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Nucleation stage of ferrocolloid phase separation induced by an external magnetic field

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Abstract

We consider an initial stage of the origination of droplike aggregates in a ferrocolloid made metastable by a strengthening of an external magnetic field, when emerging nuclei are still not large enough to affect ferrocolloid properties appreciably. Expressions for the growth rate of a high-elongated ellipsoidal shaped aggregate, for the critical nucleus volume and for the nucleation rate are presented.

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1. Introduction

Stable colloidal suspensions of the particles of ferro- and ferri-magnetic materials in liquids that are known as ferrocolloids (magnetic fluids, ferrofluids) offer unique properties [1–3] that have attracted attention of researches. The small sizes of dispersed ferroparticles (∼10 nm) provide the particles with an inherent magnetic moment. The stabilization of suspension is usually obtained by coating the magnetic grains with surfactant layer which allows to neglect the influence of van-der-Waals forces [1,2]. As a result, the ferroparticles interact with each other through the steric repulsion of surfactant coats and the dipole–dipole interaction of particle magnetic moments. The high fluidity of magnetic fluids is combined with a perceptible ability to interact with magnetic field which is being the essence of their practical application.

Among the most attractive phenomena is the phase separation of ferrocolloids [4–9], accompanied by the existence of droplike aggregates. These aggregates can be considered as fluids [6,7,9] with interfacial tension surface, representing, essentially,

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a highly concentrated ferrocolloidal phase suspended in a dilute matrix in the form of droplets [4,5,7,9]. Typical dimensions of droplike aggregates are of the order of approximately 1–5 μm, i.e. the number of ferroparticles comprising the aggregate is approximately 10^4–10^6.

From the view point of statistical mechanics the existence of droplike aggregates may be considered as a result of violation of thermodynamic stability in a system of dispersed particles that leads to their condensation [10,11]. Therefore, phase separation in ferrocolloids is treated further as a 1st order phase transition of the "colloidal-gas–colloidal-liquid" type. Two main reasons for the separation of colloidal systems are known [9,10]: (i) decrease in temperature; (ii) an increase in electrolyte concentration in ionic-stabilized dispersions. In magnetic fluids still another type of phase separation is experimentally observed, i.e. phase separation in magnetic field [4–8]. In this case, at equilibrium conditions a magnetic field increase is equivalent to a temperature lowering. Such phenomenon looks like a non-trivial phase transition of the condensation type, induced by an external magnetic field. It should be noted that similar phenomena are observed in electro-rheological suspensions [12] and polar liquid crystals [13].

In principle, existing statistical thermodynamic models of magnetic fluids [14–18] have demonstrated that, in a system of particles interacting through the non-central dipole–dipole potential, the condensation may occur in the absence of a magnetic field at a temperature below a certain critical one, the latter is dependent on the value of the ferroparticle magnetic moments. This is associated with the fact that non-central dipole–dipole interaction of particle magnetic moments displays itself on the whole as an effective interparticle attraction. In an external field this effective attraction strengthens [16–18], thus a magnetic field stimulates the process of phase separation in ferrocolloids.

There exist various methods of taking into account the magneto-dipole interaction when developing the thermodynamic theory of ferrocolloid. The earliest theories [14,15] are based on the well-known mean-field model by Weiss. Natural as it may be, these theories predict a paramagnetic to ferromagnetic IInd order phase transition which is never observed in fluid-like magnetic systems [19]. Concerning the phase separation process, the mean-field model predicts the concentrated ferrocolloidal phase to be spontaneous magnetized. However, in the absence of a magnetic field the observed droplike aggregates are spherical shaped [6,7,9]. This fact testifies that the aggregates are magnetic disordered. That is why the corresponding mean-field theory appears to be questionable. Nonetheless, there are some experiments which show that the theory is applicable when the magnetic field is strong enough [19].

Attempts to use the mean-spherical model [16,17], which was originally developed for polar liquids [20], and the thermodynamic perturbation method [18,21] proved far more successful. The models [16–18] are appropriate to describe well experimental data on magnetostatic properties of real magnetic fluids [17–19, 21–23]. Obviously, these models have the coincident fields of adequativity and are valid for ferrocolloids with low or moderate concentrations of magnetic phase under the presence of an arbitrary valued uniform magnetic field. The mathematical technique of the mean-spherical

model, however, happens to be so complicated as to prevent the author of Refs. [16,17] from studying other equilibrium properties of magnetic fluids affected by an external field. Therefore, the further results are based on the hard sphere perturbation theory applied to magnetic fluids in Refs. [18,21]. The model leads to rather simple expressions for magnetostatic properties and thermodynamic functions of the ferrocolloid in the presence of an external field. Those expressions have been proved to agree reasonably well with the available experimental evidence [22]. The basic model can be generalised to polydisperse magnetic fluids and to the systems in which the interparticle interaction includes both molecular attractive and electrostatic repulsive forces, whithout additional difficulties of the fundamental nature. On the basis of perturbation model the kinetic theory of the phase separation process in colloids in the absence of an external field has been developed in Refs. [24,25].

