

Density-functional theory for the interfacial properties of a dipolar fluid

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 111

(<http://iopscience.iop.org/0953-8984/3/1/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:03

Please note that [terms and conditions apply](#).

Density-functional theory for the interfacial properties of a dipolar fluid

P I Teixeira† and M M Telo da Gama

Departamento de Física, Faculdade de Ciências de Lisboa e Centro de Física da Matéria Condensada, Avenida Professor Gama Pinto 2, P-1699 Lisboa Codex, Portugal

Received 17 April 1990

Abstract. We have studied the interfacial properties of a model dipolar fluid using a generalization of the density functional mean-field approximation. The generalization consists in weighting configurations in the mean-field average of the perturbative part of the energy by the low-density approximation of the radial distribution function. This leads to a bulk phase diagram which depends explicitly on the strength of the multipole moments, in contrast with the results of the simpler version of the theory.

The calculated surface tension and density-orientational profile are in fair agreement with computer simulation (molecular dynamics) results: the addition of a dipole moment causes the surface tension to increase and there is interfacial ordering induced by purely multipolar forces. An extension of the theory to binary fluid mixtures is also briefly discussed.

1. Introduction

In recent years the subject of molecular orientation at fluid interfaces has received some attention. Orientation phenomena are believed to play an important role in catalysis as well as in processes involving biological membranes. The most striking example of a system exhibiting surface order is a liquid crystal (LC). However, LCs are remarkably difficult to study theoretically, owing to the complexity of shapes and interactions of their molecules. Hence a detailed microscopic theory can only be applied to drastically simplified models of LCs to provide some insight into the qualitative behaviour of the real systems.

On the other hand, fluids of smaller quasi-spherical multipolar molecules are simple enough to be amenable to microscopic treatment, while retaining many interesting interfacial properties, as revealed by some recent computer simulation (Townsend *et al* 1985, Wilson *et al* 1987, Matsumoto and Kataoka 1988, 1989) and experimental (Goh *et al* 1988) studies. Polar fluids such as water, hydrogen chloride and methanol are of great importance in chemistry and biology, as are homonuclear diatomics such as hydrogen and nitrogen, in which quadrupolar interactions are thought to be relevant. Furthermore, from a study of these systems, information can be obtained which may be pertinent to LCs, whose richness of modern technological applications (Shanks 1982) makes them worth investigating.

†Present address: Faculty of Mathematical Studies, University of Southampton, Southampton SO9 5NH, UK.

We emphasize that the difficulties involved in a detailed microscopic treatment of such systems stem not only from the complexity of intermolecular interactions but mainly from the fact that we wish to consider *non-uniform three-dimensional* fluids, i.e. systems where the translational symmetry of the bulk phases is broken at an interface. This introduces non-trivial complications which hinder the application of more complex approximations developed for homogeneous liquids.

Gubbins and co-workers developed separate theories for the surface tension and density-orientational profile of fluids characterized by anisotropic interaction potentials. In their theories for the surface tension (Gray and Gubbins 1975, Haile *et al* 1976a, Gubbins *et al* 1977) they introduced a drastic approximation for the density profile (the Fowler approximation). As for the density-orientational profile, their earlier ' μ -expansion' (Haile *et al* 1976b) predicts that multipolar-like interactions are unable to cause any interfacial ordering. The more elaborate 'f-expansion' theory (Thompson *et al* 1981) nevertheless predicts orientational ordering in the surface due to electrostatic forces. This latter theory was used to study a model fluid in which the intermolecular potential consists of site-site Lennard-Jones (LJ) terms plus a quadrupole-quadrupole term. Predictions are in qualitative agreement with molecular dynamics (MD) simulation results for chlorine by the same workers (Thompson and Gubbins 1981). However, surface tension and structure are calculated independently and using different approximations.

Tarazona and co-workers have also developed a perturbative expansion for the Helmholtz free energy of a molecular fluid interface (Tarazona and Navascués 1982) which allowed them to calculate simultaneously the surface tension and the density-orientational profile. This theory was later generalized using the density-functional formalism (Chacón *et al* 1983) but it failed to predict any interfacial ordering induced by purely multipolar intermolecular potentials.

More recently, Gubbins and co-workers used the f-expansion and a YBG-type equation (Gubbins 1980) to study the liquid-vapour interface of a Stockmayer fluid (Eggebrecht *et al* 1987a). They also performed an MD simulation of the same system and found qualitative agreement between theoretical and simulation results; dipoles tend to lie parallel to the interface on the liquid side and the surface tension increases with increasing strength of the dipole moment. Calculations also showed that molecules favour perpendicular orientations on the vapour side but the simulation data are inconclusive in this region. This investigation was of paramount importance since it established that interfacial ordering *can* be induced by purely multipolar forces.

In this paper we develop a density-functional theory similar to that of Tarazona and co-workers in order to clarify whether this type of theory can predict interfacial ordering as a result of purely multipolar interactions. The main advantage of density-functional theories is that they allow us to calculate microscopic (density-orientation profile) and macroscopic (surface tension and adsorption) quantities simultaneously and self-consistently.

This paper is arranged as follows: in section 2 we write down an (exact but intractable) expression for the Helmholtz free energy of a non-uniform fluid characterized by anisotropic pair potentials and introduce a new approximation which is particularly suitable for treating multipolar fluids. In section 3 we apply the theory to a model dipolar fluid. In section 4 we present our results for the phase diagram, density-orientational profile and surface tension. Comparison is also made with the simulation results of Eggebrecht *et al*. Finally in section 5 we briefly discuss some possible extensions of the theory and make some concluding remarks.

2. Modified mean-field theory for molecular fluids

The grand potential free energy Ω of a non-uniform one-component fluid is the minimum of the functional (Evans 1979)

$$\Omega[\rho(r, \omega)] = \mathcal{F}[\rho(r, \omega)] + \int dr d\omega \rho(r, \omega) V_{\text{ext}}(r, \omega) - \mu \int dr d\omega \rho(r, \omega) \quad (1)$$

where $\rho(r, \omega)$ is the density-orientational profile in the presence of the external potential $V_{\text{ext}}(r, \omega)$ and μ is the equilibrium chemical potential. $r = (x, y, z)$ is the set of position coordinates and $\omega = (\varphi, \theta, \chi)$ the set of orientation coordinates (Euler angles) of a molecule. $\mathcal{F}[\rho(r, \omega)]$ is a unique functional of the density which is independent of the external potentials and represents the intrinsic Helmholtz free energy of the inhomogeneous fluid.

