

Evolution of the fractal-like aggregate system in colloids

Ekaterina Elfimova, Alexey O. Ivanov, and Andrej Yu. Zubarev

Urals State University, Lenin Avenue, 51, 620083, Ekaterinburg, Russia

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The evolution of a colloidal fractal-like aggregate system is studied theoretically with account for the reduction of the single-particle concentration in the space between these growing aggregates. Two different mechanisms of the initial aggregate formation are considered. They are heterogeneous aggregation, when the initial aggregates appear on foreign nuclei (the biggest particles, pollution, etc.), and homogeneous nucleation, when the initial clusters appear due to a random meeting and combination of single Brownian particles. The principles of colloid supersaturation decrease and the aggregate distribution in size are obtained in both cases as well as the internal structure of the clusters. Unlike the usual condensation-type phase transition, the system of discrete clusters is formed at the final stage of the aggregation process. The internal particle distribution in these clusters does not obey the universal scaling power law, which differs from the model case of separate cluster growth in an infinite colloidal medium with permanent concentration of free particles.

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I. INTRODUCTION

Microscopic structures, the formation of which is omnipresent in colloidal dispersions, have a crucial influence on the rheological, hydrodynamic, optical, and other physical properties of such systems. The structure of existing aggregates in colloids is determined by the interparticle interactions present in a system. A sufficient number of experiments evidence the formation of loose branched clusters in colloids [1–10]. As these divaricate aggregates exhibit a self-similarity, the fractal approach appears to be a very effective tool in colloidal microstructure descriptions.

Fractal cluster formation is widely studied in computer simulations. Starting with the classical aggregation models [11–13], they are used to simulate the spatial alignment of particles according to the mechanisms of motion, interparticle interactions, and kinetics of coagulation predefined in the computer experiment. The results of simulations are undoubtedly useful for a deeper understanding of real natural experiments. However, the direct comparison of the properties obtained in simulations to the real physical observables of colloidal systems is not so accurate. It happens because one cannot simulate the diffusion motion for each particle in large systems simultaneously. Also, the influence of physical and chemical properties on the cluster structure could not be easily extracted from the simulations. For this, a theoretical modeling of fractal cluster growth is essential.

Unlike computer simulations and natural experiments, the number of which is in fact large in the field of cluster formation in colloids, there is a lack of theoretical models. Here only two main classes of the theoretical approaches could be named. The first one goes back to Von Smoluchowski's classical theory [14] and is usually based on a solution of the coagulation kinetic equation system. Thus, for example, Refs. [4, 15–17] are devoted to analytical and numerical studies of the Von Smoluchowski's kinetic equations. In this way exact solutions were found for the systems with a constant coagulation kernel, and the self-similar behavior has been studied for the various dependences of the kernels on aggregate sizes, including those under conditions of sedimentation

and shear flow. But it is worth mentioning that such an approach gives information about the number of aggregates only; no data concerning cluster internal structure could be obtained. The second class of theoretical models contains works mainly focused on the explanation of computer simulations, and these models are devoted to the study of the physical properties of the systems with given fractal structures inside (for example, [18–24]). So none of these approaches give the cluster distribution together with the aggregate internal structure.

The present paper is aimed at an analysis of diffusion-limited aggregation (DLA) in an *ensemble* of colloidal clusters with arbitrary structure. In this case there is a competition for nonaggregated particles, the concentration of which may decrease. So the basic question—how does the decay of supersaturation influence the rate of cluster formation and cluster internal structure?—is addressed in this work. It should be noted that there are two different scenarios for the aggregation of colloidal particles. Like for the condensation of molecules during the first-order phase transition we can observe either homogeneous aggregation of particles, when the initial aggregates form due to occasional combination of particles, or heterogeneous aggregation, when specific strange nuclei preexist in a system (large particles or pollution, for example, can play the role of these nuclei). Below, both ways of aggregation are considered on the basis of a previously developed model [25], which describes single-cluster growth in an infinite inexhaustible medium. A brief overview of this model is given in Sec. II. In Sec. III we develop a theoretical model which describes the colloidal supersaturation decrease due to the simultaneous growth of a cluster ensemble. Theoretical predictions obtained for the case of heterogeneous aggregation are presented in Sec. IV. Homogeneous aggregation is described in Secs. V and VI. The last section of the paper (Conclusion) is devoted to a summary of the work.

II. MATHEMATICAL MODEL OF SINGLE-AGGREGATE GROWTH

Let us consider a colloidal system with initial volume concentration of particles being equal to c_0 and containing a

number of aggregates. Following the model of [25], we consider all aggregates being averaged over all their orientations. In this case each single aggregate is spherically symmetrical and is bounded by a sphere of radius R . The aggregate evolution may be studied on the basis of the mathematical model developed in Ref. [25], which consists of the set of differential equations

$$\begin{aligned} \frac{\partial n}{\partial t} &= \frac{D}{r^2} \frac{\partial}{\partial r} \left[\left(1 - \frac{\varphi}{\varphi_m} \right) r^2 \frac{\partial}{\partial r} \left(\frac{n}{1 - \varphi/\varphi_m} \right) \right] - \frac{\partial \varphi}{\partial t}, \\ \frac{\partial \varphi}{\partial t} &= \alpha n \varphi - \beta \varphi (\varphi_m - \varphi), \quad r < R, \\ \Delta c &= 0, \quad r > R, \end{aligned} \quad (1)$$

and the number of boundary conditions

$$\begin{aligned} \varphi \frac{dR}{dt} &= \nu [\alpha c \varphi - \beta \varphi (\varphi_m - \varphi)], \\ D \frac{\partial c}{\partial r} - D \left(1 - \frac{\varphi}{\varphi_m} \right) \frac{\partial}{\partial r} \left(\frac{n}{1 - \varphi/\varphi_m} \right) &= (n + \varphi - c) \frac{dR}{dt}, \\ \ln \left(\frac{n}{1 - \varphi/\varphi_m} \right) &= \ln c, \quad r = R, \\ c &\rightarrow c_\infty, \quad r \rightarrow \infty. \end{aligned} \quad (2)$$

