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Abstract
A mean-field theory is presented which describes the basic observations of
recent experiments revealing rich wetting behaviour of n-alkane/methanol
mixtures at the liquid–vapour interface. The theory is based on a microscopic
lattice-gas model from which a Cahn–Landau phenomenological approach is
derived. Besides the physics associated with the short-range components of the
intermolecular interactions, the effects of the long-range tails of the net van der
Waals forces between interfaces are also taken into account. The tricritical
wetting transition, which is featured in the theory when long-range forces
are ignored, is replaced by a critical prewetting transition when these forces
are included. The experimental observations agree to a large extent with the
predictions of the theory for short-range tricritical wetting.

1. Introduction

Recent experiments have shown that a binary liquid mixture of linear or 'normal' alkane and
methanol at ambient pressure (1 atm) displays a first-order wetting transition if the wetting
temperature T_w is well below the consolute temperature T_c and a 'short-range critical wetting'
transition if T_w is very close to T_c [1, 2]. The latter is the case for n-nonane and methanol. The
'substrate' in these wetting experiments is the saturated vapour phase.

   The observation of short-range critical wetting in adsorbed binary liquid mixtures is
surprising. Indeed, due to the presence of van der Waals forces, which induce an algebraically
decaying long-ranged surface–interface interaction favouring wetting, a first-order wetting
transition should be expected [3–7, 10]. Alternatively, if the van der Waals forces oppose
wetting, no wetting transition should occur, unless the leading van der Waals interaction
amplitude changes sign at some temperature, resulting in 'long-range critical wetting' [7–10],
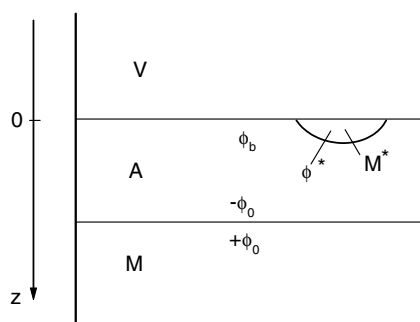
Figure 1. The configuration of the system: along the vertical direction z the vapour phase (V) is on top, the alkane-rich phase (A) is in the middle, and the methanol-rich phase (M) is at the bottom. Two-phase coexistence between phases A and M is realized at the position of the A/M interface. The order parameters on both sides of this interface take the values ϕ_0 and $-\phi_0$. The liquid–vapour interface is situated at a higher position, leading to a slight undersaturation of the A phase with methanol, and order parameter ϕ_b. The droplet consists of a metastable phase M*, with order parameter ϕ^*, slightly different from ϕ_0. The calculation of the spreading coefficient at the V/A interface takes into account the surface free energies of the V/A, V/M*, and M*/A interfaces.

observed experimentally in pentane on water [11]. However, in our present system, within the experimentally accessible range of small film thicknesses (up to 100 Å), the van der Waals forces can be neglected compared to exponentially decaying mean-field (MF) and fluctuation-induced (FI) interactions [1, 2].

Remarkably, the experimental results for the surface specific heat exponent agree with the predictions of the MF theory, and disagree strongly with renormalization group predictions [12–15]. Furthermore, Monte Carlo simulations of short-range critical wetting [16] also disagree with the RG predictions [15, 17] but agree with the experiments. These facts suggest that the non-classical critical region around the transition, in which deviations from MF behaviour show up, is too small to be relevant for experiment or simulation.

Our aim in this paper is to give a theoretical description of the experimentally observed crossover [18] between the regimes of first-order wetting and 'short-range critical wetting' in this system, *which for purely short-range forces would occur via a tricritical wetting point*. In view of the observed consistency between experiment and MF theory, we adopt the point of view of the classical theory of Cahn–Landau type. We include the van der Waals forces as a weak perturbation. We neglect thermal fluctuation effects, but incorporate the influence of the vicinity of bulk criticality at the MF level. That is, the divergence of the bulk correlation length is included in the theory, but with the MF value for the critical exponent. In this way, the interplay of wetting and critical adsorption is allowed for. This paper gives a brief summary of a detailed research article [19].

2. Theoretical model

In this section we give a brief description of our theoretical approach. We adopt the philosophy of lattice-gas modelling which is often applied to binary alloys [20]. We consider a nearest-neighbour spin-1 Ising model on a three-dimensional simple cubic (SC) or face-centred cubic (FCC) lattice. The spin variable takes the value +1 (methanol molecule), −1 (alkane molecule) or 0 (vacancy). The methanol-rich phase sits at the bottom of the recipient, the alkane-rich phase is in the middle, and the vapour is on top (figure 1).

