

## Nonfractal colloidal aggregation

Michael L. Broidé\* and Yves Garrabos

*Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, Université Paris Nord, F-93430 Villetaneuse, France*

Daniel Beysens

*Service de Physique de l'Etat Condensé, Centre d'Etudes de Saclay, F-91191 Gif sur Yvette CEDEX, France*

(Received 16 October 1992)

We have investigated the growth kinetics and aggregate structure for temperature-induced aggregation of silica colloids in a binary mixture of 2,6-lutidine and water. Using static light scattering, we find that the structure factor obeys Porod's law, the average cluster mass  $\bar{M}(t) \sim t$ , and the average cluster radius  $\bar{R}(t) \sim t^{1/3}$ . This indicates that the clusters are compact,  $\bar{M} \sim \bar{R}^3$ , and that the rate of aggregation is diffusion limited. Such a dense structure suggests that the bonds between the colloids are not rigid, in contrast to what is currently found for colloidal aggregation of solid particles.

PACS number(s): 64.70.Ja, 82.70.Dd, 05.40.+j, 82.65.Dp

Solid colloidal particles suspended in either gas or liquid tend to form fractal structures when they aggregate [1]. Examples include carbon colloids forming soot in the atmosphere and gold colloids forming aggregates in aqueous solution [2]. These ramified structures arise because the bonds, being rigid and permanent, "record" the random way that clusters collide to form an aggregate. In contrast, liquid colloidal particles, such as emulsions and aerosols [3], tend to form dense aggregates, since touching droplets can coalesce.

In this paper, we describe an experimental system which suggests that it is possible to generate dense-packed aggregates with solid colloids. The system consists of silica microspheres suspended in a binary mixture of lutidine and water. We believe that the observed dense structure occurs because the bonds between the silica spheres are not rigid and the aggregates are able to restructure themselves. Our results are consistent with the work of Gurfein, Beysens, and Perrot [4], who showed that aggregation is associated with the adsorption of one of the fluid components (lutidine) on the silica's surface.

Silica spheres  $0.173 \pm 0.043 \mu\text{m}$  in radius were prepared using the Stöber method [5]. These charge-stabilized spheres were then suspended in a binary mixture of freshly distilled 2,6-lutidine (Merck-Schuchardt) and water (Milli-Q). As has been previously demonstrated [6], the spheres aggregate in the *one-phase* region of the binary mixture above a threshold temperature  $T_a$ , which depends on lutidine concentration. The same phenomenon has also been observed using polystyrene spheres [7], suggesting that the phenomenon is general. A distinguishing

feature of this aggregation process is that it is reversible: if the temperature is reduced below  $T_a$ , the spheres completely disaggregate.

The exact mechanism that triggers aggregation is still not known, and little theoretical work has been done [8,9]. One of the objectives of this investigation was to determine the growth kinetics and aggregate structure to help elucidate the aggregation mechanism.

The characteristics of the two samples used in this study are listed in Table I. The two samples are essentially the same except for the concentration of silica. The temperature for demixing (coexistence)  $T_{\text{cx}}$  and the threshold temperature for aggregation  $T_a$  were determined from turbidity measurements.

The onset of aggregation is accompanied by a rapid and dramatic increase in the sample's turbidity. By examining the rate at which the turbidity increased, we were able to determine how the rate of aggregation depends on temperature. We found that for  $(T_a + 0.1 \text{ K}) < T < (T_{\text{cx}} - 0.1 \text{ K})$ , the rate of aggregation was independent of temperature for both samples. The light-scattering measurements reported here were performed in this plateau region. For  $T_a < T < (T_a + 0.1 \text{ K})$ , the rate increased dramatically, and for  $(T_{\text{cx}} - 0.1 \text{ K}) < T < T_{\text{cx}}$ , the rate increased slightly. We have not yet identified the physical origin for these different aggregation regimes. We suspect that the regime,  $T_a < T < (T_a + 0.1 \text{ K})$  is due to variations in the size and surface properties of the spheres that make up the sample.

The angular distribution of scattered light was mea-

TABLE I. Characteristics of samples used. Concentrations:  $x_L$  = weight fraction of lutidine,  $x_s$  = weight fraction of silica,  $c_s$  = number of silica spheres/cm<sup>3</sup>. Temperatures:  $T_a$  = aggregation threshold,  $T_{\text{expt}}$  = aggregation experiment,  $T_{\text{cx}}$  = coexistence.

