



Mean field theories and ferromagnetic ordering in ferrofluids

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Abstract

This paper addresses basic questions concerning spontaneous “ferromagnetic” order in ferrofluids. We obtain the exact equation connecting the one-particle distribution function with the pair correlation function. We study four expressions for the pair correlation function in terms of the one-particle distribution function, and only one of them results in the spontaneous orientational order. This self-consistent uncoupling is used in the density functional approach and proves to be equivalent to the mean field model. In this case an influence of dipole–dipole interaction is overestimated and so the theoretical prediction of ferromagnetic order in ferrofluids has to be considered as questionable.

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In the last decade the problem of long-range orientational ordering in dipole fluids was being actively discussed. The possibility of such state practical realization is not only of great interest from the principal physical viewpoint, but is of no doubt important for many applications. It was in the beginning of 1980’s when the orientational order (“ferromagnetic state”) was predicted by using of the Weiss mean field method for accounting the dipole–dipole interaction in ferrofluids [1]. In 1990’s, after the publication of computer modeling results [2], the interest for the problem arose again. In these and later papers [3] the following fact was pointed out: while resting spatially disordered the polar fluid undergoes the phase transition resulting in the appearance of an orientational order. The subsequent theories [4] proved (!?) the existence of “liquid paramagnetic–liquid ferromagnetic” phase transition, the conditions of which turned out to be dependent on the shape of the container with a ferrofluid. The highly elongated ellipsoid of revolution is the most suitable and, in this case, the direction of spontaneous magnetization coincides with the major semiaxis of ellipsoid. It is worth noting that the mean spherical approximation [5] and the thermodynamic perturbation theory [6,7] do not predict the magnetic ordering. The last mentioned

result also cannot be obtained by using the mean field theory by Onsager [8], the modified mean field model [8] and the recently developed theory [10].

A modern approach to the theoretical prediction of spontaneous orientational ordering in dipole fluids is based on the following algorithm: thermodynamic energy is expressed as a functional on the one-particle distribution function $g_1(\Omega_1)$. This function determines the probability for the randomly chosen magnetic particle 1 to be oriented along the $\Omega_1(\omega_1; \zeta_1)$ direction. Minimization of the energy functional leads to the equation for the one-particle distribution function, one of the solution of which is anisotropic in the orientational space Ω , even in the absence of an external field. Here we are not going to dwell on the peculiarities of the computer simulations and physical reasons of the spontaneous orientational ordering in ferrofluids. The mean field approaches and the approximations, which are important for obtaining the ferromagnetic state, will be discussed.

The function $g_1(\Omega_1)$ fulfills the normalization condition and determines the magnetization M of ferrofluid

$$\int g_1(\omega_1) d\Omega_1 = 1$$

$$M(H) = nm \frac{1}{2} \int_0^\pi \cos \omega_1 g_1(\omega_1) \sin \omega_1 d\omega_1, \quad (1)$$

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where n is the ferroparticle concentration and m is the particle magnetic moment; $\mathbf{H}||Oz$ stands for an external magnetic field which is parallel to major axis Oz of the container with ferrofluid in a shape of infinitely elongated ellipsoid of revolution. Applying to ferrofluids the one-particle distribution function g_1 depends only on the angle ω_1 between the orientation of a magnetic moment of randomly chosen ferroparticle 1 and an external field direction. On the basis of BBGKI formalism [11] the differentiation of function $g_1(\omega_1)$ with respect to ω_1 leads to the equation [7], connecting the one-particle distribution function with the pair correlation function $g_2(\mathbf{r}_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \equiv g_2(12)$

$$\frac{dg_1(\omega_1)}{d\omega_1} = -\alpha \sin \omega_1 g_1(\omega_1) - \frac{n}{kT} \int d\mathbf{\Omega}_2 \int d\mathbf{r}_{12} \frac{dU_d(12)}{d\omega_1} g_2(12),$$

$$d\mathbf{\Omega}_i = (4\pi)^{-1} \sin \omega_i d\omega_i d\zeta_i,$$

$$d\mathbf{r}_i = r_i^2 dr_i \sin \theta_i d\theta_i d\varphi_i. \quad (2)$$

Here U_d is the dipole–dipole interaction energy, $\alpha = mH/kT$ has a meaning of the Langevin parameter and the integration over $d\mathbf{r}_i$ and $d\mathbf{\Omega}_i$ correspond with the averaging over all positions and orientations of the i th ferroparticle. Eq. (2) is exact and includes all the corrections influenced by the multi-particle correlations. In the case of negligibly weak interparticle interaction Eq. (2) gives the solution for an ideal paramagnetic gas $g_1(\omega_1) \equiv g_0(\omega_1) = (\alpha/\sinh \alpha) \exp(\alpha \cos \omega_1)$, (3)

$$M = M_L(\alpha) = n m L(\alpha), \quad L(\alpha) = \coth \alpha - 1/\alpha,$$

where M_L stands for the Langevin magnetization.