The break of thermodynamic stability of a colloid is followed by the origination of initial critical nuclei of a new colloidal phase, by their transformation into macroscopic droplike aggregates and by ensuing growth of those aggregates in a metastable environment. 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 [26]. The first one corresponds to the initiation of the critical new phase nuclei which further form either the macroscopic new phase elements in a metastable molecular system or the droplike 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 justly 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 feed-back between the process of aggregate formation and growth dependent on a transient degree of metastability (e.g., a value of the supersaturation) and that of gradual reducing of metastability by the growing aggregates. At last, the third stage of final coalescence corresponds to the Ostwald ripening process when the mentioned 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 [26,27]. Recently such a theory has been worked out for colloids in Ref. [24]. In present research we should focus our attention on the fundamental problem concerning the influence of a magnetic field on the kinetics of nucleation stage of ferrocolloid phase separation from metastable state. This problem has been examined in Ref. [35], where an expression for diffusion-limited growth rate of a concentrated ferrocolloidal drop in a metastable fluid has been obtained. Using the calculated data as the base, a final stage of Ostwald ripening has been considered and the self-similar solutions both for the drop mean length ($\sim t^{1/2}$) and the drop concentration ($\sim t^{-7/6}$) have been proposed. While determining the ferroparticle concentration profiles, the author of Ref. [35] have used

the quasi-cylindrical solution of the stationary diffusion equation in the vicinity of a drop and the self-similar solution of this equation in spherical geometry far from a drop. The asymptotic joining of the two non-consistent expressions has brought the author to a physically meaningless result: the drop growth rate obviously depends on time and decreases up to zero even at a constant metastability. This inconsistent conclusion calls into question the further results of Ref. [35], and the problem remains unsolved.

2. Equilibrium phase separation

Let us consider a sterical stabilized magnetic fluid containing identical spherical particles (diameter d, magnetic moment m), suspended in a neutral liquid carrier. Ferroparticles interact with each other through the short-range hard sphere potential modelling the repulsion of surfactant coats and through the long-range dipole–dipole interaction $U_d(ij)$ of particle magnetic moments. As it has been shown in Refs. [18,21], the latter displays itself as an effective interparticle attraction which intensity is conveniently described by the parameter $\gamma = m^2/d^3kT$. This parameter characterizes the value of the interaction energy of two contacting ferroparticles, with respect to the thermodynamic temperature. The intensity of ferroparticle attraction increases in external field $\mathbf{H}_0$, the interaction of particle magnetic moments with magnetic field is described by the Langevin parameter $\alpha = mH_0/kT$.

If α and γ exceed some critical values α_c and γ_c, peculiar van der Waals loops make their appearance on the curves of ferroparticle chemical potential v and osmotic pressure P, being regarded as functions of the concentration φ of the particles by volume. Those loops determine regions in which a macroscopically homogeneous state of the magnetic fluid becomes unstable and, as a concequence, the magnetic fluid is bound to be separated into two homogeneous phases characterized by the equilibrium values φ_{I} and φ_{II} of the concentration. The conditions of co-existence of the phases mentioned are evidently determined by the equations:

$$v(\varphi_{\mathrm{I}}) = v(\varphi_{\mathrm{II}}), \qquad P(\varphi_{\mathrm{I}}) = P(\varphi_{\mathrm{II}})\,. \tag{1}$$

$$v(\varphi) = kT\left[\ln\varphi - \varphi + \frac{\varphi(8-5\varphi)}{(1-\varphi)^2} - \varphi(2-\varphi)G(T,H,\varphi)\right],$$

$$P(\varphi) = \frac{kT}{v}\varphi\left[\frac{1+\varphi+\varphi^2-\varphi^3}{(1-\varphi)^2} - \varphi G(T,H,\varphi)\right],$$

$$G(T,H,\varphi) = \frac{1}{2v}\left(\frac{\alpha}{\sinh\alpha}\right)^2 \int d\mathbf{r} \iint d\boldsymbol{\Omega}_1 d\boldsymbol{\Omega}_2 \left[-\frac{U_d(12)}{kT} + \frac{1}{2}\left(-\frac{U_d(12)}{kT}\right)^2 - \cdots\right] \exp\left(\frac{\mathbf{m}_1\cdot\mathbf{H}_0 + \mathbf{m}_2\cdot\mathbf{H}_0}{kT}\right) g_0(r,\varphi),$$

where the osmotic pressure and chemical potential are written on the basis of the hard sphere perturbation theory [18,21] by singling out the hard sphere constituent

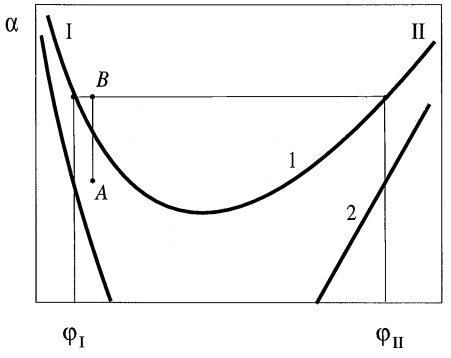

Fig. 1. Equilibrium phase diagram of a magnetic fluid with a magneto-dipole interaction parameter $\gamma_c(\infty)<\gamma<\gamma_c(0)$ (curve 1) and $\gamma>\gamma_c(0)$ (curve 2); I – gas-like phase, II – liquid-like phase.

in the form of well-known Carnahan–Starling approximation [28]. The interparticle magneto-dipole interaction is taking into account as a perturbation with the help of quantity G which contains the hard sphere radial distribution function $g_0(r,\varphi)$. The integration over $d\boldsymbol{\Omega}_i$ corresponds with averaging over the all possible directions of the magnetic moment of ith ferroparticle.

