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PERTURBATIONAL STATISTICAL THEORIES OF MAGNETIC FLUIDS

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The theories that account for the colloidal structure of a magnetic fluid give far better results than the gas-type or mean-field models. We show this by using standard perturbative approaches of colloidal science and expressing the magnetization *M(H)* and the initial magnetic susceptibility χ as Taylor series about the Langevin values $M_L(H)$ and χ_L. One of the methods surveyed enables the structural study of the ferrocolloid through the analysis of the pair distribution function. We give a polar plot of this object when an external magnetic field H is present, showing the effect it has on the otherwise isotropic suspension.

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1. Introduction

The magnetic fluids (ferrocolloids) are suspensions of solid magnetic particles dispersed in a liquid carrier. The perturbative methods [4] of the statistical study of liquids are well suited to colloids as well [5]. The use of these methods improves [10, 11] the results of the 'traditional' approach to a ferrocolloid as being a Langevin gas of magnetic particles, i.e. an ideal paramagnetic gas: The 'traditional' approach neglects the interactions between particles, either steric (the particles are coated with a layer of a surfactant solution to keep them apart) or magnetic (there is a dipole moment associated with each magnetic particle), while the theories here presented do take these interactions into consideration, them being the very building blocks of structure and of physical manifestations. Of these latter, magnetization and initial magnetic susceptibility are investigated, experimental data sustaining our conclusions being quite consistent [1, 2, 3, 10, 11].

The final result of all approaches is the effect a 'Langevin + deviations' splitting in the physical properties investigated, showing how the hard-sphere colloidal structure adjusted by the dipolar interaction contributes to the 'traditional' gas-type manifestations of the magnetic liquid. The aim of this paper is to review the perturbative means of dealing with such ‘un-traditional’ behavior. A complete but lengthy, unpublished version of this work is avaible [9].

2. Theoretical basis

The theories presented differ in the way that the energy of interparticle interaction is broken into a 'reference' part and a 'perturbation'. The case at hand is that of monodisperse suspensions of spherical particles, generalizations being possible but generally cumbersome. The total energy of the N dipolar hard spheres which model the surfactant-coated magnetic particles suspended in the carrier liquid, is, when placed in an external magnetic field **H**:

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$$H_N = \sum\sum_{i<j=1}^{N} U_S(ij) + \sum\sum_{i<j=1}^{N} \left[\frac{\mathbf{m}_i \cdot \mathbf{m}_j}{r_{ij}^3} - 3\frac{(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] + \sum_{i=1}^{N} (-\mathbf{m}_i \cdot \mathbf{H}) \qquad (1)$$

with $U_S(ij)$ the hard sphere repulsion of radius d between particles i and j, the expression in the square brackets, hereafter denoted by $U_D(ij)$, is the interaction energy between dipoles associated with spheres i and j, and then $U_{MAG}(i)$ - the energy of the dipole i in the external field **H**. Here $\mathbf{m}_i$ is the magnetic moment of the i-th particle and $\mathbf{r}_{ij}$ is the position vector of the center of the sphere j with respect to that of sphere i. The potentials are manifestly pairwise and independent of the concentration n.

2.1 The algebraic perturbation method

This is a rigorous method of perturbing the liquid of dipolar hard spheres, by switching on a weak external field; it was first described by V.I. Kalikmanov in 1992 and subsequently developed [1]. The perturbational technique used by Kalikmanov is a rigorous procedure devised by Ruelle in [8].

