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Structure and anisotropy of colloid aggregates

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We study the complex, disordered structure of clusters formed by several kinetic aggregation processes. By expanding the structure factor into spherical harmonics, detailed information about both the structure and anisotropy of the clusters at all length scales is obtained. The scaling of the expansion terms with cluster mass and order of the expansion is investigated. For cluster-cluster aggregates, we find that the fractal dimension, which reflects the scaling of the orientationally averaged structure, also describes the scaling of the spherical harmonics, which reflect the anisotropies of the structure. By contrast, clusters formed by single-particle diffusion-limited aggregation do not appear to exhibit the same degree of scale invariance. Cluster-cluster aggregates are found to exhibit considerably more anisotropy than those formed by single-particle diffusion. The consequences of the anisotropies for quasielastic light scattering experiments are discussed.

I. INTRODUCTION

Random growth processes, such as colloidal aggregation, typically form highly disordered, complex structures. Nevertheless, many of these structures can be quantitatively characterized in terms of their behavior upon change of length scale and the dilation symmetry which they exhibit. This is frequently expressed in terms of a single exponent, the fractal dimension d_f, which reflects the scaling of the mass of the cluster with its radius, $M \propto R^{d_f}$.[1-3] The internal structure of the cluster can also be described in terms of the fractal dimension by means of the pair-correlation function, which also exhibits a scaling form, $g(r) \propto r^{d_f-3}$, in three dimensions. This description of the structure has led to great strides in our understanding of the physical properties of the clusters as well as the kinetic growth processes which lead to their formation. However, the pair correlation function reflects an orientationally averaged description of the cluster and can not, by itself, fully describe the very complex structure of an aggregate. By its very nature, a random aggregate is not radially symmetric, and a description that goes beyond the fractal dimension is needed to fully describe its structure. Indeed, there are many physical properties of aggregates that explicitly depend on the anisotropies of its structure.

In this paper we consider one description of the structure of random aggregates which explicitly accounts for their anisotropy. Their structure is expressed as an expansion in terms of spherical harmonics.[4] Such a decomposition has been performed in real space,[5] and has been used to investigate second-order light scattering.[6] However, second-order light scattering depends on three- and four-particle correlations. Here we consider only two-particle correlations, and study the multipole expansion in momentum space. We use the Fourier transform of the pair-correlation function, the structure factor, which for a fractal aggregate also reflects the fractal geometry in its scaling with wave vector, $S(k) \propto k^{-d_f}$. The scaling of the multipole expansion terms, both with cluster mass as the aggregate size increases and with length scale, through the k dependence, for a given cluster, was determined. To compare with experiments we use aggregates generated by two different models for cluster-cluster aggregation, diffusion-limited cluster-cluster aggregation (DLCA) and reaction-limited cluster-cluster aggregation (RLCA). To further elucidate their properties, the scaling of the multipole terms of these clusters was compared with those generated by single-particle diffusion-limited aggregation (DLA).

The fractal nature of colloidal aggregates has been established experimentally through light,[7] neutron,[8] and x-ray scattering.[9] These static scattering experiments determine orientationally averaged quantities, and provide a measure of the fractal dimension through the static structure factor. These measurements average out all the asymmetries in the structure of the aggregates. By contrast, quasi-elastic light scattering, which probes the fluctuations of the scattered light due to the diffusive motion of the aggregates, is directly sensitive to the structural

anisotropy when $kR_g > 1$. Both translational and rotational diffusion of the aggregates contribute to the decay of the autocorrelation function of the scattered light measured by quasielastic light scattering. A study of these rotational contributions allows the asymmetries of the aggregates to be investigated. This leads in a natural way to a decomposition of the temporal autocorrelation function into an infinite series of multipole terms representing the anisotropies of the aggregates in increasingly fine detail, with each term having a characteristic relaxation time. This directly reflects the structural anisotropies of the clusters, since the initial value of the autocorrelation function is just the static structure factor. This connection between the anisotropies of the structure and their importance for the dynamic behavior raises the issue of possible scaling forms for the multipole terms, since they add up to $S(k)$ which scales as $kR_g^{-d_f}$ for $kR_g > 1$.

