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# Non-linear evolution of a system of elongated droplike aggregates in a metastable magnetic fluid

Alexey O. Ivanov\*, Andrej Yu. Zubarev

*Urals State University, 620 083 Ekaterinburg, Russia*

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## Abstract

We study the evolution of a system of drop-like aggregates suspended in a macroscopically homogeneous magnetic fluid made metastable by strengthening of an external magnetic field with account of both the reduction in metastability and the continuing initiation of new nuclei in the metastable surroundings. The growing aggregates are highly elongated ellipsoidal shaped and are distributed over volume. The distribution density is governed by a kinetic equation which neglects of fluctuations in the growth rate of a single aggregate. The approximate solutions for supersaturation and diverse characteristics of the distribution density has been found as functions of time. An influence of emerging aggregates on the macroscopic ferrocolloid properties is illustrated by the example of the time dependence of magnetization and effective viscosity. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The break up thermodynamic stability of a colloid is followed by the origination of initial critical nuclei of a new colloidal phase, by their transformation into macroscopic drop-like aggregates and by ensuing growth of those aggregates in a metastable environment. This phase separation can occur as a result of a fall of temperature, an increase in the ionic strength of a solvent, and the presence of a polymeric solute that is not capable of being completely adsorbed by the surface of colloidal particles [1–5]. The aggregates are characterized by the volume particle concentration that

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\* Corresponding author. Tel.: +7 343 2 557541; fax: +7 343 2 557401; e-mail: alexey.ivanov@usu.ru.

differs from that of the ambient colloid, and the whole process strikingly resembles a gas–liquid-phase transition in molecular systems [1,2]. In magnetic fluids still another type of phase separation is experimentally observed, i.e. phase separation in a magnetic field [6–12]. Such a phenomenon looks like a non-trivial phase transition of the condensation type, induced by an external magnetic field. In this case, the demagnetization effects lead to an approximately ellipsoidal shape of the drop-like aggregates stretched along the external field direction [8–10,12]. Common methods of equilibrium thermodynamics suffice to understand under what conditions the phase separation is bound to start [1,2,5,13]. However, they are certainly inapplicable to elucidate what happens next and so must be replaced by suitable kinetic methods.

In a theoretical research it is reasonable to distinguish three basic stages of the evolution of a particulate system that follows the preliminary stage of the development of a metastable state [14]. The first one corresponds to the initiation of critical new phase nuclei which further form either macroscopic new phase elements in a metastable molecular system or drop-like aggregates in a colloid. A fact of great consequence for a theoretical treatment is that, during this initial stage, the state of the colloid is practically not affected by the emerging nuclei so that each of them can correctly be regarded as evolving under the constant metastability condition. The second, intermediate stage covers a combined process of the growth of existing aggregates and of the initiation of additional nuclei in the circumstance of permanently reducing metastability of the parent colloid. An analysis of this stage is greatly complicated by the presence of negative feedback between the process of aggregate formation and growth dependent on a transient degree of metastability (e.g., a value of the supersaturation) and by the gradual reduction of metastability by the growing aggregates. At last, the third stage of final coalescence corresponds to the Ostwald ripening process when the dependence is of primary importance but the origination of new nuclei almost ceases and may be safely overlooked.

As far as the first stage is concerned, a relevant theory can be put forward by following common trends specific to the theory of nucleation in molecular systems [14,15]. Recently, such a theory has been worked out for colloids in Ref. [16]. An initial stage of the origination of drop-like aggregates in a ferrocolloid made metastable by strengthening of an external magnetic field has been considered in Ref. [17]. As shown in Ref. [17], at real conditions the supercritical aggregate nuclei can be regarded as highly elongated ellipsoids of revolution even in a weak magnetic field ( $H \sim 10\text{--}50$  Oe). By taking into account the interrelations between the aggregate volume and elongation degree [8,9,12,17], the expressions for the growth rate of a highly elongated aggregate, for the critical nucleus volume and for the nucleation rate have been obtained under the conditions when the emerging nuclei are still not large enough to affect the ferrocolloid properties appreciably.

The necessity of allowing simultaneously for the nucleation and the growth of new phase elements has been confirmed in Refs. [18,19]. Nevertheless, models suggested in the last papers rely, in fact, on a concept of constant nucleation rate, which may actually be true merely at the initial stage of the process.

There are a great deal of works in which attempts were made to study the time dependence of the spectrum of a particulate system evolving in a metastable environment. Among those, papers on batch crystallization [20,21], on bulk condensation of a vapour [22,23] and on the initiation of a reaction at a solid surface by means of origination and subsequent evolution of islands of a new phase [24,25] have to be mentioned. On the whole, the application of such models has met with appreciable success as pertains to the formulation of a general method of tackling the problem concerning the dynamics of the intermediate stage of the new phase evolution. An effective method of overcoming the existing mathematical difficulties has been demonstrated in Ref. [21] on example of a batch crystallization process. In addition, a similar approach has been applied to the problem of evolution of spherical drop-like aggregates in colloids with central [26] and dipole [27] interparticle interactions. Recently, this approach has been generalized to situations when there are noticeable fluctuations of the aggregates growth rate and the onflow of colloidal particles to a growing aggregate from the bulk of a metastable colloid is of essentially non-linear nature [28].

A theory of Ostwald ripening was developed by Lifshitz and Slyozov [29] (also recently in Ref. [30]) under complete neglect of fluctuations of the growth rate of a single aggregate.

In the case of large initial degree of metastability, the phase separation may originate from the thermodynamic absolute unstable state. The kinetics of such a process, known as spinodal decomposition (see, for example, Refs. [31,32]), possesses some differences of principal nature. Analysis of the spinodal decomposition phenomenon in magnetic fluids affected by the external field was carried out in Refs. [33,34].

All the theories mentioned above have been carried out with respect to spherical or quasi-spherical shape of new phase elements. In the present research we will focus our attention on the fundamental problem concerning the influence of a magnetic field on the kinetics of the intermediate stage of a ferrocolloid phase separation from a metastable state. We intend to consider the subsequent evolution of the assemblage of ellipsoidal supercritical aggregates when the degree of metastability of the parent magnetic fluid can no longer be thought of as invariable and independent of the assemblage history.

