

Structure factor scaling in aggregating systems

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We study the structure factor of evolving two-phase systems such as aggregating colloids and spinodally decomposing fluids. We interpret the total structure factor as described well by the product of cluster-cluster and single-cluster structure factors, each with their own characteristic length, the mean cluster nearest-neighbor separation, and the cluster size, respectively. Both length scales are thus relevant to the total structure factor. For systems with moderate to strong cluster-cluster correlations, this product causes an apparent peak in the structure factor. For compact clusters, i.e., clusters with a fractal dimension equal to the spatial dimension, this peak obeys the experimentally observed scaling law. However, for fractal clusters the two length scales evolve differently, hence scaling cannot occur. Despite this, our simulations show an apparent scaling when the system is dense enough so that the two length scales are comparable in magnitude. When this occurs, each length scale eliminates the individual effect of the other from the total structure factor leaving a peak. These results explain both the lack of scaling early and the scaling observed later in experiments on aggregating colloids. An important conclusion is that the position of this peak q_m does not represent a true length scale of the system. [S1063-651X(98)08501-8]

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I. INTRODUCTION

Recently, a number of studies have appeared that measured the wave-vector-dependent scattered light intensity $I(q,t)$ from dense aggregating colloids [1–5] undergoing diffusion-limited cluster aggregation (DLCA). $I(q,t)$ was found to exhibit a maximum at a position q_m , which increased in intensity while q_m decreased with time. For late stages of aggregation near the gel point, the scattered intensity was found to scale according to

$$I(q,t) \sim q_m^{-\alpha} F(x), \quad (1a)$$

$$F(x) \sim x^{-\beta}, \quad x \gg 1 \quad (1b)$$

$$x = q/q_m. \quad (1c)$$

For colloids of noncompact, fractal aggregates $\alpha = \beta = D$, the mass fractal dimension of the aggregate. Remarkably, Eqs. (1) are identical in form to the structure factors measured for fluids undergoing spinodal decomposition except that in this case $\alpha = d$ and $\beta = d + 1$, where d is the spatial dimension [6–8]. Similar structure factors have also been observed for other nonequilibrium systems [9,10]. The source of the universality of Eqs. (1) has been speculated to lie in some feature of the growth kinetics common to all these systems, but no such mechanism has yet been found. The question remains in what manner all these phenomena are related.

For aggregating colloids the general interpretation of Eqs. (1) is that the peak implies a special length scale q_m^{-1} , induced by the aggregation kinetics, which in some manner brings order to the system [2,11–16]. Physical identification of q_m^{-1} has been ambiguous with attempts having been made to correlate it to the cluster mean nearest-neighbor separation R_{NN} , depletion zones surrounding the growing clusters, or shoulders in the real-space correlation function. There are,

however, two length scales in the system: the cluster nearest-neighbor separation and the cluster size [5,12,15]; if the fractal dimension of the cluster is not equal to the space dimension, these two lengths are not linearly proportional. Thus other questions arise regarding how one length scale implied by q_m^{-1} arises out of a two-length-scale system and how to account for the dynamic scaling of Eqs. (1), which is incompatible with two length scales.

In this paper we address these questions and establish a general explanation of Eqs. (1). We show that the total structure factor observed in experiment is a combination of two structure factors: the single-cluster structure factor, which involves the cluster size R_g , and the cluster-cluster structure factor, which involves the mean nearest-neighbor distance R_{NN} . For compact clusters, i.e., $D = d$, R_g and R_{NN} are proportional, so there is only one independent length scale, hence scaling is achieved at all times. For fractal clusters, $D < d$, so R_g and R_{NN} are independent, hence scaling should not occur. In fact, experiments [1,4] on aggregating colloids show that when the system is not dense, i.e., when $R_g \ll R_{NN}$, scaling does not occur. Remarkably, however, experiment, previous simulations, and our simulations to be described below show scaling in dense systems when $R_g \lesssim R_{NN}$ despite $D < d$. We show that this scaling occurs when the slope changes in the two structure factors near R_g^{-1} and R_{NN}^{-1} overlap in a manner that eliminates their individual effects in the total structure factor and leaves a peak. Thus an important conclusion of our work is that the peak in the total structure factor at q_m does *not* indicate a fundamental length scale of the system because it is an artifact of this unusual overlap. We also describe how the visibility of the peak is related to the cluster-cluster correlation. Our general conclusion is that the features common to all these experiments, dense aggregating colloids, spinodally decomposing fluids, etc., are simply conservation of mass and light scattering (or the scattering of waves in general), which probes the system