Here $H_N = H_0 + H_{MAG}$ making it clear that the perturbed system is the magnetic fluid put in the external field, while the reference liquid is the magnetic fluid 'as is': $H_0 = H_S + H_D$. By use of the Mayer functions corresponding to the dipole-field interactions H_{MAG}, the ratio of the partition function of the perturbed system to the partition function of the reference system can be put in the exponential form through use of Ruelle's theorem. This exponential series converges rapidly after its second term if the Langevin parameter mH / kT = α <1, which is precisely the expression of the condition that the field be small [1]. The j-th coefficient of the series is given by algebraic (rational) combinations of the j-particle correlation functions of the dipolar hard spheres, [1, 8]. We must note that we only need the 2-particle correlation functions but the actual calculations use the perturbational expression of it [4]. Tedious work leads to the following expression for the free energy [1, 9]:

$$\beta F - \beta F_0 = -N\frac{\alpha^2}{6} - \frac{\alpha^2}{54} n^2 V d^3 \gamma \left[4\pi + \gamma d^3 n \frac{\pi^2}{9} \right] \qquad (2)$$

Here $\gamma = m^2/(kTd^3)$ is the coupling constant of the dipolar interaction and V is the volume of the liquid. The magnetization is easily seen to be [6]:

$$M(H) = \chi_L \left[1 + \frac{4\pi\chi_L}{3} + \frac{(4\pi\chi_L)^2}{144} \right] H \qquad (3)$$

and consequently the initial magnetic susceptibility is

$$\chi = \chi_L \left[1 + \frac{4\pi\chi_L}{3} + \frac{(4\pi\chi_L)^2}{144} \right] \qquad (4)$$

Eq. 3 and Eq. 4 emphasize that the magnetic behaviour of the suspension deviates from the ideal Langevin pattern.

2.2. Thermodynamic perturbations

The method developed by Yu. Buyevich and A. O. Ivanov in [2] it is a standard hard-sphere

perturbation theory of the partition function [4, 6, 7].

Here $H_N = H_0 + H_D$ with $H_0 = H_S + H_{MAG}$, i.e. the perturbation is the dipolar interaction H_D and the reference liquid is made up of 'magnetic noninteracting hard spheres' - this is a Langevin gas of hard spheres. H_{MAG} is used actually as a device which offers the possibility of employing the standard results of non-spherical perturbations of a spherical hard core potential [4]. So, the field is incorporated into the angle averaging technique:

$$\frac{1}{4\pi}\int_0^{2\pi} d\zeta \int_{-1}^{1} d(\cos\omega) \rightarrow \frac{1}{4\pi}\int_0^{2\pi} d\zeta \int_{-1}^{1} e^{\alpha\cos\omega} d(\cos\omega) \tag{5}$$

where ξ and ω are the azimuthal and the polar angles of the magnetic moment with respect to the direction of **H,** for convenience the direction of the z axis. This incorporation of the field also makes it easy to separate a Langevin contribution of ideal paramagnetic gas-type in the partition function, and consequently in the magnetization and the initial magnetic susceptibility [2, 9]:

$$M(H) = M_L(H)\left[1 + \frac{4\pi}{3}\chi_L\right] \tag{6}$$

$$\chi = \chi_L(1 + \frac{4\pi}{3}\chi_L) \tag{7}$$

Here $M_L(H)$ is the Langevin value of the magnetization, $M_L(H) = \chi_L H = nmL(\alpha)$, with $L(\alpha) = \coth\alpha - \frac{1}{\alpha}$ the Langevin function. Eq. 6 and Eq. 7 also show deviations of the magnetic behaviour from the ideal Langevin pattern. Notably, the latter expressions are the same with that for O(1) deviation from the Langevin pattern in the algebraic result (Eqs. 3 and 4).

2.3. Perturbations of the pair distribution function

The last method reviewed, a.k.a. 'the BBGKY method', is a standard hard-sphere perturbation theory of the colloidal 2-particle correlation function, a technique stemming directly from the theories of liquid state [4, 5]. The method was put forward by A.O. Ivanov and O.B. Kuznetzova [3].

