Journal of Magnetism and Magnetic Materials 122 (1993) 119–122
North-Holland

journal of magnetism and magnetic materials

Spontaneous magnetic order in strongly coupled ferrofluids

H. Zhang [1] and M. Widom

LASSP, Cornell University, Ithaca, NY 14853, USA

Using the dipolar hard-sphere fluid as a model, we study the spontaneous magnetization of ferrofluids. Mean field theory suggests magnetic order will occur in a strongly coupled ferrofluid. At fixed low density, the system phase separates at low temperature into a dilute nonmagnetic gas and a dense, magnetically ordered liquid. We focus our study on the effect of positional randomness, which is not included in conventional mean field studies. Our results show that a positionally unstructured ferrofluid exhibits magnetic order at low temperatures, provided its density is high enough. Freezing the solvent inhibits phase separation. In this case, positional randomness prevents magnetic order in a dilute frozen ferrofluid.

1. Introduction

Rosensweig [1] discusses the stability of ferrofluids against agglomeration. However, the agglomerated or condensed phase may itself be a useful ferrofluid [2]. In any case, it requires the same attention as the dilute phase in our effort to understand the phase diagram of ferrofluids. The separation of ferrofluids into a dense phase and a dilute one could resemble a liquid–gas phase coexistence [2–8]. However, the circumstances, if any, leading to spontaneous magnetic order in the dense phase remain unknown. Bacri et al. [2] observed a liquid–gas phase coexistence in ionic ferrofluids under zero applied field. They did not report that the dense phase was magnetized.

The complexity of ferrofluids arises from the long-range, anisotropic dipole–dipole interaction. The dipolar hard-sphere fluid captures this central feature while simplifying the short-range interaction. Agreement between its predictions and experiments on ferrofluids reveals the effects of the dipolar interaction and hard-core repulsion, while discrepancies yield information on the role of other short-range interactions of the dipolar particles with each other or with the solvent. Remarkably, even within the confines of dipolar hard-sphere fluids, the issue of magnetic ordering has not been settled theoretically. In the absence of magnetic order, the orientation-averaged interaction between two dipoles amounts to a $1/r^6$ attraction, leading de Gennes and Pincus [3] to conjecture a gas–liquid phase coexistence like the conventional van der Waals fluid. Later studies [4–6] investigated the boundaries between isotropic gas and isotropic liquid phases and the critical point at which the distinction between gas and liquid phases vanish.

The inclusion of magnetic order changes the thermodynamic behavior because now averaging orientations fails to remove the $1/r^3$ interaction, and the sample shape becomes important [3,5,8,9]. Indeed, in failing to consider elongated needle-shaped samples, one finds [7] no possibility of magnetic ordering in unstructured ferrofluids. By introducing a magnetic order parameter and treating the demagnitizing field correctly, at low temperatures one finds phase coexistence between an isotropic gas and a magnetic liquid [8]. At high temperatures the isotropic gas and magnetic fluid phases meet in a continuous symmetry-breaking phase transition. Thus instead of an ordinary gas–liquid critical point one finds a tricritical point [9].

Computer simulations of strongly coupled hard and soft spheres [10] do observe spontaneous magnetization at moderate and high densities. But the absence of magnetic order in frozen ferrofluids [11] indicates a need for caution. Conventional mean field theory does not account for local fluctuations [5], which tend to suppress mag-

Correspondence to: Dr H. Zhang, LASSP, Cornell University, Ithaca, NY 14853, USA.

[1] *Permanent address:* Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA.

netic order [12]. We find the inclusion of such fluctuations alters mean field predictions significantly. For example, at zero temperature, where mean field theory predicts magnetization at all densities [8], our results show that there is a critical volume fraction ($\phi_c \approx 0.295$) below which spontaneous magnetization is suppressed, and above which magnetic order persists.