Here $\varphi(t, r)$ is the volume concentration of particles, forming the aggregate skeleton, depending on time t and on the distance r from the formal aggregate center; $n(t, r)$ stands for the volume concentration of “free” (nonaggregated) particles, diffusing in the cluster pores; $c(r)$ has a meaning of the particle volume concentration outside the aggregates and c_∞ is associated with the mean particle concentration in the interaggregate colloid bulk; D is the particle diffusivity; the kinetic coefficients α and β describe the processes of “free” particle combination to the aggregate skeleton and its recombination, respectively; ν is the coefficient being equal by the order of magnitude to the particle radius; φ_m is the concentration of a random dense packing. A detailed discussion of the physical meaning of Eqs. (1) and (2) is given in Ref. [25]. Unlike this model, here we take into account that the mean bulk “free” particle concentration c_∞ depends on time. The third equation in Eqs. (1) is valid under the usual assumption of low aggregate growth rate as compared with the diffusion relaxation rate on the characteristic spatial length R . This means that the following inequality holds true:

$$\frac{1}{R} \frac{dR}{dt} \ll \frac{D}{R^2}.$$

The asymptotic analysis of the models (1) and (2) shows that the solution stability is characterized by some critical aggregate radius R_0 :

$$R_0 = \frac{D}{\nu \alpha K} \frac{c_\infty - K}{\varphi_m}, \quad K = \frac{\beta}{\alpha} \varphi_m. \quad (3)$$

For the case of large aggregates with $R > R_0$ the stable in time solution may be written in the form

$$\varphi(t, r) = \varphi_m \sqrt{\frac{R_0}{r}}, \quad n(t, r) = K \left[1 - \frac{\varphi(t, r)}{\varphi_m} \right], \quad (4)$$

and the following boundary relations are valid:

$$\varphi(t, R) = \varphi_m \left(\frac{R_0}{R} \right)^{1/2}, \quad \frac{dR}{dt} = \sqrt{\frac{D \alpha \nu K}{\varphi_m}} \sqrt{\frac{c_\infty - K}{R}}, \quad (5)$$

For smaller aggregates $R < R_0$ the only physically meaningful solution is

$$\varphi(t, r) = \varphi_m, \quad n(t, r) = 0. \quad (6)$$

These aggregates, the radii R of which are less than R_0 , have a homogeneous dense internal structure. The volume concentration φ in these aggregates does not depend on r and is close to the concentration φ_m of the random dense packing.

Thus, the critical radius R_0 has the meaning of the changeover aggregate size, and we get the following steady-state solution for the structure of large single aggregates ($R > R_0$). The aggregate contains the central dense core of radius R_0 and the surrounding zone, in which the aggregate becomes more and more loose. The point is that inside this loose region the angle-averaged particle concentration φ in a cluster depends on the distance r to the formal aggregate center according to the power law $\varphi(r) \sim r^{-(3-d_f)}$ [for three-dimensional (3D) clusters], which is the main feature of fractal clusters. Thus, the fractal cluster dimension d_f is obtained to be equal to the universal value $d_f = 2.5$, Eqs. (4), and it is independent of the physical and chemical parameters α , β , D , c_∞ , φ_m , and ν of the colloidal system. This value is very close to the experimental results, $d_f = 2.56 \pm 0.3$ for IgG aggregates [1], 2.52 ± 0.05 [2] and 2.4 ± 0.1 [3] for quartz particles, 2.32 ± 0.05 for calcium carbonate particles [6], and 2.5 for aggregates of porphyrins [7], and is also in good agreement with the results of the computer DLA model, $d_f = 2.51 \pm 0.06$ [11,12] and $d_f = 2.495 \pm 0.005$ [13], as well as with results of other models for 3D clusters.

It is of principal importance that only expressions (4) are obtained under the assumption that the mean concentration c_∞ is constant and does not depend on time. For the relations of Eqs. (5) this assumption is not required.

It is worth mentioning that the parameter K has the meaning of the combination-recombination equilibrium concentration at the aggregate boundary. So the cluster growth rate (5) depends on the difference between this equilibrium value and the mean bulk concentration c_∞ . In the case of their equality $c_\infty = K$ the aggregate growth stops and the aggregation process stabilizes. The point is that the difference $\Delta = c_\infty - K$ plays a part of colloid *supersaturation* similar to the condensation in supersaturated gases. This analogy is of vital importance because the aggregate ensemble evolution in *super saturated* colloids might be studied with the help of the colloid phase separation kinetic theory developed in Refs. [26,27].

III. KINETIC AND BALANCE EQUATIONS

Let us study the evolution of a system of fractal-like colloidal aggregates suspended in a macroscopically homogeneous supersaturated colloid under the conditions when both the reduction in supersaturation and the continuing initiation of new aggregates in the supersaturated surroundings are taken into account. The growing aggregates are distributed over size, and the distribution density $f(t, R)$ is governed by a kinetic equation

$$\frac{\partial f(t, R)}{\partial t} + \frac{\partial}{\partial R} \left[\frac{dR}{dt} f(t, R) \right] = 0, \quad (7)$$

under complete neglect of the fluctuations of the diffusionally controlled growth rate of a single aggregate (5). We presume the function $f(t, R)$ to be normalized to the number concentration $N(t)$ of the aggregates:

$$\int_0^\infty f(t, R) dR = N(t). \quad (8)$$

The supersaturation decreases due to the growth of the cluster ensemble. This decrease should be described with the help of the mass balance condition which can be presented in the form

$$\frac{d\Delta}{dt} = -4\pi \int_0^\infty f(t, R) R^2 \frac{dR}{dt} [\varphi(R) + n(R) - c(R)] dR, \quad (9)$$

$$\Delta(t=0) \equiv c_\infty(t=0) - K = c_0 - K = \Delta_0,$$

where c_0 is the total initial concentration of disperse particles in the system. The physical meaning of Eq. (9) is quite clear: the number of single particles in the interaggregate space decreases due to their combination to the boundaries of all aggregates.

