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2000 J. Phys.: Condens. Matter 12 A471

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## Strongly dipolar fluids at low densities

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Received 12 August 1999

**Abstract.** We propose a simple statistical mechanical theory for a strongly dipolar fluid at low densities, based on the analogy between a system of polydisperse linear chains and the equilibrium structure of these fluids as revealed by computer simulations. At low densities, both steric and dipolar interactions between long chains are weak and thus the dipolar fluid is well described as an ideal gas of polydisperse chains. We have further investigated how the residual dipolar interaction between monomers and/or additional isotropic attractions between the spheres cause the dissociation of the chains and/or the condensation of the dipolar fluid.

### 1. Introduction

In recent years there has been renewed interest in the thermodynamic and structural properties of dipolar fluids. Numerical simulations revealed an entirely new behaviour, not predicted by existing theories: formation of chain-like structures for strongly dipolar fluids (with [1–3] or without [4,5] an applied magnetic field) at low densities, the appearance of a ferromagnetically ordered fluid phase [6, 7] and the absence of liquid–vapour condensation unless external magnetic fields [1, 3] or isotropic attractions between the spheres are turned on [8]. Various theoretical approaches were proposed to investigate these new features: integral equations [9] and density functional theory [10] were used to describe the ferromagnetic fluid phase, and models for associating fluids, treated within mean-field approximations, were used to describe the absence of condensation of dipolar hard spheres (DHS) and the onset of chain formation at low densities [11–14].

### 2. Independent chains

We consider a system of hard spheres with radius  $\sigma$  and embedded dipoles of strength  $\mu$ , interacting through the pair potential

$$\phi_{DHS} = \begin{cases} \infty & r_{12} < \sigma \\ -\frac{\mu^2}{r_{12}^3} [3(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12}) - \hat{\mu}_1 \cdot \hat{\mu}_2] & r_{12} \geq \sigma. \end{cases} \quad (1)$$

$r_{12}$  is the distance between the centres of the spheres,  $\hat{r}_{12}$  the unit interdipolar vector, and  $\hat{\mu}_1$  and  $\hat{\mu}_2$  the unit dipolar vectors of spheres 1 and 2, respectively. We define the reduced dipole

moment (or square root of the inverse reduced temperature) as

$$\mu^* = \left( \frac{\mu^2}{k_B T \sigma^3} \right)^{1/2}. \quad (2)$$

$k_B$  is Boltzmann's constant and  $T$  the absolute temperature.

The dipole–dipole potential (1) has a global minimum when the dipoles of two spheres at contact are aligned ‘head to tail’. It is expected that, at sufficiently high dipole moments, this structure will reveal itself, at least locally. Indeed, snapshots of equilibrium configurations [4, 14] show that dipolar spheres self-assemble forming linear structures that may span the simulation box, indicating that the dipole–dipole potential induces strong many-body spatial and angular correlations, at low density and temperature (large reduced dipole moment).

A direct calculation of these many-body correlations is not feasible by simulation or theoretically. In fact, standard mean-field theory based on the hard-sphere reference system does not describe the onset of chain formation. An approach that is useful both in the analysis of simulation results and in a theoretical description has been used, namely that of assuming that the many-body correlations are described accurately by the size distribution function of an assembly of chains [1, 2, 4, 5, 11, 12, 14]. The equilibrium structure of the system is then given in terms of the thermal distribution of chain lengths.

