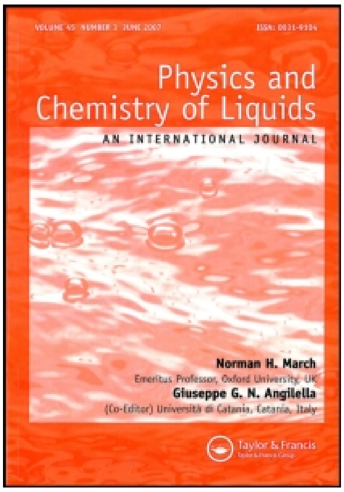

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VAPOUR-LIQUID COEXISTENCE IN A QUASI TWO-DIMENSIONAL HARD DIPOLAR FLUID

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The liquid-gas phase behavior of a quasi two-dimensional fluid has been calculated using Zwanzig thermodynamic perturbation theory. The molecular model is that of hard disks with an inmmersed three dimensional point dipole. Calculations show the fluid phase coexistence for values of temperature lower than the critical temperature.

Keywords: Perturbation theory; dipolar fluid; vapour-liquid equilibria

1. INTRODUCTION

Two-dimensional fluids have been used as model systems to study the behaviour of films adsorbed at a solid surface as well as the phase behavior of monolayers at a fluid-fluid interface. The phase behaviour in monolayers arise from the lateral interactions occurring at the interface [1].

We are attempting to study the phase behaviour of lipid monolayers at the oil/water interface. Lipids have a polar amphiphilic head and a non-polar hydrophilic tail which, in this interface, play a very minor role in its phase behaviour.

The simplest polar system we can think of consists of hard dipoles whose centre of mass lies at the interface. We are specifically

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concerned with the lateral interactions in this system which we model as indicated below.

In this work we present a calculation of the phase coexistence curve based on Zwanzig's thermodynamic perturbation theory.

In order to describe such interactions, we have assumed that the constituent fluid molecules can be modelled as hard disks with an immersed three dimensional point dipole. The reference system is a monodisperse fluid of hard disks.

A sketch of the theoretical approach is presented in the following section. The thermodynamic properties and results are presented in sections III and IV, respectively. Finally a brief discussion of the results is presented in Section V.

2. THEORY

We assume that the molecules (i and j) of the fluid, separated by a distance r_{ij}, interact via the pair potential:

$$u(r_{ij}) = u_{HD}(r_{ij}) + u_{dd}(r_{ij}) \tag{1}$$

where $u_{HD}(r_{ij})$ is the hard disk pair potential and $u_{dd}(r_{ij})$ the three dimensional dipole-dipole interaction pair potential given by:

$$u_{dd}(r_{ij}) = -\frac{\mu^2}{4\pi\varepsilon_0 r_{ij}^3}[2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)] \tag{2}$$

where θ_i and θ_j are the angles between the two dipole vectors and the vector $\mathbf{r}_{ij}$ is the vector joining the centers of the dipolar hard disks. In Eq. (2) only the lateral interactions on the interface are taken into account.

In the Zwanzig thermodynamic perturbation theory the Helmholtz free energy (HFE) is written as:

$$A^* = A_0^* + A_1^* + A_2^* + A_3^* + \dots; \quad A^* = \beta A/N. \tag{3}$$

Here, A_0^* is the free energy of HD which is taken from Gonzalez *et al.* [2] as follows. We fitted the equation of state from Ref. 2, by a Padé-like approximant, which reads

$$\beta P/\rho = 1/(1-\eta)^2 + c_1\eta^2/(1-\eta)^2 - c_2\eta^4/(1-\eta)^3; \quad \eta = \pi\sigma^2/4. \tag{4}$$

with $\beta = (k_B T)^{-1}$; k_B the Boltzman constant, ρ the number density and σ the disk diameter.

On integrating Eq. (4) the excess free energy is given by:

$$\begin{aligned}\frac{A - A^{id}}{Nk_B T} &= (c_1 + 3c_2 - 1)\ln(1-\eta) - c_2(1-\eta) + (c_1 + 3c_2 + 1)/(1-\eta) \\ &\quad - c_2/2(1-\eta)^2 - (c_1 + 3c_2/2 + 1);\ c_1 = 0.0851, c_2 = 0.0157\end{aligned} \tag{5}$$

The results obtained from Eqs. (4–5) are in very good agreement with the computer simulations results of Henderson [3] and of Erpenbeck and Luban [4].

Finally, Eq. (3) can be written as a sum of two terms, with the second term on the r.h.s. a Padé approximant proposed by Stell [5]

$$A^* = A_0^* + A_{2DD}^*/(1 - A_{3DD}^*/A_{2DD}^*), \tag{6}$$

where

$$A_{2DD}^* = -\frac{\pi}{3}\frac{\rho^*}{T^{*2}} I_2(\rho^*), \tag{7}$$

$$A_{3DD}^* = \frac{\pi}{27}\frac{\rho^{*2}}{T^{*3}} I_3(\rho^*), \tag{8}$$

and

$$I_2(\rho^*) = \int \frac{g_0(r^*)}{r^{*5}} dr^*.$$

$g_0(r)$ is the pair distribution function of the hard disk reference system [2] and

$$I_3(\rho^*) = \int g_0(123)\varphi(123)dr^*.$$

$\varphi(123) = (1 + 3\cos\alpha_1\cos\alpha_2\cos\alpha_3)/(r_{12}r_{13}r_{23})^3$ is the usual Axilrod-Teller three body contribution [6]. The three particle distribution function $g_0(123)$ is assumed to be given by the Kirkwood superposition approximation [6].

