Spinodal-Type Dynamics in Fractal Aggregation of Colloidal Clusters

Marina Carpineti and Marzio Giglio

Dipartimento di Fisica, Università di Milano, via Celoria 16, Milano 20133, Italy

The aggregation of dense colloidal solutions has been investigated by means of low-angle static light scattering. We show that the scattered pattern exhibits a finite-q-vector peak, whose intensity and position q_m change with time. We find that the intensity distributions scale according to $S(q/q_m,t) = q_m(t)^{-d}F(q/q_m)$, in agreement with the scaling law for spinodal decomposition. While $d=3$ for spinodal decomposition, here scaling requires that $d=d_f$, the fractal dimension of the clusters.

The spinodal decomposition (SD) is a phase-separation process that has been investigated in a large number of quite dissimilar systems like small-molecule liquid mixtures [1-4], metallic alloys [5,6], polymer blends [7,8], inorganic glasses [9], and thermodynamically unstable colloidal systems [10]. The peculiar feature of SD is that the long-wavelength diffusion coefficient becomes negative so that fluctuations grow instead of decaying. The fastest-growing fluctuation occurs at a finite wave vector and this gives rise to the well-known ring in the pattern of scattered radiation. The intensity and radius of the ring change in time as the thermodynamically stable state is approached. In spite of the diversity of the physical systems, universal features in the dynamics are observed. It should also be pointed out that other phase-separating systems, although not exactly falling in the class of SD, exhibit the same behavior [11,12].

Colloidal aggregation is another area where a substantial amount of work has been produced in recent years [13]. In this case also diffusion plays an essential role. Monomers diffuse to form fractal clusters, and the clusters themselves diffuse to coalesce into even larger clusters and so on.

In this paper we will show that colloidal aggregation exhibits the same features of SD in spite of the fact that nothing anomalous occurs to the diffusion coefficient of the monomers and clusters. By using very-low-angle static light scattering and high monomer concentration, we present for the first time clear evidence of a ring in the scattered intensity pattern. We will show that during the later stages the dynamics is in agreement with the scaling predictions of Marro, Lebowitz, and Kalos [14], also put forward by Furukawa [15] and by Binder and Stauffer [16].

The position of the scattered peak q_m and the scaled structure factor $S(q/q_m,t)$ are related by the equation

$$S(q/q_m,t) = q_m(t)^{-d}F(q/q_m), \qquad (1)$$

where $F(q/q_m)$ is a time-independent scaling function. For ordinary spinodal decomposition, $d=3$, while here we find that the relation holds if we take $d=d_f$, where d_f is the fractal dimension of the clusters. The surprising similarities between these results and those related to the spinodal decomposition are likely to suggest some underlying common mechanism in the dynamics of these irreversible processes.

The measurements have been performed on a solution of polystyrene spheres 0.0190 μm in diameter in a water–heavy-water mixture. The mixture was adjusted so as to make the solution isopycnic, in order to avoid differential sedimentation problems. The monomer concentration is $c=8.25\times10^{13}$ cm^{-3} (volume fraction $\Phi=2.96\times10^{-4}$), more than 2 orders of magnitude larger than in previous works [17-20]. The aggregation was induced by adding a divalent salt to the solution. Runs were taken at various MgCl$_2$ concentrations slightly above the critical flocculation value (4-8 mM). By so doing, the reaction proceeds on manageable time scales in spite of the high value of c.

The low-angle light scattering setup has already been described elsewhere [19] and only a brief account will be given here. A parallel beam of He-Ne laser light impinges on a cuvette. The scattered light and the transmitted beam are collected by a lens. A multielement sensor array is placed in the back focal plane. Each element has an annular shape, and is centered around a tiny hole which allows the focused transmitted beam to pass clear of the sensing elements. Consequently, each sensor collects light scattered around a given angle θ. The thickness and the average radius of the elements are geometrically spaced and cover scattering angles $0.18° < \theta < 12.1°$ corresponding to the wave-vector range $4.15\times10^2 < q < 2.78\times10^4$ cm^{-1}. Here $q=(4\pi/\lambda)\sin(\theta/2)$.