In the following we recall the derivation of the free energy of an ideal mixture of polydisperse chains [11–14]. Consider a system of  $N$  monomers in volume  $V$ , assembled as non-interacting chains of length  $i = 1, \dots, N$ . If  $M_i$  is the number of chains of length  $i$ , the partition function is

$$Z = \prod_{i=1}^N \frac{q_i^{M_i}}{M_i!} \quad (3)$$

where  $q_i$  is the partition function of a chain with  $i$  monomers. The number of monomers is conserved and thus

$$N = \sum_{i=1}^N i M_i. \quad (4)$$

In the thermodynamic limit, the Helmholtz free-energy density,  $f$ , is derived from (3):

$$\beta f = \sum_{i=1}^{\infty} \rho_i (\ln \rho_i - 1 - \ln \tilde{q}_i) \quad (5)$$

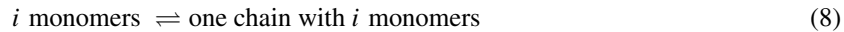
where  $\rho_i = M_i/V$  and  $\tilde{q}_i = q_i/V$ . In this limit, the constraint (4) becomes

$$\rho = \sum_{i=1}^{\infty} i \rho_i. \quad (6)$$

The Helmholtz free energy (5) is expected to describe the system at low densities, when the interactions between monomers of different chains can be neglected [12]. From (5), the chemical potential of species  $i$ , i.e., of chains of length  $i$ , is found to be

$$\beta \mu_i = \ln \rho_i - \ln \tilde{q}_i. \quad (7)$$

Chemical equilibrium among chains is obtained through reactions that conserve the number of monomers, such as



implying that the chemical potentials satisfy

$$\mu_i = i \mu_1. \quad (9)$$

Using (7) and (9) the density of a chain of length  $i$  is

$$\rho_i = \left( \frac{\rho_1}{\bar{q}_1} \right)^i \bar{q}_i. \quad (10)$$

The explicit calculation of the distribution of chain lengths requires an approximation for the partition function of individual chains. The latter may be written as

$$q_i = \frac{1}{h^{3i} i!} \int d p^{3i} \exp \left( -\beta \sum_{k=1}^{3i} \frac{p_k^2}{2m} \right) q_i^C \quad (11)$$

where  $h$  is Planck's constant,  $m$  the mass of a monomer and  $p^{3i}$  the set of cartesian coordinates of the linear momenta of the monomers.  $q_i^C$  is the configurational partition function:

$$q_i^C = \int d\vec{r}_1 \cdots d\vec{r}_i d\omega_1 \cdots d\omega_i \exp(-\beta\phi(\vec{r}_1, \dots, \vec{r}_i, \omega_1, \dots, \omega_i)) \quad (12)$$

with  $\vec{r}_k$  the position vector of a dipolar hard sphere in the chain and  $\omega_k$  the set of angles that describe the orientation of the dipole.  $\phi$  is the sum of the potentials (1) between all pairs of spheres in the chain. Integrating the momenta in (11) we find for the partition function of a chain

$$q_i = \left( \frac{q_1}{V} \right)^i \frac{q_i^C}{i!} \quad (13)$$

with  $q_1 = V/\lambda^3$  and  $\lambda$  the de Broglie wavelength of a monomer.

We proceed by calculating  $q_i^C$ , using an approximate method that is valid for short-ranged interactions in the limit of strong dipoles, i.e., for long chains [12, 14]. The result is

$$q_i^C = V \exp[(i-1)S_0] \quad (14)$$

where  $S_0$ , the free energy of a bond (divided by  $-k_B T$ ), is given by [15]

$$S_0 = 2\mu^{*2} + \ln \left( \frac{\pi\sigma^3}{24\mu^{*6}} \right) - \frac{3}{2\mu^{*2}}. \quad (15)$$

Substituting (14) and (13) in (10), we obtain for the density of chains of length  $i$  [14]

$$\rho_i = \rho_1^i \frac{\exp[(i-1)S_0]}{i!}. \quad (16)$$

The distribution function  $\rho_i$  depends on the translational partition function through the factorial  $i!$ ; this differs from the findings of other works on dipolar chains [11, 12, 16], surfactant systems [17] and living polymers [18]. The translational partition function of the aggregates is usually neglected (set to 1) and the inclusion of this factor is not discussed in the literature (with the exception of [16]). If the chains (or, more generally, the aggregates) are solid-like, then this factor does not appear in the distribution function since the monomers are distinguishable. This assumption, however, is not reasonable for the dipolar hard-sphere fluid, since it has been shown [4, 14] that the spheres diffuse through all of the chains in the course of equilibrium simulation runs.