Sample	$x_L$ (%)	$x_s$ (%)	$c_s$ (cm <sup>-3</sup> )	$T_a$ (°C)	$T_{\text{expt}}$ (°C)	$T_{\text{cx}}$ (°C)
A	20.0	0.15	$3.8 \times 10^{10}$	33.100	33.311	33.868
B	20.2	0.077	$2.0 \times 10^{10}$	33.440	33.597	33.783

sured as a function of time for scattering angles between  $1.00^\circ$  and  $15.4^\circ$ , corresponding to a wave-vector range of  $2.36 \times 10^3 < q < 3.62 \times 10^4 \text{ cm}^{-1}$ . The incident intensity was provided by a 5-mW He-Ne laser. The scattered light from the sample cell was collimated by a collection lens onto a viewing screen. An image of this screen was then recorded by an 8-bit video camera for subsequent analysis. Small corrections were made for the dark count of the camera, sample turbidity, and the form factor for the unaggregated spheres. Scattering from the binary mixture was negligible compared to scattering from the colloids. All scattering distributions represent an azimuthal average of the scattered intensity.

Sample cells with an optical path of 2 mm, were placed in a thermostated water bath, with a temperature stability of  $\pm 1 \text{ mK}$ , at 5 mK below  $T_a$ . Aggregation was initiated by rapidly raising the temperature to  $T_{\text{expt}}$  (Table I); it took about 2 min for the temperature of the sample and bath to reach equilibrium.

Figure 1(a) shows the time evolution of the scattered intensity of sample A. Similar curves were obtained for sample B, except the time scale was different. We find that the scattered intensity can be fit over the measured range of  $q$  by the simple function

$$I(q) = I_0 / [1 + (q\bar{R})^2 / 10]^\alpha, \quad (1)$$

with  $\alpha = 2$ . This functional form has been used successfully in previous studies of fractal aggregation [10,11], where, however,  $\alpha$  is lower and of order unity. (We should mention that for salt-induced slow aggregation of our silica spheres, we also find that  $\alpha \sim 1$ , as is expected for reaction-limited cluster aggregation).

The fact that our data is consistent with Porod's law  $I(q\bar{R} \gg 1) \sim q^{-4}$  suggests that the aggregates in our system have a sharp, nonfractal interface with the solvent. Large-angle scattering measurements up to  $q = 2.6 \times 10^5 \text{ cm}^{-1}$  confirm that the structure factor obeys Porod's

law. To interpret this finding, we note that the index of refraction of pure lutidine ( $n = 1.48$ ) is close to that of silica ( $n = 1.46$ ) [6]. If the aggregates are indeed surrounded by a lutidine-rich layer, then this layer would provide a good index-matched matrix for the silica spheres. Note that this matrix prevents us from probing how the spheres are arranged within an aggregate.

The factor of 10 in Eq. (1) was chosen so that at low  $q$  this equation corresponds to  $I(q)$  for a sphere of radius  $\bar{R}$ , namely,  $I(q\bar{R} \ll 1) \sim 1 - (q\bar{R})^2 / 5$ .

For  $t < 6 \text{ min}$ , corresponding to  $\bar{R} < 1 \mu\text{m}$ , the fit of Eq. (1) to the scattered intensity from sample A is excellent [Fig. 1(a)]. At later times, the fit becomes progressively worse. Sample B exhibits a similar trend: for  $t < 9.3 \text{ min}$ , corresponding to  $\bar{R} < 1 \mu\text{m}$ , the fits are good; for later times, there are deviations. The fact that the deviations begin at the same  $\bar{R}$ , and not the same level of turbidity, suggests that it is not due to multiple scattering. The transmission at which deviations begin in sample A is 59%, in sample B, 78%. (Control experiments indicate that multiple scattering is negligible for transmissions above 50%.) Most likely, the change in  $I(q)$  is due to gravitational settling of the clusters, as discussed below.

In Fig. 1(b), we have scaled seven intensity distributions for sample A between  $3.0 < t < 6.0 \text{ min}$ . This alignment demonstrates that  $I(q, t)$  has the factored form

$$I(q, t) = I_0(t) F(q\bar{R}), \quad (2)$$

where  $F(x)$  is time independent. Comparing Eqs. (1) and (2) implies that  $F(x) = (1 + x^2 / 10)^{-2}$ .

