

Kinetics of a magnetic fluid phase separation induced by an external magnetic field

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We study the processes of nucleation and subsequent evolution of a system of droplike aggregates suspended in a macroscopically homogeneous magnetic fluid made metastable by strengthening of an external magnetic field. The growing aggregates are highly elongated ellipsoidal shaped and are distributed over volume. Expressions for the growth rate of an aggregate, the critical nucleus volume, and the nucleation rate have been obtained. The aggregate distribution density is governed by a kinetic equation with neglect of fluctuations in the growth rate of a single aggregate. The approximate solutions for supersaturation and diverse characteristics of the distribution density have been found as functions of time. The kinetics of evolution of a system of ellipsoidal aggregates in the presence of a magnetic field differs essentially from the corresponding kinetics of a system of spherical droplets. [S1063-651X(97)13605-4]

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I. INTRODUCTION

Magnetic fluids (ferrofluids, ferrocolloids), stable colloidal suspensions of the one-domain particles of ferro- and ferrimagnetic materials in liquids, offer unique properties [1–3] that have attracted the attention of researchers. The small sizes of dispersed ferroparticles (diameter $d \sim 10$ nm) provide the particles with an inherent magnetic moment m of the constant value. The stabilization of suspension is usually obtained by coating the magnetic grains with a surfactant layer which allows us to neglect the influence of the 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 latter interaction is responsible for the phase separation of magnetic fluids [4–9], accompanied by the existence of droplike aggregates. These aggregates can be considered as fluids [6,7,9] with an interfacial tension surface, representing, essentially, 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 viewpoint of statistical mechanics the existence of droplike aggregates may be considered as a result of the violation of thermodynamic stability in a system of dispersed particles that leads to their condensation [10,11]. Therefore, phase separation in magnetic fluids is treated further as a first order phase transition of the “colloidal gas — colloidal liquid” type. Two main reasons for the separation of colloidal systems are known [9–12], a decrease in temperature or an increase in electrolyte concentration in ionic stabilized dispersions. In magnetic fluids still another type of phase separation is experimentally observed: phase separation in a magnetic field [4–8] under isothermal conditions. In this case, at equilibrium conditions, a uniform magnetic field increase is equivalent to an effective temperature lowering. Such phenomenon looks like a nontrivial phase transition of the condensation type, induced by an external magnetic field.

In principle, existing statistical thermodynamic models of

magnetic fluids [13–20] have demonstrated that, in a system of particles interacting through a noncentral 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 (i.e., on the diameters of the magnetic cores). This is associated with the fact that a noncentral dipole-dipole interaction of magnetic moments of particles displays itself on the whole as an effective interparticle attraction. In a uniform external field this effective attraction strengthens [16–18,20], thus a magnetic field stimulates the process of phase separation in magnetic fluids. The equilibrium phase diagrams of ferrocolloids, under the conditions of such a magnetic field induced phase separation, were experimentally studied in Refs. [6–8,21,22] and theoretically calculated in Refs. [16–18,20]. It was shown that even weak and moderate external fields (~ 30 – 300 Oe) may result in the break of the thermodynamic stability of a ferrocolloid. During the phase separation under the presence of a magnetic field the occurring droplike aggregates are spindle shaped and stretched along the external field direction.

In the present research we should focus our attention on the problem of the theoretical description of the kinetic process of ferrocolloid phase separation from a metastable state induced by a uniform magnetic field. The break of thermodynamic stability of a magnetic fluid is followed by the origination of critical nuclei of a new phase, by their transformation into macroscopic droplike aggregates and by the ensuing growth of those aggregates in a metastable environment.

As far as nucleation is concerned, a relevant theory can be put forward by following common trends specific to the theory of nucleation in molecular systems [23]. Recently such a theory has been worked out for colloids in Ref. [24]. The nucleation kinetics essentially depend on the shape of emerging nuclei. An analysis, presented in Sec. II, shows that even in weak magnetic fields the shape of a droplike aggregate with good accuracy may be approximated by a highly elongated ellipsoid of revolution, the elongation of which is dependent on the aggregate volume. The aggregate growth rate, in a supersaturated ferrocolloidal environment,

is determined in Sec. III under the assumption that this growth is limited by a diffusional transport of ferroparticles to the aggregate surface. On the basis of the classical Volmer-Frenkel-Zel'dovich nucleation theory in Sec. IV, the expressions for the nucleation rate and the critical aggregate volume are obtained.

The necessity of allowing simultaneously for the nucleation and the growth of new phase elements has been acknowledged in Refs. [25,26]. Such 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 magnetic fluid, is covered by the so-called intermediate stage of phase transition. 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 that of the gradual reducing of metastability by the growing aggregates [27,28]. Proposed in Ref. [28] a method for solving the problem has been applied to study the evolution of spherical droplike aggregates in colloids [29] in the absence of the external field. A similar approach, based on the analysis of the kinetic equation for volume distribution function of highly elongated ellipsoidal aggregates, is used in Sec. V–IX. An integral equation, describing the metastability reduction with time, is obtained in Sec. VI and approximately solved in Sec. VII. The evolution of the integral characteristics of the aggregate system and of the aggregate distribution function are investigated in Secs. VIII and IX, respectively.

We shall consider a sterically stabilized magnetic fluid containing identical spherical ferroparticles, suspended in a neutral liquid carrier. The ferrocolloid is supposed to be thermodynamically stable in the absence of a magnetic field. But if a weak uniform external magnetic field \mathbf{H}_0 is present, a macroscopically homogeneous state of the magnetic fluid becomes unstable and, as a consequence, the magnetic fluid with the initial volume particle concentration φ_0 is bound to be separated into two homogeneous phases characterized by the equilibrium values φ_I and φ_{II} of the concentration ($\varphi_I < \varphi_{II}$). At the thermodynamic equilibrium state the co-existing phases are separated by a plane interfacial surface which is parallel to an external field.

