

SEPARATION KINETICS OF FERROCOLLOIDS IN THE ABSENCE OF A MAGNETIC FIELD

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Formation of drop aggregates in ferrocolloids is described by using the general concepts of phase transition theory. The nucleation stage is analyzed within the framework of Frenkel–Zel'dovich's theory, allowing for diffusional mass transfer. The main focus is studying the evolution of the aggregate size density distribution function when the system supersaturation is intensively removed.

Among various forms of stability loss by colloidal systems, of greatest importance is apparently their separation accompanied by formation of a system of relatively coarse drop aggregates suspended in the surrounding matrix colloidal phase. In this case, the particle distribution in both phases remains random, and their concentrations can substantially differ [1-3].

Two main approaches to describing the phase separation of such a type are known. The first is based on studying the kinetics of adding or losing single particles by aggregates and represents the natural generalization of the classical Smolukhovskiy method [4, 5]. The second approach is based on analyzing the properties of the equilibrium states of the colloidal suspensions by the methods of thermodynamics and statistical physics. In this case, the drop aggregates are considered as separations of a new phase that appear due to a colloid transition into the thermodynamically metastable state [6, 7].

In the early 1970's colloid separation was described within the framework of the formal extension of Van der Waals' condensation theory to the system of dispersed particles [1]. In this situation, the formation of concentrated colloid "drops" in a weakly concentrated colloidal medium (or small-concentration "bubbles" in a highly concentrated phase) is considered as a phase transition at the 1st kind. It is shown in [8] that particle concentration in the co-existing phases must be determined from the constancy of the chemical potential of the dispersed particles.

A similar approach has been also used for analyzing the phase separation of ferrocolloids [9-11] at equilibrium, whose specific features are now studied in detail: diagrams of the phase stability of the ferrocolloid are plotted, critical parameters of the phase transition vs temperature and external magnetic field are analyzed. It is found that appearing drop aggregates are a strongly concentrated "liquid" ferrocolloid phase which has no magnetic ordering without a magnetic field. The properties of such a concentrated colloid [3] are examined.

Strictly speaking, the obtained phase diagrams [10] refer to the equilibrium separation into two phases with a flat interface. In experiment, the separation is accompanied by the appearance of different size drop aggregates which are spherical due to the existing interphase tension in the absence of a magnetic field. It is clear that determining the spectrum of the size distribution of the aggregates is a problem which cannot be, in principle, solved by the methods of equilibrium statistical thermodynamics and requires reference to the kinetic theory of phase transitions.

Separating a new phase in the metastable medium can be conventionally subdivided into three successive stages. In the first stage described by the theories of Frenkel–Zel'dovich et al., in the metastable colloid the near-critical nuclei are formed due to fluctuations, and in the sufficiently small time after the start of the process steady flow of nuclei through a critical potential barrier is formed. Effectively, at this stage the metastability degree does not change, and each nucleus can be considered irrespective of the onset and growth of other nuclei.

At the second, intermediate stage the bulk of the new phase is separated. The growth of the aggregates occurs with the onset of new supercritical nuclei that depends on the instantaneous metastability degree of the matrix colloid. Its change is, in its turn, determined by the number and growth rate of aggregates. Despite some recent success in describing this stage for vapor condensation and mass crystallization [12-16], this problem is not developed practically for colloid separation.

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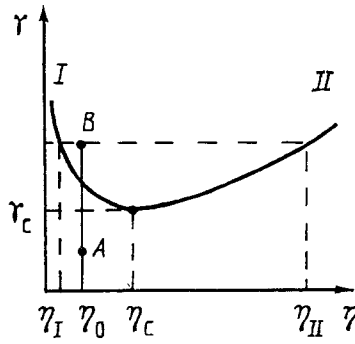


Fig. 1. Phase diagram of the ferrocolloid.

The final recondensation stage practically corresponds to the complete absence of metastability and the cease in formation of new supercritical nuclei, and the growth of large separations of a new phase occurs with the disappearance of the small ones. The theory of the system evolution at this stage was constructed by I. M. Lifshits and V. V. Slezov [17] under some very substantial simplifying assumptions.