For dilute solutions of aggregates, the scattered intensity can be written as [12]

$$I(q, t) \propto \int_0^\infty c(M, t) M^2 P(qR) dM, \quad (3)$$

where  $c(M, t) dM$  is the concentration of aggregates with mass in the range  $M$  to  $M + dM$ , and  $P(qR)$  is the structure factor for a cluster of size  $R$ . For cluster-cluster aggregation, the mass distribution exhibits dynamic scaling [13]:  $c(M, t) = \bar{M}^{-2} \phi(M/\bar{M})$ , where  $\bar{M}(t)$  is the average cluster mass, and  $\phi(z)$  is time dependent. This form for the size distribution insures that the concentration of colloids is constant throughout the aggregation process. Substituting this expression into Eq. (3), and changing the variables of integration from  $M$  to  $R$  by using  $M \propto R^{d_f}$ , one finds

$$I(q, t) \propto \bar{M}(t) \int_0^\infty y^{3d_f-1} \phi(y^{d_f}) P(q\bar{R}y) dy, \quad (4)$$

where  $y = R/\bar{R}$ . This expression provides a theoretical interpretation for the experimental quantities  $I_0(t)$  and  $F(x)$ :

$$I_0(t) \propto \bar{M}(t), \quad F(x) \propto \int_0^\infty y^{3d_f-1} \phi(y^{d_f}) P(xy) dy. \quad (5)$$

The above analysis demonstrates that the scaling of the scattering intensity, Eq. (2), is a direct consequence of the scaling of  $c(M)$ .

In Fig. 2, we plot the time dependence of the parameters  $I_0$  and  $\bar{R}$ , which we deduced from fitting Eq. (1) to the measured intensity distributions. The experimental uncertainty in these parameters is a reflection of how well

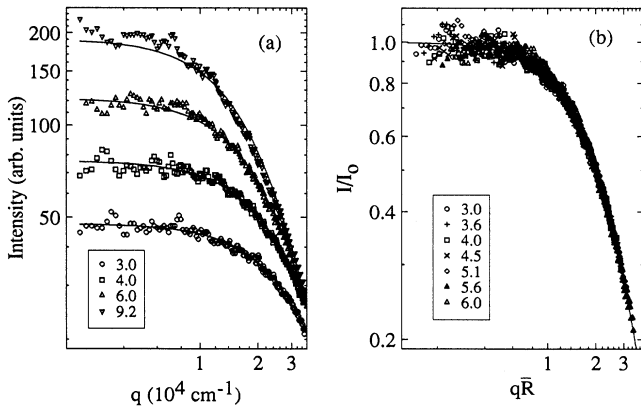


FIG. 1. (a) Scattered intensity distributions for sample A measured at four different times. Up to  $t = 6 \text{ min}$ , the fit to Eq. (1) is excellent; for later times there are systematic deviations. (b) Scaled intensity distributions over indicated range of time. Alignment of data demonstrates that the mass distribution of aggregates exhibits dynamic scaling over this range of time. Solid line is Eq. (1).

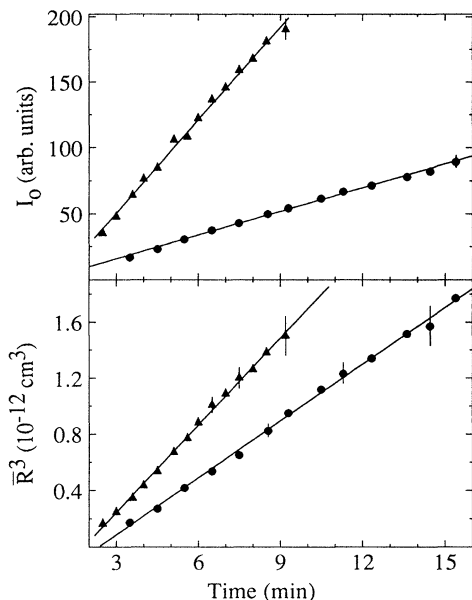


FIG. 2. Time dependence of fitting parameters  $I_0$  and  $\bar{R}$  in Eq. (1) for sample A ( $\blacktriangle$ ) and sample B ( $\bullet$ ). Lines represent linear fits to  $I_0(t)$  and  $\bar{R}^3(t)$  with  $\bar{R}$  in  $\mu\text{m}$  and  $t$  in min. Sample A:  $I_0 = -20.5 + 23.6t$ ;  $\bar{R}^3 = -0.376 + 0.207t$ . Sample B:  $I_0 = -2.13 + 6.00t$ ;  $\bar{R}^3 = -0.319 + 0.135t$ . The negative constant terms in the fits reflect the fact that it took about 2 min for the bath and sample to reach equilibrium.