The spin-1 Ising model Hamiltonian reads

$$\mathcal{H}(s) = -J \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i - \Delta \sum_{\langle ij \rangle} (s_i s_j^2 + s_j s_i^2) - E \sum_{\langle ij \rangle} s_i^2 s_j^2 - M \sum_i s_i^2 \qquad (2.1)$$

where the angle brackets $\langle ij \rangle$ indicate that the sums are over nearest neighbours on the lattice. The Ising couplings can be defined as follows: $J = (\epsilon_{MM} + \epsilon_{AA} - 2\epsilon_{AM})/4$, $H = (\mu_M - \mu_A)/2$, $\Delta = (\epsilon_{MM} - \epsilon_{AA})/4$, $E = (\epsilon_{MM} + \epsilon_{AA} + 2\epsilon_{AM})/4$, $M = (\mu_A + \mu_M)/2$ (here we introduced the pair interaction energies $\epsilon_{MM}, \epsilon_{AA}, \epsilon_{AM}$ and chemical potentials μ_A and μ_M for methanol (M) and alkane (A) molecules).

Since the vapour phase is dilute and the liquid phases are dense, we can map the spin-1 model onto a spin-1/2 model *with a free surface* and the following bulk Hamiltonian:

$$\mathcal{H}_{\text{bulk}} = -J \sum_{\langle ij \rangle} s_i s_j - H_{\text{bulk}} \sum_i s_i \qquad (2.2)$$

where the bulk field is given by

$$H_{\text{bulk}} = H + q\Delta. \qquad (2.3)$$

Here q is the coordination number of a lattice.

The surface contribution to the Hamiltonian, $\mathcal{H}_{\text{surf}}$, is given by

$$\mathcal{H}_{\text{surf}} = -J \sum_{\langle ij \rangle} s_i s_j - H_{\text{surf}} \sum_i s_i \qquad (2.4)$$

where the surface field H_{surf} takes the form

$$H_{\text{surf}} = H_{\text{bulk}} - m\Delta \qquad (2.5)$$

with $m = 1$ for the SC lattice, and $m = 4$ for the FCC lattice.

To the Ising Hamiltonian we now apply the MF approximation and subsequently make the continuum approximation to obtain the Cahn–Landau theory [21]. Additionally, we take into account that the mixture is at, or very close to, two-phase coexistence in bulk.

The Cahn–Landau surface free-energy functional of the concentration-like order parameter $\phi(z)$ reads [22]

$$\gamma[\phi] = \int_0^\infty \mathrm{d}z \left\{ \frac{c^2}{4} \left(\frac{\mathrm{d}\phi}{\mathrm{d}z} \right)^2 + f(\phi(z)) \right\} - \int_{z^*}^\infty \mathrm{d}z \, h(z)\phi(z) - h_1\phi_1 - g\frac{\phi_1^2}{2}. \qquad (2.6)$$

Here in the second integral we include the long-range tails of the van der Waals interactions between molecules. A long-range substrate–adsorbate field $h(z)$ takes into account the net effect of the substrate–adsorbate adhesive and adsorbate–adsorbate cohesive contributions. We consider the following approximation for $h(z)$:

$$h(z) = a_3/z^3 + \mathcal{O}(1/z^4). \qquad (2.7)$$

In our type of system the long-range interactions favour wetting by the methanol-rich phase; therefore we have $a_3 > 0$, which is referred to as 'agonistic' long-range forces (LRF) [3].

The reduced free-energy density $f = F/(Nk_BT_c)$ (F is the free energy, N is the number of cells in the lattice-gas representation of our system, and T_c represents the *consolute point*) can be expanded in terms of the order parameter ϕ. We obtain for the reduced free energy

$$f(\phi) = \text{constant} - h\phi - (1 - T/T_c)\phi^2/2 + (T/T_c)\phi^4/12 \qquad (2.8)$$

where h stands for the reduced bulk field, $h = H_{\text{bulk}}/k_BT_c$.

The last two terms in (2.6) constitute a surface contact energy which depends on the surface value of the order parameter, $\phi_1 = \phi(z = 0)$. For the surface field we have the simple relation [21]

$$h_1 = H_{\text{surf}}/k_BT_c \qquad (2.9)$$

and for the enhancement we have, for $T \approx T_c$,

$$g = -mK_c. \tag{2.10}$$

We conclude that, since $g < 0$, first-order as well as critical wetting transitions are possible.

The gradient-squared coefficient $c^2/4$ in (2.6) is related to microscopic interaction energies and thermodynamic quantities in the following way [21]:

$$c^2/2 = J/k_B T_c \equiv K_c \tag{2.11}$$

and can be estimated through the experimental values for the surface tension γ_{MA} of the methanol/alkane interface.