Here too $H_N = H_0 + H_D$ and $H_0 = H_S + H_{MAG}$ just as before, with H_{MAG} accounted for by the same technique of angle averaging. The only difference is that the perturbed object is the $g_2(\mathbf{r}_{12}, \omega_1, \omega_2)$ 2-particle correlation function of the reference 'Langevin gas of hard spheres' above. The magnetization M(H) is given by a straightforward expression involving the 1-particle correlation function, $g_1(\omega_1)$:

$$M(H) = \frac{nm}{2}\int_{-1}^{1} \cos\omega g_1(\omega) d(\cos\omega) \tag{8}$$

and use of a BBGKY-type hierarchy gives us the experimentally-inaccesible g_1 in terms of the experimentally-accesible (e.g. through the structure factor) g_2.

This latter function is determined by perturbation with O(1) in the dipolar interaction [3, 9]:

$$g_2(\mathbf{r}_{12}, \omega_1, \omega_2) = g_d + (a+b)(3\cos^2\theta_{12} - 1) + c + d \tag{9}$$

apart from terms that do not matter for the calculations of physical properties. Such an expression offers the possibility of further studying the structural properties of the ferrocolloid, e.g. the structural anisotropy = the dependence of g_2 on the interparticle polar angle θ_{12} (see Section 4). The terms in Eq. (9) are:

$g_d(r_{12})$ the hard sphere pair distribution function

a the dipolar perturbational contribution

b, c, d terms that account for the mean field contribution and also for the hard sphere structure

Using the BBGKY the differential equations makes it possible to write down O(2) results::

$$M(H) = M_L(H)\left[1+\frac{4\pi}{3}\frac{dM_L(H)}{dH}+\frac{1}{2}\left(\frac{4\pi}{3}\right)^2 M_L(H)\left(\frac{d^2M_L(H)}{dH^2}\right)+\frac{(4\pi)^2}{144}\left(\frac{dM_L(H)}{dH}\right)^2+K\right] \quad (10)$$

dropping out the terms (abbreviated by the constant K) that do not contribute to the initial susceptibility, which is:

$$\chi = \chi_L\left[1+\frac{4\pi\chi_L}{3}+\frac{(4\pi\chi_L)^2}{144}\right] \quad (11)$$

We used $\frac{1}{1\pm x^2} = 1\mp x + x^2 \mp x^3 + \ldots$ to write down expressions of $\frac{dL(\alpha)}{d\alpha}$ and $\frac{d^2L(\alpha)}{d\alpha^2}$, and have again separated the contribution of Langevin type, showing that the magnetic properties are controlled by the interparticle correlations attained by both types of interaction: steric and dipolar. Eq. (11) is the same with the algebraic results (Eq. (4)), and that represents a mutual validation of the two methods, but Eq. (11) is better than Eq. (3) because it is valid no matter if the field is low or high.

3. Range of validity and order of approximation

Writing down a hard sphere perturbative series, Sections 2.2. and 2.3, is usually restricted to O(1) in the perturbation and in the density, because of computational difficulties [2, 3, 9]. This makes the BBGKY method of Section 2.3 very useful, as O(1) in the perturbative series of the 2-particle correlation function (also O(1) in the concentration) is converted into thermodynamical O(2) results, i.e. magnetization, through the specific device of the method, which uses the BBGKY hierarchy [3, 9]. We remark here that the first term of Eq. (10) is actually computed by means of the O(1) term in the virial series for the hard sphere partial distribution function g_d [7].

Choosing the dipolar hard spheres as the reference fluid, Section 2.1, enables one to use a method that gives O(2) thermodynamical results in the perturbation and density, but is limited to low fields [1, 9].

3.1 Algebraic perturbations (O(2) perturbative series, O(2) thermodynamics, low fields)

The choice of the reference system makes H_{MAG} be the perturbation, so that the method works in low fields (a meaningful expression of 'low' is α <1). Even though initially developed at low concentrations of the dispersed phase, n < 1%, careful analysis [1] by Szalai et al. of the integrals involved showed that the method is valid through all concentrations of practical interest $0 < nd^3 < 0.95$. In [1] it is also shown that the theory is in good agreement with experimental findings for weakly to moderately coupled dipoles: γ < 2.5.

