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Phase separation in bidisperse ferrocolloids

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Abstract

The peculiarities of the phase separation of polydisperse ferrocolloids have been investigated using thermodynamic perturbation theory for the analysis of a model bidisperse system. The phase stability region is determined completely by a small number of large particles present in the system.

1. Introduction

From the principal point of view, well-known statistical and thermodynamical models [1–4] have shown that ferrocolloids allow for ferroparticle condensation in the absence of a magnetic field at temperatures lower than a certain critical temperature, the latter depending on the value of the ferroparticle magnetic moment. This is caused by the fact that the noncentral dipole–dipole interaction of the particle magnetic moments displays itself on the whole as an effective interparticle attraction. In an external field this effective attraction strengthens [4], and thus the magnetic field stimulates the process of phase separation in ferrocolloids.

However, a number of circumstances exist which leave the problem open. First, the sizes of the particle magnetic cores in real ferrocolloids (~ 8 – 10 nm), taking into account the nonmagnetic layers on their surfaces, give typical values of the energy of the magneto-dipole interparticle interaction of the

order of ~ 0.1 – $0.5kT$. A potential well of such a depth is not sufficient for condensation to occur. Various authors [1–4] give values of the potential minimum required for a phase transition in the range 2 – $4.5kT$, i.e. an order larger than is realized experimentally. Taking into account the van der Waals attraction does not help to resolve the contradiction. The influence of van der Waals forces is negligible due to the solvation layers [5]. In addition, all existing theories are based on the assumption of monodispersity, and they are unable to explain a number of effects in principle (e.g. the difference in the dispersities of weakly and strongly concentrated phases [6]). Thus, by not taking into account the polydispersity of ferrocolloids, one can only assume a qualitative description of the process of phase separation. In addition, experiments indicate a number of effects caused by polydispersity [6–9], a general analysis of which leads to the conclusion that a major role is played by a small number of large particles.

2. Thermodynamic model

The major problem in the theoretical modelling of thermodynamic properties of ferrocolloids is to take

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into account non-central dipole–dipole interaction of the magnetic moments of ferroparticles in the presence of an external magnetic field H . By considering this interaction as a perturbation for a cylindrical container with the ferrocolloid stretched along the field, Buyevich and Ivanov [4] obtained an expression for the thermodynamic potential, which for polydisperse system assumes the form

$$\begin{aligned} \Phi = & N_0 \mu_0^0(P, T) \\ & + \sum_i N_i \left[\mu_i^0(P, T) + kT \ln \varphi_i - kT \ln \frac{\sinh \alpha_i}{\alpha_i} \right] \\ & - kT \ln Q_s - kT \sum_{ij} N_i \varphi_j \left(\frac{d_i + d_j}{2d_j} \right)^3 G_{ij}(T, H), \\ \alpha_i = & \frac{m_i H}{kT}, \end{aligned} \quad (1a)$$

$$\begin{aligned} G_{ij}(T, H) = & 4\gamma_{ij} L(\alpha_i) L(\alpha_j) + \frac{4}{3} \gamma_{ij}^2, \\ \gamma_{ij} = & \frac{8m_i m_j}{kT(d_i + d_j)^3}, \end{aligned} \quad (1b)$$

where the summation over i and j is done over all fractions of discretely distributed ferrophase; φ_i is the volume concentration of particles of the i th fraction having diameter d_i and magnetic moment m_i ; μ_i^0 is the chemical potential of a single ferroparticle, and μ_0^0 is the chemical potential of a pure liquid consisting of N_0 molecules. The configurational integral Q_s takes account of spherically symmetric interactions (steric repulsion, van der Waals forces, etc.). Expression (1) also contains terms corresponding to a liquid solvent, to an ideal paramagnetic ferroparticle gas, and to a contribution of the magneto-dipole interaction described by parameter $G_{ij}(T, H)$. These quantities are positively determined and increasing functions of the external magnetic field. The latter corresponds to the fact that the magneto-dipole interaction in a ferrocolloid manifests itself as an effective interparticle attraction that grows in intensity in the magnetic field.

