

## Virial Expansions for Low Dimensional Ferrofluids

M. Widom and H. Zhang

Department of Physics, Carnegie-Mellon University, Pittsburgh, Pa. 15213

### Abstract

Ferrofluids are colloidal suspensions of magnetic particles which we model as a dilute gas of dipolar hard spheres. At low particle density the osmotic pressure and magnetic susceptibility may be expanded in a virial series. We evaluate the second virial coefficients for fluids confined to a line, or to a plane, as well as ordinary three dimensional fluids in ellipsoidal containers. We focus our attention on anisotropy of the magnetic susceptibility and point out the role of particle chaining in determining the magnetic anisotropy of low dimensional ferrofluids.

### Introduction

Dipolar hard sphere fluids are a widely studied model in statistical mechanics [1]. The motivations for this study include the application to the study of fluids of molecules [2] whose interactions are dominated by electric dipole moments  $\mu$  at large separation, and the application to ferrofluids [3] and electro-rheological fluids [4]. A further motivation is the anisotropy of the dipolar interaction

$$\phi(\mathbf{r}_{12}) = \frac{3(\boldsymbol{\mu}_1 \cdot \hat{\mathbf{r}}_{12})(\boldsymbol{\mu}_2 \cdot \hat{\mathbf{r}}_{12}) - \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} \quad (1)$$

which ranges from ferromagnetic when  $\mathbf{r}_{12} \parallel \boldsymbol{\mu}_1$  to antiferromagnetic when  $\mathbf{r}_{12} \perp \boldsymbol{\mu}_1$ . In three dimensions there are additional subtleties since the interaction is long range, so that physical properties become dependent on the shape of the container in which the fluid is held.

One consequence of the anisotropy of the dipolar interaction (1) is a tendency for spheres to align into chains, with each dipole moment pointing towards a nearest neighbor along the chain (see Figure 1.) The degree of chain formation depends both on the number density  $\rho$  of particles, and on the strength of the dipolar interaction. A reduced dipolar coupling constant may be defined

$$\lambda = \frac{\mu^2}{k_B T a^3} \quad (2)$$

where  $a$  is the hard sphere diameter. For typical dipolar molecules this coupling is not large and ranges from  $\lambda \approx 0.06$  for  $\text{CHCl}_3$  to  $\lambda \approx 0.5$  for  $\text{H}_2\text{O}$  at their Boyle temperatures [2]. For room temperature ferrofluids, however, it is quite possible to achieve  $\lambda \approx 1 - 10$ , and for electrorheological fluids  $\lambda$  may reach 1000. These strongly coupled colloidal materials thus represent a parameter range less widely investigated than the weaker couplings characteristic of molecules. In particular, chain formation is pronounced in the colloidal materials, but not in the molecules. In tandem with the stronger coupling, however, we may expect interesting phenomena even at fairly low particle density.

This paper addresses the magnetic anisotropy resulting from the onset of chain formation in low dimensional ferrofluids. Our principal conclusion is that correlations among particle positions serve to enhance susceptibility to fields in the parallel (infinite length) directions because chains can respond to the field as a coherent unit. At the same time, susceptibility to fields in the perpendicular (finite length) directions is diminished because the long chains cannot rotate into alignment with the field. We illustrate these points by examining the second virial coefficients.