3. Crossover from first-order to critical wetting

Within the short-range forces framework we are interested in three cases: first-order wetting, tricritical wetting, and critical wetting, which are distinguishable by the value of some dimensionless parameter κ. It easy to see [23] that in our model *tricritical wetting* occurs for

$$\kappa \equiv \sqrt{12}g/c\phi_0 = -2 \tag{3.12}$$

critical wetting takes place for $\kappa < -2$ and first-order wetting results for $\kappa > -2$ (which includes also $g > 0$).

Within the model, we analyse the temperature behaviour of the layer thickness, the adsorption, and the pertinent surface free energies at fixed chemical potential very close to two-phase coexistence using the phase portrait technique. The wetting layer thickness corresponds to the region occupied by a methanol-rich film, when a sufficient amount of methanol is adsorbed at the alkane/vapour interface. In the experiments, the layer thickness is calculated from the measured ellipticity by modelling the film as a slab with sharp interfaces. This approximation certainly breaks down very close to T_c. We employ here a more reliable parameter, such as the adsorption or coverage. This is a measure of the total adsorbed amount per unit area, obtained by integrating the concentration excess. Importantly, the adsorption is, to a first approximation, directly proportional to the experimentally measured ellipticity [1,2].

The spreading coefficient, which depends on the interfacial tensions γ_{VA}, γ_{VM}, and γ_{MA}:

$$S = \gamma_{VA} - (\gamma_{VM} + \gamma_{MA}) \tag{3.13}$$

can also be determined experimentally, since it can be expressed in terms of measured contact angles. For tricritical and critical wetting the calculation of the spreading coefficient is non-trivial (see the caption of figure 1).

The singular behaviour of S at wetting is described by the power law, for T approaching T_w from below,

$$S = S_0(T_w - T)^{2-\alpha_s} \tag{3.14}$$

where α_s is the surface specific heat exponent. At bulk two-phase coexistence ($h = 0$) the Cahn–Landau theory produces the MF results for short-range forces, $\alpha_s = 1$ (first-order), $\alpha_s = 1/2$ (tricritical), and $\alpha_s = 0$ (critical) [24]. Within our model, slightly off two-phase coexistence, we obtain that for first-order wetting there is a zero-crossing, so S is linear about T_w, implying $\alpha_s = 1$. For tricritical wetting, fits to the calculated curve give $\alpha_s \approx 0.5$, and for critical wetting, we find $\alpha_s \approx 0$. In conclusion, the tricritical and critical wetting transitions at $h = 0$ are already well approximated by the behaviour of S slightly off coexistence. This is valid for systems with short-range forces. In order to compare the theory with experiments

on real fluids, however, it is indispensable to include the LRF in the description, which is the task to which we now turn.

The basic characteristic of our approach is that we take the LRF amplitude a_3 to be an *adjustable parameter*, since we will ignore all higher-order terms in (2.7). The magnitude of our LRF amplitude is unknown, but we assume that its sign is consistent with that of the Hamaker constant [25]. Our approach is a *perturbative* one, in which the LRF are treated as a weak contribution. That is, the amplitude a_3 is taken to be small, so its effect on the spreading coefficient S is small. Our purpose will be to test the influence of weak agonistic LRF on critical wetting and the crossover to first-order wetting, in systems which are slightly away from bulk coexistence.

One can check the value of a_3 which follows from the Hamaker constant pertaining to the experiments. Calculation gives $a_3 \approx 0.030$ [19]. We remark that a_3 can be considered to be a constant, independent of T, while the Hamaker constant is proportional to $a_3\phi_0$, where ϕ_0 denotes the bulk order parameter which goes to zero at the upper consolute point T_c of the liquid mixture. In the following the LRF amplitudes for our calculations will be denoted as 'weak' provided that they are small compared to this estimate.

For the three different mixtures we estimate the bulk and surface fields, and the surface coupling enhancement, and calculate the adsorption as a function of temperature. As input to these calculations we use molecular constants and experimental values for the liquid–liquid (M/A) interfacial tension. We also use the fact that the liquid–vapour interface is at a height of about 0.5 cm above the liquid–liquid interface. We interpret the results on the basis of the knowledge of the properties of the short-range theory and the effect of adding weak LRF, and compare with the experimental findings [18].

For the nonane/methanol mixture the calculated adsorption curve clearly reveals a continuous transition, in every respect reminiscent of the critical wetting phenomenon in the case of short-range forces, although the prediction from all previous theoretical works is that the short-range critical wetting transition must become a first-order wetting transition when LRF favouring wetting are present. Moreover, the experimentally observed adsorption curve, through ellipticity measurements, is similar to this theoretical one [19].