Eq. (1) fits the data. Based on the theoretical work of van Dongen and Ernst [13], we fit the following functions to  $I_0$  and  $\bar{R}$ :  $I_0 = (A + Bt)^z$  and  $\bar{R} = (C + Dt)^w$ , where  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $z$ , and  $w$  are free parameters of the fit. We found that for both samples,  $z \sim 1$  and  $w \sim \frac{1}{3}$ , suggesting that the growth exponents are independent of the silica concentration. This led us to simply set  $z = 1$  and  $w = \frac{1}{3}$ . Figure 2 demonstrates that this assignment is in complete accord with our data.

Summarizing the above, we find that  $I_0$ , which is proportional to  $\bar{M}$ ,  $\sim t$  and  $\bar{R}^3 \sim t$ . This implies that  $\bar{M} \propto \bar{R}^3$ . This expression indicates that the clusters in our system have a dense, nonfractal structure. This conclusion is consistent with the fact that the large- $q$  behavior of  $I(q)$  decays like  $q^{-4}$  and not  $q^{-d_f}$ , as is expected for fractal aggregates.

The Smoluchowski rate equation predicts [13] that, in general,  $\bar{M} \sim t^{1/(1-\lambda)}$ , where  $\lambda$  is the homogeneity exponent of the reaction kernel  $K_{ij}$ . For our system, we conclude that  $\lambda = 0$ . The Brownian kernel also has this value for  $\lambda$ , and it has the form  $K_{ij} = 2kT(R_i + R_j)(R_i^{-1} + R_j^{-1})/3\eta$ , where  $R_i$  is the radius of a cluster of  $i$  spheres,  $kT$  is the thermal energy, and  $\eta$  is the solvent viscosity. This kernel models fractal and nonfractal diffusion-limited aggregation. For the Brownian kernel,  $(\bar{R}/R_1)^{d_f} \sim (t/t_0)$ , where  $t_0 = 3\eta/4kTc_s$  [14].

Substituting numbers into the above expression, we find that  $\bar{R}^3 \sim 0.0439t \mu\text{m}^3$  for sample A, and  $\bar{R}^3 \sim 0.0230t \mu\text{m}^3$  for sample B. The experimentally measured slopes in Fig. 2 are about a factor of 5 larger than

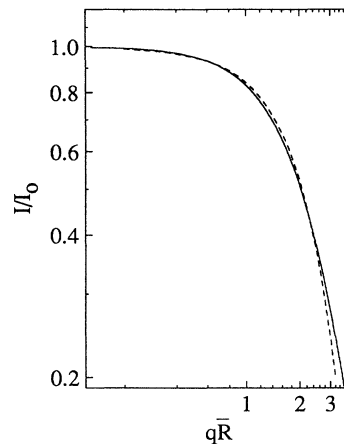


FIG. 3. Comparison of empirical scaled intensity distribution used to fit data, Eq. (1), solid line, and calculated distribution based on Eq. (6), dotted line.

the above predictions.

Usually, one finds that experimental aggregation rates are less than the Brownian limit, so our finding is at first puzzling. A possible explanation is that  $R_1$  is larger than the bare silica radius due to an adsorbed layer of lutidine. The theoretical expression for the rate can be corrected by using  $5^{1/3}R_1$  for the monomer radius instead of  $R_1$ . This implies that the average distance between the centers of the colloids within an aggregate is  $\sim 3.4R_1$ . Gurfein, Beysens, and Perrot [4] found that the interparticle spacing in a sedimented phase of such aggregates is  $(3.0 \pm 0.3)R_1$ , in close accord with the above model.

