The nature of the phase transition in dipolar fluids

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Monte Carlo computer simulations of a quasi two dimensional (2D) dipolar fluid at low and intermediate densities indicate that the structure of the fluid is well described by an ideal mixture of self-assembling clusters. A detailed analysis of the topology of the clusters, of their internal energy and of their size (or mass) distributions further suggests that the system undergoes a phase transition from a dilute phase characterized by a number of disconnected clusters to a condensed phase characterized by a network or spanning (macroscopic) cluster that includes most of the particles in the system.

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The condensation of simple fluids results from the free energy balance of the high entropy gas and the low energy liquid phases. This transition appears to be generic in simple fluids interacting through isotropic intermolecular potentials that are repulsive at short distances and attractive otherwise. The dipolar hard sphere fluid (DHS) is a model where hard (or soft) spheres with an embedded central dipole interact through the dipole-dipole potential. As the average dipolar interaction between two dipoles (weighted by the Boltzmann factor) is attractive one may expect a phase behavior analogous to that of simple fluids. A recent calculation of the free energy of the DHS at several temperatures, using Monte Carlo (MC) simulations [1], suggests the presence of an isotropic fluid-fluid transition at low densities, lending some support to the analogy with simple fluids. However, the structure of DHS at those low densities is drastically different. Numerical simulations of DHS [2] for dipolar interaction strengths of the order of the thermal energy, have shown that the anisotropy of the dipolar potential promotes the formation of self-assembled aggregates (chains, rings and more complex clusters - see fig. 1) in sharp contrast with the isotropic compact clusters observed in simple fluids. Moreover, the pair correlation function of DHS is strongly peaked at contact and the internal energy is nearly independent of the density at odds with the behavior of simple fluids.

Association theories [3,4,5,7], that include the effect of cluster formation in the thermodynamics, describe well the slow variation of the internal energy with the density and the size (or mass) distribution of the clusters. The simplest theoretical approach (based on simulation results [2,5,7]) assumes that the only effect of the dipolar interactions is to drive cluster formation. Thus, the

\[ \beta f = \sum_{N=1}^{N_p} \phi(N) \left( \ln \phi(N) - 1 - \ln q(N) \right), \]

where \( \beta = (k_B T)^{-1} \) (\( k_B \) is Boltzmann’s constant). \( \phi(N) \) and \( Vq(N) \) are, respectively, the density and the partition function of clusters of size \( N \). The free energy \( f \) is minimized with respect to the densities \( \phi(N) \), subject to a normalization condition \( N_p/V = \sum_{N=1}^{N_p} N \phi(N) \), yielding the set of equations [3]

\[ \phi(N) = q(N) \exp \left( N \beta \mu(N_p, \rho) \right), \]

where \( \mu(N_p, \rho) \) is the chemical potential of a system with \( N_p \) particles and density \( \rho = N_p/V \). In general [3], the
partition function $q(N)$ may be written as

$$q(N) = F(N) \exp(-\beta \lambda N), \quad (3)$$

where $\lambda$ is the free energy per particle of an infinite cluster and $-\beta^{-1} \ln(VF(N))$ is a sublinear correction (in $N$) to that free energy. The substitution of eqs. (2) and (3) in the normalization condition results in,

$$\rho = \sum_{N=1}^{N_p} NF(N) \exp[\beta (\mu(N_p, \rho) - \lambda) N], \quad (4)$$

and defines implicitly $\mu(N_p, \rho)$. The phase behavior of the system is obtained from the equation of state $\mu(\rho) \equiv \lim_{N_p \to \infty} \mu(N_p, \rho)$, i.e., the thermodynamic limit of eq. (4). This limit depends crucially on the convergence sum $\rho_t \equiv \sum_{N=1}^{\infty} NF(N)$. If $\rho_t$ diverges, then $\mu(\rho)$ is an analytic increasing function of $\rho$, bounded by $\lambda$ ($\mu(\rho) < \lambda$). Consequently, when $\rho_t$ diverges, the system does exhibit any phase transition. On the other hand, if $\rho_t$ is finite, $\mu(\rho)$ converges non-uniformly to the function: $\mu(N_p) \equiv \rho(\rho)$ (given through eq. (5)) if $\rho < \rho_t$; and $\lambda$ if $\rho \geq \rho_t$. Then, for finite $\rho_t$, $\mu(\rho)$ is singular at $\rho = \rho_t$, signaling a phase transition at this density: when $\rho < \rho_t$ the system consists of small disconnected clusters ($\mu(\rho) < \lambda$) and when $\rho \geq \rho_t$ any excess particles (with respect to $\rho_t$) condense in an 'infinite', spanning cluster ($\mu(\rho) = \lambda$). This transition is similar to a variety of other transitions - lamellae formation in systems of disk-like micelles, emulsification failure in microemulsions, Bose-Einstein condensation, etc.- where condensation is not driven by the interactions between 'particles' (or aggregates). Previous applications of association theories to the DHS considered chain and ring formation only and failed to predict a phase transition. Indeed, infinite chains and rings have the same configurational entropy and internal energy per particle. Their behavior is similar to that of self avoiding random walks with $F(N) \propto (N^{\gamma-1} + N^{-3+\epsilon})$, where $\gamma$ and $\epsilon$ are universal exponents known from polymer theory. Since $\gamma \geq 1$, $\rho_t \to \infty$ and the absence of a phase transition follows from eq. (4). However, chains and rings are only the simplest self-assembled clusters in DHSs and the previous argument may not hold in general. In this letter we present evidence for the occurrence of a phase transition in DHSs by analyzing the distribution functions of various types of clusters obtained from extensive Monte Carlo (MC) DHS simulations. Understanding the existence and nature of this phase transition is important for applications based on dispersions of ferromagnetic nanoparticles, where strong dipolar interactions are present, as well as for theoretical reasons. In fact, the interplay between cluster formation and condensation is a general problem, relevant in a variety of other theoretical contexts.

