PHYSICAL REVIEW E, VOLUME 64, 041403

Internal structure of colloidal aggregates

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(Received 8 February 2001; published 21 September 2001)

A nonlinear model of diffusion-limited growth of three-dimensional colloidal aggregate has been developed. The conditions of internal combination/recombination balance has been considered. Obtained solution shows that the aggregate contains the central dense core and the surrounding loose region, in which the aggregated particle concentration decreases as a power function, according to the fractal cluster properties. The fractal dimension d_f has been found to be independent on physical and chemical properties of colloidal system. The obtained universal value $d_f = 2.5$ is in a good agreement with the known experimental and numerical results. The model may be useful for the analysis of a wide class of aggregation phenomena.

DOI: 10.1103/PhysRevE.64.041403 PACS number(s): 82.70.Dd, 61.43.Hv

Problems of aggregative stability of colloids and kinetics of aggregation represent one of the basic topics in colloid science. Traditional approaches to the theoretical analysis of aggregation processes go back to the Smoluchowski's classical model [1] and are based on solution of system of kinetic equations of coagulation. A lot of papers concerning the analytical and numerical studies of the Smoluchowski kinetic system are available (see, for example, [2–4]). Exact solutions have been found for the constant coagulation kernel; and the self-similar behavior has been analyzed for the various dependencies of aggregation kernels on aggregate sizes, including those under sedimentation conditions and in shear flows. Numerous comparisons with the experimental data have been carried out.

At the same time, such approach entails little attention to the internal structure of colloidal aggregates. The similar process of aggregation of molecules and small particles to form clusters is a central problem in many fields of applied sciences; examples are coagulated aerosols, chemical precipitation from a supersaturated matrix, growing crystals from a supercooled melt, and others. The aggregates formed in all cases have extremely complicated multibranched forms like dendrites and are called ''fractal clusters.'' Advanced methods of numerical simulations [5–8] have demonstrated that in such structures the angle averaged concentration φ of particles in a cluster depends on the distance r to the formal cluster center according to the power law: $\varphi(r) \sim r^{d_f - 3}$ [for three-dimensional (3D) clusters]. The power exponent d_f is called ''fractal cluster dimension'' and its determination is a key problem in large number of computer and theoretical studies on evolution of fractal clusters [5–14].

Computer analysis, however, entails a number of substantial drawbacks while applying to colloid aggregation. In fact, it is impossible to simultaneously simulate the diffusion motion of large number of particles in colloidal system. Moreover, it is quite difficult to trace the dependence of cluster structure on specific physicochemical conditions that are realized in a colloid. Therefore, it is important to develop the analytical models of aggregation process in colloidal dispersions, combining the possibility of obtaining information on the spatial structure of separate clusters with the determination of principles of evolution of an aggregate ensemble. This paper is devoted to the development of a corresponding model of the growth of a separate aggregate forming due to the attachment of single particles.

Unlike the known theoretical models of fractal clusters, such as: the diffusion-limited aggregation (DLA) mean-field theories [5,13,14]; the probability scaling approaches [10,11]; the ''branched growth'' models [12] and others, we do not study detailed peculiarities of the fractal structure of colloidal aggregates. Our model does not contain any suggestions on the internal aggregate structure, and we are interested only in an averaged description of the latter one. We take into account that the particle diffusion inside the aggregate and the combination/recombination processes are complicated by the presence of the excluded volume. Due to the very slow diffusion motion of colloidal particles, we analyze the conditions when the aggregate growth is limited by the diffusional transport of particles to the aggregate. In this case the balance between the internal combination/recombination processes have to be established. The main physical result is that in such conditions the growing aggregate is characterized by the power dependence of the aggregated particle concentration φ on the spatial coordinate, that is like a fractal cluster. The analytically determined value of the fractal dimension $d_f = 2.5$ is independent of physical and chemical properties of colloidal system. This universal value is closely coincident with the results of experimental studies [15–19] and with the fractal dimension of classical DLA regime.

