Low-Density Fluid Phase of Dipolar Hard Spheres

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Unexpectedly, recent computer simulation studies [Weis and Levesque, Phys. Rev. Lett. **71**, 2729 (1993); Leeuwen and Smit, *ibid.* **71**, 3991 (1993)] failed to find a liquid phase for dipolar hard spheres. We argue that the liquid was not observed because the dipolar spheres form long chains which interact only weakly. To support this argument we derive a simple theory for noninteracting chains of dipolar spheres and show that it provides a reasonable description of the low-density fluid phase.

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The liquid state of matter is common and, apparently, well understood [1]. Substances varying from the noble gases to complex and highly nonspherical organic molecules all exhibit a liquid phase coexisting with a vapor. This has been understood since the work of van der Waals over a century ago [1]. Essentially, in a liquid the interactions between the repulsive cores of the molecules (which increase the pressure) are greater than in the gas but so are the attractive interactions (which decrease the pressure). It is a balance between the repulsive and attractive interactions that enables two fluid phases at different densities to have the same chemical potential and pressure and so to coexist. Reducing the temperature increases the effect of the attractive part of the potential so it is tempting to assume that at sufficiently low temperature, if the intermolecular potential contains an attractive part, there will be a liquid phase [2]. It may turn out that vapor-liquid coexistence is metastable with respect to a fluid-solid transition but we would still expect a van der Waals loop in the pressure.

It was therefore something of a shock when computer simulation failed to find a liquid phase for the dipolar hard-sphere potential [2–4]. Simulations at temperatures well below the expected, and theoretically predicted [5], critical temperature revealed no sign of coexistence. What the simulations did show was that the dipolar spheres formed long, quite straight, chains at these low temperatures [2,4,6]. It is tempting to speculate that the formation of chains is somehow responsible for the lack of a liquid phase. We examine this idea by showing that, due to the highly anisotropic nature of the interaction between dipolar spheres, chain formation is energetically favorable [7]. Then, we derive a theory for chains of dipolar spheres and show that once chains have formed there is little driving force for the formation of a liquid phase. The results of our simple theory are in reasonable agreement with computer simulation and we are able to extend our calculations to densities far below those studied by simulation. The chains dominate over a very large density range at low temperatures and that in this density range the thermodynamic functions, particularly the energy and chemical potential, vary very slowly with density.

The interaction potential for a pair of dipolar hard spheres is

$$u_2(12) = \begin{cases} -\dfrac{\mu^2}{4\pi\epsilon_0 r_{12}^3}[2\cos\theta_1\cos\theta_2 & \\ \quad -\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)], & r_{12} > \sigma\,, \\ \infty & r_{12} < \sigma\,, \end{cases} \tag{1}$$

where θ_1 and θ_2 are the angles between the two dipole vectors and the vector $\mathbf{r}_{12}$ which joins the centers of the two dipolar hard spheres. ϕ_1 and ϕ_2 are the azimuthal angles about $\mathbf{r}_{12}$ [8]. σ is the diameter of the spherical hard core, μ is the dipole moment, and ϵ_0 is the permittivity of free space. The notation (12) represents the relative coordinates of molecules 1 and 2 with coordinates (1) and (2), respectively.

Of course, this is a long ranged potential; doubling the distance between two dipolar hard spheres reduces the energy of interaction by a factor of 8 whereas the energy decreases by a factor of 64 for two Lennard-Jones molecules [1]. However, the potential is highly anisotropic and has two pronounced minima corresponding to nose-to-tail configurations. The minima of the potential correspond to the maximum of the angular function in (1) and $r_{12} = \sigma$. At these minima the energy of a pair of molecules is $-2\beta^* k_B T$, where $\beta^* = \mu^2/4\pi\epsilon_0\sigma^3 k_B T = 1/T^*$ defines our energy scale. T is the temperature and k_B is Boltzmann's constant. There are other local minima with the pair of molecules side by side and antiparallel but their energy is only $-\beta^* k_B T$. The low energy states are those for which the molecules are nose to tail, forming chains of molecules. As the temperature T^* decreases the weighting, by the Boltzmann factor, configurations in which the dipolar spheres are nose to tail will increase exponentially. The dipolar spheres form long chains because only then can they minimize their energy (there are also ringlike configurations but the qualitative effect of rings is the same as that of chains, so for the moment we ignore them).