In this paper we show that these multipoles do indeed have scaling properties. They describe the anisotropies on all length scales smaller than the cluster size. However, we find that the introduction of the multipole terms does not require the introduction of additional fractal dimensions. We show that for cluster-cluster aggregates the scaling of the multipole terms is determined solely by the value of d_f. Furthermore, we find that DLCA clusters have a larger anisotropy than RLCA clusters, as is intuitively expected, since their fractal dimension is lower and they are less dense. By contrast, DLA clusters do not seem to exhibit the same scaling behavior as the cluster-cluster aggregates.

II. BACKGROUND

The structure factor of the clusters is given by

$$S(k)=\left|\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right|^2 , \tag{1}$$

where the summation extends over each of the particles, at positions $\mathbf{r}_i$, which comprise the cluster. This structure factor directly reflects the polarized light scattered by the cluster composed of N identical particles if they are small compared to the inverse scattering wave vector k^{-1}, so the scattering from each is isotropic. In order to ensure that this structure factor properly reflects the total scattered light, we have not normalized it by N^2, so that $S(0)=N^2$. The position of each particle in the cluster is given by a vector $\mathbf{b}_i$ from the center of mass of the cluster; this vector has an orientation Ω_i relative to an arbitrary axis fixed to the cluster. The orientationally averaged scattering from the cluster can be written as a series of multipole expansion terms[4]

$$S(k)=\sum_l S_l(k) , \tag{2}$$

where

$$S_l(k)=\sum_{m=-l}^{l}\left|\sum_{i=0}^{N} j_l(kb_i)Y_{lm}(\Omega_i)\right|^2 . \tag{3}$$

Here $j_l(kb_i)$ are the spherical Bessel functions of order l, and $Y_{lm}(\Omega_i)$ the spherical harmonics of order l,m.

To calculate the multipole expansion terms $S_l(k)$, we use clusters generated by off-lattice computer simulations using various aggregation models. In order to compare to experimentally realizable conditions, we restrict ourselves to three dimensions, and examine clusters obtained from simulations of diffusion-limited cluster-cluster aggregation (Refs. 10 and 11) and reaction-limited cluster-cluster aggregation.[12] In DLCA, the colloid aggregation process begins with a set of monomers which are free to diffuse. When two monomers touch, they form a permanent, rigid dimer. This process continues, with both clusters and monomers diffusing and bonding to form larger and larger clusters, with most growth occurring through collisions of clusters of roughly equal size. For RLCA there is only a small probability that two clusters will stick together when they collide. Many collisions are required before two clusters stick, allowing all possible bonding configurations to be sampled. Reaction-limited aggregation is slower than diffusion-limited aggregation, and forms denser clusters. This is reflected by the fractal dimensions, which are 1.8 for DLCA and 2.1 for RLCA. Reaction-limited aggregation produces a much broader distribution of cluster sizes, with growth occurring by combination of clusters of all sizes with nearly equal probability. Both aggregation conditions have been observed experimentally,[13] and the measured fractal dimensions are in accord with those obtained by the computer simulations. For comparison, we also examine clusters generated by simulations of single-particle diffusion-limited aggregation,[14,15] in which single particles diffuse freely until they touch a cluster grown from a seed particle. The chief distinctions between DLA and the cluster-cluster aggregation systems are that DLA clusters have a well-defined center and have a higher fractal dimension, $d_f \approx 2.5$.

III. RESULTS

In Fig. 1 we show the multipole expansion terms $S_l(k)$ for DLCA clusters with 900 particles, for $l=0$ to 7. Each curve represents an average of 20 different clusters of the same mass. For these clusters, the average radius

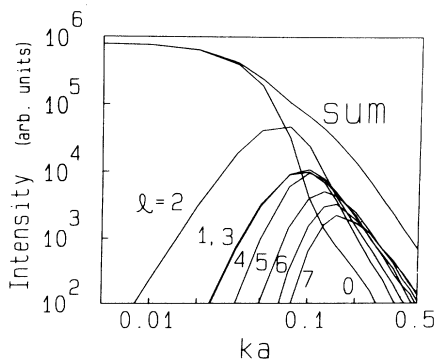

FIG. 1. Multipole terms averaged over 20 DLCA clusters of 900 particles each, plotted as a function of ka, where a is the monomer radius. Multipole terms for $l=0$ to 7 are shown; the uppermost curve is the sum of these terms.

