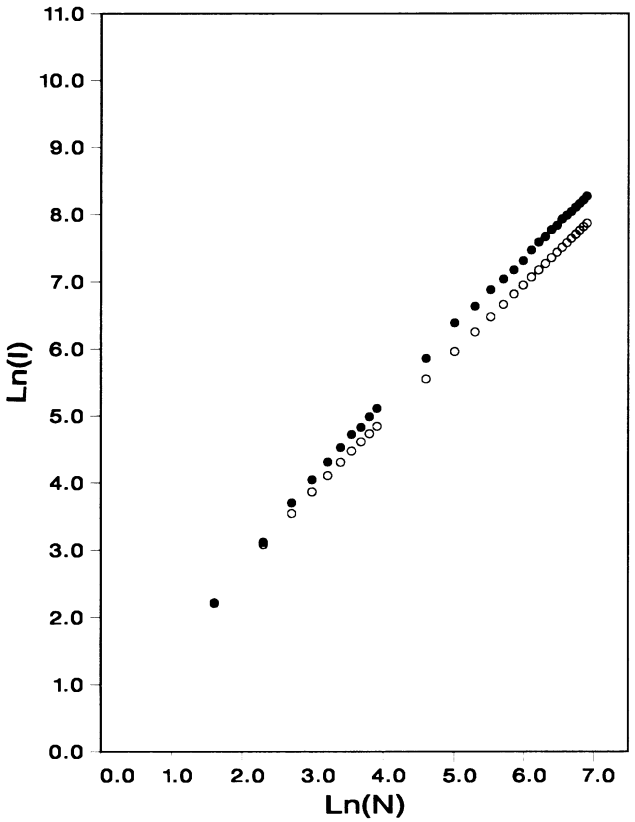

FIG. 1. Intensity of second-order light scattering vs size of DLA clusters. Solid circle, total intensity; open circle, contribution from two-body correlations.

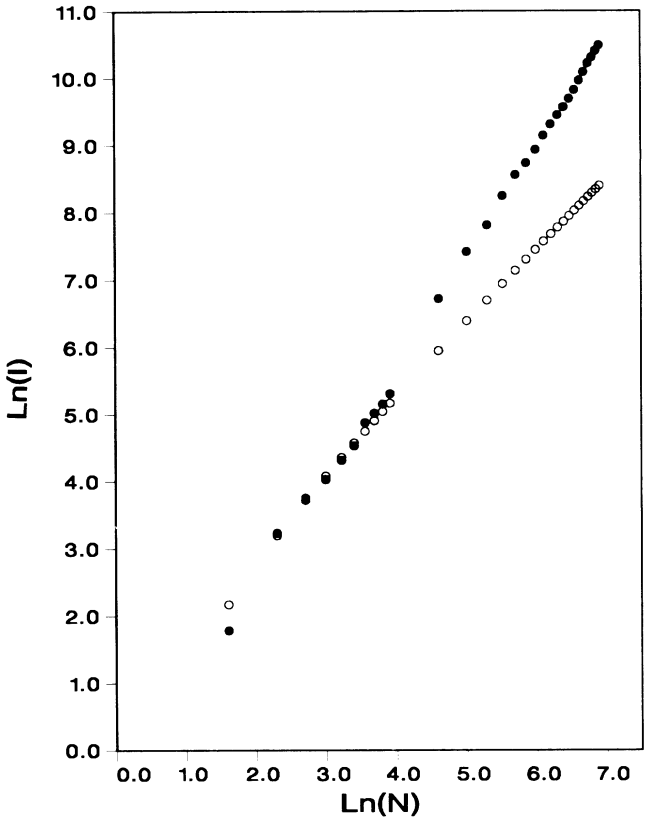

FIG. 2. Intensity of second-order light scattering vs size of BPC's. Solid circle, total intensity; open circle, contribution from two-body correlations.

with $D \approx 2.5$ for DLA's and $D \approx 2.55$ for BPC's.

As mentioned earlier, since the scaling behavior of the two-body distribution function is determined by D via (2), it follows that the differences in second-order light-scattering intensities are due to differences in the contributions from *many-* (i.e., three- and four-) body correlations. To explore this point quantitatively, we rewrite the SOLS intensity (5) as

$$I^{(2)} \propto \left\{ \left\langle \sum_{i \neq j} [T_{xz}(ij)]^2 \right\rangle + \left\langle \sum_{i \neq j \neq k} T_{xz}(ij) T_{xz}(jk) + \sum_{i \neq j \neq k \neq l} T_{xz}(ij) T_{xz}(kl) \right\rangle \right\}. \tag{7}$$

Here the first term in curly brackets includes the pair-distribution effects, while the second ensemble average corresponds to the three- and four-particle contributions. The open circles in Figs. 1 and 2 show our results for the two-body terms in $I^{(2)}$. It is not surprising that, *for both types of cluster,* these terms obey the same scaling law ($\sim N^{1.1}$), consistent with the fact that both aggregates are characterized by the same D. Note also that the SOLS intensity for DLA is dominated by the two-body terms, whereas that for BPC includes significant contributions from three- and four-particle correlations, their relative importance increasing with N.