The equilibrium density $\rho_0(r, \omega)$ is determined by minimizing equation (1), and the surface tension can then be calculated from

$$\gamma A = \Omega - \Omega_{\text{bulk}} = \Omega + pV \quad (2)$$

where p is the bulk pressure and V the volume of the system.

Let us consider a fluid characterized by a pairwise intermolecular potential $\varphi(r_1, r_2, \omega_1, \omega_2)$. In this case, it can be shown (Evans 1979) that

$$\begin{aligned} \mathcal{F}[\rho(r, \omega)] = & \mathcal{F}_{\text{ref}}[\rho(r, \omega)] + \frac{1}{2} \int_0^1 d\alpha \int dr_1 dr_2 d\omega_1 d\omega_2 g(r_1, r_2, \omega_1, \omega_2; \alpha) \\ & \times \rho(r_1, \omega_1) \rho(r_2, \omega_2) \varphi_p(r_1, r_2, \omega_1, \omega_2) \end{aligned} \quad (3)$$

where we have defined a 'perturbative' interaction

$$\varphi_p(r_1, r_2, \omega_1, \omega_2) = \varphi(r_1, r_2, \omega_1, \omega_2) - \varphi_{\text{ref}}(r_1, r_2, \omega_1, \omega_2). \quad (4)$$

In equation (3), $\mathcal{F}_{\text{ref}}[\rho(r, \omega)]$ corresponds to an initial (non-equilibrium) reference system in which the particles interact via a pairwise potential $\varphi_{\text{ref}}(r_1, r_2, \omega_1, \omega_2)$ and the density is $\rho(r, \omega)$. $g(r_1, r_2, \omega_1, \omega_2; \alpha)$ is the pairwise distribution function for a fluid with density $\rho(r, \omega)$ and in which the pairwise potential is $\varphi_\alpha(r_1, r_2, \omega_1, \omega_2)$ given by

$$\varphi_\alpha(r_1, r_2, \omega_1, \omega_2) = \varphi_{\text{ref}}(r_1, r_2, \omega_1, \omega_2) + \alpha[\varphi(r_1, r_2, \omega_1, \omega_2) - \varphi_{\text{ref}}(r_1, r_2, \omega_1, \omega_2)]. \quad (5)$$

This is the familiar coupling constant algorithm, where α parametrizes a linear integration path between the reference system and the real system.

Equation (3) is an *exact* result. However, the pairwise distribution function of the non-uniform system is in general not known. Thus we shall first assume that g depends on the position coordinates only through $r_{12} = |r_1 - r_2|$, which amounts to replacing the *pairwise* distribution function of the non-uniform system by the *radial* distribution function of the uniform system. This latter function is again not known exactly. Although good approximate theories have been derived and applied to homogeneous systems, calculations for interfaces would be too complicated and of little practical interest. Therefore it is usual to resort to the simplest mean-field (MF) approximation, i.e.

$$g(r_{12}, \omega_1, \omega_2; \alpha) = 1. \quad (6)$$

However, if φ_p is an electrostatic interaction (i.e. one term or a combination of terms

from the multipolar series expansion) the MF contribution to the free energy of an isotropic bulk phase is zero, since (Gray and Gubbins 1984)

$$\frac{1}{2}\rho^2 V \int dr_{12} d\omega_1 d\omega_2 \varphi_p^{\text{mult}}(r_{12}, \omega_1, \omega_2) = 0. \quad (7)$$

Consequently the MF bulk phase diagram of a multipolar fluid in this approximation does not depend on the strength of multipole moments, which is unrealistic for all but the lowest moments.

The simplest way to correct this is to use for $g(r_{12}, \omega_1, \omega_2; \alpha)$ the low-density approximation

$$g(r_{12}, \omega_1, \omega_2; \alpha) = \exp[-\beta\varphi_\alpha(r_{12}, \omega_1, \omega_2)] \quad (8)$$

where $\beta = 1/k_B T$, k_B being Boltzmann's constant and T the temperature. This we call the *modified mean-field* (MMF) approximation.

The 'perturbative' contribution to the free energy is now

$$\begin{aligned} \frac{k_B T}{2} \int dr_1 dr_2 d\omega_1 d\omega_2 \exp[-\beta\varphi_{\text{ref}}(r_{12}, \omega_1, \omega_2)] \{1 - \exp[-\beta\varphi_p(r_{12}, \omega_1, \omega_2)]\} \\ \times \rho(r_1, \omega_1)\rho(r_2, \omega_2). \end{aligned} \quad (9)$$

Note that by expanding the exponentials in (9) in a Taylor series we are able to improve systematically on the MF theory in the low-density limit. The MF is recovered if we retain only first-order terms in β . For reasons of analytical simplicity we shall be interested in the first correction to MF, i.e. we shall retain terms up to second order in the series expansions.

In this MMF approximation it is still assumed that the Helmholtz free energy of the reference system can be treated in a local-density approximation (see e.g. Telo da Gama (1984) for details). The grand potential free energy can then be written in the form

$$\begin{aligned} \Omega[\rho(r, \omega)] = \int f_{\text{ref}}(\rho(r)) dr + \int dr d\omega \rho(r, \omega) [V_{\text{ext}}(r, \omega) - \mu] \\ + \frac{k_B T}{2} \int dr_1 dr_2 d\omega_1 d\omega_2 \exp[-\beta\varphi_{\text{ref}}(r_1, r_2, \omega_1, \omega_2)] \\ \times \{1 - \exp[-\beta\varphi_p(r_1, r_2, \omega_1, \omega_2)]\} \rho(r_1, \omega_1)\rho(r_2, \omega_2). \end{aligned} \quad (10)$$

3. Application to a model dipolar fluid

Let us consider a model dipolar fluid characterized by the potential

$$\varphi_{\text{ref}}(r) = \begin{cases} +\infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \quad \varphi_p(r, \omega_1, \omega_2) = \begin{cases} 0 & r \leq \sigma \\ -4\varepsilon(\sigma/r)^6 + \varphi_{\text{dd}}(r, \omega_1, \omega_2) & r > \sigma \end{cases} \quad (11)$$

where σ is the hard-core diameter, ω_1 and ω_2 are the orientations of the two molecules, r is the intermolecular separation and ε is a measure of the strength of the spherically

symmetric part of the perturbation†. φ_{dd} is the interaction between two dipoles of equal strength μ_D given by

$$\varphi_{dd}(r, \omega_1, \omega_2) = -(\mu_D^2/r^3)[3(\hat{\mu}_1 \cdot \hat{r})(\hat{\mu}_2 \cdot \hat{r}) - \hat{\mu}_1 \cdot \hat{\mu}_2] \quad (12)$$

where $\hat{\mu}_1$ and $\hat{\mu}_2$ are unit vectors along the dipole moments and \hat{r} is a unit vector along the intermolecular axis.

