

LETTER TO THE EDITOR

On a statistical theory of magnetic fluids

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Abstract. An approach leading to a statistical theory of magnetic fluids is proposed for the first time. It is shown that magnetic fluid can be treated as a combination of two subsystems: (i) magnetic dipoles and (ii) molecules of a solvent fluid contained in cells with a potential field. The contributions from these subsystems to the thermodynamic properties of a magnetic fluid are additive quantities. The basic model of a magnetic fluid is justified by means of the thermodynamic perturbation theory for non-ideal systems. It is argued that the emergence of aggregates in magnetic fluids is a first-order phase transition. The densities of coexisting phases and the critical parameters are estimated.

A magnetic fluid is a colloidal suspension of ferromagnetic particles dispersed in the usual classical fluid (Shliomis 1974, Rosensweig 1979). The ferromagnetic particles are a system of strongly interacting magnetic dipoles and they influence the thermal properties of the fluid substantially. Until now magnetic fluids have been investigated by means of hydrodynamic models where the solvent fluid is treated as a continuous medium (Isaev and Kashevsky 1980, Maugin and Drouot 1983). However, it is impossible to study the thermal properties of magnetic fluids (magnetisation, specific heat, surface tension etc) without a correct assessment of the interparticle interactions. Phase transitions and the appearance of aggregates are of great interest (Krueger 1980). Therefore the construction of a statistical theory of magnetic fluids is a current problem.

Let us consider a magnetic fluid of volume V , containing N solvent molecules and n ferromagnetic particles. It is assumed that the particles are spherical, consist of a single domain, have a magnetic moment, s , $|s| = \text{const}$, and a diameter $d \sim 50\text{--}150 \text{ \AA}$. In order to prevent coagulation each ferromagnetic particle is enveloped in a surfactant layer, the thickness of this layer being $\sigma_s \sim 10 \text{ \AA}$. The system is subject to the action of a magnetic field H_e . In the temperature range in question, $T \sim 200\text{--}400 \text{ K}$, the total change in the internal energy of the ferromagnetic particles, ΔU_f , is negligible compared with the change in the internal energy of the solvent, ΔU_L , as $\Delta U_f/\Delta U_L \sim \varphi_V$ (φ_V is the volume concentration of the particles), so the internal structure of the particles can be neglected.

Let us use the following notation: q_j ($j = 1, \dots, N$) are the coordinate vectors of the molecules, r_α ($\alpha = 1, \dots, n$) are the coordinate vectors of ferromagnetic particles, θ_α , φ_α are the angular coordinates of the particle magnetic moments s_α and $\vec{r}_\alpha = (r_\alpha, \theta_\alpha, \varphi_\alpha)$. The partition function for the magnetic fluid in a magnetic field is

$$Z = \left(\frac{kT}{2\pi\hbar^2} \right)^{3(N+n)/2} M^{3n/2} m^{3N/2} \frac{Q}{N!n!} \tag{1}$$

where M and m are the masses of the particles and molecules, respectively. In the configuration integral,

$$Q = \int d^n \bar{r} d^N q \exp\left(-\frac{U}{kT}\right) = \int d^n \mathbf{r} \exp\left(-\frac{\tilde{U}}{kT}\right) \int d^N \mathbf{q} \exp\left(-\frac{\hat{U}}{kT}\right) \quad (2)$$

the system potential energy is $U = \tilde{U} + \hat{U}$, where

$$\tilde{U} = \sum_{i < j} \varphi_{ij} + \sum_{\alpha, i} \tilde{\varphi}_{\alpha i} \quad \text{and} \quad \hat{U} = \sum_{\alpha < \beta} \Psi_{\alpha\beta} + \sum_{\alpha} \tilde{\Psi}_{\alpha}.$$

It consists of the interactions of four types. (i) The interactions of molecules described by the pair potentials φ_{ij} . (ii) The interactions between molecules and particles described by the potentials $\tilde{\varphi}_{\alpha i}$. (iii) The interactions between ferromagnetic particles described by the potentials

$$\Psi_{\alpha\beta} = \Psi_{\alpha\beta}^{\text{dd}} + \Psi_{\alpha\beta}^{\text{s}}$$

where

$$\Psi_{\alpha\beta}^{\text{dd}} = \frac{s_{\alpha} s_{\beta}}{r_{\alpha\beta}^3} - \frac{3(s_{\alpha} \mathbf{r}_{\alpha\beta})(s_{\beta} \mathbf{r}_{\alpha\beta})}{r_{\alpha\beta}^5}$$

is the usual dipole-dipole interaction potential, and $\Psi_{\alpha\beta}^{\text{s}}$ is a short-range potential caused by the surfactant, $\mathbf{r}_{\alpha\beta} = \mathbf{r}_{\alpha} - \mathbf{r}_{\beta}$. (iv) The interactions of particles with the external magnetic field, $\tilde{\Psi}_{\alpha} = -S_{\alpha} H_e$. We shall assume that the potentials φ_{ij} and $\tilde{\varphi}_{\alpha i}$ have spherically symmetric asymptotics.