## **2. Basic equations**

Let us study the evolution of a system of drop-like ellipsoidal aggregates suspended in a macroscopically homogeneous metastable magnetic fluid at the intermediate stage of phase transition under the conditions when both the reduction in metastability (the decrease in the parent ferrocolloid supersaturation) and the continuing initiation of new nuclei in the metastable surroundings are taken into account. The degree of metastability is supposed rather small so that it is possible to consider the supercritical aggregate nuclei as macroscopic objects. The growing aggregates are distributed over volume and

the distribution density  $f(t, V)$  is governed by a kinetic equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V} \left( \frac{dV}{dt} f \right) = 0, \quad t > 0, \quad V > V_*, \quad (1)$$

under complete neglect of fluctuations of the diffusionally controlled growth rate of single aggregate. We presume the function  $f(t, V)$  to be normalized to the number concentration  $N(t)$  of the aggregates. The determination of the quantity  $dV/dt$  as a function of aggregate volume  $V$  has been the objective of Ref. [17]. In the case of highly ellipsoid elongation, the aggregate volume growth rate may be approximately written:

$$\frac{dV}{dt} = \left( \frac{4\pi}{3} \right)^{2/3} \frac{3D}{\varphi_{II} c_*^{2/3} |\ln(c_*/2)|} \left( \frac{V}{V_*} \right)^{\beta-1/3} \Delta(t),$$

$$\beta = \frac{3}{7} - \frac{5}{7 \ln(V_*/B)} - \frac{\ln 2}{\ln(c_*/2) \ln(V_*/B)}, \quad B = \frac{4\pi^7 \sigma^3}{3H^6} \frac{\mu_I^3}{(\mu_{II} - \mu_I)^6}, \quad (2)$$

where  $V_*$  and  $c_*$  have the meaning of the volume and semiaxes ratio of the critical aggregate,  $\Delta$  is the absolute supersaturation of the metastable magnetic fluid, and  $D$  is the coefficient of mutual Brownian diffusion of the ferroparticles down a concentration gradient. The parameter  $B$  relates the aggregate volume  $V$  to the elongation degree  $c$ :  $V \approx B/c^7 |\ln c|^3$  [17]. This relationship is dependent on an external magnetic field strength  $H_0$ , on the interfacial tension  $\sigma$  acting on the drop-like aggregate surface, and on the magnetic permeabilities  $\mu_I$  and  $\mu_{II}$  of a dilute ferrocolloidal surroundings with ferroparticle volume concentration  $\varphi_I$  and of a dense magnetic fluid substance of the aggregate characterized by the concentration  $\varphi_{II}$  ( $\varphi_{II} \gg \varphi_I$ ). For real magnetic fluid at separation conditions [8–12]:  $\sigma \sim 5\text{--}10 \times 10^{-4}$  erg/cm<sup>2</sup>,  $H \sim 50$  Oe,  $\mu_I \sim 1\text{--}2$ ,  $\mu_{II} \sim 20\text{--}40$ , the order of value of  $B$  may be easily defined:  $B \sim 10^{-23}\text{--}10^{-25}$  cm<sup>3</sup>. Considering that critical aggregate contains some tens or hundreds of ferroparticles, we arrive at the strong ratio  $V_*/B \sim 10^6\text{--}10^8$  and, consequently, the highly elongated shape of supercritical aggregates,  $c \leq c_* \ll 1$ .

Initial and boundary conditions imposed upon physically meaningful solutions of Eq. (1) are of the form

$$\left. \frac{dV}{dt} f \right|_{V=V_*} = J[\Delta(t)] = C\Delta(t) \exp \left[ -E \frac{\Delta_0^2}{\Delta(t)^2} \right], \quad f(0, V) = 0. \quad (3)$$

The above representation of the nucleation rate  $J$  results from Ref. [17]. Here  $C \approx \text{const}$ ,  $\Delta_0$  is an initial value of the supersaturation and  $E$  stands for the dimensionless activation energy referred to initial supersaturation. The quantity  $E$  is commonly much larger than unity and depends on a magnetic field strength (see Table 1, Ref. [17]).

In order to close the set of Eqs. (1)–(3) it is necessary to define the supersaturation as a function of parameters specific to an assemblage of growing aggregates. A requirement of conservation of the overall number of ferroparticles in the system

under study leads to the mass balance equation

$$\Delta(t) = \Delta_0 - (\varphi_{II} - \varphi_I) \int_{V_*}^{\infty} Vf(t, V) dV, \quad \Delta(0) = \Delta_0. \quad (4)$$

Since the characteristic volume of aggregates during the intermediate stage of their growth considerably exceeds the volume of the critical nucleus, it is permissible to regard the latter quantity as negligibly small  $V^{1/3} - V_*^{1/3} \approx V^{1/3}$  in the expression given by Eq. (2). It is consistent with the neglect of possible coalescence processes specific to this stage. The aggregate distribution density is clearly little affected by this simplification only in the vicinity of the point  $V \sim V_*$ , but it does not change in the region of interest  $V \gg V_*$ .

The set of Eqs. (1)–(4) includes only two external dimension parameters – the mutual diffusivity  $D$  and the nucleation rate  $J$ . They enable us to construct time and volume scales,  $t_0$  and  $V_0$ , intrinsic to the evolution process under study:

$$V_0 = \left[ \left( \frac{4\pi}{3} \right)^{2/3} \frac{D\Delta_0}{\varphi_{II}J_0} \frac{3}{c_*^{2/3} |\ln c_*| V_*^{\beta-1/3}} \right]^{1/(2-\beta)}, \quad t_0 = \frac{1}{J_0 V_0}, \quad J_0 = J(\Delta_0). \quad (5)$$

It is also convenient to introduce dimensionless variables and parameters according to the relations

$$s = \frac{V}{V_0}, \quad \tau = \frac{t}{t_0}, \quad \omega(\tau) = \frac{\Delta(t)}{\Delta_0}, \quad q = \frac{\varphi_{II} - \varphi_I}{\Delta_0}, \quad F(\tau, s) = V_0^2 f(t, V). \quad (6)$$

Eqs. (1)–(4) in dimensionless variables (Eq. (6)) are

$$\frac{\partial F}{\partial \tau} + \omega(\tau) \frac{\partial}{\partial s} (F \cdot s^\beta) = 0, \quad \tau > 0, \quad s > 0, \quad \frac{ds}{d\tau} = s^\beta \omega(\tau),$$

$$F(0, s) = 0, \quad |F \cdot s^\beta|_{s=0} = \exp[Eg(\tau)], \quad g(\tau) = 1 - \omega(\tau)^{-2}, \quad (7)$$

$$\omega(\tau) = 1 - q \int_0^\infty sF(\tau, s) ds, \quad \omega(0) = 1. \quad (8)$$

It is this set that is investigated in the remainder of the paper.