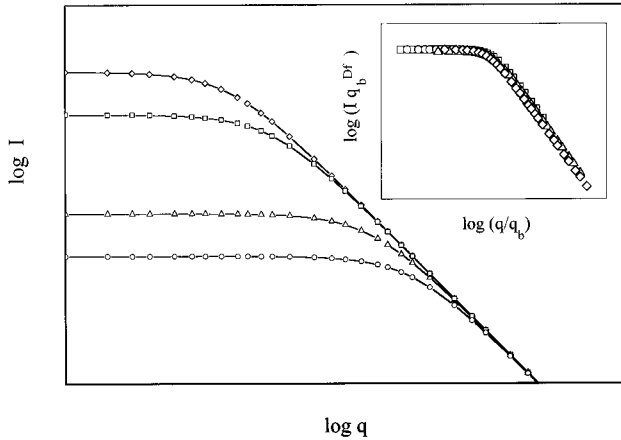


FIG. 1. Sketch of the scattered intensity as a function of wave vector q for a dilute aggregating system at various times. The inset shows single curve scaling of these intensities where q_b is the value of q at the bend in $S(q)$ and D is the cluster fractal dimension.

with a characteristic length q^{-1} . Beyond this, the nature of the kinetics is ancillary, serving to affect the visibility of the features in the structure factor, e.g., the peak, but not directly responsible for them.

II. THEORETICAL DISCUSSION

A. Heuristic example

For heuristic purposes we first consider the simple case of a very dilute aggregating system. This will allow us to demonstrate the importance of mass conservation and the scattering characteristic length scale q^{-1} and to deemphasize the importance of the kinetics for scaling of the scattered light intensity. For a monodisperse system of clusters, the scattered intensity is given by [17,18]

$$I_{SC}(q) = N_C \sigma_{scat}^{mono} S_{SC}(qR_g), \quad (2)$$

where N_C is the number of clusters of radius of gyration R_g with N monomers per cluster each with a scattering cross section of σ_{scat}^{mono} . The single-cluster structure factor $S_{SC}(qR_g)$ is strictly a function of the dimensionless product qR_g , the characteristic length of the cluster being R_g . For our purposes here its exact form is not important, but its limiting behavior is

$$S_{SC}(qR_g) = \begin{cases} N^2, & qR_g \ll 1 \\ N^2(qR_g)^{-D}, & qR_g \gg 1. \end{cases} \quad (3a)$$

$$(3b)$$

For a fractal, $N = k_0(R_g/a)^D$, where a is the monomer radius and k_0 is a constant near unity [19]. Mass conservation during aggregation implies a constant number of monomers N_m in the complete system given by

$$N_m = N_C N. \quad (4)$$

Figure 1 is a sketch of the scattered intensity at various stages of aggregation for a very dilute system. At low q there is a q -independent Rayleigh regime. At higher q , a bend in

the curves occurs when the characteristic length scale of the scattering q^{-1} becomes comparable to the characteristic length scale of the aggregating system, which when very dilute is the cluster size R_g . If we define the bend in the curve to be at $q_b = R_g^{-1}$, then Eqs. (2)–(4) yield

$$I(q) = N_m \sigma_{scat}^{mono} q_b^{-D} F(q/q_b). \quad (5)$$

Equation (5) has the same form as Eq. (1), i.e., it scales in the same manner. This scaling is a simple result of (i) mass conservation, (ii) the single-valued nature of the single-cluster structure factor dependence on qR_g , and (iii) the fact that there is only one length scale accessible to the q range of the experiment, R_g . Moreover, it occurs regardless of the kinetics of aggregation. Thus, whereas the remarkable discovery was that dense aggregating systems exhibit scaling, we see that a very dilute aggregating system scales in accord with Eqs. (1) as well.

The structure factor for the very dilute system in Eq. (2) is inadequate for dense systems because it neglects intercluster, or cluster-cluster, effects. As we will soon see, these cluster-cluster effects introduce two more length scales that can be relevant to scattering data analysis.

