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Cluster aggregation under diffusion

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Abstract

Cluster aggregation limited by cluster diffusion is one of the possible pathways leading to aggregation phenomena as different as phase separation or colloidal gelation. The imprinting of the irreversible diffusion-limited aggregation is observable in the evolution of the scattered intensity $I(q,t)$ and in its dynamical scaling relations. We discuss a recent model for describing the evolution of the scattered intensity both for growing eucledean and fractal clusters.

1. Introduction

Diffusion is one of the possible mechanisms limiting the process of aggregation in unstable systems. The irreversible aggregation in colloidal systems under high salt concentration, the kinetics of phase separation under deep quench conditions, or the growth of crystalline phases from a supercooled melt, are different examples of diffusion-limited growth [1–3].

All these aggregating systems are characterized by the developement during the aggregation time of a peculiar correlation among clusters, which manifests itself in a ring in the scattered intensity $I(q,t)$, whose intensity and size change continuously in time. The shape of $I(q,t)$ and its evolution during the aggregation process convey information on the leading aggregation mechanism [4]. The scattered intensity at different times can sometimes be scaled on a common master curve by plotting $q_m^d I(q/q_m)$ as a function of the scaled wave vector q/q_m, q_m being the peak position [4], suggesting an underlying scaling in space and time of the ordering process.

We review here a simple mean field theory [5] which has been proposed to describe the growth of clusters under diffusion-limited cluster aggregation (DLCA). We discuss how the fractal nature of the growing clusters affects the scaling properties in space and time.

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2. Theory

Fig. 1 shows three snapshots, at different times, of a two-dimensional Brownian dynamics simulation of the phase separation in a Lennard-Jones fluid after a deep quench. The insets in the panels show enlarged portions of the same configurations, to visualize the cluster structure. The system is quenched at time $t = 0$ from a high T (120 K for Argon) to a T (24 K) significantly below the critical temperature (about 60 K). Under such deep quench conditions, atoms never *evaporate* from an already formed cluster, so that the phase separation proceeds via irreversible diffusion-limited aggregation. In contrast to the simple models of cluster–cluster diffusion, links between different atoms are not frozen in, so clusters can change shape during the growth. This produces, at the early stage of the separation shown in Fig. 1, the formation of rather compact clusters. At later times, not documented in Fig. 1, a cluster fractal structure develops.

The simple process of diffusion and aggregation is able to account for the cluster–cluster correlation which develops in time and which shows up in a growing peak in the scattered intensity. In Ref. [5] we have shown that the mass concentration $c(r,t)$ at distance $r > 2R(t)$ from the origin, knowing that one cluster of mass $M(t)$ and radius $R(t)$ is at the origin, evolves in time (for compact clusters) as [6]

$$c(r,s) = c_o \left[1 - \frac{F(r/(2s^{1/2}))}{F(\lambda)}\right], \quad r \geqslant 2R(s) \tag{1}$$

$$c(r,s) = 0, \qquad r \leqslant 2R(s). \tag{2}$$

$F(x)$ is given by

$$F(x) = \operatorname{erf} c(x), \quad d = 1; \tag{3}$$

$$F(x) = \operatorname{Ei}(-x^2), \quad d = 2; \tag{4}$$

$$F(x) = \frac{e^{-x^2}}{x} - \sqrt{\pi}\operatorname{erf} c(x), \quad d = 3. \tag{5}$$

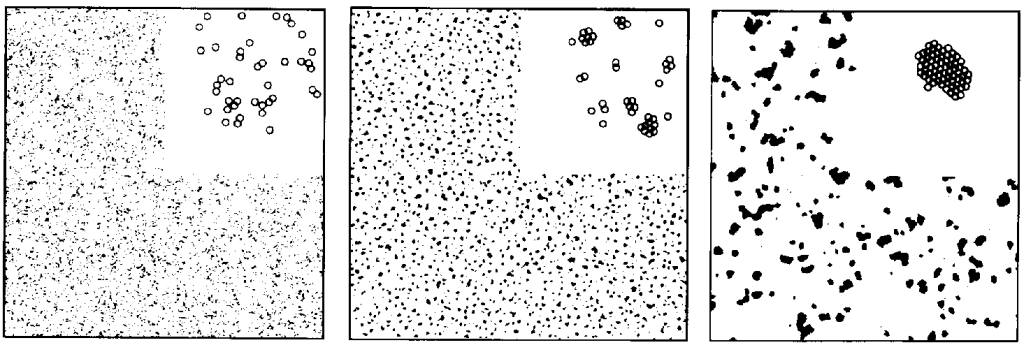

Fig. 1. Three snapshots at different times during the phase separation of a Lennard-Jones fluid following a quench from the stable to the unstable region.