### 3. Integral equation for the supersaturation

Let us introduce the new functions

$$u(\tau, s) = s^\beta F(\tau, s), \quad \theta(\tau) = \int_0^\tau \omega(\tau') d\tau'. \quad (9)$$

From Eq. (7) we get a boundary problem for  $u(\tau, s)$ :

$$s^{-\beta} \frac{\partial u}{\partial \theta} + \frac{\partial u}{\partial s} = 0, \quad u(0, s) = 0, \quad u(\tau, 0) = \exp[Eg(\tau)], \quad (10)$$

which can be solved with the help of method of characteristics. The solution of kinetic Eq. (7) satisfying the initial conditions can be written in a form

$$F(\tau, s) = s^{-\beta} \cdot u[\theta(\tau) - y(s)] \cdot H[\theta(\tau) - y(s)], \quad y(s) = \int_0^s x^{-\beta} dx = \frac{s^{1-\beta}}{1-\beta}, \quad (11)$$

where  $H(z)$  is the Heaviside step-function, and the function  $u(z)$  satisfies the boundary condition, Eq. (10):

$$u[\theta(\tau)] = \exp\{E[1 - \omega(\tau)^{-2}]\}. \quad (12)$$

The characteristics of the partial differential Eq. (10) gives us the value at a time  $\tau$  of dimensionless volume  $s(\tau, \zeta)$  of an aggregate which appeared at a moment  $\zeta$ :

$$y[s(\tau, \zeta)] = s(\tau, \zeta)^{1-\beta}/(1-\beta) = \theta(\tau) - \theta(\zeta), \\ s_m(\tau) = s(\tau, 0) = [(1-\beta)\theta(\tau)]^{1/(1-\beta)}. \quad (13)$$

Here  $s_m(\tau)$  can be considered as a maximal volume of aggregates. In order to make use of Eq. (11) we need to know a functional dependence of the dimensionless supersaturation  $\omega(\tau)$  on the function  $\theta(\tau)$  defined in Eq. (9). This dependence has to be found by means of substituting  $F(\tau, s)$  (Eq. (11)) into the mass balance equation in Eq. (8):

$$\omega(\tau) = 1 - q \int_0^{s_m(\tau)} s^{1-\beta} u[\theta(\tau) - y(s)] ds, \quad (14)$$

where the upper limit of integration  $s_m(\tau)$  appears after taking into account the Heaviside step-function  $H[\theta - y]$ . Changing the integration variable  $s$  to  $\zeta$  according to Eq. (13)

$$y(s) = \theta(\tau) - \zeta, \quad dy(s) = s^{-\beta} ds = -d\zeta, \\ s = 0 \rightarrow \zeta = \theta(\tau), \quad s = s_m(\tau) \rightarrow \zeta = 0,$$

and using Eqs. (12) and (13) we get an integral equation for the dimensionless supersaturation as a function of  $\theta$ :

$$\omega[\theta(\tau)] = 1 - Q \int_0^{\theta(\tau)} [\theta(\tau) - \zeta]^{1/(1-\beta)} \exp\{E[1 - \omega(\zeta)^{-2}]\} d\zeta, \\ Q = q(1-\beta)^{1/(1-\beta)} \sim 5-10. \quad (15)$$

This equation describes the dynamics of changes in the supersaturation caused by the growth of aggregates.

#### 4. Kinetics of the metastability reduction

The supersaturation is governed by the strongly non-linear functional integral equation given in Eq. (15) which could hardly be handled to yield an exact solution in an explicit form. However, there is a large parameter in the exponent of the integrand in Eq. (15) due to the dimensionless activation energy  $E$  of the critical nucleus formation being much larger than unity. Since the function  $g(\tau)$  defined in Eq. (7) is negative, there appears a sharply decreasing function in that integrand, and this gives the opportunity to get an approximate solution. The same approach is common in the theory and has been put into effect through the use of an iteration method in Refs. [22,23] and of the Laplace method in Refs. [21,27,28].

At small dimensionless times we get from Eq. (15) an asymptotic:

$$\omega(\zeta) \approx 1, \quad g(\zeta) \approx 0, \quad \omega(\theta) \approx 1 - \frac{Q}{\delta} \theta^\delta, \quad \delta = \frac{2 - \beta}{1 - \beta} \approx \frac{11}{4}, \quad (16)$$

the region of validity of which is obvious  $\theta \ll (\delta/Q)^{1/\delta}$ . Time dependence of  $\omega(\tau)$  can be estimated with due regard for the relation  $\theta(\tau) \approx \tau$  following from Eq. (33) at small  $\tau$ :

$$\omega(\tau) \approx 1 - \frac{Q}{\delta} \tau^\delta, \quad \tau \ll (\delta/Q)^{1/\delta}, \quad (17)$$

instead of Eq. (16). At sufficiently large  $\theta$  an approximate solution of integral Eq. (15) may be obtained under the conditions when the large values of parameter  $E$  is taken into account. Since  $E$  is larger than unity and the function  $g(\zeta)$  is negative (Eq. (7)),  $\exp[Eg(\zeta)]$  is rapidly decreasing as  $\zeta$  is growing. It shows, as usual, that the main contribution to the integral in Eq. (15) is promoted by the nearest vicinity of the point  $\zeta = 0$ , which permits expanding the slowly changing function  $(\theta - \zeta)^{1/(1-\beta)}$  in a Taylor series. Following Ref. [28] we get

$$\omega(\theta) = 1 - Q \int_0^\theta \left[ \theta^{1/(1-\beta)} - \frac{1}{1-\beta} \theta^{\beta/(1-\beta)} \zeta + \dots \right] \exp[Eg(\zeta)] d\zeta. \quad (18)$$

For reasons given, the above integrals converge very quickly, which allows both the upper limit of integration to be put equal to infinity and small-time asymptotics (Eq. (16)) to be used for  $\omega(\zeta)$ . Therefore, it is easy to obtain an approximate expression

$$\omega[\theta(\tau)] = 1 - \varepsilon_1 \theta(\tau)^\gamma + \varepsilon_2 \theta(\tau)^{\gamma-1} + \dots, \quad \gamma = 1/(1-\beta) \approx 7/4,$$

$$\varepsilon_1 = Q \int_0^\infty \exp[Eg(\zeta)] d\zeta, \quad \varepsilon_2 = Q \gamma \int_0^\infty \zeta \exp[Eg(\zeta)] d\zeta,$$

$$g(\zeta) = 1 - \left( 1 - \frac{Q}{\delta} \zeta^\delta \right)^{-2}, \quad (19)$$

which is valid at sufficiently large times from the beginning of the evolution process. Coefficients  $\varepsilon_j$  can be calculated with the help of the relation

$$\exp[Eg(\zeta)] \approx \exp\left(-\frac{2EQ}{\delta} \zeta^\delta\right),$$

following from Eq. (19), which yields after integration

$$\begin{aligned} \varepsilon_1 &\approx \frac{Q}{\delta} \left(\frac{\delta}{2EQ}\right)^{1/\delta} \Gamma\left(\frac{1}{\delta}\right) \approx 0.99(E^{-4}Q^7)^{1/11} \sim 1-1.5, \\ \varepsilon_2 &\approx \frac{Q^\gamma}{\delta} \left(\frac{\delta}{2EQ}\right)^{2/\delta} \Gamma\left(\frac{2}{\delta}\right) \approx 0.95(E^{-8}Q^3)^{1/11} \sim 0.1-0.2, \end{aligned} \tag{20}$$

$\Gamma(z)$  being the Eulerian gamma function. It can be readily demonstrated that not only  $\varepsilon_2/\varepsilon_1 \approx (EQ)^{-4/11} \ll 1$  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. (18).