3. THERMODYNAMIC PROPERTIES

The phase equilibria between the fluid phases (*a*) and (*b*) at a given pressure and temperature is calculated by numerically solving the equations: $\mu^*(\rho^{*(a)}, T^{*(a)}, P^{*(a)}) = \mu^*(\rho^{*(b)}, T^{*(b)}, P^{*(b)})$, $P^{*(a)} = P^{*(b)}$ and $T^{*(a)} = T^{*(b)}$; μ^* is the reduced chemical potential, at given pressure and temperature.

The expressions for the Gibbs free energy and pressure are: $G^* = A^* + P^*/\rho^* T^*, P^* = \rho^{*2} T^*(\partial A^*/\partial \rho^*)_{T^*}$. Reduced variables for pressure, temperature and density are, respectively, with μ the molecule dipole moment $P^* = P\sigma^5/\mu^2$; $T^* = kT\sigma^3/\mu^2$; $\rho^* = \rho\sigma^2$.

4. RESULTS

In Figure 1 we present the results for the coexistence curve of the vapour and liquid phases for the dipolar fluid studied in this work. As noted, the shape of the coexistence curve is similar to those found in real polar fluids. It also verifies the law of rectilinear diameters.

In Figure 2 we present the vapour-pressure line which ends at the critical point which, in reduced units, is given by the values $T^* = 0.34211953$, $P^* = 0.0801344$ and $\rho^* = 0.46285481$.

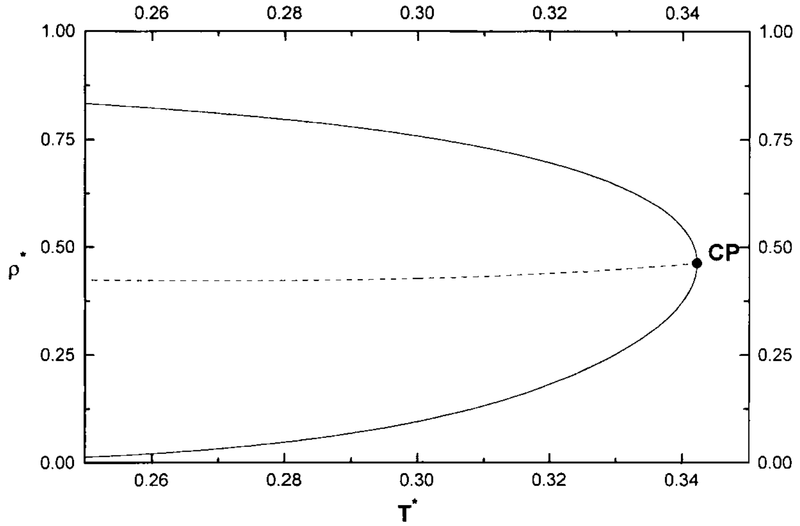

FIGURE 1 Vapour-liquid coexistence curve for the dipolar hard disk fluid. The broken line shows $(\rho_g + \rho_l)/2$. CP is the calculated critical point of the fluid.

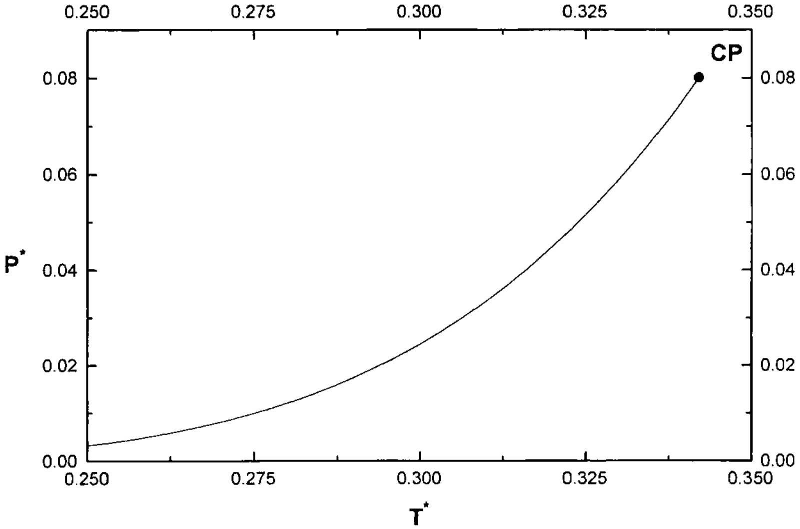

FIGURE 2 Vapour-pressure curve for the dipolar hard disk fluid. CP is the calculated critical point.

5. DISCUSSION

The results presented in this work cannot be compared with computer simulations of a corresponding model dipolar system for the following reasons. First, it has been found that in computer simulations of the equivalent three-dimensional system there is no liquid phase present as dipoles form head to tails chains [7] which, while minimizing the free energy [8] prevent condensation. Second, although to our knowledge there is no published results for the two-dimensional system it is widely accepted that this two-dimensional dipolar fluid does not have a liquid phase either. Finally, and although the system studied in this work is no strictly a two dimensional system (the dipolar interactions are the lateral interactions of three dimensional dipoles), preliminary results suggest the existence of chains in this case as well [9]. Nevertheless we believe our results are meaningful. The work by van Leeuwen and Smit [10] suggests that mean field theories such as that used in this work, on averaging the dipolar interactions, somehow appear to introduce forces other than the strictly dipolar forces which are used in computer simulations. In fact, the recent work of Kiyohara *et al.* [11] shows clearly that the inclusion of dispersion forces, although much weaker than the dipole interactions, are sufficient to break up the chains and allow for the existence of a liquid phase.

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