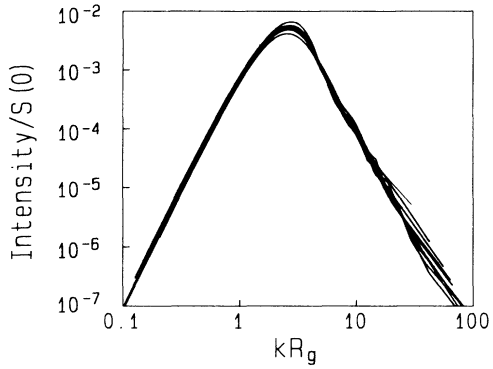

FIG. 2. Scaled $l=2$ multipole terms for DLCA clusters of 100 to 1000 particles. Each curve is the average of 20 clusters of the same mass, with the amplitude of the multipole term scaled by $S(0)$.

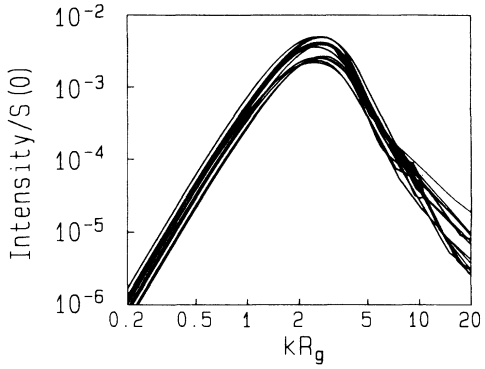

FIG. 4. Scaled $l=2$ multipole terms for RLCA clusters of 50 to 1000 particles. Each curve is the average of several clusters of the same mass, with the amplitude of the multipole term scaled by $S(0)$.

of gyration is $R_g \approx 19.7a$, where a is the radius of a monomer. Qualitatively similar results are obtained for other clusters with different masses. At all length scales larger than the cluster size, $kR_g < 1$, the internal structure of the cluster is not resolved, and the cluster appears as a point scatterer, which means that at small wave vectors $S(k)$ is a constant. In the multipole expansion, we see that at small wave vectors the $l=0$ isotropic term is constant, dominating all the other multipole terms, so that the sum is independent of k. At larger wave vectors corresponding to shorter length scales, $kR_g > 1$, the interior structure of the clusters is resolved. Here the $l=0$ term decreases, and the higher-order multipole terms become important. Each of the higher-order terms is small at low wave vectors, rises to a maximum value at some intermediate wave vector, and then decreases at higher k.

The dependence of the multipole expansion terms on cluster mass, and on k for a given mass, provides new insights into the scale invariance of these clusters. We begin by studying the dependence on cluster mass, allowing us to assess the variation of the cluster asymmetry with its size.

All clusters, both physical and simulated, are objects of finite extent. They possess a characteristic length scale, the cluster size, which is conveniently measured by their radius of gyration. If the multipole expansion terms exhibit scaling between clusters of different masses, R_g must be the only characteristic length scale for each cluster. If the asymmetry is scale-invariant, the $Y_{lm}(\Omega_i)$ terms in Eq. (3) will not depend on the size of the cluster. Rather, the scale dependence will be reflected only in the spherical Bessel functions, which depend on the radius of the cluster through the argument kb_i, and on the number of particles N that make up the cluster, determining the limit on the sum. This implies that the amplitudes of the multipole expansion terms should be normalized by $S(0)=N^2$ to compare clusters of different masses. Therefore, we investigate the scale invariance of the cluster asymmetry by scaling the magnitude of the multipole terms by N^2 and scaling the wavevector by R_g. If the asymmetry is scale invariant, the normalized multipole terms should lie on a single universal curve for each value of l.

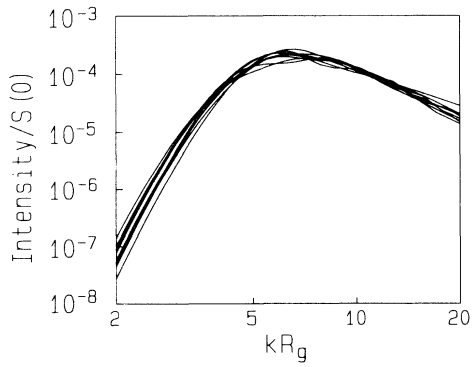

FIG. 3. Scaled $l=7$ multipole terms for DLCA clusters of 100 to 1000 particles. Each curve is the average of 20 clusters of the same mass, with the amplitude of the multipole term scaled by $S(0)$.