The differential equation  $d\theta(\tau)/d\tau = \omega(\theta)$  results from Eqs. (9) and (19). Its solution at the evident initial condition  $\theta(0) = 0$  is

$$\tau = \int_0^{\theta(\tau)} \frac{d\theta}{1 - \varepsilon_1\theta^\gamma + \varepsilon_2\theta^{\gamma-1}}. \tag{21}$$

Asymptotics, Eqs. (19) and (21) are adequate at sufficiently large  $\theta(\tau)$ . A corresponding estimate gives the following restriction imposed on this function from below Eqs. (19) and (21) to be valid:

$$\theta(\tau) > (\delta/2EQ)^{1/\delta} \approx 1.1(EQ)^{-4/11} \approx \varepsilon_2/\varepsilon_1 \ll 1.$$

Thus, we have obtained a pertinent approximate solution of the integral equation in Eq. (15) that determines relative supersaturation  $\omega(\tau)$  as an implicit function of dimensionless time  $\theta(\tau)$ .

It is worth noting that the usage of further terms of series in Eq. (18) is impossible in a straightforward way because it would give rise to terms with negative exponents of the type of  $\theta^{\gamma-n}$ ,  $n = 2, 3, \dots$ ,  $\gamma - n < 0$ , which diverge at  $\tau$  coming to zero. This is due to violation of the necessary conditions of the transition from Eq. (18) to Eq. (19) and, in particular,  $\varepsilon_j$  cannot be regarded now as independent of  $\tau$ . Allowance for such a dependence brings about a correct but somewhat cumbersome mathematical problem instead of the one that has been studied.

The behaviour of function  $\omega(\tau)$  in conformity with approximate formulae, Eqs. (19)–(21), is demonstrated in Fig. 1. It agrees sufficiently well with results of an exact numerical solution of the integral Eq. (15) which are shown in Fig. 1 by dots. This proves the above approximation to be reasonably correct.

It should be noted that, in compliance with the developed theory, the supersaturation entirely vanishes for a finite time  $\theta_*$  that can be presented, by virtue of Eq. (19),



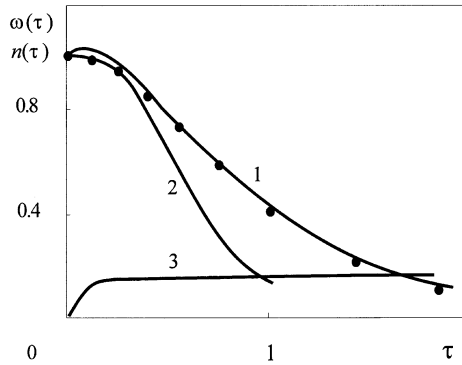


Fig. 1. Time dependence of the dimensionless supersaturation  $\omega(\tau) = \Delta(t)/\Delta_0$  (curves 1, 2 and dots) and dimensionless aggregate concentration  $n(\tau) = N(t)V_0$  (curve 3) for a metastable magnetic fluid characterized by the activation energy  $E = 18.3$  (see Table 1, Ref. [1]); dots – numerical solution of the integral Eq. (15), curve 1 – approximate expressions, Eqs. (19)–(21), curve 2 – small time asymptotics, Eq. (16).

through the approximate relation

$$\theta_* = \varepsilon_1^{-1/\gamma} + \frac{1}{\gamma} \frac{\varepsilon_2}{\varepsilon_1} + O\left[\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^2\right]. \tag{22}$$

This inference is surely inaccurate because of the neglect of distinctions in the equilibrium particle concentration of the parent magnetic fluid at the surfaces of the aggregates of different volume. It amounts to ignoring processes of particle redistribution between the aggregates which have much in common with coalescence and recondensation processes in two-phase molecular systems. The latter processes affect the final stage of the new phase formation in molecular and the Ostwald ripening process in colloidal systems and should be accounted for during this late stage.

Eq. (22) permits an estimate of the duration of the second intermediate stage studied here to be made as

$$\theta_m \approx \varepsilon_1^{-1/\gamma} = \varepsilon_1^{\beta-1} \approx \varepsilon_1^{-4/7} \approx (E^{16/77} Q^{-4/11}). \tag{23}$$

Values of  $\tau_m$  corresponding to Eqs. (22) and (23) are to be found in accordance with the definition of  $\theta$  in Eq. (9) and with allowance for the representation of  $\omega(\tau)$  in Eq. (19).

### 5. Integral characteristics of a system of aggregates

The evolution of the system of growing aggregates can sometimes be described with a sufficient accuracy with the help of moments of the aggregate size distribution. Among those moments are the number concentration  $N(t)$  of the aggregates and the

mean dimensionless volume  $\langle s(\tau) \rangle$ :

$$n(\tau) = N(t)V_0 = \int_0^\infty F(\tau, s) ds = \int_0^{\theta(\tau)} \exp[EG(\zeta)] d\zeta,$$

$$\langle s(\tau) \rangle = \frac{1}{n(\tau)} \int_0^\infty sF(\tau, s) ds = \frac{(1 - \beta)^\gamma}{n(\tau)} \int_0^{\theta(\tau)} (\theta - \zeta)^\gamma \exp[EG(\zeta)] d\zeta, \tag{24}$$

$n(\tau)$  being the number of aggregates within the volume  $V_0$ . At small times we obtain, similar to Eq. (26):

$$n(\tau) \approx \theta(\tau) \approx \tau \ll 1, \quad \langle s(\tau) \rangle \approx (1 - \beta)^\gamma \theta(\tau)^\gamma / \delta. \tag{25}$$

At large times, when Eq. (19) is approximately valid, we have

$$n(\tau) \approx \left( \frac{\delta}{2EQ} \right)^{1/\delta} \frac{\Gamma(1/\delta)}{\delta} = \frac{\varepsilon_1}{Q} \approx 0.99(EQ)^{-4/11},$$

$$\langle s(\tau) \rangle \approx (1 - \beta)^\gamma [\theta(\tau)^\gamma - \varepsilon_2 \theta(\tau)^{\gamma-1} / \varepsilon_1], \tag{26}$$

where  $\theta(\tau)$  is implicitly expressed in Eq. (21). These formulae are derived analogously to those in the preceding section.