2. Theory and results

Although the mean field theories [4–8] and computer simulations [10] of dipolar hard-sphere fluids discussed in the introduction address mobile particles capable of redistributing themselves to accommodate magnetic order, we claim that mobility is not essential. Thus, we consider a fixed, random, distribution of particles and set the pair correlation function $g(\boldsymbol{r}) = 1$ outside the hard core diameter. This assumption is consistent with the frozen ferrofluid experiments [11] except for our neglect of the randomly oriented easy axes of real crystalline particles. It may also be consistent with the computer simulations in the sense that Wei and Patey [10] reported no dramatic change in $g(\boldsymbol{r})$ associated with the onset of magnetic order. To accentuate the point that the fluctuations considered are due to the random environment as opposed to thermal randomness, we focus our attention on the state at $T = 0$, where thermal fluctuations vanish.

Klein et al. [13] pioneered a self-consistent theory of randomly positioned point dipoles. Assume that each dipole feels a field distribution $P(\boldsymbol{H})$, with mean $\boldsymbol{H}_0$ and width δ. Conventional mean field sets $\delta = 0$. Since dipole moments tend to align with an applied field, $P(\boldsymbol{H})$ determines the distribution of dipole orientation $Q(\hat{\mu})$. The dipole moment distribution, and the dipole positions, in turn determine the field distribution $P(\boldsymbol{H})$. The allowed field distributions $P(\boldsymbol{H})$ may thus be determined self-consistently. Vugmeister and Glinchuk [12] applied this theory to the study of orientational ordering in random point dipoles, and concluded that local fluctuations due to positional randomness prevent the emergence of long-range orientational order even at $T = 0$.

However, we note that in real systems, the closeness of neighboring dipoles is limited by the hard-sphere diameter. Neglecting this minimum separation alters the qualitative behavior of the system since the dipole–dipole interaction diverges rapidly at zero distance. As a result, in a point dipole system, where neighboring dipoles can get infinitely close, the field distribution $P(\boldsymbol{H})$ is a Lorentzian squared with a spread proportional to the dipole density. Orientational order does not occur. When infinite closeness is not allowed, the field distribution $P(\boldsymbol{H})$ is close to a Gaussian with a spread proportional to the square root of dipole density. Indeed, when a minimum dipole separation a is incorporated, our study shows that long-range orientational order does emerge when the dipole volume fraction exceeds a certain critical value ϕ_c.

Following Klein's notation, we let the dipole moment of particle i be

$$\boldsymbol{p}_i = p\hat{\mu}_i, \tag{1}$$

where p is the magnitude which is fixed and the same for all dipoles, and $\hat{\mu}_i$ is the orientation. Each dipole is subject to the same field distribution $P(\boldsymbol{H})$, which results in the same orientation probability distribution $Q(\hat{\mu})$. At $T = 0$, for dipoles that can assume arbitrary orientations, $\hat{\mu}$ is always parallel to the local field $\boldsymbol{H}$, so that

$$Q(\hat{\mu}) = \int_0^\infty P(H\hat{\mu})H^2 \, \mathrm{d}H. \tag{2}$$

To study the field felt by a dipolar particle located at the origin, we assume each of the remaining dipoles has zero probability in the region $r < a$, and uniform probability $1/V$ outside the region, V being the volume of the system. We decouple the contribution of different particles to the field at the origin by taking the Fourier transform of $P(\boldsymbol{H})$:

$$F(\boldsymbol{\rho}) \equiv \int \mathrm{d}^3\boldsymbol{H} \, P(\boldsymbol{H}) \exp(-\mathrm{i}\boldsymbol{\rho}\cdot\boldsymbol{H}) \tag{3}$$

$$= \exp(-nW_1(\boldsymbol{\rho}) - \mathrm{i}nW_2(\boldsymbol{\rho})), \tag{4}$$

where $n = 1/V$ is the number density of dipoles, and

$$W_1(\boldsymbol{\rho}) = \int \mathrm{d}^2\hat{\mu}\, Q(\hat{\mu}) \times \int_{r>a} \mathrm{d}^3\boldsymbol{r}\{1 - \cos[(p/r^3) \times (3(\boldsymbol{\rho}\cdot\hat{\boldsymbol{r}})(\hat{\mu}\cdot\hat{\boldsymbol{r}}) - \boldsymbol{\rho}\cdot\hat{\mu})]\}, \quad (5)$$

$$W_2(\boldsymbol{\rho}) = \int \mathrm{d}^2\hat{\mu}\, Q(\hat{\mu}) \times \int_{r>a} \mathrm{d}^3\boldsymbol{r}\, \sin[(p/r^3)(3(\boldsymbol{\rho}\cdot\hat{\boldsymbol{r}})(\hat{\boldsymbol{\mu}}\cdot\hat{\boldsymbol{r}}) - \boldsymbol{\rho}\cdot\hat{\mu})]. \quad (6)$$