Nucleation Stage. Let us consider the phase diagram of the ferrocolloid in the absence of a magnetic field (Fig. 1). On it is the phase equilibrium line, below which the region of stability of a space-uniform colloid state is located. Above, there is the region where the colloid is in the equilibrium state of the separation into phases with concentrations η_I and η_{II} at the flat boundary of the interphase interface. The phase diagram shown in the figure is obtained for ferrocolloids within the framework of the mean-spherical approximation [10] ($\gamma_c = 4.445$, $\eta_c = 0.055$), as well as when the interparticle dipole-dipole interaction typical of ferrocolloids is taken into account by using thermodynamic perturbation theory [11, 18] ($\gamma_c = 2.461$, $\eta_c = 0.130$). It should be noted that the phase diagram of the non-magnetic colloid has the same form under sufficiently intensive interparticle attraction conditions [7, 18].

Let us consider the ferrocolloid with an initial dispersed phase concentration η_0 in the stable uniform state (point A in Fig. 1). When lowering the temperature, the point representing the system state on the phase diagram will move vertically upwards and intersect the phase equilibrium line, reaching point B. In this situation, the colloid transits to the metastable state, and the kinetic process of the phase separation starts developing and the quantity $\Delta_0 = \eta_0 - \eta_I$ serves as the initial concentrated supersaturation.

Under real conditions, concentrated phase II is separated in the form of spherical drop aggregates. The presence of a curved interphase surface will affect the conditions of local thermodynamic equilibrium between the aggregate and the surrounding colloidal medium. Account of this factor and calculation of the minimal work of nucleation of the aggregate were given in [11] where the following presentation is obtained for a critical radius:

$$a_* = \frac{2\sigma v}{kTK\Delta}, \quad K = \frac{\eta_{II} - \eta_I}{1 - \eta_I} \left(\frac{\partial \mu}{\partial \eta} \right)_{\eta=\eta_I}, \quad (1)$$

where the coefficient K describes the deviations of the ferroparticle system properties from the ideal gas ones; expression (1) accordingly differs from the classical one [19] by the presence of the coefficient K.

Aggregate nuclei having radii greater than a_* grow, participating in decreasing the metastability degree (supersaturation). The kinetics of this decrease mainly depends on what physical processes determine the growth of individual aggregate. For colloids to separate it is obvious that this growth will be limited by the diffusional supply of particles from the matrix colloid to the aggregate surface. Thus, a law of the rate of varying the spherical aggregate radius appears which includes an "excess" of particles due to concentration supersaturation

$$(\eta_{II} - \eta_I) \frac{d}{dt} \left(\frac{4}{3} \pi a^3 \right) = -4\pi a^2 D \frac{d\eta}{dr} \Big|_{r=a+0}. \quad (2)$$

Since the characteristic time of setting the steady diffusional flow is of the order of $\tau_D \sim a^2/D$ and the characteristic time of varying the drop size is $\tau_a \sim 1/(da/dt)$,* we have [7]

*As in Russian original — Publisher.

$$\frac{\tau_D}{\tau_a} = \frac{a^2/D}{a^2/D\Delta} \sim \Delta \ll 1. \quad (3)$$

This means that for determination of a spherically symmetric concentration profile around the aggregate we can solve the quasi-stationary problem [11, 19]

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 D(\eta) \frac{d}{dr} \eta(r) \right] = 0, \quad \eta(r \rightarrow a + 0) = \eta_1, \quad (4)$$

where the concentration of the colloidal sphere near the aggregate surface is determined from the condition of local thermodynamic equilibrium between the aggregate and the surrounding colloid.

Using the obtained presentations, we obtain expressions for the frequency of forming supercritical nuclei per unit volume and for the aggregate growth law

$$\begin{aligned} \frac{da}{dt} &= \frac{D(\eta_1)}{\eta_{11} - \eta_1} \frac{a - a_*}{a^2} \Delta(t), \quad J(\Delta) = Q(\gamma) \Delta \exp[-E(\gamma)/\Delta^2], \\ Q(\gamma) &= \Gamma [\eta_1 D(\eta_1)] / (4\pi v^2) (kT/\sigma)^{1/2}, \quad E(\gamma) = (\sigma/kT)^3 (16\pi v^2/3K^2), \end{aligned} \quad (5)$$

on the basis of Ya. B. Zel'dovich's theory [19]. Here, the preexponential multiplier Q and the relative activation energy, E , of forming a critical nucleus depend on a magnetodipole interaction parameter γ that characterizes the intensity of effective interparticle attraction. In principle, the numerical coefficient Γ cannot be expressed in terms of the macroscopic variables [19].

