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Orientation and association at the liquid–vapour interface of dipolar fluids

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Abstract

Recent simulation and experimental results on molecular alignment at the liquid–vapour interface of dipolar fluids are in disagreement with the predictions of all existing theories. We discuss these problems in the context of our earlier work on association in dipolar fluids and propose new theoretical approaches to tackle them.

1. Introduction

There seems to exist a certain degree of cultural prejudice against surfaces, with things superficial usually being deemed of lesser pith and moment [1]. This is most unjustified as regards the liquid–vapour (LV) interface of a fluid, which is the seat of a host of fascinating phenomena [2]. These are a consequence of the fact that a molecule residing in the interfacial region finds itself in a very different environment to inside the bulk, on account of its reduced number of neighbours. The stronger attraction towards the denser liquid phase results in the existence of a surface tension, or excess free energy associated with the interface.

Of the plethora of fluids of Nature and industry, there are many where multipolar interactions play an important role. Recall that multipole moments are the ingredients of classical electromagnetism's description of a discrete distribution of charges. If such a distribution is spatially asymmetric, then the lowest non-zero moment of an overall neutral body is the dipole moment; if it has a degree of axial symmetry, this is reflected in the quadrupole moment. In what follows we restrict ourselves to permanent multipoles, i.e., those that are caused by the particular equilibrium geometry of a molecule. The interactions between (even point) multipoles are highly anisotropic, as they couple the molecular axes with the intermultipole vector. Two parallel dipoles will repel each other if placed side by side, but attract each other if placed head to tail, whereas the minimum-energy configuration of two

quadrupoles is T-shaped. In addition, dipolar forces are long ranged, which produces subtle effects relating to system size and the nature of the boundary conditions [3].

At the LV interface, the anisotropy of the multipolar interactions, combined with the strong density gradient, gives rise to preferential alignment of the molecular axes [4, 5]. The width of the interface is of the order of the bulk correlation length ξ , which is microscopic far from the LV critical point [6]. Any orientational order will therefore be confined within a few molecular layers. (We shall not discuss here the surfaces and interfaces of *bulk* ordered fluids, such as liquid crystals (LCs); for a review see [7].) One might then reasonably ask, what is the relevance of molecular alignment that extends over such a short distance, and moreover is in many cases weak (as will be seen below)? Consider the wall of a living cell: this is a lipid bilayer, whose interior is highly hydrophobic. In order that hydrophilic species, such as ions, may be exchanged between the cell and the outside world, channels must exist which are protein molecules oriented such that they span the membrane. In a different context, catalysts work in part by arranging individual molecules in such a way that their relevant groups are exposed to attack by other reactants.

A number of theories have been developed for the density-orientation profile of fluids with anisotropic interactions, including dipoles and quadrupoles. Gubbins and co-workers' u -expansion [8], as well as Tarazona and co-workers' perturbative expansions of the Helmholtz free energy of a molecular fluid interface [9, 10], both failed to predict any interfacial ordering arising from purely multipolar intermolecular potentials: the multipolar contribution enters through its unweighted angular average, which vanishes in an unpolarized medium. Later, Gubbins and co-workers used their f -expansion [11] and an Yvon–Born–Green-type equation [12] to study the LV interface of a Stockmayer fluid [13]. They showed that dipoles favour parallel orientations on the liquid side of the interface, and perpendicular on the vapour side. This investigation was of paramount importance since it established that interfacial ordering *can* be induced by multipolar forces alone.