To close the problem (7)–(9) one needs to write down the initial and boundary conditions for the aggregate distribution density $f(t, R)$. These conditions are determined by the specific nature of the initial aggregate formation. By analogy with the kinetic theory of the first-order phase transitions in molecular fluids, two different basic mechanisms of nucleation may be specified in colloid aggregation. The first of them is based on the heterogeneous formation of initial aggregates due to the presence of foreign nucleation centers. The second one is connected with homogeneous aggregation, when the initial aggregates are formed as a result of a random meeting and combination of Brownian particles.

IV. HETEROGENEOUS AGGREGATION

We consider here the first heterogeneous way of aggregation. As a rule, it leads to faster aggregation (condensation) both in the colloidal and molecular systems. So we assume that each unit volume of a colloidal system contains a certain fixed number N of nucleation centers. For maximal simplification of the problem's mathematical side, we suppose that the parameters of the system are such that the radius of these nucleation centers, R_c , is bigger than the changeover value

$R_0 = D\Delta_0 / \nu\alpha K\varphi_m$, Eqs. (3). This means that the aggregates, at the very beginning of their appearance, have a fractal-like structure. Then, we assume that the characteristic time of the nucleation is small in comparison with the growth time of the aggregates. This means that we may suppose that all aggregates appear at the same time $t=0$. The whole initial volume concentration $\Phi = 4\pi R_c^3 N / 3$ of the aggregate nuclei is considered to be much less than the colloid volume concentration c_0 —that is, $\Phi \ll c_0$.

Under these inessential simplifications, the cluster distribution density is defined as a delta function

$$f(t, R) = N\delta(R - R(t)), \quad (10)$$

where the time-dependent aggregate radius $R(t)$ is to be determined from the following set of equations [see Eqs. (4), (5), and (9)]:

$$\frac{dR}{dt} = \sqrt{\frac{D\alpha\nu K \Delta(t)}{\varphi_m R(t)}}, \quad R(0) = R_c, \quad (11)$$

$$\frac{d\Delta}{dt} = -4\pi N \left(1 - \frac{K}{\varphi_m}\right) DR(t)\Delta(t), \quad \Delta(0) = \Delta_0. \quad (12)$$

For further analysis it is convenient to introduce the dimensionless time variable τ , dimensionless supersaturation $\omega(\tau)$, and aggregate size $S(\tau)$, according to the relations

$$\tau = t \sqrt{\frac{\nu\alpha K D \Delta_0}{\varphi_m R_c^3}}, \quad \omega(\tau) = \frac{\Delta(t)}{\Delta_0}, \quad S(\tau) = \frac{R(t)}{R_c}. \quad (13)$$

Combining Eqs. (11), (12), and (13) we get the nonlinear set of differential equations

$$\frac{d\omega}{d\tau} = -5I\omega(\tau)S(\tau), \quad \frac{dS}{d\tau} = \sqrt{\frac{\omega(\tau)}{S(\tau)}}, \quad (14)$$

$$\omega(\tau=0) = 1, \quad S(\tau=0) = 1,$$

describing both the evolution of the cluster sizes and the time decrease of the supersaturation and containing the only physical parameter I :

$$I = \frac{3}{5}\varphi_m \left(1 - \frac{K}{\varphi_m}\right) \frac{\Phi}{\Delta_0} \sqrt{\frac{R_0}{R_c}} \ll 1. \quad (15)$$

The phase diagram of the first-order differential system (14) in the plane (S, ω) is determined by the equation

$$\frac{d\omega}{dS} = -5I\omega^{1/2}S^{3/2}, \quad \omega(S=1) = 1. \quad (16)$$

Its solution

$$\omega(S) = [1 - I(S^{5/2} - 1)]^2 \quad (17)$$

is demonstrated in Fig. 1. Evidently, the aggregation process stops when the supersaturation ω becomes equal to zero. So we come to the first principal conclusion, that unlike the single aggregate growth model [25] the present model of aggregate ensemble evolution results in finite cluster sizes when the aggregation comes to the end. This largest radius S_* appears to be defined by the unique parameter I :

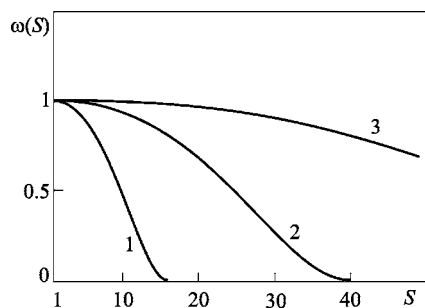


FIG. 1. Decrease of the relative colloid supersaturation ω during the growth of the aggregate dimensionless radius S for the heterogeneous aggregation. The values of parameter I are 10^{-3} (curve 1), 10^{-4} (curve 2), and 10^{-5} (curve 3).

$$S_* = [(I+1)/I]^{2/5} \approx I^{-2/5} \gg 1.$$

Hence, unlike condensation phase transitions in molecular systems, heterogeneous colloid aggregation should be over at the stage of formation of the discrete clusters. Since the initial volume concentration of the nucleation centers Φ is considered as being much less than the total colloid volume concentration c_0 (and Δ_0 as well), the parameter I is much less than unity. For the values $I \sim 10^{-5}$ it follows that the cluster size increases hundreds of times during the aggregation process. On the other hand, the final volume concentration of the aggregate ensemble Φ_* must not exceed unity when $\omega \approx 0$ and $S \approx S_*$:

$$\Phi_* = \Phi S_*^3 = \frac{5\Delta_0}{3(\varphi_m - K)} \sqrt{\frac{R_c}{R_0}} I^{-1/5} < 1.$$