In what follows, we are going to study the kinetics of phase separation of a dilute magnetic fluid ($\varphi_0 \ll 1$). In so doing, the inequality for concentrations φ_I and φ_{II} is valid ($\varphi_I < \varphi_0 \ll \varphi_{II}$). Hence, the magnetization M_I of the low concentrated phase may be neglected as compared with the magnetization M_{II} of the high concentrated phase ($M_{II} \gg M_I$). In closing, we shall consider the separation in a weak magnetic field, so the ferrocolloid magnetization is directly proportional to the field strength.

II. QUASIEQUILIBRIUM SHAPE OF DROPLIKE AGGREGATE

Let us consider a single droplike aggregate placed in a magnetic fluid under separation conditions. 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 the aggregate with a given volume V may be deter-

mined under the conditions of its energy minimum. Experimental studies [6,7,30] and theoretical analyses [31] have demonstrated that the magnetic fluid drop in an external field is spindle shaped. A simple ellipsoidal approximation also shows good agreement with experimental observations [6,7,30] in weak-to-moderate magnetic fields.

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 the aggregate surface S and the 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. [30–32]). However, this dependence reveals at large strength of an external field in the vicinity of the saturation magnetization of magnetic fluid (Ref. [30]). Therefore, parameter σ will be treated as an effective interfacial tension which remains constant along the surface of the droplike aggregate

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

Here $c = b/a$ is the ratio between the 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 μ_I ($\mu_{II} \gg \mu_I$). The internal magnetic field H_2 is uniform in the case of the ellipsoidal shape of the volume V . Thus for the energy F_m we obtain, according to Ref. [33],

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

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

where n is the demagnetization factor.

In the quasiequilibrium state the aggregate shape may be determined under the condition of minimization of total energy with respect to semiaxis ratio $c: d(F_s + F_m)/dc = 0$. The rather complicated expression of quasiequilibrium shape factor c upon the dimensionless magnetic field and aggregate volume is presented in Ref. [30]. The distinctive feature of this expression is the occurrence of hysteresis loops [6,7] on the curves $c(V)$ in the case of a sufficiently large value of $\mu_{II}(\mu_{II}/\mu_I > 20)$. In this area the magnetic fluid drop undergoes a jumplike elongation, the main features of such a process have been experimentally studied in Refs. [6,7,30]. The analysis of the dependence $c(V)$ shows that the ellipsoidal drop becomes highly elongated ($a \gg b$, $c \ll 1$) if the combination $H_0 V^{1/6} \sigma^{1/2}$ exceeds a certain value which is approximately equal to 1. Thus, for typical values of interfacial tension $\sigma \sim 10^{-4}$ erg/cm² [6,7,30] and weak magnetic fields $H_0 \sim 10$ Oe we obtain the volume $V \sim 1 - 10 \times 10^{-18}$ cm³. The latter is of the order of the ferroparticle volume v ($d \sim 10$ nm, $v \sim 10^3$ nm³). In consequence, the droplike aggregates in the magnetic fluid may be regarded as highly

elongated ellipsoids of revolution. In so doing, the relationship between aggregate volume V and semiaxis ratio c takes the simple asymptotic form

$$V \approx \frac{B}{c^7 |\ln c|^3}, \quad B \equiv \frac{4\pi^7 \sigma^3}{3H_0^6} \frac{\mu_I^3}{(\mu_{II} - \mu_I)^6}, \quad c \ll 1, \quad V \gg B. \quad (3)$$

One can see from asymptotic equation (3) that a large increase of aggregate volume V is accompanied with a small decrease of ratio c .

III. A MODEL OF THE GROWTH OF AGGREGATES

Because the potential barrier preventing a new particle from adhering to an aggregate is hardly expected to be large, the growth of the aggregate with volume particle concentration φ_2 is likely to be limited by the rate of the diffusional transport of particles to the aggregate surface. Then

$$\varphi_2 \frac{dV}{dt} = - \int_S \mathbf{j} \cdot d\mathbf{s}, \quad (4)$$

where \mathbf{j} is the ferroparticle flux density in the metastable phase. The characteristic time for establishing a stationary concentration field in the vicinity of the growing aggregate is evidently much less than the time required to change the aggregate volume substantially. This means that the ferroparticles diffusion can be considered in the quasistationary approximation

$$\operatorname{div} \mathbf{j} = 0, \quad \mathbf{j} = -D(\nabla \varphi + \varphi \nabla u), \quad \varphi|_{\infty} = \varphi_{\infty}, \quad \varphi|_S = \varphi_1, \quad (5)$$

$$D = \frac{kT}{3\pi\eta d}, \quad u = -\ln \frac{\sinh(\alpha_1)}{\alpha_1}, \quad \alpha_1 = \frac{mH_1}{kT},$$

where η stands for the viscosity of the pure matrix liquid, D is the coefficient of mutual Brownian diffusion of the particles down a concentration gradient, 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 ukT is dependent on a local value of magnetic field strength H_1 in low concentration phase, and $-D\varphi\nabla u$ is the particle flux density caused by the inhomogeneities of magnetic field H_1 .

The boundary condition at the aggregate surface contains the quasiequilibrium concentration φ_1 of the diluted phase in the vicinity of the aggregate. This concentration can be determined with the help of the conditions of chemical and mechanical equilibrium of the aggregate when both the bubble and the magnetic pressures are taken into account

$$\nu(\varphi_1) = \nu(\varphi_2), \quad P(\varphi_1) + \sigma K = P(\varphi_2) + 2\pi M_{2n}^2. \quad (6)$$

Here the ferroparticle chemical potential ν and osmotic pressure P are regarded as functions of the concentration φ of the particles by volume, K is the curvature of the interface, and M_{2n} is the normal to the surface component of magnetization in high concentration ferrocolloidal phase.

