

Phase separation in model polydisperse ferrofluids

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The influence of polydispersity on the phase equilibrium properties of a dipolar system with additional short-range (repulsive+attractive) interactions (modeled by a shifted Lennard-Jones pair potential) is studied by means of Gibbs ensemble Monte Carlo simulations. The critical temperature and density as well as the magnetization at the critical point are calculated as a function of the applied magnetic field, and the obtained results are compared with the data determined in a monodisperse equivalent of the system.

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Ferrofluids or magnetic fluids are stable colloidal dispersions of small magnetic particles (with a diameter of 4–14 nm) in liquid carriers [1]. The particles have permanent magnetic dipole moments, which are proportional to their volumes. For such systems, fluid-fluid phase transitions have not only been predicted but also experimentally observed [2]. Ferrofluids are generally treated as dipolar fluids, where only the colloidal particles are explicitly taken into account [3]. Investigations of the influence of anisotropic interactions, as in dipolar fluids, yielded numerous theoretical reports on the phase behavior of dipolar systems [4,5]. Although, at fairly low temperatures, vapor-liquid phase equilibrium might exist for pure dipolar interactions [6], this coexistence commonly requires the (for real ferrofluids ever present) van der Waals attraction [3].

In real ferrofluids the nanoparticles can have different sizes and different magnetic moments. The polydispersity in the particle size or in the magnetic moment affects the equation of state for the system. Size polydispersity, for example, has been shown to have a large effect on the coexistence densities of fluids [7]. Recently, some reports on the influence of polydispersity on the phase behavior of dipolar systems appeared in the literature [8,9], although these studies have been carried out exclusively for bidisperse systems.

In our previous paper [10] we studied the influence of polydispersity on the equilibrium magnetic properties of dipolar liquids. In this Brief Report, our main concern is the influence of polydispersity on the vapor-liquid coexistence properties of a dipolar system with realistic polydispersity. Phase equilibrium density curves are calculated and the critical points are estimated as a function of the applied external field and the obtained results are compared with the data determined in a monodisperse equivalent of the system.

The system consists of spherical particles of diameter σ_i , which have permanent point dipole (magnetic) moments m_i . The short range repulsive interaction and the van der Waals attraction between particles i and j are modeled by a shifted Lennard-Jones pair potential:

$$\varphi_{ij}^r = 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r_{ij} - \zeta} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij} - \zeta} \right)^6 \right], \quad (1)$$

where ε is the energy parameter, r_{ij} is the interparticle distance, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, and ζ is an additional size parameter. Shifting in the distance scale allows a crude approximation to take into account the fact that, due to the presence of stabilizing nonmagnetic layers, the particle size in ferrofluids exceeds the magnetic core diameter σ_i .

The dipole-dipole potential between particles i and j is given by

$$\varphi_{ij}^d = \frac{1}{4\pi\mu_0} \left[\frac{\mathbf{m}_i \cdot \mathbf{m}_j}{r_{ij}^3} - 3 \frac{(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (2)$$

where μ_0 is the permeability of vacuum, and the interaction of dipole moments with an external field \mathbf{H} can be written as

$$\varphi_i^{\text{ext}} = -\mathbf{m}_i \cdot \mathbf{H}. \quad (3)$$

The particle polydispersity is described by the gamma distribution [11]

$$f(x) = \frac{\zeta}{x_0} \left(\frac{x}{x_0} \right)^a \frac{\exp(-x/x_0)}{\Gamma(a+1)}, \quad (4)$$

where x is the magnetic core diameter of particles, x_0 and a are the parameters of the distribution, Γ denotes the gamma function, and ζ is taken as the unit length [to render $f(x)$ dimensionless]. For spherical particles $\sigma=x$, and the magnetic moment reads

$$m = \mu_0 M_d \frac{\pi}{6} x^3, \quad (5)$$

where M_d represents the bulk magnetization of the ferromagnetic component.