The solution to this paradox lies entirely in the fact that the system is not at bulk two-phase coexistence. Actually, off coexistence the system does not display first-order wetting but features a prewetting line, which is very short in temperature as well as in bulk field, for very weak LRF. Under those circumstances the bulk field due to the gravitational effect is large enough to make the system sneak *underneath* the prewetting critical point, and show a continuous transition instead of a first-order one.

The calculation of the exponent α_s associated with the spreading coefficient for the continuous prewetting transition, the interpretation of the result, and the comparison with the experimentally measured value are reported in the more detailed paper [19]. This is also the case for the other systems discussed below.

For the decane/methanol system we obtain a remarkable result, as far as the temperature-dependent adsorption is concerned. The addition of weak LRF drives the transition very weakly first order, as is demonstrated in figure 2. The similarity of the adsorption curve of figure 2 and the typical vertical adsorption signal for tricritical wetting is striking. There is hardly a way to distinguish the tricritical adsorption singularity from a genuine weak first-order jump of the order parameter. The hysteresis is so minute that the lower and upper spinodal points SP_l and SP_u practically coincide in temperature.

In the case of undecane/methanol, weak LRF already drive the transition clearly first order. Since the system is very close to the prewetting critical point, the hysteresis is much smaller than that of the typical first-order adsorption signal.
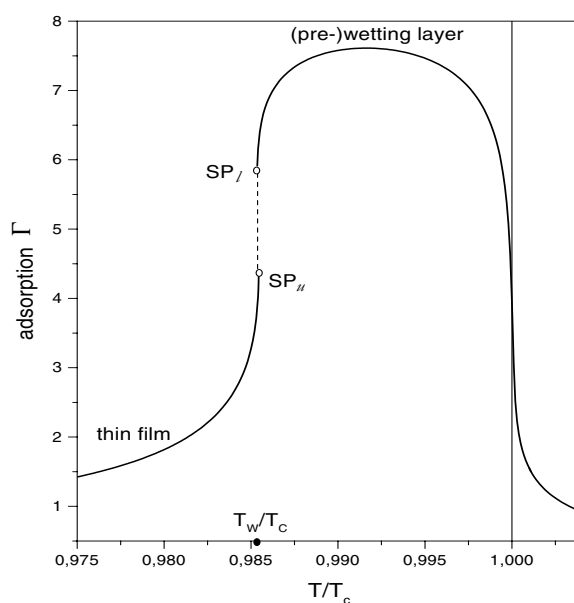
Figure 2. The theoretical adsorption curve for the binary liquid mixture decane/methanol slightly away from bulk two-phase coexistence. The excess of methanol adsorbed at the liquid–vapour interface is plotted versus temperature. The prewetting transition is weakly first order and occurs at $T/T_c \approx 0.986$. Critical adsorption takes place at the consolute point $T = T_c$. The prewetting transition is almost continuous as it lies in the immediate vicinity of the prewetting critical point. There is no hysteresis: the lower spinodal SP_l and the upper spinodal SP_u almost coincide in temperature. For this calculation, weak LRF have been assumed, and the prewetting transition is strongly reminiscent of short-range tricritical wetting.

4. Conclusions

We show that systems slightly off coexistence can behave qualitatively differently from those at coexistence. The most spectacular example that we have found in this regard is the possibility of a wetting transition that exhibits all the features of short-range critical wetting under circumstances in which, strictly speaking, the wetting transition at coexistence is always of first order. This is the case when the LRF are agonistic, and consequently short-range first-order wetting remains first order, and short-range critical wetting must turn into a first-order transition, asymptotically, for vanishing undersaturation.

The methods that we have employed and the theory that we have developed rely fully on the MF description of the interacting many-body system. Why should the MF theory be sufficient in this case? The most decisive justification of this is that MF critical behaviour is observed experimentally, in contrast with the subtle predictions of advanced functional renormalization group approaches [15, 17], but in close agreement with Monte Carlo simulations [16], for equivalent Ising-like systems with short-range forces. Another main reason is that, as soon as van der Waals forces are added to the theory, the upper critical dimension above which MF critical exponents are valid is lowered from $d_u = 3$ (short-range forces) to $d_u < 3$.

We have opted for a perturbative theory in which we examined the effect of weak LRF on the wetting transitions dictated by the theory incorporating short-range forces. This is perfectly in line with the experimental fact that the physics predicted by the theory involving

short-range forces is in good accord with the observed continuous wetting phenomenon in nonane/methanol [1, 2]. The most remarkable of our findings is that, slightly off two-phase coexistence, the LRF *are* perturbative, while all previous theoretical works indicated that, at coexistence, critical wetting is ruled out for agonistic LRF. As we emphasized, our results can be explained as a consequence of the action of a small bulk field, turning macroscopic wetting layers into mesoscopic ones.

Acknowledgments

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