The corresponding magnetization component in the low concentration phase M_{1n} can 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 Eqs. (6) let us make some obvious assumptions. The ellipsoid elongation coincides with the direction of magnetization vector \mathbf{M}_2 . Therefore, in the case of the highly elongated aggregate, the contribution of the normal to the surface component M_{2n} to the mechanical equilibrium condition (6), as a first approximation, may be considered as negligibly small. This approximation breaks down near the tips of the droplet where the lines of a local magnetic field are modified. But the estimation given below shows that the tip areas make the contribution to the aggregate growth rate of the order of $c \ll 1$. And so, the aggregate growth is controlled mainly by the ferroparticle absorption on the ellipsoid side surface.

By taking for granted that the concentration shifts due to the interface curvature are relatively small, $|\delta\varphi_1| = |\varphi_1 - \varphi_I| < \varphi_I$, $|\delta\varphi_2| = |\varphi_2 - \varphi_{II}| \ll \varphi_{II}$, and by carrying out an averaging procedure over the interface, we arrive at a set of linear algebraic equations to find the concentration shifts. Making simple calculations we obtain the expressions for quasiequilibrium averaged concentrations φ_1 and φ_2 which are constant along the aggregate surface and can be used in the boundary problem (5)

$$\varphi_1 = \varphi_I + \frac{\bar{\sigma}U}{\sqrt{V^3}}, \quad \varphi_2 \approx \varphi_{II},$$

$$U \equiv \frac{\partial \nu / \partial \varphi_{II}}{(\partial P / \partial \varphi_{II})(\partial \nu / \partial \varphi_I) - (\partial P / \partial \varphi_I)(\partial \nu / \partial \varphi_{II})}. \quad (7)$$

Here $\bar{\sigma}$ is an effective parameter which appears in Eqs. (6) during averaging procedure over the interface, this parameter will be determined later.

Due to the ellipsoidal shape of the aggregate it is convenient to solve the boundary problem (5) with the help of ellipsoidal coordinates [33,34]. Then let us analyze this problem taking the highly elongated shape of the aggregate into account. In this case the magnetic field inside the aggregate approximately equals to the external field $H_2 \approx H_0$. According to this, the magnetic field outside the aggregate is also approximately equal to the external one $H_1 \approx H_0$ on an average. In the vicinity of the ellipsoid side surface a magnetic field is approximately constant ($\alpha_1 \approx \text{const}$), 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 $j_D \sim D\varphi_{\infty}/b$. The total diffusion flux on the ellipsoid side surface $I_D \sim abj_D \sim D\varphi_{\infty}a$. "Convective" flux density is detectable 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 the highly elongated aggregate, the strong inequality $I_D \gg I_{\alpha}$ holds true. On the basis of such an assumption the magnetic convective flux $-D\varphi\nabla u$ allows itself 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 the familiar differential equation for determining the concentration profile in the vicinity of an

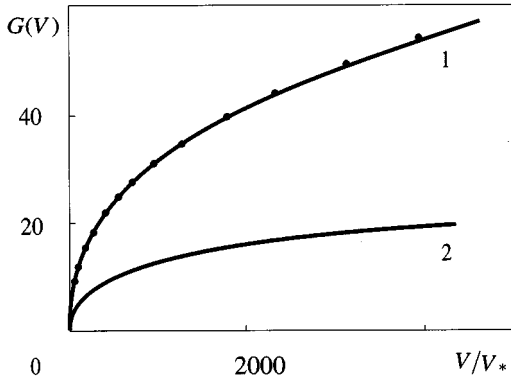


FIG. 1. Dependence of the dimensionless aggregate growth rate $G(V) = (dV/dt)(3/4\pi)^{2/3}\varphi_{II}/3D\Delta V_*^{1/3}$ on relative aggregate volume V/V_* : curve 1, expression (11); curve 2, diffusion limited growth rate for spherical droplet $G(V) \sim (V/V_*)^{1/3}$; dots, numerical solution of Eqs. (8) and (3).

aggregate. This equation is similar to the problem of a dielectric ellipsoid placed in an electric field [33]. By using the solution from Ref. [33] and Eqs. (7) we get the growth rate of a highly elongated ellipsoidal aggregate

$$\varphi_{II} \frac{dV}{dt} = 3 \left(\frac{4\pi}{3} \right)^{2/3} D \frac{V^{1/3} - V_*^{1/3}}{c^{2/3} |\ln c|} \Delta, \quad V_*^{1/3} = \frac{\bar{\sigma}U}{\varphi_\infty - \varphi_I}, \quad c \ll 1. \quad (8)$$

Here the parameter V_* means the critical volume of the aggregate nucleus, in the case $V > V_*$ the aggregate grows, otherwise $V < V_*$ the aggregate recedes. The quantity $\Delta = \varphi_\infty - \varphi_I$ plays the role of the absolute supersaturation of the parent magnetic fluid.

The diffusion limited growth rate of an ellipsoidal aggregate (8) differs from the well-known classical growth rate of a spherical droplet [24,35] by the presence of function $f(c)$ dependent on the semiaxis ratio. In the case $c=1$ ($a=b$, sphere) this function must get the value $f(1)=1$, in the limit $c \rightarrow 0$ ($a \gg b$) the divergence law $f(c) = 1/c^{2/3} |\ln c| \rightarrow \infty$ takes place [see expression (8)]. 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 aggregate volume is demonstrated in the Fig. 1. Here the dots present expression (8) with an account of the interrelation between aggregate volume V and semiaxis ratio c given by formulas (3).

