What Makes a Polar Liquid a Liquid?

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We report computer simulations of the phase behavior of dipolar (ferro) fluids. We consider a model in which the dispersive interactions can be varied independently from the dipolar (magnetic) interactions. The simulation results show that a minimum amount of dispersive energy is required to observe liquid-vapor coexistence. If the dispersive energy is below this threshold, as for example in the dipolar hard-sphere fluid, the system forms chains of dipoles aligning nose to tail. Our simulations did not give any evidence that these "polymerlike" systems phase separate into a liquid and vapor phase.

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The seminal work of Alder and Wainwright has shown that hard-sphere interactions alone are sufficient to observe a fluid-solid phase transition [1]. For a vapor-liquid phase transition attractive forces are required to provide the cohesive energy to stabilize the liquid phase [2]. Since all common molecular fluids have a liquid phase, it is tempting to assume that, if attractive forces are present, vapor-liquid equilibria will always be observed at sufficiently low temperature. This point of view is, however, too simplistic. For example, experiments on colloidal suspensions have shown that "liquid-vapor" phase coexistence is only observed when the range of the attractive forces is sufficiently large as compared to the diameter of the colloidal particles [3]. If the range is too small, the (metastable) critical temperature is lower than the triple temperature and hence no vapor-liquid equilibrium is observed.

In this Letter, we consider the effects of dipolar interactions on the vapor-liquid curve. In particular, we pose the question whether dipolar interactions are sufficient to stabilize a liquid phase. Since all polar fluids have a liquid phase, one might be inclined to assume that the answer to this question is affirmative. However, in real polar fluids the dispersive van der Waals forces can never be ignored and hence we cannot conclude that dipolar forces alone suffice to stabilize the liquid phase. The effects of dipolar interactions can also be investigated in a ferrofluid, i.e., a colloidal suspension of ferromagnetic particles dispersed in a magnetically passive liquid. Bacri *et al.* [4] have shown that these systems have a vapor-liquid phase transition. Ferrofluids are particularly interesting since the anisotropic magnetic (dipolar) interactions can be varied independently from the isotropic dispersive interactions.

To study these systems using computer simulations, we introduce a model dipolar/ferrofluid in which the particles interact via a pair potential of the following form:

$$U_{\lambda,\mu}(\mathbf{r}_{ij},\boldsymbol{\mu}_i,\boldsymbol{\mu}_i) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \lambda\left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{\mu^2}{r^3}\left[\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j - \frac{3}{r^2}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})\right],$$

where μ is the dipole moment and $\boldsymbol{\mu}_i$ is the orientation of the dipole of particle i, $\mathbf{r}_{ij}$ is the distance between the particles, and λ controls the strength of the dispersive interactions. Note that we focus on a ferrofluid in zero magnetic field.

It is interesting to consider some limiting cases of this model. For $\lambda = 1$, the model is identical to the Stockmayer fluid [2] for which the vapor-liquid curve has been calculated using computer simulations [5,6]. For $\lambda = 0$, the model reduces to a dipolar soft-sphere fluid which is similar to the dipolar hard-sphere fluid. For the dipolar hard-sphere fluid, the existence of a liquid phase also appears to be well established. Since the orientationally averaged interaction between two dipoles is a van der Waals–like $1/r^6$ attraction, de Gennes and Pincus conjectured a vapor-liquid coexistence similar to that of a conventional van der Waals fluid [7]. Kalikmanov [8] used this conjecture to estimate the critical point. Also more sophisticated liquid theories such as mean spherical approximation [9] and perturbation theory [10] predicted the occurrence of a vapor-liquid curve. Finally, simulations of Ng *et al.* [11] lent support to the theoretical predictions of the existence of liquid-vapor coexistence in a dipolar hard-sphere fluid.