The free-energy density of the reference system is

$$f_{\text{ref}}(\rho(r, \omega)) = f_{\text{hs}}(\rho(r)) + \rho(r)k_B T \langle \log[4\pi\hat{f}(r, \omega)] \rangle \quad (13)$$

where $\hat{f}(r, \omega)$ is the orientational distribution function, $\langle A \rangle = \int A \hat{f}(r, \omega) d\omega$ and $f_{\text{hs}}(\rho(r))$ is the free-energy density of a system of hard spheres, e.g. in the Percus-Yevick compressibility approximation (see, e.g., Telo da Gama 1984). The second term on the right-hand side of equation (13) is the contribution to the free-energy density due to the loss of entropy caused by the orientational order. For an isotropic fluid, $\hat{f}(r, \omega) = 1/4\pi$ and this term vanishes.

We further note that, since we are considering spherical molecules, any surface-induced orientational ordering will be due entirely to the anisotropy of the 'perturbative' part of the interaction. Hence, by 'orientation of a molecule' is meant 'orientation of a molecular dipole'.

We now specialize to the case of a planar interface of area A in the X - Y plane. The grand potential functional (10) can now be written

$$\begin{aligned} \frac{\Omega[\rho(z), \hat{f}(z, \omega)]}{A} &= \int f_{\text{hs}}(\rho(z)) dz + k_B T \int \rho(z) \langle \log[4\pi\hat{f}(z, \theta)] \rangle dz - \mu \int \rho(z) dz \\ &+ \frac{1}{2} \int dz_1 d\omega_1 \int dz_2 d\omega_2 \varphi_{\text{eff}}(|z_1 - z_2|, \omega_1, \omega_2) \rho(z_1) \hat{f}(z_1, \omega_1) \\ &\times \rho(z_2) \hat{f}(z_2, \omega_2). \end{aligned} \quad (14)$$

φ_{eff} can be calculated analytically if we expand the exponentials to second order and write φ_{dd} as a sum of spherical harmonics (Gray and Gubbins 1984). This will allow us to perform most angular integrations analytically, which is a major simplification. Details of this calculation are presented in the appendix. Substituting for φ_{eff} in equation (14) we obtain an expression for the grand potential functional in terms of the density profile and the *orientational order parameters*, defined as

$$\eta_1(z) = \langle P_1(\cos \theta) \rangle = \int P_1(\cos \theta) \hat{f}(z, \theta) d\omega \quad (15a)$$

$$\eta_2(z) = \langle P_2(\cos \theta) \rangle = \int P_2(\cos \theta) \hat{f}(z, \theta) d\omega \quad (15b)$$

$P_1(\cos \theta)$ and $P_2(\cos \theta)$ being Legendre polynomials. These give the fraction of molecules aligned in the zz direction.

Minimization of the grand potential functional (see, e.g., Telo da Gama 1984) yields

$$\begin{aligned} \mu &= \mu_{\text{hs}}(\rho(z)) + k_B T \langle \log[4\pi\hat{f}(z, \theta)] \rangle + \int dz' \varphi_0(|z - z'|) \rho(z') - \int dz' \varphi_1(|z - z'|) \\ &\times \rho(z') \eta_1(z') \eta_1(z) - \int dz' \varphi_2(|z - z'|) \rho(z') \eta_2(z') \eta_2(z) - \int dz' V(|z - z'|) \\ &\times \rho(z') [\eta_2(z) + \eta_2(z')] \end{aligned} \quad (16a)$$

†Note that the depth of the attractive potential well is 4ϵ .

$$\hat{f}(z, \theta) = \exp[\alpha_1(z)P_1(\cos \theta) + \alpha_2(z)P_2(\cos \theta)] / \int d\omega \exp[\alpha_1(z)P_1(\cos \theta) + \alpha_2(z)P_2(\cos \theta)] \quad (16b)$$

where $\mu_{\text{hs}} = \partial f_{\text{hs}} / \partial \rho$ is the chemical potential of a uniform hard-sphere fluid,

$$\alpha_1(z) = \frac{1}{k_B T} \int \varphi_1(|z - z'|) \rho(z') \eta_1(z') dz' \quad (17a)$$

$$\alpha_2(z) = \frac{1}{k_B T} \left(\int V(|z - z'|) \rho(z') dz' + \int \varphi_2(|z - z'|) \rho(z') \eta_2(z') dz' \right) \quad (17b)$$

and $\varphi_0, \varphi_1, \varphi_2$ and V are also given in the appendix. The solution of the Euler–Lagrange equation is now reduced to the solution of a one-dimensional integral equation, equation (16a), for $\rho(z)$ and the consistency relations (15) for the orientational order parameters. These equations are solved numerically by an iterative procedure. For details of the numerical solution see, e.g., Telo da Gama (1984). By straightforward manipulation of equations (15) and use of equation (16b), the orientational order parameters can be expressed in terms of known functions (see, e.g., Abramowitz and Stegun 1964).

4. Results

The phase diagram is calculated by solving the two simultaneous equations that express the constancy of the pressure and the chemical potential in a two-phase system and we use for p and μ the constant-density limit obtained from our density functional theory. Hence the dipolar contribution to the free energy of the bulk phases arises only as a *second-order* effect in φ_{dd} .