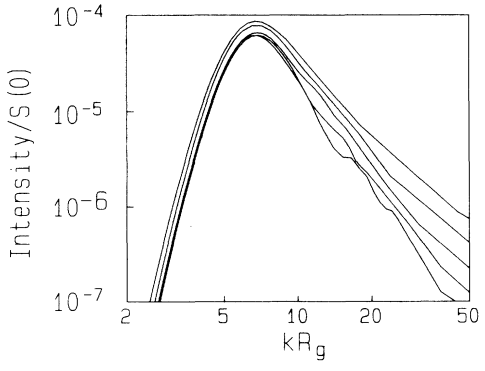

FIG. 5. Scaled $l=7$ multipole terms for DLA clusters of 625 to 10 000 particles. Each curve is the average of several clusters of the same mass, with the amplitude of the multipole term scaled by $S(0)$.

The results when this scaling is performed for the $l=2$ multipole terms for a series of DLCA clusters of 100–10 000 particles are shown in Fig. 2. To reduce fluctuations, each curve is the mean of the expansion terms for 20 clusters of identical mass. The scaled amplitudes for the $l=7$ multipole terms for the same set of clusters are shown in Fig. 3. In both cases, the scaled amplitudes of the multipole terms for each cluster mass fall on a single curve. Similar results are obtained for all other multipole terms. Therefore we conclude that the structural asymmetry of these DLCA clusters is scale invariant.

In Fig. 4 we show a similar plot of the $l=2$ multipole terms for a series of RLCA clusters of masses 50–1800. We again find scaling behavior, although there is considerably more deviation between the individual curves than exists for the DLCA clusters. Nevertheless, these are random fluctuations, within which the asymmetry of the RLCA clusters is scale invariant. For comparison, the scaled amplitudes for the $l=7$ multipole terms for a series of single-particle DLA clusters of masses 625–10 000 are shown in Fig. 5. While the overall shapes of the curves are very similar, for the DLA clusters there is a definite trend in the scaling behavior, as the magnitudes of the scaled multipole expansion terms decrease as the cluster mass increases, for all kR_g. Thus the single-particle DLA clusters do not exhibit the same scaling as the cluster-cluster aggregates. This is consistent with other simulation results[16] which indicate that two-dimensional DLA clusters have a more complex structure than RLCA and DLCA clusters. For DLA clusters more than one scaling exponent or fractal dimension may be required to describe their structure.[17–19]

The contrasting behavior of the single-particle and cluste-cluster aggregates is better demonstrated by investigating the variation of the peaks of the scaled multipole terms with cluster mass. This is shown for the $l=2$ and 7 multipole terms for DLCA clusters in Fig. 6 and for the $l=2$, 3, and 7 multipole terms for the RLCA clusters in Fig. 7. In both cases there are fluctuations but no clear trend, again illustrating the scale invariance of the asymmetry of the cluster-cluster aggregates. By contrast, as shown in Fig. 8, for the DLA clusters a clear trend is evident, as the scaled peak heights of all the multipole terms decrease with increasing cluster mass. This implies that

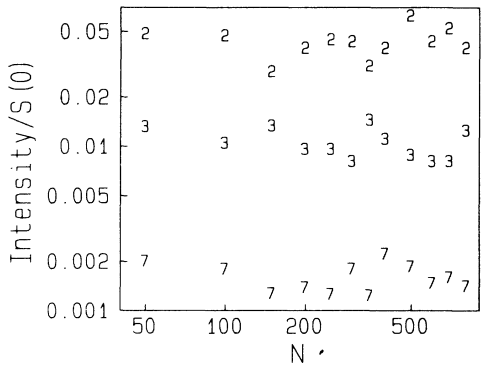

FIG. 7. The peak values of the $L=2$, 3, and 7 multipole terms, scaled by $S(0)$, for RLCA clusters.

the DLA clusters become more isotropic as their mass increases. This mass dependence is most pronounced for the $l=2$ multipole term, but still remains for the higher orders. Thus the asymmetry of the DLA clusters does not exhibit the same scaling between clusters of different masses as that of cluster-cluster aggregates.

The origin of this behavior for the DLA clusters is unclear. We emphasize that we have investigated clusters only up to $N=10\,000$. It is known that many of the features exhibited by DLA clusters are not manifest until very large sizes are achieved. Thus it is possible that the lack of exact scale invariance exhibited by these smaller DLA clusters is not inherent to the clusters themselves; rather it may reflect the fact that scale invariance is achieved more rapidly for cluster-cluster aggregates than for single-particle aggregates. Thus, at higher masses, it is possible that DLA clusters will also exhibit the same scale invariance and mass dependence as the cluster-cluster aggregates. Nevertheless, it is clear that if it exists this scale invariance is achieved only at much larger cluster masses. This may be due to the fact that the DLA clusters have a very well-defined center,[20] the seed particle, unlike the cluster-cluster aggregates. This effect may be further exacerbated by the relatively higher fractal dimension which causes R_g to increase much more slowly with N than for the cluster-cluster aggregates.