As is known (Shliomis 1974) the ratio of the ferromagnetic particle concentration to the concentration of molecules is very low,

$$n/N \sim 10^{-7} - 10^{-9}. \quad (3)$$

We use this fact to simplify the integral for Q in equation (2). Let us divide the physical space into n cells in such a way that each cell contains one particle and a number of solvent molecules. The mean number of molecules per cell is $N_0 = N/n \sim 10^7 - 10^9$.

The following assumptions are plausible. (a) The energy of interaction between molecules of different cells is negligible compared with the energy of interaction between molecules of the same cell (the corresponding error in calculation of the energy is $\sim (N_0)^{-1/3}$). (b) The interaction of each ferromagnetic particle with molecules of only a specific cell is taken into account. As the particle is much larger than a molecule, and due to the power decrease of $\tilde{\varphi}_{\alpha i}$ with distance (Barash and Ginzburg 1984), one can conclude that the corresponding error in the energy calculation is less than about $(N_0)^{-1/3}$. In view of these two assumptions, the cells can be treated as independent systems, and the configuration integrals over the coordinates of molecules in every cell, Q_{Δ} , are all equal. Thus the expression (2) is reduced to

$$Q = [N!/(N_0!)^n] Q_f Q_{\Delta}^n \quad (4)$$

where

$$Q_f = \int_V \dots \int d^n \bar{r} \exp\left(-\frac{\tilde{U}}{kT}\right) \quad Q_{\Delta} = \int_{V_{\Delta}} \dots \int d^{N_0} \mathbf{q} \exp\left(-\frac{\hat{U}_{\Delta}}{kT}\right)$$

and the subscript Δ means that the molecules contained in a single cell of volume V are examined. The factor of $N!/(N_0!)^n$ in (4) represents the number of various distributions

of molecules between the cells. Using (4), one obtains the system free energy, $\mathcal{F} = -kT \ln Z$,

$$\mathcal{F} = -kT \ln Q_f - nkT \ln Q_\Delta - kT \ln \left[\left(\frac{kT}{2\pi\hbar^2} \right)^{3(N+n)/2} \frac{M^{3n/2} m^{3N/2}}{n!(N_0!)^n} \right] \quad (5)$$

Thus Q_f describes the magnetic properties of the magnetic fluid, and Q_Δ describes the properties of the solvent in the field of $\tilde{\varphi}$. The most important consequence from (5) is the additivity of the thermodynamic quantities in both components of the magnetic fluid. For example when the potentials φ_{ij} and $\tilde{\varphi}_{\alpha i}$ have spherical symmetry, we obtain an expression for pressure:

$$p = -(\partial \mathcal{F} / \partial V)_{T, N, n, H_e} = p_\Delta + p_f$$

$$p_f = \frac{kT}{v_f} - \frac{1}{6n} \frac{1}{(4\pi)^2 v_f^3} \int_V \int \frac{\partial \Psi_{12}}{\partial r_{12}} \tilde{F}_2(\tilde{r}_1, \tilde{r}_2) d\tilde{r}_1 d\tilde{r}_2$$

$$p_\Delta = \frac{kT}{v_0} - \frac{1}{6N_0} \frac{1}{v_0^3} \int_{V_\Delta} \int |q_1 - q_2| \varphi'(|q_1 - q_2|) F_2(q_1, q_2) dq_1 dq_2 \\ - \frac{1}{3N_0} \frac{1}{v_0^2} \int_{V_\Delta} |q| \tilde{\varphi}' \left(\left| q - 0.5d_f \frac{q}{|q|} \right| \right) F_1(q) dq \quad (6)$$

where we have introduced the notation $v_0 = V/N$, $v_f = V/n$, $d_f = d + 2\sigma_s$. Two types of correlation functions are present in (6): $F_1(q)$, $F_2(q_1, q_2)$ and $F_1(\mathbf{r})$, $\tilde{F}_2(\tilde{r}_1, \tilde{r}_2)$. The subsystems being independent, each type of the correlation functions can be obtained from an independent chain of Bogolyudov equations (Fischer 1963). Mathematical simulation methods (Zamalin *et al* 1977) or perturbation theory (Zelener *et al* 1981) can also be used to obtain the correlation functions. Note that in the thermodynamic limit, $N \rightarrow \infty$, $n \rightarrow \infty$, $V \rightarrow \infty$, $N/V = \text{const}$, $n/N \rightarrow 0$, expression (6) is reduced to the corresponding expression for a homogeneous fluid (Fischer 1963).

Strictly speaking, the interaction potentials are not known, yet the properties of the magnetic fluids can be investigated by means of the following approach. We propose a 'reference model' with approximate potentials. The difference between the exact potentials and those in the reference model can be taken into account by means of various versions of the thermodynamic perturbation theory for non-ideal systems (Zelener *et al* 1981). As the subsystems are independent, this procedure can be performed for every subsystem separately.