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

$$z - \ln z = y, \quad y \rightarrow \infty, \quad z(y) \approx y \left(1 + \frac{\ln y}{y} + \dots \right). \quad (9)$$

After evident calculations we obtain from Eq. (3)

$$c = c(V) \approx c_* \left(\frac{V}{V_*} \right)^{1/7} \left[\frac{\ln(V_*/B)}{\ln(V/B)} \right]^{3/7}, \quad (10)$$

where B is determined in Eq. (3), and c_* is the semiaxis ratio of the aggregate with critical volume V_* . Expression (10) may be simplified by taking into account that the order of the value of ratio V_*/B is about 10^7 [see Eq. (3)]. Then we may expand function $c(V)$ from Eq. (10) into the power series over V_*/V . Ultimately, we obtain from Eqs. (8) and (10)

$$G(V) \equiv \frac{dV}{dt} \left(\frac{3}{4\pi} \right)^{2/3} \frac{\varphi_{II}}{3D\Delta V_*^{1/3}} = \frac{V^{1/3} - V_*^{1/3}}{c_*^{2/3} |\ln(c_*/2)| V_*^{1/3}} \left(\frac{V}{V_*} \right)^{\beta-1/3}, \quad (11)$$

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

$$\ln(V_*/B) \gg 1.$$

The accuracy of the expression for growth rate (11) may be estimated from Fig. 1 (curve 1 and dots), for the values $V/V_* \leq 10^4$ the relative error does not exceed 5%. Curve 2 (Fig. 1) presents the classical growth rate of a spherical droplet $G(V) \sim (V/V_*)^{1/3}$. The rather convenient expression (11) allows itself to be integrated in order to analyze in explicit form the aggregate volume evolution with respect to time $V(t)$.

IV. NUCLEATION KINETICS

A shift in the magnetic fluid free energy ΔF , caused by the presence of a new phase nucleus, may be written as follows [33,35]:

$$\Delta F = \int_{V_0-V} \left[f_1(\varphi_1, H_1) + \frac{1}{2} M_1(H_1 - H_0) \right] dV + \int_V \left[f_2(\varphi_2, H_2) + \frac{1}{2} M_2(H_2 - H_0) \right] dV - f_1(\varphi_\infty, H_0) V_0 + \sigma S, \quad (12)$$

where f is a free energy density, and V_0 is the total volume of a metastable system. In the case of a highly elongated aggregate, by using the assumption $H_1 \approx H_2 \approx H_0$ (Sec. III), we get the expression for minimal work of nucleus formation [24,35]

$$A \approx -V \frac{\varphi_{II}}{\varphi_I} \frac{kT}{v} \Delta + \sigma \kappa(c) V^{2/3}, \quad (13)$$

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 for critical volume

$$V_*^{1/3} = \frac{2}{3} \frac{v}{kT} \frac{\varphi_I}{\varphi_{II}} \frac{\sigma \kappa(c_*)}{\Delta}. \quad (14)$$

Equations (14) and (3) allow us to calculate the volume of critical nucleus V_* and corresponding ratio of ellipsoid semiaxis c_* .

A separating magnetic fluid is characterized by the following typical values of parameters: ferroparticle diameter $d \sim 10\text{--}20$ nm; interfacial tension $\sigma \sim (5\text{--}10) \times 10^{-4}$ erg/cm² [6,7,9,30–32]; external field strength $H_0 \sim 10\text{--}100$ Oe; volume concentrations of coexisting phases $\varphi_I \sim 0.01\text{--}0.05$, $\varphi_{II} \sim 0.2\text{--}0.4$; magnetic permeabilities of phases $\mu_I \sim 1\text{--}2$, $\mu_{II} \sim 20\text{--}40$ [7,20,36]; and temperature $T \approx 300$ K.

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

Expressions (14) and (8) must evidently lead to coinciding values of critical volume V_* . Doing so, the effective averaged parameter $\bar{\sigma}$ (7) may be determined. By expanding $A(V^{1/3})$ in Taylor a 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

$$A \approx \frac{\sigma \kappa(c_*)}{3} V_*^{2/3} - \sigma \kappa(c_*) (V^{1/3} - V_*^{1/3})^2 + \dots \quad (15)$$

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_* .

Equation (15) strikingly resembles a familiar expression of the classical Zel'dovich's theory of nucleation [35]. When building this relation, both spontaneous origination of initial nuclei and the probability of their passing over the critical potential barrier can be treated quite similarly to the treatment specific to molecular systems. Omitting standard calculation, we are able to write a conclusive expression of the nucleation rate as [24,35]

$$J = C \frac{\varphi_I \varphi_{II}}{v^2} \left(\frac{kT}{\sigma \kappa(c_*)} \right)^{1/2} \lim_{v \rightarrow V_*} \left(\frac{1}{V^{1/3} - V_*^{1/3}} \frac{dV}{dt} \right) \times \exp \left(- \frac{\sigma \kappa(c_*)}{3} V_*^{2/3} \right), \quad (16)$$

C being a numerical coefficient which could not be expressed in terms of macroscopical variables and parameters in principle. Formula (16) 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 of the theory of generation of stable molecular nuclei of a new phase by Zel'dovich. 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 the influence of the supersaturation on the nucleation rate is controlled by an exponential factor

$$J \sim \Delta \exp[-E(\Delta)], \quad E(\Delta) = \frac{4}{27} \left[\frac{\sigma \kappa(c_*)}{kT} \right]^3 \left(\frac{\varphi_I v}{\varphi_{II} \Delta} \right)^2, \quad (17)$$

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

where the physical meaning of E is that of a relative activation energy for the formation of a single critical nucleus referred to the actual supersaturation. In the case of spherical nuclei $\kappa(c_*) = (36\pi)^{1/3}$ the nucleation rate (17) becomes the classical one. Using the typical values of parameters in Eq. (17) gives us the order of value of activation energy $E \sim 10\text{--}50$. Taking into account the dependences of $\varphi_I, \varphi_{II}, c_*$ on magnetic field H_0 , the analysis of Eq. (17) 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 a higher magnetic field. This result is confirmed by all known experimental evidences [4–9,21,22,30].