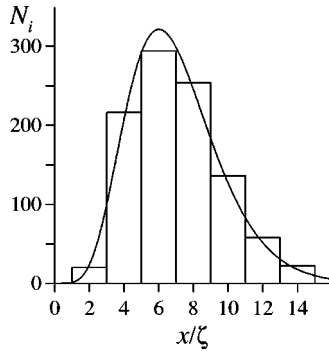


FIG. 1. Discretization of the particle distribution.

Constant volume and temperature Gibbs ensemble Monte Carlo (GEMC) calculations have been performed using $N = 1000$ particles. The production period in the simulations varied between 300 000 and 400 000 cycles. In the case of the larger particles in the polydisperse system the identity exchange algorithm was utilized [12] because the probability of a successful normal particle transfer was prohibitively low.

Standard long-range corrections were applied for the Lennard-Jones-type interaction. The long-range dipolar interactions were treated using the Ewald summation with conducting boundary condition [13]. The results for the dipolar (magnetic) fluids are presented in reduced units, where the mean magnetic core diameter is used for σ : $T^* = kT/\varepsilon$ is the reduced temperature with k being the Boltzmann constant, $\rho^* = N\sigma^3/V$ is the reduced density, $p^* = p\sigma^3/\varepsilon$ is the reduced pressure, and $M^* = M/\sqrt{4\pi\varepsilon/(\mu_0\sigma^3)}$ is the dimensionless magnetization.

Furthermore, the dimensionless form of the external magnetic field is $H^* = H\sqrt{4\pi\mu_0\sigma^3/\varepsilon}$, and $m^{*2} = m^2/(4\pi\mu_0\varepsilon\sigma^3)$ is the reduced squared magnetic moment. For the magnetic coupling, $\lambda = m^{*2}/T^* = 1$ was adopted at $T^* = 1$. This choice implies that the average reduced magnetic moment was unity in all calculations. It should be noted, however, that the mean magnetic moment \bar{m} in the polydisperse system is not proportional to $\bar{x}^3 = \sigma^3$ [where $\bar{x} = x_0(a+1)$], but to the mean cubed core diameter, $\bar{x}^3 = x_0^3(a+1)(a+2)(a+3)$. For the parameters of the gamma distribution, $x_0/\zeta = 1$ and $a = 6$ were taken, thus the resultant shape of the distribution is typical of real ferrofluids if the *unit length is set to 1 nm* [2,10]. The discretization of the particle distribution density necessary for molecular simulation with a limited number of particles is illustrated in Fig. 1. The exact mean core diameter is reproduced within 1%, while for the mean magnetic moment the discrete and the continuous distributions provide the same value. In the simulations the equilibrium magnetization can be obtained from the expression

$$\mathbf{M} = \frac{1}{\mu_0} \left\langle \sum_{i=1}^N \frac{\mathbf{m}_i}{V} \right\rangle, \quad (6)$$

where the brackets denote ensemble average. The calculated magnetization values are compared with the saturation magnetization of the ideal ferrocolloid gas,

$$M_s = \frac{\bar{m}}{\mu_0} \left\langle \frac{N}{V} \right\rangle. \quad (7)$$

Clusters are defined on the basis of the pair energies of the interacting particles [14]. Two particles are considered to be bound if their potential energy is less than 75% of their contact energy in perfect coagulation.

The phase coexistence was studied at fixed number densities and polydispersity of the (starting) parent phase. This corresponds to the experimental procedure that involves adding a prescribed quantity of particles with a given degree of polydispersity to a vessel of fixed volume and observing possible phase separations. Although phase separation results in coexisting phases with different particle distribution density, the procedure allows the conservation of the applied distribution for the whole system. If we finally restrict ourselves to two-phase coexistence and monomodal distribution, we can avoid the problem associated with the infinite dimensionality of the full phase diagram of polydisperse systems, and our system can be treated as a quasi one-component system.