At present, relatively little is known about the struc-

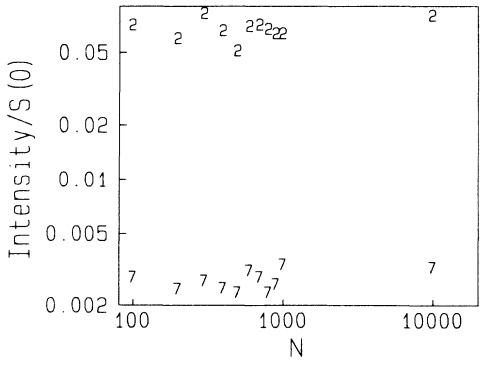

FIG. 6. The peak values of the $l=2$ and $l=7$ multipole terms, scaled by $S(0)$, for DLCA clusters.

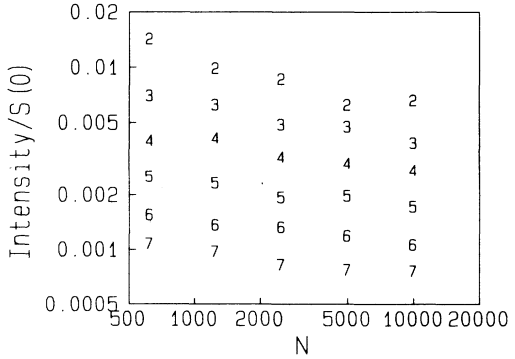

FIG. 8. The peak values of the $L=2$–7 multipole terms, scaled by $S(0)$, for DLA clusters.

ture of three-dimensional off-lattice DLA clusters. Quite extensive simulations using both lattice and off-lattice models indicate that the cluster radius of gyration grows with increasing cluster size according to the power law,

$$R_g \sim N^{\beta}, \tag{4}$$

where the exponent β has a value of about 0.40, corresponding to $d_f \approx 2.50$. However, measurements of the two-point density correlation function and the generalized dimensions,[21] D_q, indicate that the short-length-scale internal structure can be described by a somewhat smaller effective fractal dimension (or dimensions). We do not have a simple model for the structure of either two-dimensional or three-dimensional DLA clusters which is consistent with all, or even most, of the results obtained from simulations, which are necessarily finite sized.

Figures 6–8 also allow a comparison of the relative amount of asymmetry in the different types of clusters. Since each l term is scaled by $S(0)=N^2$, they give a quantitative measure of the anisotropy. For example, the peak value of the $l=2$ terms for the DLCA clusters is 0.07, while for the RLCA clusters the peak value is 0.04, reflecting the greater degree of anisotropy of the DLCA clusters. Furthermore, the magnitude of the $l=2$ terms of all DLA clusters from $N=625$ to 10 000 is substantially lower than those of the cluster-cluster aggregates. Thus there is a clear trend toward less asymmetry and more isotropic clusters as d_f increases. This might be intuitively expected, since as d_f decreases the objects naturally become more tenuous.

Further insight about the k dependence of the multipole terms can be obtained by investigating the analytic properties of the expansion in Eq. (3). The wave-vector dependence of $S_l(k)$ is determined by the spherical Bessel function $j_l(kb_i)$. If $kR_g \ll 1$, then $kb_i \ll 1$ for all i and $j_l(kb_i) \propto (kb_i)^l$. Thus, for $l \geq 2$ and $kR_g \ll 1$, $S_l(k) \propto k^{2l}$. Therefore, only the isotropic term S_0 contributes significantly for $kR_g \ll 1$, as expected, and as seen clearly in Fig. 1.