There is an implicit assumption in all of this, that the energy is essentially the sum of $N - 1$ pair terms; that the molecules do not arrange themselves in some more complicated way with an even lower energy. However, the formation of structures more ordered than simple chains will be highly unfavorable at low densities. Also, and this is an important point, if we only consider nearest neighbor interactions in a chain the configurational energy will be a little above $-2\beta^* k_B T$ but the energy of a close-packed antiferromagnetic solid is only $-2.56\beta^* k_B T$ [7] and Onsager's lower bound on the energy [9] is $-4\beta^* k_B T$. A fluid of noninteracting chains has an energy almost as low as a close-packed lattice even when we count only the interaction of nearest neighbors. As observed by de Gennes and Pincus [7] the formation of chains almost saturates the interaction between dipolar spheres. But if it is not possible to lower the energy of a fluid below that of essentially noninteracting chains there is no driving force for the formation of a liquid phase. In the van der Waals picture of a fluid, two fluid phases can coexist because the lower excluded volume entropy of the denser phase is counterbalanced by its lower energy. If the energy saturates then the van der Waals mechanism for vapor-liquid coexistence no longer applies.

This saturation of the attractive part of the interaction may be contrasted with the situation for molecules which interact via a spherically symmetric potential. These molecules minimize their energy by clustering; each molecule will be surrounded by and interact equally with around 12 other molecules. It is straightforward to see that this clustering will lead to the formation of a liquid.

We now use our simple physical picture of the low temperature gas of dipolar hard spheres to develop a statistical mechanical theory. If our ideas are correct then the predictions of this theory should agree with the pseudoexact computer simulation data [3,6]. Our starting point is the pressure p, related to the logarithm of the grand partition function Ξ, expressed as an activity expansion. The activity z is simply related to the chemical potential μ_p by

$$z = q_P(T)\exp(\beta\mu_p)\,, \tag{2}$$

where $\beta = 1/k_B T$ and q_P is the one molecule momentum partition function. The activity expansion of the pressure is exactly given in terms of an infinite sum of graphs, where graphs are combinations of integrals and symmetry numbers, see [1,10] for descriptions and definitions of graphs.

$$\beta p V = \ln\Xi = \int d(1)z(1) + \left\{\begin{matrix}\text{sum of all connected graphs of}\\ \text{black circles } z, \text{ and } f \text{ bonds}\end{matrix}\right\}, \tag{3}$$

where V is the volume of the system and $f = \exp[-\beta u_2(12)] - 1$ is the Mayer f function. A connected graph is a graph with at least two circles and with the circles linked together by bonds so that every circle of the graph is connected to every other circle by a sequence of circles and bonds. Following the usual practice we have left z expressed as a function of position and orientation $z(1)$; however, we do not consider a fluid in an external field so z is just a constant.

Our picture of a dilute gas of dipolar hard spheres is one of noninteracting chains of the dipolar spheres. If we also neglect all interactions within a chain except for nearest neighbor interactions then the chains are ideal and their theoretical treatment is simple [11,12]. So, for noninteracting ideal chains of dipolar spheres, (3) simplifies to

$$\beta p V = \int d(1)z(1) + \left\{\begin{matrix}\text{sum of all linear chain graphs of}\\ \text{black circles } z, \text{ and } f \text{ bonds}\end{matrix}\right\}, \tag{4}$$

where a linear chain graph is composed of z circles and f bonds such that the only f bonds are between successive z circles. A chain graph with n z circles factorizes into $n - 1$ pair integrals, each of which is $-2B_2$, divided by a symmetry number: always equal to 2. B_2 is the second virial coefficient of the dipolar sphere fluid. Then, summing all chain graphs gives

$$\beta p = z - \frac{z^2 B_2}{1 + 2zB_2}\,. \tag{5}$$

This is the correct result for the pressure of an ideal gas of ideal chains [13]. The number density ρ is obtained from

$$\rho = z\left(\frac{\partial\beta p}{\partial z}\right)_{V,T} = z - \frac{2zB_2 + 2z^2B_2^2}{(1 + 2zB_2)^2}\,. \tag{6}$$

