

Phase Separation of Polydisperse Ferrofluids

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The phenomenon of magnetic fluid phase separation, accompanied by the formation of droplike aggregates, was first observed over thirty years ago [1]. These aggregates can be considered as fluids with an interfacial tension surface, representing, essentially, a highly concentrated ferrocolloidal phase suspended in a dilute matrix in a form of droplets. 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 . Later the phenomenon was thoroughly studied experimentally [2], and three main reasons, which can lead to phase separation, were revealed: (a) a decrease in temperature; (b) a strengthening of a magnetic field; (c) an increase of the solvent ionic strength for ionic ferrofluids.

In principle, known theoretical models [3] 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 particle magnetic moment. This is associated with the fact that the noncentral dipole-dipole interaction of ferroparticle magnetic moments displays itself on the whole as an effective interparticle attraction. In an external field this effective attraction strengthens, thus a magnetic field stimulates the process of phase separation in ferrofluids. But the problem is that in computer simulations of dipolar fluids with hard or soft spheres no vapor-liquid transition has been observed [4]. Only when the van der Waals attraction is added to the magnetic dipolar interaction, the phase transition can be found in Stockmayer fluids [5]. So, the question is: what is the

driven force for the phase separation in real ferrofluids? Is it really influenced by the dipolar interaction only? And what is the part of van der Waals attraction in the phase separation of ferrofluids?

To answer these questions we examine first the van der Waals interaction in a system of identical spherical ferroparticles coated by a surfactant layer of the width l :

$$U_w(r) = -\frac{A}{12} \left(\frac{d^2}{r^2} + \frac{d^2}{r^2 - d^2} + 2 \ln \frac{r^2 - d^2}{r^2} \right) \quad (1)$$

Here A is the Hamaker constant, r stands for the particle center-to-center distance, and d is the diameter of particle solid grain. For typical parameters $d=10 \text{ nm}$ and $l=2 \text{ nm}$ we obtain the contact value approximately

$$U_w(r = d + 2l) \approx 0.01A \quad (2)$$

For ferrite colloids in hydrocarbons ($A \approx 3 \cdot 10^{-19} \text{ J}$) it means that the contact van der Waals energy at room temperatures is comparable with the thermal energy $kT \approx 4 \cdot 10^{-21} \text{ J}$. At the same time, the commonly used long-range approximation of expression (1)

$$U_w(r) \approx -\frac{A}{36} \left(\frac{d}{r} \right)^6 \quad (3)$$

gives the contact value

$$U_w(r = d + 2l) \approx 0.0037A, \quad (4)$$

which is three times smaller than the real one (2). This estimation shows that the van der Waals energy should not be neglected when we describe the conditions of violation of ferrofluid thermodynamic stability. Next we develop a simple model based on the thermodynamic perturbation method. The main advantage of this model is that it

may be easily extended to the case of polydisperse ferrofluids as well as for various kinds of the central interparticle interaction. The test of the model on Stockmayer fluids results in rather accurate description of the critical point and the phase diagram. The comparison for the reduced critical temperature T_c^* is presented in Table for various values of the reduced magnetic moment μ and reduced magnetic field H^* .

μ	H^*	T_c^* computer simul. [5]	T_c^* model
0	0	1.316(6)	1.306
1	0	1.41(1)	1.409
1	1	1.44(1)	1.428
1	2	1.49(1)	1.471
1	3	1.51(1)	1.517
$\sqrt{2}$	0	1.60(1)	1.669
$\sqrt{3}$	0	1.82(1)	2.016

The model is used for theoretical investigation of the phase separation conditions with major attention to the influence of ferroparticle polydispersity. The equilibrium phase stability region is completely determined by a small number of large particles. Highly concentrated droplike aggregates formed upon separation take up several percent of the volume of a system and cover virtually the entire large particle fraction. Our analysis also demonstrates that van der Waals interaction plays a significant part in ferrofluid phase separation, its influence is comparable with the part of dipolar forces.

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