The same qualitative picture as regards interfacial order has been corroborated by all subsequent theoretical treatments. The present authors constructed a modified mean-field (MMF) theory by approximating the radial distribution function (RDF) in the Helmholtz free energy functional [14] by its low-density limit, rather than the long-distance limit as is done in ordinary mean-field (MF) theory [15]. This established that the density-functional (DF) formalism is able to predict the same surface-induced alignment as the Gubbins *et al* integral equation. Teixeira and Telo da Gama's MMF approach was refined by Frodl and Dietrich [16, 17], who removed the additional approximation (of only quantitative consequences) of retaining only terms to second order in the expansion of the RDF. They then proceeded to a very detailed study of the bulk and interfacial properties of the Stockmayer fluid which yielded scaling relations for the density and order parameter profiles, $\rho(z)$ and $\alpha_2(z)$ respectively [17]:

$$\rho(z, \tau \rightarrow 0) = \rho_c + A_\rho \tau^\beta F_\rho(z/\xi), \quad (1)$$

$$\alpha_2(z, \tau \rightarrow 0) = \tau^{\beta+2\nu} \overline{F}_{\alpha_2}(z/\xi), \quad (2)$$

where $\tau = (T_c - T)/T_c$ is the reduced temperature, ξ is the bulk correlation length, $\beta = \frac{1}{2}$ and $\nu = \frac{1}{2}$ are, respectively, the (MF) bulk order parameter and correlation length critical exponents, A_ρ is a non-universal amplitude, $F_\rho(y)$ is a universal scaling function, $\overline{F}_{\alpha_2}(y)$ is a limiting function conjectured to be universal apart from a non-universal amplitude, and the subscript c refers to quantities at the LV critical point. The order parameter $\alpha_2(z)$ is defined as

$$\alpha_2(z) = \frac{5}{4\pi} \langle P_2(\cos \theta) \rangle, \quad (3)$$

where $P_2(x) = \frac{1}{2}(3 \cos^2 \theta - 1)$ is the second Legendre polynomial and θ is the angle between the dipole moment and the z -axis, assumed perpendicular to the (flat) LV interface. Sullivan and co-workers derived more general versions of Teixeira and Telo da Gama's MMF theory by following the more conventional approach for generating corrections to MF theory [18] and fixing its unrealistic low-temperature behaviour [19]. Furthermore, they included in their model potential also dipole–quadrupole and quadrupole–quadrupole terms. Iatsevitch and Forstmann [20] solved the Lovett–Mou–Buff–Wertheim [21, 22] equation for the density-orientation profile of a Stockmayer fluid, using an interpolation of the direct correlation function between those for the bulk phases calculated using the RHNC closure of the Ornstein–Zernike equation [23]. Still, the basic qualitative conclusion remains unchanged: dipoles tend to lie parallel to LV interface on its liquid side, and perpendicular on its vapour side.

A qualitative explanation can be given of the orienting tendency of dipoles at the LV interface, in terms of the interaction between a real dipole and its image dipole. This was first provided by Frodl and Dietrich [17], which we now reproduce. Consider two homogeneous half-spaces, $z > 0$ and $z < 0$, each filled with dielectric media of permittivities ϵ_+ and ϵ_- , respectively. Then the energy E required to place a dipole of strength m at a distance $z > 0$ from the (assumed sharp) interface at $z = 0$ making an angle θ with the normal is [24]

$$E = -\frac{m^2}{16} \frac{\epsilon_- - \epsilon_+}{\epsilon_+(\epsilon_- + \epsilon_+)} \frac{1 + \cos^2 \theta}{z^3}. \quad (4)$$

At a fixed distance z , E attains its minimum value for $\theta = 0$ or π if $\epsilon_+ < \epsilon_-$ and for $\theta = \pi/2$ if $\epsilon_+ > \epsilon_-$. The preferred orientation of the dipole is therefore perpendicular to the interface if it is located in the medium of smaller permittivity (i.e., lower density) or parallel to the interface if it is instead in the medium with larger permittivity (i.e., higher density).