Dependence on dimensionless time of  $n(\tau)$  is shown also in Fig. 1. It can be seen that  $n(\tau)$  becomes practically constant and coincides with its asymptotic value in Eq. (26) after a rather short length of time. This is easy to understand because the nucleation rate represents a sharply increasing exponential 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. As is seen from Fig. 1, the process of formation of new supercritical nuclei (increase in aggregate concentration  $n(\tau)$ ) goes on during the period of time when the small-time asymptotic solution, Eq. (16), is adequate (see curves 2 and 3). This result lends support to the validity of using the small-time asymptotics, Eq. (16), in exponential function in the integral Eq. (18).

Time dependence of the mean volume of the aggregates is illustrated in Fig. 2. At the end of the intermediate stage of the evolution (i.e., at  $\tau \approx \tau_m$ ,  $\tau_m$  being defined by Eqs. (23) and (21) the mean aggregate volume reaches its maximal value that can be shown to be equal to

$$\langle s(\tau_m) \rangle \approx \varepsilon_1^{-1} \approx 0.43(E^4 Q^{-7})^{1/11}.$$

The reduction of metastability during the intermediate stage is formally attended by the increasing of the critical nucleus volume  $V_*(t) \sim \Delta(t)^{-3}$ ,  $s_*(\tau) \sim \omega(\tau)^{-3}$ . Such expected dependence is shown in the Fig. 2 (curve 3). Dimensionless critical volume  $s_*(\tau)$  is much less than the mean volume  $\langle s(\tau) \rangle$  everywhere over the region of time  $\tau < \tau_m$ . This gives proof to the neglect of recondensation process during the intermediate stage of phase transition.

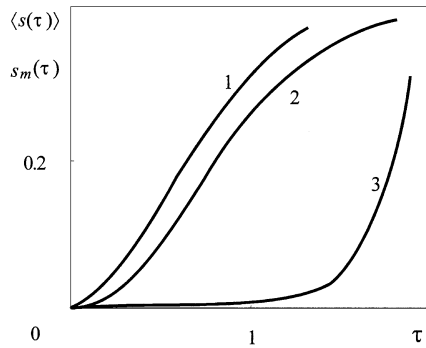


Fig. 2. Time dependence of the maximum aggregate volume  $s_m(\tau)$ , Eq. (13) (curve 1) and the mean aggregate volume  $\langle s(\tau) \rangle$ , Eq. (26) (curve 2) in comparison with the expected time dependence of the critical aggregate volume  $s_*(\tau) \sim \omega(\tau)^{-3}$  (curve 3).

The growth of an ellipsoidal aggregate is accompanied by its elongation. Whereas the aggregate volume increases by several orders of magnitude, the corresponding semiaxes ratio decreases in several times. It can be readily seen from the shape condition of an aggregate (see Section 1 and Ref. [17]).

## 6. Evolution of the volume distribution density

The volume distribution density is obtained in a dimensionless form in Eqs. (11) and (12) and is fully determined if  $\omega(\tau)$  and, consequently,  $\theta(\tau)$  are known. That is why the above results concerning the decline of the supersaturation allow  $F(\tau, s)$  to be calculated as a function of dimensionless time and of relevant parameters. In the field of adequacy of large-time asymptotics, Eq. (19), the distribution density can be written in a form

$$F(\tau, s) = s^{-\beta} \exp\{Eg[\theta(\tau) - y(s)]\} H[\theta(\tau) - y(s)], \quad (27)$$

$$g(z) = 1 - (1 - \varepsilon_1 z^\gamma + \varepsilon_2 z^{\gamma-1})^{-2},$$

where the function  $y(s)$  is defined in Eq. (11) and the functional relation between  $\tau$  and  $\theta(\tau)$  is given by the Eq. (21).

The evolution of the dimensionless distribution density is presented in Fig. 3 where the measure of an area under the curves is equal to the dimensionless aggregate concentration  $n(\tau)$ . At small times the distribution density constitutes a very high and narrow function of the dimensionless aggregate volume. This is caused by the active nucleation process at the beginning of the intermediate stage. After the period of continuing initiation of new nuclei the aggregate concentration in the system becomes constant (see curve 3 in the Fig. 1). It means that subsequent evolution of the distribution density goes on under the condition of constancy of the area measure under the curve. As is clear from Eqs. (2) and (7) the various points of the function  $F(\tau, s)$  move towards the

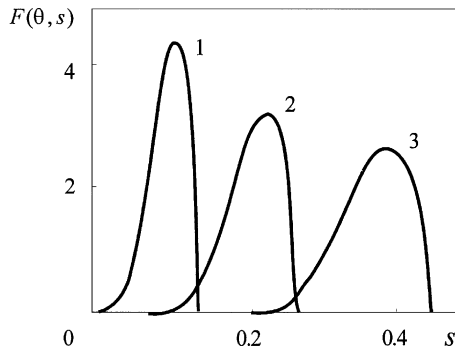


Fig. 3. Dimensionless distribution density at subsequent time moments:  $\theta = \theta_m/2$  (curve 1);  $3\theta_m/4$  (curve 2);  $\theta_m$  (curve 3).

right in the Fig. 3 (i.e., in the space of dimensionless volumes) at a rate  $ds/d\tau$ . Since the rate of such motion represents the increasing function of dimensionless volume  $s$ , then the function  $F(\tau, s)$  becomes more spreading. This means that the distribution density of the aggregates by volume is characterized by increasing dispersion. In accordance with this, the maximum value of the function  $F(\tau, s)$  is the decreasing function of  $s$  (see curves 1–3 in Fig. 3).

The emergence of aggregates affects rheological, thermophysical and other properties of magnetic fluids to considerable extent, their evolution making those properties time dependent. By using the corresponding methods of the macroscopic theory of multiphase and heterogeneous media, the time evolution of such properties may be predicted with the help of the known aggregate distribution density, Eq. (27). To demonstrate these time dependences we shall consider the evolution of ferrocolloid magnetization and effective viscosity during phase-separation process.