Expressions (8) and (11) for the aggregate growth rate dV/dt , Eq. (14) for the critical nucleus volume V_* and Eqs. (16) and (17) 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 largest part by a dimensionless activation energy E [see Eq. (17)] 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 semiaxis 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 initial supersaturation $\Delta_0 = \varphi_0 - \varphi_I$ of the original magnetic fluid.

Dependence of the mentioned parameters on the external field strength H_0 is presented in Table I. Equilibrium concentrations φ_I and φ_{II} of coexisting ferrocolloidal phases were determined for various H_0 on the basis of first-order hard sphere perturbation theory [17,18,20,36]. For given initial concentration (for example, $\varphi_0 = 0.045$) strengthening of a magnetic field leads to an appreciable increase in supersaturation. 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 lowers the volume of critical nucleus and raises the probability of its formation. Nevertheless, the height of the energy barrier is such as to yield rather large values of E at reasonable supersaturations. 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.

V. INTERMEDIATE STAGE: BASIC EQUATIONS

Let us next study the evolution of a system of droplike ellipsoidal aggregates suspended in a macroscopically homogeneous metastable magnetic fluid during 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 growing aggregates are distributed over volume and the distribution density $f(t, V)$ is governed by a kinetic equation

TABLE I. Dimensionless activation energy E , number of particles per critical aggregate N_* , critical value of aggregate volume V_* related to ferroparticle volume v , and semiaxis ratio for critical aggregate c_* as functions of external field strength H_0 for a magnetic fluid with initial volume concentration $\varphi_0=0.045$; equilibrium concentrations φ_I, φ_{II} and the corresponding values of the Langevin parameter $\alpha=mH_0/kT$ are also shown.

H_0 (Oe)	α	φ_I	φ_{II}	Δ	c_*	V_*/v	N_*	E
51	1.42	0.038	0.264	0.007	0.046	5.1×10^3	1.3×10^3	128
53	1.47	0.035	0.270	0.010	0.052	1.8×10^3	489	65.7
55	1.53	0.032	0.275	0.013	0.055	839	231	40.7
57	1.58	0.030	0.280	0.015	0.057	454	127	28.1
60	1.67	0.028	0.287	0.017	0.058	220	63	18.3
65	1.80	0.024	0.299	0.021	0.059	83	30	10.5
70	1.94	0.022	0.307	0.023	0.059	45	14	7.3

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V} \left(\frac{dV}{dt} f \right) = 0, \quad t > 0, \quad V > V_*, \quad (18)$$

under complete neglect of fluctuations of the diffusionaly controlled growth rate of a 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 and actual value of absolute supersaturation Δ has been the objective of Sec. III [see expressions (8) and (11)].

Initial and boundary conditions imposed upon physically meaningful solutions of Eq. (18) are of the form

$$\frac{dV}{dt} f|_{V=V_*} = J[\Delta(t)] = C\Delta(t) \exp \left[-E \frac{\Delta_0^2}{\Delta(t)^2} \right], \quad f(0, V) = 0. \quad (19)$$

The above representation of the nucleation rate J results from Sec. IV [see expression Eq. (17)]. Here $C \approx \text{const}$, Δ_0 is an initial value of the supersaturation, and $E \equiv E(\Delta_0)$ stands for the dimensionless activation energy referred to as initial supersaturation. The quantity E is commonly much larger than unity and depends on a magnetic field strength (see Table I).

In order to close the set of equations (18), (19), and (11), 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

$$\Delta(t) = \Delta_0 - \varphi_{II} \int_{V_*}^{\infty} V f(t, V) dV, \quad \Delta(0) = \Delta_0. \quad (20)$$

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 expression (11). 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 equations (18)–(20) and (11) includes only two external dimensionless 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 processes under study

$$V_0 = \left[\left(\frac{4\pi}{3} \right)^{2/3} \frac{D\Delta_0}{\varphi_{II} J_0 c_*^{2/3} |\ln(c_*/2)| V_*^{\beta-1/3}} \right]^{1/(2-\beta)}, \quad (21)$$

$$t_0 = \frac{1}{J_0 V_0}, \quad J_0 = J(\Delta_0).$$

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

$$F(\tau, s) = V_0^2 f(t, V), \quad s = \frac{V}{V_0}, \quad \tau = \frac{t}{t_0}, \quad \omega(\tau) = \frac{\Delta(t)}{\Delta_0}, \quad (22)$$

$$q = \frac{\varphi_{II}}{\Delta_0}.$$

Equations (18)–(20) and (11) in dimensionless variables (22) are

$$\frac{\partial F}{\partial \tau} + \omega(\tau) \frac{\partial}{\partial s} (F s^\beta) = 0, \quad \tau > 0, \quad s > 0, \quad \frac{ds}{d\tau} = s^\beta \omega(\tau), \quad (23)$$

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

$$\omega(\tau) = 1 - q \int_0^\infty s F(\tau, s) ds, \quad \omega(0) = 1. \quad (24)$$

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

VI. INTEGRAL EQUATION FOR THE SUPERSATURATION

Let us introduce the new functions

$$u(\tau, s) = s^\beta F(\tau, s), \quad \theta(\tau) = \int_0^\tau \omega(\tau') d\tau'. \quad (25)$$