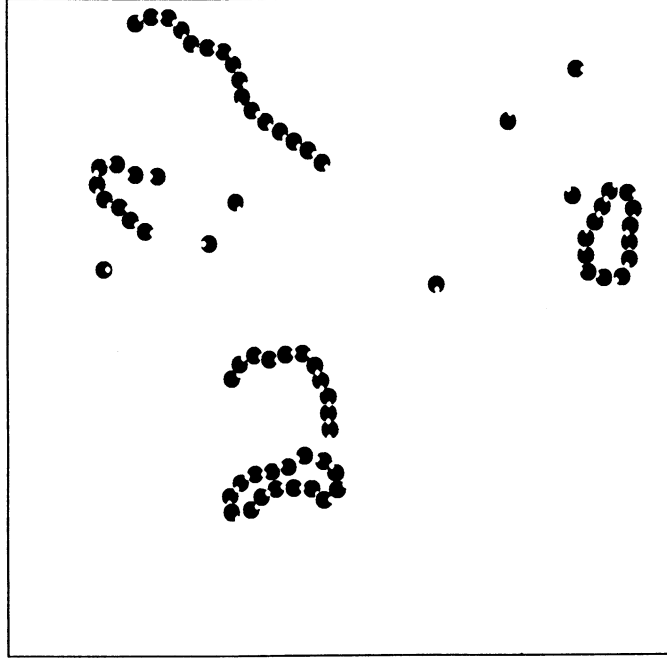


Figure 1: Instantaneous configuration from Monte Carlo simulation of a two dimensional dipolar fluid (white dots locate North Poles) with  $\lambda = 5$  and  $\rho = 0.045$ .

### Virial Expansion

We calculate the second virial coefficients in the equations of state for pressure and magnetic susceptibility

$$\beta P = \rho + B_2 \rho^2 + \dots, \quad \chi = \frac{1}{3} \beta \mu^2 \rho + M_2 \rho^2 + \dots \quad (3)$$

We recognize the leading terms in eq. (3) from the ideal gas law and from the Langevin susceptibility formula. For one and two dimensional spaces, where the magnetic susceptibility is anisotropic, we must distinguish between susceptibilities in the parallel and perpendicular directions. In three dimensions the susceptibility depends on shape through the demagnetization formula

$$\chi^{shape} = \frac{\chi^i}{1 + 4\pi N \chi^i} \quad (4)$$

where  $N$  is the demagnetization factor and  $\chi^i$  is the *intrinsic* shape independent susceptibility. We consider highly prolate spheroids for our calculations of  $\chi$  in three dimensions so that the demagnetization factor  $N = 0$ . Note also that we use CGS units.

Formulas for the virial coefficients are derived by expanding the grand canonical potential in terms of cluster integrals in the presence of a weak magnetic field [5]. The

Table 1: Second Virial Coefficients. First group 1-d, second group 2-d, final group 3-d.

Coefficient	Weak Coupling Series	Strong Coupling Limit
$B_2$	$a(1 - \frac{\lambda^2}{15} - \frac{\lambda^4}{275})$	$\frac{-ae^{2\lambda}}{36\lambda^3}$
$M_2^{\parallel}$	$\frac{2\lambda^2 a^4}{9}(1 + \frac{2}{25}\lambda + \frac{7}{100}\lambda^2 + \frac{16}{1925}\lambda^3 + \frac{37}{8575}\lambda^4)$	$\frac{5a^4 e^{2\lambda}}{54\lambda^2}$
$M_2^{\perp}$	$\frac{-\lambda^2 a^4}{9}(1 + \frac{2}{25}\lambda + \frac{1}{25}\lambda^2 + \frac{16}{1925}\lambda^3 + \frac{13}{8575}\lambda^4)$	$\frac{-a^4 e^{2\lambda}}{54\lambda^2}$
$B_2$	$\frac{\pi a^2}{2}(1 - \frac{\lambda^2}{6} - \frac{\lambda^4}{125})$	$\frac{-\pi a^2 e^{2\lambda}}{36\lambda^3}$
$M_2^{\parallel}$	$\frac{\pi \lambda^2 a^6}{9}(1 + \frac{\lambda}{20} + \frac{2}{35}\lambda^2 + \frac{4}{875}\lambda^3 + \frac{61}{15925}\lambda^4)$	$\frac{\pi a^6 e^{2\lambda}}{27\lambda^2}$
$M_2^{\perp}$	$\frac{-2\pi \lambda^2 a^6}{9}(1 + \frac{\lambda}{20} + \frac{4}{175}\lambda^2 + \frac{4}{875}\lambda^3 + \frac{1}{1225}\lambda^4)$	$\frac{-\pi a^6 e^{2\lambda}}{54\lambda^2}$
$B_2$	$\frac{2\pi a^3}{3}(1 - \frac{\lambda^2}{3} - \frac{\lambda^4}{75})$	$\frac{-\pi a^3 e^{2\lambda}}{18\lambda^3}$
$M_2^i$	$\frac{4\pi \lambda^2 a^6}{27}(1 + \frac{\lambda^2}{25} + \frac{4\lambda^4}{1225})$	$\frac{\pi a^6 e^{2\lambda}}{27\lambda^2}$