We show in Fig. 1 a sequence of intensity distributions at various times after the start of the aggregation process. The run was at 8-mM salt concentration, and is quite representative of all the runs taken at various salt concentrations, the only differences being dilation of the time scale and slight changes of d_f. At variance with all the previous observations via static light scattering from aggregating colloids, no maximum is observed at $q\sim0$. Instead the curves show a peak at a finite value of q. The peak height increases in time, and the peak position q_m shifts to smaller and smaller values in a way which is strongly reminiscent of the spinodal decomposition dynamics. It should also be pointed out that at large q all the distributions collapse onto the same asymptotic curve. This behavior is well known, and always occurs in the ag-
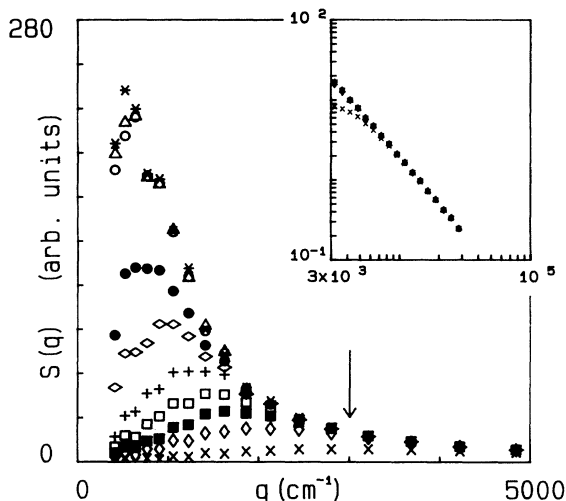
FIG. 1. Plots of a limited number of scattered intensity distributions of various times during the aggregation, for 8-mM $MgCl_2$ salt concentration. The curves cover a range from $t = 722$ to 60753 s (from bottom to top). The last three curves refer to $t = 18200$ s (O), $t = 51754$ s ($\triangle$), and $t = 60753$ s ($*$). They show the saturation effect (see text). The large-q asymptotic behavior of the curves is shown on a log-log plot in the inset. The arrow indicates the lowest q displayed in the inset. Notice that the q interval is much larger, and all the curves fall on the same power-law decay. The fractal dimension is $d_f = 1.90 \pm 0.02$.

gregation of colloidal clusters. As it has been pointed out [19], this behavior reflects the conservation of the total number of monomers in the scattering volume. We show in the inset the plot of the asymptotic part on a log-log scale. One can observe that the data can be fitted quite nicely with a power law. The exponent, which gives the fractal dimension, is $d_f = 1.90 \pm 0.02$. Finally, the terminal stages indicate a saturation effect. Roughly after $t = 18200$ s, the curves show little sign of change as time goes on. The peak position and height remain locked to a terminal value over a very substantial amount of time. For convenience, the dynamics can be divided into three phases: an early stage, a later ripening stage, and a terminal time-invariant stage. It is more convenient to start with the description of the last two stages.

In order to verify whether the data scale according to Eq. (1), we present in Fig. 2 plots of the universal function $F(q/q_m)$ as a function of q/q_m (in plotting the data, we have chosen $d = d_f = 1.9$). Only the later and terminal stages are shown here. The data fall remarkably well onto the same scaling function. However, while $d = 3$ is the reported value for spinodal decomposition, here the collapse onto a single curve is obtained only if $d = d_f$. This is a *necessity* stemming from the fact that the tails of the intensity distribution of the raw unscaled functions collapse onto the same asymptotic power law (inset in Fig. 1). Consequently, since scaling implies a contraction of the x axis of the order of $1/q_m$, rescaling of the y axis
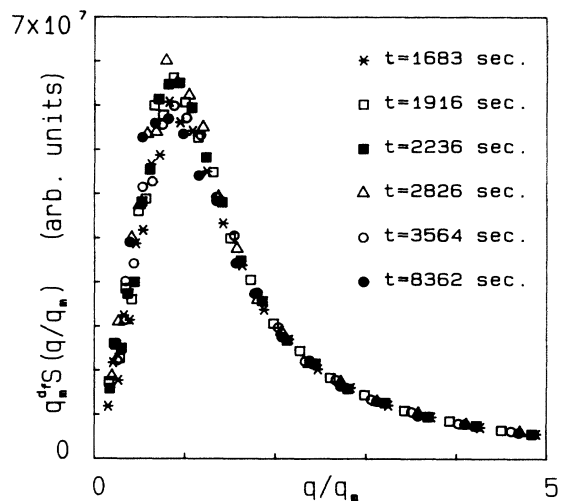

FIG. 2. Plots of the scaled functions $q_m^{d_f} S(q/q_m)$ as a function of q/q_m. The curves refer to the same run of Fig. 1. The data are for the later stages of the aggregation only.

to superimpose again the tails of the scaled functions *necessarily* requires multiplication by $q_m^{d_f}$. Furthermore, the shape of the scaled function $F(x)$ cannot be of the form proposed so far [15]. While we cannot propose here the explicit form, it must remain true that the asymptotic behavior at large x is a power law with the exponent equal to $-d_f$.