The vapor-liquid coexistence results of our polydisperse system are compared with those of a monodisperse system. The monodisperse fluid is characterized by uniform σ and m , with the additional specification that $m^* = 1$. However, it should be mentioned that we have to make a compromise at this point. As $\bar{m} \propto \bar{x}^3$ and $\bar{x}^3 \neq \bar{x}^3$ for the polydisperse fluid, the monodisperse fluid can be considered either to have a different mean core diameter or different M_d (i.e., different ferromagnetic component) than those of the polydisperse fluid. According to the applied model, m^* decreases by about one-third if we take the same \bar{x} as well as M_d for the two systems. As the choice of σ is somewhat arbitrary, the equivalent monodisperse system might be the one with the same volume fraction of the magnetic cores as the polydisperse system (at the same number density). This means that, instead of the mean core diameter, the mean cubed core diameter would be identical for the two systems. Disregarding the volume fraction, this choice does not concern our numerical results presented in reduced units.

We started the calculations at $T^* = 1$, where the density of the parent phase of the polydisperse system ρ_0 was chosen so that the vapor pressure of the monodisperse fluid at this temperature is reproduced. Raising the temperature, the coexistence density curves behave ordinarily up to a point for which the density of either phase becomes equal to the density of the parent phase. At this end point of phase equilibrium one phase coexists with an infinitesimal amount of the other phase. The coexistence density curves meet at the critical temperature T_c only if the density of the parent phase is equal to the critical density ρ_c . Accordingly, the critical point of our polydisperse system can be determined solely by an iterative procedure. First, a pseudocritical density is estimated for a selected $\rho_0^{(0)}$ using the GEMC results at various temperatures up to the end point. Assuming a Wegner expansion [15] and neglecting the contribution from the gap exponent [16], the vapor (V) and the liquid (L) densities can be fitted to the expression

TABLE I. Coexistence densities and average percentage of particles in clusters at $T^*=1.0$. Here the coexistence pressure of the polydisperse system is identical to the vapor pressure obtained for the monodisperse system ($p^*=0.0306$).

Fluid	ρ_L^*	ρ_V^*	Dimer % (L)	Dimer % (V)	Trimer % (L)
monodisperse	0.4392	0.0421			
polydisperse	0.3021	0.0360	2.2	0.8	0.2

$$\rho_{L,V} = \rho_c \pm B(1 - T/T_c)^\beta + C(1 - T/T_c), \quad (8)$$

where B and C are parameters and β is the critical exponent which is set to its exact nonclassical value, 0.325. The coexistence curves are then determined by GEMC for $\rho_0^{(1)} = \rho_c^{(0)}$, and the procedure is repeated until $\rho_c^{(n)}$ agrees with $\rho_0^{(n)}$ within the uncertainty of the calculation. This procedure necessitates 3–5 iterations in the present case.

Essentially for an entropic reason, polydispersity affects the coexisting phases in such a way that the difference between the more and less ordered phases is reduced. Table I shows that, at the same temperature and pressure, the saturated liquid density of the polydisperse fluid notably deviates from that of the monodisperse fluid. However, the marked contrast between the two liquid phases almost disappears when considering the proportion of volume occupied by the magnetic cores to the system volume (volume fraction). Note, from the definition of volume fraction, $\phi_{\text{monodisperse}} = \rho^*(\pi/6)$ and $\phi_{\text{polydisperse}} = \rho^*(\pi\bar{x}^3/6\bar{x}^3)$, where $\bar{x}^3 > \bar{x}^3$, and these mean values are different in the coexisting polydisperse vapor and liquid phases. At this state point $\phi_{\text{polydisperse}}$ turns out to be slightly greater than $\phi_{\text{monodisperse}}$ for the vapor phases. The distributions of particles obtained here in the coexisting polydisperse phases are typical of the other state points examined: the larger particles predominantly belong to the denser phase. The dissimilarity manifests itself also in the formation of clusters. Approximately 3% of the particles are organized in randomly distributed short and flexible clusters in the denser polydisperse phase at zero external field, while in the monodisperse phases no cluster formation can be found (according to our cluster definition). It is interesting to note that this qualitative picture was found to be valid at other temperatures and in the presence of the external magnetic field, although, obviously, some increase of the amount of clusters with the field strength can be observed. Even at strong fields, less than 5% of the particles of the polydisperse liquid phases are organized in clusters and less than 0.1% of the particles of the monodisperse phases are present in dimers or trimers.