At the thermodynamic equilibrium state the coexisting phases are separated by a plain interfacial surface which is parallel to an external field. The critical parameters of phase transition γ_c and φ_c are dependent on magnetic field strength. For example, the mean spherical approximation (Ref. [16]) gives the values $\gamma_c(H_0=0)=4.45$, $\varphi_c(H_0=0)=0.055, \gamma_c(H_0\to\infty)=3.06, \varphi_c(H_0\to\infty)=0.085$; the 1-st order perturbation theory (Ref. [18]) yields $\gamma_c(0)=2.82, \varphi_c(0)=0.130, \gamma_c(\infty)=1.69, \varphi_c(\infty)=0.130$. Phase diagram for a magnetic fluid is shown in the coordinates $\varphi-\alpha$ at various values of magneto-dipole interaction parameter γ. The point A (Fig. 1) corresponds to a spatially homogeneous magnetic fluid with the initial volume concentration φ_0. The increasing of external field strength (growth of α) is attended with the changing of ferrocolloid state to the two-phase region (point B, Fig. 1). The system begins to separate into low and high concentrated phases ($\varphi_{\rm I}$ and $\varphi_{\rm II}$, respectively). In what follows, we are going to study the kinetics of phase separation of dilute magnetic fluid ($\varphi_0\ll 1$). In doing so, the inequality for concentrations $\varphi_{\rm I}$ and $\varphi_{\rm II}$ is valid: $\varphi_{\rm I}\ll\varphi_{\rm II}$. Hence the magnetization $M_{\rm I}$ of low concentrated phase may be neglected as compared with magnetization $M_{\rm II}$ of high concentrated phase ($M_{\rm II}\gg M_{\rm I}$). In closing, we shall consider the separation in a weak magnetic field, so the ferrocolloid magnetization is directly proportional to field strength: $M=\chi H_0, \chi=\text{const.}$ – initial susceptibility of magnetic fluid.

3. Quasi-equilibrium shape of droplike aggregate

Let us consider a single droplike aggregate placed in separating magnetic fluid. It seems natural to suppose that the relaxation of an aggregate shape to the most

energetical advantageous one is very quick as compared with the change of the aggregate volume V. Thus, the shape of aggregate with a given volume V may be determined under the conditions of its energy minimum. Experimental studies [6,7,29] and theoretical analysis [30] have demonstrated that the magnetic fluid drop in an external field is spindle-shaped.

The attempts to calculate the exact shape of a ferrocolloid drop placed in a uniform magnetic field have been made in Refs. [30,35]. However, there exist some reasons, on which the results of Refs. [30,35] cannot be considered as correct. First, the dependence of the interfacial tension both on a magnetic field strength and on a mutual orientation of the drop surface and a magnetic field have not been taken into account. Second, an influence of the tip effects have been neglected, while just here the capillary and magnetic forces are especially strong. Besides that, a magnetic field is non-uniform inside the spindle-shaped drop. The author of Refs. [30,35] has faced the last problem while determining the drop growth rate and has neglected the magnetic field inhomogeneities. Hence, the calculations of a drop shape in Refs. [30,35] have been carried out with an accuracy excess.

The problem of a magnetic field inhomogeneity disappears in the case of ellipsoidal shape of a droplike aggregate. This assumption has been used in Ref. [6] during an analysis of the experimental data, concerning the elongation of the ferrocolloidal drops under the influence of an external magnetic field. As has been shown in Ref. [6], the simple ellipsoidal approximation results in a good agreement with the experimental evidences in the weak and moderate magnetic fields. In a strong magnetic field a natural discrepancy, caused by the tip effects, is observed. Later the conclusions of Ref. [6] have been confirmed in experimental researches [7,29]. The above mentioned success is the basis for a choice of a simple ellipsoidal shape of a droplike aggregate as a first approximation.

By using the results of Ref. [6] we consider the droplike aggregate as an ellipsoid of revolution stretched along the external field direction. This shape is dependent on the balance between the surface energy F_s and the excess magnetic energy F_m. The energy F_s is determined by the values of aggregate surface S and interfacial tension σ. The latter depends both on the magnetic field strength and on the local mutual orientation of the surface and vector $\mathbf{H}_0$ (Refs. [29–31]). However, this dependence reveals at large strength of external field in the vicinity of the saturation magnetization of magnetic fluid (Refs. [29,31]). Therefore, parameter σ will be treated as an effective interfacial tension which remains constant along the surface of droplike aggregate:

$$F_s = \int_S \sigma \, ds \approx \sigma S = 2\pi\sigma \left(\frac{3V}{4\pi}\right)^{2/3} c^{2/3} \left(1 + \frac{\arcsin\sqrt{1-c^2}}{c\sqrt{1-c^2}}\right). \tag{2}$$

Here $c = b/a$ is the ratio between ellipsoid semiaxes b and a.

The excess magnetic energy F_m is connected with the fact that volume V characterized by magnetic permeability μ_{II} is placed in a medium characterized by magnetic permeability $\mu_{\mathrm{I}}(\mu_{\mathrm{II}} \gg \mu_{\mathrm{I}})$. The internal magnetic field H_2 is uniform in the case of

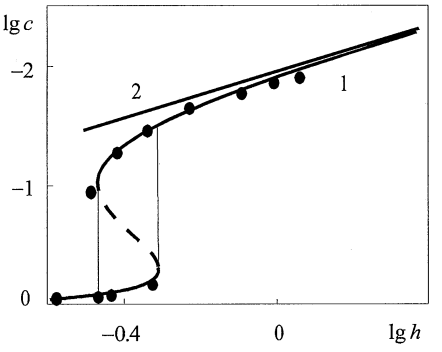

Fig. 2. Dependence of an ellipsoidal drop semiaxe ratio c on the dimensionless parameter $h=(3V/4\pi)^{1/6}H_0(\mu_1/4\pi\sigma)^{1/2}$: curve 1 – numerical minimization of the total energy of Eqs. (2) and (3) with respect to ratio c; curve 2 – asymptotic expression Eq. (4); dots – experimental data from Ref. [7], an elongation hysteresis loop is shown.

ellipsoidal shape of a volume V. Thus for the energy F_m we obtain [32]:

$$F_m = -\frac{VH_0^2}{8\pi}\mu_1\frac{\mu_{II}-\mu_I}{\mu_I+n(\mu_{II}-\mu_I)}, \tag{3}$$

$$n \equiv \frac{c^2}{2(1-c^2)^{3/2}}\left[\ln\left(\frac{1+\sqrt{1-c^2}}{1-\sqrt{1-c^2}}\right)-2\sqrt{1-c^2}\right],$$

where n is the demagnetization factor.