The associated solution for the boundary motion is

$$R(s) = \lambda s^{1/2}; \tag{6}$$

λ depends only on the ratio between the initial solution density and the density of the growing cluster. The scaled time $s = D_o t^{2/(2+\gamma d)}$, accounting for the dependence of the diffusion coefficient D with the cluster mass ($D = 2D_o M^{-\gamma}$). We have assumed that the initial conditions are given by $c(r \geqslant 2R(0), 0) = c_o$ and $c(\infty, t) = c_o$, reflecting the initial homogeneous state and the absence of correlation between very distant clusters.

The growing cluster acts as a trap for the nearby clusters, decreasing the probability of finding clusters close to its sticky boundaries. The scaling properties of the solution show that plots of $c(r,s)$ vs. $r/s^{0.5}$, or by virtue of Eq. (6) vs. $r/R(s)$, for different s values will collapse on a single master curve. The master curve depends only on c_o. The size of the depletion region will be larger, the smaller the initial density. The analytic solution of the model also shows that the growth of the radius of the average euclidean cluster is controlled by the same exponent as the growth of the depletion region. The fact that the same scaled variable controls both radius and size of the depletion region already suggests that the system is characterized by only *one* characteristic length.

The Fourier transform of Eq. (1) gives the structure factor, whose leading term in the small q expansion is q^2, as imposed by mass conservation. $c(r,s)$ being a function of the scaled variable $r/2s^{1/2}$, $S(q,s)$ also scales in time as $qs^{1/2}$ or, by Eq. (6), as $qR(s)$. The total scattered intensity $I(q,t)$ measured experimentally can be approximated as the product of the previously calculated $S(q,t)$ and of the so-called cluster form factor $P(q,t)$, a well-known function for any d [7]. $P(q,t)$ is proportional to the mass of the scatterer, i.e. in our case to the mass of the average cluster and it is a function of qR only, i.e. of the same scaled variable of $S(q,t)$. At high q, where $S(q,t) \approx 1$, $P(q,t)$ goes as $(R(t)q)^{-(d+1)}$. This implies that the total scattered intensity will also be a scaled function of qR, with a q^2 behavior at small q and a $q^{-(d+1)}$ behavior at high q. Moreover, a plot of $I(qR(t))/M(t)$ vs. $qR(t)$ will show a remarkable data collapse. The scaling form depends only on the initial concentration c_o. On lowering c_o the $I(q,t)$ maximum will eventually move out from the finite experimental window [8]. Fig. 2(a) shows the scaling form for the total scattered intensity $I(qR(t))/M(t)$ vs. $qR(t)$ for three different initial monomer concentrations. $I(qR(t))/M(t)$ has been evaluated as a product of $S(q,t)$ and $P(q,t)$, where $S(q,t)$ is the Fourier transform of Eq. (1) and $P(q,t)$ is the form factor calculated for a slightly polydisperse ($\delta R/R = 0.2$) assembly of spheres [9]. The power-law growth of the mass is given by $M(t) \sim t^{d/(2+\gamma d)}$. In three dimensions and with the $\gamma = 1/d$ value for Stokes–Einstein diffusion we recover the Smoluchowski result $z = 1$ [10].

We now turn to the case where the aggregation process produces fractal clusters [11]. It is known that the growth of fractal clusters is limited in time and space. Fractal clusters tend to fill the space, being characterized by an average density which decreases with the cluster size. When clusters reach a space-filling configuration, gelation occurs. One single cluster fills up all the available space. When the growing cluster is a fractal, a new length scale related to the average cluster size at the gelation point R_f