A more interesting regime is found when $kR_g > 1$, where the fractal structure is resolved. In this regime, the static structure factor, which is the sum of all the multipole terms, scales as k^{-d_f}. The k dependence of the individual multipole terms is determined by the form of the spherical Bessel functions. For large values of l the first peak of $j_l(x)$ occurs when $x \approx l$. Hence higher-order multipoles have their peak values at larger values of kR_g, as seen in Fig. 1. Furthermore, for $x \gg l$, $j_l(x)=x^{-1}\sin(x-l\pi/2)$. Therefore, all the multipole terms with $kR_g > l$ will be roughly equal in magnitude; this result is also seen in Fig. 1. Due to the initial k^{2l} dependence of the multipole terms at $x < l$, only those terms which have reached or passed their peaks ($kR_g > l$) will contribute significantly to the static structure factor. Therefore, for any given value of $kR_g \gg 1$, the number of multipole terms contributing will be roughly kR_g, with each term contributing roughly the same amount. Since the sum must scale as k^{-d_f}, and the number of terms is proportional to k, the k dependence of each term must be $k^{-(d_f+1)}$, in the limit of large l and k.

To investigate the scaling of the analytic form of the multipole terms, we calculate the mean amplitude of the peak of each term, normalized by the N^2, for clusters of 100 to 1000 particles. In Fig. 9, we show a logarithmic plot of these mean peak amplitudes for l from 2 to 11 as a function of α_l', where α_l' is the value at which the lth spherical Bessel function reaches its first maximum. This is given by[22]

$$\alpha_l' = (l+\tfrac{1}{2}) + 0.8086(l+\tfrac{1}{2})^{1/3} - 0.236\,68(l+\tfrac{1}{2})^{-1/3} + \cdots \tag{5}$$

which approaches l for large l. A least-squares fit to these data gives a slope of -2.86, very close to the value of $-(d_f+1) \approx -2.78$, as predicted above. We can also investigate the slope of an individual multipole term at large k. We choose the $l=11$ term, which should come closest to reaching the scaling limit. As shown in Fig. 10, we find that the slope is -2.76, again very close to $-(d_f+1)$, as predicted. Similar behavior is observed for the scaled average of the multipole terms calculated from RLCA clusters of 50 to 1800 particles. This is shown in Fig. 11, which is a logarithmic plot of the peaks of the multipole terms as a function of α_l'. Here the measured

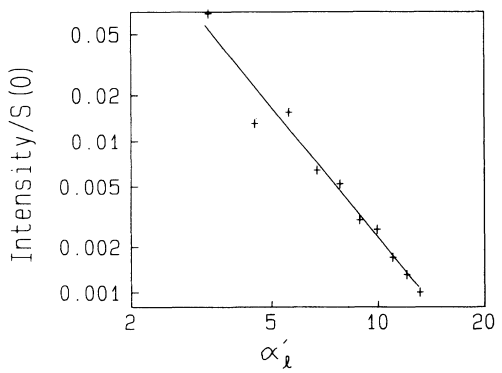

FIG. 9. The average peak value for $S_l(k)/S(0)$ for DLCA clusters of 100 to 1000 particles, vs α_l', the first maximum of the lth spherical Bessel function.

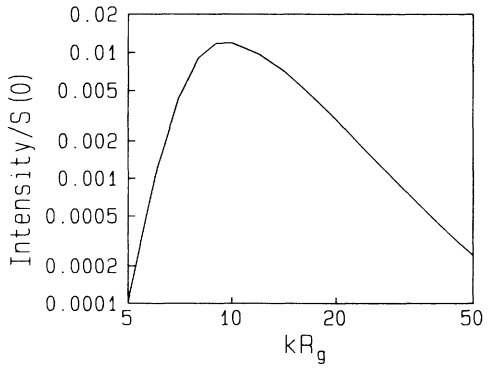

FIG. 10. The $l=11$ multipole term, averaged over 20 DLA clusters each with 900 particles. The amplitude is scaled by $S(0)$.

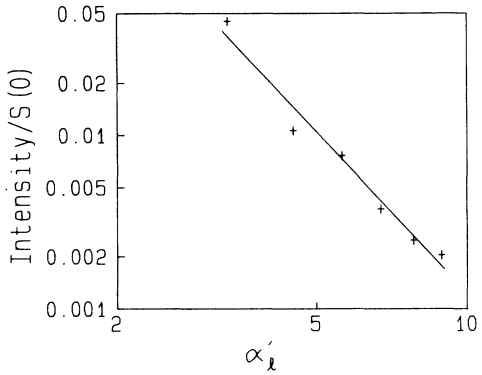

FIG. 11. The average peak value for $S_l(k)/S(0)$ for RLCA clusters of 50 to 1000 particles, vs α'_l, the first maximum of the lth spherical Bessel function.

slope is 3.1, in excellent agreement with our prediction of $d_f+1=3.1$.