zero field case yields the pressure equation of state, while the field dependence of the free energy yields the magnetic susceptibility. The integrations required to calculate virial coefficients cannot be performed in closed form. It is not difficult, however, to evaluate them in the limits of either weak or strong coupling as shown in Table 1. For the three dimensional case,  $B_2$  agrees with the known result of Keesom [6], while  $M_2$  reproduces both the weak coupling result of Buckingham and Joslin [7] modified to the case of a very prolate ellipsoid, and the strong coupling result of de Gennes and Pincus [8]. The one and two dimensional results are new.

Let us examine the strong coupling limits for evidence of chain formation. Following the ideas of Jordan [9] we consider chemical equilibrium between isolated spheres, with density  $\rho_1$ , and dimers, with density  $\rho_2$ . These densities obey

$$\rho_2 = B\rho_1^2, \quad \rho_1 + 2\rho_2 = \rho, \quad (5)$$

where  $B \equiv -B_2 > 0$  because we are in the strong coupling limit, and chains of length three or greater are neglected since we are only examining second virial coefficients. The calculation can be generalized to relate the densities of chains of all lengths to corresponding many particle cluster integrals.

Now consider the contributions to the susceptibility from monomers and dimers separately. We treat the dimers as rigid rods with effective dipole moment  $2\mu$  constrained to point in the particle space, while the monomers are free to rotate in three dimensions. In one dimension we predict

$$\chi^{\parallel} = \frac{1}{3}\beta\mu^2\rho_1 + \beta(2\mu)^2\rho_2, \quad \chi^{\perp} = \frac{1}{3}\beta\mu^2\rho_1. \quad (6)$$

Now, setting  $\rho_1 = \rho - 2B\rho^2$  and  $\rho_2 = B\rho^2$ , we identify the second magnetic virial coefficient with the coefficients of  $\rho^2$  in the susceptibility eq. (6). This yields

$$M_2^{\parallel} = \frac{10}{3}\beta\mu^2 B, \quad M_2^{\perp} = \frac{-2}{3}\beta\mu^2 B. \quad (7)$$

Likewise, in two dimensions we predict

$$\chi^{\parallel} = \frac{1}{3}\beta\mu^2\rho_1 + \frac{1}{2}\beta(2\mu)^2\rho_2, \quad \chi^{\perp} = \frac{1}{3}\beta\mu^2\rho_1. \quad (8)$$

Substituting again for  $\rho_1$  and  $\rho_2$  we obtain

$$M_2^{\parallel} = \frac{4}{3}\beta\mu^2 B, \quad M_2^{\perp} = \frac{-2}{3}\beta\mu^2 B. \quad (9)$$

Finally, in three dimensions, we predict

$$\chi^i = \frac{1}{3}\beta(\rho_1\mu^2 + \rho_2(2\mu)^2) \quad (10)$$

which results in

$$M_2 = \frac{2}{3}B. \quad (11)$$

The validity of these relations (equations (7),(9), and (11)) between the mechanical and magnetic virial coefficients may be checked by inspection of the strong coupling results in Table 1.