In figure 1 we present bulk phase diagrams calculated for different values of the reduced dipole moment $\mu_D^* = \mu_D / (\epsilon \sigma^3)^{1/2}$. For small dipolar strengths ($\mu_D^* \leq 0.5$) the phase diagram is hardly affected, whereas for large μ_D^* (> 1.5) the effect on the critical temperature is substantial (see table 1). In this approximation, the critical density seems to be independent of the dipole strength. The rise in critical temperature approximately obeys the law

$$k_B \Delta T_c / \epsilon \sim (\mu_D^*)^4 \quad (18)$$

where $\Delta T_c = T_c(\mu_D^*) - T_c(0)$. It follows from figure 1 that the steepness of the density profile at a given temperature increases with increasing dipole moment, as the difference between coexisting liquid and vapour densities also increases.

Engbrecht *et al* (1987a) argued that, for such models as point multipoles, the singlet density distribution is invariant to a rotation through π (i.e. the system is invariant under multipole reversal) and therefore all odd-numbered order parameters should vanish. Indeed we found η_1 to be zero to first and second orders in this approximation and believe this to hold for arbitrarily higher orders. Since η_1 is the only meaningful order parameter in the MF limit (first-order terms only), we expect that any orientational ordering will be due to second-order terms and will reveal itself through non-zero values of η_2 .

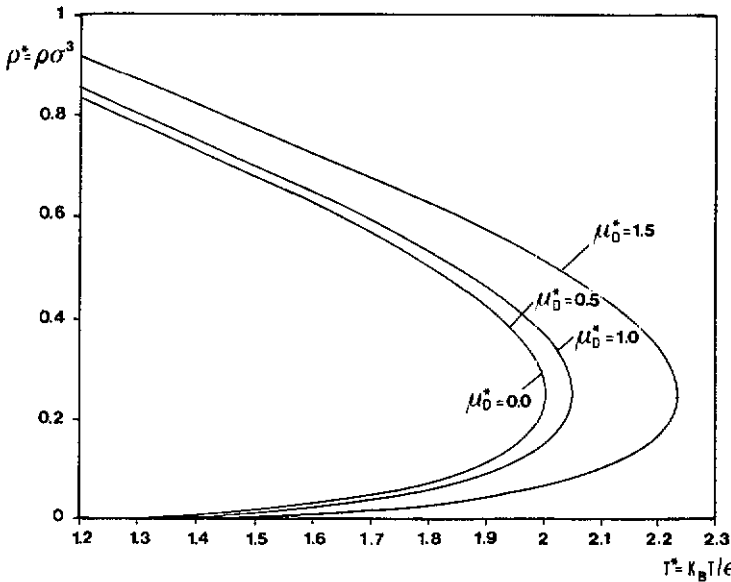


Figure 1. Phase diagrams for four different strengths of the reduced dipole moment. Note the increase in the critical temperature. The curves for $\mu_D^* = 0.0$ and $\mu_D^* = 0.5$ are nearly coincident.

Table 1. Critical temperatures for several reduced dipole strengths. In weakly polar liquids, T_c^* is almost independent of μ_D^* .

μ_D^*	0.00	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
T_c^*	2.00	2.00	2.00	2.02	2.05	2.12	2.23	2.41	2.64

In figure 2 we show η_2 for $T^* = 1.0$ and four reduced dipole moments. The molecules prefer to lie parallel to the interface ($\eta_2(z) < 0$) on the liquid side, while on the vapour side perpendicular orientations ($\eta_2(z) > 0$) are favoured. However, for realistic dipole strengths ($\mu_D^* \sim 1$) the degree of orientational order is small, i.e. of the order of a few per cent. As expected, the orientational structure is washed out as the temperature increases, for the entropy term in the free energy becomes dominant.

In figure 3 we compare our results for $\hat{\rho}_2(z) = (5/4\pi)\rho(z)\eta_2(z)$ with those of the simulation by Eggebrecht *et al* (1987b). Although the present theory slightly overestimates the degree of interfacial order, the overall agreement is fair, given the fact that there is considerable scatter in the simulation data. Figure 4 shows the density-orientational profile $\rho(z, \theta)$ at three different z -values (measured relative to the Gibbs dividing surface). $\rho(z, \theta)$ has a maximum for $\theta = \pi/2$ on the liquid side ($z < 0$) and two symmetric maxima for $\theta = 0$ and $\theta = \pi$ on the vapour side ($z > 0$) (compare with figure 11 of Eggebrecht *et al* (1978a)).

This orientational structure can be understood in terms of a lowering of the free energy. The minimum-energy configuration of a pair of dipoles is top to bottom, and it

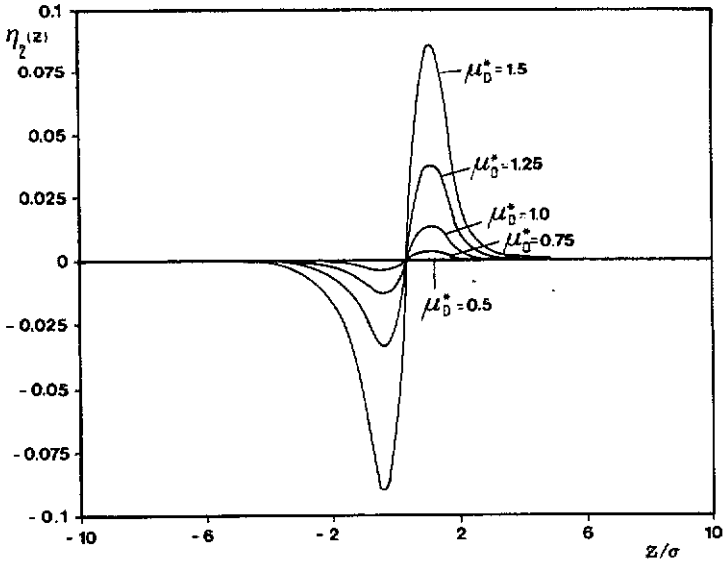


Figure 2. Orientational order parameter η_2 at $T^* = 1.0$ for five different dipole strengths. The curve for $\mu_D^* = 0.5$ is coincident with the z axis.

