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

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Abstract

The phase separation kinetics in a ferrofluid made metastable by a strengthening of an external magnetic field has been studied theoretically at the nucleation, intermediate and Ostwald ripening stages of the phase transition.

Keywords: Kinetics; Phase separation; Magnetic fluids

1. Introduction

In magnetic fluids a unique type of concentrational phase separation is experimentally observed [1,2]: "ferrocolloidal gas–ferrocolloidal liquid" phase transition induced by an external magnetic field. During this process the ferrofluid with initial ferroparticle concentration φ_0 separates into two phases (I and II) of the concentrations φ_{I} and $\varphi_{\mathrm{II}} (\varphi_{\mathrm{I}} < \varphi_0 \ll \varphi_{\mathrm{II}})$ [3]. In real situations the highly concentrated phase II is suspended in the diluted phase I in the form of droplike aggregates, which typical dimension are of the order of 1–5 μm, i.e. the number of ferroparticles comprising the aggregate is approximately 10^5–10^7. In what follows, we are going to present the main results of the kinetic theory describing the evolution of a system of droplike aggregates in a magnetic fluid containing identical spherical ferroparticles. The ferrocolloid is supposed to be thermodynamically stable in the absence of a magnetic field. But if a weak uniform external field $\boldsymbol{H}$ is applied, a macroscopically homogeneous state of the magnetic fluid becomes unstable and the phase separation process is bound to start.

2. Nucleation kinetics

The nucleation kinetics essentially depends on the shape of emerging nuclei. It is well known [1,2] that the shape of a droplike aggregate with good accuracy may be approximated by an ellipsoid of revolution, the elongation of which is dependent on the aggregate volume V, on the interfacial tension σ, on the magnetic permeabilities of phases μ_{I}, μ_{II} and on an external field strength. The analysis made in Ref. [4] shows that in the

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presence of a weak-to-moderate magnetic field ($H \sim 10$–100 Oe) the droplike aggregates may be regarded as highly elongated ellipsoids, and the relationship between the aggregate volume and semiaxis ratio c takes the form

$$V \approx \frac{B}{c^7|\ln c|^3}, \quad B = \frac{4\pi^7\sigma^3}{3H^6}\frac{\mu_{\rm I}^3}{(\mu_{\rm II}-\mu_{\rm I})^6}, \quad c \ll 1. \tag{1}$$

In the case of highly elongated ellipsoids the problem of an aggregate growth rate in supersaturated ferrocolloidal environment can be solved analytically under the assumption that this growth is limited by a diffusional transport of ferroparticles to the aggregate surface [4]:

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

$$V_*^{1/3} = \frac{2}{3}\frac{v}{kT}\frac{\varphi_{\rm I}}{\varphi_{\rm II}}\frac{\sigma\kappa(c_*)}{\Delta}, \quad \kappa(c_*) = \frac{S}{V^{2/3}} \approx \left(\frac{9\pi^4}{16c_*}\right)^{1/3}. \tag{3}$$

Here v and D are the ferroparticle volume and diffusion coefficient, S is an ellipsoid surface, $\Delta = \varphi - \varphi_{\rm I}$ stands for a ferrofluid supersaturation and is defined as a difference between the actual value of the ferrofluid concentration φ and the concentration of the diluted ferrofluid phase I. Parameters V_* and c_* have the meanings of the critical aggregate volume and the corresponding value of the semiaxes ratio ($c_* \ll 1$): in the case $V > V_*$ the aggregate grows, otherwise $V < V_*$ it dissolves.

By using expressions (1)–(3) both the spontaneous origination of initial aggregate nuclei can be treated quite similar to the classical Volmer–Frenkel–Zel'dovich theory of nucleation. According to this, an influence of the supersaturation on the nucleation rate J is governed by the exponential factor [5]

$$J \sim \Delta \exp[-E(\Delta)], \quad E(\Delta) = \frac{\pi^4}{12c_*}\left(\frac{\sigma}{kT}\right)^3\left(\frac{\varphi_{\rm I}v}{\varphi_{\rm II}\Delta}\right)^2. \tag{4}$$

Taking into account the dependences of $\varphi_{\rm I}$, $\varphi_{\rm II}$, c_*, Δ on a magnetic field within the equilibrium phase separation conditions [3], the analysis of Eq. (4) comes to the conclusion that the nucleation rate J increases sharply under the strengthening of an external field. In other words, the process of phase separation in ferrofluids goes on more rapidly in the presence of a higher magnetic field.

3. Intermediate stage

The further evolution of a system of droplike aggregates at the intermediate stage of phase transition is investigated under the conditions when both the reduction in metastability and the continuing initiation of new nuclei are taken into account [5]. The aggregates are distributed over volume and the distribution density $f(t, V)$ is governed by the kinetic equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V}\left(\frac{\mathrm{d}V}{\mathrm{d}t}f\right) = 0, \tag{5}$$

$$\left|\frac{\mathrm{d}V}{\mathrm{d}t}f\right|_{V=V_*} = J[\Delta(t)], \quad f(0, V) = 0, \tag{6}$$

with account for a requirement of conservation of the overall number of ferroparticles in the system under study:

$$\Delta(t) = \Delta_0 - (\varphi_{\rm II} - \varphi_{\rm I})\int_{V_*}^{\infty} V f(t, V)\,\mathrm{d}V, \quad \Delta(0) = \Delta_0. \tag{7}$$

The method of solving the boundary problem (5)–(7) was described in Ref. [5]. The solution is applicable down to the begining of Ostwald ripening and defines the diverse characteristics of distribution density which gives the total information about the evolution of the aggregate system. Fig. 1 demonstrates the characteristic time dependence of the dimensionless supersaturation and the mean aggregate volume. The evolution of the dimensionless distribution density is presented on the Fig. 2 where curves 1–3 correspond to the increasing time moments. The time evolution of the magnetic, rheological and other properties of magnetic fluids under the phase separation process may be predicted with the help of the known aggregate volume distribution density (some examples one may find in Ref. [5]).

