MAGNETIC PROPERTIES OF FERROCOLLOIDS:
THE EFFECT OF INTERPARTICLE INTERACTIONS

Institute of Continuous Media Mechanics, USC of the USSR Acad. Sci. 614061, Perm, USSR

Several new experimental results on the initial susceptibility of magnetic fluids are presented and discussed from the theoretical point of view.

1. Introduction

Experimental data recently obtained compel us to revise the conventional concept of a magnetic fluid (MF) as an ideal gas of magnetic particles suspended in a liquid matrix. Even attributing the deviation of MF magnetization from the Langevin law to the polydispersedness of magnetic grains, it is impossible to explain our experimental results [1,3] on either temperature, concentration or frequency dependence of the initial susceptibility $\chi$, as well as the data by other authors [4-6], in the framework of a simple paramagnetic model. The latter predicts the linear increase of $\chi$ with the solid phase volume fraction $\eta$, the Curie-type temperature behavior ($\chi \sim 1/T$) and simple dynamical response $\chi \sim (1 + i\omega\tau)^{-1}$ based on a single characteristic time of relaxation.

As a matter of fact, only in highly-diluted colloids the susceptibility is proportional to the concentration: the linearity of $\chi(\eta)$ dependence fails already for $\eta \geq 1\%$. In no one of the studied MF samples (see also refs. [5,6]) the Curie law was observed. Instead the non-monotonic behavior $\chi(T)$ with the maximum at certain point $T_0$ has been found. The profile of the dispersion curves $\chi(\omega)$ implicates an extremely wide relaxation time spectrum: $\tau_{\text{max}}/\tau_{\text{min}} \approx 10^3-10^8$.

With no doubt, all these effects originate from the interparticle interactions in ferrocolloids. The first attempts of a theoretical treatment of such phenomena have been made in refs. [7-9]. In refs. [8,9] the mean-field model (MFM) with the molecular field constant equal to the Lorentz value $4\pi/3$ was proposed. The free-energy density expression used in refs. [8,9] differs from the standard Weiss theory by taking into account the excluded-volume effects. Due to that in addition to the usual second-order phase transition into a uniform spontaneously magnetized state ($M \neq 0$ for $H = 0$) the first-order transition in a certain concentration and temperature range has been predicted. The latter transition in principle could be interpreted as the agglomeration of MF but unfortunately it does really exist only under the assumption that even at $H = 0$ the nuclei of the new phase have a needle-like form: if a magnetic droplet is spherical, its demagnetization field exactly compensates the Lorentz term. Thus the conclusions of MFM being in reasonable agreement with the experiment at $H \rightarrow \infty$ entirely contradict it at $H = 0$. This is evidently due to the fact that MFM ignores concentration fluctuations and spatial correlations of MF particles, which become negligible only in $H \rightarrow \infty$ limit. In the present paper we discuss the so-called mean-spherical model (MSM) based on a special choice of a pair-correlation function. This theory is free from the above mentioned shortcomings of MFM.

2. Theory

Let us treat MF as a system of point dipoles with magnetic moments $m$ positioned in the centres of non-permeable spheres of diameter $d$. 

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Thus the particle pair-potential is

\[ u(r) = \begin{cases} \infty & (r < d), \\ u_{dd} & (r \geq d), \end{cases} \]

where \( u_{dd} \) is the dipole–dipole interaction. Thermodynamics of MSM with the potential (1) has been developed in refs. [10,11]. As it has been shown in ref. [12], MSM pretty well describes the dipolar system in the intermediate volume fraction \( \eta = \pi n d^3 / 6 \leq 0.2 \) (here \( n \) is the particle number concentration) and dipole-interaction constant \( \lambda = m^2 / d^3 k_B T \geq 5 \) range. These values of \( \eta \) and \( \lambda \) are relevant to the majority of real MF samples.

According to ref. [11] the chemical potential of MF in the MSM approximation is

\[ \kappa = k_B T \left( \ln \frac{\eta}{1 - \eta} + \eta^2 - 13 \eta + 14 \frac{2(1 - \eta)^3}{2} - 8 \lambda b \right). \]

(2)

The first two terms are due to the steric effects, the last originates from the dipolar interaction. Parameter \( b \) in (2) is determined by the equations

\[ q(x) = (1 + 2x)^2 / (1 - x)^4. \]

From expression (2) it follows that in the considered system the first-order phase transition of a gas-liquid type is possible. For the critical point position equations \( \partial \kappa / \partial \eta - \partial^2 \kappa / \partial \eta^2 = 0 \) yield \( n_C = 0.0555 \), \( \lambda_C = 4.445 \); the corresponding phase diagram is presented in fig. 1. In the low temperature range (\( \lambda > \lambda_C \)) the dipolar system can exist in either “gaseous” (1), “liquid” (2) or “mixed” (1 + 2) state. At \( \lambda < \lambda_C \), when there is no phase separation, the initial susceptibility is given by the expression

\[ \chi = \frac{nm^2}{3k_B T} q(-b), \]

(3)

which is in a good agreement with the results of the concentration dependence \( \chi(\eta) \) measurements of kerosene-based colloidal solutions of magnetite – see curve 1 in fig. 2. At \( \lambda > \lambda_C \) MF with the initial volume fraction \( \eta \) is separated into two phases differing by the concentration of magnetic grains: \( \eta_A < \eta \) in phase 1 and \( \eta_B > \eta \) in phase 2.