How well are these predictions verified? Gubbins and co-workers [25] performed a Molecular Dynamics (MD) simulation of the Stockmayer fluid and indeed found parallel alignment on the liquid side of the interface, in qualitative accord with theory, but simulation data were inconclusive for the vapour side. The same fate befell another MD simulation of the same system, by Nordholm and co-workers [26], as well as simulations of TIPT4 water (as modelled by Sullivan *et al* [18, 19]), by Pohorille and co-workers [27–29], and by Matsumoto and Kataoka [30, 31]: whereas dipoles in the liquid could be reliably said to prefer parallel orientations, no such certainty was borne out as regards the vapour. Very recently, however, Winkelmann and co-workers [32] carried out very careful MD simulations of a thin layer of: (i) Stockmayer molecules; and (ii) dipolar Lennard-Jones (LJ) dumbbells of small elongation. In both cases, molecular orientation was parallel to the interface, on the liquid as well as on the vapour side, which is at variance with all theories. Thorough checks were conducted to ensure that this was not a finite-size effect. It thus appears that the discrepancy is real, and needs to be explained.

On the experimental front, studies are much less abundant. Early second-harmonic-generation studies of the LV interfaces of water [33] and of aqueous solutions of phenol and *p*-cresol [34–36] showed preferential alignment which could be due to dipolar interactions, but this technique is only sensitive to a net polarization at the interface; moreover, interpretation of its results carries some ambiguity. More recently, Law and co-workers [37] reported evidence for spatial variation of orientational order at the critical liquid–liquid interface of the ionic mixture triethyl-*n*-hexylammonium + triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) in the solvent diphenyl ether, using Brewster angle ellipsometry. They also checked [38] that the scaling function $\bar{F}_{\alpha_2}(z/\xi)$ in equation (2), now for the concentration profile $v \equiv v(z)$ of the polar component through the critical liquid–liquid interface of the mixtures carbon

disulphide + cyclohexane and 2-nitroanisole + cyclohexane, has the form

$$\alpha_2(z) \sim m^*4 \frac{d^2v}{dz^2}, \quad (5)$$

as follows from a suggestion by Sluckin [4, 39] and from Frodl and Dietrich's work [17]. Here, $m^* = m/\sqrt{\epsilon\sigma^3}$ is the dipole strength reduced by the LJ well depth ϵ and the molecular hard-sphere diameter σ . This is consistent with the MF result for a polymer–solvent interface [40] that

$$S(z) \sim \frac{d^2v}{dz^2} - v \frac{dv}{dz} - \frac{2}{3} \left(\frac{dv}{dz} \right)^2 \quad (6)$$

where $S(z) = \langle \cos^2 \theta_n - \frac{1}{3} \rangle$ is the order parameter for the n th monomer in a chain (taking into account that the second derivative term dominates $S(z)$). For the critical concentration profile $v(z) - v_c \propto \tanh(z/2\xi)$, both equations (5) and (6) give $\alpha_2(z)$ of the shape predicted by the theories of the LV interface reviewed above [38, figure 1].

Law and co-workers subsequently turned their attention to the (non-critical) LV interface of the (critical) polar–non-polar mixtures 2-nitroanisole + cyclohexane and 4-nitroanisole + cyclohexane [41] and were able to confirm the theoretical prediction of parallel alignment of the dipoles on the liquid side of the interface; their experiments were not sensitive to molecular behaviour on the vapour side. However, they also found that their results suggested

$$\alpha_2(z) \sim v^2, \quad (7)$$

instead of equation (5). Alongside the failure of dipoles on the vapour side of the interface to do what was expected of them [32], this is another mystery that requires clarification. In the next section we propose a scheme for answering the first of these questions.

2. How to favour parallel alignment

At this stage we ask ourselves: how can we get the dipoles to lie parallel to the LV interface on the vapour side so as to explain the results of Winkelmann *et al*? To answer this, let us see what we can learn from other systems that also exhibit interfacial order. First and foremost amongst these are LCs. The simplest mechanism that can induce long-range orientational order as is obtained in the simplest LC phase, the nematic, is a highly anisotropic molecular shape. Then, as theorized by Onsager [42], at sufficiently high densities the gain in translational entropy associated with having the long axes of molecules all pointing in the same direction outweighs the loss in rotational entropy thus incurred. Now, it is also known that a prolate (i.e., rod-like) shape favours parallel alignment at both the N–V and I–V interfaces [7, and references therein]. It would then appear that a mechanism that could promote dipole association on the vapour side of the interface would also favour parallel alignment. And we might just have one such mechanism at our disposal: as revealed by simulation [43–46] and later rationalized by theory [47–49], dipoles at low densities tend to aggregate into chains—hence the extended objects that we need to get the required ordering behaviour.

