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The Influence and Interpretation of Surface Parameters for Wetting Transitions in Ternary Mixtures[1]

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Starting from a microscopic Hamiltonian defined on a semi-infinite cubic lattice, and employing a mean-field approximation, the surface parameters relevant for wetting in confined ternary mixtures are derived. These are found in terms of the microscopic coupling constants, and yield a physical interpretation of their origins. In comparison with the standard expression for the surface free-energy density, several new terms arising from the derivation are identified. The influence of the surface parameters on a predicted unbinding transition in a mixture of oil, water, and amphiphile demonstrate that existing results are robust to the addition of the extra surface terms.

KEY WORDS: complex fluids; lattice models; mean-field theory; wetting transitions.

1. INTRODUCTION

A popular starting point for the study of wetting or unbinding in both simple and complex fluids is the appropriate Ginzburg-Landau (GL) theory. In particular, for the case of wetting of a substrate in the plane $z=0$ by an adsorbate, the GL theory is based on a surface free-energy functional of the form,

$$\mathcal{H}_{\mathrm{GL}}[\phi]=\int_{\mathbf{r}\geqslant 0} \mathrm{d}^d\mathbf{r}\,\{\mathcal{L}_V[\phi,\nabla\phi,\ldots]+\delta(z)\mathcal{L}_S[\phi,\ldots]\}, \tag{1}$$

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where $\phi(\mathbf{r})$ is the bulk order parameter and d is the spatial dimension. For the case of simple fluids ϕ represents a local density, and $\mathcal{L}_V \equiv \mathcal{L}_V[\phi, \nabla\phi] = K(\nabla\phi)^2/2 + f(\phi)$ where $K > 0$ and $f(\phi)$ is a double-welled bulk free-energy density with two equal minima at coexistence. In this case the substrate-adsorbate energy is usually accepted to take the form

$$\mathcal{L}_S \equiv \mathcal{L}_S[\phi_1] = -h_1\phi_1 - g\phi_1^2/2, \tag{2}$$

where $\phi_1 = \phi(\mathbf{y}, z = 0)$ is the surface order parameter, h_1 is the surface field, and g is the surface-coupling enhancement [1,2]. The motivation for this expansion is not clear *a priori* since, in general, ϕ_1 is not anticipated to vanish on approach to the critical temperature T_c; however, derivations based on lattice mean-field theory broadly support the expansion [3].

In this paper, we are primarily interested in ternary mixtures of oil, water, and amphiphile [4]. Such mixtures are predicted to display a wide range of different structures, with bulk mean-field phase diagrams capturing many of the features found in experimental studies. For example, at low amphiphile concentrations a monolayer of surfactant molecules is formed at the oil–water interface leading to a decrease of the surface tension. As the amphiphile concentration is increased, a number of distinct structured phases are possible, such as the lamellar phase which consists of regular one-dimensional arrays of monolayers separated alternately by oil-rich and water-rich domains. If this array is disordered, one instead obtains the microemulsion phase. One can use a single scalar order parameter model of the form of Eq. (1) to model these fluids, with the order parameter $\phi(\mathbf{r})$ interpreted as the local concentration difference between oil and water.

Due to the presence of small, or even negative surface tensions in ternary mixtures, the simple model discussed above can become unstable so that higher-order gradient terms are required leading to an expansion for $\mathcal{L}_V$ of the form,

$$\mathcal{L}_V \equiv \mathcal{L}_V[\phi, \nabla\phi, \nabla^2\phi] = c(\nabla^2\phi)^2 + g(\phi)(\nabla\phi)^2 + f(\phi) - \mu\phi, \tag{3}$$

where the amphiphile degrees of freedom have been integrated out but with their properties influencing c, f, and g. The bulk free-energy density $f(\phi)$ has three minima corresponding to homogeneous oil, water, and microemulsion phases, while μ is the chemical potential difference between oil and water. From scattering experiments it is known that $g(\phi)$ is positive in the pure oil and water phases, but may be negative in the microemulsion phase. In contrast c is always positive, stabilizing the system, and for simplicity may be assumed constant.

For studies of confined ternary mixtures the substrate-adsorbate energy density has been proposed to take the form (employing conventional notation for ternary mixtures),

$$\mathcal{L}_S \equiv \mathcal{L}_S[\phi_1, \nabla\phi_1] = \mu_s\phi_1 + \omega_s\phi_1^2 + g_s(\nabla\phi_1)^2, \tag{4}$$

with $\nabla\phi_1 = \nabla\phi|_{z=0+}$ the local gradient of ϕ [5,6]. Here the local surface field (or chemical potential) μ_s describes the preference of the wall for one of the phases, while ω_s is the analogue of the standard surface enhancement term. The gradient term (with coefficient g_s) is required for correctly determining the wall conditions associated with minimizing the GL free energy. The main purpose of this work is to test the validity of Eq. (4) by deriving connections with the parameters of an appropriate lattice model. In particular we seek to find a physical interpretation of the parameter g_s.