Simple estimates show that when the initial colloid volume concentration c_0 has typical values of about $\sim 0.02-0.04$, the kinetic coefficient ratio $\beta/\alpha = K/\varphi_m$ is about $\sim 0.01-0.1$, the maximal aggregate concentration taking the value $\Phi_* \sim 0.3-0.5$. Here we take into account that the random volume packing concentration of the aggregate dense core is $\varphi_m \sim 0.5$. It means that the average distance between the cluster boundaries is rather small at the final stage of the aggregation process and the model needs to take into account the cluster contact interaction and the excluded volume effects in the diffusion of the single c particles in outer aggregate space as well as the possibility of cluster percolation and formation of a continuous spatial cluster net. In other words, cluster-cluster interaction effects become prevalent at this stage. However, due to the rather low spatial mobility of clusters as compared with the single-particle mobility, the rate of cluster-cluster aggregation should be substantially smaller than the rate of particle-cluster aggregation, which is studied here. Moreover, the theory of the effective properties of heterogeneous systems shows that the excluded volume presence results in minor changes of the particle effective diffusion through the heterogeneous medium and in outer aggregate space. So it seems possible to divide the aggregation process into two subsequent stages: particle-cluster aggregation and cluster-cluster aggregation. Since we study here the first stage only, we limit our consideration to the first (left) part of the phase diagram in Fig. 1.

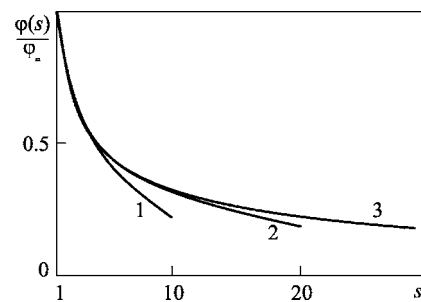


FIG. 2. The relative aggregated particle concentration $\varphi(s)/\varphi_m$ as a function of the dimensionless distance $s=r/R_c$ from the aggregate center. For curves 1–3 the values of the parameters are the same as in Fig. 1, curves 1–3.

Let us return to the spatial distribution of aggregated φ particles into the clusters. Since we consider the steady-state solution, Eqs. (4) and (5), of the partial boundary problem, Eqs. (1) and (2), this internal spatial distribution is independent of time. It means that the cluster internal structure is determined entirely by the aggregated particle concentration $\varphi(S)$ which is formed at the aggregate boundary S . During the cluster growth the concentration φ at the point $s=r/R_c$ remains the same as it was when this point belongs to the aggregate boundary. Taking into account this property of the moving boundary partial differential model (1), (2), (11), and (12), the internal spatial distribution of the cluster skeleton particles might be presented in the form

$$\varphi(s) = \varphi_m \sqrt{\frac{R_0}{R_c}} \sqrt{\frac{\omega(s)}{s}}, \quad \omega(s) = [1 - I(s^{5/2} - 1)]^2. \quad (18)$$

Naturally, this solution is valid only for the case when the distance to the cluster center s is larger than the radius of the nucleation center, which is unity in dimensionless units. So expression (18) describes the loose fractal-like region of the aggregate, similar to the single-cluster solution (4). Some dependences (18) are presented in Fig. 2 for the case when the relative supersaturation ω is larger than 0.5 (left sides of curves 1–3 in Fig. 1). One can see that the internal aggregate structure is quite similar to the case of the single cluster, when the supersaturation is still rather high and the average distance between the aggregates is much larger than their sizes. For this aggregation stage the internal spatial distribution of the aggregated particles is very accurately described by the approximate power dependence, which easily follows from expression (18):

$$\varphi(s) \approx \varphi_m \sqrt{\frac{R_0}{R_c}} s^{-(1+5I)/2}. \quad (19)$$

So we obtain the cluster fractal dimension being equal to the value $d_f = 2.5(1-I)$, which is slightly less than the universal fractal dimension $d_f = 2.5$ in the single-aggregate growth model (Sec. II). This small difference is a result of the supersaturation decrease due to the simultaneous growth of the aggregate ensemble.

At the aggregate periphery a deviation from the universal scaling law $\varphi(s) \sim s^{d_f-3}$ becomes more visible. It is fully understandable from the physical point of view: the central parts of the aggregates are formed in the case when the colloid supersaturation is close to the initial one, the effects of the colloid exhaustion are weak, and the approximation of single-aggregate growth is quite accurate. However, the supersaturation decrease with time affects the boundary value $\varphi(S)$ and the subsequent distribution $\varphi(s)$. In this cluster region the distribution $\varphi(s)$ is not power like, and the exact functional dependence is determined by the physical and chemical parameters of the colloid.

V. HOMOGENEOUS AGGREGATION: A MODEL

The homogeneous regime of the initial aggregate formation is specified by another boundary condition describing the aggregate flux J in the space of their sizes:

$$f(t,R) \frac{dR}{dt} \Big|_{R=R_c} = \frac{\alpha \nu K}{R_c^4} \sqrt{\frac{R_0}{R_c}} J(\Delta),$$

where the value R_c is considered as the critical nuclei radius. Introducing the dimensionless aggregate distribution density $F(\tau,S) = f(t,R) R_c^4$, the mathematical model (5), (7), and (9) of the homogeneous aggregation in dimensionless units (13) takes the form

$$\frac{\partial F}{\partial \tau} + \frac{\partial}{\partial S} \left(\frac{dS}{d\tau} F \right) = 0, \quad \frac{dS}{d\tau} = \sqrt{\frac{\omega}{S}}, \quad (20)$$

$$F(0,S) = 0, \quad F(\tau,S) \frac{dS}{d\tau} \Big|_{S=1} = J[\omega(\tau)], \quad (21)$$

$$\frac{d\omega}{d\tau} = -4\pi \left(1 - \frac{K}{\varphi_m} \right) \frac{\varphi_m}{\Delta_0} \sqrt{\frac{R_0}{R_c}} \int_1^\infty \omega^{1/2} S^{3/2} F(\tau,S) \frac{dS}{d\tau} dS, \quad (22)$$

$$\omega(\tau=0) = 1,$$

where $S=1$ stands for the dimensionless radius of the critical nucleus. The additional function

$$\theta(\tau) = \int_0^\tau \sqrt{\omega(\tau')} d\tau' \quad (23)$$

is easily seen to be introduced for further convenience. This function determines the size of the aggregate $S(\tau, \xi)$ at a time τ , which is initially formed at a time ξ :

$$S(\tau, \xi) = \left\{ 1 + \frac{3}{2} [\theta(\tau) - \theta(\xi)] \right\}^{2/3}, \quad (24)$$

$$S_m(\tau) = S(\tau, 0) = \left[1 + \frac{3}{2} \theta(\tau) \right]^{2/3}.$$

So at any time the largest clusters have the radius $S_m(\tau)$ and these clusters are nucleated at the starting time of the aggregation process.