The adequacy of perturbation theory is confirmed by experimental data on the magnetic properties.

Quite simple expressions for the magnetization M and the initial magnetic susceptibility χ_0 ,

$$\begin{aligned} M(H) = & M_L(H) \left[1 + \frac{4\pi}{3} \frac{dM_L(H)}{dH} \right], \\ \chi_0 = & \chi_L \left(1 + \frac{4\pi}{3} \chi_L \right), \end{aligned} \quad (2a)$$

$$\begin{aligned} M_L(H) = & \sum_i n_i m_i L(\alpha_i) \\ \equiv & \sum_i n_i m_i \left(\coth \alpha_i - \frac{1}{\alpha_i} \right), \\ \chi_L = & \sum_i \frac{n_i m_i^2}{3kT}, \end{aligned} \quad (2b)$$

describe well the experimental magnetization curves $M(H)$, and the concentration $\chi_0(\varphi)$ and temperature $\chi_0(T)$ dependencies of the initial susceptibility [4,10].

3. Bidisperse ferrocolloids

The peculiarities brought by the polydispersity into the process of phase separation can be estimated even in an example of a two-fraction system. As is well known, the distribution of magnetic cores of ferroparticles with respect to their diameters $f(x)$ is successfully described by a log-normal or gamma distribution [6,11,12], whose maximum lies in the region 6–8 nm (Fig. 1). The mean value of the magnetic core diameter usually lies in the interval

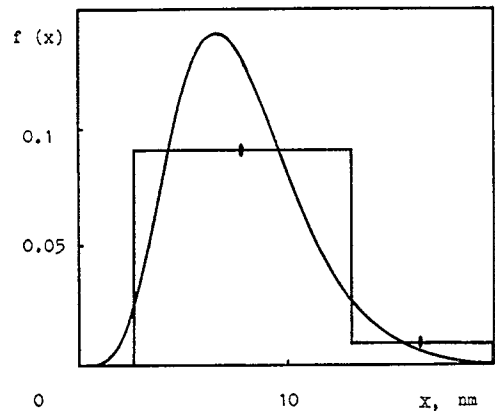


Fig. 1. Ferroparticle size distribution function and model bidisperse distribution.

$\langle x \rangle \sim 7\text{--}9$ nm. When coming from a real distribution to a model bidisperse one (Fig. 1) it is reasonable to adopt the following principles:

(1) The diameter of one of the fractions x_1 (small particles) should be chosen as the mean diameter $\langle x \rangle$ of the distribution $f(x)$.

(2) The fraction mole portions $v_1 = N_1/(N_1 + N_2)$ and $v_2 = 1 - v_1$ and the diameter x_2 of the second fraction (large particles) should be determined by the conditions of equality of the experimentally observed saturation magnetization and initial susceptibility, i.e. the mean magnetic moment $\langle m \rangle \sim \langle x^3 \rangle$ and the mean squared magnetic moment $\langle m^2 \rangle \sim \langle x^6 \rangle$.

Thus a model bidisperse distribution has the following properties: the main fraction consists of particles with magnetic core diameters $x_1 \approx 7\text{--}9$ nm and mole portions $v_1 \approx 90\text{--}95\%$; the second fraction consists of a small number of large particles, $x_2 \approx 14\text{--}17$ nm, $v_2 \approx 5\text{--}10\%$. Taking into consideration the fact that the summary thickness of the existing nonmagnetic layer and surfactant envelope is approximately $l \approx 3$ nm, we come to the particle diameters $d_i = x_i + 2l$: $d_1 \approx 13\text{--}15$ nm, $d_2 \approx 20\text{--}23$ nm. Due to the large difference in the magnetic core diameters, the dimensionless energy of the magneto-dipole interaction γ_{ij} between particles of different fractions (1b) varies considerably. For magnetite particles at a room temperature we obtain $\gamma_{11} \approx 0.1\text{--}0.3$, $\gamma_{22} \approx 2.5\text{--}3$. Thus, the main fraction consists of particles with negligibly weak interparticle attraction, whereas the interaction between large particles is quite intensive.