Note that the critical nuclei are considered as macroscopic formations containing a great deal of particles and having a surface tension. For this, their critical radius a_* first should not be too small, i.e., the supersaturation degree of the initial ferrocolloid should be not sufficiently large.

Using diffusional model (2) for the aggregate growth requires a concrete value of the gradient diffusion coefficient of ferroparticles. A radical step in constructing the Brownian diffusion theory for concentrated colloids was made by Batchelor [20] who obtained an expression

$$D(\eta) = B(\eta) \frac{\eta}{1 - \eta} \left(\frac{\partial \mu}{\partial \eta} \right)_{P,T} \quad (6)$$

from general thermodynamic considerations.

A considerable number of studies (e.g., [21-23]) has shown that the sedimentation mobility $B(\eta)$ is a decreasing function of concentration. There exist many expressions which describe this dependence, e.g.:

$$B(\eta) = \frac{1}{3\pi\eta_B d} \frac{M_1(\eta)}{M_2(\eta)}, \quad M_1(\eta) = 1 - \eta, \quad M_2(\eta) = (1 - \eta)^{-5/2}. \quad (7)$$

These are rather simple and describe the experiments with particle sedimentation in suspensions well.

In expression (6), account of the cancelled-volume effects [20, 22, 24] bound up with the particle impermeability results in the gradient diffusion coefficient serving as increasing function of concentration. The presence of interparticle attraction somewhat decreases the value of the diffusion coefficient. A similar result was also obtained for ferrocolloids [25] where, based on approach (6), it was shown that for sufficiently large values of the magnetodipole interaction parameter ($\gamma \leq 2$) the gradient diffusion coefficient nonmonotonically depends on concentration, and this enables one to explain the specific features of the hydrostatic height particle distribution in the gravity field.

Interphase Tension Coefficient. As is seen from (5), the nucleation kinetics substantially depends on the value of the interphase tension coefficient, whose value is affected by the particle concentration in the co-existing phases and by the interparticle interaction rate. We are not able to discuss the problem of determining ferrocolloid interphase tension in detail here, therefore, we must confine ourselves to a short illustration of the method used.

Consideration of the aggregates as thermodynamic objects corresponds to the assumption of the aggregate radius a being much greater than the ferroparticle diameter. In this case, to a first approximation it is possible to neglect the effects

caused by the curvature of the phase interface and to use the quantity σ obtained for a flat interphase surface. Replacing the transient region by the "equimolecular" interface and using the known model of "liquid with a normal density up to the equimolecular interface being in contact with a constant-density gas" [26], we obtain an expression

$$\sigma = \frac{\pi}{8v^2} \int_0^\infty dr \int d\Omega_1 d\Omega_2 r^4 \frac{dU}{dr} [\eta_{II}^2 g_{II}(r, \Omega_1, \Omega_2) - 2\eta_I \eta_{II} g_{I,II}(r, \Omega_1, \Omega_2) + \eta_I^2 g_I(r, \Omega_1, \Omega_2)], \quad (8)$$

where integration with respect to $d\Omega_i$ corresponds to the averaging over all possible directions of the magnetic moment of the i -th particle.

For functions g_I and g_{II} we use the approximation

$$g_J = \exp(-U_d/kT) g_{0J}(r), \quad J = I, II, \quad (9)$$

conforming to thermodynamic perturbation theory [11, 25].

In such an approach (8), the greatest difficulty is observed in determining the function $g_{I,II}$ because there are no rigorous methods of calculating the interphase correlations. In some cases [27], the linear superposition of the phase distribution functions with given unknown coefficients is adopted. The simplest approximation of such a type is

$$g_{I,II}(r, \Omega_1, \Omega_2) = \frac{1}{2} [g_I(r, \Omega_1, \Omega_2) + g_{II}(r, \Omega_1, \Omega_2)]. \quad (10)$$

Using expressions (9) and (10) in (8), we arrive at the interphase tension coefficient

$$\sigma = \frac{kTd}{4v} (\eta_{II} - \eta_I) \{G_p (\eta_{II} - \eta_I) - 3 [\eta_{II} g_{0,II}(d) - \eta_I g_{0I}(d)]\},$$

$$g_{0J}(d) = \frac{2 - \eta_J}{2(1 - \eta_J)^3}, \quad J = I, II, \quad (11)$$

$$G_p = \frac{2\pi}{vd} \int_d^\infty dr r^3 \int d\Omega_1 d\Omega_2 [\exp(-U_d/kT) - 1].$$

Of course, for the curved interface the coefficient σ will somewhat differ, in magnitude, from the value corresponding to the flat boundary. However, from general theory [26, 27] it follows that the correction bound up with the curvature will be of an order of magnitude $\sim d/a \ll 1$, and due to the roughness of approximation (10) the small quantities of such an order should be neglected.