The method of characteristics allows us to find a solution $F(\theta, S)$ of the first-order partial differential boundary prob-

lem (20) and (21) as a function of the aggregate dimensionless radius S and the new introduced effective time variable θ :

$$F(\theta, S) = \begin{cases} \sqrt{S} \frac{J \left[\omega \left(\theta - \frac{2}{3} S^{3/2} + \frac{2}{3} \right) \right]}{\sqrt{\omega \left(\theta - \frac{2}{3} S^{3/2} + \frac{2}{3} \right)}}, & 0 \leq S \leq S_m(\tau), \\ 0 & S > S_m(\tau), \end{cases} \quad (25)$$

where J is the same as in Eq. (21).

This expression becomes sensible when the functional dependence of the relative supersaturation $\omega(\theta)$ on the function $\theta(\omega(\tau))$ is determined. Substituting the aggregate distribution over sizes (25) into the mass balance equation (22), taking into account the limitation on the aggregate radiuses $0 \leq S \leq S_m$, and changing the integration variable S to ζ according to the relations

$$\frac{2}{3}(S^{3/2} - 1) = \theta - \zeta, \quad -d\zeta = S^{1/2} dS,$$

$$S = 1 \rightarrow \zeta = \theta, \quad S = S_m(\tau) \rightarrow \zeta = 0,$$

we get the memory-type integro-differential equation having a major importance in the homogeneous aggregation:

$$\frac{1}{\sqrt{\omega(\theta)}} \frac{d\omega(\theta)}{d\theta} = -4\pi \left(1 - \frac{K}{\varphi_m} \right) \frac{\varphi_m}{\Delta_0} \sqrt{\frac{R_0}{R_c}} \int_0^\theta \times \left[1 + \frac{3}{2}(\theta - \zeta) \right]^{2/3} \frac{J(\zeta)}{\sqrt{\omega(\zeta)}} d\zeta. \quad (26)$$

This equation is quite similar to those obtained in the kinetic theory of colloid phase separation [26,27]. By analogy with these theories we may expect that the supersaturation will totally vanish only in the infinite-time limit ($\tau \rightarrow \infty$) so that the effective time variable $\theta(\tau)$ will remain finite. It means that the upper integral limit (26) does not exceed some maximal value θ_m during the aggregation process. Hence, similar to the heterogeneous case the largest clusters will grow up to the radius $S_m(\theta_m)$ and will be of finite size at the end of the aggregation process.

The same technique gives the expression for the aggregate concentration N , Eq. (8):

$$R_c^3 N[\theta(\tau)] = \int_0^{\theta(\tau)} \frac{J(\zeta)}{\sqrt{\omega(\zeta)}} d\zeta. \quad (27)$$

Both considered models (heterogeneous and homogeneous) coincide if we assume a δ -function aggregate flux through the critical nucleus barrier:

$$J(\theta) = \sqrt{\omega(\theta)} N R_c^3 \delta(\theta).$$

Therefore, for further analysis we may represent the aggregate flux in the form

$$J(\theta) = \sqrt{\omega(\theta)} N_0 R_c^3 \tilde{J}(\theta), \quad N(\tau) = N_0 \int_0^{\theta(\tau)} \tilde{J}(\xi) d\xi, \quad \tilde{J}(0) = 1, \quad (28)$$

where the supersaturation-dependent factor $\tilde{J}(\omega)$ determines the number of aggregates in a unit volume of a colloid and the parameter N_0 stands for the characteristic coefficient of the nucleation process. It is well known from the nucleation theory that this coefficient cannot be calculated directly within statistical thermodynamics. With the help of this expression, the basic equation (26) for the supersaturation takes the form

$$\frac{1}{\sqrt{\omega(\theta)}} \frac{d\omega(\theta)}{d\theta} = -5I \int_0^\theta \left[1 + \frac{3}{2}(\theta - \xi) \right]^{2/3} \tilde{J}(\xi) d\xi,$$

$$I = \frac{3}{5} \varphi_m \left(1 - \frac{K}{\varphi_m} \right) \frac{\Phi_0}{\Delta_0} \sqrt{\frac{R_0}{R_c}} \ll 1, \quad \Phi_0 = \frac{4\pi}{3} R_c^3 N_0, \quad (29)$$

and the parameter I has the same meaning as for the case of heterogeneous aggregation. Evidently, the use of delta-function aggregate flux $\tilde{J}(\theta) = \delta(\theta)$ results in the equation

$$\frac{d\omega}{dS_m} = -5I\omega^{1/2} S_m^{3/2}, \quad \omega(S_m = 1) = 1,$$

which coincides with Eq. (16) since all aggregates have the same radius S_m in this case.

The last parameter, characterizing the aggregation process, is the mean aggregate radius $\langle S \rangle$:

$$\langle S \rangle \equiv \frac{\int_0^\infty SF(\theta, S) dS}{\int_0^\infty F(\theta, S) dS} = \frac{\int_0^\theta \left[1 + \frac{3}{2}(\theta - \xi) \right]^{2/3} \tilde{J}(\xi) d\xi}{\int_0^\theta \tilde{J}(\xi) d\xi}, \quad (30)$$

which is equal to the maximal radius S_m for the δ -function aggregate flux.