The remainder of the paper is arranged as follows. In the next section we calculate the surface contact energy in terms of the microscopic coupling constants of a semi-infinite lattice model, generalizing earlier work [7] to arbitrary dimensions and providing a more detailed discussion of the origins of the surface terms. Our analysis leads to extra terms not accounted for in Eq. (4). In Section 3, we discuss the influence of the extra terms on predictions of a wetting transition in a ternary mixture and summarize our main results.

2. DERIVATION AND INTERPRETATION OF SURFACE PARAMETERS FOR TERNARY MIXTURES

We base our study on a simple three-component lattice model which has molecules of either oil, water, or amphiphile located on each site of a d-dimensional cubic lattice. The properties of the amphiphile are introduced via a term which reduces the energy of configurations in which an amphiphile molecule sits between oil and water, but increases the energy in configurations in which the amphiphile sits between two oil or water molecules. The model is most conveniently formulated as a spin-1 magnetic system via a nonlinear variable mapping (see, for example, Ref. 4 for full details). In this formulation the Hamiltonian for the bulk system, ignoring surface effects, is

$$\begin{aligned}\mathcal{H}_B = &-\sum_{\langle ij\rangle}\left[J_B S_i S_j + K_B S_i^2 S_j^2 + C_B(S_i^2 S_j + S_i S_j^2)\right]\\ &-\sum_i (H_B S_i - \Delta_B S_i^2) - L_B \sum_{[ijk]} S_i(1 - S_j^2)S_k,\end{aligned} \tag{5}$$

where the spin variable S_i takes the values 1, 0, and -1, representing the water, amphiphile, and oil molecules, respectively. The parameter $L_B < 0$ is the strength of the amphiphilic interaction, while the coupling constants J_B, K_B, C_B, H_B, and Δ_B can be found in terms of the chemical potentials of the three components and the various two-particle interactions [4]. The notation $\langle .. \rangle$ indicates sums over nearest neighbor sites, and $[\ldots]$ denotes sums over three linearly adjacent sites. In our analysis, we will assume a balanced system in which there is symmetry between the oil and water phases, so that the symmetry breaking fields $C_B = H_B = 0$.

The Hamiltonian $\mathcal{H}_B$ is an extended version of the familiar Blume-Emery-Griffiths (BEG) model with the last term in Eq. (5) providing the only difference with the standard BEG model [8]. To further extend the model to include surface effects, we need to add an extra term $\mathcal{H}_S$ describing the interactions between spins lying on the surface;

$$\begin{aligned}\mathcal{H}_S = &-\sum_{\langle ij \rangle}\Big[J_S S_i S_j + K_S S_i^2 S_j^2 + C_S(S_i^2 S_j + S_i S_j^2)\Big] \\ &-\sum_i (H_S S_i - \Delta_S S_i^2) - L_S \sum_{[ijk]} S_i(1 - S_j^2) S_k, \end{aligned} \tag{6}$$

so that the total Hamiltonian for the system is $\mathcal{H} = \mathcal{H}_B + \mathcal{H}_S$. In $\mathcal{H}_S$ the sums only involve sites on the surface hyperplane, denoted by $i = 1$. In general, the surface couplings will differ from their bulk counterparts, and so the fields C_S and H_S will not be zero despite the assumed symmetry in the bulk.

We employ a lattice mean-field approximation in order to calculate the contribution to the mean-field free energy due to the presence of the surface [9]. In this approach the system is described by the set $\{M_i, Q_i;\ i \geqslant 1\}$ where i is used to label the $(d-1)$-dimensional hyperplanes parallel to the surface. Specifically $M_i = \langle S_j \rangle$ and $Q_i = \langle S_j^2 \rangle$ are the thermodynamic expectation values of S_i and S_i^2, respectively. Note, the averages are taken over all sites j in hyperplane i, so that the subscripts of M and Q refer to the appropriate hyperplane, whereas the subscript of S refers to the lattice site. Within this approximation the excess surface contact energy that we seek, F_S, can be found as the difference in free energy of the two situations shown schematically in Fig. 1. In case (I) one considers the free energy for the semi-infinite system with $M_i = M_0$ and $Q_i = Q_0$ for all $i > 1$, where M_0 and Q_0 represent the values for a typical homogeneous solution. In case (II) one determines the free energy of a semi-infinite system with bulk couplings everywhere and with dangling bonds connecting the surface spins to spins just outside the surface.