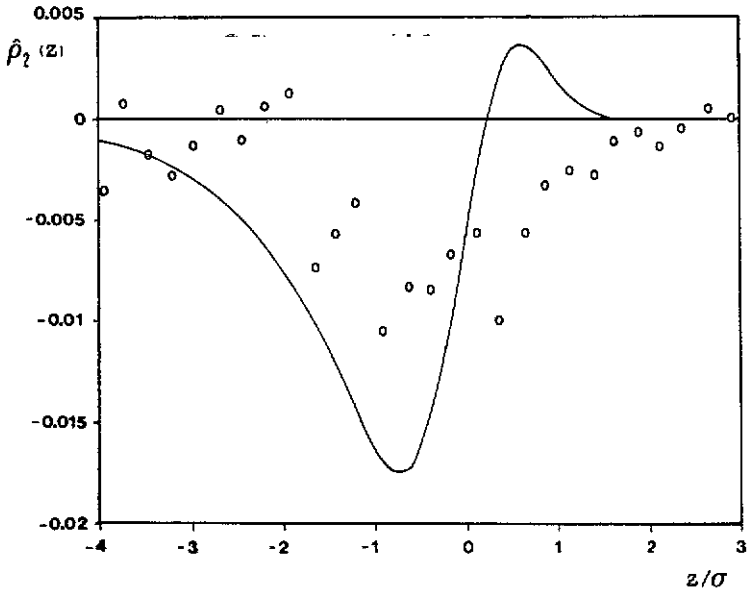


Figure 3. β_2 at $T^* = 2.00$ for $\mu_D^* = 2.31$ (—). Computer simulation data (O) (Eggebrecht *et al* 1987(b) for the same reduced temperature ($T_r = T/T_c$) and reduced dipole moment ($\beta_D = \mu_D/(k_B T_c \sigma^3)^{1/2}$) are also shown. The theory overestimates the degree of orientational order.

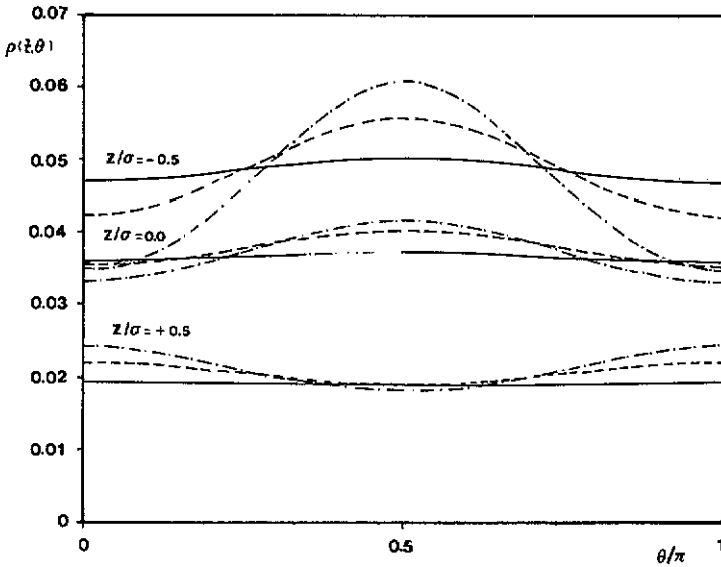


Figure 4. Density-orientational profile at three different z -values (measured relative to the Gibbs dividing surface): —, $\mu_D^* = 1.22$ at $T^* = 1.35$; ---, $\mu_D^* = 1.78$ at $T^* = 1.55$; -·-·-, $\mu_D^* = 2.31$ at $T^* = 2.00$. Temperatures and dipole moments were chosen such that reduced temperatures ($T_r = T/T_c$) and reduced dipole moments ($\hat{\mu}_D = \mu_D/(k_B T_c \sigma^3)^{1/2}$) are the same as in figure 11 of Eggebrecht *et al* (1987a).

is reasonable to expect that dipoles on the liquid side of the interface will adopt it in order to minimize the number of nearest parallel and antiparallel neighbours. On the vapour side, energy constraints are not so severe and dipoles can orient themselves either antiparallel or perpendicular to those in the liquid. The former configuration has a lower energy but also a very low entropy, and this is why in our view the latter is adopted.

We also considered the effect of including a quadrupole–quadrupole interaction term to first order (setting the dipole moment to zero). No orientational ordering was observed in this case and no symmetry arguments explain such a result. There are nonetheless indications that quadrupole-induced interfacial ordering may arise if quadrupole–quadrupole terms to second order are included (Sullivan 1989). Thus we may conclude that the simplest MF approximation does not predict any preferential alignment due to quadrupolar forces.

In figure 5 we plot our results for the surface tension for different strengths of the reduced dipole moment. The addition of a dipole moment causes the surface tension to increase in a non-linear fashion. However, if we plot γ^* against reduced temperature $T_r (= T/T_c$ where T_c is the critical temperature) instead, the surface tension curves are nearly coincident, which suggests that the effect of the dipole on the surface tension is due mainly to its effect on the phase diagram. This is consistent with the finding that the degree of orientational order is small.

In table 2 we compare the results of our calculations with those of the simulation. The simulation used a different intermolecular potential; so we scaled the dipole moments and the surface tension by T_c . The theory slightly overestimates both the

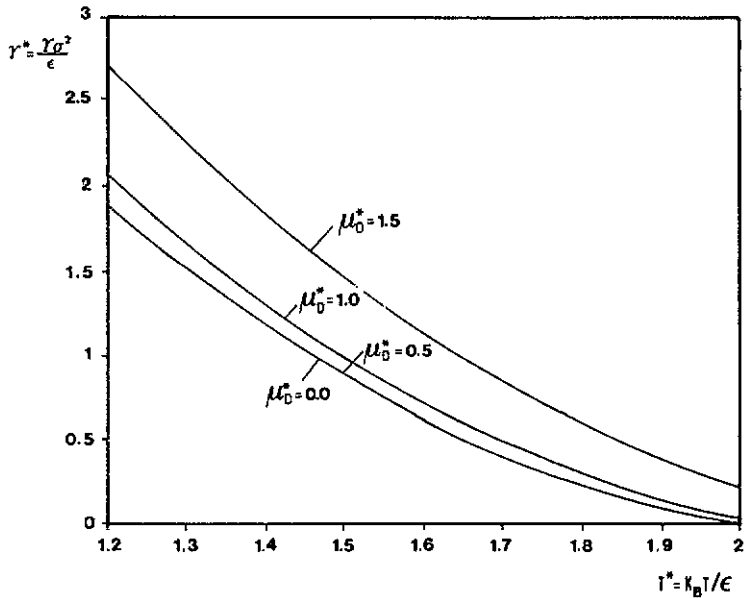


Figure 5. Temperature dependence of the reduced surface tension ($\gamma^* = \gamma\sigma^2/\epsilon$) for four different dipole strengths. The curves for $\mu_D^* = 0.0$ and $\mu_D^* = 0.5$ are nearly coincident.