VI. HOMOGENEOUS AGGREGATION: EVOLUTION OF THE AGGREGATE ENSEMBLE

The general approach for analytical solving Eq. (29) is formulated in Refs. [26,27] and is based on consideration of the short- and long-time asymptotic solutions.

At the beginning of the aggregation process, when the number of aggregates is small and the supersaturation is approximately equal to the initial value, we may use in the right-hand sides of expressions (27) and (29) the constant initial value of the aggregate flux $\tilde{J}(0) = 1$, and then

$$\theta(\tau) \approx \tau, \quad N(\tau) \approx N_0 \theta(\tau), \quad S_m(\tau) \approx 1 + \theta(\tau), \quad \langle S(\tau) \rangle \approx 1 + \theta(\tau)/2,$$

$$\omega(\tau) \approx 1 - 2.5I\theta(\tau)^2, \quad \theta(\tau) \ll [2.5I]^{-1/2}. \quad (31)$$

So the number of aggregates and their radii grow linearly in time, whereas the saturation decreases very slowly. During

this initial stage of the aggregation process, the supersaturation might be determined as a power function of the largest aggregate radius S_m :

$$\omega(\tau) \approx S_m(\tau)^{-5I}.$$

Hence, the internal structure of the initially formed and growing clusters is described by the powerlike spatial dependence of the skeleton concentration φ , similar to expressions (18) and (19)—that is, $\varphi(s) \sim s^{-(1+5I)/2}$. And the fractal dimension takes the value $d_f = 2.5(1-I)$, which is slightly less than those with universal constant 2.5.

At sufficiently large θ an approximate solution of the integral equation (29) may be obtained under the condition when the functional properties of the aggregate flux $\tilde{J}(\omega)$ are taken into account. Obviously, this flux represents a sharply decreasing function of the supersaturation, similar to the nucleation process in supersaturated gases. It means that the integrand function $\tilde{J}(\xi)$ in Eq. (29) is rapidly decreasing as ξ is growing. This shows that the main contribution to the integral is given by the nearest vicinity of the point $\xi \approx 0$, which permits an expansion of the slowly changing function $\left[1 + \frac{3}{2}(\theta - \xi) \right]^{2/3}$ in a Taylor series. Following [27] we get

$$\frac{1}{\sqrt{\omega(\theta)}} \frac{d\omega(\theta)}{d\theta} = -5I \int_0^\theta \left[\left(1 + \frac{3}{2}\theta \right)^{2/3} - \left(1 + \frac{3}{2}\theta \right)^{-1/3} \xi + \dots \right] \tilde{J}(\omega(\xi)) d\xi. \quad (32)$$

For the reasons given, the above integrals converge very quickly, which allows both the upper limit of integration to be put equal to infinity and the short-time asymptote (31) to be used for $\omega(\xi)$. Therefore, it is easy to obtain an approximate expression

$$\omega(\theta) \approx (1 - \varepsilon_1 \theta^{5/3} + \varepsilon_2 \theta^{2/3} - \dots)^2,$$

$$\varepsilon_1 = \left(\frac{3}{2} \right)^{5/3} I \int_0^\infty \tilde{J}(\omega(\xi)) d\xi, \quad \varepsilon_2 = \frac{5}{2} \left(\frac{3}{2} \right)^{2/3} I \int_0^\infty \xi \tilde{J}(\omega(\xi)) d\xi, \quad (33)$$

which is valid at sufficiently long times after the beginning of the aggregation process. It can be readily demonstrated that not only $\varepsilon_2/\varepsilon_1 \ll 1$, but also $\varepsilon_{j+1}/\varepsilon_j \ll 1$ at any $j=1, 2, \dots$. It justifies using merely a few initial terms in the series in Eq. (33). The differential equation $d\theta(\tau)/d\tau = \sqrt{\omega(\theta)}$ results from Eqs. (33) and (23). Its solution at the evident initial condition $\theta(0)=0$ is

$$\tau = \int_0^{\theta(\tau)} \frac{d\theta}{(1 - \varepsilon_1 \theta^{5/3} + \varepsilon_2 \theta^{2/3})}. \quad (34)$$

The asymptotic formulas (33) and (34) are adequate at sufficiently large $\theta(\tau)$. A corresponding estimation gives the following restriction imposed on this function from below Eqs. (33) and (34) to be valid:

$$\theta(\tau) > \varepsilon_2/\varepsilon_1.$$

Thus we have obtained a pertinent approximate solution of the integral equation (29) that determines the relative supersaturation $\omega(\tau)$ as an implicit function of dimensionless time τ .

It is worth noting that the use of further terms of the series in Eq. (33) is impossible in a straightforward way because it would give rise to terms with negative exponents of the type $\theta^{5/3-j}$, $j=2,3,\dots$, which diverges as θ goes to zero. This is due to violation of the necessary conditions of the transition from Eq. (32) to Eq. (33) and, in particular, ε_j cannot be regarded now as independent of θ . Allowance for such a dependence brings about a correct but somewhat cumbersome mathematical problem, instead of the one that has been studied. In compliance with the developed theory, the supersaturation entirely vanishes for a finite value θ_m , which can be presented, by virtue of Eq. (33), through the approximate relation

$$\begin{aligned} \theta_m &\approx \varepsilon_1^{-3/5} + \frac{3}{5} \frac{\varepsilon_2}{\varepsilon_1} \approx \frac{2}{3} \left[I \int_0^\infty \tilde{J}(\omega(\zeta)) d\zeta \right]^{-3/5} \gg 1, \\ S_m(\theta_m) &\equiv S_* \approx \left[I \int_0^\infty \tilde{J}(\omega(\zeta)) d\zeta \right]^{-2/5} = \left(\frac{IN_m}{N_0} \right)^{-2/5}. \end{aligned} \quad (35)$$

Here $N_m=N(\tau \rightarrow \infty)$ is the total number of aggregates in a unit volume of a colloid and the parameter S_* stands for the final value of the radius of the largest aggregates; it approximately coincides with those defined in the case of heterogeneous aggregation.