The partial differential model may be formulated on the basis of coexisting interpenetrating media conception under the following assumptions.

(1) All colloidal particles are divided in two main classes: the aggregated particles, united into the cluster skeleton, and the ''free'' particles inside and outside the aggregate volume. The cluster structure is described by the volume concentration $\varphi(t,r)$ of aggregated particles, coexisting with the ''free'' particles of $n(t,r)$ concentration inside the aggregate volume. Outside the aggregate only the ''free'' particles exist with the concentration $\sigma(t,r)$. Due to interparticle bonds, the hydrodynamic mobility of aggregated φ particles is neglected as compared with the diffusional motion of ''free'' n particles. We assume the angle averaged situation. So, all the concentrations depend only on the distance r from the aggregate center.

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(2) The aggregate volume is formally bounded by the sphere (radius Σ) passing over the outermost particle of aggregate skeleton. The boundary motion $\Sigma(t)$ is limited by the rate of diffusional transport of ‘‘free’’ particles from the bulk of colloid to the formal aggregate surface.

(3) A diluted colloidal system is considered. Outside the aggregate the particle concentration $\sigma(t,r)$ is small enough, so the interparticle interaction is negligible. The evolution of spontaneously formed aggregate is dependent on the kinetics of attachment of ‘‘free’’ particles to the aggregate skeleton. The probability of such attachment is proportional to the aggregated particle concentration and is sufficiently large in comparison with the probability of single particle-particle coagulation. The attachment is supposed to be reversible and the recombination process is also taken into account. It should be pointed out that the recombination probability may be very small, but this process always takes place in real colloids.

(4) Inside the aggregate the φ and n particles are considered as the coexisting interpenetrating media. The particle attachment and breaking to/from the aggregate are convenient to describe with the help of nonlinear mass-exchange terms in diffusion equation.

According to these assumptions the diffusion flux $\mathbf{j}$ of n particles inside the aggregate is controlled by inhomogeneities of chemical potential μ:

$$\mathbf{j}=\beta n \boldsymbol{\nabla}\mu, \quad \mu=kT\ln\left(\frac{n}{1-\varphi/\varphi_m}\right), \tag{1}$$

where β stands for the particle hydrodynamic mobility. While defining the chemical potential μ we assume that the particle-particle coagulation is resulted by the presence of narrow and deep interparticle energy minimum. The narrowness of this minimum allows us to neglect the interparticle interaction up to the particle-particle contact, after that a single ‘‘free’’ particle transfers to a skeleton one. At the same time, the aggregated particles occupy a volume excluded for the ‘‘free’’ particles. The last condition leads to the dependence of chemical potential μ on the concentration φ. We use the simplest van der Waals approximation (1), where φ_m stands for the random, close packing concentration ($\varphi_m \sim 0.4-0.6$).

Hence, the diffusion equations for the ‘‘free’’ particles take the form

$$\frac{\partial n}{\partial t}=D\left(\boldsymbol{\nabla}\left[\left(1-\frac{\varphi}{\varphi_m}\right)\boldsymbol{\nabla}\left(\frac{n}{1-\varphi\varphi_m}\right)\right]\right)-\frac{\partial\varphi}{\partial t}, \quad 0\leqslant r<\Sigma(t), \tag{2}$$

$$\partial\sigma/\partial t=D\Delta\sigma, \quad r>\Sigma(t), \quad \sigma(\infty)=\sigma_\infty, \quad D=\beta kT. \tag{3}$$

The last term in Eq. (2) has the mass-exchange meaning and describes the evolution of aggregate structure. We assume that the aggregation kinetics is defined by the local probabilities of the attachment of ‘‘free’’ particles to the aggregate skeleton and the breaking of particles from the aggregate, complicated by the presence of interparticle bonds between the aggregated particles,

$$\frac{\partial\varphi}{\partial t}=an\varphi-b\varphi(\varphi_m-\varphi), \quad a,b\approx\text{const}, \quad 0\leqslant r<\Sigma(t). \tag{4}$$