Separating the Bulk of a New Phase. The evolution of a system at the intermediate stage of the separation process is followed by a rapid growth of aggregates. In this case, the critical radius varies inconsiderably and has a value which is much less than the characteristic radius of the bulk of the aggregates. Therefore, as a simplification we shall assume $a_* = 0$ below. It should be noted that generally speaking, for the aggregate growth rate in Eq. (5) some random perturbations

$$\frac{da}{dt} = \Psi + \sqrt{2W} \xi(t), \quad \Psi = \frac{D(\eta_I)}{\eta_{II} - \eta_I} \frac{\Delta(t)}{a}, \quad (12)$$

are imposed on the averaged component of the aggregate growth rate. Here the coefficient W characterizes the probability of a fluctuational variation of the aggregate radius. As a whole, the last addend in (12) describes the fluctuations in the growth rate of the same-size aggregates. In this case, the radius density distribution function of the drop aggregates changes according to the Fokker-Planck evolution equation [28]

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial a} (\Psi f) = \frac{\partial}{\partial a} \left(W \frac{\partial f}{\partial a} \right), \quad f(0, a) = 0, \quad (13)$$

under the boundary condition

$$[\Psi f - W (\partial f / \partial t)]_{a \rightarrow +0} = J(\Delta), \quad (14)$$

that reflects the continuation of the appearance of new supercritical nuclei of aggregates, and $J(\Delta)$ is assigned by expression (5).

The balance equation for the number of dispersed particles at separation of a system with the assigned initial supersaturation Δ_0 is of the form

$$\Delta(t) = \Delta_0 - \frac{4}{3} \pi (\eta_{II} - \eta_I) \int_0^{\infty} a^3 f(t, a) da. \quad (15)$$

The system of equations (12)-(15) completely describes the separation kinetics at the stage of separating the bulk of a new phase but it is very difficult to solve it in virtue of nonlinearity. As a simplification, we shall consider that the fluctuations of the aggregate growth rate are very weak and can be neglected, i.e., we assume that the coefficient W equals zero.

Let us include the natural space and time scales

$$l_0 = \left[\frac{D(\eta_I) \Delta_0}{\eta_{II} - \eta_I} J_0^{-1} \right]^{1/5}; \quad t_0 = \left\{ \left[\frac{D(\eta_I) \Delta_0}{\eta_{II} - \eta_I} \right]^3 J_0^2 \right\}^{-1/5},$$

as well as the dimensionless variables and parameters

$$\begin{aligned} s &= \frac{a}{l_0}; \quad \tau = \frac{t}{t_0}; \quad c(\tau) = \frac{\Delta(t)}{\Delta_0}, \quad F = l_0^4 f, \\ p &= \frac{E(\gamma)}{\Delta_0^2}, \quad q = \frac{4\pi}{3} \frac{\eta_{II} - \eta_I}{\Delta_0}, \quad J_0 = J(\Delta_0). \end{aligned} \quad (16)$$

In the notation of (16), system (12)-(15) assumes the form

$$\begin{aligned} \frac{\partial F}{\partial \tau} + c \frac{\partial}{\partial s} \left(\frac{F}{s} \right) &= 0, \quad \left[\frac{F(\tau, s)}{s} \right]_{s=0} = \exp[\rho(1-c^{-2})], \\ F(0, s) &= 0, \quad ds/d\tau = c(\tau)/s, \\ c(\tau) &= 1 - q \int_0^{\infty} s^3 F(\tau, s) ds, \quad c(0) = 1. \end{aligned} \quad (17)$$

A solution to the kinetic equation for $F(\tau, s)$ is of the form

$$F(\tau, s) = sG[\theta(\tau) - y(s)] H[\theta(\tau) - y(s)], \quad (18)$$

where the functions

$$\theta(\tau) = \int_0^{\tau} c(\tau) d\tau, \quad y(s) = \int_0^s s ds = s^2/2 \quad (19)$$

have been included.