Substituting (16) in (6), we obtain for the total density of spheres

$$\rho = \rho_1 \exp(\rho_1 e^{S_0}). \quad (17)$$

The density of free monomers,  $\rho_1$ , is calculated through this relation, for a given  $\rho$  and,  $\mu^*$ , and, using (16), the equilibrium chain distribution is determined. The mean chain length,  $\bar{N}$ , is easily calculated from (16) and (17), and is found to be

$$\bar{N} = \frac{\rho e^{S_0}}{\exp(\rho_1 e^{S_0}) - 1}. \quad (18)$$

The equilibrium chain length distribution obtained from (16) underestimates the number of long chains and this difference becomes more pronounced at high values of the dipole moment [14]. A comparison of theory and simulation [5] (see table 1) also shows that the inclusion of  $i!$  eliminates the (order-of-magnitude) discrepancies found in previous work [12]. For the lowest density and highest dipole moment, the present theoretical results are in quantitative agreement with simulation. We conclude that the living polymer theory is capable of describing semi-quantitatively the structure of a dipolar system in the strongly dipolar regime.

**Table 1.** Mean chain length: comparison of the theoretical results of [14], those from [12] and the simulations of [5].  $\rho^*$  is the reduced density and  $\mu^*$  the reduced dipole moment defined in the text.

$\rho^*$	$\mu^*$	$\bar{N}$ from [5]	$\bar{N}$ from [12]	$\bar{N}$ from [14]
0.3	2.0	2.7	1.94	1.36
0.3	2.5	5.2	7.09	2.79
0.3	3.0	16.5	60.0	6.19
0.3	3.5	27.0	966	11.2
0.2	3.5	24.6	789	10.8
0.1	2.0	2.6	1.43	1.16
0.1	2.5	6.7	4.36	2.18
0.1	3.0	24.5	34.8	5.27
0.1	3.5	24.2	558	10.2
0.05	3.5	30.4	395	9.57
0.02	2.0	2.3	1.11	1.04
0.02	3.5	8.4	250	8.75

### 3. Interactions

The free energy (5) cannot be used to calculate the phase diagram since it neglects interactions. A perturbative calculation of the excess free energy due to the hard-core and dipolar interactions between the chains requires knowledge of the (many-body) anisotropic correlations that characterize the ideal system. This difficulty is overcome by assuming that a chain consists of independent linear segments of length  $\ell$ . The interacting system is formed by these segments and free monomers. The excess (mean-field) free energy is calculated from the effective interactions between segments and free monomers, in the limit  $\ell \gg \sigma$  [12, 13, 19]. In spite of the limitations of this mean-field approximation, a qualitative agreement with simulation results is obtained.

The excess hard-core free energy of the system of segments is approximated by [12, 13]

$$\beta f_{ch}^{HC}(\rho) = \frac{3}{8}\rho \frac{4\eta - 3\eta^2}{(1-\eta)^2} = \frac{3}{8}\beta f_{CS}(\rho) \quad (19)$$

where  $\eta = (\pi/6)\sigma^3\rho$ . Similarly, the excess free energy of the free monomers is [12, 13]

$$\beta f_{ch}^{HC}(\rho) = \frac{5}{8}\rho_1 \frac{4\eta_1 - 3\eta_1^2}{(1-\eta_1)^2} = \frac{5}{8}\beta f_{CS}(\rho_1) \quad (20)$$

where  $\eta_1 = (\pi/6)\sigma^3\rho_1$ .