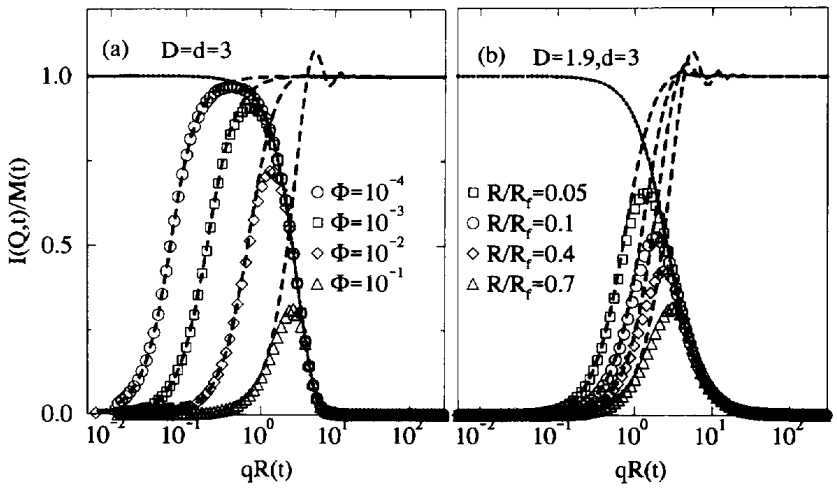

Fig. 2. (a) Scaling form for the total scattered intensity, $I(qR(t))/M(t)$ vs. $qR(t)$ for three different initial monomer concentrations, for $D = d = 3$. (b) $I(qR(t))/M(t)$ as a function of $qR(t)$ for four different times in the case of $D = 1.9$ and $d = 3$. Dashed and dotted lines show the structure factor and form factor contributions, respectively.

is expected to arise. The model proposed in Ref. [5] shows that in the fractal cluster case, the radius growth is faster than $s^{1/2}$ so that the size of the depletion region shrinks on increasing time, and becomes zero at gelation, when the fractal clusters fill the space completely. The change in the time dependence of the cluster growth compared to the time dependence of the growth of the depletion region brings as a consequence that the $c(r,t)$ profile does not scale anymore with $R(t)$. $c(r,t)$ progressively approximates a step function. As a consequence, the scattered intensity at geletion becomes independent of the initial concentration. This prediction has recently been confirmed for irreversible colloidal aggregation [12]. Fig. 2(b) shows the time evolution of the total scattered intensity as a function of $qR(t)$. As for the compact cluster case, the scattered intensity scaled by the cluster mass, i.e. by $R^D(t)$, is shown as a function of $qR(t)$. Data collapse is observed only for $P(qR(t),t)/M(t)$, while $S(qR(t),t)$ moves to smaller and smaller $qR(t)$ values. As shown in Ref. [13], the shape of the depletion region depends only on the ratio between $R(t)$ and R_f.

The growth of the mass is not a pure power-law, diverging very close to gelation. For early time, we showed in Refs. [5, 13] that $M \sim t^{D/[D(1+\gamma)-(d-2)]}$, the same exponent predicted by the Smoluchowski approach for fractal clusters.

3. Conclusions

In summary, we have discussed a simple model [5] to describe the origin and the development of the spatial correlatations among clusters during DLCA. The origin of the correlation is ascribed to the formation of a depletion zone around the growing clusters [3]. From the model we have calculated the dynamic exponents controlling the time

dependence of the average mass and of the radius of the aggregates, obtaining the same exponents predicted by the Smoluchowski equations [10]. We have also calculated the scattered intensity and its evolution during the aggregation process. We have shown that a peak in $I(q,t)$ arises as a manifestation in Fourier space of the existence of a depletion zone around the growing clusters. The model shows that $I(q,t)$ truly scales, during the whole aggregation process, only for compact growing clusters where correlations have the same scaling behavior as the size of the growing cluster. $I(q,t)$ can be scaled as $I(qR,t) \sim M(t)F(qR) \sim R^d(t)F(qR)$. The function $F(qR)$ is not universal, but depends on the difference in density of the cluster compared to the bulk density.

When the growing cluster is a fractal, the theory predicts an absence of scaling in the time development of the scattered intensity. The reason for such a difference is shown to arise from the different time scales of $R(t)$ and $c(r,t)$. While cluster growth is controlled by the fractal dimension, the mass diffusion is still controlled by the dimensionality of the space in which diffusion takes place. Only close to gelation, when clusters are very close, the growth of the cluster takes over the diffusional process and an apparent scaling may be observed. Samples with different initial monomer concentration are predicted to show the same scattering pattern if compared at the same R/R_f value.

Before concluding, we note that irreversible aggregation in the compact cluster case is strongly related to the phase separation problem. As seen in Fig. 1, irreversible aggregation can be seen as a phase separation process in deep quench limit, when separation proceeds only along a path of decreasing total energy and cluster breaking is very rare. In such conditions, mechanisms like the evaporation–condensation are less effective than diffusion and coalescence of the entire clusters. The $M(t)$ dependence we find is the same as that obtained from the Binder–Stauffer diffusion–reaction mechanism for droplet coarsening [14]. The q^2 and q^{-4} limit in $I(q,t)$ in the late stage decomposition in the deep quench coincides with the $I(q,t)$ behavior during aggregation predicted by our model when $d = 3$. Our exact results support the view that the scaling function is not universal and depends strongly on the initial conditions and coarsening process.

Acknowledgements

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