3.2 Thermodynamic perturbations (O(1) perturbative series, O(1) thermodynamics, arbitrary fields)

The angle averaging device enables the use in an arbitrary field. Even though hard sphere perturbations work primarily at high densities of the dispersed phase, this method functions best when the volume fraction of the hard spheres is in the range 6% - 12% , mostly because of the limitation imposed on the perturbative series by considering only O(1) terms. This happens because of difficulties related to the calculation of the relevant integrals. The method also works at low densities $0.1\% < n < 6\%$ where U_D is weak and does not influence the fundamental structure of the hard spheres or the corresponding physical properties [4]. Formally, this method is a high temperature approximation, a.k.a. HTA [2, 11], but a better criterion for the convergence of the series involved is that the effect of the perturbation on the structure of the colloid be small [4, 2]. This method works for $\gamma < 4 \div 5$.

3.3 Perturbations of the pair distribution function - The BBGKY method (O(1) perturbative series, O(2) thermodynamics, arbitrary fields)

The angle averaging device enables use in an arbitrary field. Hard spheres perturbations work as usual when the volume fraction of the hard spheres motivates peturbational techniques. The method is in very good agreement with experimental findings up to high concentrations n ~ 18% of the magnetic phase; low concentrations being covered by this approximation on the same grounds as above. In fact, the same criterion of convergence of the perturbative series applies as before: the effect of the perturbation on the structure of the suspension be small, rather than the HTA $U_D << kT$. This method works for $\gamma < 4 \div 5$. The success of this method is justified by the following argument: g_2 is intimately connected with the structure of the ferrocolloid and the structure of the colloid is primarily influenced by the hard-spheres, and not by the fluctuations around hard spheres, so that consideration of O(1) terms in the perturbative series for g_2 suffices (compare with the method above which retains O(1) in the perturbation, and consequently in the density, in the expression of the partition function, which is not a direct indication on the structure but rather on the full physical behaviour). O(2) in the density is attained by the specific device of re-obtaining the thermodynamics from the microscopic analysis through use of 1- and 2-particle correlation functions, connected by the BBGKY hierarchy.

4. Further studies

All the theories pesented here apply to polar fluids as well. Care must be taken when computing the dielectric constant of the polar fluid by the method of Section 2.3: an additional term is needed in the perturbative series of g_2 [3]. The theory of Section 2.1 was actually devised for use with polar fluids [1].

The method of thermodynamic perturbations retains in its very structure the opportunity of equilibrium thermodynamic studies (e.g. the phase diagram, phase separation) by use of the Carnahan-Starling model of the hard spheres reference liquid, and even that of (tentative) considerations on nonequilibrium properties (see [2] for further comments).

Determination of g_2 is itself important as this correlation function is a central object in the study of colloidal suspensions. The two probabilities $g_2(\theta_{12} = 0)$ and $g_2(\theta_{12} = \pi/2)$, obtained by integrating with respect to the angles ω_1, ω_2 and ϕ_{12}, are such that their ratio (which is the anisotropy of g_2) shows a dependence on the r_{12} distance, typical to the liquid state, specifically of

the first virial coefficient in the perturbative expression of $g_d(12)$, see Eq. (10) and [7]. This is a direct manifestation of the short range order induced by the field on the magnetic hard spheres, similar to that already showed by a simple liquid of hard spheres. This phenomenon can be observed from the data plotted in Fig. 1 below, calculated for H=100 kA/m and n=10% sample concentration, and this packing of the 'magnetic hard spheres' is one aspect missed by the 'traditional' gas-type or mean field models. The smooth profile of the curve in Fig. 1 is due to the perturbation U_D (which also makes the two probabilities above be un-equal).