A clearer picture now begins to emerge: past theories of dipole-induced order at the LV interface should be augmented with chain formation. Let us explore various ways in which this can be achieved.

One possibility is to combine our theories for the LV interface [15] and for associating dipoles at low densities [49]. It is, however, notoriously difficult to estimate reliably the interactions between aggregates of different lengths [50], which are central to the correct orientational behaviour. Moreover, in [49] it was assumed that the chains are long, whereas

at the LV interface they are expected to be quite short due to the presence of attractive interactions [50].

Alternatively, one could derive a statistical associating field theory (SAFT) along the lines of [51], but now with angle-dependent pair potentials. The problem here is that SAFT is formulated in terms of the monomer density only, which means that a given molecule will interact in exactly the same way whether it is associated or not. Therefore no shape effect results.

In view of the above difficulties, we have opted, in a first stage, to treat our system as a mixture of dipolar monomers (species 1) and dimers (species 2). In other words, we assume weak association, which we do not treat self-consistently: the degree of association is an annealed variable. Monomers of course interact with one another via the full hard-sphere + attractive $1/r^6$ tail + dipole–dipole potential:

$$\phi_{11}(\mathbf{r}_{12}, \omega_1, \omega_2) = \begin{cases} +\infty & r \leq \sigma \\ -\epsilon \left(\frac{\sigma}{r_{12}} \right)^6 + \phi_{dd}(\mathbf{r}_{12}, \omega_1, \omega_2) & r > \sigma, \end{cases} \quad (8)$$

where \mathbf{r}_{12} is the intermolecular vector, $r_{12} = |\mathbf{r}_{12}|$, ω_i is the orientation of molecule i , and ϕ_{dd} is the interaction between two dipoles of equal strength m given by

$$\phi_{dd}(\mathbf{r}_{12}, \omega_1, \omega_2) = -\frac{m^2}{r_{12}^3} [3(\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{m}}_2 \cdot \hat{\mathbf{r}}_{12}) - \hat{\mathbf{m}}_1 \cdot \hat{\mathbf{m}}_2], \quad (9)$$

where $\hat{\mathbf{m}}_i$ is a unit vector along dipole moment \mathbf{m}_i and $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$ is a unit vector along the intermolecular axis.

On the other hand, it is assumed that the *dipolar* part of the interaction between two monomers bonded in a dimer saturates: this is consistent with the approximations made in [47, 49, 50]. Consequently, a dimer only interacts with monomers and with other dimers via the spherically symmetric parts of the potentials due to its constituent monomers (i.e., a site–site ‘LJ’ potential):

$$\phi_{12}(\mathbf{r}_{12}, \omega_1, \omega_2) = \sum_{\alpha=1}^2 \phi_{LJatt}(r_{\alpha}), \quad (10)$$

$$\phi_{22}(\mathbf{r}_{12}, \omega_1, \omega_2) = \sum_{\alpha,\beta=1}^2 \phi_{LJatt}(r_{\alpha\beta}), \quad (11)$$

where the sums run over the LJ centres in each molecular species (1 in a monomer, 2 in a dimer) and

$$\phi_{LJatt}(r_{12}) = \begin{cases} +\infty & r_{12} \leq \sigma \\ -\epsilon \left(\frac{\sigma}{r_{12}} \right)^6 & r_{12} > \sigma. \end{cases} \quad (12)$$

ϕ_{12} and ϕ_{22} can be expanded in spherical harmonics for ease of computation [54]. According to theory and simulation [52, 53], LJ dimers have opposite alignment behaviour to dipoles at the LV interface: perpendicular on the liquid side, and parallel on the vapour side—as we require.