From Eqs. (23) we get a boundary problem for $u(\tau, s)$ which can be solved with the help of a method of characteristics. This solution, satisfying the initial conditions, can be written in a form

$$F(\tau, s) = s^{-\beta} u(\theta(\tau) - y(s)) H(\theta(\tau) - y(s)),$$

$$y(s) = \int_0^s x^{-\beta} dx = \frac{s^{1-\beta}}{1-\beta}, \tag{26}$$

where $H(z)$ is the Heaviside step function, and the function $u(z)$ satisfies the boundary condition (23)

$$u[(\theta(\tau))] = \exp\{E[1 - \omega(\tau)^{-2}]\}. \tag{27}$$

The characteristics of the partial differential equation (23) gives us the value at a time τ of dimensionless volume $s(\tau, \xi)$ of an aggregate that appeared at a moment ξ

$$y[s(\tau, \xi)] = \frac{s(\tau, \xi)^{1-\beta}}{(1-\beta)} = \theta(\tau) - \theta(\xi),$$

$$s_m(\tau) = s(\tau, 0) = [(1-\beta)\theta(\tau)]^{1/(1-\beta)}. \tag{28}$$

Here $s_m(\tau)$ can be considered as a maximal volume of aggregates. In order to make use of Eqs. (26) and (27) we need to know a functional dependence of the dimensionless supersaturation $\omega(\tau)$ on the function $\theta(\tau)$ defined in Eq. (25). This dependence has to be found by means of substituting $F(\tau, s)$ Eq. (26) into the mass balance equation in Eq. (24). Changing the integration variable s to ζ according to Eq. (28)

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

$$s=0 \rightarrow \zeta = \theta(\tau), \quad s=s_m(\tau) \rightarrow \zeta=0,$$

and using Eqs. (27) and (28) we get an integral equation for the dimensionless supersaturation as a function of θ

$$\omega[(\theta(\tau))] = 1 - Q \int_0^{\theta(\tau)} [\theta(\tau) - \zeta]^{1/(1-\beta)} \times \exp\{E[1 - \omega(\zeta)^{-2}]\} d\zeta, \tag{29}$$

$$Q = q(1-\beta)^{1/(1-\beta)} \sim 5 - 10.$$

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

VII. KINETICS OF THE METASTABILITY REDUCTION

The supersaturation is governed by the strongly nonlinear functional integral equation given in Eq. (29), 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. (29), due to the fact that the dimensionless activation energy E of the critical nucleus formation is much larger than unity. Since the function $g(\tau)$ defined in Eq. (23) is negative, a sharply decreasing function shows up in that integrand, and this gives the opportunity to get an approximate solution. The same approach is common in the theory and has been developed using the iteration method in

Ref. [27] and Laplace's method in Refs. [28,29]. At small dimensionless times we get from Eq. (29) asymptotic estimates

$$\omega(\zeta) \approx 1, \quad g(\zeta) \approx 0, \quad \omega(\theta) \approx 1 - \frac{Q}{\delta} \theta^\delta,$$

$$\delta = \frac{2-\beta}{1-\beta} \approx \frac{11}{4}, \tag{30}$$

the region of validity of which is obvious: $\theta \ll (\delta/Q)^{1/\delta}$. The time dependence of $\omega(\tau)$ can be estimated by using the equality $\theta(\tau) \approx \tau$ following from Eq. (25) at small τ .

At sufficiently large θ an approximate solution of integral equation (29) 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 (23), $\exp[EG(\zeta)]$ is rapidly decreasing as ζ is growing. This shows that the main contribution to the integral in Eq. (29) is given by the nearest vicinity of the point $\zeta=0$, which permits expansion of the slowly changing function $(\theta-\zeta)^{1/(1-\beta)}$ in a Taylor series. Following [29] we get

$$\omega(\theta) = 1 - Q \int_0^\theta \left[\theta^{1/(1-\beta)} - \frac{1}{1-\beta} \theta^{\beta/(1-\beta)} \zeta + \dots \right] \times \exp[EG(\zeta)] d\zeta. \tag{31}$$

For the reasons given, the above integrals converge very quickly, which allows both the upper limit of integration to be put equal to infinity and small times asymptotics (30) to be used for $\omega(\zeta)$. Therefore, it is easy to obtain an approximate expression

$$\omega(\theta(\tau)) = 1 - \varepsilon_1 \theta(\tau)^\gamma + \varepsilon_2 \theta(\tau)^{\gamma-1} + \dots,$$

$$\gamma = 1/(1-\beta) \approx 7/4, \tag{32}$$

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

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

which is valid at sufficiently large times after the beginning of the evolution process. Coefficients ε_j can be approximately calculated with the help of the Eulerian γ function $\Gamma(z)$

$$\varepsilon_1 \approx \frac{Q}{\delta} \left(\frac{\delta}{2EQ} \right)^{1/\delta} \Gamma\left(\frac{1}{\delta}\right) \approx 0.99(E^{-4}Q^7)^{1/11} \sim 1 - 1.5, \tag{33}$$

$$\varepsilon_2 \approx \frac{Q\gamma}{\delta} \left(\frac{\delta}{2EQ} \right)^{2/\delta} \Gamma\left(\frac{2}{\delta}\right) \approx 0.95(E^{-8}Q^3)^{1/11} \sim 0.1 - 0.2.$$

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 Eqs. (31) and (32). The differential equation

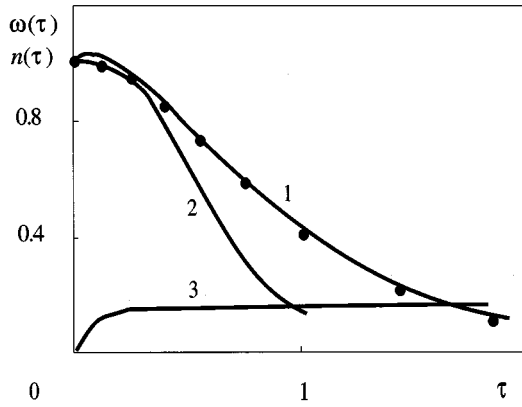


FIG. 2. Time dependence of the dimensionless supersaturation $\omega(\tau) = \Delta(t)/\Delta_0$ (curves 1, 2, and dots) and dimensionless aggregate concentration $n(\tau) = N(t)V_0$ (curve 3) for a metastable magnetic fluid characterized by the activation energy $E = 18.3$ (see Table I); dots, numerical solution of the integral equation (29); curve 1, approximate expressions (32)–(34); curve 2, small time asymptotics (30).