Having established the role of the higher-order correlations, it is nevertheless most difficult to calculate them directly. Further insight into their differences in DLA's and BPC's can, however, be gained from the nearest-neighbor distributions.[21] By evaluating $g(r)$ at r = lattice constant, we find that each DLA particle has approximately two nearest neighbors, reflecting the branched polymer nature of the aggregate's local structure. For cubic-lattice BPC's, on the other hand, each particle has approximately three nearest neighbors, consistent with these clusters being formed at the percolation threshold ($p = p_c = 0.25$): A bond can be placed in each of two cubic-lattice directions, so that about half of the adjacent sites are occupied. Thus the local anisotropy and the many-body correlations arise from the different nearest-neighbor geometries of DLA's and BPC's.

In conclusion, we have presented an analysis of the second-order light scattering from two different fractal objects, diffusion-limited aggregates and bond-percolation clusters. Since these two objects have similar mass-size fractal dimensionalities ($D \approx 2.5$), they cannot be distinguished via first-order scattering experiments. However, it is easily appreciated that these two fractals are structurally different from one another, and analyses of simulation results[22-24] have shown that, unlike the percolation clusters, the center of a two-dimensional DLA is a special point for which the radial and tangential correlations are different. Thus it is natural to seek supplemental properties which are amenable to direct experimental measurement for characterizing them. We have suggested the usefulness of measuring and calculating the size-scaling behavior of the second-order light scattering. We have shown in particular that the $I^{(2)} \sim N^x$ exponents are significantly different for DLA's and BPC's, and that this difference arises from the competing contributions of the three- and four-particle correlations. Further studies of this kind will be important for elucidating the nature of local anisotropy in these basic fractal structures.

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[1]B. B. Mandelbrot, *The Fractal Geometry of Nature* (W. H. Freeman, New York, 1982).

[2]*On Growth and Form: Fractal and Nonfractal Patterns in Physics,* NATO Advanced Study Institute Series E, Vol. 100, edited by H. E. Stanley and N. Ostrowsky (Martinus Nijhoff, Dordrecht, 1986).

[3]*Kinetics of Aggregation and Gelation,* edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).

[4]B. B. Mandelbrot, J. Fluid Mech. **62**, 331 (1974).

[5]H. G. E. Hentschel and I. Procaccia, Physica (Amsterdam) **8D**, 435 (1983).

[6]T. E. Halsey, P. Meakin, and I. Procaccia, Phys. Rev. Lett. **56**, 854 (1986).

[7]T. C. Halsey, M. H. Jensen, L. P. Kadanoff, I. Procaccia, and B. Shraimen, Phys. Rev. A **33**, 1141 (1986).

[8]L. de Arcangelis, S. Redner, and A. Coniglio, Phys. Rev. B **31**, 4725 (1985).

[9]P. Meakin, H. E. Stanley, A. Coniglio, and T. A. Witten, Phys. Rev. A **32**, 2364 (1985).

[10]B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[11]S. H. Chen and J. Teixeira, Phys. Rev. Lett. **57**, 2583 (1986); J. Teixeira, *Experimental Methods for Studying Fractal Aggregates,* in Ref. 2, pp. 145–162.

[12]D. S. Cannell and C. Aubert, *Aggregation of Colloidal Silica,* in Ref. 2, pp. 187–197.

[13]W. M. Gelbart, Adv. Chem. Phys. **26**, 1 (1974), and Philos. Trans. Roy. Soc., Ser. A **293**, 359 (1979).

[14]B. M. Ladanyi and T. Keyes, Mol. Phys. **37**, 1809 (1979), and J. Chem. Phys. **76**, 2047 (1982).

[15]T. Keyes, G. Seeley, P. Weakliem, and T. Ohtsuki, "Collision Induced Light Scattering from Growing Clusters: Depolarization by Fractals," to be published, and J. Chem. Soc. Faraday Trans. 2, to be published.

[16]T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).

[17]P. Meakin, Phys. Rev. A **27**, 604, 1495 (1983).

[18]W. M. Gelbart, in *Intermolecular Spectroscopy,* edited by J. van Kranendonk (North-Holland, Amsterdam, 1980).

[19]See Ref. 10, pp. 31 and 115.

[20]M. Thibeau, G. C. Tabisz, B. Oksengorn, and B. Vodar, J. Quant. Spectrosc. Radiat. Transfer **10**, 839 (1970).

[21]P. Dimon, S. K. Sinha, D. A. Weitz, C. R. Safinya, C. S. Smith, W. A. Varady, and H. M. Lindsay, Phys. Rev. Lett. **57**, 595 (1986).

[22]T. C. Halsey and P. Meakin, Phys. Rev. A **32**, 2546 (1985).

[23]P. Meakin and T. Vicsek, Phys. Rev. A **32**, 685 (1985).

[24]M. Kolb, J. Phys. (Paris), Lett. **46**, L631 (1985).