Rearranging (6) gives a cubic equation for z in terms of ρ and so enables us to obtain the chemical potential and hence the free energy as a function of ρ and T. The configurational energy u can be obtained by differentiating the free energy with respect to temperature. B_2 is a function (only) of T; we calculate it using the expression of Joslin [14]. The average chain length l is equal to the total number density divided by the total number of chains. The pressure of ideal chains, over $k_B T$, is just this total number density of chains, therefore $l = \rho/\beta p$.

We now have the thermodynamic functions and l which we may compare with the results of computer simulation. Caillol [3] performed simulations at $T^* = 0.18$. At the densities we are interested in, $\rho^* = \rho\sigma^3 \leq 0.1$, the pressure is too small to be measured in the simulation but at $\rho^* = 0.98$ simulation gives $\beta u = -8.82$ and $\ln z = -6.39$ which may be compared with our results of $\beta u = -6.06$ and $\ln z = -5.79$. The simulations of Levesque and Weis [6] are at the much lower temperature of $T^* = 0.0816$. Their data provide a severe test of our theory as at this very low temperature B_2 is huge, $B_2(0.0816) = -5.39 \times 10^6 \sigma^3$. This may be compared with the second virial coefficient for hard spheres $B_2(\infty) = 2\pi/3$. Simulations for ρ^* in the range 0.01–0.1 give $\beta u \simeq -26$ while in this range our theory gives $\beta u \simeq -21.2$. Both simulation and theory predict that the energy is essentially constant over a decade in density, indeed theory predicts that βu changes only by about 0.05 (0.2%). The molecules form linear aggregates which interact weakly; as such their behavior will be similar to that of a one-dimensional fluid. Just as in a typical one-dimensional fluid each molecule interacts only with two others, and so the interaction energy easily saturates [15]. Without an energy which decreases with density, there is no driving force for a vapor-liquid transition.

At sufficiently low density βu, of course, tends to 0 but this occurs at much lower densities of around 10^{-8} (see Fig. 1). Remarkably, the energy is almost constant over a density range of 4 decades. The chemical potential (also shown in Fig. 1) is similarly almost constant over the same density range. So, we predict that due to the saturation of the interaction between the dipolar spheres the energy and chemical potential are almost constant over a very large density range. The average chain length l does change in this density region, as can be seen in Fig. 2. At the densities simulated [6] l is greater than the number of molecules used in the simulation so we are unable to compare the theoretical l with that of simulation. Note that l has increased to above 10 at $\rho^* = 10^{-5}$. Over the density range 10^{-5}–10^{-1} where the energy is constant the fraction of molecules which are part of a chain and are not an end sphere varies only from above 0.8 to essentially 1. With this in mind it is less surprising that the energy is nearly constant.

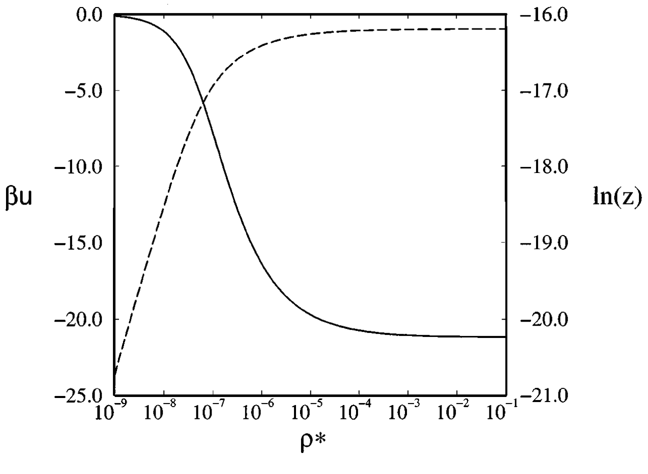

FIG. 1. The configurational energy u divided by $k_B T$ (solid curve) and the chemical potential $\ln(z)$ (dashed curve), as a function of the reduced density ρ^* at a temperature of $T^* = 0.0816$.