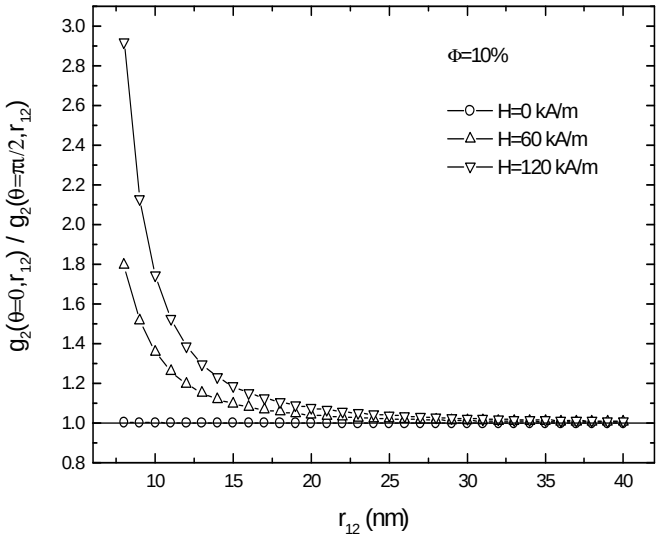

Fig. 1. The dependence of the anisotropy on the spacing between particles (first virial approximation).

This structural anisotropy is due to the external field **H**. The field enables arrangements of the magnetic particles conformal with the prescriptions of U_D ($\theta_{12}=0$ is more probable than $\theta_{12}=\pi/2$ when the magnetic moments are ordered parallel to the z axis, i.e. in the limit of infinite field).

This effect is dependent on the interparticle distance r_{12} ($U_D \sim 1/r_{12}^{\,3}$) and is important on a scale of approx. 30 nm, as can be seen in Fig.2 below, which is a polar plot of $g_2(\theta_{12}, r_{12})$ as a function of θ_{12}, for values of 12, 15, and 30 nm of the r_{12} interparticle distance, calculated for H=100kA/m. The effect increases with the value H of the external imposed magnetic field **H**, as shown by the polar plot of $g_2(H, \theta_{12})$ as a function of θ_{12}, for values of 0, 60 and 120 kA/m of the magnitude H of the external imposed field **H** and r_{12} =10 nm of the interparticle distance. Both plots are drawn for n=10% sample concentration (we have again integrated on the ω angles and on the azimuthal $\mathbf{r}_{12}$ angle, ϕ_{12}):

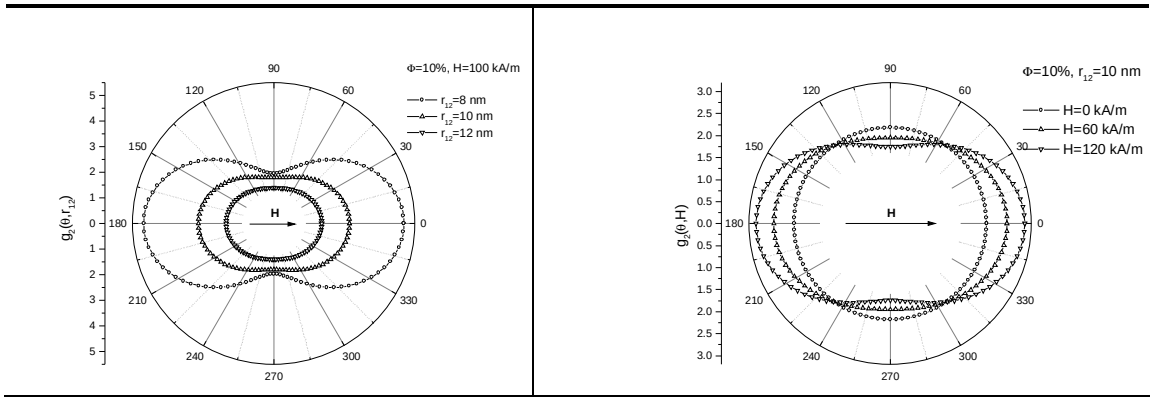

Fig. 2. Polar plot of the interparticle correlation function $g_2(12)$, showing the anisotropy, the **H** and the r_{12} dependence as accounted by Eq. 9.