In quasi-equilibrium state the aggregate shape may be determined under the condition of minimization of total energy with respect to ratio c: $d(F_s+F_m)/dc=0$. Dependence of quasi-equilibrium shape-factor c upon the dimensionless magnetic field is presented on Fig. 2 in comparison with experimental data of Pshenichnikov, Ref. [7]. The distinctive feature of curves on Fig. 2 is the occurence of hysteresis loops in the case of sufficiently large value of $\mu_{II}(\mu_{II}/\mu_I>20)$. In this area the magnetic fluid drop undergoes a jump-like elongation, the main features of such process have been experimentally studied in Refs. [6,7,29]. The Fig. 2 shows that the ellipsoidal drop becomes high-elongated ($a\gg b,c\ll 1$) if the combination $H_0V^{1/6}\sigma^{-1/2}$ exceeds a certain value which is approximately equal to 1. Thus, for typical values of interfacial tension $\sigma\sim10^{-4}$ erg/cm^2 [6,7,29] and weak magnetic fields $H_0\sim10$ Oe we obtain the volume $V\sim1$–10×10^{-18} cm^3. The latter corresponds in order of value with the ferroparticle volume v ($d\sim10$ nm, $v\sim10^3$ nm^3). In consequence, the droplike aggregates in magnetic fluid may be regarded as high-elongated ellipsoids of revolution. In so doing, the relationship between aggregate volume V and semiaxes ratio c takes the simple asymptotic form:

$$V\approx\frac{B}{c^7|\ln c|^3},\quad B=\frac{4\pi^7\sigma^3}{3H_0^6}\frac{\mu_I^3}{(\mu_{II}-\mu_I)^6},\quad c\ll1,\quad V\gg B. \tag{4}$$

One can see from asymptotic Eq. (4) and Fig. 2 that a major increase of aggregate volume V is attended with a minor decreasing of ratio c.

4. Equilibrium conditions at an interface between colloidal phases

Consider next equilibrium at a distorted interface under the conditions when both the bubble and the magnetic pressures are taken into account:

$$v(\varphi_1) = v(\varphi_2), \qquad P(\varphi_1) + \sigma K = P(\varphi_2) + 2\pi M_{2n}^2 . \tag{5}$$

Here K is the curvature of the interface, and M_{2n} is the normal to the surface component of magnetization in high concentrated ferrocolloidal phase. The correspondent magnetization component in low concentrated phase M_{1n} allows to be neglected in comparison with M_{2n}.

The curvature K and normal magnetization M_{2n} represent rather complex functions of the surface coordinates. In order to simplify the mathematical structure of Eq. (5) let us make some obvious assumptions. The ellipsoid elongation coincides with the direction of magnetization vector $\mathbf{M}_2$. Therefore, in the case of high-elongated aggregate the normal component M_{2n} allows to be considered as negligibly small at the great majority of the surface. This assumption becomes untrue in two areas of ellipsoid apices. These areas are much less than the total surface of an aggregate. Hence, as a first approximation, the normal to the surface component of aggregate magnetization will be considered as equals to zero ($M_{2n} \approx 0$).

By taking for granted that the concentration shifts due to the interface curvature are relatively small, $|\delta\varphi_1| = |\varphi_1 - \varphi_{\mathrm{I}}| < \varphi_1, |\delta\varphi_2| = |\varphi_2 - \varphi_{\mathrm{II}}| \ll \varphi_{\mathrm{II}}$, and by carrying out an averaging over the interface, we arrive at a set of linear algebraic equations to find the concentration shifts:

$$\frac{\partial v}{\partial \varphi_{\mathrm{I}}}\delta\varphi_{\mathrm{I}} - \frac{\partial v}{\partial \varphi_{\mathrm{II}}}\delta\varphi_2 = 0, \qquad \frac{\partial P}{\partial \varphi_{\mathrm{I}}}\delta\varphi_1 - \frac{\partial P}{\partial \varphi_{\mathrm{II}}}\delta\varphi_2 = -\frac{\bar{\sigma}}{V^{1/3}} . \tag{6}$$

Here $\bar{\sigma}$ is an effective parameter which appears in Eq. (5) during averaging procedure over the interface, this parameter will be determined later. Making simple calculations we obtain the expressions for quasiequilibrium averaged concentrations φ_1 and φ_2 which are constant along the aggregate surface:

$$\varphi_1 = \varphi_{\mathrm{I}} + \frac{\bar{\sigma}}{V^{1/3}}U, \qquad \varphi_2 \approx \varphi_{\mathrm{II}} ,$$

$$U = \frac{\partial v/\partial \varphi_{\mathrm{II}}}{(\partial P/\partial \varphi_{\mathrm{II}})(\partial v/\partial \varphi_1) - (\partial P/\partial \varphi_{\mathrm{I}})(\partial v/\partial \varphi_{\mathrm{II}})} . \tag{7}$$

5. A model of the growth of aggregates

Because the potential barrier preventing a new particle from adhering to an aggregate is hardly to be expected to be large, the growth of the aggregate is likely to be limited

by the rate of diffusional transport of particles to the aggregate surface. Then

$$\varphi_{\mathrm{II}}\frac{dV}{dt} = -\int_S \mathbf{j}\,ds\,, \tag{8}$$

where $\mathbf{j}$ is the ferroparticle flux density in a metastable magnetic fluid.