We have performed extensive MC simulations in the canonical ensemble for systems of hard spheres with diameter $\sigma$ and dipole strength $m$, interacting through the pair potential,

$$U_{DHS} = U_{HS} - m^2 \sum_{i,j} [(\hat{\mu}_1 \cdot \hat{r}_{12})(\hat{\mu}_2 \cdot \hat{r}_{12}) - \hat{\mu}_1 \cdot \hat{\mu}_2]. \quad (5)$$

$\hat{r}_{12}$ is the distance between spheres 1 and 2, $U_{HS}$ the hard-sphere potential ($= \infty$ if $\hat{r}_{12} < \sigma$, 0 otherwise), $\hat{r}_{12} = \frac{\hat{r}_{12}}{r_{12}}$ the unit interparticle vector and $\hat{\mu}_1, \hat{\mu}_2$ the unit vectors in the direction of the dipole moments of spheres 1 and 2, respectively. The centers of the spheres and their dipole moments were constrained to lie on the same plane, and the dipole interaction was considered only through $\hat{r}_{12}$. Previous simulations performed at reduced densities $\rho^* \equiv \sigma^2 N_p / A = 0.025, 0.03125, 0.0375, 0.05, 0.075, 0.1, 0.15, 0.2$ ($A$ is the area of the simulation box). For $\rho^* > 0.2$, two or more additional particles within this circle, $\rho$ is an end, an interior or a junction particle, respectively. Two particles belong to the same cluster if their separation is less than $r_c$ and the topology of each cluster is determined by the number of ends and junctions: rings have interior particles only, chains have two ends and no junctions.
and networks have at least one junction. The cut off $r_c$ must be $\approx \sigma$ and in this work we took $r_c = 1.15\sigma$.

Both the total internal energy of the system and the internal energy of the clusters decrease $\approx 0.5\%$ when the density is increased from $\rho^* = 0.025$ to 0.1. At all densities, the difference between these two energies is of the order of 0.5%, and well defined size distributions are observed even though the clusters break and recombine during a simulation run. Thus, as in previous works $^{5,6}$, the description of the system as an ideal mixture of self-assembling clusters is justified.

The theory entailed in eqs. $^{2,3,4}$ is easily generalized to include $N$-clusters with different topologies. Each $N$-cluster is classified according to its number of ends, $n_1$, and junctions, $n_3$. The partition function of an $N$-cluster is now $Vq(N, n_1, n_3)$, with,

$$q(N, n_1, n_3) = F(N, n_1, n_3) \exp(-N\beta \lambda(x_1, x_3)),$$

where $\lambda(x_1, x_3)$ is the free energy per particle of an infinite cluster with a fraction of ends $x_1 \equiv n_1/N$ and a fraction of junctions $x_3 \equiv n_3/N$, and $-\beta^{-1}\ln V F(N, n_1, n_3)$ is the sublinear correction to that free energy. The generalization of eq. $^2$ for the density of $N$-clusters with topology $(n_1, n_3)$ is,

$$\phi(N, n_1, n_3) = F(N, n_1, n_3) \exp(\beta N(\mu - \lambda(x_1, x_3))).$$

The partition functions of chains and rings are approximated by those of self avoiding random walks (SARW) with internal energies given by $E_0(N) = -N\epsilon_0 + 2\epsilon_1$ (chains) and $E_r(N) = -N\epsilon_0 + \epsilon_r/N$ (rings). Here, $\epsilon_0$ is a “bond” energy, i.e. the internal energy per particle of an infinite chain or ring, $\epsilon_1$ is the energy cost of an end, and $\epsilon_r/N$ a long-range correction to the energy of a ring. The resulting size distributions are given, at fixed $\rho^*$, by $\phi(N, 2, 0) \propto N^{\gamma - 1} \exp(\beta(\mu - \lambda_0)N)$ and $\phi(N, 0, 0) \propto N^{-3+\alpha} \exp(\beta(\mu - \lambda_0)N + \beta \epsilon_r/N)$, where $\lambda_0 = \lambda(0, 0)$. In fig. we plot these predictions (with $\gamma = 1.34$ and $\alpha = 0.5$ of 2D SARW $^3$) for $\rho^* = 0.1$ and the simulation results. The remarkable agreement found at this density is also observed at $\rho^* < 0.1$.