$G(\theta)$ is satisfied with the functional equation obtained under the boundary condition for $F(\tau, s)$ in (17)

$$G[\theta(\tau)] = \exp\{p[1 - c(\tau)^{-2}]\}. \quad (20)$$

Solving the equation for s from (17) yields the dimensionless radius of the aggregates which have appeared at a time ξt_0 by a time τt_0 ($\tau > \xi$) in the form

$$s(\tau, \xi) = \sqrt{2[\theta(\tau) - \theta(\xi)]}. \quad (21)$$

The coarsest aggregates have at time τt_0 the dimensionless radius $s_m(\tau) = s(\tau, 0)$.

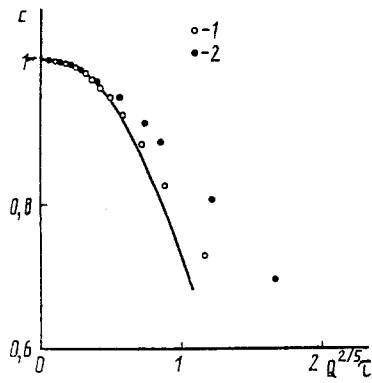


Fig. 2

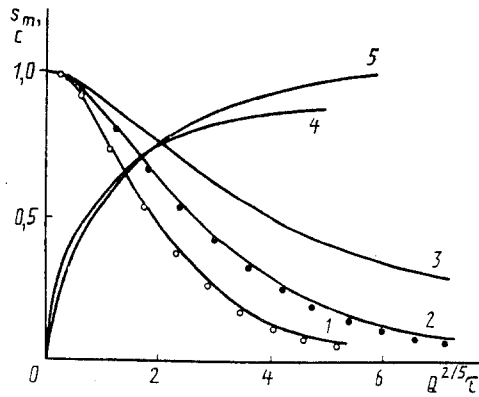


Fig. 3

Fig. 2. Supersaturation variation at small times after the start of the process: curve, asymptotic (24); points, numerical calculation at $p = 13.8$ (1) and 67.5 (2).

Fig. 3. Time variation of the supersaturation and maximum radius of aggregates: points, the same as in Fig. 2; 1, 2) expression (25) at $p = 13.8$ and 67.5 , respectively; 3) solution [11] at $p = 67.5$; 4 and 5) maximum radius corresponding to curves 1 and 2.

By substituting (18) into balance equation (17), at any constant τ we replace the integration variable s by ξ according to the following relations:

$$\theta(\xi) = \theta(\tau) - y(s), \quad d\theta(\xi) = c(\xi) d\xi = -s ds, \quad (22)$$

and in this case, the values $\xi = \tau$ and $\xi = 0$ of the variable ξ correspond to the boundaries $s = 0$ and $s = s_m$ of the interval of integration with respect to s . Upon using (20) and (21), we obtain the nonlinear integral equation for the time variation of the metastability degree

$$c(\tau) = 1 - Q \int_0^\tau h(\xi, \tau) c(\xi) \exp[\rho g(\xi)] d\xi, \quad (23)$$

$$h(\xi, \tau) = [\theta(\tau) - \theta(\xi)]^{3/2}, \quad Q = 2\sqrt{2}q; \quad g(\xi) = 1 - c(\xi)^{-2}.$$

At small times after the start of the process, the nonanalytic relation

$$c(\tau) = 1 - \frac{2}{5} Q \theta(\tau)^{5/2}, \quad (24)$$

describing the kinetics of escaping the system from the nucleation stage, follows from the asymptotics $\xi \rightarrow 0$, $c(\xi) \approx 1$, $\theta(\xi) \approx \xi$, $g(\xi) \approx 0$. Figure 2 plots the dimensionless supersaturation variation at small times after the start of the process. The points stand for the numerical solutions of Eq. (23) obtained by the iterative procedure at time variations with a step $\Delta\tau = 0.0025$. The solution error does not exceed 0.0008 in dimensionless supersaturation units c .