Figure 2 shows the vapor-liquid phase equilibrium curves for our polydisperse system and for its monodisperse equivalent (i.e., in both cases, $\bar{m}^* = 1$). The most striking feature of the figure is the relatively narrow coexistence envelopes obtained for the polydisperse system. As H^* increases, the better alignment of the dipoles along the field direction gives stronger dipolar interactions, especially in the denser coexisting phase. Thus the coexistence envelopes broaden with

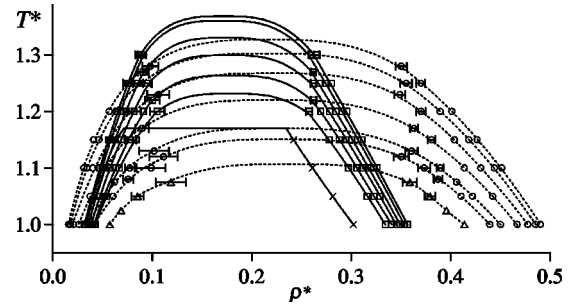


FIG. 2. Coexistence densities at different external magnetic fields for the monodisperse fluid (circles) and for the polydisperse fluid for which the density of the parent phase is identical to the critical density (squares). The curves from bottom to top correspond to vapor-liquid equilibrium results at $H^* = 0, 1, 2.5, 5, 10,$ and 20 , respectively. Crosses denote coexistence points at $H^* = 0$ for the polydisperse fluid for which the density of the parent phase is chosen so that the vapor pressure of the monodisperse fluid is reproduced at $T^* = 1.0$. Triangles are plotted only for comparison: they represent the results for a monodisperse fluid with $m^* = 0.6806$, where the mean magnetic core diameter as well as the bulk magnetization of the ferromagnetic component are the same as those of the polydisperse fluid.

the field strength, which is consistent with the results reported by Stevens and Grest [5] and Boda *et al.* [17] for the monodisperse Stockmayer fluid with $m^* = 1$. In contrast with these works, we have explored in our calculations the extremely strong field regime, $H^* \geq 5$. The coexistence envelope of our shifted Stockmayer model is much narrower than that of the original Stockmayer model [17]. The introduction of the additional size parameter ζ yields smaller liquid and greater vapor densities, as well as a lower critical temperature. Our preliminary calculations with the unshifted polydisperse model showed that this qualitative statement remains valid also for the polydisperse model, but the changes are smaller.

The critical properties are compiled in Table II. In agreement with earlier findings, [5,17], ρ_c^* changes only slightly in both systems here. For the polydisperse system, T_c^* is significantly greater and ρ_c^* is significantly smaller than the corresponding monodisperse value. The differences slightly decrease with the field strength, which can be anticipated from

TABLE II. Critical properties at different magnetic fields. The numbers in parentheses represent the estimated uncertainties in the last digit.

H^*	Monodisperse fluid			Polydisperse fluid		
	T_c^*	ρ_c^*	ϕ_c	T_c^*	ρ_c^*	ϕ_c
0	1.151(5)	0.229(4)	0.120	1.232(5)	0.179(3)	0.138
1	1.170(5)	0.227(4)	0.119	1.264(5)	0.179(3)	0.138
2.5	1.220(4)	0.221(4)	0.116	1.300(5)	0.175(3)	0.135
5	1.268(5)	0.221(4)	0.116	1.331(5)	0.173(3)	0.133
10	1.303(4)	0.215(3)	0.113	1.361(5)	0.171(3)	0.132
20	1.327(4)	0.217(3)	0.114	1.369(5)	0.172(3)	0.132

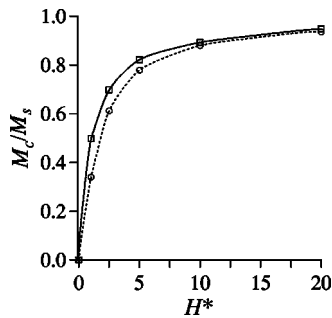


FIG. 3. Critical magnetization relative to the saturation magnetization of the ideal ferrocolloid gas as a function of the external magnetic field for the monodisperse fluid (circles) and for the polydisperse fluid (squares).

the relative changes of the widths of the coexistence density curves as a function of the field strength. Table II contains also the calculated volume fractions of magnetic cores demonstrating the greater ability of the polydisperse system to fill the accessible space.