An intuitive understanding of the magnitude of the anisotropies for clusters with different fractal dimensions d_f can be obtained by comparing DLCA and DLA clusters, with the same number of particles. We consider the scaled structure factors $S(x)/N^2$ as a function of $x=kR_g$. The scaled structure factors for both types of clusters must have the same value as $x\rightarrow 0$, and both must begin to decrease with $x\sim 1$. However, since $d_f\approx 2.5$ for DLA and $d_f\approx 1.8$ for DLCA, the scaled structure factor for the DLA clusters must decrease more rapidly than that of the DLCA clusters, so that for $x>1$, $S(x)_{\rm DLA}<S(x)_{\rm DLCA}$. Since the number of multipole terms contributing to $S(x)$ is roughly equal to x and is the same in both cases, these terms must be smaller for the DLA clusters than for the DLCA clusters. This is indeed observed in Figs. 6 and 8. This interpretation demonstrates that the anisotropies reflected in the multipole terms are a natural consequence of the scaling behavior of the clusters. Thus the existence of the anisotropies does not necessitate the introduction of additional fractal dimensions to describe the structure.

IV. APPLICATIONS TO QUASIELASTIC LIGHT SCATTERING

The results obtained here have direct consequences for dynamic light scattering from fractal clusters and have been used to determine the contributions of rotational diffusion to quasielastic light scattering.[4] Here we investigate some interesting consequences of the scaling behavior of the multipole terms on the autocorrelation function. We can express the temporal autocorrelation function in terms of the dynamic structure factor,

$$S(k,t)=\sum_l S_l(k)e^{-Dk^2t}e^{-l(l+1)\Theta t}\ . \tag{6}$$

This is a sum over the multipole terms, each having its own decay rate. At a given k, the temporal autocorrelation function separates the contribution of each multipole, because the decay rate for each term varies as $l(l+1)$. In writing Eq. (6), we assume that the translational diffusion coefficient D can be described by a single hydrodynamic radius R_H using the Stokes relation $D=k_BT/6\pi\eta R_H$. This approximation is suitable as long as the overall anisotropy of the cluster is not too large, a condition met experimentally. We also assume that the rotational diffusion coefficient of a cluster, $\Theta=k_BT/8\pi\eta R_H^3$, depends on the same hydrodynamic radius. The experimentally measured autocorrelation function would then be a sum over the dynamic structure factors of all the clusters in the scattering volume, assuming they are sufficiently dilute to be noninteracting.

We first examine the behavior in the hydrodynamic limit ($kR_g\ll 1$). We consider the first cumulant Γ_1 for the decay of the autocorrelation function,[23]

$$\Gamma_1=-\lim_{t\rightarrow 0}\frac{d}{dt}\ln S(k,t)\ . \tag{7}$$

Using Eq. (6), for a set of identical anisotropic scatterers, we have

$$\Gamma_1=\frac{\sum_l S_l(k)[k^2D+l(l+1)\Theta]}{\sum_l S_l(k)}\ . \tag{8}$$

In the hydrodynamic limit as $k\rightarrow 0$, $S_0(k)\rightarrow A$ and $S_2(k)\rightarrow Bk^4$, where A and B are constants; thus

$$\lim_{k\rightarrow 0}\Gamma_1\rightarrow\frac{Ak^2D+Bk^4(k^2D+6\Theta)}{A+Bk^4}=k^2D\ , \tag{9}$$

demonstrating that in the small wave-vector limit, the first cumulant is due purely to translational diffusion, as expected.

The situation is somewhat different in the case of the second cumulant, Γ_2. To investigate this, we consider the Q factor, defined as Γ_2/Γ_1^2, which is often regarded as indicative of polydispersity for isotropic particles. We obtain

$$Q=\frac{\left[\sum_l S_l(k)\right]\left[\sum_l[k^2D+l(l+1)\Theta]^2S_l(k)\right]}{\left[\sum_l[k^2D+l(l+1)\Theta]S_l(k)\right]^2}-1\ . \tag{10}$$

Again, using only the $l=0$ and $l=2$ terms, which are the dominant terms as $k\rightarrow 0$,

$$\lim_{k\rightarrow 0}Q=\frac{A^2k^4D^2+36ABk^4\Theta^2}{A^2k^4D^2}-1=\frac{36B}{A}\left[\frac{\Theta}{D}\right]^2\ . \tag{11}$$