## 7. Magnetization of separating ferrocolloid

As growing aggregates have the shape of highly elongated ellipsoids of revolution, the demagnetization effects become negligibly small. In this case the magnetization of the separating system  $M_{sep}$  can be additively defined under the mixture rule through the quasi-equilibrium magnetizations of coexisting phases I and II. The latter depends on the current values of ferroparticle concentration in phases and should be determined with allowance for interparticle dipole–dipole interaction of ferroparticle magnetic moments. Analysis of this problem on the basis of thermodynamic perturbation theory [13] has resulted in a simple expression which most advantageously describes the experimental ferrocolloid magnetization curves [13,35]:

$$M(\varphi, \alpha) = M_L(\varphi, \alpha) \left[ 1 + \frac{4\pi}{3} \frac{dM_L(\varphi, \alpha)}{d\alpha} \right],$$

$$M_L(\varphi, \alpha) = M_s(\varphi)(\coth \alpha - 1/\alpha), \quad \alpha = mH/kT. \quad (28)$$

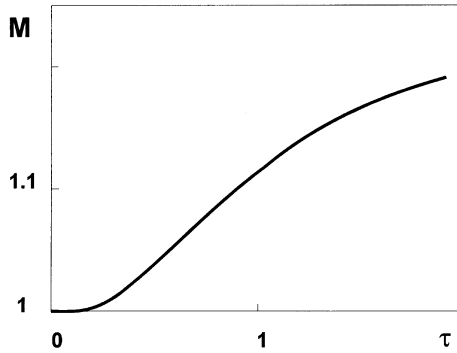


Fig. 4. Time dependence of the relative magnetization  $\mathbf{M} = M_{sep}(\tau)/M(\varphi_0)$  from expressions, Eqs. (28) and (29).

Here  $\alpha$  is the Langevin parameter defined as an energy of magnetic moment  $m$ , interacted with an external magnetic field  $H$ , related to thermal energy  $kT$ . The magnetization of an ideal paramagnetic gas  $M_L$  depends on the dimensionless magnetic field  $\alpha$  and saturation magnetization  $M_s$  being a function of ferroparticle concentration  $\varphi$ .

Assuming the relaxation time of magnetization in phases to quasi-equilibrium values to be small in comparison with the characteristic evolution time of the aggregate system, we come to approximate but qualitatively correct formulae for the magnetization of ferrocolloid during phase-separation process:

$$M_{sep}(\tau) = M[\varphi_1(\tau)][1 - K(\tau)] + M(\varphi_{II})K(\tau),$$

$$K(\tau) = \int_0^\infty Vf(t, V) dV = \frac{\varphi_0 - \varphi_1(\tau)}{\varphi_{II} - \varphi_I} = \frac{\Delta_0}{\varphi_{II} - \varphi_I} [1 - \omega(\tau)],$$

$$\varphi_0 = \varphi_I + \Delta_0, \quad \varphi_1(\tau) = \varphi_I + \Delta(\tau), \quad M(\varphi_{II}) \gg M(\varphi_1). \tag{29}$$

Here  $\varphi_0$  is an initial concentration of ferrocolloid transferred in a metastable state by strengthening of the external magnetic field.

Fig. 4 demonstrates the time dependence of magnetization  $M_{sep}$  related to magnetization  $M(\varphi_0)$  of the initial homogeneous metastable ferrocolloid. The magnetization of highly concentrated drop-like aggregates exceeds by far the corresponding one in a metastable environment. A general fraction of the system volume  $K(\tau)$ , engaged in aggregates, also increases with time, reaching its maximum value  $(\varphi_0 - \varphi_I)/(\varphi_{II} - \varphi_I)$  at  $\tau \rightarrow \infty$ . The influence of these factors surpasses the reduction of magnetization in diluted phase caused by a decrease of the current concentration  $\varphi_1$ . As a result the magnetization of separating system is increased with time (Fig. 4). This means, in the phase-separation region the ferrocolloid magnetostatic curve becomes dependent on the measurement time. Such an effect was experimentally found in Ref. [36],

an influence of the aggregation process has been suggested as a possible explanation.

When the intermediate stage of phase transition is completed, the magnetization  $M_{sep}$  exceeds the magnetization  $M(\varphi_0)$  on some tens of percents. It leads to the occurrence of characteristic bowing on ferrocolloid magnetization curve observed in experiments [37]. The presence of similar bowings may be considered as one of the indirect factors indicating a phase separation of magnetic fluids.

## 8. Effective viscosity

Let us consider a stationary flow of an incompressible magnetic fluid containing drop-like highly elongated aggregates stretched along an external field direction. The flow is assumed to be so weak that the following conditions hold true:

- The shear Peclet number, constructed on the sizes of all aggregates representing interests and on the diffusion coefficient of single ferroparticles, is much less than unity. Therefore, it is possible to neglect the influence of the convective particle flux on the aggregate surfaces. Thus, the aggregate growth rate does not depend on the magnetic fluid flow.
- The viscous hydrodynamic stresses on the aggregate surfaces are much less than both capillary and Maxwell stresses. Consequently, the shape of aggregates can be also considered as independent of the ferrocolloid flow.
- The hydrodynamic moment of forces, turning aggregate, is more weak as compared to the magnetic torque. Therefore, the aggregates may be regarded as stationary oriented and the axis of symmetry of each of them differs little from an external field direction.
- The effective viscosity of the concentrated substance of aggregates is appreciably higher than the viscosity of diluted metastable magnetic fluid. Especially, it is displayed far from the critical point of phase transition. Thus, as a first approximation, we may accept that the strongly viscous drop-like aggregates exert such effect on the magnetic fluid flow as hard particles coincidentally sized and shaped.
- The distance between aggregates is rather large that it is possible to neglect their hydrodynamic and magnetic interactions.

By the above assumptions and using the known results of the hydromechanics of suspension-containing ellipsoidal particles [38], the components of macroscopic hydrodynamic stress tensor are defined by the expression

$$\sigma_{ik} = \sigma_{ik}^s + \sigma_{ik}^a, \quad (30)$$

$$\sigma_{ik}^s = \eta_0 \left\{ 2\gamma_{ik} + \int_0^\infty Vf(t, V) [-\rho(V)e_j e_l \gamma_{jl} \delta_{ik} + 2\alpha(V)\gamma_{ik} + (\zeta(V) + \beta(V)\lambda(V))(e_i e_j \gamma_{jk} + e_k e_j \gamma_{ji}) + \beta(V)(\omega_{ij} e_j e_k + \omega_{kj} e_j e_i)] \right\}$$

$$+ (\chi(V) - 2\lambda(V)\beta(V))e_i e_k e_j e_l \gamma_{jl}] dV \Big\},$$

$$\sigma_{ik}^a = \frac{1}{2} \int_0^\infty f(t, V) q(V) (e_i e_j H_j H_k - e_k e_j H_j H_i) dV, \quad i, j, k, l = x, y, z.$$

Here  $e_i$  are the components of the unit vector  $\mathbf{e}$  directed toward the aggregate axis of symmetry,  $\eta_0$  stands for the viscosity of the liquid carrier,  $\delta_{ik}$  is the Kronecker delta-tensor,  $\omega_{ik} = (\partial u_i / \partial x_k - \partial u_k / \partial x_i) / 2$ ,  $\gamma_{ik} = (\partial u_i / \partial x_k + \partial u_k / \partial x_i) / 2$ , and  $u_i$  are the components of the ferrocold velocity vector. The quantities  $\gamma_{ik}$  and  $\omega_{ik}$  have the meaning of the symmetric and anti-symmetric parts of the tensor of the flow velocity gradient, repeating indices in Eq. (30) mean summation. The meaning of functions  $\alpha(V), \beta(V), \zeta(V), \rho(V), \chi(V), q(V), \lambda(V)$  are given in the Appendix.