Since for both limits of our model the existence of a liquid phase appears to be well established, a detailed study of this model is not expected to reveal new qualitative insights. It turned out, however, that below a certain value of λ *no* phase coexistence could be observed in our simulations. For low values of λ, the dipoles align nose to tail and form chains at conditions close to the coexistence curve.

To determine the vapor-liquid curve of our model as a

function of λ, the Gibbs-ensemble Monte Carlo technique has been used [12,13]. In the Gibbs-ensemble technique, simulations of the vapor and liquid phase are carried out in parallel. Monte Carlo moves which allow for changes in the volume and number of particles ensure that the two boxes are in thermodynamic equilibrium with each other. The coexistence densities can be determined directly from the two systems. Systems of at least 512 particles were studied and the long-range dipolar interactions were handled with the Ewald-summation technique using "tin-foil" boundaries [14]. Further details on the simulations can be found in Ref. [6]. The reduced temperature and density are defined using the dipolar hard-sphere fluid as a reference, i.e., $T^* = k_B T\sigma^3/\mu^2$ and $\rho^* = \sigma^3\rho$. The parameters are such that for $\lambda = 1$ the model reduces to a Stockmayer fluid with $\mu^{*2} = \mu^2/\epsilon\sigma^3 = 4$.

In Fig. 1 the phase diagrams for λ =1–0.35 are presented. The lower the value of λ the more difficult it becomes to exchange particles between the liquid and the gas phase. Besides the already low probability of finding an empty space, the probability that a randomly oriented dipole has the "correct" orientation to be accepted turned out to be very small. To enhance the acceptance of the exchange step, we have used the configurational-bias Monte Carlo technique to bias the orientation of the dipole [15]. This resulted in an increase of the acceptance of the exchange step by a factor 3 to 4 depending on the conditions.

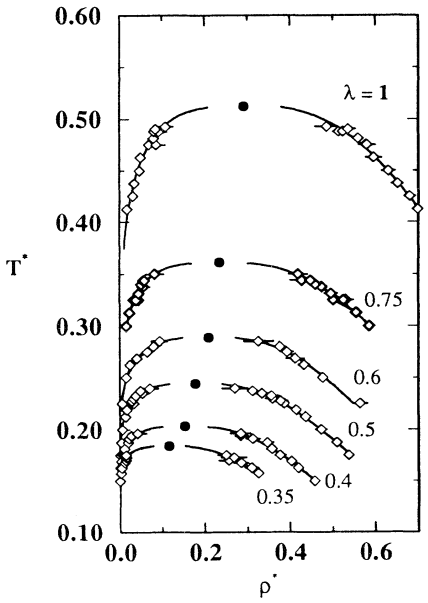

FIG. 1. Vapor-liquid curves of the model dipolar fluids for various values of λ as obtained from the Gibbs-ensemble simulations. The points are the simulation data; the solid lines are fits to the simulations (see Ref. [6]). The critical point is estimated using the methods described in Ref. [6]. The results for $\lambda = 1$ correspond to the Stockmayer fluid with $\mu^* = 2$ and are taken from Ref. [6].

In Fig. 2 the critical temperature and density are shown as a function of λ. As expected, the critical temperature is lowered due to the decrease of the dispersive interactions. More surprising is the decrease in the critical density. The predictions of the various theories and the simulation results of Ng *et al.* for the dipolar hard-sphere fluid are shown as well in Fig. 2. If we extrapolate our results to $\lambda = 0$ [16], we arrive at a much lower critical temperature and density than predicted by the theories and simulations of Ng *et al.* These results are in line with the recent simulations of Caillol [17]. Caillol performed Gibbs-ensemble and NPT simulations for the dipolar hard-sphere fluid for $T^* = 0.18$ and 0.22 and could not detect any vapor-liquid coexistence. Our results show that if there is a coexistence curve it should be expected at a much lower temperature and density.