The scaled function $F(x)$ exhibits a marked minimum at low q and possibly $F(0) = 0$. Quite generally, this implies that the integral of the net density correlation function vanishes. It has been pointed out to us by Degiorgio that this behavior is the same as that observed in neutron scattering from semiconductor microcrystallites in a glassy matrix [11,21]. Depletion regions are formed around the denser crystallite core, and mass is conserved over the overall volume. The width of the low-q hole is related to the size of the depletion region, while the position of the half height of the peak at larger q is related to the size of the denser core. The scaling observed in our system therefore implies that the ratio of the average linear dimensions of these two regions remains a constant throughout the later stages of the aggregation process. Incidentally, such a picture is in qualitative agreement with the graphical representation of simulations of Brownian aggregation shown in Ref. [22]. Indeed, long-wavelength modulations in the density can be appreciated across the semirandom cluster spatial distribution.

The terminal time-independent state occurs when the intercluster distance equals the average cluster diameter. More quantitatively, during the aggregation process fractal clusters are formed and their linear dimension is described by a gyration radius R_g.

The number of monomers contained in a cluster is

$$n(\text{cluster}) = (R_g/R_0)^{d_f}, \tag{2}$$

while the volume enclosing the cluster is of the order of R_g^3. Consequently, the density of monomers inside a cluster *decreases* as the size of the clusters grows. The coalescence of two clusters leads to a cluster occupying a volume larger than the one occupied by the individual clusters. It is easy to calculate the intercluster distance [23]

$$d = [(1/n_0)(R_g/R_0)^{d_f}]^{1/3}.$$ (3)

n_0 is the monomer number density and R_0 the monomer radius. When the cluster diameter equals the distance d, all the available space is filled with closely packed clusters. No further ripening due to cluster coalescence can occur. In fact this would require extra volume in addition to that originally occupied by the two clusters, but such volume is no longer available. In Fig. 1 the data taken at times longer than $t = 18200$ s still show a pronounced peak at a finite wave vector, although the low-q limb is partially outside the explored range. This implies that indeed the clusters in the terminal stage retain their individual structure, and each denser core is surrounded by a lower density region. We have made some preliminary measurements with a longer focal length to explore the low-q limb at the terminal stage. The data are not of very good quality, because of the small signal at extremely low q, but it appears that the deep hole at $q \sim 0$ is preserved. Therefore the depleted region of the cluster boundary balances out the inner denser core to conserve density over the typical cluster volume. Taking into account that the monomer concentration is $c = 8.25 \times 10^{13}$ cm^{-3}, and taking $1/q_m$ as the average radius, we find that the terminal diameter is 28.6 μm to be compared with the value $d = 23.6$ μm obtained from Eq. (3). In view of the crudeness of the estimate based on Eq. (3), it is quite satisfying to notice a reasonable agreement between the two values. We have also made measurements at lower monomer concentration ($c = 8.25 \times 10^{12}$ cm^{-3}). In this case the peak shifts outside the low-q range is not visible anymore.

We discuss now the earlier phases for $t < 1683$ s. The results in Fig. 3 do not scale according to Eq. (1) if we take d equal to the fractal dimension. Typically, the peak height grows faster than expected, a behavior also reported for polymer mixtures [7]. As we pointed out, however, the choice $d = d_f$ is unavoidable if we want to superimpose the tails of the scaled functions. So we are left with an inconsistency, and a possible explanation on how to resolve it is that perhaps in the early stages one unique scale length is no longer adequate to describe the system. A hypothesis to be tested in future studies is that the diameter of the depleted region does not scale with the diameter of the denser core.

Finally, we discuss the time behavior of the peak intensity $S(q_m)$ and of q_m. It is often assumed [24] that they should behave according to power laws characterized, respectively, by the exponents γ and $-\Phi$, although in the
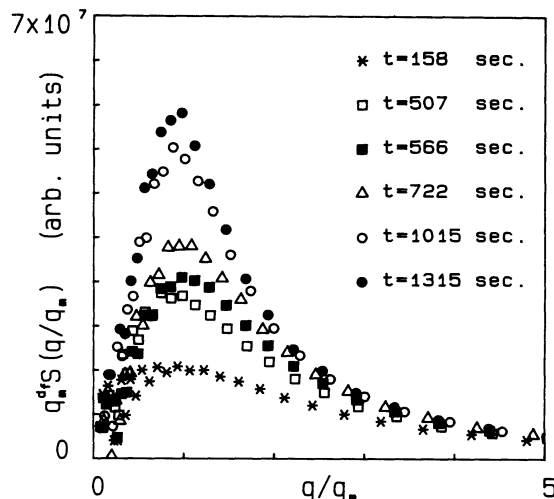

FIG. 3. Plots of the scaled functions, as in Fig. 2, but referring to the earlier stages. The curves do not scale if $d = d_f$ is used in Eq. (1). The peak intensity grows faster than expected on the basis of the scaling function.