$d\theta(\tau)/d\tau = \omega(\theta)$ results from Eqs. (25) and (32). Its solution at the evident initial condition $\theta(0) = 0$ is

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

Asymptotics (32) and (34) are adequate at sufficiently large $\theta(\tau)$. A corresponding estimate gives the following restriction imposed on this function from below Eqs. (32) and (34) 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. (29) 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 the series in Eq. (32) 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 as τ goes to zero. This is due to violation of the necessary conditions of the transition from Eq. (31) to Eq. (32) and, in particular, ε_j cannot be regarded now as independent of τ . Allowance for such a dependence brings about a correct but somewhat cumbersome mathematical problem, instead of the one that has been studied.

The behavior of function $\omega(\tau)$ in conformity with approximate formulas (32)–(34) is demonstrated in Fig. 2. It agrees sufficiently well with results of an exact numerical solution of the integral equation in Eq. (29) which are shown in Fig. 2 by dots. This proves the above approximation to be reasonably correct. In compliance with the developed theory, the supersaturation entirely vanishes for a finite value θ_* that can be presented, by virtue of Eq. (34), through the approximate relation

$$\theta_* = \varepsilon_1^{-1/\gamma} + \frac{1}{\gamma} \frac{\varepsilon_2}{\varepsilon_1} + O\left(\left(\frac{\varepsilon_2}{\varepsilon_1}\right)^2\right). \quad (35)$$

This inference is surely inaccurate because it ignores the processes of particle redistribution between the aggregates, which have much in common with the coalescence and recondensation processes in two-phase molecular systems. The latter processes affect the final stage of the new phase formation in the molecular systems and the Ostwald ripening process in colloidal systems and should be accounted for during this late stage. A kinetic theory of Ostwald ripening in magnetic fluids represents an important but rather difficult problem. In many respects it is caused by the strong anisotropy of the droplike aggregates and the tip effects [5].

Equation (35) permits an estimate of the duration of the intermediate stage of phase transition studied here to be made as

$$\theta_m \approx \varepsilon_1^{-1/\gamma} = \varepsilon_1^{\beta-1} \approx \varepsilon_1^{-4/7} \approx (E^{16/77} Q^{-4/11}). \quad (36)$$

Values of τ_m corresponding to Eqs. (35) and (36) are to be found in accordance with the definition of θ in Eq. (25) and with allowance for the representation of $\omega(\tau)$ in Eq. (32).

VIII. INTEGRAL CHARACTERISTICS OF A SYSTEM OF AGGREGATES

The evolution of a system of growing aggregates can sometimes be described, with 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 $\langle s(\tau) \rangle$

$$n(\tau) = N(t)V_0 = \int_0^\infty F(\tau, s) ds = \int_0^{\theta(\tau)} \exp[EG(\zeta)] d\zeta, \quad (37)$$

$$\begin{aligned} \langle s(\tau) \rangle &= \frac{1}{n(\tau)} \int_0^\infty s F(\tau, s) ds \\ &= \frac{(1-\beta)^\gamma}{n(\tau)} \int_0^{\theta(\tau)} (\theta - \zeta)^\gamma \exp[EG(\zeta)] d\zeta, \end{aligned}$$

$n(\tau)$ being the number of aggregates within the volume V_0 . At small times we obtain, similarly to Eq. (30),

$$n(\tau) \approx \theta(\tau) \approx \tau \ll 1, \quad \langle s(\tau) \rangle \approx (1-\beta)^\gamma \theta(\tau)^\gamma / \delta. \quad (38)$$

At large times, when Eq. (32) is approximately valid, we have

$$n(\tau) \approx \left(\frac{\delta}{2EQ}\right)^{1/\delta} \frac{\Gamma(1/\delta)}{\delta} = \frac{\varepsilon_1}{Q} \approx 0.99(EQ)^{-4/11}, \quad (39)$$

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

where $\theta(\tau)$ is implicitly expressed in Eq. (34). These formulas are derived analogously to those in the preceding section.

Dependence on the dimensionless time of $n(\tau)$ is shown also in Fig. 2. It can be seen that $n(\tau)$ becomes practically constant and coincides with its asymptotic value in Eq. (39) after a rather short period of time. This is easy to understand because the nucleation rate represents a sharply increasing exponential function of the supersaturation and becomes

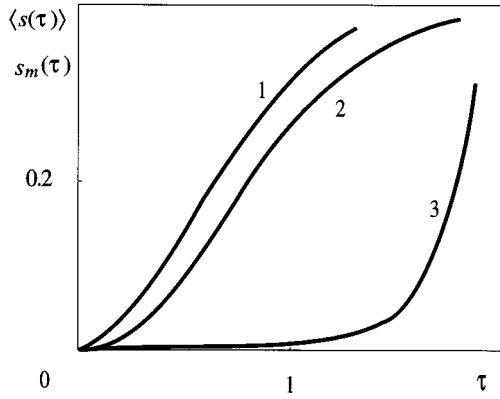


FIG. 3. Time dependence of the maximum aggregate volume $s_m(\tau)$ (28) (curve 1) and the mean aggregate volume $\langle s(\tau) \rangle$ (39) (curve 2) in comparison with the expected time dependence of the critical aggregate volume $s_*(\tau) \sim \omega(\tau)^{-3}$ (curve 3).