4. Phase stability

The equilibrium conditions for the coexistence of weakly and highly concentrated ferrocolloid phases are determined in a standard way by the equality of the chemical potentials of ferroparticles of the two fractions μ_1 and μ_2 , and the molecules of the liquid solvent μ_0 under isothermal and isobaric conditions:

$$\mu_i(\varphi_1^I, \varphi_2^I) = \mu_i(\varphi_1^{II}, \varphi_2^{II}), \quad i = 0, 1, 2, \quad (3a)$$

$$k\varphi_j^I + (1 - k)\varphi_j^{II} = \varphi_j, \quad j = 1, 2, \quad (3b)$$

where the superscripts denote phases I and II, φ_j is the volume concentration of j fraction in the original

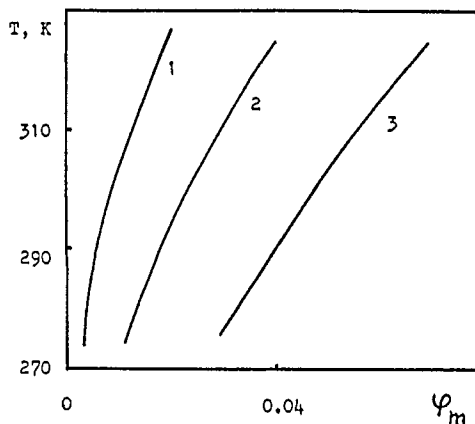


Fig. 2. Phase diagram of bidisperse ferrocolloid: critical temperature as a function of magnetic phase concentration. Curves 1–3 correspond to magnetic field strengths $H = 10$ (1), 5 (2), and 0 (3) kA/m.

ferrocolloid, and $k = V_1/V$ is the volume portion of phase I in the system.

The chemical potentials of the fractions and the liquid are calculated using thermodynamic potential (1) and an approximation [13] of the configurational integral Q_s for a system of hard spherical particles. A decrease in temperature and an increase in magnetic field (i.e. growth in the values γ_{ij} and G_{ij}) result in the appearance of bends on curves of chemical potentials μ_i as functions of concentrations φ_1 and φ_2 , these bends are analogous to the van der Waals loops. In these regions of concentrations, temperatures and magnetic fields, the stability of a spatially homogeneous ferrocolloid state breaks down and coexisting phases originate. The phase stability curve, dividing the regions of homogeneous and two-phase states of the ferrocolloid, can naturally be determined in the space of three measured quantities: the temperature T , the external magnetic field strength H and the magnetic phase concentration in the whole system, φ_m . Figs. 2–4 show phase diagrams in the planes $\varphi_m\text{--}T$, $\varphi_m\text{--}H$, $T\text{--}H$ for the following magnetic colloid: $x_1 = 8$ nm, $v_1 = 0.94$, $x_2 = 16.5$ nm, $v_2 \equiv 1 - v_1 = 0.06$, which corresponds to Fig. 1 [6]. In all cases the region of higher temperatures and weaker magnetic fields corresponds to the stable homogeneous state. The most important result is that only the fraction of large particles (which are small in number) is thermodynamically unstable. Thus even a slight change in

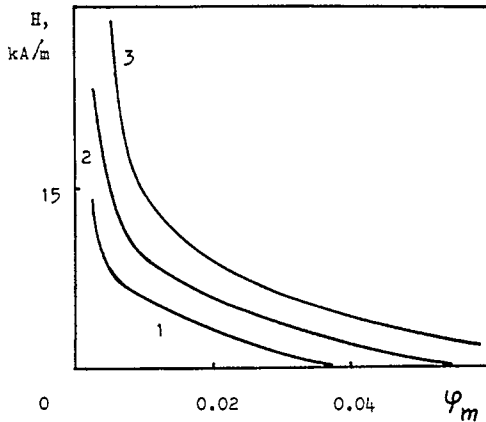


Fig. 3. Phase diagram of bidisperse ferrocolloid: critical value of the magnetic field as a function of magnetic phase concentration. Curves 1–3 correspond to temperatures $T = 280$ (1), 300 (2), and 320 (3) K.