Table 2. Reduced liquid and vapour densities ($\rho^* = \rho\sigma^3$) and reduced surface tension ($\hat{\gamma} = \gamma\sigma^2/k_B T_c$) for two different strengths of the reduced dipole moment ($\mu_D = \mu_D/(k_B T_c \sigma^3)^{1/2}$), obtained by simulation (MD) and with the present theory (MMF).

μ_D	T_r	ρ_l^{*md}	ρ_l^{*mmf}	ρ_g^{*md}	ρ_g^{*mmf}	$\hat{\gamma}_{md}$	$\hat{\gamma}_{mmf}$
0.84	0.72	0.702	0.714	0.0023	0.0106	0.437	0.512
1.33	0.67	0.743	0.811	0.0013	0.0025	0.487	0.591

coexisting bulk densities (by a few percent) and the surface tension (by approximately 20%).

5. Conclusions

The theory described in this paper is the simplest self-consistent approximation for the interfacial properties of fluids characterized by multipolar interactions which yields a non-zero contribution to the free energy of the bulk phases. This results in a bulk phase diagram which depends explicitly on the strength of the multipole moments.

We have applied the theory to a simple model of a dipolar fluid and found that it predicts that orientational ordering can be induced by purely multipolar forces. Results are in fair agreement with those of a computer simulation of a Stockmayer fluid. Discrepancies can be traced to the fact that we have approximated the radial distribution function by its low-density limit and truncated the series expansions at second order.

Moreover, the simulation did not use quite the same intermolecular potential as we did and there is some uncertainty in the critical temperatures used to reduce the simulation data (Eggebrecht *et al* 1987a).

We also found that the effect of the dipole on the surface tension is due mainly to the changes in the phase diagram caused by the dipolar contribution to the bulk free energy.

The present theory can be straightforwardly generalized to binary or ternary mixtures. We successfully developed one such extension (to a polar–non-polar binary mixture) (Teixeira 1990) but the agreement with existing experimental data for the surface tension (for a CH_2Cl_2 – CS_2 mixture) was no better than that achieved using a simple MF theory and a choice of spherically symmetric interaction potentials (Aracil *et al* 1989). Thus we believe the strength of our theory to lie in the fact that it can successfully predict dipole (and possibly quadrupole) induced interfacial orientational ordering.

Acknowledgment

P I Teixeira gratefully acknowledges the financial support of the Portuguese Instituto Nacional de Investigação Científica in the form of an M.Sc. scholarship.

Appendix: evaluation of the effective potential φ_{eff}

Expanding the exponentials in (10) to second order in a Taylor series, we obtain

$$\begin{aligned} \beta\varphi_{\text{eff}}(z, \omega_1, \omega_2) &= \int_0^{2\pi} d\varphi \int_0^{+\infty} R dR \exp[-\beta\varphi_{\text{ref}}(R, z, \varphi)] \\ &\quad \times \{1 - \exp[-\beta\varphi_p(R, z, \varphi, \omega_1, \omega_2)]\} \\ &= \int_0^{2\pi} d\varphi \int_0^{+\infty} R dR \left(\beta\varphi_p(R, z, \varphi, \omega_1, \omega_2) \right. \\ &\quad \left. - \frac{1}{2!} (\beta\varphi_p(R, z, \varphi, \omega_1, \omega_2))^2 + \dots \right). \end{aligned} \quad (\text{A1})$$

We shall retain terms to second order in the dipole–dipole interaction and to first order in the quadrupole–quadrupole interaction. This involves evaluating integrals of the type

$$\bar{\chi}(z, \omega_1, \omega_2) = \int_0^{2\pi} d\varphi \int_0^{+\infty} R dR \chi(R, z, \varphi, \omega_1, \omega_2) \quad (\text{A2})$$

where $\chi = \varphi_{\text{LJat}}, \varphi_{\text{LJat}}^2, \varphi_{\text{dd}}, \varphi_{\text{dd}}^2, \varphi_{\text{LJat}}\varphi_{\text{dd}}, \varphi_{\text{qq}}$. Evaluation of integrals containing just the spherically symmetric terms is straightforward; so we restrict our attention to multipolar contributions. Conventions adopted for spherical harmonics and Clebsch–Gordan

coefficients are those of Gray and Gubbins (1984), which serves as a general reference for this appendix.

A1. Evaluation of $\overline{\varphi_{dd}}$

We start by writing φ_{dd} as a sum of spherical harmonics (Gray and Gubbins 1984):

$$\varphi_{dd}(r, \omega_1, \omega_2) = \begin{cases} -\frac{\mu_D^2}{r^3} 4\pi \left(\frac{8\pi}{15}\right)^{1/2} \sum_{m_1 m_2 m} C(112; m_1 m_2 m) \\ \quad \times Y_{1m_1}(\omega_1) Y_{1m_2}(\omega_2) Y_{2m}^*(\omega) & r > \sigma \\ 0 & r \leq \sigma. \end{cases} \quad (A3)$$

For $z > \sigma$ we have

$$\overline{\varphi_{dd}}(z, \omega_1, \omega_2) = -\mu^2 4\pi \left(\frac{8\pi}{15}\right)^{1/2} \sum_{m_1 m_2 m} C(112; m_1 m_2 m) Y_{1m_1}(\omega_1) Y_{1m_2}(\omega_2) \\ \times \int_0^{+\infty} \frac{R dR}{(R^2 + z^2)^{3/2}} \int_0^{2\pi} Y_{2m}^*(\omega) d\varphi. \quad (A4)$$

The angular integral in (A4) is proportional to δ_{m0} and the integral over R vanishes. It follows that $\overline{\varphi_{dd}}$ is zero for $z > \sigma$.

If we now have $z \leq \sigma$, two cases must be considered: $r \leq \sigma$ if $R^2 \leq \sigma^2 - z^2$ and $r > \sigma$ if $R^2 > \sigma^2 - z^2$. From the potential separation it results that $\overline{\varphi_{dd}}$ can be calculated from (A4) if the lower limit of the integral over R is changed to $\sqrt{\sigma^2 - z^2}$. Hence

$$\overline{\varphi_{dd}}(z, \omega_1, \omega_2) = -(2\pi\mu^2/\sigma^3)(z^2 - \sigma^2)[\cos \theta_1 \cos \theta_2 - \frac{1}{2}\sin \theta_1 \sin \theta_2 \cos(\varphi_1 - \varphi_2)] \quad (A5)$$

for $z \leq \sigma$.