Linearly on  $\omega_{ik}$  and  $\gamma_{ik}$  approximation, the vector  $\mathbf{e}$  components in the expression for the symmetric part of the stress tensor  $\sigma^s$  need to be treated such as in a stationary medium. In the case of a coordinate system with symmetry axis  $z$  parallel to an external field  $\mathbf{H}$  direction, the unit vector  $\mathbf{e}$  components in a stationary ferrocold can be defined as  $e_i = \delta_{iz}$ . The non-equilibrium values of vector  $\mathbf{e}$  components, appearing in the expression for the anti-symmetric part of the stress tensor  $\sigma^a$ , can be found with the help of a balance equation for the quasi-hard ellipsoidal aggregate placed in a shear flow [38]:

$$\omega_{lm} + \lambda(V) e_j (e_m \gamma_{lj} - e_l \gamma_{mj}) = \frac{q(V)}{6\eta_0 V \delta(V)} e_k H_k (e_l H_m - e_m H_l), \tag{31}$$

where the function  $\delta(V)$  is given in the Appendix. With the help of Eq. (31) the components  $e_l$  may be simply determined for any geometry of a flow. Let us consider three characteristic examples.

1. The flow velocity  $\mathbf{u}$  is perpendicular to the aggregate axis of symmetry and the value  $u$  linearly changes along this axis, i.e.

$$u_x = 2\omega z, \quad \omega = \text{const}, \quad u_y = u_z = 0, \quad \gamma_{xz} = \gamma_{zx} = \omega_{xz} = -\omega_{zx} = \omega.$$

In this case for effective magnetic fluid viscosity we get from Eqs. (30) and (31):

$$\begin{aligned} \sigma_{xz} = 2\eta_1 \omega, \quad \eta_1 = \eta_0 \Big\{ & 1 + \int_0^\infty V f(t, V) \left[ \alpha(V) + \frac{1}{2} (\zeta(V) + \beta(V)\lambda(V) + \beta(V)) \right. \\ & \left. + \frac{3}{2} \delta(V)(1 + \lambda(V)) \right] dV \Big\}. \end{aligned} \tag{32}$$

2. The flow velocity is aligned with the aggregate axis of symmetry and its value linearly varies along the perpendicular axis, i.e.

$$u_z = 2\omega x, \quad u_x = u_y = 0, \quad \gamma_{xz} = \gamma_{zx} = \omega_{zx} = -\omega_{xz} = \omega, \quad \sigma_{zx} = 2\eta_2 \omega,$$

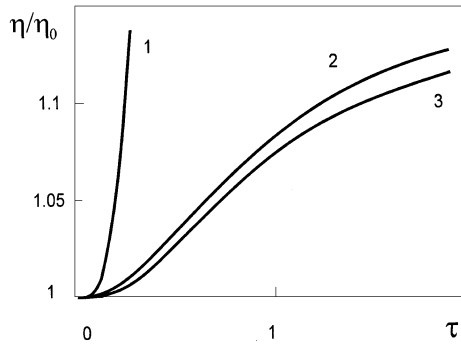


Fig. 5. Time evolution of the relative effective viscosity for three given flow geometries, figures at the curves correspond to expressions, Eqs. (32)–(34). The effective viscosity  $\eta_1$  for the first flow geometry is presented with the scale factor  $10^{-3}$ .

$$\eta_2 = \eta_0 \left\{ 1 + \int_0^\infty V f(t, V) \left[ \alpha(V) + \frac{1}{2}(\zeta(V) + \beta(V)\lambda(V) - \beta(V)) + \frac{3}{2}\delta(V)(1 - \lambda(V)) \right] dV \right\}. \tag{33}$$

3. The flow velocity is directed perpendicular to the aggregate axis of symmetry and its value linearly changes along another perpendicular axis, i.e.

$$u_x = 2\omega y, \quad u_y = u_z = 0, \quad \gamma_{xy} = \gamma_{yx} = \omega_{xy} = -\omega_{yx} = \omega,$$

$$\sigma_{xy} = 2\eta_3\omega, \quad \eta_3 = \eta_0 \left\{ 1 + \int_0^\infty V f(t, V) \alpha(V) dV \right\}. \tag{34}$$

Fig. 5 shows the time evolution of the effective viscosities in all given geometries of ferrocolloid shear flow. In the second and third cases the effective viscosity slowly increases with time. The presence of drop-like aggregates results in that, upon termination of the intermediate stage of phase transition the effective viscosity on 10–20% exceeds the viscosity of a homogeneous magnetic fluid.

Another situation develops in the first case. At the given geometry the drop-like aggregates are extended across the flow, and the gradient aspires to turn them along the flow direction. Stronger counteracting influence of an external magnetic field brings in the occurrence of large additional hydrodynamic stresses. Because of this, the effective viscosity rapidly grows on some decimal orders. Naturally, in this case, the approach, Eq. (30), cannot be applicable and the curve 1 in Fig. 5 has a purely illustrative character.



## 9. Discussion

While summing up findings, we are able to state that the evolution of the system of drop-like ellipsoidal aggregates in a metastable magnetic fluid at the stage of major emergence of those aggregates can be described with a high accuracy by purely analytical methods, with merely occasional application of simple numerical methods. Essentially, the same inference pertains the numerous processes of the new phase formation in molecular and colloid systems. As compared with the latter, the magnetic-field-induced phase separation in magnetic fluids is substantially governed by the mutual dependence between the volume of an aggregate and its shape. An elongation of the aggregate during its growth is attended by an increase of both the interfacial surface and the concentration gradient in the vicinity of the side surface. The latter is caused by the relative decrease (as compared with a sphere) of transverse size of an ellipsoid. Consequently, the aggregate elongation results in the higher value of growth rate in comparison with the growth of spherical droplets. On the other hand, the large aggregate surface hinders the process of formation of initial aggregates and tends to an increase of the critical nucleus activation energy. Nevertheless, the rate of nucleation and the kinetics of intermediate stage of phase transition go on more rapidly in a magnetic fluid made metastable by an external field. This is due to the fact that a small strengthening of magnetic field implies a significant increase of initial supersaturation (see Table 1 in Ref. [1]). The latter exerts primary control over the kinetics of phase-separation process.