We have calculated the equilibrium magnetization along the coexistence curves as well, but found it difficult to compare the results obtained at different densities. Therefore the magnetization at the critical point relative to the saturation magnetization of the ideal ferrocolloid gas (M_c/M_s) was estimated assuming that, near the critical point, M^* exhibits similar scaling behavior to that of ρ^* . As Fig. 3 shows, at weak magnetic fields the polydisperse system reveals considerably greater M_c/M_s values. We think the presence of weak aggregates, which are continuously forming and breaking in the polydisperse system, is partly responsible for the en-

hancement of the magnetization. The results suggest that the particles with magnetic moments larger than the mean magnetic moment have greater importance, probably due to their greater ability to form clusters [10]. However, this figure also demonstrates that the difference in magnetic properties between the polydisperse and monodisperse systems becomes progressively smaller with increasing H^* . At strong fields the magnetization no longer depends on the distribution of the magnetic moments, but on their average, and so the relative magnetization appears to tend to the same limiting value in both systems.

In summary, vapor-liquid coexistence properties were determined in a polydisperse dipolar fluid. The experimentally available examples of such fluids are the magnetic fluids in which vapor-liquid-like phase separations, i.e., coexistence of a dense liquid phase with a diluted liquid phase, are also possible. Taking into account the realistic situation, i.e., polydispersity in size and interaction strength, a considerable reduction of the width and upward shift of the critical point were introduced into the phase diagram. The application of an external magnetic field enhances the dissimilarity of the coexisting phases in both the monodisperse and polydisperse systems, but the expected saturation effect at higher fields, especially in the relative magnetization at the critical point, becomes more pronounced in the polydisperse system.

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- [1] R. E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, England, 1985).
 - [2] F. Cousin, E. Dubois, and V. Cabuil, *J. Chem. Phys.* **115**, 6051 (2001).
 - [3] P. I. C. Teixeira, J. M. Tavares, and M. M. Telo da Gama, *J. Phys.: Condens. Matter* **12**, R411 (2000).
 - [4] M. E. van Leeuwen and B. Smit, *Phys. Rev. Lett.* **71**, 3991 (1993).
 - [5] M. J. Stevens and G. S. Grest, *Phys. Rev. E* **51**, 5976 (1995).
 - [6] P. J. Camp, J. C. Shelley, and G. N. Patey, *Phys. Rev. Lett.* **84**, 115 (2000).
 - [7] L. Bellier-Castella, H. Xu, and M. Baus, *J. Chem. Phys.* **113**, 8337 (2000).
 - [8] V. Russier, *J. Colloid Interface Sci.* **174**, 166 (1995).
 - [9] A. O. Ivanov, *J. Magn. Magn. Mater.* **201**, 234 (1999).
 - [10] T. Kristóf and I. Szalai, *Phys. Rev. E* **68**, 041109 (2003).
 - [11] M. I. Shliomis, A. F. Pshenichnikov, K. I. Morozov, and I. Yu. Shurubor, *J. Magn. Magn. Mater.* **85**, 40 (1990).
 - [12] A. Z. Panagiotopoulos, *Int. J. Thermophys.* **10**, 447 (1989).
 - [13] S. W. de Leeuw, J. W. Perram, and E. R. Smith, *Proc. R. Soc. London, Ser. A* **373**, 27 (1980).
 - [14] D. Levesque and J. J. Weis, *Phys. Rev. E* **49**, 5131 (1994).
 - [15] F. J. Wegner, *Phys. Rev. B* **5**, 4529 (1972).
 - [16] L. Vega, E. de Miguel, L. F. Rull, G. Jackson, and I. A. McLure, *J. Chem. Phys.* **96**, 2296 (1992).
 - [17] D. Boda, J. Winkelmann, J. Liszi, and I. Szalai, *Mol. Phys.* **87**, 601 (1996).