Evaluation of $\overline{\varphi_{L3ar}\varphi_{dd}}$ is straightforward, since this term has the same angular dependence as $\overline{\varphi_{dd}}$. Its z -dependence is given by $H(z)$ in equation (A14).

A2. Evaluation of $\overline{\varphi_{dd}^2}$

For $z > \sigma$ we have

$$\overline{\varphi_{dd}^2}(z, \omega_1, \omega_2) = \mu^4 \frac{128\pi^3}{15} \sum_{\substack{m_1 m_2 m \\ m'_1 m'_2 m'}} C(112; m_1 m_2 m) Y_{1m_1}(\omega_1) Y_{1m_2}(\omega_2) \\ \times C(112; m'_1 m'_2 m') Y_{1m'_1}(\omega_1) Y_{1m'_2}(\omega_2) \int_0^{+\infty} \frac{R dr}{(R^2 + z^2)^3} \\ \times \int_0^{2\pi} Y_{2m}^*(\omega) Y_{2m'}^*(\omega) d\varphi. \quad (A6)$$

The angular integral in (A6) is proportional to $\delta_{m+m'0}$ and it again follows, noting that $m' = m'_1 + m'_2 = -m \Rightarrow m'_2 = -(m'_1 + m)$, that

$$\begin{aligned} \overline{\varphi_{dd}^2}(z, \omega_1, \omega_2) &= \mu^4 \frac{128\pi^3}{15} \sum_{m_1 m_2 m'_1} C(112; m_1 m_2 m) C(112; m'_1 - (m'_1 + m) - m) \\ &\times Y_{1m_1}(\omega_1) Y_{1m_2}(\omega_2) Y_{1m'_1}(\omega_1) Y_{1-(m'_1+m)}(\omega_2) \\ &\times \int_0^{+\infty} \frac{R dR}{(R^2 + z^2)^3} \int_0^{2\pi} Y_{2m}^*(\omega) Y_{2-m}^*(\omega) d\varphi \end{aligned} \quad (A7)$$

where m_1, m_2 and m'_1 run from -1 to $+1$ and $m = m_1 + m_2 = -m'$. Hence

$$\overline{\varphi_{dd}^2}(z, \omega_1, \omega_2) = (3\pi\mu^4/16)(1 + \cos^2 \theta_1)(1 + \cos^2 \theta_2)(1/z^4) \quad (A8)$$

for $z > \sigma$.

Now let $z \leq \sigma$. Likewise $\overline{\varphi_{dd}^2}$ is again given by (A7) if the lower limit of the integral over R is replaced by $\sqrt{\sigma^2 - z^2}$. Hence

$$\begin{aligned} \overline{\varphi_{dd}^2}(z, \omega_1, \omega_2) &= (\pi\mu^4/16\sigma^4)(10 - 10 \cos^2 \theta_1 - 10 \cos^2 \theta_2 + 18 \cos^2 \theta_1 \cos^2 \theta_2) \\ &+ (\pi\mu^4/\sigma^4)(-1 + \frac{5}{2} \cos^2 \theta_1 + \frac{5}{2} \cos^2 \theta_2 - 6 \cos^2 \theta_1 \cos^2 \theta_2)(z^2/\sigma^2) \\ &+ (9\pi/4)(\mu^4/\sigma^4)[\frac{1}{2}(3 \cos^2 \theta_1 - 1)\frac{1}{2}(3 \cos^2 \theta_2 - 1)](z^4/\sigma^4) \end{aligned} \quad (A9)$$

for $z \leq \sigma$.

A3. Evaluation of φ_{qq}

Similarly we write φ_{qq} as a sum of spherical harmonics (Gray and Gubbins 1984):

$$\varphi_{qq}(r, \omega_1, \omega_2) = \begin{cases} \frac{Q^2 8\pi}{r^5} \frac{(70\pi)^{1/2}}{15} \sum_{m_1 m_2 m} C(224; m_1 m_2 m) \\ \quad \times Y_{2m_1}(\omega_1) Y_{2m_2}(\omega_2) Y_{4m}^*(\omega) & r > \sigma \\ 0 & r \leq \sigma. \end{cases} \quad (A10)$$

First, for $z > \sigma$,

$$\begin{aligned} \overline{\varphi_{qq}}(z, \omega_1, \omega_2) &= \frac{8\pi}{15} (70\pi)^{1/2} Q^2 \sum_{m_1 m_2 m} C(224; m_1 m_2 m) Y_{2m_1}(\omega_1) Y_{2m_2}(\omega_2) \\ &\times \int_0^{+\infty} \frac{R dR}{(R^2 + z^2)^{5/2}} \int_0^{2\pi} Y_{4m}^*(\omega) d\varphi. \end{aligned} \quad (A11)$$

The angular integral in (A11) is again proportional to δ_{m0} and the integral over R vanishes. Therefore $\overline{\varphi_{qq}}$ is zero for $z > \sigma$.

Now for $z \leq \sigma$ we substitute $\sqrt{\sigma^2 - z^2}$ for the lower limit of the integral over R in (A11). Hence we finally obtain

$$\overline{\varphi_{qq}}(z, \omega_1, \omega_2) = (3\pi Q^2/2\sigma^3) \times [P_2(\cos\theta_1)P_2(\cos\theta_2) + \frac{1}{2}\sin^2\theta_1\sin^2\theta_2\cos 2(\varphi_1 - \varphi_2) - \frac{1}{2}\sin(2\theta_1)\sin(2\theta_2)\cos(\varphi_1 - \varphi_2)] \times [5(z/\sigma)^4 - 6(z/\sigma)^2 + 1] \quad (\text{A12})$$

for $z \leq \sigma$.