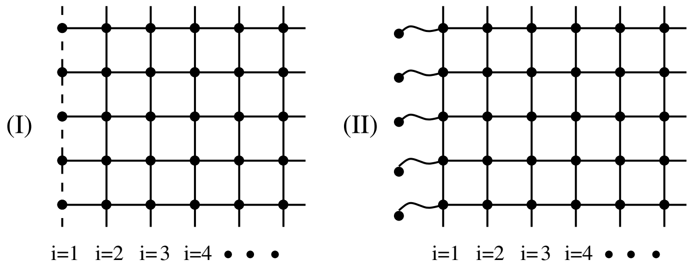

Fig. 1. Schematic representation of the two systems discussed in the main text. Solid and dashed lines correspond to bulk couplings (J_B, K_B, ...) and surface couplings (J_S, K_S, ...), respectively, while the index i identifies the various $(d-1)$-dimensional hyperplanes.

Following this approach yields

$$\begin{aligned} F_S(M_1, Q_1, M_0) = & -H_S M_1 + (\Delta_S - \Delta_B) Q_1 - \left(\frac{2d-2}{2} J_S - \frac{2d-1}{2} J_B \right) M_1^2 \\ & - \left(\frac{2d-2}{2} K_S - \frac{2d-1}{2} K_B \right) Q_1^2 - 2(d-1) C_S M_1 Q_1 \\ & + L_B M_0 (1 - Q_1) M_1 - (d-1)(L_S - L_B)(1 - Q_1) M_1^2. \end{aligned} \quad (7)$$

In order to connect this expression to the corresponding energy density in the continuous GL theory, it is appropriate to rewrite F_S purely in terms of M_1 and differences of M_i's involving the surface hyperplane $i=1$, which can be transformed to local gradients when going to the continuous GL theory. This can be achieved by solving self-consistency equations in the standard mean-field approximation (details are given in Refs. 7 and 9) leading to an expansion for Q_1 in terms of the surface order parameter M_1 and the local difference $\Delta M_1 \equiv M_2 - M_1$. Substituting into Eq. (7) leads to the appropriate expansion for the surface contact energy,

$$F_S(M_1, \Delta M_1) = \mu_s M_1 + \omega_s M_1^2 + g_1 \Delta M_1 + g_s (\Delta M_1)^2 + k_1 M_1 \Delta M_1, \quad (8)$$

which defines the various surface parameters. Note the explicit M_0 dependence has been adsorbed into the definition of the surface parameters. From Eq. (8) we can derive the corresponding GL theory energy density to first approximation by a Taylor expansion of M_2 about M_1, and associating M with the order parameter ϕ. This indicates that the substrate-adsorbate energy proposed in Eq. (4) should be replaced by the more general form,

$$\mathcal{L}_s [\phi_1, \nabla\phi_1] = \mu_s \phi_1 + \omega_s \phi_1^2 + g_1 (\nabla\phi_1)\cdot\mathbf{n} + g_s (\nabla\phi_1)^2 + k_1 \phi_1 (\nabla\phi_1)\cdot\mathbf{n}, \quad (9)$$

where $\mathbf{n}$ is the outwardly directed surface normal. Here we have naively assumed that the surface parameters are not affected by the transformation from lattice mean-field theory to the continuous GL theory. In practice one does not expect this to be true, with the parameters in $\mathcal{L}_s$ differing from those in F_S by terms proportional to the difference in phase space from the bulk critical point; however, such modifications are not relevant for the observations discussed below.

The most notable result of our derivation is the presence of two additional terms in $\mathcal{L}_s$, one linear in $\nabla\phi_1$, and one cross term of the form $\phi_1\nabla\phi_1$, neither of which can be ignored by simple symmetry considerations. The coefficients of both terms (g_1 and k_1 respectively) are found to contain contributions proportional to the surface field and enhancement of the amphiphile molecules. The local chemical potential μ_s is typically dominated by the surface field H_S, and a term proportional to the bulk coupling constant L_B. The presence of this term can be anticipated from the penultimate contribution in Eq. (7), and is directly attributable to the property of the amphiphile to locally self organize the system (for a non-amphiphilic ternary mixture, or a mixture with a very weak amphiphile $L_B \approx 0$ and so this contribution would vanish from μ_s). The enhancement term ω_s accounts for the interactions of all molecules (both oil or water, and amphiphile) at the surface and their entropy (i.e., missing neighbors), which in general are different as compared to the bulk. The origin of g_s is one of the main goals of this work, with earlier studies choosing to interpret g_s as the local chemical potential of the amphiphile [5]. While a contribution of this form (proportional to the effective surface field $\Delta_S - \Delta_B$) is indeed found, an additional term is also present and is related to the difference between the interaction couplings (being proportional to $(2d-2)K_S-(2d-1)K_B$). Thus, in general, g_s, g_1, and k_1 all act both as a surface field and surface enhancement for the amphiphilic molecules. Full expansions for all of the surface parameters in $d=3$ are given in Ref. 7. We conclude this section by considering two special cases in further detail.