For the magnetic subsystem the reference model is a system of particles with a centrally symmetric potential W , chosen in such a way that the first coefficients in the virial expansions for the reference model and for the real system are identical:

$$\exp[-\beta W(|\mathbf{r}_{ij}|)] = \langle \exp(-\beta \Psi_{ij}) \rangle_{\omega_i, \omega_j} \quad \beta = 1/kT$$

where $\langle \rangle_{\omega_i, \omega_j}$ stands for averaging over the different orientations of the magnetic moments of the particles. The perturbation is the difference between Ψ and W and the interaction of ferromagnetic particles with the external field H_e . An appropriate reference model for the solvent fluid subsystem is a system of molecules interacting with the potential φ_{ij} and, in addition, interacting with particles as if they were hard spheres. Here the perturbation is the attractive part of the potential $\tilde{\varphi}_{\alpha i}$.

Using the method described by Ruelle (1969) and by Zelener *et al* (1981), one can express the free energy given in (5) via the free energy of the reference model and a number of generalised group integrals:

$$\mathcal{F} = \mathcal{F}_0 - kT \sum_{j=1}^{\infty} \frac{(\sinh \alpha/\alpha - 1)^j}{v_0^j j!} b_j - nkT \sum_{j=1}^{\infty} \frac{1}{v_0^j j!} u_j$$

$$\mathcal{F}_0 = -kT \ln Q_f^0 - nkT \ln Q_{\Delta}^0 - kT \ln \left[\left(\frac{kT}{2\pi\hbar^2} \right)^{3(N+n)/2} \frac{M^{3n/2} m^{3N/2}}{n!(N_0!)^n} \right]. \quad (7)$$

Here $\alpha = sH_c/kT$, Q_f^0 and Q_{Δ}^0 are the configuration integrals for the reference model, b_j and u_j depend on the correlation functions of the reference model and on the difference between the model potentials and the real potentials (Zelener *et al* 1981). The series converge rapidly, if the perturbation energies are small ($\alpha \ll 1$, $\beta\bar{\varphi} \ll 1$).

One of interesting phenomena discovered in magnetic fluids is the appearance of aggregates (Krueger 1980). We shall consider this effect on the basis of the suggested approach for the case $H_c = 0$. The thermodynamics of the magnetic subsystem is determined completely by the reference model with the configuration integral Q_f^0 , where the particles interaction potential W is spherically symmetric and at distances $r \geq d_f$ can be presented as (Chan and Henderson 1984)

$$W = -\frac{1}{2}x^2 + O(x^4) \quad (8)$$

where $x = \beta s^2/r^3$, $\beta = 1/kT$ and at distances $r < d_f$ it is positive and tends to infinity. In view of (8), the magnetic subsystem behaves like the Lennard-Jones liquid. The parameters of the Lennard-Jones potential (Fischer 1963) are

$$\varepsilon = \beta s^4/3d_f^6 \quad \sigma = d_f. \quad (9)$$

The suggested analogy makes it possible to treat the appearance of aggregates in magnetic fluids as a first-order phase transition of the vapour-liquid type. The critical parameters of this transition, i.e. the temperature, T_c , and the density of the ferromagnetic particles, ρ_f^c , can be obtained from the corresponding states law (Fischer 1963),

$$kT_c/\varepsilon(T_c) \approx 1.3 \quad d_f^3 \rho_f^c \approx 0.3. \quad (10)$$

The compatible solution of (9) and (10) is

$$kT_c = (1.3/3)^{1/2} s^2/d_f^3 \quad (11)$$

or, in the dimensionless form, $\lambda_c = 1.52$, where $\lambda = s^2/kTd_f^3$. For $T > T_c$ ($\lambda < \lambda_c$) there are no aggregates. The estimate of the critical value of λ , obtained here in a simple manner, coincides with the result of Tsebers (1982) calculated within the framework of the mean-field theory.

For temperatures close to T_c ($|\Delta T/T_c| \ll 1$, so that $|\Delta\varepsilon/\varepsilon(T_c)| \ll 1$) the corresponding states law enables one to obtain the ratio δ of the ferromagnetic particle concentrations in strongly and weakly condensed phases.

For magnetite particles (the saturation magnetisation of magnetite is $M_f = 450$ G, $s = \frac{1}{2}M_f\pi d^3$) having a diameter $d = 120$ Å, the above estimates are

$$T_c \approx 400 \text{ K} \quad \rho_f^c \approx 1.1 \times 10^{17} \text{ cm}^{-3} \quad \delta(T = 300 \text{ K}) \approx 10.$$

Note, in conclusion, that the results presented support a hypothesis by de Gennes and Pincus (1970) that the phase diagrams of magnetic fluids are similar to that of the usual van der Waals liquid.

It is reasonable to expect that experimental investigations of the structure factor, correlation functions, the behaviour of T_c as a function of d_f and M_f , combined with the present approach and mathematical simulation methods, will make it possible not only to specify the potentials, but also to calculate reliably the thermodynamic properties of magnetic fluids.

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