The implementation of this approach requires the knowledge of $q(N, n_1, n_3)$ for networks (i.e. for $n_3 \neq 0$) and simulation results for the various cluster distribution functions. Unfortunately this is not possible at present, as the number of configurations of a network of $N$ monomers, with $n_1$ ends and $n_3$ junctions, is not known and simulations do not yield reliable distribution functions for clusters with arbitrary topologies. In order to proceed, we note that an increase in the number of junctions and ends of a $N$ cluster increases the internal energy, while it decreases the volume available to branches, decreasing the translational entropy of the network. However, the number of possible branched architectures increases, increasing the configurational entropy of the network. We may then conjecture that, at fixed $N$, the function $q(N, n_1, n_3)$ will exhibit a maximum for some $(\tilde{n}_1(N), \tilde{n}_3(N))$. If, in the spirit of the saddle-point approximation, only this maximum is considered the mean density of networks of size $N$, $\phi_n(N)$, is,

$$\phi_n(N) = F(N, \tilde{n}_1, \tilde{n}_3) \exp(\beta N(\mu - \lambda(\tilde{x}_1, \tilde{x}_3))),$$

where $\tilde{x}_1 \equiv \tilde{n}_1(N)/N$ and $\tilde{x}_3 \equiv \tilde{n}_3(N)/N$. Substituting this (and the corresponding expressions for chains and rings) in eq. $^4$ yields the equation of state. Further analysis requires the knowledge of the functions $F$, $\tilde{n}_1(N)$ and $\tilde{n}_3(N)$. In fig. we plot the mean fraction of ends and junctions of $N$-networks, at three different densities, obtained from the simulations. Approximating $\tilde{n}_1(N)$ and $\tilde{n}_3(N)$ by these quantities, one obtains, in the large $N$ limit, $\tilde{n}_3(N) \approx c_3 N$, where $c_3$ is constant (if a slight dependence on $\rho^*$ is neglected) and $\tilde{n}_1 \approx c_1 N^{\eta}$, with $c_1$ and $\eta$ constant. Comparison with the result for chains shows (fig.) that $0 < \eta < 1$. As a consequence, the internal energy of a $N$-network can be approximated by $-\epsilon_0 N + \epsilon_1 c_1 N^{\eta} + \epsilon_3 c_3 N$, where $\epsilon_3$ is the energy cost of a junction. We note that the linear term may be incorporated into the free energy per particle of the infinite cluster $\lambda(0, c_3)$. The sublinear term must be accounted for through the energetic part of $F(N)$. Then, using eq. $^5$ and the simulation results of fig. $^5$ we may write,

$$\phi_n(N) = F_S(N) \exp[-\beta \epsilon_1 c_1 N^{\eta} + \beta N(\mu - \lambda(0, c_3))],$$

where $\beta^{-1}\ln V F_S(N)$ is the excess entropy of a finite $N$-network ($F_S(N)$ is expected to scale with some power of $N$ $^5$).

Finally we turn to the analysis of the equation of state eq. $^4$. Using the approximations described previously ($\phi(N, 2, 0) + \phi(N, 0, 0)) \propto (N^{\gamma - 1} + N^{-3+\alpha}) \exp(\beta(\mu -$
the slopes are always negative, indicating that \( \Delta \) is always more negative than that of networks, meaning the transition is discontinuous at \( \rho^* \). The existence of the transition is related to the properties of the clusters responsible for the condensation of ends stabilizes the infinite network, since \( 0 < \eta < 1 \). The full phase diagram of the DHS at low densities may be studied by generalizing the methods described in this letter. Nevertheless we stress that the phase transition mechanism is the same in both approaches. We acknowledge D. Levesque and P.I.C. Teixeira for a critical reading of this manuscript and for their valuable suggestions.

Recently, the thermodynamics of a self-assembling system of chains and networks (with no rings and no attractive interactions between clusters) was studied using a mean-field (MF) approximation \[12\]. The approximations used in that work for the distributions of chains and networks prevent a quantitative comparison with the results of this letter. Nevertheless we stress that the phase transition mechanism is the same in both approaches.

Combining a detailed analysis of extensive MC simulations and a theory that includes non-linear clusters, we confirmed the existence and clarified the nature of the phase transition of the low density DHS fluid. We have shown that the transition is driven by the formation of a macroscopic network, with a large configurational entropy that overcomes the cost in internal energy and the loss of translational entropy of the phase with high connectivity as predicted by a previous MF calculation \[12\].

The full phase diagram of the DHS at low densities may be studied by generalizing the methods described in this letter. However, the entropy driven transition may be preempted by the stabilization of other condensed phases (ordered or not) that are not considered in this framework. This is unlikely to occur at the low densities of the simulations described here but may prevent a critical point to be observed.

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