At long times, when Eq. (33) is approximately valid, we get for the density of clusters N , the radius of the largest clusters S_m and the mean aggregate size $\langle S \rangle$:

$$\begin{aligned} N(\tau) &= N_m, \quad S_m(\tau) \approx [3\theta(\tau)/2]^{2/3}, \\ \langle S(\tau) \rangle &\approx \left[\frac{3}{2} \theta(\tau) \right]^{2/3} - \left[\frac{3}{2} \theta(\tau) \right]^{-1/3} \frac{\int_0^\infty \zeta \tilde{J}(\omega(\zeta)) d\zeta}{\int_0^\infty \tilde{J}(\omega(\zeta)) d\zeta} + \dots \\ &= S_m(\tau) - \frac{2}{5} \left(\frac{3}{2} \right)^{2/3} \frac{\varepsilon_2}{\varepsilon_1} \theta(\tau)^{-1/3} + \dots, \end{aligned} \quad (36)$$

where $\theta(\tau)$ is implicitly expressed in Eq. (34). These formulas are derived analogously to expression (33). So the mean aggregate size approaches the largest aggregate radius. It means that the cluster distribution by size becomes more narrow during the evolution process.

The evolution of the dimensionless distribution density $F(\tau, S)$ is presented in Fig. 3, where the measure of the area under the curves is equal to the dimensionless aggregate concentration $R_c^3 N(\tau)$. At short times the distribution density is a wide function of the dimensionless aggregate size. This is bound up with the active nucleation process at the beginning of the aggregation. After the period of continuing initiation

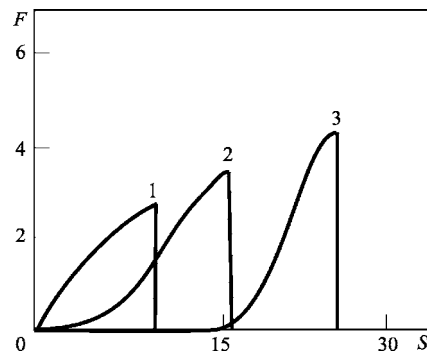


FIG. 3. Dimensionless aggregate distribution density at subsequent time moments: $\theta = \theta_m/4$ (curve 1), $\theta = \theta_m/2$ (curve 2), and $\theta = \theta_m$ (curve 3).

of new cluster nuclei the aggregate concentration in the system becomes approximately constant. It means that the subsequent evolution of the distribution density goes on under the condition that the area under the curve remain constant. As is clear from expression (20) the various points of the function $F(\tau, S)$ move towards the right in Fig. 3 (i.e., in the space of dimensionless radius) at a rate $dS/d\tau$. Since the rate of such motion is a decreasing function of dimensionless size S , then the function $F(\tau, S)$ contracts. This means that the aggregate distribution density over radii is characterized by a decreasing width. In accordance with this, the maximum value of the function $F(\tau, S)$ is an increasing function of S (see curves 1–3, Fig. 3).

The presented analytical dependences are valid only for the case when the aggregate flux \tilde{J} is a sharply decreasing function of the dimensionless supersaturation. Otherwise, the integral equation (29) needs a numerical solution. This solution may be based on the iteration technique for an operator equation of the type: $d\sqrt{\omega(\theta)}/d\theta = \hat{A}(\zeta)\omega(\zeta)$, where \hat{A} is a contracting operator. The solution for the i th iteration allows us to find the function $\omega_{i+1}(\theta)$: $d\sqrt{\omega_{i+1}(\theta)}/d\theta = \hat{A}(\zeta)\omega_i(\zeta)$. And the initial value $\omega_0(\theta) = 1$ can be regarded as the zeroth iteration. The numerical procedure shows that beginning from the third iteration the deviation is less than a percent for all physically meaningful dependences of the aggregation flux \tilde{J} on the supersaturation ω .

The behavior of the function $\omega(\tau)$ in conformity with approximate expressions (31), (33), and (34) is demonstrated in Fig. 4 for various power dependences of the aggregate flux \tilde{J} on dimensionless supersaturation ω : $\tilde{J}(\omega) = \omega^5$ (curve 1) and $\tilde{J}(\omega) = \omega^{15}$ (curve 2). We use here the power dependence $\tilde{J}(\omega) = \omega^k$ since it means that the critical nuclei is formed by k particles. The analytical solutions are in good agreement with the numerical solution of the problem. The difference between curves 1 and 2 is mainly devoted to the intensity of the nucleation process. At the beginning of the aggregation these intensities are equal. But in case 2 the initiation of aggregate nuclei stops earlier than in case 1 and the total number of aggregates N_m differs substantially. This difference is shown in Fig. 5, where the time dependence of the aggregate concentration is presented. One can see that $N(\tau)$

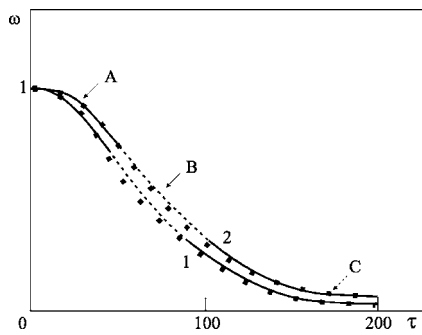


FIG. 4. Time evolution of dimensionless supersaturation $\omega(\tau)$ for various power dependences of the aggregate flux \tilde{J} and for constant value of the parameter $I=10^{-5}$: $\tilde{J}(\omega)=\omega^5$ (curve 1) and $\tilde{J}(\omega)=\omega^{15}$ (curve 2). Each curve consists of three zones: zone A corresponds to the small-time asymptote (31), zone C is the long-time solution (33) and (34), and zone B is the transition region. The numerical solution is indicated by dots.

becomes practically constant after a rather short length of time. This is easy to understand because the nucleation rate $\tilde{J}(\omega)=\omega^k$, $k=5$ and 15 (curves 1 and 2, respectively), represents a sharply increasing power function of the supersaturation and becomes negligible when the latter quantity falls below a certain level. After that, new critical nuclei cease to occur and the evolution proceeds at the expense of diffusional exchange by particles alone.