### Discussion

From the virial coefficients in Table 1 we see that particle correlations enhance the parallel susceptibility in low dimensions, while suppressing the perpendicular susceptibility. In three dimensions only enhancement is observed, since we consider the susceptibility of an infinitely prolate ellipsoid in the direction for which the demagnetization factor vanishes. From the strong coupling limits we find an attractive interpretation of these results in terms of chain formation. Chains increase the effective magnetic moment of the spheres by a factor of the number  $\bar{n} \approx 1 + B\rho$  of particles in the chain (provided the chain is effectively rigid), while the number of such chains falls off like  $1/\bar{n}$ . Thus the parallel susceptibility grows proportionally to  $\bar{n}$ . But the chains do not contribute substantially to the perpendicular susceptibility because rotation into the field direction is inhibited.

Since we restricted our attention here to second virial coefficients, we can consider only monomers and dimers. That is, our results are valid for  $1 \leq \bar{n} \ll 2$ . Furthermore, in the context of virial expansions we find thermodynamic functions are analytic functions of  $\rho$ . The magnetic anisotropy, for instance, is guaranteed to grow as  $\rho^2$  for sufficiently small  $\rho$ . Examining Figure 2 we see that the magnetic anisotropy  $\chi^a \equiv \chi^{\parallel} - \chi^{\perp}$  grows as the difference of second magnetic virial coefficients times the second power of density

$$\chi^a \approx (M_2^{\parallel} - M_2^{\perp})\rho^2 \quad (12)$$

for densities  $\rho \ll 1/B \approx 0.07$ . The straight line is the prediction of eq. (12) using the strong coupling formulas for the virial coefficients taken from Table 1. The line lies slightly below the low density data, presumably because the virial coefficients are not given exactly by the strong coupling formula.

But once  $B\rho \approx 1$  the virial expansion cannot be truncated at low order. At densities comparable to  $1/B$  the data begins to turn over, so that  $\chi^a$  varies effectively as  $\rho^x$  with  $x < 2$ . The configuration shown in Figure 1 represents such a case. Indeed, it becomes attractive to model the ferrofluid as a living polymer solution [10]. In this case one finds (within a mean field approximation)  $\bar{n} \sim \rho^{1/2}$  and corresponding nonanalytic behavior of thermodynamic functions. For chains short compared to their persistence length  $\lambda a$  [8] the chain is essentially a rigid rod, and we expect the exponent of magnetic anisotropy  $x = 3/2$ . For long chains (in two and three dimensions only) we must modify the relations between chain length and susceptibility to represent the stretching of chains along the field direction. For ideal chains this yields  $x = 1$ , but when chain fluctuations, excluded

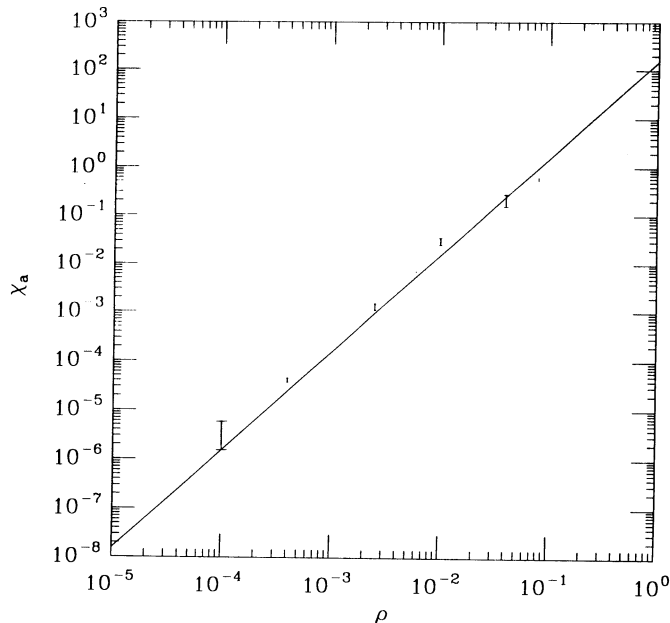


Figure 2: Magnetic anisotropy  $\chi^a$  as a function of particle density  $\rho$  in two dimensions. Data come from Monte Carlo simulations, while the straight line represents  $(M_2^{\parallel} - M_2^{\perp})\rho^2$  using the strong coupling limits of  $M_2$ .

volume effects, and the presence of rings (inspect Figure 1) are considered [10,11] we expect the exponent to shift slightly.