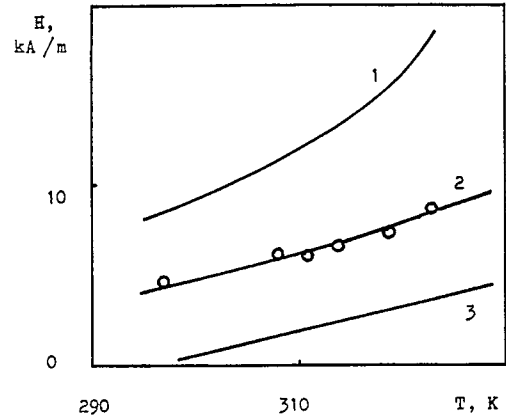


Fig. 4. Phase diagram of a bidisperse ferrocolloid: temperature dependence of the critical magnetic field strength. Curves 1–3 correspond to magnetic phase concentrations $\varphi_m = 1\%$ (1), 2.4% (2), and 5% (3); dots, experimental data from A.F. Pshenichnikov et al. (private communication).

their number causes an essential shift in the two-phase region boundary. As Figs. 2–4 show, a transfer from a monodisperse to even a model bidisperse system results in phase separation at room temperature.

Behind the phase stability boundary the ferrocolloid is in the separated state. The character of the changes in the basic parameters of coexisting phases can be seen in Table 1. Phase I occupies practically the whole volume of the system and consists of particles of fraction 1 with a negligibly low portion of large particles of fraction 2. Phase II contains the majority of large particles, whose concentration grows with decreasing temperature or a strengthening magnetic field, and can reach the maximum

possible value for the liquid state. The volumetric portion of phase II in the whole system $1 - k$ at room temperature and weak fields is a few percent. Under real conditions this phase manifests itself in the form of a large number of droplet-like aggregates suspended in a weakly concentrated phase I. Due to the high concentration of the magnetic phase and the large size of particles, the mean magnetic moment of droplet aggregates $\langle m^{II} \rangle$ is several times larger than the moment $\langle m \rangle$ in the original phase. The magnetic permeability of the substance in phase II is up to $\sim 30\text{--}40$, which corresponds with well-known experimental results [8,9].

Table 1

Parameters of a separated bidisperse ferrocolloid: $x_1 = 7.8$ nm, $x_2 = 16.5$ nm, $v_1 = 0.94$, $v_2 = 0.06$, $l = 3$ nm, $\varphi_m = 0.05$, $\langle m \rangle = 1.8 \times 10^{-19}$ A m²

T (K)	H (kA/m)	φ_m^I	φ_m^{II}	$\langle m^I \rangle$ (10^{-19} A m ²)	$\langle m^{II} \rangle$ (10^{-19} A m ²)	k
270	0	0.039	0.170	1.33	9.73	0.90
275	0	0.040	0.165	1.36	9.43	0.91
280	0	0.041	0.161	1.41	9.10	0.92
285	0	0.042	0.156	1.46	8.73	0.93
290	0	0.044	0.151	1.53	8.33	0.94
295	0	0.046	0.146	1.62	7.87	0.96
300	0	0.049	0.140	1.74	7.39	0.98
300	1	0.047	0.142	1.70	7.55	0.97
300	5	0.039	0.165	1.34	9.40	0.91
300	10	0.036	0.181	1.23	10.39	0.90
300	15	0.035	0.187	1.21	10.65	0.90
300	20	0.035	0.190	1.21	10.75	0.90

5. Conclusions

The bulk phase separation of a ferrocolloid induced by a magnetic field is determined by the fraction of large particles. Changes in the parameters of a separated ferrocolloid presented in Table 1 are typical of other dispersities. Due to a certain non-uniqueness in the approximation of a real ferrocolloid by a bidisperse system it is hardly reasonable to try to reach accurate quantitative agreement with experimental results on phase separation. However, all the basic features listed in the introduction can be successfully explained even by the example of a two-fraction ferrocolloid.

In the case of a real size distribution of ferroparticles (log-normal or gamma distribution) the peculiarities of the phase separation process would remain, as mentioned above. A detailed analysis of such problems may be considered as a natural extension of this research.

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