Gravitational settling could also increase the aggregation rate above the Brownian limit [11]. To assess this possibility, we calculated the time it takes a spherical cluster to settle a distance equal to its radius, and the time it takes a cluster to diffuse the same distance. We found that for clusters larger than  $0.6 \mu\text{m}$  in radius, the settling time is less than the diffusion time. This reveals that the Brownian kernel, which assumes that clusters move solely by diffusion, may not be valid late in the aggregation process. A change in the kernel would alter the rate of aggregation, the form of the size distribution, and the structure factor. The above analysis suggests that the change we observe in the structure factor for  $\bar{R} > 1 \mu\text{m}$  is due to gravitational settling.

Having established that  $d_f = 3$  in this system, we now return to Eq. (5) for  $F(x)$ . Assuming that clusters are indeed spherical, we use the Rayleigh-Gans-Debye approximation [12] for the structure factor of an aggregate. This leads to

$$F(x) \propto \int_0^\infty y^5 \phi(y^3) J_{3/2}^2(xy) dy, \quad (6)$$

where  $J_{3/2}$  is the Bessel function of order  $\frac{3}{2}$ . The cluster mass distribution for the Brownian kernel can be approximated by  $\phi(z) \sim e^{-az}$  for large  $z$ , where  $a$  is an adjustable parameter [13]. We have carried out the above integration numerically for  $a = 1$  to 10. We find that  $a = 4$  yields an  $F(x)$  that agrees well with the empirical form, Eq. (1), used to fit the scattering data over the measured range

$0.15 < q\bar{R} < 3.5$ ; see Fig. 3. This agreement demonstrates that the form of Eq. (1) is consistent with a reasonable theoretical model for the aggregation process. We stress that this model has only one free parameter and thus feel the agreement to the light-scattering data is significant.

In summary, we find that the Brownian kernel predicts the correct growth exponent for  $\bar{M}$ , accounts for the shape of the measured structure factor, and, to within a factor of 5, correctly predicts the time scale for the aggregation process. We thus conclude that the clusters in our system stick as soon as they collide, and that there is no energy barrier to aggregation. We believe that the aggregates are dense because the bonds that hold them together are fluidlike and can rotate. Our results are consistent with the idea that prior to aggregating, a layer of lutidine

forms on the silica. Lutidine adsorption has also been observed in silica gels [15].

We gratefully acknowledge valuable discussions with Roland Aschauer, Andrew Cumming, Catherine Allain, and Michel Cloitre. Toni VanDeKop performed the numerical integration of Eq. (6). Special thanks to the scientists and technicians at SPEC CE Saclay for their suggestions and expert technical support. This work has been partially supported by the French Ministère de la Recherche et de la Technologie and the Centre National d'Etudes Spatiales. The Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions is affiliated with the Centre National de la Recherche Scientifique.

---

\*Current address: Physics Department, Lewis & Clark College, Portland, OR 97219. Electronic address: broide@lclark.edu

- [1] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
- [2] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, *Nature* **339**, 360 (1989).
- [3] B. J. Olivier, C. J. Sorenson, and T. W. Taylor, *Phys. Rev. A* **45**, 5614 (1992).
- [4] V. Gurfein, D. Beysens, and F. Perrot, *Phys. Rev. A* **40**, 2543 (1989).
- [5] W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
- [6] D. Beysens and D. Estève, *Phys. Rev. Lett.* **19**, 2123 (1985).
- [7] P. D. Gallagher, M. L. Kurnaz, and J. V. Maher, *Phys. Rev. A* **46**, 7750 (1992).
- [8] T. J. Sluckin, *Phys. Rev. A* **41**, 960 (1990).
- [9] H. T. Dobbs, G. A. Darbellay, and J. M. Yeomans, *Europhys. Lett.* **18**, 439 (1992).
- [10] D. S. Cannell and C. Aubert, in *On Growth and Form*, edited by H. E. Stanley and N. Ostrowsky (Nijhoff, Dordrecht, 1986), p. 187.
- [11] D. Asnaghi, M. Carpineti, M. Giglio, and M. Sozzi, *Phys. Rev. A* **45**, 1018 (1992).
- [12] M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic, New York, 1969).
- [13] P. G. J. van Dongen and M. H. Ernst, *Phys. Rev. Lett.* **54**, 1396 (1985).
- [14] G. M. Hidy and D. K. Lilly, *J. Colloid Interface Sci.* **20**, 867 (1965).
- [15] B. J. Frisken, F. Ferri, and D. S. Cannell, *Phys. Rev. Lett.* **66**, 2754 (1991).