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 diffusion exchange by particles alone. As is seen from Fig. 2 the process of formation of new supercritical nuclei [an increase in aggregate concentration $n(\tau)$] goes on during the period of time when the small time asymptotic solution (30) is adequate (see curves 2 and 3). This result lends support to the validity of using the small time asymptotics (30) in exponent function in the integral equation (31).

Time dependence of the mean volume of the aggregates is illustrated in Fig. 3. At the end of the intermediate stage of the evolution (that is, at $\tau \approx \tau_m$), 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 with the increasing of the critical nucleus volume $V_*(t) \sim \Delta(t)^{-3}$ and $s_*(\tau) \sim \omega(\tau)^{-3}$. Such expected dependence is shown in Fig. 3 (curve 2). 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 the recondensation process during the intermediate stage of phase transition.

IX. EVOLUTION OF THE VOLUME DISTRIBUTION DENSITY

The volume distribution density is obtained in dimensionless form in Eqs. (26) and (27) and is fully determined if $\omega(\tau)$ and, consequently, $\theta(\tau)$ are known. This 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. When the large time asymptotics (34) is adequate, the distribution density can be written in the form

$$F(\tau, s) = s^{-\beta} \exp\{Eg[\theta(\tau) - y(s)]\} H[\theta(\tau) - y(s)], \quad (40)$$

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

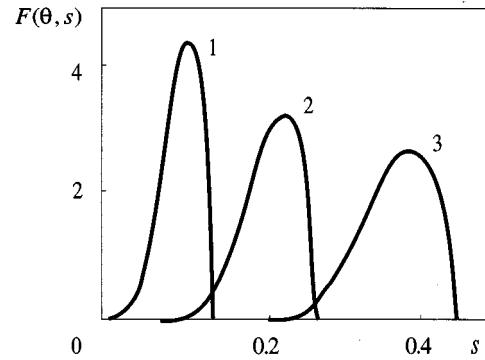


FIG. 4. Dimensionless distribution density at subsequent time moments: $\theta = \theta_m/2$ (curve 1), $3\theta_m/4$ (curve 2), and θ_m (curve 3).

where the function $y(s)$ is defined in Eq. (26) and the functional relation between τ and $\theta(\tau)$ is given by Eq. (34).

The evolution of the dimensionless distribution density is presented in Fig. 4, where the measure of the area under the curves is equal to the dimensionless aggregate concentration $n(\tau)$. At small times the distribution density is a very high and narrow function of the dimensionless aggregate volume. This is bound up with 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, Fig. 2). It means that subsequent evolution of the distribution density goes on under the condition that the area under the curve remains constant. As is clear from expressions (23) the various points of the function $F(\tau, s)$ move towards the right in Fig. 4 (i.e., in the space of dimensionless volumes) at a rate $ds/d\tau$. Since the rate of such a motion is an increasing function of dimensionless volume s , then the function $F(\tau, s)$ spreads. This means that the volume distribution density of the aggregates is characterized by an increasing dispersion. In accordance with this, the maximum value of the function $F(\tau, s)$ is a decreasing function of s (see curves 1–3, Fig. 4).

X. DISCUSSION

To sum up we are able to describe with high accuracy by purely analytical methods, with merely occasional application of simple numerical methods, the initiation and subsequent evolution of the system of droplike ellipsoidal aggregates in a magnetic fluid under the presence of an external magnetic field. Essentially the same approach could be applied to numerous processes of new phase formation in molecular and colloid systems. As compared with the latter, the magnetic field induced phase separation in magnetic fluids is essentially controlled by the mutual relation between the volume of an aggregate and its shape. An elongation of the aggregate during its growth is accompanied 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 that for a sphere) of the transverse size of the ellipsoid. Consequently, the aggregate elongation results in a higher value of growth rate in comparison with that 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 the 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 the magnetic field implies a significant increase of initial supersaturation (see Table I). The latter exerts primary control over the kinetics of the phase separation process.

The validity of the developed theory is somewhat restricted by certain underlying conditions imposed on characteristic time scales of involved processes, 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 highly elongated ellipsoid with semiaxis ratio $c_* \ll 1$ (see Table I). The last requirement is surely fulfilled for a magnetic fluid, except for a region of very high initial 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.

The continuing nucleation plays a role only at an early phase of the 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 5% 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. General evolution laws happen to be universal in the case of the diffusion kinetics of phase separation when expressed in terms of the special time variable $\theta(\tau)$, defined in Eq. (25). These universal laws for the diffusion limited aggregate growth in the small and large time asymptotics have the form

$$\omega(\theta) \approx 1 - Q\theta^\delta/\delta, \quad \langle s(\theta) \rangle \sim \theta^\gamma, \quad n(\theta) \approx \theta, \\ \theta \ll (\delta/Q)^{1/\delta},$$

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

both for the magnetic fluid phase separation induced by an external field, and for the phase separation of a colloid made metastable by a fall of temperature or an increase in the ionic strength of a solvent [24,29]. All the differences consist in the various values of exponents δ and γ . In the case of magnetic field induced phase separation we get, from Sec. VII: $\gamma \approx 7/4$, $\delta \approx 11/4$. When the phase separation takes place under the absence of an external field, the corresponding value of exponents were determined in Ref. [29]: $\gamma = 3/2$, $\delta = 5/2$.

The pertinent volume and time scales of the evolution process equal V_0 and t_0 defined by Eq. (21). 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 the actual phase separation process help to enable one to judge the nucleation rate J . Emergence of aggregates affects rheological, thermophysical, and other properties of magnetic fluids to an extremely 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 (40).

Unfortunately, the authors have failed to find reliable experiments on the kinetics of the phase separation process in magnetic fluids checked against 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 a similar theory [28] with some experiments on batch crystallization, which lends additional support to the present theory.

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