For values of $\lambda < 0.3$, we could not detect phase coexistence using the Gibbs ensemble. At conditions where

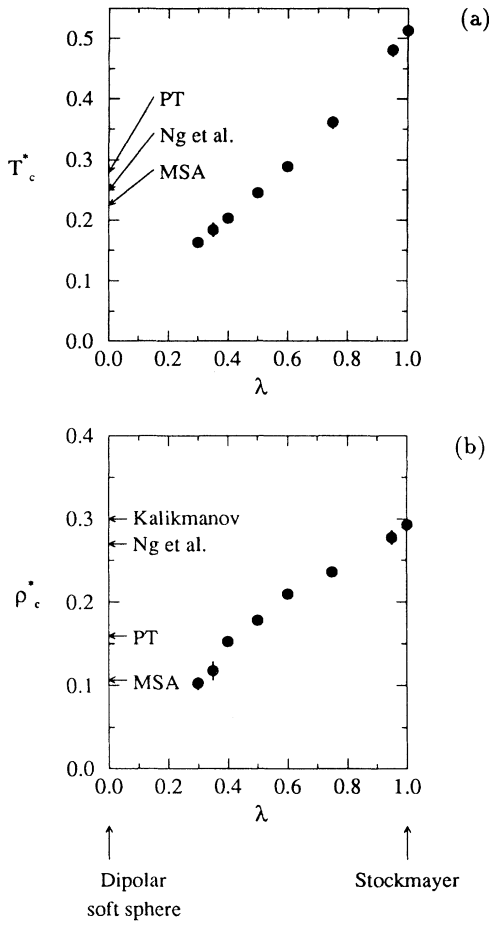

FIG. 2. Critical temperature (a) and critical density (b) as a function of λ. The arrows indicate the various estimates of the critical temperatures for the dipolar hard-sphere fluid (see text). Note that the estimate of Kalikmanov [8] of the critical temperature ($T_c = 0.66$) does not fit on the scale.

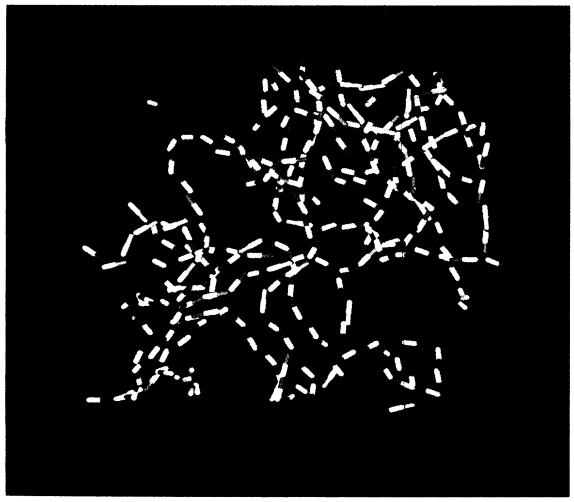

FIG. 3. Snapshot of the dipolar fluid ($\lambda = 0.2$, $T^* = 0.125$, and $\rho^* = 0.073$). The particles are shown as capped sticks, with the long axes of the stick parallel to the dipole. The plus side of the dipole is colored red, the minus side white.

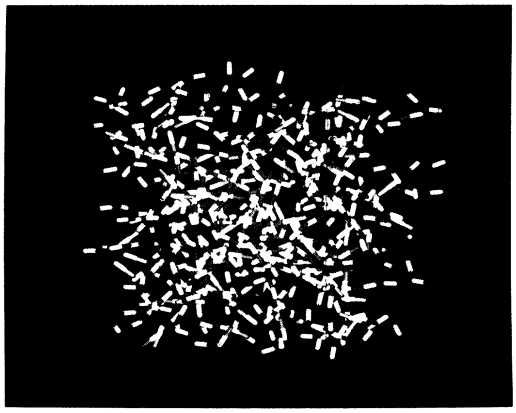

FIG. 4. Snapshot of liquid coexistence density of the dipolar fluid ($\lambda = 0.3$, $T^* = 0.14$, and $\rho^* = 0.3$). See also the caption to Fig. 3.