The local kinetic coefficients a and b evidently depend on chemical and physical properties of colloidal system. Of the great importance is the structure of the last term in Eq. (4) (recombination). The number of recombined particles is proportional to the number of aggregated particles in a unit volume, that is, the last term is proportional to φ. On the other hand, the recombination probability should be a decreasing function of the number of interparticle bonds and should be dependent on the presence of the free volume in local vicinity of the aggregated particle. In close packing region ($\varphi \approx \varphi_m$) the recombination should tend to be zero. We have used the simplest dependence $\sim\varphi(\varphi_m-\varphi)$ in Eq. (4) to take these assumptions into account.

The following conditions would be fulfilled at the aggregate boundary $\Sigma(t)$.

(1) The continuation of chemical potentials of ‘‘free’’ particles

$$\ln\left(\frac{n}{1-\varphi/\varphi_m}\right)=\ln\sigma, \quad r=\Sigma(t). \tag{5}$$

(2) The mass balance equation

$$D\frac{\partial\sigma}{\partial r}-D\left(1-\frac{\varphi}{\varphi_m}\right)\frac{\partial}{\partial r}\left(\frac{n}{1-\varphi/\varphi_m}\right)=(n+\varphi-\sigma)\frac{d\Sigma}{dt}, \quad r=\Sigma(t). \tag{6}$$

(3) The boundary motion equation

$$\varphi\frac{d\Sigma}{dt}=\nu[a\sigma\varphi-b\varphi(\varphi_m-\varphi)], \quad r=\Sigma(t). \tag{7}$$

where ν is the length dimension coefficient, which may be considered approximately to be equal to the particle radius. Hence, the aggregate boundary is determined by the balance between the diffusional transport of particles and the kinetics of aggregation.

The developed model represents the system of nonlinear partial differential equations complicated by the presence of unknown moving boundary. It is well known that the time relaxation of solution of mentioned class of partial problems is determined by the time dependence of moving boundary $\Sigma(t)$ with the character time $\tau_\Sigma=\Sigma/(d\Sigma/dt)$. The time evolution of aggregate structure is controlled by the kinetic equation (4), the solution of which is characterized by the aggregation time $\tau_a=1/a$. In the case of sufficiently large cluster size and slow growth we should consider the steady-state regime of aggregation kinetics: $\tau_a \ll \tau_\Sigma$, $\partial\varphi/\partial t\approx 0$. It means that the internal balance between the combination/recombination processes is established. In order to explain the solution it is convenient to introduce the function $\rho=n/(1-\varphi/\varphi_m)$, standing for the ‘‘free’’ particle concentra-

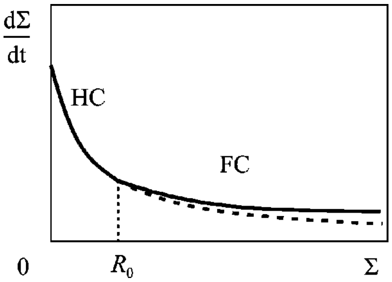

FIG. 1. Character dependence of the growth rate on the aggregate size, solid curve—stable regimes, dashed curve—unstable HC growth rate.

tion defined over the volume, which is not occupied by aggregated particles. Thus, the kinetic equation (4) takes the form

$$\frac{\partial\varphi}{\partial t}=a\varphi\left(1-\frac{\varphi}{\varphi_m}\right)(\rho-K)\approx 0,\qquad K=\frac{b}{a}\varphi_m\ll 1,$$

$$\varphi(t,r=0)=\varphi_m. \tag{8}$$

It is easy to see that two kinds of solution of the models (1)–(8) exist. The first one represents the homogeneous aggregate ''core'' (HC),

$$\varphi(r)=\varphi_m,\qquad \rho(\Sigma)=\sigma(\Sigma)=\frac{D\sigma_\infty}{D+a\nu\varphi_m\Sigma},$$

$$\frac{d\Sigma}{dt}=\frac{a\nu D\sigma_\infty}{D+a\nu\varphi_m\Sigma}. \tag{9}$$

In this case the aggregate structure is similar to liquid drops and the aggregates of such kind arise during the phase separation of colloids [2].