The evolution of mean aggregate size is shown in Fig. 6 under the same conditions as those for the curves plotted in Figs. 4 and 5. The obtained analytical solution also demonstrates a good coincidence with the numerical solution. We see that faster nucleation (curve 1) results in smaller aggregates at the end of the aggregation process. It is obvious since we study here the conditions of equal initial supersaturation. So for both cases 1 and 2 the total number of single particles, which can be involved in aggregation, is the same.

Another point following from Fig. 4 is that the supersaturation decrease is weakly dependent on the power k of the nucleation rate $\tilde{J}(\omega)=\omega^k$. But it depends drastically on the physical and chemical conditions which are realized in a colloid. In the present model these conditions are described by a parameter $I \ll 1$. The influence of this parameter on the time decrease of dimensionless supersaturation is illustrated in Fig. 7; the curves are plotted for $k=10$. The qualitative time

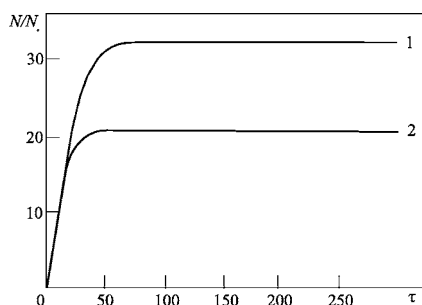


FIG. 5. Time evolution of the dimensionless number concentration $N(\tau)/N_0$ of aggregates under the same conditions as those for curves 1 and 2 in Fig. 5.

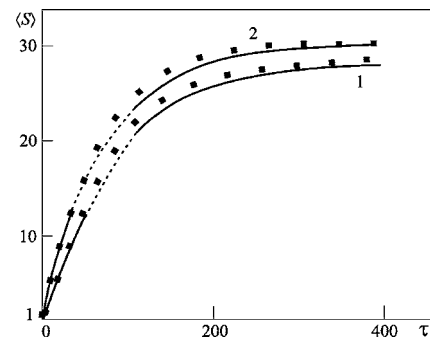


FIG. 6. Time evolution of the mean aggregate size $\langle S(\tau) \rangle$ under the same conditions as those for curves 1 and 2 in Fig. 5. The numerical solution is indicated by dots.

behavior for all curves 1–3 is the same, but they strongly differ quantitatively.

The spatial dependence of aggregated particle concentration $\varphi(r)$ resembles the one for heterogeneous aggregation (Fig. 2). Strictly speaking, the internal structure of aggregates does not obey the universal scaling power law $\varphi(r) \sim r^{-(3-d_f)}$ for both cases of homogeneous and heterogeneous nucleation. The reason is that the decrease of colloid supersaturation results in an additional influence on the aggregate growth rate instead of the one caused by the diffusion motion of single particles and their attachment to the aggregate skeleton. But in real time the aggregation process is rather slow, so for some time scale the spatial distribution $\varphi(r)$ may be fitted by this power function. On the one hand, it gives rise to a definition of the time-dependent fractal dimension which also must depend on the chemical and physical specificities of a colloid. But as evidenced by the foregoing, the deviations of the fractal dimension from the universal value 2.5 are weak. On the other hand, the experimental techniques are able to measure only the ensemble-averaged values of the fractal dimension. So we can hardly imagine that the weak time dependence of the fractal cluster internal structure may be observed.

VII. CONCLUSION

On the basis of the previously developed model [25] of separate colloidal aggregate growth we study the kinetics of

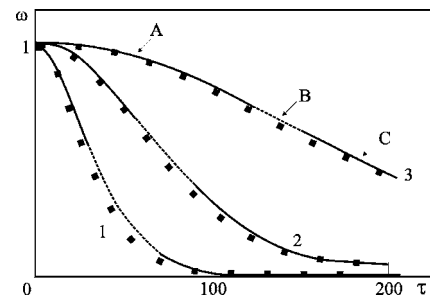


FIG. 7. Time evolution of dimensionless supersaturation $\omega(\tau)$ for the same power dependence of the aggregate flux $\tilde{J}=\omega^{10}$ and for different values of the parameter $I=10^{-4}, 10^{-5}, 10^{-6}$ (curves 1, 2, 3, respectively). The numerical solution is indicated by dots.

colloidal aggregation under condition when both the aggregate distribution over size and the particle balance law in the colloid are taken into account. Diffusion-limited particle-cluster aggregation is investigated. But unlike the DLA approach our results are devoted to the situation when the internal combination-recombination dynamic equilibrium balance is established in each growing aggregate. The effect of the colloid supersaturation decrease during the aggregate ensemble growth is a focus of our attention. Two main physical conclusions follow from our analysis for both the heterogeneous and homogeneous regimes of the initial aggregate formation. First, the system of discrete, finite-size clusters is formed at the final stage of aggregation process. This result is different from the classic condensation-type phase transition kinetics when the simply connected new dense phase is formed.

The second conclusion is connected to the internal structure of the aggregates. For the case of a single cluster, growing in an infinite colloidal medium with permanent concentration of free particles, the previous model [25] has predicted analytically the power spatial behavior of the

aggregated particle concentration according to the fractal cluster properties. The universal fractal dimension $d_f=2.5$ was shown to be independent of the physical and chemical characteristics of the colloidal system. In the present case, the colloid supersaturation reduction due to the simultaneous growth of the aggregate ensemble leads to a situation when the internal power spatial dependence of the aggregated particles is established only at the beginning of the aggregation process. And the fractal dimension is obtained to be slightly less than the universal value 2.5. Moreover, at the final stage of the aggregation, the particle distribution in the clusters does not obey any power law and depends on the physical and chemical characteristics of the colloid.

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