Formation of chain aggregates in magnetic fluids: an influence of polydispersity

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Abstract

The formation of chain-like aggregates in polydisperse ferrofluids is studied theoretically on the basis of the model bidisperse system, consisting of two fractions of small and large ferroparticles. Various topological structures of chains, containing the particles of both fractions, are considered. The equilibrium chain distribution is obtained with the help of the density functional approach. It was found that in real conditions the majority of large particles and the minority of small particles are connected in short chains of 1–3 large particles in the middle and 1–2 small particles at the edges. The chain distribution is greatly dependent on the mole portion of the large particle fraction.
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It is well known that the presence of various types of aggregates influences greatly the macroscopical properties of magnetic fluids. Due to the non-central dipole–dipole interaction, the most typical aggregate structure in ferrofluids is a chain one. The chain formation was studied numerically and theoretically (see, for example Refs. [1–5]), but only the monodisperse model systems were considered. Usually such studies are based on Frenkel's theory [6] and the following assumptions are adopted: (a) particles are treated as identical spheres of volume v with constant magnetic moment; (b) structures that differ from those of linear chains are ignored; (c) only the interaction between the nearest neighboring particles in every chain is taken into account; (d) interaction between chains is not considered.

The final problem is to find the minimum of free energy functional (1) under condition (2) (see, for example, Ref. [2]):

$$F = kT \sum_{n=1}^{\infty} g(n)\left[\ln \frac{g(n)v}{e} - \varepsilon(n-1)\right] \to \min, \qquad (1)$$

$$\frac{\rho}{v} = \sum_{n=1}^{\infty} ng(n). \qquad (2)$$

Here kT is the thermal energy, n is the number of particles in a chain. The function $g(n)$ stands for the number of chains, consisting of n particles, per unit volume. Expression (1) follows from Frenkel's theory of heterophase fluctuations [6]; the first term is the free energy of an ideal gas of chains, and the second term describes the energy of a chain consisting of n particles with the dimensionless energy of interparticle interaction $\varepsilon > 0$. Condition (2) represents the mass balance equation, and ρ has the meaning of volume particle concentration.

Naturally, the presence of a large particle fraction in practically used ferrofluids demands for taking into account the polydispersity in theoretical models. The peculiarities brought by the polydispersity into the chain formation process can be estimated even in an example of a two-fraction system. So, the bidisperse model is regarded. To use Frenkel's theory and obtain the free energy functional, one needs to find the energy of all topologically different chains. The algorithm, allowing to account for all chains having different energies and consequently different structures, was worked out.

Let n and m be the number of large and small particles per chain, respectively; vector $\mathbf{E} = (\alpha, \beta, \gamma)$—the energy vector: $\alpha, \beta, \gamma > 0$—the energies of the coupling dipole–dipole interaction between the particles of fractions "large–large", "small–small" and "large–small" divided

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by thermal energy kT, respectively. Thus, the energies of all chains, consisting of n large and m small particles, are described by the scalar product $\langle \mathbf{E}, \mathbf{S}_i \rangle$, where coordinates of $\mathbf{S}_i = (a_i, b_i, c_i)$ are the numbers of α, β, γ interparticle bonds and satisfy

$$a_i + b_i + c_i = n + m - 1. \tag{3}$$

All different solutions of Eq. (3) are shown in Fig. 1, but not all of them describe the structure of real chains; hence by imposing additional restrictions on $\mathbf{S}_i$, the number of topologically different chain structures $I(n, m)$ could be obtained. Thus, functional (4) and mass balance equations (5) and (6) are the natural generalization of problem (1)–(2), where the function $g(i, n, m)$ stands for the number of chains per unit volume of the system with structure $i \in \{I(n, m)\}$, consisting of n and m particles, and ρ_n, ρ_m, v_n and v_m—the particle concentrations and volumes of fractions n and m:

$$F = kT \sum_{n+m>0}^{\infty} \sum_{i=1}^{I(n,m)} g(i,n,m) \left[\ln \frac{g(i,n,m)v_n}{e} - \langle \mathbf{S}_i, \mathbf{E} \rangle \right]$$
$$\rightarrow \min, \tag{4}$$

$$\frac{\rho_n}{v_n} = \sum_{n+m>0}^{\infty} \sum_{i=1}^{I(n,m)} ng(i,n,m), \tag{5}$$

$$\frac{\rho_m}{v_m} = \sum_{n+m>0}^{\infty} \sum_{i=1}^{I(n,m)} mg(i,n,m). \tag{6}$$

Using the Lagrange method, expression (7) for $g(i, n, m)$ follows from problem (4)–(6):

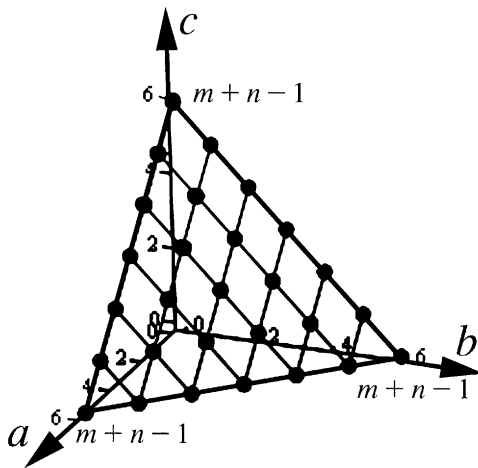$$g(i,n,m,) = \frac{\exp(\lambda_1 n + \lambda_2 m + \langle \mathbf{S}_i, \mathbf{E} \rangle)}{v_n}, \tag{7}$$

Fig. 1. Surface of solutions of Eq. (3). This surface allows us to determine the number of α, β, γ interparticle bonds (a_i, b_i, c_i, respectively) for each topologically various structure of the chain, consisting of n large particles and m small ones.

where λ_1 and λ_2 are the Lagrange multipliers, which should be determined from balance conditions (5) and (6) numerically.