We are interested in the low-order moments of $P(\boldsymbol{H})$, and thus the small ρ region is most important. We define the long-range magnetic order parameter $\boldsymbol{L}$ as

$$\boldsymbol{L} \equiv \int \mathrm{d}^2\hat{\mu} Q(\hat{\mu})\hat{\mu}. \quad (7)$$

$W_2(\boldsymbol{\rho})$, which controls the location of the peak in $P(\boldsymbol{H})$, is related to $\boldsymbol{L}$ through the simple relation

$$W_2(\boldsymbol{\rho}) = \frac{4\pi}{3} p\boldsymbol{\rho}\cdot\boldsymbol{L}. \quad (8)$$

Note that $W_2(\boldsymbol{\rho})$ is independent of particle size a at fixed p. $W_1(\boldsymbol{\rho})$ controls the width and shape of the peak in $P(\boldsymbol{H})$. In the absence of orientational order, $Q(\hat{\mu}) = 1/4\pi$, and

$$W_1(\boldsymbol{\rho}) = \frac{4\pi p^2}{9a^3}\rho^2 + \mathrm{O}\left(\frac{p^4\rho^4}{a^9}\right). \quad (9)$$

The correction in $W_1(\boldsymbol{\rho})$ due to magnetic order is $\sim L^2$. We are interested in the low order moments of $P(\boldsymbol{H})$, and thus the small ρ region is most important, and eq. (9) suffices for examining the onset of order. Our result (9) showing $W_1(\boldsymbol{\rho}) \sim \rho^2/a^3$ contrasts with the result $W_1(\boldsymbol{\rho}) \sim \rho$ obtained [12,13] for point particles with $a = 0$.

Our expressions (9) and (8) for $W_1(\boldsymbol{\rho})$ and $W_2(\boldsymbol{\rho})$ define $F(\boldsymbol{\rho})$, the Fourier transform of the field distribution $P(\boldsymbol{H})$. For small ρ, $F(\rho)$ is close to a Gaussian, while it is exponentially small for large ρ. Neglecting deviations from the Gaussian, an inverse Fourier transform leads us to

$$P(\boldsymbol{H}) = \frac{1}{(2\sqrt{\pi}\,\delta)^3} \exp\left[-(\boldsymbol{H} - \boldsymbol{H}_0)^2/4\delta^2\right], \quad (10)$$

where the peak field $\boldsymbol{H}_0 = (4\pi/3)np\boldsymbol{L}$ is exactly equal to the mean field predicted by the mean field theory, and the Gaussian spread

$$\delta = \sqrt{\frac{4\pi p^2 n}{9a^3}}\,. \quad (11)$$

We regain the point dipole result [12,13] by taking the nonphysical limit $a \to 0$ at fixed p. Since δ diverges in the limit $a \to 0$, $P(\boldsymbol{H})$ approaches a Lorentzian squared. We consider here the physical case where p and a are fixed. For small ϕ, H_0 vanishes more rapidly than δ, thus the fluctuations dominate the mean field and there is no magnetization. For large δ, H_0 dominates δ and magnetization is possible. We find a criticle volume fraction $\phi_c > 0$ at which magnetization becomes nonzero. Now, $\boldsymbol{L}$ determines $P(\boldsymbol{H})$ through eq. (10), which further determines $Q(\hat{\mu})$ through eq. (2), which finally determines $\boldsymbol{L}$ through eq. (7). This loop forms the self-consistent condition which we use to find the critical volume fraction

$$\phi_c \equiv \frac{\pi}{6} n_c a^3 = \frac{3\pi}{32} \approx 0.295. \quad (12)$$

Note that ϕ_c is a numerical constant, independent of both p and a provided they are nonzero.