B. General situation

To understand the most general scattering situation consider the total structure factor for a system of N_m monomer particles given by

$$S_{tot}(q) = \sum_i^{N_m} \sum_j^{N_m} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}. \quad (6)$$

In Eq. (6) \vec{r}_i is the position of the i th monomer. Equation (6) factors if we write \vec{r}_i as the sum of the positions of the centers of mass of the a th cluster $\vec{r}_{c.m.,a}$ and the position of the k th monomer in the cluster relative to this center of mass $\vec{\delta}_k$:

$$\vec{r}_i = \vec{r}_{c.m.,a} + \vec{\delta}_k. \quad (7)$$

Then Eq. (6) becomes

$$S_{tot} = \sum_a^{N_C} \sum_b^{N_C} \sum_k^N \sum_l^N e^{i\vec{q} \cdot (\vec{r}_{c.m.,a} - \vec{r}_{c.m.,b} + \vec{\delta}_k - \vec{\delta}_l)}. \quad (8)$$

If the clusters are monodisperse, i.e., all have the same N , the factorization occurs

$$S_{tot} = \sum_a^{N_C} \sum_b^{N_C} e^{i\vec{q} \cdot (\vec{r}_{c.m.,a} - \vec{r}_{c.m.,b})} \sum_k^N \sum_l^N e^{i\vec{q} \cdot (\vec{\delta}_k - \vec{\delta}_l)}, \quad (9)$$

which we rewrite as

$$S_{tot} = S_{CC}(q) S_{SC}(q). \quad (10)$$

Equations (9) and (10) define the cluster-cluster (CC) and single-cluster (SC) structure factors. For polydisperse clusters Eq. (10) is inexact, but, as we will see by simulation below, it is a good approximation. Usually, for instance, our simple example above, the length scale involved in the cluster-cluster structure factor is too large to be observable in

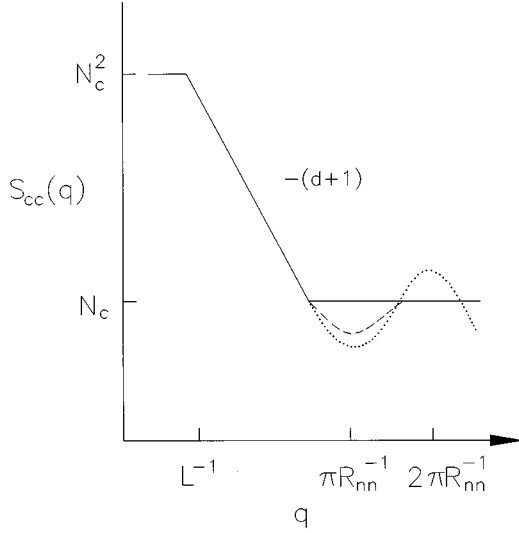


FIG. 2. Cluster-cluster structure factor $S_{CC}(q)$. N_C is the number of clusters in the scattering volume, L is the size of the scattering volume, R_{NN} is the mean cluster-cluster center-of-mass separation, and d is the spatial dimension. The solid line is for random positioning of the clusters, the dashed line is for moderate correlation between clusters, and the dotted line is for strong correlations between clusters.

a scattering experiment, hence $S_{CC}(q)$ is a constant equal to N_C as in Eq. (2). However, for dense systems, either colloids or spinodally decomposing fluids, the length scale inherent in $S_{CC}(q)$ falls into the experimental range, which might lead to variation with q , which must be accounted for.