the coexistence curve is expected, we observed the formation of chains of dipoles aligning nose to tail. A typical snapshot of such a configuration is shown in Fig. 3. It is important to note that we did not observe chain formation in the Gibbs-ensemble simulations of the liquid phase for $\lambda \geq 0.3$ (see Fig. 4). We also used NPT simulation at zero pressure starting with a high density liquid. If there is phase coexistence, these NPT simulations would equilibrate to a density close to the coexistence density. We observed that chains already formed at densities higher than the expected liquid coexistence density. The system formed a "glassy" structure with chains that percolated. Because of this percolation most volume changes were rejected and the density did not further decrease. After repeated heating, to break up the chains, the simulations ended in the gas state which suggests that there is no stable liquid phase.

The results presented in this work suggest that if there is a vapor-liquid phase transition for the dipolar hard-sphere fluid, it is at much lower temperatures and densities than predicted by most theories. Furthermore, contrary to what is assumed in most theoretical work on this subject, we observe that under conditions where a critical point is expected, the structure of the dipolar hard-sphere fluid is very different from that of a typical "simple" liquid. In fact, the microscopic structure of the dipolar hard-sphere fluid resembles that of a polydisperse mixture of "living" linear polymers and ring polymers. We did not find any evidence that this system undergoes a liquid-vapor transition.

The simulations indicate that a minimum amount of dispersive energy is required to observe a van der Waals–like vapor-liquid curve. In ferrofluids it is possible to prepare colloidal suspensions in which the magnetic interactions can be varied independently from the dispersive interactions. With such systems the results of the simulations may be tested. Furthermore, chain formation in these colloidal systems may be further investigated. The formation of chains introduce an additional correlation length in the system which can have a critical exponent different from the Ising-like one. It would therefore be interesting to further investigate the critical behavior of these systems at conditions where the percolation of dipoles occurs close to two-phase region. This work, together with the recent studies of Wei and Patey [18] and Weis *et al.* [19] on the formation of liquid crystalline phases in simple dipolar fluids, shows that these systems are much more interesting than expected.

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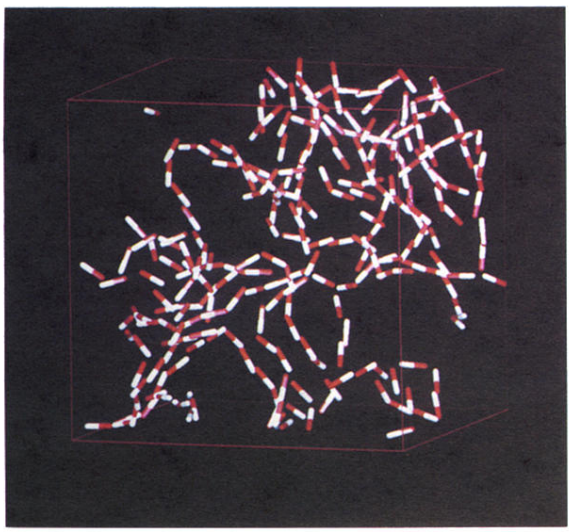

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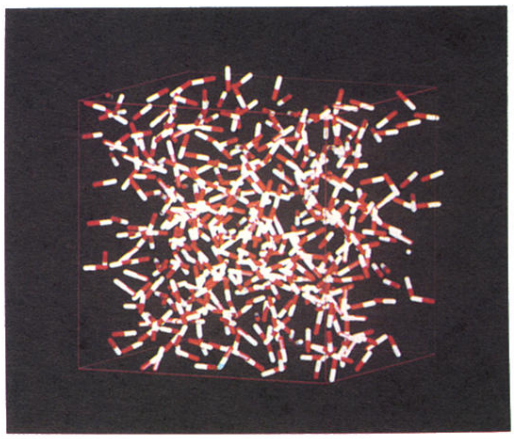

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