Moving from a real continuous particle distribution by size to a model bidisperse one, it is reasonable to adopt the following principles [7]: (a) the size of one of the fractions x_m should be chosen as the mean diameter of the continuous distribution; (b) fraction mole portions v_n, v_m and size x_n of the large particle fraction should be determined by the conditions of equality of the experimentally observed saturation magnetization and initial susceptibility; that is, the mean magnetic moment and the mean squared magnetic moment. Thus, a model bidisperse distribution has the following properties. The main fraction consists of small particles with magnetic core diameter $x_m \sim 7-9$ nm, and mole portion $v_m \sim 90-98\%$. The second fraction consists of small number of large particles $x_n \sim 14-17$ nm and $v_n \sim 5-10\%$. Allowing for the existence of the nonmagnetic and solvent layers for magnetite particles at room temperatures, the following values of the coupling energies are obtained: $\beta \sim 0.2-0.3$, $\gamma \sim 1-1.5$, $\alpha \sim 5-7$. Hence, the main fraction consists of particles with the weak interparticle attraction, whereas the interaction between large particles is quite intensive.

It appeared that not only the energies of interaction but also the volume concentrations influence the number and structure of chains. The chain formation in the above-mentioned bidisperse ferrofluid was analyzed at magnetic phase concentration 1–5%. It was found that the majority of small particles $\sim 40-80\%$ and only $\sim 2-10\%$ of large particles were nonaggregated. Due to the great amount of m particles in the system, their couples are sufficiently probable. The majority of chains consist of large particles in the middle and two–three small particles at the edges. The most typical topological chain configuration appears to be as shown in Fig. 2. Most of such chains contain one large particle and two small ones. Chains consisting of several small particles, placed in the middle of a chain, are extremely rare.

The problem of calculation of the mean number of particles per chain is worth discussing. The mean number of large particles per chain is observed to be $\sim 2-3$. Nevertheless, the total mean number of particles
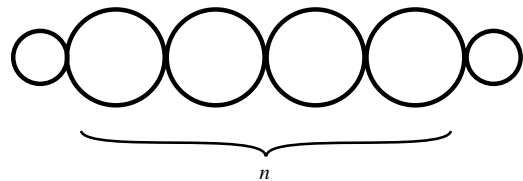

Fig. 2. Most typical topological chain structure. The chains consist of 1–2 large particles in the middle and 1–2 small particles along the edges.
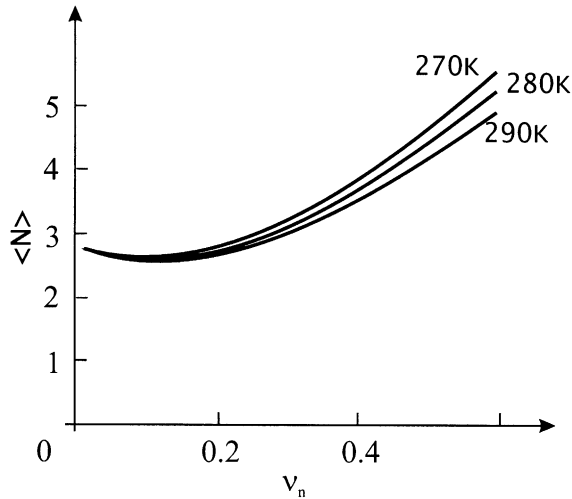
Fig. 3. Dependence of the mean chain length $\langle N \rangle$ on the mole portion v_n of the large particle fraction in bidisperse ferrofluid with the magnetic phase concentration 5% for various temperatures.

Here we state $n + m \geqslant 2$ because the nonaggregated particles are excluded from the account. This number— $\langle N \rangle$—strongly depends on the concentration of n fraction and less on temperature. Fig. 3 demonstrates the dependence of $\langle N \rangle$ on the mole portion v_n of the large particle fraction under different temperatures. The presence of minimum is the consequence of the most probable chain structure transformation.

In conclusion, the analysis presented above shows that in a model bidisperse ferrofluid, almost all the large particle fraction is connected in chains. However, the total number of chains is comparatively small due to the low molar portion of this fraction. In spite of the high small particle fraction molar portion the majority of them are nonaggregated. This is the result of the very weak interparticle dipole–dipole interaction between the small particles.

per chain, defined as the total number of chains divided by the total number of particles, slowly grows with the increasing concentration and the decreasing temperature and varies over ~ 1.1–2.0. These low values are caused by the large number of single small particles. But as it was observed, the majority of large particles were connected in chains. So, it is important to find the mean chain length $\langle N \rangle$:

$$\langle N \rangle = \frac{\sum_{n+m \geqslant 2}^{\infty} \sum_{i=1}^{I(n,m)} (m+n) g(i,n,m)}{\sum_{n+m \geqslant 2}^{\infty} \sum_{i=1}^{I(n,m)} g(i,n,m)}. \tag{8}$$

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