The characteristic time of establishing of a stationary field of concentration in the vicinity of the growing aggregate is of the order of value $\tau_D = V^{2/3}/D$, whereas the order of time required to change the aggregate volume substantially is determined by $\tau_V = V/(dV/dt) \approx V^{2/3}/D\delta$ so that

$$\frac{\tau_D}{\tau_V} \sim \frac{V^{2/3}/D}{V^{2/3}/D\delta} = \delta \ll 1, \qquad \delta = \frac{\varphi_0 - \varphi_{\mathrm{I}}}{\varphi_{\mathrm{II}}}\,. \tag{9}$$

Here D is the coefficient of mutual Brownian diffusion of the particles down a concentration gradient and φ_0 is the initial concentration of ferroparticles by volume. This inequality (9) means that diffusion can be considered in the quasi-stationary approximation:

$$\begin{aligned} &div\,\mathbf{j} = 0, \quad \mathbf{j} = -D(\nabla\varphi + \varphi\nabla u), \quad \varphi|_\infty = \varphi_\infty, \quad \varphi|_S = \varphi_1\,, \\ &D = \frac{kT}{3\pi\eta d}, \quad u = -\ln\frac{\sinh(\alpha_1)}{\alpha_1}, \quad \alpha_1 = \frac{mH_1}{kT}\,. \end{aligned} \tag{10}$$

where η stands for the viscosity of the pure matrix liquid. The boundary conditions at the aggregate surface contains the quasi-equilibrium averaged concentration φ_1 determined in Eq. (7); the current concentration of a metastable phase φ_∞ may be regarded as a slow function of time. The one-particle Langevin free energy of an ideal paramagnetic gas $u \cdot kT$ is dependent on a local value of magnetic field strength H_1 in low-concentrated phase, and $-D\varphi\nabla u$ is the particle flux density caused by the inhomogeneities of magnetic field H_1.

In order to solve Eq. (10) let us enter the coordinate axes x, y, z with the origin placed at the center of an aggregate. The direction of x is parallel to the axis of symmetry. Due to the ellipsoidal shape of an aggregate it is convenient to solve the boundary problem, Eq. (10), with the help of ellipsoidal coordinates [33] ξ, ζ which are related to x, y, z:

$$\begin{aligned} &x = \pm\left[\frac{(\xi + a^2)(\zeta + a^2)}{a^2 - b^2}\right]^{1/2}, \qquad y^2 + z^2 = \frac{(\xi + b^2)(\zeta + b^2)}{b^2 - a^2}\,, \\ &\xi \geqslant -b^2, \quad -a^2 \leqslant \zeta \leqslant -b^2\,. \end{aligned} \tag{11}$$

In ellipsoidal coordinates the aggregate boundary is described by the surface $\xi = 0$. In general one cannot find the analytical solution of the boundary problem defined by Eqs. (10) and (11). Then let us analyze this problem under the conditions when the high-elongated shape of an aggregate is taken into account. In this case the magnetic field inside the aggregate approximately equals the external field, $H_2 \approx H_0$. According

to this, the magnetic field outside the aggregate, on an average, also approximately equals to external one, $H_1 \approx H_0$. In the vicinity of the ellipsoid side surface a magnetic field is approximately constant ($\alpha_1 \approx$ const.), so the magnetic "convective" flux density $j_\alpha = -D\varphi(\partial u/\partial\alpha_1)\nabla\alpha_1$ is negligibly small. The diffusion flux density here is of the order of value $j_D \sim D\varphi_\infty/b$. The total diffusion flux on the ellipsoid side surface $I_D \sim abj_D \sim D\varphi_\infty a$. "Convective" flux density is detectible only in the vicinity of the ellipsoid apices where $j_\alpha \sim D\varphi_\infty \alpha/b$. Total "convective" flux on ellipsoid apex surface $I_\alpha \sim j_\alpha b^2 \sim D\varphi_\infty \alpha b$. So in the case of high-elongated aggregate a strong inequality $I_D \gg I_\alpha$ holds true. On the basis of such assumption the magnetic "convective" flux $-D\varphi\nabla u$ allows to be neglected as compared with diffusional flux $-D\nabla\varphi$. This simplification is obviously valid for dilute metastable magnetic fluid, $|\ln\varphi_1| \gg |\ln(\sinh\alpha/\alpha)|$. Thereafter, we obtain familiar differential equation for determining the concentration profile in vicinity of an aggregate:

$$\frac{d}{d\xi}\left(R_\xi \frac{d\varphi}{d\xi}\right) = 0, \qquad R_\xi = (\xi + b^2)\sqrt{\xi + a^2}\,,$$

$$\varphi(\xi = 0) = \varphi_1, \quad \varphi(\xi = \infty) = \varphi_\infty\,. \tag{12}$$

Eq. (12) is similar to the problem of dielectric ellipsoid placed in an electric field [32]. The solution of Eq. (12) is to be written as [32]

$$\varphi(\xi) = \varphi_\infty + \frac{\varphi_1 - \varphi_\infty}{\mathrm{Arth}\sqrt{1 - c^2}}\,\mathrm{Arth}\sqrt{\frac{a^2 - b^2}{\xi + a^2}}\,. \tag{13}$$