The second kind of solution is characterized by the power dependence of concentration $\varphi(r)$ and, thus, resembles a fractal cluster (FC),

$$\varphi(r)=\sqrt{\frac{\varphi_m D(\sigma_\infty-K)}{a\nu K r}},\qquad \rho(r)=K=\sigma(\Sigma),$$

$$\frac{d\Sigma}{dt}=\sqrt{\frac{Da\nu K}{\varphi_m}\,\frac{(\sigma_\infty-K)}{\Sigma}}. \tag{10}$$

Here we use the steady-state approximation $\partial\sigma/\partial t\approx 0$ for Eq. (3). This is valid only in the case, when the character diffusion time $\tau_D=\Sigma^2/D$ is much less than the growth time τ_Σ, that evidently follows from Eqs. (9) and (10).

Analyzing the stability of solutions we have to take into account that for mentioned class of partial models this stability is totally dependent on the boundary growth rates. A similar situation, for example, takes place in the processes of unidirectional solidification of melts. It should be noted that we do not consider the instabilities of branches in DLA clusters. Our approach considers on average all the inhomogeneities in the spatial displacement of skeleton particles. Figure 1 shows the dependence of growth rate on the aggregate size.

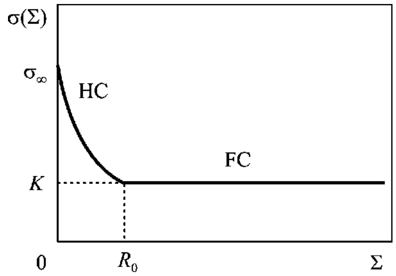

FIG. 2. Evolution of the boundary value of ''free'' particle concentration with the aggregate growth.

Analyzing the growth conditions we come to the conclusion that for the aggregate size of radii $0<\Sigma(t)<R_0$, the HC (9) grows more rapidly. Consequently, this kind of solution must be stable and more probable. Otherwise, the aggregate evolves as FC (10) for the larger sizes $\Sigma(t)>R_0$. The changeover radius R_0 is equal to

$$R_0=\frac{D}{\nu a K}\,\frac{\sigma_\infty-K}{\varphi_m}. \tag{11}$$

The evolution of the boundary value of ''free'' particle concentration $\sigma(r=\Sigma)$ is presented on Fig. 2. The changeover of the regimes HC and FC also takes place at $\Sigma(t)=R_0$. So, for the large aggregates $[\Sigma(t)>R_0]$ we get the following solution for the aggregate structure (see Fig. 3). The aggregate contains the central dense core and the surrounding zone, in which the aggregate becomes more and more loose. The point is that inside this loose region the aggregated particle concentration φ decreases as a power function,

$$\varphi(r)=\varphi_m(R_0/r)^{1/2},\qquad R_0\leqslant r\leqslant\Sigma. \tag{12}$$

Thus, the fractal cluster dimension d_f is obtained to be equal to the universal value $d_f=2.5$ and is independent on the physical and chemical parameters $a,b,D,\sigma_\infty,\varphi_m,\nu$ of colloidal system. This value is very close to the experimental results: $d_f=2.56\pm0.3$ for IgG aggregates [15]; 2.52 ± 0.05 [16] and 2.4 ± 0.1 [17] for quartz particles; 2.32 ± 0.05 for calcium carbonate particles [18]; 2.5 for aggregates of porphyrins [19]. Our result is also very close to the known result of DLA model $d_f=2.51\pm0.06$ [5,6] and $d_f=2.495\pm0.005$ [8] for 3D clusters. It should be noted that the present solution is valid only in the limit of very ''slow'' aggregate