If we now treat the interaction between monomers, ϕ_{11} , in the MMF approximation [15], and all others in the MF approximation, the grand potential functional will read [14, 55]

$$\begin{aligned}
\Omega[\{\rho_i(\mathbf{r}, \omega)\}] &= \int d\mathbf{r} d\omega f_{hs+hd}(\{\rho_i(\mathbf{r}, \omega)\}) - \sum_{i=1}^2 \int d\mathbf{r} \mu_i \rho_i(\mathbf{r}) \\
&+ k_B T \sum_{i=1}^2 \int d\mathbf{r} \rho_i(\mathbf{r}) \langle \log[4\pi \hat{f}_i(\mathbf{r}, \omega)] \rangle_i \\
&+ \frac{k_B T}{2} \int d\mathbf{r}_1 d\omega_1 \int d\mathbf{r}_2 d\omega_2 \exp[-\phi_{11}^{hs}(\mathbf{r}_{12})/k_B T] \\
&\times \{1 - \exp[-\phi_{11}^p(\mathbf{r}_{12}, \omega_1, \omega_2)/k_B T]\} \rho_1(\mathbf{r}_1, \omega_1) \rho_1(\mathbf{r}_2, \omega_2) \\
&+ \int d\mathbf{r}_1 d\omega_1 \int d\mathbf{r}_2 d\omega_2 \rho_1(\mathbf{r}_1, \omega_1) \phi_{12}^p(\mathbf{r}_{12}, \omega_1, \omega_2) \rho_2(\mathbf{r}_2, \omega_2) \\
&+ \frac{1}{2} \int d\mathbf{r}_1 d\omega_1 \int d\mathbf{r}_2 d\omega_2 \rho_2(\mathbf{r}_1, \omega_1) \phi_{22}^p(\mathbf{r}_{12}, \omega_1, \omega_2) \rho_2(\mathbf{r}_2, \omega_2), \quad (13)
\end{aligned}$$

where $\rho_i(\mathbf{r}, \omega)$ and μ_i are, respectively, the density-orientational profile and the chemical potential of species i , and $\langle A \rangle_i = \int d\omega A \hat{f}_i(\mathbf{r}, \omega)$, with $\hat{f}_i(\mathbf{r}, \omega)$ the orientational distribution function of species i . In equation (13) the superscript p denotes the non-hard parts of potentials $\phi_{ij}(\mathbf{r}_{12}, \omega_1, \omega_2)$ ($i, j = 1, 2$), the hard parts of which are hs (hard sphere) and hd (hard dimer). A local density approximation for the reference part of the potentials is implicit, and is usually valid at the weakly structured LV interface. We take for f_{hs+hd} the Honnell–Hall free energy density (FED) [56]:

$$\begin{aligned}
\frac{f_{hs+hd}}{k_B T} &= \rho_1 \left[\log(\Lambda_1^3 \rho_1) - 1 + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \right] \\
&+ \rho_2 \left[\log(\Lambda_2^3 \rho_2) - 1 + b_3 \log(1 - \eta) + \frac{\eta(b_1 - b_2\eta)}{(1 - \eta)^2} \right], \quad (14)
\end{aligned}$$

where Λ_i is the de Broglie thermal wavelength of species i , $\eta = \pi(\rho_1 + 2\rho_2)\sigma^3/6$ is the total packing fraction, and $b_1 = 8.21199$, $b_2 = 6.3091$, $b_3 = 2.75503$. Equation (14) reduces to the Carnahan–Starling [57] and Tildesley–Streett [58] FEDs in the limits of pure monomers and pure dimers, respectively.

The equilibrium density-orientation profiles would now follow by standard functional minimization of the grand potential functional [15, 55], which would furnish a quantitative test of the qualitative arguments adduced above. Given the smallness of the competing effects (and recall that the degree of alignment is a few per cent at most), it is a non-trivial matter to judge the reliability of the various approximations involved. This work is in progress.

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