Figure 2 shows the general behavior of $S_{CC}(q)$. Two length scales are relevant: the overall system size, i.e., the size of the scattering volume L , and the mean nearest-neighbor cluster separation R_{NN} . At very low q such that $q < L^{-1}$, the clusters scatter coherently; since there are N_C clusters, $S_{CC}(q) = N_C^2$. For $L^{-1} \leq q < R_{NN}^{-1}$ the Porod regime of the scattering volume is obtained where $S_{CC}(q) \sim q^{-(d+1)}$. Jumping ahead to $q \gg R_{NN}^{-1}$, $S_{CC}(q) = N_C$, a constant due to the incoherent addition of N_C waves. This is the regime usually encountered in nondense systems. The regime near $q \sim R_{NN}^{-1}$ requires special attention. For a highly structured system of clusters in which R_{NN} is well defined, i.e., it has a narrow distribution, a damped oscillation occurs in $S_{CC}(q)$ with minima at $\pi R_{NN}^{-1}, 3\pi R_{NN}^{-1}, \dots$, and maxima at $2\pi R_{NN}^{-1}, 4\pi R_{NN}^{-1}$. This is depicted by the dotted line in Fig. 2. An example of analogous behavior is the behavior of the single-cluster structure factor for clusters of touching monomers of radius a (hence a well-defined monomer distance), which shows oscillatory behavior with half period π/a [20]. As the cluster system becomes less structured, i.e., as the distribution in R_{NN} broadens, the oscillatory behavior washes out. We will see in our simulations below that for a dense DLCA system that is moderately structured what remains of the oscillation is a dip below a shoulder near $4.5R_{NN}^{-1}$, which is near the middle of πR_{NN}^{-1} and $2\pi R_{NN}^{-1}$. This behavior is depicted in Fig. 2 by the dashed line. For unstructured systems of clusters the dip washes out completely, as depicted by the solid line.

Figure 3 graphically demonstrates the product in Eq. (10),

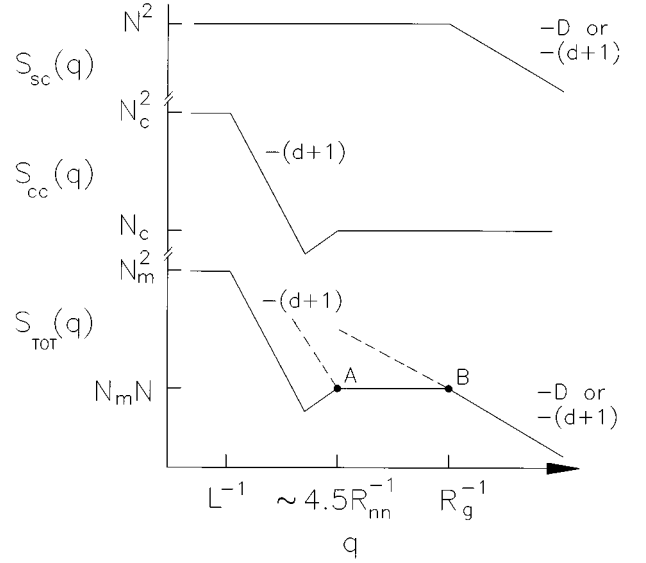


FIG. 3. Sketch of the structure factors as a function of wave vector for a dilute system of aggregates. $S_{tot}(q) = S_{CC}(q)S_{SC}(q)$. The length scales are as follows: L , scattering volume size; R_{NN} , cluster-cluster mean nearest-neighbor separation; and R_g , cluster size. The quantities are as follows: N_m , total number of monomers in the scattering volume; N_C , number of clusters; N , number of monomers per cluster where $N_m = N_C N$; d , spatial dimension; and D , fractal dimension. Dotted lines represent the evolution of points A and B as N increases during aggregation.

which leads to the total structure factor. The upper curve is the single-cluster structure factor as discussed in Fig. 1. The single characteristic length is the cluster size, which we take as the cluster radius of gyration R_g . For $q > R_g^{-1}$, if the cluster is a mass fractal, the slope on this log-log plot is $-D$; if the cluster is compact, it will have a well-defined surface hence Porod scattering will occur with a slope of $-(d+1)$. In either case for $q < R_g^{-1}$ the constant Rayleigh regime is obtained with $S_{SC}(q) = N^2$ due to coherent addition of the N waves scattered from the N monomers in the cluster. The second curve in Fig. 3 is $S_{CC}(q)$ for a moderately structured system of clusters (i.e., the dashed line of Fig. 2). The bottom curve in Fig. 3 shows the product of the upper two curves, i.e., $S_{tot} = S_{CC}S_{SC}$. For a moderately structured system of clusters a broad peak in $S_{tot}(q)$ occurs. This is the peak seen in dense aggregating and spinodally decomposing systems, which we now describe in detail.