By using this expression in Eq. (8) with account of Eq. (7) we get the growth rate of an ellipsoidal aggregate:

$$\varphi_{\mathrm{II}}\frac{dV}{dt} = 3\left(\frac{4\pi}{3}\right)^{2/3} D\frac{V^{1/3} - V_*^{1/3}}{\mathrm{Arth}\sqrt{1 - c^2}}\frac{\sqrt{1 - c^2}}{c^{2/3}}(\varphi_\infty - \varphi_1)\,, \tag{14}$$

$$V_*^{1/3} = \frac{\bar{\sigma}U}{\varphi_\infty - \varphi_{\mathrm{I}}}\,.$$

Here the parameter V_* has a meaning of critical volume of aggregate nucleus, in the case $V > V_*$ the aggregate grows, otherwise $V < V_*$ the aggregate reduces. For high-elongated ellipsoid Eq. (14) takes the form ($c \ll 1$):

$$\varphi_{\mathrm{II}}\frac{dV}{dt} = 3\left(\frac{4\pi}{3}\right)^{2/3} D\frac{V^{1/3} - V_*^{1/3}}{c^{2/3}|\ln c|}\Delta\,, \tag{15}$$

where the quantity $\Delta = \varphi_\infty - \varphi_{\mathrm{I}}$ plays the role of the absolute supersaturation of the parent magnetic fluid (see Fig. 1).

The diffusion limited growth rate of an ellipsoidal aggregate, Eq. (14), differs from well-known classical growth rate of spherical droplet [24,27] by the presence of function $f(c) = \sqrt{1 - c^2}/c^{2/3}\mathrm{Arth}\sqrt{1 - c^2}$. In the case $c = 1$ ($a = b$, sphere) we get the

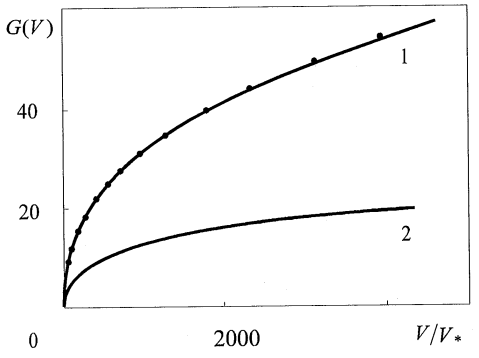

Fig. 3. Dependence of the dimensionless aggregate growth rate $G(V)=(dV/dt)(3/4\pi)^{2/3}\varphi_{II}/3DV_*^{1/3}$ on relative aggregate volume V/V_*; curve 1 – expression Eq. (19); curve 2 – diffusion limited growth rate for spherical droplet $G(V)\sim(V/V_*)^{1/3}$; dots – numerical solution Eqs. (15) and (4).

value $f(1)=1$, in the limit $c\to 0$ ($a\gg b$) the divergence law $f(c)=1/c^{2/3}|\ln c|\to\infty$ takes place (see Eq. (15). The function $f(c)$ is proportional to the growth rate dV/dt under the conditions of equality of other parameters. Hence, the more elongated aggregate grows more rapidly. It is the reasonably expected result which is caused by increasing of the aggregate surface during elongation. The dependence of the dimensionless growth rate $G(V)=(dV/dt)(3/4\pi)^{2/3}\varphi_{II}/3D\Delta V_*^{1/3}$ upon the aggregate volume is demonstrated in Fig. 3. Here the dots represent Eq. (15) with account of interrelation between aggregate volume V and the semiaxes ratio c.

In order to get the explicit form of dV/dt as function of V it is convenient to use the asymptotic expansion:

$$z-\ln z=y,\quad y\to\infty,\quad z(y)\approx y\left(1+\frac{\ln y}{y}+\cdots\right). \tag{16}$$

After evident calculations we obtain from Eq. (4):

$$c=c(V)\approx c_*\left(\frac{V_*}{V}\right)^{1/7}\left[\frac{\ln(V_*/B)}{\ln(V/B)}\right]^{3/7}, \tag{17}$$

where B is determined in Eq. (4), and c_* is the semiaxes ratio of the aggregate with critical volume V_*. Eq. (17) may be simplified by taking into account that the order of value of ratio V_*/B is about 10^7 (see Eq. (4)). Then we may write:

$$\left[\frac{\ln(V_*/B)}{\ln(V/B)}\right]^{\lambda}\approx 1+\frac{V-V_*}{V_*}\frac{(-\lambda)}{\ln(V_*/B)}+\cdots\approx\left(\frac{V}{V_*}\right)^{-\lambda/\ln(V_*/B)}, \tag{18}$$

$$0<\lambda\sim 1,\quad \ln(V_*/B)\gg 1,\quad 0<\frac{\lambda}{\ln(V_*/B)}\ll 1.$$

By using the approximations of Eqs. (17) and (18) we obtain from Eq. (15):

$$G(V)=\frac{dV}{dt}\left(\frac{3}{4\pi}\right)^{2/3}\frac{\varphi_{\mathrm{II}}}{3D\Delta V_*^{1/3}}=\frac{V^{1/3}-V_*^{1/3}}{c_*^{2/3}|\ln(c_*/2)|V_*^{1/3}}\left(\frac{V}{V_*}\right)^{\beta-1/3}, \tag{19}$$

$$\beta=\frac{3}{7}-\frac{5}{7\ln(V_*/B)}-\frac{\ln 2}{\ln(c_*/2)\ln(V_*/B)}.$$

The accuracy of the expression for growth rate, Eq. (19), may be estimated from Fig. 3 (curve 1 and dots), for the values $V/V_*\leqslant 10^4$ the relative error does not exceed 5%. The curve 3 (Fig. 3) presents the classical growth rate of a spherical droplet $G(V)\sim(V/V_*)^{1/3}$. The rather convenient expression, Eq. (19), allows to be integrated in order to analyse in explicit form the aggregate volume evolution with respect to time, $V(t)$.

