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Interfacial phase transitions

M M Telo da Gama

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

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Abstract. We review the thermodynamic and structural behaviour of interfaces between two coexisting phases in 3D. In particular we look at fluid–fluid interfaces in ternary systems. The (microscopic) interface between two phases may (under some circumstances) exhibit structural changes that will drastically change the thickness of the transition region. Examples of these are wetting transitions. Here, we will review theoretical as well as experimental results for wetting transitions in binary and ternary (surfactant) mixtures.

1. Introduction

In this paper we review theoretical as well as experimental results for wetting transitions in surfactant mixtures. Since several comprehensive reviews on wetting transitions have been published [1–3], we give only a very brief introduction to the subject. We will, however, discuss in some detail the results for systems with surfactants. These, in addition to their obvious technological importance, are also interesting from a theoretical point of view and have not been treated in great detail by any of the previous reviews.

In particular we will describe the *microscopic* theories developed to reproduce their characteristic phase behaviour and unique interfacial properties, namely the ultra-low interfacial tensions and the (non-) wetting of the oil–water interface by the middle phase (microemulsion).

2. Wetting and pre-wetting [1–3]

Let us consider a situation where the thermodynamic parameters of a (multicomponent) system have been adjusted so that three distinct phases A, B and C coexist at a triple point. When the interfacial free energies γ_{AB} , γ_{AC} and γ_{BC} satisfy triangle inequalities

$$\gamma_{AB} < \gamma_{AC} + \gamma_{BC} \quad (1)$$

(and cyclic permutations of A, B and C) the situation is called non-wetting. The inverse, $\gamma_{AB} > \gamma_{AC} + \gamma_{BC}$, does not occur at equilibrium since the system can lower its interfacial free energy by interposing a macroscopic wetting layer of C between phases A and B.

This situation is called wetting and the phase C is said to wet the AB interface. The interfacial free energy of the latter is now

$$\gamma_{AB} = \gamma_{AC} + \gamma_{BC}. \quad (2)$$

In some systems it happens that non-wetting occurs along a triple line up to a certain point where the interface becomes wet. This is called a wetting transition, and it can be brought about by a variation of the temperature or some equivalent thermodynamic field variable. Depending on the nature of the interactions it is either a discontinuous (first-order) or continuous (higher-order) transition. Beyond that point the layer of C is macroscopically thick on the triple line. Continuity then suggests that near three-phase coexistence there should be a thick layer with composition close to that of C at the AB interface, with a thickness that diverges as the triple line is approached. This transition to the complete wetting regime is always continuous. In this case the most important singularity that characterizes the wetting behaviour of the systems is the divergence of the film thickness l as coexistence is approached in the complete wetting regime, i.e.

$$l \sim |\Delta\mu|^{1/\delta_s}, \quad \Delta\mu \rightarrow 0^-, \quad T_C < T < T_W \quad (3)$$

where the exponent δ_s depends on the nature of the intermolecular forces and, for systems with dispersion interactions ($1/r^6$), $\delta_s = -3$, in line with the experimental values for a variety of systems [1–3].

Clearly a theory of wetting transitions has to address two main questions:

- (i) Why (i.e. where and when) do wetting transitions occur?
- (ii) How are wetting transitions characterized (i.e. what are the values of the critical exponents)?

The second of these questions seems to have been (fully) answered. In particular for fluids, where (first-order) wetting transitions have been observed, the agreement between theoretical and experimental results is very encouraging [1–3].

By contrast, the answer to the first of these questions is far from satisfactory. Wetting transitions display a very delicate sensitivity to details of the atomic interactions as a direct consequence of the small value of the bulk correlation length at T_W . At the moment, and despite several advances in the theory of non-uniform fluids, the systems that can be studied in detail are limited to highly idealized model Hamiltonians. In the last few years, however, a couple of continuum and lattice models have been proposed to describe the behaviour of ternary surfactant mixtures. Although the results of these calculations cannot give more than (vague) guidelines to the behaviour of real ternary surfactant systems, they have been quite successful at least as far as describing the global phase behaviour and interfacial properties of these systems is concerned.

3. Surfactant mixtures

It is well known that oil and water do not mix. The addition of a small amount of amphiphile (typically a few per cent) causes oil and water to form a single isotropic phase. This phase, although isotropic, is believed to be not homogeneous, but made of coherent regions of oil and water that are separated by the amphiphile. This picture is confirmed (to some extent) by scattering experiments, but the detailed structure of these phases is not yet clearly understood [4, 5].