Thus we obtain the surprising result that the Q factor does not go to zero in the small-wave-vector limit, as would be expected for pure translation of identical clusters. Therefore the anisotropy can lead to changes in the second cumulant, even in the hydrodynamic limit, where one normally expects the internal structure of the clusters to be unresolved. However, care must be taken in comparing this calculated result for a set of monodisperse anisotropic scatterers to experimental measurements. Most experimental samples exhibit a polydispersity in size, which gives a contribution to Q due to their different de-

cay rates from translational diffusion. Furthermore, as $k \to 0$, the contribution of rotational diffusion to Q may become undetectable under typical experimental conditions, since rotational diffusion yields a very fast but very small decay added to the large, slow decay due to translational diffusion. Thus the contribution of rotational diffusion can easily be lost in the experimental noise.

We can also use the scaling of the multipoles to determine the first cumulant $\Gamma_1(k)$ at large values of kR_g. In general, for a monodisperse system,

$$\Gamma_1(k) = \frac{\sum_{l=0}^{\infty} S_l(k)[k^2 D + l(l+1)\Theta]}{\sum_{l=0}^{\infty} S_l(k)} . \quad (12)$$

We use the scaling behavior to write each multipole term in its large-wave-vector limit, $S_l(k) = Ak^{-(d_f+1)}$, where A is a constant, and take $l(l+1) \to l^2$. Since only those terms which are near or past their peak values will contribute, the sums in Eq. (12) are restricted to $l \leq \alpha k R_g$, where α can be expected to be slightly larger than 1. Therefore,

$$\Gamma_1(k) = \frac{(\alpha k R_g) k^2 D + \frac{1}{3}(\alpha k R_g)^3 \Theta}{\alpha k R_g} . \quad (13)$$

Using $\Theta = 3D/4R_H^2$,

$$\Gamma_1(k) = k^2 D \left[1 + \frac{\alpha^2}{4\beta^2} \right] , \quad (14)$$

where $\beta = R_H/R_g$ is the ratio between the hydrodynamic radius and the radius of gyration of the cluster. For DLCA clusters, this ratio has been calculated to be $\beta = 0.87$, while for RLCA clusters $\beta = 0.96$.[24,25] We can compare these scaling limits to explicit calculations of Γ_1/k^2 obtained from the multipole expansion terms.[4] For DLCA clusters, with $\beta = 0.87$, the limiting value at large kR_g is found to be $\Gamma_1/k^2 = 1.7D$. This gives $\alpha = 1.5$ in Eq. (14), a value slightly larger than 1, as expected.

From Eq. (14), we see that Γ_1/k^2 can be considered the "effective" diffusion coefficient measured by quasielastic light scattering. It has a value of D, the translational diffusion coefficient, when $kR_g \ll 1$, and then rises to a higher limit for $kR_g \gg 1$. Interestingly, the value of this higher limit depends on the ratio of R_H to R_g for the clusters. However, it still scales with D, and therefore with cluster mass, in the same way as the low-kR_g limit. The intermediate values of Γ_1/k^2, when $kR_g \approx 1$, cannot be determined by scaling arguments; however, explicit calculations of Γ_1/k^2 generally show a smooth transition between the two limits.[4] We note that Ball[26] has used a completely different approach to find $\Gamma_1/k^2 \to D(1 + 1/2\beta^2)$ for fractal clusters in the large-wave-vector limit. This is consistent with our result if $\alpha = \sqrt{2}$, which is close to the value of $\alpha = 1.5$ obtained from our calculation.

V. CONCLUSIONS

We have performed a multipole expansion of the structure factors for three-dimensional clusters simulated with several different aggregation models, allowing us to investigate the scaling of the anisotropy. The observed behavior of the multipole expansion terms for DLCA and RLCA clusters demonstrates that the anisotropies of these clusters are scale invariant. We find that for cluster-cluster aggregates, the scaling of the multipole expansion terms can be understood without the use of any fractal dimensions other than the global fractal dimension. In contrast, for single-particle DLA clusters, the anisotropy of the clusters decreases as the cluster size increases, for the range of sizes we have examined. These results are consistent with the ideas that cluster-cluster aggregates have a self-similar fractal geometry but that DLA clusters have a more complex, possibly self-affine, structure. We observe increasing anisotropy in aggregation clusters with decreasing fractal dimension. Finally, we demonstrated how the scaling of the multipole terms of the cluster-cluster aggregates provides useful insights into quasielastic light scattering from fractal aggregates.

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