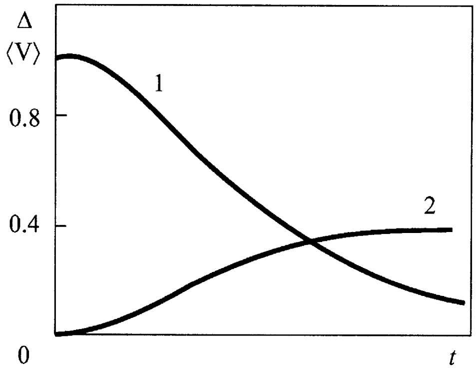

Fig. 1. Dimensionless time dependences of the dimensionless supersaturation (curve 1) and the mean aggregate volume (curve 2).

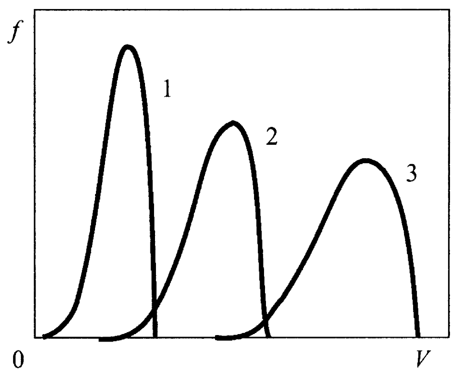

Fig. 2. Aggregate distribution density vs. dimensionless aggregate volume at the increasing time moments (curves 1–3) during the intermediate stage of the phase separation process.

4. Ostwald ripening kinetics

The final stage of phase transition corresponds to the Ostwald ripening process when the dependence of the critical aggregate volume on supersaturation (3) is of primary importance but the origination of new nuclei almost ceases and may by safely overlooked. A mathematical model includes the kinetic equation for the aggregate distribution density (5), the mass balance equation (7) and the aggregate growth rate (2), which is dependent both on the aggregate volume and on the volume of the critical aggregate.

On the basis of the classical method of Lifshitz and Slyozov [6] we find that the model demon-

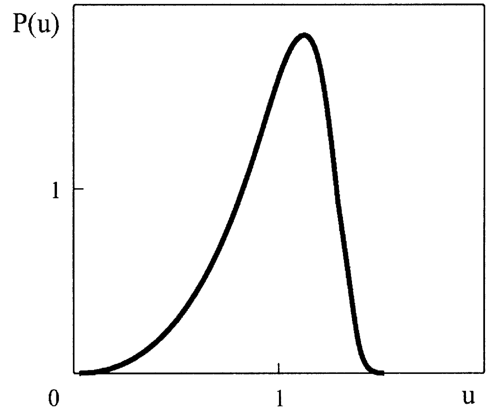

Fig. 3. Self-similar aggregate distribution density as a function of the dimensionless aggregate size during the Ostwald ripening process.

strates the self-similar solution for the aggregate distribution density as a function of the self-similar variable $u = V^{1/3}/V_*^{1/3}$ of a form

$$f(t, V^{1/3}) \sim P(u)(\ln t)^{8/9} t^{-14/9}, \quad t \to \infty . \tag{8}$$

The self-similar function $P(u)$ is plotted in Fig. 3.

The Lifshitz–Slyozov method of attacking the problem also allows us to construct the asymptotic time dependences for the critical aggregate volume V_*, for the absolute supersaturation Δ, for the mean number of droplike aggregates per unit volume N and for the mean aggregate volume $\langle V \rangle$:

$$V_*^{1/3}(t) \sim t^{7/18}(\ln t)^{-2/9}, \quad \Delta(t) \sim (\ln t)^{5/18} t^{-1/3}, \quad t \to \infty , \tag{9}$$

$$N(t) \sim (\ln t)^{2/3} t^{-7/6}, \quad \langle V(t) \rangle \sim t^{7/6}(\ln t)^{-2/3}, \quad t \to \infty . \tag{10}$$

We would like to remind that according to the classical case the similar laws for spherical new phase elements have the following scaling forms: $V_*^{1/3} \sim t^{1/3}$, $\Delta \sim t^{-1/3}$, $N \sim t^{-1}$, $\langle V \rangle \sim t$. Our asymptotics (9) and (10) differ from the classical results and coincide with the conclusions of the Ref. [7]. During the analysis of the Ostwald ripening kinetics, the author of Ref. [7] has neglected the logarithmic dependence and has obtained the self-similar solutions as the power functions. The point is that the exponents for the time evolution of the drop concentration ($\sim t^{-7/6}$) and of the mean drop volume ($\sim t^{-7/6}$) coincide with expressions (10) with the logarithmic accuracy.

5. Conclusion

To sum up we are able to describe by analytical methods the evolution of the system of droplike ellipsoidal aggregates in a ferrofluid under the presence of an external magnetic field during all the stages of the phase separation process. As compared with the growth of the spherical new phase elements, the magnetic field-induced phase separation in ferrofluids is essentially controlled by the mutual relation between the volume of the droplike aggregates and their shape. An ellipsoidal shape of the aggregates leads to the non-classical relation for the critical aggregate volume which is dependent not only on the ferrocolloid supersaturation, but on the critical aggregate semiaxis ratio as well. This special feature results in the self-similar time-evolution laws which differ from the classical theories. The general conclusion is that the system of highly elongated ellipsoidal aggregates evolves faster in comparison with the system of spherical drops.

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