General evolution laws happen to be universal in the case of the diffusion kinetics of phase separation, however, when expressed in terms of special time variable  $\theta(\tau)$  defined in Eq. (9). These universal laws for the diffusion-limited aggregate growth in the small-time and large-time asymptotics have the form

$$\begin{aligned}\omega(\theta) &\approx 1 - Q\theta^\delta/\delta, & \langle s(\theta) \rangle &\sim \theta^\gamma, & n(\theta) &\approx \theta, & \theta &\ll (\delta/Q)^{1/\delta}, \\ \omega(\theta) &\approx 1 - \varepsilon_1\theta^\gamma + \varepsilon_2\theta^{\gamma-1}, & \langle s(\theta) \rangle &\sim (\theta^\gamma - \varepsilon_1\theta^{\gamma-1}/\varepsilon_2), & n(\theta) &\approx (QE)^{-1/\delta}, \\ \varepsilon_1 &\approx Q(EQ)^{-1/\delta}, & \varepsilon_2 &\approx Q(EQ)^{-2/\delta}, & \theta_m &\approx \varepsilon_1^{-1/\gamma}, & \theta &> \varepsilon_2/\varepsilon_1,\end{aligned}$$

both for the magnetic fluid phase separation induced by an external field and for the phase separation of a colloid [5–7] made metastable by a fall of temperature or an increase in the ionic strength of a solvent [8]. All the differences consist in the various values of exponents  $\delta$  and  $\gamma$ . In the case of magnetic field induced phase separation we get from Sections 3 and 4:  $\gamma \approx 7/4$ ,  $\delta \approx 11/4$ . When the phase separation takes place under the absence of an external field, the corresponding value of exponents were determined in Ref. [7]:  $\gamma = 3/2$ ,  $\delta = 5/2$ .

The pertinent volume and time scales of the evolution process equal  $V_0$  and  $t_0$  defined by Eq. (5). The first scale is representative of the ultimate volume of an aggregate attained at the end of the intermediate stage of the evolution. Similarly,  $t_0$  has the meaning of the period of time during which the supersaturation falls to zero.

Measurements of those scales in actual phase-separation process help to enable one to judge about the nucleation rate  $J$ .

The continuing nucleation plays a role only at an early phase of intermediate stage because of an abrupt drop in the nucleation rate caused by a seemingly insignificant decrease in the supersaturation. (If a transient value of the supersaturation is only five percent smaller than the initial one, this rate can be proved to be diminished by a factor  $\exp(0.1E)$  which can be quite tremendous at large  $E$ .) After that the nucleation may be neglected.

Unfortunately, the authors have failed to find out reliable experiments of the kinetics of phase-separation process in magnetic fluids which could suffice to provide for a conclusive check of the developed theory. However, it seems to be certain that the theory is implicitly corroborated by the general bulk of available experimental evidence. Moreover, there is an excellent agreement of the theory of the same kind [21] with some experiments on batch crystallization, which lends an additional support to the theory of the present paper as well.

In conclusion, we point out that the above asymptotic expression of the distribution of the aggregates over volume presents an initial condition that should be used while dealing with the final stage of Ostwald ripening. An analysis, of this final stage presents a tempting object of future research.

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## Appendix

The functions used in Section 8 are expressed through characteristic elliptic integrals

$$\alpha_0 = \int_0^{\infty} \frac{ds}{(a^2 + s)Q}, \quad \beta_0 = \int_0^{\infty} \frac{ds}{(b^2 + s)Q}, \quad \alpha'_0 = \int_0^{\infty} \frac{ds}{(b^2 + s)^2 Q},$$

$$\beta'_0 = \int_0^{\infty} \frac{ds}{(a^2 + s)(b^2 + s)Q}, \quad \alpha''_0 = \int_0^{\infty} \frac{s ds}{(b^2 + s)^2 Q},$$

$$\beta''_0 = \int_0^{\infty} \frac{s ds}{(a^2 + s)(b^2 + s)Q},$$

$$Q = (b^2 + s)\sqrt{(a^2 + s)}.$$

Such integrals arise during the solving of the hydrodynamic problems on a flow around a particle in the shape of an extended ellipsoid of revolution [38]. Strictly speaking, the quantities used in Section 8  $\alpha, \beta, \zeta, \rho, \xi, q, \lambda, \delta$  are the functions of the ellipsoid shape factor  $c = b/a$  ( $a$  and  $b$  stand for the ellipsoid semi-axes). In the considered case of high-elongated drop-like aggregates ( $c \ll 1$ ), we have from Ref. [38]

$$\begin{aligned}\alpha(V) &= \alpha[c(V)] = 1/ab^4\alpha'_0 \approx 2, & \lambda(V) &= \lambda[c(V)] = (1 - c^2)/(1 + c^2) \approx 1, \\ \beta(V) &= \beta[c(V)] = 3\lambda[c(V)]\delta[c(V)] \approx -1/c^2 \ln c, \\ q(V) &= V(\mu_{II} - 1)^2/4\pi(\mu_{II} + 1), \\ \zeta(V) &= \zeta[c(V)] = \frac{4}{(a^2 + b^2)ab^2\beta'_0} - \frac{2}{ab^4\alpha'_0} \approx O(c^2), \\ \chi(V) &= \chi[c(V)] = \frac{2\alpha''_0}{ab^4\alpha_0\beta''_0} - \frac{8}{ab^2(a^2 + b^2)\beta'_0} + \frac{2}{ab^4\alpha'_0}, \\ \rho(V) &= \rho[c(V)] = \frac{2(\alpha''_0 - \beta''_0) + 3ab^2(\alpha_0\alpha''_0 - \beta_0\beta''_0)}{3AB^4\alpha'_0\beta''_0}, \\ \delta(V) &= \delta[c(V)] = \frac{2}{3} \frac{a^2 + b^2}{ab^2(a^2\alpha_0 + b^2\beta_0)} \approx -1/3c^2 \ln c.\end{aligned}$$

The dependence of these functions on aggregate volume  $V$  in Eqs. (32)–(34) can be received under the condition when the interrelation between the volume and the shape of the growing aggregates is taken into account (see Section (2) and Ref. [17]).

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