The phase behaviour of these systems is also interesting, since the disordered fluid can coexist simultaneously with oil-rich and water-rich phases. By varying an external parameter the two critical end points that limit the three-liquid-phase coexistence region can be reached [6].

A third interesting property of ternary surfactant systems is that at the triple line the interfacial tension between oil and water can be two or three orders of magnitude smaller than its value without amphiphile [7]. Furthermore, in systems with good surfactants the oil–water interface is not wetted by the microemulsion middle phase, while in systems with shorter chain amphiphiles it is [6, 8].

It has also been shown recently that in simple three-component systems (e.g. water, hexadecane and C_6E_2) a temperature-driven (first-order) wetting transition of the oil–water interface involving wetting by the middle phase can be observed, a few degrees below the upper critical end point [9].

It is precisely the relationship between these various properties of three-component systems that poses the most challenging questions and that (to some extent) several microscopic models are beginning to answer [10–12]. Here we will not review the phenomenological approach (Landau theory [13]) to the phase behaviour and interfacial properties of microemulsions, since we believe that the study of microscopic models has taught us more, in particular by helping to demystify the somewhat complex behaviour of these systems.

In microscopic approaches, the starting point is a Hamiltonian that describes the interactions in the system, and the free energy follows by standard statistical mechanical manipulations (approximations). Several of these Hamiltonians have been proposed (most of them on a lattice, with a few exceptions that explicitly considered continuum models), all of which incorporate at least some form of anisotropic interaction between the amphiphile and the other components. All produce oil-rich and water-rich phases, a uniform fluid phase, and/or other phases with more structure. The orders of the phase transitions between these phases are to some extent still controversial, and this problem as well as the identification of the microemulsion are discussed in detail (for lattice models) in a recent review by Gompper and Schick [10].

The results for the interfacial properties have been scarcer since, in addition to the calculation of the (global) bulk phase diagram, one needs to consider several (coupled) spatially varying order parameters. The numerical problems involved in solving the resulting equations in the simplest cases (planar geometry, symmetrical mixtures) are non-trivial, even at the level of Landau theory.

4. Interfacial properties: wetting transitions

At least five different models have been proposed and studied in some detail, including interfacial properties. Of these, three are lattice models [14–16] and two are based on continuum Hamiltonians [11, 12]. The basic (common) ingredient of all of them is the presence of three different chemical species *a*, *b* and *c* with at least anisotropic interactions between the amphiphile (*c*) and the other two species. In the model developed by Widom and co-workers [14] the particles are placed on the bonds of the lattice, while in that of Schick and co-workers [15] the particles are on lattice sites. In the model introduced by Alexander [16] the water and oil are placed on lattice sites and the amphiphiles on bonds. Given sufficiently ‘complex’ interactions between the three species (*a*, *b*, *c*) all of these models are capable of describing the correct phase behaviour

of ternary surfactant mixtures [10]. In the two continuum models [11, 12] three different chemical species are also considered with anisotropic interactions between the amphiphile and the other two species. The global phase diagram, including lyotropic phases, has not yet been investigated for these systems [11], since the numerical calculations are in general harder to carry out, and the models cannot be mapped into well known systems; this is, in fact, one of the great disadvantages of continuum models versus lattice models. The single most obvious advantage of using continuum models in this context is that if layered phases are found they will not have any of the unrealistic (lattice-dependent) characteristics of the layered phases found in lattice models [10].

Finally, most of the models can predict ultra-low tensions. In two of the lattice models this is attributed to the existence of a tricritical point and the stability of a layered phase at $T = 0$ [10]. We believe that this is also responsible for the low tensions (at least) in one of the continuum models [11], although a better understanding of the global phase diagram is required before this can be ascertained with any certainty.

As to the wetting behaviour, the models predict wetting of the oil–water interface by the middle phase in systems with weak amphiphiles, and non-wetting in systems with very good surfactants, in agreement with experiments.

A temperature-driven [11, 15] (or otherwise-driven [15]) wetting transition was also predicted for systems with intermediate amphiphiles, and this was recently confirmed by experiment [9].

A much stronger relation between the structure of the middle phase and the wetting properties at the oil–water interface has been predicted by Gompper and Schick on the basis of a Landau theory [17], and is being currently investigated by experiment [18].

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