As the system is invariant in the X - Y plane, the orientational distribution function $\hat{f}(z, \omega)$ depends on ω only through θ , and terms in $\cos(\varphi_1 - \varphi_2)$ average to zero and can be omitted. The final expression for the effective potential is then

$$\begin{aligned} \varphi_{\text{eff}}(z, \theta_1, \theta_2) = & A(z) + B(z) \cos\theta_1 \cos\theta_2 + \varphi_{qq}(z) [\frac{1}{2}(3\cos^2\theta_1 - 1)\frac{1}{2}(3\cos^2\theta_2 - 1)] \\ & - (\beta/2)\{C(z) + D(z)(1 + \cos^2\theta_1)(1 + \cos^2\theta_2) + E(z)(10 - 10\cos^2\theta_1 \\ & - 10\cos^2\theta_2 + 18\cos^2\theta_1\cos^2\theta_2) + F(z)(-1 + \frac{5}{2}\cos^2\theta_1 + \frac{5}{2}\cos^2\theta_2 \\ & - 6\cos^2\theta_1\cos^2\theta_2) + G(z)[\frac{1}{2}(3\cos^2\theta_1 - 1)\frac{1}{2}(3\cos^2\theta_2 - 1)] \\ & + H(z) \cos\theta_1 \cos\theta_2\} \end{aligned} \quad (\text{A13})$$

where

$$\begin{aligned} A(z) &= \begin{cases} -2\pi\epsilon\sigma^6/z^4 & |z| > \sigma \\ -2\pi\epsilon\sigma^2 & |z| \leq \sigma \end{cases} & B(z) &= \begin{cases} 0 & |z| > \sigma \\ -(2\pi\mu^2/\sigma^3)(z^2 - \sigma^2) & |z| \leq \sigma \end{cases} \\ C(z) &= \begin{cases} 16\pi\epsilon^2/5(\sigma^{12}/z^{10}) & |z| > \sigma \\ 16\pi\epsilon^2\sigma^2/5 & |z| \leq \sigma \end{cases} & D(z) &= \begin{cases} (3\pi\mu^4/16)(1/z^4) & |z| > \sigma \\ 0 & |z| \leq \sigma \end{cases} \\ E(z) &= \begin{cases} 0 & |z| > \sigma \\ \pi\mu^4/16\sigma^4 & |z| \leq \sigma \end{cases} & F(z) &= \begin{cases} 0 & |z| > \sigma \\ (\pi\mu^4/\sigma^4)(z^2/\sigma^2) & |z| \leq \sigma \end{cases} \\ G(z) &= \begin{cases} 0 & |z| > \sigma \\ (9\pi/4)(\mu^4/\sigma^4)(z^4/\sigma^4) & |z| \leq \sigma \end{cases} & H(z) &= \begin{cases} (64\pi\mu^2\epsilon/21)(\sigma^6/z^7) & |z| > \sigma \\ (16\pi\mu^2\epsilon/\sigma^3)(z^2/3 - \sigma^2/7) & |z| \leq \sigma \end{cases} \\ \varphi_{qq}(z) &= \begin{cases} 0 & |z| > \sigma \\ (3\pi Q^2/2\sigma^3)(5(z/\sigma)^4 - 6(z/\sigma)^2 + 1) & |z| \leq \sigma \end{cases} \end{aligned} \quad (\text{A14})$$

where σ , ϵ are LJ parameters, μ is the dipole moment, Q is the quadrupole moment. θ_1 (θ_2) is the angle between the dipole moment of a molecule at z_1 (z_2) and the positive z axis and $z = z_1 - z_2$.

The effective potential terms used in the evaluation of the order parameters and grand potential (equations (14), (16) and (17)) are linear combinations of the above:

$$\varphi_0(z) = A(z) - \beta C(z)/2 - (8\beta/9)D(z) - (8\beta/3)E(z) \quad (\text{A15a})$$

$$\varphi_1(z) = -B(z) + \beta H(z)/2 \quad (\text{A15b})$$

$$\varphi_2(z) = (2\beta/9)D(z) + 4\beta E(z) - (4\beta/3)F(z) + \beta G(z)/2 - \varphi_{qq}(z) \quad (\text{A15c})$$

$$V(z) = (4\beta/9)D(z) - (4\beta/3)E(z) + \beta F(z)/6. \quad (\text{A15d})$$

References

- Abramowitz M and Stegun I 1964 *Handbook of Mathematical Functions* (New York: Dover)
 Aracil J, Luengo G, Almeida B S, Telo da Gama M M, Rubio R G and Diaz Peña M 1989 *J. Phys. Chem.* **93** 3210

- Chacón E, Tarazona P and Navascués G 1983 *J. Chem. Phys.* **79** 4426
- Eggebrecht J, Gubbins K E and Thompson S M 1987a *J. Chem. Phys.* **86** 2286
- Eggebrecht J, Thompson S M and Gubbins K E 1987b *J. Chem. Phys.* **86** 2299
- Evans R 1979 *Adv. Phys.* **28** 143
- Goh M C, Hicks J M, Kemnitz K, Pinto G R, Bhattacharyya K, Eiseenthal K B and Heinz T F 1988 *J. Phys. Chem.* **92** 5074
- Gray C G and Gubbins K E 1975 *Mol. Phys.* **30** 179
- 1984 *The Theory of Molecular Fluids* (Oxford: Clarendon)
- Gubbins K E 1980 *Chem. Phys. Lett.* **76** 329
- Gubbins K E, Haile J M and McDonald I R 1977 *J. Chem. Phys.* **66** 364
- Haile J M, Gray C G and Gubbins K E 1976a *J. Chem. Phys.* **64** 2569
- Haile J M, Gubbins K E and Gray C G 1976b *J. Chem. Phys.* **64** 1852
- Matsumoto M and Kataoka Y 1988 *J. Chem. Phys.* **88** 3233
- 1989 *J. Chem. Phys.* **90** 2398
- Shanks I A 1982 *Contemp. Phys.* **23** 65
- Sullivan D 1989 private communication
- Tarazona P and Navascués G 1982 *Mol. Phys.* **47** 145
- Teixeira P I 1990 *MSc Thesis* University of Lisbon
- Telo da Gama M M 1984 *Mol. Phys.* **52** 585
- Thompson S M and Gubbins K E 1981 *J. Chem. Phys.* **74** 6467
- Thompson S M, Gubbins K E and Haile J M 1981 *J. Chem. Phys.* **75** 1325
- Townsend R M, Gryko J and Rice S A 1985 *J. Chem. Phys.* **82** 4391
- Wilson M A, Pohorille A and Pratt L R 1987 *J. Phys. Chem.* **91** 4873