6. Nucleation kinetics

Shift in the magnetic fluid free energy ΔF caused by the origination of a new phase nucleus may be written as follows [27]:

$$\Delta F=\int\limits_{V_0-V}\left[f_1(\varphi_1,H_1)+\frac{1}{2}M_1(H_1-H_0)\right]dV + \int\limits_{V}\left[f_2(\varphi_2,H_2)+\frac{1}{2}M_2(H_2-H_0)\right]dV-f_1(\varphi_\infty,H_0)V_0+\sigma S, \tag{20}$$

where f is a free energy density, and V_0 is a total volume of a metastable system. In the case of high-elongated aggregate by using the assumption $H_1\approx H_2\approx H_0$ (Sections 4 and 5) we get the expression for minimal work of nucleus formation [24,26,27]:

$$A=\frac{\varphi_{\mathrm{II}}}{v}V\cdot[v_2(\varphi_{\mathrm{II}},H_0)-v_1(\varphi_1,H_0)]+\sigma S. \tag{21}$$

Expanding the chemical potential of low-concentrated phase $v_1(\varphi_1)$ in Taylor series near the point $\varphi_1=\varphi_{\mathrm{I}}$ and taking into account the equilibrium conditions, Eq. (1), we obtain:

$$A\approx -V\frac{\varphi_{\mathrm{II}}}{\varphi_{\mathrm{I}}}\frac{kT}{v}\Delta+\sigma\kappa(c)V^{2/3}, \tag{22}$$

where $\kappa(c)=S/V^{2/3}$. The microaggregate will be at quasi equilibrium if the equality $\partial A/\partial V=0$ holds true. Hence this equality leads to the expression:

$$V_*^{1/3}=\frac{2}{3}\frac{v}{kT}\frac{\varphi_{\mathrm{I}}}{\varphi_{\mathrm{II}}}\frac{\sigma\kappa(c_*)}{\Delta}. \tag{23}$$

Eqs. (23) and (4) allow us to calculate the volume of critical nucleus V_* and corresponding ratio of ellipsoid semiaxes c_*.

A separating magnetic fluid is characterized by the following typical values of parameters:
– ferroparticle diameter $d\sim$10–20 nm;
– interfacial tension $\sigma\sim$5–10 $\times 10^{-4}$ erg/cm^2 [6,7,9,29–31];
– external field strength $H_0\sim$10–100 Oe;
– volume concentrations of coexisting phases $\varphi_{\mathrm{I}}\sim$0.01–0.05, $\varphi_{\mathrm{II}}\sim$0.2–0.4;
– magnetic permeabilities of phases $\mu_{\mathrm{I}}\sim$1–2, $\mu_{\mathrm{II}}\sim$20–40 [7,34];
– temperature $T\approx 300$ K.

Thus, for real degrees of supersaturation $\Delta\sim 10^{-2}$ we obtain the values of critical nucleus volume $V_*\sim$100–1000v and the semiaxes ratio $c_*\sim$0.04–0.07. The critical aggregate contains several tens or hundreds of ferroparticles and is high elongated ($c_*\ll 1$). It should be noted that the critical volume is a drastically decreasing function of a magnetic field strength.

Eqs. (23) and (14) must evidently lead to coinciding values of critical volume V_*. Doing so the effective averaged parameter $\bar{\sigma}$, Eq. (7), may be determined:

$$\bar{\sigma}=\bar{\sigma}(c)=\frac{2}{3}\frac{v}{kT}\frac{\varphi_{\mathrm{I}}}{\varphi_{\mathrm{II}}}\frac{\sigma\kappa(c)}{U}\,. \tag{24}$$

By expanding $A(V^{1/3})$ in Taylor series near the point $V^{1/3}=V_*^{1/3}$ we obtain, accurately to terms of the second order in the supersaturation inclusively, an expression

$$A\approx\frac{\sigma\kappa(c_*)}{3}V_*^{2/3}-\sigma\kappa(c_*)(V^{1/3}-V_*^{1/3})^2+\cdots \tag{25}$$

for the minimal work necessary to form a nucleus which differs from the classical one by the presence of $\kappa(c_*)$. The latter represents the slow function of V_*.

Eq. (25) strikingly resembles a familiar expression of the classical Zel'dovich's theory of nucleation [27]. When building on this relation, both the spontaneous origination of initial nuclei and the probability of their passing over the critical barrier of potential can be treated quite similar to the treatment specific to molecular systems. Omitting standard particulars of the calculation, we are able to write a conclusive expression of the nucleation rate as [24,27]

$$J=C\frac{\varphi_{\mathrm{I}}\varphi_{\mathrm{II}}}{v^2}\left(\frac{kT}{\sigma\kappa(c_*)}\right)^{1/2}\lim_{V\to V_*}\left(\frac{1}{V^{1/3}-V_*^{1/3}}\frac{dV}{dt}\right)\exp\left(-\frac{\sigma\kappa(c_*)}{3}V_*^{2/3}\right), \tag{26}$$