At sufficiently large times after the start of the process, the asymptotic solution to Eq. (23) can be obtained on the grounds that the parameter p determined in (16) is great in magnitude ($p \gg 1$). In this case, the exponential function in the integrand in (23) decreases from a maximum value at $\xi = 0$ with increasing ξ more rapidly than the $h(\xi, \tau)$ and $c(\xi)$ change. Taking into account that the main contribution to the integral in (23) is made by the nearest vicinity of the point $\xi = 0$, we can expand $h(\xi, \tau)$, $c(\xi)$ in a Taylor series. Finally, we have

$$c(\tau) = 1 - \varepsilon_1 \theta(\tau)^{3/2} + \varepsilon_2 \theta(\tau)^{1/2} - \dots, \quad (25)$$

$$\varepsilon_1 = Q \int_0^\infty \exp[\rho g(\xi)] d\xi, \quad \varepsilon_2 = \frac{3}{2} Q \int_0^\infty \xi \exp[\rho g(\xi)] d\xi,$$

where the upper limit of τ integration (23) tends to infinity due to a very rapid decrease in $\exp[\rho g(\xi)]$.

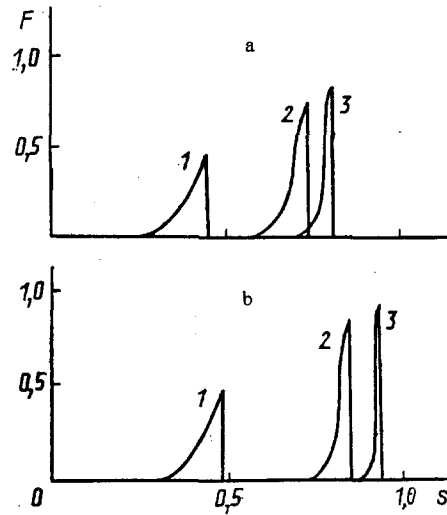


Fig. 4. Evolution of the dimensionless radius density distribution function of aggregates at $\gamma = 2.6$ (a) and 2.5 (b) and $c = 94\%$ (1), 49% (2), and 27% (3).

To determine the parameters ε_i in [11] the self-consistent method of closing problem (25) was used. However, comparison with the numerical solution of equation (23) has shown that this closure yields a very rough estimate of ε_i (Fig. 3). Therefore, here to calculate the parameters ε_i dependent on the form of the function $c(\xi)$, we use the small time asymptotic (24), assuming that the corresponding integrals in (25) converge sufficiently rapidly. In this situation, the coefficients ε_i can be approximately calculated as the explicit functions of the parameters p , Q .

Taking into account in (25) that $c(\tau) = d\theta/d\tau$, we obtain the differential equation for the function $\theta(\tau)$, whose solution is presented in the form of the implicit function

$$\tau = 2 \int_0^z \frac{z dz}{1 - \varepsilon_1 z^3 + \varepsilon_2 z}, \quad \theta(\tau) = z(\tau^2), \quad (26)$$

$$\varepsilon_1 \approx 0,9701 Q^{3/5} p^{-2/5}, \quad \varepsilon_2 \approx 0,83506 Q^{1/5} p^{-4/5}.$$

Comparison with the numerical solution of Eq. (23) (Fig. 3) has shown that obtained asymptotic (25), (26) yields a sufficiently exact solution. Agreement with the numerical solution is improved by decreasing the parameter p . This may appear to be surprising as the large value of the parameter p is the condition for asymptotic expansion (25) to be used. However, as is seen from Fig. 2, the increase in p means the elevation of the activation energy of forming a critical nucleus and, naturally, the more slow reduction of the supersaturation. In this case, the range of τ narrows, over which small time asymptotic (24) is valid. This means that determining the parameters ε_i in terms of this asymptotic results in underestimating their values and, accordingly, in a somewhat reduction of the supersaturation.

The relation $c[\theta(\tau)]$ determined in (25), (26) enables one to obtain the expression for the function $G[\theta(\tau) - y(s)]$, in an explicit form, and also $\theta(\tau) - y(s)$ can be given as $\theta(\tau) - y(s) = [s_m^2(\tau) - s^2]/2$. Finally, from (18), (20) we obtain an expression for the size density distribution function of the drop aggregates

$$F(\tau, s) = s \exp \{ p [1 - [1 - \varepsilon_1 \omega^3(\tau, s) + \varepsilon_2 \omega(\tau, s)]^{-2}] \} \times \\ \times H[s_m(\tau) - s], \quad \omega(\tau, s) = \sqrt{[s_m^2(\tau) - s^2]/2}. \quad (27)$$

The specific feature of the obtained distribution lies in the presence of a sharp peak at $s \approx s_m$ and

$$\left. \frac{\partial F}{\partial s} \right|_{s \rightarrow s_m - 0} = 1,$$

which is characteristic of the diffusional model for the aggregate growth.