Consider the evolution of $S_{tot}(q)$ with time. As the system aggregates, the number of monomers per aggregate N increases. The characteristic length scales are related to N by

$$R_g \sim N^{1/D}, \quad (11a)$$

$$R_{NN} \sim L(N/N_m)^{1/d}. \quad (11b)$$

For a given experiment L and N_m are constant. A colloidal system with either DLCA or RLCA (reaction-limited cluster aggregation) kinetics yields fractal clusters with $D < d$. Thus the two length scales R_g and R_{NN} will have different N dependences, hence different time dependences. The N dependences are shown as dashed lines in Fig. 3. Two different length scales implies that the system cannot scale. This ex-

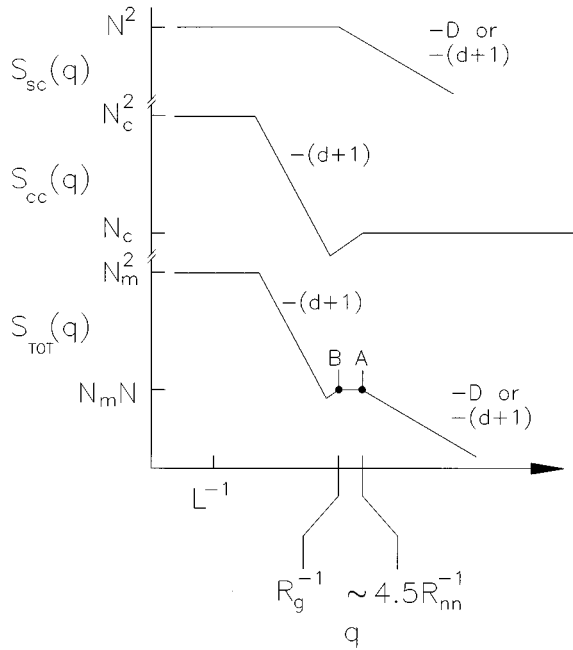


FIG. 4. Sketch of the structure factors as a function of wave vector for a dense system of aggregates. The length scales are as follows: L , scattering volume size; R_{NN} , cluster-cluster mean nearest-neighbor separation; and R_g , cluster size. The quantities are as follows: N_m , total number of monomers in the scattering volume; N_c , number of clusters; N , number of monomers per cluster where $N_m = N_c N$; d , spatial dimension; and D , fractal dimension.

plains why scaling is not seen in the early stages of colloid aggregation because the length scales differ enough so that both are *clearly visible in the total structure factor*.

If compact clusters are formed, as they are during spinodal decomposition, then $D = d$ and $R_g \propto R_{NN}$, i.e., they have the same dependence on time. This implies only one independent length scale, hence scaling can occur. By Fig. 3, the q_m value for the broad peak is proportional to both R_g^{-1} and R_{NN}^{-1} , which are both proportional to $N^{-1/d}$; thus $q_m \sim N^{-1/d}$. The magnitude of the peak is NN_m . It follows that $NN_m \sim q_m^{-d}$, thus $q_m^{-d} I(q/q_m)$ scales the structure factor. Finally, note that if the clusters are compact, the single-cluster structure factor will show Porod scattering for $q > R_g^{-1}$, i.e., $S_{SC}(q) \sim q^{-(d+1)}$. Thus Eqs. (1) are obtained and this explains the behavior of structure factor measurements on spinodally decomposing systems.

Next consider what happens in a dense system, where ‘dense’ will be used to imply $R_{NN} \lesssim 4.5R_g$. We pick this definition because it is in this regime that the q -dependent parts of the cluster-cluster and single-cluster structure factors overlap. Such a situation is drawn in Fig. 4. Note that points A and B of Fig. 3 are now reordered in Fig. 4, i.e., $q_A = 4.5R_{NN}^{-1} > q_B = R_g^{-1}$ rather than $q_A < q_B$. This leaves a peak in the total structure factor. In the simplified drawing of Fig. 4 both length scales are still present in $S_{tot}(q)$. Thus the conclusions above follow for the same reasons: no scaling for noncompact fractal clusters and scaling for compact clusters. Figure 4, however, is too simple because the bends at q_A and q_B are system dependent and gradual. If gradual, only when $4.5R_{NN}^{-1}$ is significantly different from R_g^{-1} , either greater or

less, will points A and B be resolvable and scaling not occur for fractal clusters. However, it is conceivable, and below with simulations we will show, that when points A and B are nearly the same, i.e., when $4.5R_{NN}^{-1} \approx R_g^{-1}$, the two length scales are *not clearly visible in the total structure factor*. Then the system might appear to have only one length scale and an artificial scaling might occur. Moreover, note that one of the extremes in which the length scales are obviously discernible, $4.5R_{NN}^{-1} \gg R_g^{-1}$, cannot occur because gelation would stop the aggregation before this regime could be obtained. A rough estimate of when gelation occurs is when the clusters would touch, which is when $2R_g \approx R_{NN}$.