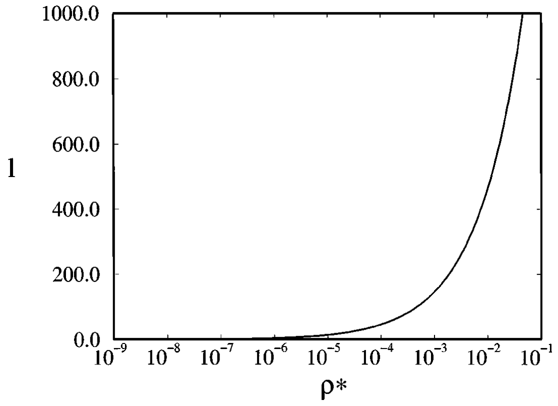

FIG. 2. The mean chain length l as a function of the reduced density ρ^* at a temperature of $T^* = 0.0816$.

In addition to treating the chains as ideal, we have neglected the possibility of rings forming [11,16]. Chains of dipolar spheres are not very flexible and this certainly discourages ring formation; few rings were seen in computer simulation. However, at very low densities ring formation is favored because the entropy cost of forming long chains is high [16]. It is difficult to assess the number of rings that will form but if significant numbers do form then the energy will saturate more quickly than we predict using our theory, which neglects ring formation.

In conclusion, because the interaction between dipolar spheres is highly anisotropic the formation of chains is highly favored. These chains are highly stable and there is little energy to be gained by their aggregation, and therefore the driving force for the formation of a liquid phase is much weaker than that found for spherically symmetric potentials. The behavior of dipolar spheres is similar to that of associating spheres [17], in particular a sphere with two sites, each mediating a highly anisotropic and short ranged interaction (typically $\simeq 0.1\sigma$). Remarkably, the enormous difference in interaction range between the associated sphere [17] and the dipolar sphere seems to make little difference at low densities. The behavior shown in Fig. 1 is general to systems which form long, linear chains; see Ref. [18] for a discussion of such systems. It is interesting to note that although a sphere with two sites does not show vapor-liquid coexistence, a sphere with four (or three) sites does [19]. With more than two sites the chains can branch and cross-link; this encourages clustering and the formation of a liquid phase. So, if we can modify the potential so that instead of two minima there are three or more we expect a liquid phase to appear; this is borne out by the computer simulations of McGrother and Jackson [20].

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[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986), 2nd ed.

[2] M. E. van Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993).

[3] J.-M. Caillol, J. Chem. Phys. **98**, 9835 (1993).

[4] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993).

[5] G. S. Rushbrooke, G. Stell, and J. S. Høye, Mol. Phys. **26**, 1199 (1973).

[6] D. Levesque and J. J. Weis, Phys. Rev. E **49**, 5131 (1994).

[7] P.-G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).

[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley, New York, 1954).

[9] L. Onsager, J. Phys. Chem. **43**, 189 (1939).

[10] T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, 537 (1961).

[11] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[12] P. C. Jordon, Mol. Phys. **38**, 769 (1979).

[13] R. P. Sear and G. Jackson (to be published).

[14] C. G. Joslin, Mol. Phys. **42**, 1507 (1981).

[15] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).

[16] R. P. Sear and G. Jackson, Phys. Rev. E **50**, 386 (1994).

[17] M. S. Wertheim, J. Chem. Phys. **87**, 7323 (1987).

[18] R. G. Petschek, P. Pfeuty, and J. C. Wheeler, Phys. Rev. A. **34**, 2391 (1986).

[19] I. Nezbeda and G. A. Iglesias-Silva, Mol. Phys. **69**, 767 (1990).

[20] S. C. McGrother and G. Jackson (to be published).