Experimental studies showing (a) the behavior accounted for in this paper, typical of the liquid state and (b) the anisotropy in the function g_2 and hence in the structure, due to the field, are consequently possible, e.g. neutron scattering or optical studies of magnetically induced dichroism. See also [2, 3, 10, 11] and a further paper of VS.

5. Conclusions

This paper has evidenced the benefits of taking into account the structure of ferrocolloids when attempting studies of macroscopic behaviour, such as magnetization and magnetic susceptibility. The teories presented [1, 2, 3], all of which are various types of well-known fluid-state perturbational methods [4, 5, 6, 7] are valid in a wider region of the parameter space (concentration of magnetic phase vs. value of imposed magnetic field) than gas-type or mean-field models, also effecting an a posteriori justification of such crude approximations. Compared to the integral-equations methods, such as the spherical-model based theories, the perturbational methods offer a better, more realistic, picture of the microscopic interaction and structure. We note here that the mean-spherical model offers good description of experimental studies (see [11]). See our Section 3.

The BBGKY method (perturbations of the 2-particle correlation function), Section 2.3, is particulary well-suited for further developments [3]. The expression of the 2-particle intercorrelation function, apart from giving information on the structure of the colloidal suspension, is a basic input in the optical investigations such as magnetically induced dichroism.

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References

[1] V. I. Kalikmanov, PRE **59**, 4085 (1999); Statistical Thermodynamics for Ferrofluids, Physica A **183** (1992), 25 - 50; Reply to ‘Comment on "Algebraic perturbation theory for pola fluids: A model for the dielectric constant"’, Phisycal Review **62**, 8851 (2000); I. Szalai, K. I. Chan, D. Henderson, Comment on "Algebraic perturbation theory for polarfluids: A model for the dielectric constant", PRE **62**, 8846 (2000).

[2] Yu. A. Buyevich, A. O. Ivanov, Equilibrium Properties of Ferrocolloids, Physica A **190**, 276 (1992); Statistical Thermodynamics for Ferrocolloids, J. Magn. Magn. Mat. **85**, 33 (1990).
[3] A. O. Ivanov, O. B. Kuznetzova, Magnetic properties of ferrocolloids: an influence of interparticle correlations, Physical Review E **64**, 041405-1 (2001); Magnetic Properties of Dense Ferrocolloids, J. Magn. Magn. Mat. **252**, 135 (2002).
[4] J. A. Barker, D. Henderson, What is "liquid"? Understanding States of Matter, RMP **48**, 587 (1976).
[5] W. van Megen, I. Snook, Equilibrium properties of suspensions, ACIS **21**, 119 (1984).
[6] L. D. Landau, E. M. Lifshitz, Statistical Physics, (in romanian), publisher 'Editura Tehnică', Bucharest, 1988.
[7] R. Balescu, Equilibrium and Nonequilibrium Statistical Mechanics, Wiley Interscience, New York, 1975.
[8] D. Ruelle, Statistical Mechanics: Rigorous Results., Benjamin, New York, 1969.
[9] L. B. Popescu: Perturbative statistical theories for the investigation of magnetic fluids (in romanian), MSc thesis, West University of Timisoara, 2004 (unpublished).
[10] L. B. Popescu, V. Socoliuc, D. Bica, L. Vekas, J. Optoelectron. Adv. Mater. **7**, 753 (2005).
[11] K. I. Morozov, A. F. Pshenichnikov, Yu. L. Raikher, M. I. Shliomis, JMMM **65**, 269 (1987); M. I. Shliomis, A. F. Pshenichnikov, K. I. Morozov, I. Yu. Shurobor, JMMM **85**, 40 (1990); K. I. Morozov, A. V. Lebedev, JMMM **85**, 51 (1990); A. F. Pshenichnikov, JMMM **145**, 319 (1995); A. F. Pshenichnikov, V. V. Mekhonoshin, A. V. Lebedev, JMMM **161**, 94 (1996).