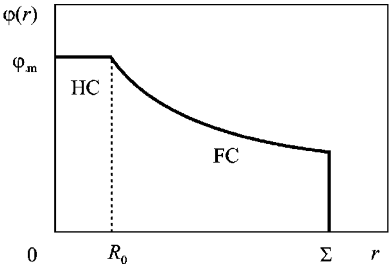

FIG. 3. Radial dependence of the aggregated particle concentration.

growth, that is $\tau_\Sigma \gg \tau_a, \tau_D$ and $d\Sigma/dt \ll a\Sigma, D/\Sigma$. So, the solution (8)–(12) represents the zero-order perturbation over the small parameter $(\Sigma/D)(d\Sigma/dt) \ll 1$, standing for the dimensionless aggregate growth rate. With the help of asymptotic methods it should be possible to find out the first-order perturbation. The last one will result in small variations of d_f over the value 2.5.

In conclusion, we have discussed the partial differential model describing the growth and the evolution of internal structure of a separate colloidal aggregate. The model predicts analytically the power spatial behavior of the aggregated particle concentration according to the fractal cluster properties. The fractal dimension $d_f = 2.5$ is found to be independent on the physical and chemical characteristics of colloidal system. It is important to note that unlike the DLA approach our results are devoted to the situation when the internal combination/recombination balance is established. The point is that this regime of aggregate evolution is characterized by the universal value of fractal dimension coincident with the same one for DLA regime.

By using the results of the model on aggregate internal structure and growth rate, the kinetics of colloid aggregation may be investigated under condition when both the aggregate distribution over size and the particle balance law in colloid will be taken into account. The model is also useful for the analysis of many problems of applied sciences, when the processes of cluster formation and growth play a significant role.

The present research was carried out within the financial support of RFBR Grant Nos. 00-02-17731, 01-02-16072, 01-01-00058, and 01-02-96430ural and RME Grant No. E00-3.2-210. The research was also made possible in part by CRDF, Award No. REC-005.

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[1] M. Von Smoluchowski, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **92**, 120 (1917).

[2] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge Univ. Press, Cambridge, 1989).

[3] A. Fernandez-Barbero *et al.*, Phys. Rev. E **53**, 4981 (1996).

[4] A. Fernandez-Barbero *et al.*, Phys. Rev. E **56**, 4337 (1997).

[5] T. A. Witten and L. M. Sander, Phys. Rev. B **27**, 5686 (1983).

[6] P. Meakin, Phys. Rev. A **27**, 1495 (1983).

[7] T. Vicsek, *Fractal Growth Phenomena*, 2nd ed. (World Scientific, Singapore, 1992).

[8] S. Tolman and P. Meakin, Phys. Rev. A **40**, 428 (1989).

[9] R. C. Ball and T. A. Witten, Phys. Rev. A **29**, 2966 (1984).

[10] L. A. Turkevich and H. Scher, Phys. Rev. A **33**, 786 (1986).

[11] T. C. Halsey, P. Meakin, and I. Procaccia, Phys. Rev. Lett. **56**, 854 (1986).

[12] T. C. Halsey, Phys. Rev. A **38**, 4789 (1988); Phys. Rev. Lett. **72**, 1228 (1994).

[13] H. Levine and Y. Tu, Phys. Rev. A **45**, 1044 (1992).

[14] V. A. Bogoyavlenskiy and N. A. Chernova, Phys. Rev. E **61**, 5422 (2000).

[15] J. Feder *et al.*, Phys. Rev. Lett. **53**, 1403 (1984).

[16] S. K. Sinha, T. Freltoft, and J. Kjems, in *Aggregation and Gelation*, edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).

[17] J. Kjems and T. Freltoft, in *Scaling Phenomena in Disordered Systems*, edited by R. Pynn and A. Skjeltorp (Plenum Press, New York, 1985).

[18] C. Allain, M. Cloitre, and M. Wafra, Phys. Rev. Lett. **74**, 1478 (1995).

[19] F. Mallamace *et al.*, Phys. Rev. Lett. **76**, 4741 (1996).