Use of the above assumption on the large value of the parameter p is supported by calculation. So, at $\gamma = 2.5$, at phase concentrations $\eta_I = 0.073$, $\eta_{II} = 0.198$ determined from the equilibrium separation conditions (see Fig. 1), and at the initial supersaturation degrees $\Delta_0 = 0.017$ and 0.027 , calculations yield $p = 67.5$ and 26.7 . At $\gamma = 2.6$, $\eta_I = 0.035$, $\eta_{II} = 0.270$, and $\Delta_0 = 0.015$ and 0.025 we have $p = 38.3$ and 13.8 , respectively. Thus, indeed, $p \gg 1$ in real situations.

Also, Fig. 3 plots the time variations of the maximum drop size $s_m(\tau)$, practically coinciding with the mean radius. The evolution of the density distribution function of the drop aggregates is shown in Fig. 4 at supersaturations amounting to 94, 49, and 27% of the initial one. Thus, already at an intermediate time when supersaturation constitutes 40-60% of the initial one, the system of the growing drops of the new phase can be very close to the dispersed one.

Unfortunately, in as much as there are no direct experimental studies of the phase separation kinetics of ferrocolloids in no magnetic field, it is impossible to make a detailed comparison of theory and experiment. However, the conclusion that the evolution of the system of drop aggregates is accompanied by narrowing their distribution function is supported by indirect data [29], showing that after the intermediate stage all aggregates have practically the same size.

In reality, the size aggregate distribution function obtained after the end of the intermediate stage must somewhat differ from the almost delta function in Fig. 4. The variance of this function is apparently determined by the term for diffusion along the radius axis not taken into account in the kinetic (evolution) equation that reflects the presence of the real fluctuations of the growth rate of the given-radius aggregates. However, as before the conclusion is valid that this function is very sharp and its radius derivative can be, in absolute magnitude, very great.

The asymptotic distribution function at the intermediate stage can be considered as the initial value for the distribution function at the final phase transition stage. As its variance is very small (the radius derivative can be very great) it becomes problematic to use the evolution equation, neglecting the diffusion term at the final stage. This means that one of the main conditions for the validity of the Lifshits-Slezov theory is not satisfied and, hence, there are no grounds to expect that as a result of this stage, the similarity size aggregate distribution will be established asymptotically. For molecular systems this is supported by the results from [30]. Therefore, the results given must stimulate further studies of the evolution of colloidal systems under phase separation.

NOTATION

η , volume concentration of a dispersed phase; η_I , η_{II} , equilibrium concentrations of ferroparticles in the co-existing phases; γ , magnetodipole interaction parameter that determines the relationship between the interaction energy of two contacting particles and the energy temperature kT ; Δ , absolute supersaturation of a medium; a , aggregate radius; v , volume of a dispersed ferroparticle; σ , interphase tension coefficient; μ , chemical potential of ferroparticles; a^* , radius of a critical aggregate nucleus; D , coefficient of the gradient Brownian diffusion of ferroparticles; r , radial coordinate taken from the center of a sample ferroparticle; η_I , particle concentration near the aggregate surface; t , time; J , frequency of forming supercritical nuclei; B , sedimentation mobility of ferroparticles; P , pressure; η_B , viscosity of a pure liquid-solvent; d , ferroparticle diameter; U , interparticle interaction potential; U_d , dipole-dipole interaction potential; g_J pairwise distribution function of particles in the phase J ; $g_{I II}$, pairwise distribution function of particles belonging to different phases; Ω_i , solid angle responsible for the orientation of the magnetic moment of the i -th ferroparticle; g_{0J} , pairwise distribution function of the solid spheres in the phase J ; $\xi(t)$, random function (white Gaussian noise); W , "diffusion coefficient in the space of the radii"; $f(t, a)$, radii distribution function of aggregates; s , τ , c , s_m , $F(\tau, s)$, dimensionless radius of aggregates, time, medium supersaturation, maximum radius of aggregates, radius distribution function of aggregates; Δ_0 , initial supersaturation; l_0 , t_0 , characteristic scales of length and time; $H(x)$, Heaviside function; p , q , Q , dimensionless parameters.

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