The excess free energy due to the dipolar interaction between chains, and between chains and free monomers may be neglected [12, 13]. By contrast, the excess free energy due to the dipolar interactions between free monomers is isotropic and attractive, resulting from a weak residual potential, since the anisotropic dipolar interactions were taken into account in

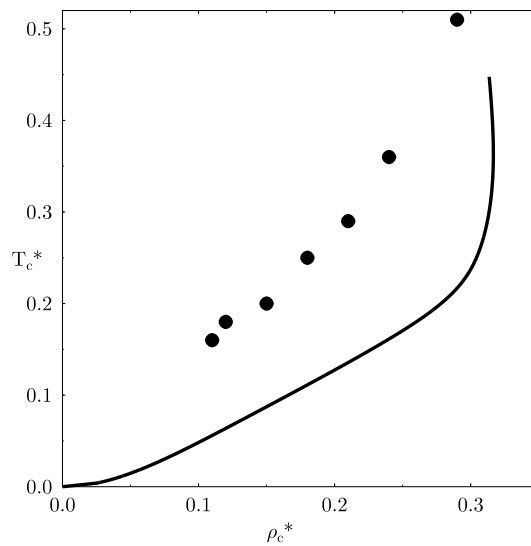
the calculation of the chain distribution function. This term is difficult to calculate and we have obtained only rough estimates [13, 19]. Thus, in the following we will calculate the properties of the DHS fluid as a function of a parameter  $A$  in terms of which the corresponding (mean-field) free energy is

$$\beta f_m^{dd}(\rho_1) = -\frac{1}{2}A\sigma^3\rho_1^2\mu^{*2}. \quad (21)$$

The critical behaviour of the DHS fluid described by the free energy (5) + (19) + (20) + (21) depends on the value of  $A$ : for  $A > A_{co} \simeq 0.284$  ordinary liquid–vapour condensation occurs between two phases of free monomers; for  $A < A_{co}$  there is chain formation at low temperatures (similarly to the ideal case) and there is no condensation. Our systematic study confirms earlier suggestions [11].

Finally, in order to compare the theory with the simulations of [8], we added to the dipole–dipole potential a Lennard-Jones tail,  $\phi_{LJ}(r) = -\epsilon_0(\sigma/r)^6$  and defined  $\lambda = \epsilon_0\sigma^3/\mu^2$  as the ratio of the dispersion to the dipolar interactions [8]. The free-energy contribution from these isotropic interactions was calculated in [12] and used in [13, 19].

For  $A < A_{co}$ , the trends of the critical temperature and density observed in the simulation are captured semi-quantitatively by the theory and are reproduced in figure 1, for  $A = 4\pi/81 < A_{co}$  [19]. The theoretical liquid–vapour critical line continues for lower values of  $\lambda$ , in contrast to the case for simulations for  $\lambda < 0.3$  which show no sign of condensation. As the critical density decreases and the mean chain length (at the critical point) increases exponentially with decreasing  $\lambda$ , these critical points become undetectable with conventional simulation algorithms. We note that at low densities and temperatures the predicted coexistence between chains may be pre-empted by the gas–solid coexistence or by an ordered (ferroelectric) liquid phase.



**Figure 1.** Comparison between the results of theory and simulation for the critical line of the dipolar fluid. The circles are estimates of the critical densities and temperatures from the simulations of [8], corresponding, from the highest to the lowest temperature, to  $\lambda = 1, 0.75, 0.6, 0.5, 0.4$  and  $0.35$ . The dashed line is the theoretical result calculated with  $A = 4\pi/81$  in (21) [19].  $\rho^* = \sigma^3\rho$  is the reduced density and  $T^*$  the reduced temperature defined in the text.

### Acknowledgments

We thank J J Weis, M A Osipov and P I C Teixeira for their collaboration at various stages of this work. JMT acknowledges the support of the Fundação para a Ciência e a Tecnologia (FCT) through Grant No PRAXIS XXI/BD/2818/94. We acknowledge the FCT for partial support through a running grant and project PRAXIS XXI/2/2.1/FIS/181/94.

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