C being a numerical coefficient which could not be expressed in terms of macroscopical variables and parameters in principle. Eq. (26) defines the mean number of supercritical nuclei arising during unit time per unit volume of a magnetic fluid and is subject to the common restrictions characteristic to the theory of generation of stable molecular nuclei of a new phase by Zel'dovich. Eq. (26) is of importance in that it reveals the very character of dependence of the nucleation rate upon all the relevant parameters. The dependence happens to be essentially the same as that for molecular systems in the absence of external field. As in the last case, this formula is of logarithmic accuracy

since the factor cannot be expressed through macroscopic parameters and so remains undeterminable. It is obvious, nevertheless, that an influence of the supersaturation on nucleation rate is governed by exponential factor:

$$J \sim \Delta \exp[-E(\Delta)], \qquad E(\Delta) = -\frac{4}{27}\left[\frac{\sigma\kappa(c_*)}{kT}\right]^3 \left(\frac{\varphi_{\mathrm{I}} v}{\varphi_{\mathrm{II}}\Delta}\right)^2,$$

$$\kappa(c_*)^3 \approx \frac{9\pi^4}{16 c_*}, \quad c_* \ll 1, \tag{27}$$

where the physical meaning of E is that of a relative activation energy of the formation of a single critical nucleus referred to actual supersaturation. In the case of spherical nuclei $\kappa(c_*) = (36\pi)^{1/3}$ the nucleation rate of Eq. (26) becomes the classical one. Using the typical values of parameters in Eq. (26) gives us the order of value of activation energy $E \sim 10$–50. Taking into account the dependences of $\varphi_{\mathrm{I}}, \varphi_{\mathrm{II}}, c_*$ on magnetic field H_0, the analysis of Eq. (10) comes to the conclusion that nucleation rate J increases sharply under the strengthening of an external field. In other words the process of phase separation in magnetic fluids goes on more rapidly in the presence of higher magnetic field. This result is confirmed by all known experimental evidences [4–9,12].

7. Discussion

Eqs. (15) and (19) for the aggregate growth rate dV/dt, Eq. (23) for the critical nucleus volume V_* and Eqs. (26) and (27) for the nucleation rate J completely describe the kinetics of the phase separation process at the nucleation stage. In order to illustrate the results obtained we choose the following parameters as meaningful representatives of properties of the nucleation process in magnetic fluids. First, the nucleation rate is determined for the greatest part by a dimensionless activation energy E (see Eq. (27)) which offers an effective height of the potential barrier to be overcome by a nucleus to ensure its subsequent growth. Second, a dimensionless volume V_*/v and semiaxes ratio c_* of the critical microaggregate as well as the total number of particles N_* being contained in that microaggregate are of great significance. These parameters depend, above all, upon the supersaturation $\Delta_0 = \varphi_0 - \varphi_{\mathrm{I}}$ of the original magnetic fluid.

Dependence of the parameters mentioned on the external field strength H_0 is presented in Table 1. Equilibrium concentrations φ_{I} and φ_{II} of co-existing ferrocolloidal phases were determined for various H_0 on the basis of 1st order hard sphere perturbation theory (see Refs. [18,21] and Eq. (1)). For given initial concentration (e.g., $\varphi_0 = 0.045$) strengthening of a magnetic field leads to an appreciable increase in supersaturation (see Fig. 1). Respectively, the critical volume, number of particles per critical aggregate and activation energy provide the sharply decreasing functions of an external field strength. This is fully understandable because a magnetic field strengthening means an increase in the degree of metastability of the parent magnetic fluid which tends to lowering of the volume of critical nucleus and rising of the probability of its formation. Nevertheless, the height of the energy barrier is such as to yield rather large

Table 1
Dimensionless activation energy E, number of particles per critical aggregate N_*, critical value of aggregate volume V_* related to ferroparticle volume v, semiaxes ratio for critical aggregate c_* as functions of external field strength H_0 for a magnetic fluid with initial volume concentration $\varphi_0 = 0.045$ and interparticle interaction parameter $\gamma = 2.77$; equilibrium concentrations φ_{I} and φ_{II} are also shown

H_0 (Oe)	φ_{I}	φ_{II}	Δ	c_*	V_*/v	N_*	E
51	0.038	0.264	0.007	0.046	5.1×10^3	1.3×10^3	128
53	0.035	0.270	0.010	0.052	1.8×10^3	489	65.7
55	0.032	0.275	0.013	0.055	839	231	40.7
57	0.030	0.280	0.015	0.057	454	127	28.1
60	0.028	0.287	0.017	0.058	220	63	18.3
65	0.024	0.299	0.021	0.059	83	0	10.5
70	0.022	0.307	0.023	0.059	45	14	7.3

values of E at reasonable supersaturations. It is worth noting that this inference will be rather useful in the studying of the intermediate stage of phase separation process since the inequality $E \gg 1$ permits mighty asymptotic methods to be employed in calculations. Both V_*/v and N_* are also large compared with unity so that the critical microaggregate contains tens or hundreds of particles when the supersaturation is sufficiently low.

The validity of the developed theory is somewhat restricted by certain underlying conditions imposed on characteristic time scales of involved processed as well as on the sizes of aggregates and nuclei which might be considered on a basis of classical thermodynamics. These conditions and ensuing restrictions are essentially the same as those in the theory of nucleation in molecular systems and, thereby, it is hardly worth discussing them in this paper. We would like, nonetheless, to place emphasis upon the most serious requirement that the critical nucleus should be sufficiently large to be regarded both as a macroscopic object liable to be explored with the help of conventional methods of classical thermodynamics and as a high-elongated ellipsoid with semiaxes ratio $c_* \ll 1$ (see table). The last requirement is surely fulfilled for magnetic fluid, save for a region of scarcely probable supersaturations.

In the opposite case of very high relative supersaturation, only a few particles suffice to originate the critical nucleus, and the above methods are not likely to be appreciable without appropriate modification. In this case, methods founded on an analysis of the kinetics of the attachment of new particles apparently have to be used and the fractal nature of clusters and the resulting microaggregates ought to be accounted for.

In the next paper the authors intend to consider the subsequent evolution of the assemblage of supercritical aggregates when the degree of metastability of the parent ferrocolloid can no longer be thought of as invariable and independent of the assemblage history.

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