In summary, it appears that as a colloidal system aggregates it can evolve from a nondense region in which both length scales are visible in the total structure factor, thus scaling does not occur, to a dense regime, limited by gelation, in which the signatures of the two lengths scales interfere and hence scaling might occur. In the next section our simulations will substantiate these claims.

III. SIMULATION RESULTS

We simulated DLCA aggregation on a two-dimensional square lattice. The lattice size was $L = 1000$ with periodic boundary conditions and the monomers had a radius of $a = \frac{1}{2}$. Initially the monomers are randomly distributed. At an intermediate time, a cluster is picked at random and moved in a random direction with a move probability to $N^{-1/D}$. If any monomer in this cluster comes into contact with a monomer in another cluster, the two clusters aggregate and form a larger cluster. N versus R_g for our clusters yielded $D = 1.45$. Runs were made with 10^3 , 10^4 , and 5×10^4 monomers on the lattice, which correspond to densities of 10^{-3} , 10^{-2} , and 5×10^{-2} , respectively. For each density the scattered intensity was an average over eighteen runs. Mean R_g and R_{NN} were calculated. Intensities were calculated for the total, single-cluster, and cluster-cluster scattering using Eq. (6) for $S_{tot}(q)$ and Eqs. (9) and (10) for $S_{CC}(q)$ and $S_{SC}(q)$.

Our simulations show R_{NN} and R_g do, as expected, grow at different rates during colloid aggregation (Fig. 5) such that $R_{NN} \sim R_g^{0.77}$. This occurs because the dimensionality of the embedding space is greater than the dimensionality of the cluster, so that as the clusters aggregate, their *relative* separation becomes smaller. According to Eqs. (11) $R_{NN} \sim R_g^{D/d}$. For our $d = 2$ simulation we find $D = 1.45$; thus $D_p/d = 0.72$ to explain the result in Fig. 5.

Figures 3 and 5 [the latter is a verification of Eqs. (11)] can be combined to describe the evolution of the light scattered intensity during colloid aggregation. In very dilute systems, R_{NN} is too large, hence $4.5R_{NN}^{-1}$ is too small, so that only the single-cluster scattering is seen (Fig. 1). In denser systems, however, $4.5R_{NN}^{-1}$ might be accessible to the experimental q range; thus *both* length scales R_{NN} and R_g will be present in S_{tot} . This is illustrated in Fig. 6, which contains the result of a $d = 2$ DLCA simulation with a monomer density of 10^{-3} . It displays the single-cluster behavior plus a modest dip for $q \leq 4.5R_{NN}^{-1}$ until the Porod regime of the scattering volume at yet smaller q . [Oscillations in this Porod regime in both Figs. 6 and 7 are due to the sharp edge of the scattering volume. Note, however, that the envelope of this

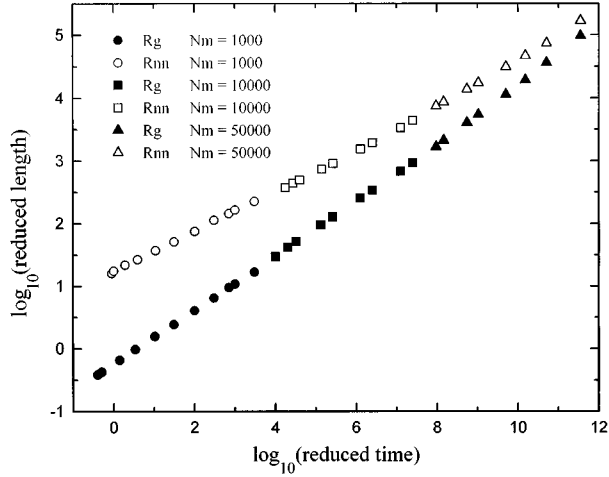


FIG. 5. Comparison of the mean cluster radius of gyration R_g and mean cluster nearest-neighbor distance R_{NN} time evolutions. This is a composite plot of three different aggregation runs with different numbers of monomers as specified, which have been rescaled so that the data are collinear.

oscillation has the Porod law slope $-(d+1) = -3$.] As described above, because R_{NN} is significantly greater than R_g , both length scales are relevant to S_{tot} ; since they have different time dependences, S_{tot} should not be scalable to a single length scale. The inset in Fig. 6 shows an attempt to do so where q_m was chosen to be in the middle of the Rayleigh regime between $4.5R_{NN}^{-1}$ and R_g^{-1} . Scaling is not achieved. This explains and demonstrates the lack of scaling observed in experimental systems during the early stages of aggregation.