The appearing droplets of a new phase (highly-magnetic if \( \eta < \eta_C \) and weakly-magnetic if \( \eta > \eta_C \)) in the absence of the external field are obviously spherical. The magnetic susceptibility of the system (1 + 2) can be calculated using the well-known result [13]

\[ \mu = \begin{cases} \mu_1 + 3c\mu_1(\mu_2 - \mu_1) / (\mu_2 + 2\mu_1) & \text{for } c \ll 1, \\ \mu_2 - 3(1 - c)\mu_2(\mu_2 - \mu_1) / (\mu_1 + 2\mu_2) & \text{for } (1 - c) \ll 1. \end{cases} \]

(4)

Here \( \mu_1 \) and \( \mu_2 \) are the permeabilities of the phases and \( c = (\eta - \eta_A) / (\eta_B - \eta_A) \) is the volume fraction of the phase 2. Near the critical point (\( \eta = \eta_C, \lambda \geq \lambda_C \)) the initial susceptibility is given by the expression

\[ \chi = \frac{nm^2}{3k_B T} q(-b), \]

which is in a good agreement with the results of the concentration dependence \( \chi(\eta) \) measurements of kerosene-based colloidal solutions of magnetite – see curve 1 in fig. 2. At \( \lambda > \lambda_C \) MF with the initial volume fraction \( \eta \) is separated into two phases differing by the concentration of magnetic grains: \( \eta_A < \eta \) in phase 1 and \( \eta_B > \eta \) in phase 2.
mixture permeability is given by a relation \([13]\)
\[
\mu^3 = (1 - c)\mu_1^3 + c\mu_2^3
\]
for \((\mu_1 - \mu_2)^2/\mu_2^2 < 1\), \((5)\)
which holds for arbitrary values of \(c\). Curve 2 in fig. 2 has been obtained with the aid of (5) for \((\mu_1 - \mu_2)^2/\mu_2^2 = 1/9\). This graph displays a characteristic bowing near point \(C\) (see fig. 1) caused by MF phase separation. Curve 3 in fig. 2 corresponds to formulae (4) with \(\lambda = 5\), its dash-lined part shows the expected behavior \(\chi(\eta)\) in the concentration region where approximations (4) fail.

Expression (3) together with formula (4), describing the influence of phase separation on \(\mu\), provides the possibility of determining the temperature dependence \(\chi(T)\) as well. In fig. 3 the comparison between theoretical and experimental values of \(\chi(T)\) is presented. MSM parameters involved in this calculation have been evaluated from the high-temperature asymptotics (exact fit at \(T = 340\) K). The decrease of \(\chi\) while cooling MF below the point of maximum \(T_0 \approx 250\) K owes to the phase transition. In this interval the temperature fall (shown by the arrow in fig. 1) produces rapid growth of the concentration \(\eta_B\) of highly-magnetic phase along with its permeability \(\mu_2\) and, simultaneously, decrease of \(\eta_A\) and \(\mu_1\). When \(\mu_2 \gg \mu_1\) the first line of (4) yields \(\chi = (1 + 3c)\chi_1 + 3c/4\pi\). Though \(c\) depends on \(\lambda\) in rather a complicated way, its definition indicates that by the order of magnitude it does not exceed \(\eta\). Therefore the decrease of \(\chi(T)\) at \(T < T_0\) is primarily due to \(\chi_1\) diminution along the branch CA of the phase diagram. The difference in curvature between theoretical peak and experimentall cusp in fig. 3 arises probably from the polydispersedness of real MF.

Since now we take for granted that due to the magnetodipole interaction colloidal particles might be associated in the droplet aggregates of the volume \(V \gg V_0\), where \(V_0\) is the volume of an “elementary” ferroparticle. In the absence of the field the aggregates are spherical and have zero magnetic moments. With allowance for the polydispersedness of MF it is natural to assume that the internal magnetic structure of the drop to some extent resembles that of the dipolar glass. This hypothesis is favoured also by the character of MF magnetic susceptibility dispersion (see fig. 4), which displays almost complete similarity to the dipolar glass spectra \(\chi(\omega)\) \([14]\). To the latter an extremely wide range of relaxation times is inherent.

For the theoretical interpretation of MF dynamic susceptibility measurements we employ a cluster model of a magnetic glass by Tholence–Tournier–Wohlfarth \([15]\). This approach treats the glass as a system of non-interacting superparamagnetic domains with magnetization-reversal time \(\tau = \tau_0 \exp(KV/k_BT)\), where \(\tau_0 \approx 10^{-9}\) s and \(V\) is the domain volume. Assuming that in each cluster the particles are coupled by the magnetodipole interaction, one gets an estimate for the effective anisotropy constant \(K \approx (md^3/\eta_B)\). Theory \([15]\) contains an adjustable function \(f(V)\) – cluster volume distribution; according to the experimental data this distribution has to be rather wide. For \(f(V)\) we choose \([1]\) the gamma-distribution of \(1/V\) viz.

\[
f(V) = \frac{V^{1 + \gamma}}{\Gamma(1 + \gamma)V^{2 + \gamma}} \exp(-V_*/V), \quad (6)
\]

where \(V_*\) and \(\gamma\) are the parameters. Averaging of the dynamic susceptibility \(\chi(V) = [1 + i\omega\tau(V)]^{-1}\) with the function (6) yields

\[
\chi' \sim \left[-\ln(\omega \tau_0)\right]^{-1 - \gamma}, \quad \chi'' \sim \left[-\ln(\omega \tau_0)\right]^{-\gamma}.
\]

This formulae for \(\gamma \approx 0.3\) provide a good agreement with the measurement results – see fig. 4.
Comparison of the absolute values of theoretical and experimental data on $\chi'$ and $\chi''$ gives the estimate $V_0 = 10V_0$. The average cluster volume $\bar{V} = V_0/\gamma$ is therefore $30V_0$ in accordance with the hypothesis of many-particle aggregates.

References