reference quoted above such behavior is shown not to be tenable over extended ranges (a number of various systems is analyzed in the reference above). For brevity we will not report here these plots. We find, however, that the data can be plotted with $\gamma = 1.02$ and $\Phi = 0.59$, deviations being more appreciable at the earlier stages. To represent these results in more compact form, we show in Fig. 4 the plot of q_m vs $S(q_m)$. It can be noticed that the ratio of γ and Φ is close to 0.58, namely, the reciprocal of the fractal dimension. In Fig. 4 the later stages are indeed characterized by such exponent. The fit is performed only for the points corresponding to scaling curves ($q < 2 \times 10^3$). The deviation at earlier stages is thus in agreement with the observation of the anomalously fast growth of $S(q_m)$.
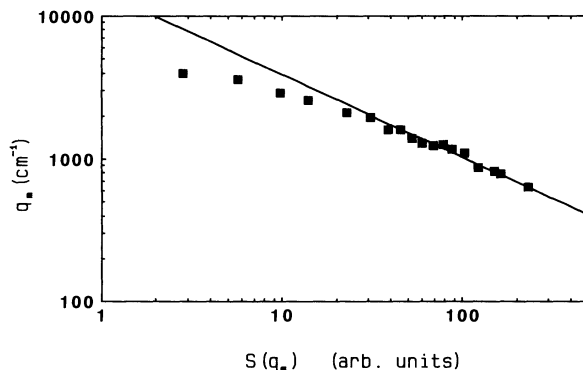

FIG. 4. Peak position as a function of peak intensity. The data at later times are compatible with a power law with an exponent $1/d_f$. At the beginning of the aggregation, the data fall below this power law, thus indicating a faster growth than at later times.

[1] J. S. Huang, W. I. Goldburg, and A. W. Bjierkaas, Phys. Rev. Lett. **32**, 921 (1974).

[2] Y. C. Chou and W. I. Goldburg, Phys. Rev. A **23**, 858 (1981).

[3] N. C. Wong and C. M. Knobler, Phys. Rev. A **24**, 3205 (1981).

[4] P. Guenoun, R. Gastaud, F. Perrot, and D. Beysens, Phys. Rev. A **36**, 4876 (1987).

[5] S. Katano and M. Iizumi, Phy. Rev. Lett. **52**, 835 (1984).

[6] B. D. Gaulin, S. Spooner, and Y. Morii, Phys. Rev. Lett. **59**, 668 (1987).

[7] P. Wiltzius, F. S. Bates, and W. R. Heffner, Phys. Rev. Lett. **60**, 1538 (1988).

[8] F. S. Bates and P. Wiltzius, J. Chem. Phys. **91**, 3258 (1989).

[9] P. Wiltzius, F. S. Bates, S. B. Dierker, and G. D. Wignall, Phys. Rev. A **36**, 2991 (1987).

[10] P. W. Rouw, A. T. J. M. Woutersen, B. J. Ackerson, and C. G. De Kruif, Physica (Amsterdam) **156A**, 876 (1989).

[11] V. Degiorgio, G. P. Banfi, G. Righini, and A. Rennie, Appl. Phys. Lett. **57**, 2879 (1990).

[12] K. Schätzel and B. J. Ackerson, Phys. Rev. Lett. **68**, 337 (1992).

[13] See, for example, *The Fractal Approach to Heterogeneous Chemistry*, edited by D. Avnir (Wiley, New York, 1989).

[14] J. Marro, J. L. Lebowitz, and M. H. Kalos, Phys. Rev. Lett. **43**, 282 (1979).

[15] H. Furukawa, Adv. Phys. **34**, 703 (1985).

[16] K. Binder and D. Stauffer, Phys. Rev. Lett. **33**, 1006 (1974).

[17] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, Proc. R. Soc. London A **423**, 71 (1989).

[18] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. Klein, R. C. Ball, and P. Meakin, J. Phys. Condens. Matter **2**, 3093 (1990).

[19] M. Carpineti, F. Ferri, M. Giglio, E. Paganini, and U. Paganini, Phys. Rev. A **42**, 7347 (1990).

[20] D. Asnaghi, M. Carpineti, M. Giglio, and M. Sozzi, Phys. Rev. A **45**, 1018 (1992).

[21] A. R. Rennie, V. Degiorgio, and G. P. Banfi, in Proceedings of the International Conference on Neutron Scattering, Oxford, United Kingdom, 1991 (to be published).

[22] R. M. Ziff, in *Kinetics of Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984), p. 191.

[23] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, Phys. Rev. A **41**, 2005 (1990).

[24] H. L. Snyder and P. Meakin, J. Chem. Phys. **79**, 5588 (1983).