2.1. Simple Fluid Limit

Firstly we consider the limiting case of a simple fluid aiming to recover known results for the surface field and enhancement. In this case the couplings K, C, Δ, and L in the bulk and surface are identically zero so that the total Hamiltonian for the system is simply

$$\mathcal{H} = -\sum_{\langle ij\rangle} J_B S_i S_j - {\sum_{\langle ij\rangle}}' J_S S_i S_j - {\sum_i}' H_S S_i, \tag{10}$$

where the primes on the last two sums indicate that only spins in the surface hyperplane are included. As expected, the variables Q_i, which are directly related to the profile of the amphiphile concentration, drop out of the results. Only the terms μ_s and ω_s are found to be nonzero; since we have reduced the problem to the case of a simple fluid we revert to the notation of Eq. (2) so that $h_1 = -\mu_s$ and $g = -2\omega_s$ are given by

$$h_1 = H_S, \quad g = (2d-2)J_S - (2d-1)J_B. \tag{11}$$

These findings are in agreement with earlier lattice mean-field results [3], providing a useful check on the consistency of our approach.

2.2. Symmetric Limit

As noted earlier there are two symmetry breaking surface fields in the model, H_S and C_S. Considering the symmetric limit where $H_S = C_S = 0$ yields many simplifications, and helps to identify the contributing factors to the various surface parameters. As discussed above μ_s does not vanish in the symmetric limit but is proportional to $L_B M_0$ with a sign dependent on the particular homogeneous phase assumed in the hyperplanes near the surface. The enhancement ω_s is qualitatively unchanged in this limit as anticipated for a surface enhancement. In contrast g_1 vanishes indicating that this term is completely induced by the symmetry breaking fields; indeed, one can further show that for any given H_S one can find a $C_S \propto -H_S$ which yields $g_1 = 0$. Finally, both g_s and k_1 are of the form $a_\Delta(\Delta_S - \Delta_B) + a_K[(2d-2)K_S - (2d-1)K_B]$ with appropriate constants a_Δ and a_K in each case. Thus, both terms play the role of surface field and enhancement for the amphiphilic molecules independently of the symmetry breaking fields.

3. DISCUSSION AND CONCLUSIONS

In the previous section we showed that the assumed GL theory substrate-adsorbate energy $\mathcal{L}_S$ given by Eq. (4) should more generally be replaced by Eq. (9). Thus, we are naturally led to evaluate how important the extra terms in $\mathcal{L}_s$ are for predictions of wetting behavior. To this end we have reanalyzed a recent study of wetting of the wall-microemulsion interface by the water-rich phase in a balanced ternary mixture [6, 10]. In that study a mean-field analysis predicted a rich surface phase diagram containing first-order and continuous (critical) wetting transitions, with the critical phase boundary given by a straight line in the (μ_s, ω_s)-plane. The parameter g_s was found to have no qualitative effect with only minor quantitative differences in the cases where $g_s > 0$, $g_s = 0$, and $g_s < 0$.

Encouragingly, repeating this analysis with the two extra surface terms included also leads to only minor quantitative changes in the location of the phase boundaries (see Ref. 7 for numerical details). The general qualitative features of the phase diagram, including the straight critical boundary all remain. The fact that the effect of g_1 and k_1 is similarly limited as that of g_s may be connected to the similar origins of the three terms as discussed in Section 2. Should this be the case, one can reasonably anticipate that the additional two terms will not play a relevant role in the study of interfacial behavior in confined ternary mixtures whenever g_s is found to be insignificant.

In conclusion, we have calculated the surface contact energy F_S for a semi-infinite mixture of water, oil, and amphiphile using a simple mean-field approximation based on a microscopic lattice model. We have shown that F_S can be expressed as an expansion in powers of the surface order parameter M_1 and the local difference ΔM_1. Our calculation suggests that two additional terms should be added to the standard GL surface free energy density $\mathcal{L}_s$. The coefficients of these two terms, along with the parameter g_s, are interpreted as combinations of a local chemical potential and surface enhancement for the amphiphilic molecules. On the basis of this interpretation, in combination with the study of a particular unbinding transition in a ternary mixture, we believe that the two additional terms will only be important if g_s is also qualitatively relevant.

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