To obtain the closed equation (2) the pair correlation function should be expressed in either the one-particle distribution function of an ideal paramagnetic gas $g_0(\omega_1)$ or the exact function $g_1(\omega_1)$. From the definition [11] the following expression, equivalent to the virial expansion, holds true

$$g_2(12) = g_0(\omega_1) g_0(\omega_2) \tilde{g}_2(12), \quad (4)$$

where the function $\tilde{g}_2(12)$ takes into account the interparticle correlations in a system of interacting ferroparticles. The solution of Eqs. (2) and (4) with the accuracy of terms $\sim U_d^2$ was considered in Ref. [7]. The results obtained for magnetic properties of dense ferrofluids and dielectric properties of polar fluids are in a good agreement with the experimental data and the computer simulations, including the ferrofluids with maximum allowable magnetic phase concentration and saturation magnetization ~ 90 kA/m. The ferrofluid magnetization [7] is expressed in a form of rather complicated series on the Langevin magnetization and equals to zero in the absence of an external field. In

other words, the exact expression (4) does not predict the existence of ferromagnetic state in ferrofluids.

The density functional approaches [4] use the self-consistent expression for the pair correlation function $g_2(12)$ in terms of the one-particle distribution function g_1 . Three various kinds of such self-consistent uncoupling exist

$$g_2(12) = g_1(\omega_1) g_0(\omega_2) \tilde{g}_2(12), \quad (5)$$

$$g_2(12) = g_0(\omega_1) g_1(\omega_2) \tilde{g}_2(12), \quad (6)$$

$$g_2(12) = g_1(\omega_1) g_1(\omega_2) \tilde{g}_2(12). \quad (7)$$

Now we are interested only in the principal physical aspect of a problem What kind of uncoupling will lead to the prediction of a spontaneous orientational order? So, in what follows, only the first order of the perturbation theory is to be considered. It means that all the interparticle correlations are determined by the central part of interaction energy. Due to the structure of right hand part of Eq. (2) this approximation corresponds to the first order of the thermodynamic perturbation on dipole–dipole potential. The solution of Eq. (2) with the uncoupling (5) gives

$$g_1(\omega_1) = (\alpha_c/\sinh \alpha_c) \exp(\alpha_c \cos \omega_1), \quad (8)$$

$$M = M_L(\alpha_c) = nm L[(m/kT)(H + 4\pi M_L/3)]$$

and represents the result of the modified mean field model, empirically suggested by Pshenichnikov [9]. In this case an effective field H_e , acting on a single particle, is determined through the Langevin magnetization. Expression (8) describes well the experimental data on magnetostatic properties of moderately concentrated ferrofluids and does not predict the ferromagnetic order even in the second order of perturbation theory [7].

Uncoupling (6) gives the one-particle distribution function in terms of Legendre polynomials, the coefficients of this expansion are dependent on the magnetization

$$g_1(\omega_1) = g_0(\omega_1) \left\{ 1 + (4\pi/3)(m/kT) \times [\cos \omega_1 - L(\alpha)] M \right\}, \quad (9)$$

$$M = M_L / [1 - (4\pi nm^2/3kT)(dL/d\alpha)].$$

The expression for magnetization (9) is valid only for diluted ferrofluids and equals to zero in the absence of an external field. The existent divergency, when $(4\pi nm^2/3kT) = 1$, is not accompanied with the orientational ordered solution, that is $g_1(\omega_1) = 1$, $H = 0$.

Using the last uncoupling (7), the solution of Eq. (2) leads to the known Weiss mean field model

$$g_1(\omega_1) = (\alpha_c/\sinh \alpha_c) \exp(\alpha_c \cos \omega_1), \quad (10)$$

$$M = M_L(\alpha_c) = nm L[(m/kT)(H + 4\pi M/3)],$$

predicting the magnetic phase transition when $(4\pi/3)(m^2n/kT) \geq 1$. This conclusion principally holds true in higher orders of the thermodynamic perturbation method [4], resulting in more complicated expressions for the one-particle distribution function. Moreover, the structure of these expressions coincides with the exponential form of (10), and the exponential factor is dependent on ferrofluid magnetization. Hence, the density functional approach represents a special case of the mean field theory. However, it is well known that expression (10) highly overestimates the initial magnetic susceptibility. The point is that only the last kind of expressions (4)–(7) predicts the spontaneous orientational ordering in ferrofluids. Apparently, this is caused by the fact that in exact virial expansion (4) all the influence of dipole–dipole interaction is determined by the pair correlation function $\tilde{g}_2(12)$. The self-consistent uncoupling (7) imposes the additional influence by way of functions $g_1(\omega_i)$. The latter also takes into account the dipole–dipole interaction, an influence of which turns out to be overestimated. Therefore, it is not a surprise that such excess account for the dipole–dipole interaction leads to prediction of a ferromagnetic state in dipolar fluids. However, uncoupling (7) is not valid even for diluted ferrofluids. Hence, the extension of these theories on more concentrated systems is incorrect. Thus, the principal physical conclusion on the possibility of ferromagnetic state in ferrofluids, arising from the mean field theories, has to be considered as questionable.

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