3. Conclusion

Although mean field theory supports the possibility of spontaneous magnetization in strongly coupled dense ferrofluids [8], studies of local fluctuations [12] assert that magnetic order is completely prevented even at $T = 0$ for point dipoles. For finite-size dipoles, we show that a critical volume fraction separates the isotropic and magnetic phases at $T = 0$. Thus we establish the possibility of magnetic order in the presence of positional randomness. Mean field theory appears reliable at moderate and high volume frac-

tions. At low volume fractions, the particle size becomes less relevant, and the field distribution approaches a Lorentzian form consistent with Vugmeister and Glinchuk [12]. If the particle positions are frozen, the system should not magnetize even as $T \to 0$. Mobile particles, however, will tend to phase separate at low temperatures, and magnetization may be possible in the dense phase.

We note, finally, that the frozen ferrofluid experiments [11] are conducted in the range $\phi \leq 0.233$, which falls in the regime where we predict no magnetization, while in the computer simulations of dipolar hard spheres [10] the magnetized phase was found for $\phi \geq 0.417$, within the regime where we predict spontaneous magnetization. Explaining the phase separation into dilute and dense non-magnetic phases observed by Bacri et al. [2] remains a challenge, but is not directly addressed by the present study. The challenge arises because conventional mean field theory [8,9] suggests the isotropic gas–isotropic liquid phase transition resulting from the effective $1/r^6$ attraction of dipolar hard spheres is pre-empted by the magnetized liquid state. Perhaps randomness in particle positions allows phase separation into an isotropic liquid prior to the onset of magnetic order [5]. We can test that hypothesis by incorporating a density shift [8,9] into the random mean field theory presented here. But it is conceivable that dipolar hard spheres simply do not possess a dense isotropic liquid state. If that turns out to be the case, then the phase separation observed by Bacri et al. [2] may result from the van der Waals attraction, or other forces not taken into account in our simplified model.

We wish to acknowledge useful discussions with S.R. Nagel, J. Marko, and B.E. Vugmeister. 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 done, and partial support at Cornell through DOE grant no. DE-FG02-89ER-45405.

References

[1] R.E. Rosensweig, Ferrohydrodynamics (Cambridge University Press, Cambridge, 1985) p. 33.
[2] J.C. Bacri, R. Perzynski, D. Salin, V. Cabuil and R. Massart, J. Colloid. Interface. Sci. 132 (1989) 43.
[3] P.G. de Gennes and P.A. Pincus, Phys. Condens. Matter 11 (1970) 189.
[4] G.S. Rushbrooke, G. Stell and J.S. Høye, Mol. Phys. 26 (1973) 1199.
[5] K.I. Morozov, A.F. Pshenichnikov, Yu.L. Raikher and M.I. Shliomis, J. Magn. Magn. Mater. 65 (1987) 269.
[6] V.I. Kalikmanov, Physica A 183 (1992) 25.
[7] P. Palffy-Muhoray, M.A. Lee and R.G. Petschek, Phys. Rev. Lett. 60 (1988) 2303.
[8] A.O. Cebers, Magnetohydrodynamics 3 (1982) 33; K. Sano and M. Doi, J. Phys. Soc. Jpn. 52 (1983) 2810.
[9] H. Zhang and M. Widom, unpublished (1992). The continuous phase transition and the tricritical point are implicit in ref. [8].
[10] D. Wei and G.N. Patey, Phys. Rev. Lett. 68 (1992) 2043 (dipolar soft spheres); J.J. Weis, D. Levesque, and G.J. Zarragoicoechea, Phys. Rev. Lett. 69 (1992) 913 (dipolar hard spheres).
[11] W. Luo, S.R. Nagel, T.F. Rosenbaum and R.E. Rosensweig, Phys. Rev. Lett. 67 (1991) 2721.
[12] B.E. Vugmeister and M.D. Glinchuk, Rev. Mod. Phys. 62 (1990) 993.
[13] M.W. Klein, C. Held and E. Zuroff, Phys. Rev. B 13 (1976) 3576.