As the system continues to evolve, $R_{NN} \rightarrow R_g$ and the dip that begins near $4.5R_{NN}^{-1}$ and the power-law regime when q

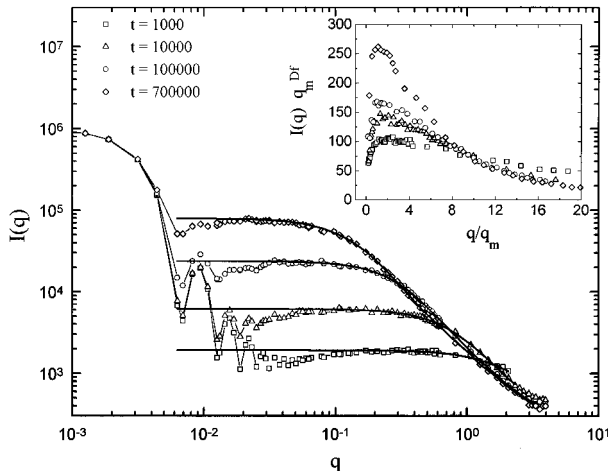


FIG. 6. Structure factor for a two-dimensional aggregating system of 1000 monomers on a 1000×1000 square lattice at various times. Units of q are a^{-1} , where a is the lattice spacing. The large feature at $q \approx 10^{-3}$ is the finite size of system. With increasing q , the feature falls off as q^{-3} and then follows a modest dip at $q \approx \pi/R_{NN}^{-1}$, a flat Rayleigh regime, a rounding at $q \approx R_g^{-1}$, and finally a power-law falloff with slope $-D$. Solid lines are the single-cluster scattered intensity. The inset shows an unsuccessful attempt to scale these curves in accord with Eq. (1).

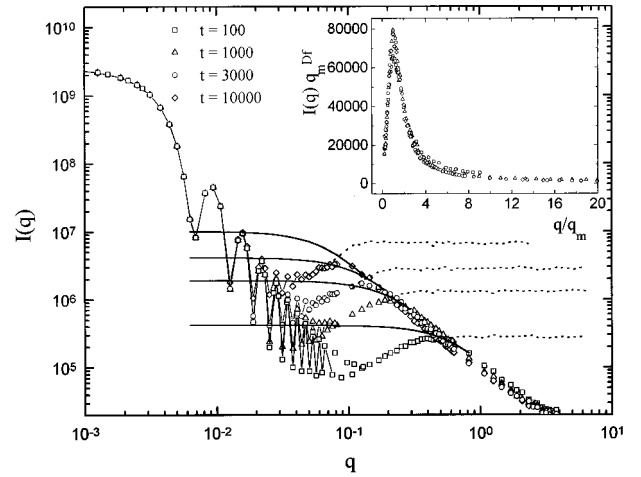


FIG. 7. Structure factor for a two-dimensional aggregating system of 50 000 monomers on 1000×1000 square lattice. Compared to Fig. 6, the dip in the range $R_{NN}^{-1} - 4.5R_{NN}^{-1}$ is greater and no flat Rayleigh regime is seen. Also shown are the single-cluster (solid line) and cluster-cluster structure factor (dotted line). These curves show how the length scales that parametrize these two structure factors R_g and R_{NN} , respectively, are no longer observable in the total structure factor. The apparent peak at q_m is therefore an artifact, but very useful since, as the inset shows, scaling in accord with Eq. (1) is achieved using the artificial q_m .