It should be possible to test these predictions experimentally. Chain formation requires  $\lambda \gg 1$ , for which ordinary ferrofluid suspensions may not be stable against gravitational settling [3]. But for a thin ferrofluid film gravitational settling is irrelevant. Finally, we comment on an interesting application of our work to the study of Ferrosmeectic liquid crystals [12]. These are lamellar structures with ferrofluid inserted between layers. If we treat the system as an assembly of noninteracting two dimensional sheets, our results suggest a magnetic anisotropy with  $\chi^{\parallel} > \chi^{\perp}$ . Even if we include interactions between layers, the texturing of the three dimensional fluid by its exclusion from layers leads to such an inequality. Because the magnetic anisotropy can be quite large, the smectic layers may be tilted by the application of modest perpendicular magnetic fields.

#### Acknowledgments

We wish to acknowledge useful discussions with R.B. Griffiths, P.G. de Gennes, S.T. Milner, G.S. Grest, and P. Fabre. This work was supported in part by NSF grant no. DMR-8918810 and by the A.P. Sloan foundation. We also wish to acknowledge the hospitality of the Cornell University Physics Department and LASSP at the time this

work was completed, and partial support through DOE grant no. DE-FG02-89ER-45405.

## References

- [1] For reviews see J.M. Deutch, *Ann. Rev. Phys. Chem.* **24**, 301 (1973); M.S. Wertheim, *ibid.* **30**, 471 (1979)
- [2] Hirschfelder, Curtiss and Boyd, *Molecular Theory of Gases and Liquids*, (Wiley, 1954). Molecular data are tabulated for the Stockmayer potential. We convert to an approximate hard sphere potential with  $a = \sqrt[3]{2}\sigma$ . The Boyle temperature (we use  $T_B = 1853^\circ K$  for  $H_2O$  and  $T_B = 3638^\circ K$  for  $CHCl_3$ ) is the zero of the second virial coefficient calculated from the Stockmayer potential.
- [3] R.E. Rosensweig, *Ferrohydrodynamics*, (Cambridge Univ., 1985)
- [4] A.P. Gast and C.F. Zukowsky, *Adv. Colloid Interface Sci.* **30**, 153 (1989); T.C. Halsey and W. Toor, *Phys. Rev. Lett.* **65**, 2820 (1990)
- [5] H. Zhang and M. Widom, To be submitted to *Mol. Phys.* (1992)
- [6] W.H. Keesom, *Comm. Phys. Lab. Leiden, Suppl.* **24b**, Section 6 (1912)
- [7] A.D. Buckingham and C.G. Joslin, *Mol. Phys.* **40**, 1513 (1980). They calculate the Clausius-Mossotti function  $\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi\chi^i}{3+4\pi\chi^i}$ . See also G.S. Rushbrooke, *Mol. Phys.* **37**, 761 (1979)
- [8] P.G. de Gennes and P.A. Pincus, *Phys. Kondens. Mater.* **11**, 189 (1970)
- [9] P.C. Jordan, *Mol. Phys.* **25**, 961 (1973). See also D.A. Krueger, *J. Colloid Interface Sci.* **70**, 558 (1979)
- [10] M.E. Cates, *J. Physique*, **49**, 1593 (1988)
- [11] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell, Ithaca, 1979)
- [12] P. Fabre, et. al., *Phys. Rev. Lett.* **64**, 539 (1990)