$>R_g^{-1}$ will eventually overlap, leaving a sharper peak as drawn in Fig. 4. Such a situation is demonstrated in Fig. 7, which contains the results of a $d=2$ DLCA simulation with a monomer density of 0.05. Note that all three structure factors have been calculated and are represented in Fig. 7. There it can be seen that Eq. (10) is verified to sufficient accuracy. Furthermore, Fig. 4 is verified in that the two shoulders in $S_{CC}(q)$ and $S_{SC}(q)$ representing the two length scales R_{NN} and R_g are not observable in $S_{tot}(q)$, which instead is left with a rounded peak. As with previous simulation work and in accord with experiment, the peak in the total structure factor grows in magnitude and its position, q_m , decreases with time. It can also be scaled in accord with Eqs. (1), as shown in the inset in Fig. 7. However, as forecast at the end of Sec. II, this peak is artificial in the sense that its position q_m^{-1} does not represent a true length scale of the system. The true length scales are R_{NN} and R_g and their effects, while clearly evident in $S_{CC}(q)$ and $S_{SC}(q)$, respectively, are undiscernible in $S_{tot}(q)$ because each interferes with the other. Moreover, we find, quite remarkably, that despite this “wipe out” of the length scales, the resultant peak in the total intensity matches very well with πR_{NN}^{-1} for all times in our aggregation simulation. However, by the logic above, this occurs by coincidence and is due to the manner in which S_{CC} intersects with S_{SC} .

IV. DISCUSSION

An important result of this work is that the position of the structure factor maximum q_m in dense aggregating colloids, spinodally decomposing fluids or other nonequilibrium systems that have structure factors described by Eqs. (1) is not directly related to a fundamental length scale of the system.

That is, q_m^{-1} is not a characteristic length of the system. Thus it is dangerous to use q_m to infer kinetic information. In some cases, for instance, in our simulations above where we found $q_m \approx \pi R_{\text{NN}}^{-1}$ to be a good approximation, it may work quite well because of a fortuitous proportionality to one of the two true characteristic lengths of the system, but no such connection is guaranteed.

Our results also give insight to the concept of kinetically induced ordering. Contrary to previous speculations, the kinetics of these various systems does *not* produce a new length scale as implied by the growth of the peak in the total structure factor. In any two-phase system there will be two length scales: the size of the entities of one of the phases and their mean separation. For colloids and later-stage spinodally decomposing systems in which droplets have formed these lengths are R_g and R_{NN} . The kinetics, however, can determine the order in these two lengths and thereby determine the visibility of the peak (actually the dip) in the total structure factor. For example, in a dilute colloidal system the initial distribution of R_{NN} is very broad, but the aggregation kinetics causes R_g to grow faster than R_{NN} so that the ensuing crowding of clusters narrows the R_{NN} distribution. This narrowing is ordering and as sketched in Figs. 2–4 creates dips and peaks in the structure factor. The weaker, or lack of, peaks for RLCA versus DLCA is due to the greater polydispersity, i.e., a broad R_g distribution, in a RLCA colloid, which in the dense, crowded system would cause a broader R_{NN} distribution, hence less distinct structure factor dips and peaks. The kinetics may also create depletion zones around the clusters as many have proposed; these will enhance the visibility of the peak, but they do not imply a new length scale.

Finally, we remark that very often overlooked is the $q \rightarrow 0$ behavior, which is either neglected or taken to be a δ func-

tion due to an “infinite” system size. This is an error. As the system grows to infinity at constant density, i.e., as $L \rightarrow \infty$, then $N_m \rightarrow \infty$ as well. Thus the overall effect on $S_{\text{tot}}(q)$ in Fig. 4 would be a relative narrowing of the system peak, but the end of its Porod regime would remain near (not exactly at) πR_{NN}^{-1} . In fact, the literature contains examples of real data that show the tail of the scattering volume Porod regime [21].

V. CONCLUSION

The total structure factor of a dense aggregating system can be described as a combination of cluster-cluster and single-cluster parts, each with their own length scale. If the clusters are compact, these two length scales are proportional and scaling in accord with experimental observation [Eqs. (1)] occurs as a consequence of mass conservation and the rules of wave scattering. The kinetics of the cluster growth is not a factor in the scaling. If the clusters are not compact but fractal, these two length scales evolve differently, hence the structure factor cannot be scaled. The apparent scaling peak in dense systems of noncompact clusters is due to the overlap of effects of these two length scales in the total structure factor in such a way as to eliminate their individual effects and leave a peak. It must be stressed that this peak is an artifact and its position q_m does not represent a true characteristic length scale of the system. The visibility of the peak increases with increasing cluster-cluster order, which can be affected by the aggregation kinetics.

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