Wetting of a symmetrical binary fluid mixture on a wall

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1. Introduction

It has long been appreciated that fluid phase transitions are influenced by geometrical confinement [1,2]. Such confinement may be imposed by rigid external constraints, for example the surfaces of porous media; or it may be an inherent feature of a system such as occurs when a liquid wetting film in equilibrium with its vapor is bound to a solid substrate [3]. In the latter case the liquid is confined between the rigid substrate and the flexible liquid-vapor interface. Depending on the strength of the substrate-fluid interactions and the proximity to liquid-vapor coexistence, a variety of surface phase transitions may occur [1].

It transpires that the surface phase behavior of a liquid film is particularly rich if the liquid possesses an additional internal degree of freedom. This situation occurs, for instance, in binary liquids, where the relative concentration of species constitutes an additional order parameter to the number density. Under appropriate conditions the density and concentration fluctuations can couple giving rise to complex wetting behavior. In this paper we describe mean field and Monte Carlo simulation studies of the wetting behavior of a symmetrical binary fluid mixture. In this a system, interactions between particles of the same species are identical, but differ from those between dissimilar species. As elucidated in ref. [4], it is possible to arrange that the bulk phase diagram of the symmetrical mixture exhibits a ‘λ’-line of continuous demixing transitions, terminating in a critical end point on the liquid side of liquid-vapor coexistence (c.f. figure 1). If such a fluid is placed in contact with a sufficiently attractive non-selective wall, complete wetting occurs at and above the critical end point temperature $T_{cep}$ as liquid-vapor coexistence is approached from the vapor side. But what happens for $T < T_{cep}$? Far from coexistence, the wetting film is sufficiently thin that demixing is suppressed. On approaching the coexistence curve, however, the film thickness grows and depending on the wall strength, the liquid may demix and wet the substrate. We find a number of novel wetting and premixing transitions associated with this process, which we outline below.

2. Ginzburg-Landau theory

The wetting behavior of the symmetrical binary fluid mixture can be probed within mean field theory via a generic Ginzburg-Landau functional incorporating two coupled order parameters. These order param-
etters are

\[ \phi(z) \equiv \rho(z) - \rho_c \]

\[ m(z) \equiv [\rho_A(z) - \rho_B(z)]/\rho(z) \]

where \( \rho(z) \) is the number density profile (\( z \) measures the distance from the wall) and \( \rho_c \) is the bulk critical density. \( \rho_A(z) \) and \( \rho_B(z) \) are the density profiles of the two species.

The Ginzburg-Landau free energy functional takes the form [5]

\[
F = \int d\rho \int dz \left\{ \frac{1}{2} \left( \frac{d\phi}{dz} \right)^2 + \frac{1}{2} \gamma \left( \frac{dm}{dz} \right)^2 \right\} + f(m, \phi) \]

\[ + \int d\rho f_s(m, \phi) \]

with bulk free energy density

\[
f(m, \phi) = -\frac{\phi^2}{2} + \frac{\phi^4}{4} + \theta \frac{m^2}{2} + \frac{m^4}{4} + \kappa(1 - \phi)m^2 - \mu\phi
\]

and bare surface free energy

\[
f_s(m, \phi) = \frac{1}{2} C_\phi \phi_o^2 - h_\phi \phi_o + \frac{1}{2} C_m m_o^2
\]

Here \( \mu \) is the chemical potential and \( \gamma \) measures the stiffness ratio of interfacial surface tensions of \( m(z) \) and \( \phi(z) \). The parameter \( \theta \) in the bulk term is a “temperature-like” variable controlling the deviation from the critical end point. The value of \( \kappa \) controls the degree of coupling between the two order parameters. On the basis of a previous study [4] we set \( \kappa = 1 \) which yields a bulk phase diagram of the topology shown in fig. 1. With regards to the surface terms, the tendency of the wall to favor mixing of a liquid film due to ‘missing neighbors’ is controlled by the \( C_m \) parameter. \( C_\phi \) and \( h_\phi \) specify, respectively, the degree of short range particle repulsion and attraction. The latter two parameters are set such as to yield a desired fluid density \( \phi_o \) at the wall, which we choose sufficiently large to ensure that the mixed liquid wets at bulk coexistence at and above \( T_{cep} \).

![Phase diagram](image1)

Fig. 1. Schematic phase diagram of the symmetrical binary fluid mixture in the density-temperature plane. Dashed line indicates critical demixing transitions, full curve the first order liquid-vapor coexistence envelope.

![Phase diagram](image2)

Fig. 2. Phase diagram in the \( \mu - \phi_o \) plane. Parameters are \( \kappa = 0.5, \theta = 0.1 \) and \( \gamma = 1.0, C_m = 0.2 \). Solid line indicates first order transition, dashed line second order transition.

Since the value of \( \phi_o \) effectively controls the wall-fluid interaction strength, we use it together with \( \mu \) to scan the wetting phase
diagram. This has been obtained by numerical minimization of equation 1. The specific wetting scenario that results depends on the choice of the parameters $\gamma$, $\theta$ and $C_m$. The results on a subcritical isotherm for a physically reasonable choice of these parameters are shown in figure 2. For sufficiently large $\phi_0$ we find a surface transition from a thin mixed film to a thick demixed film as bulk coexistence is approached. This transition can occur in a number of ways. For large $\phi_0$, there is a continuous demixing of the film as one passes through a line of continuous transitions. This line intersects and is truncated by a line of first order prewetting transitions at lower $\phi_0$. The point at which the two lines meet is a surface critical end point above which a thin and a thick demixed film coexist. The first order prewetting line continues to lower values of $\phi_0$. For states on this line below the critical end point, a thin mixed film coexists with a thick demixed film as shown in figure 3.

On decreasing the surface coupling $C_m$, it is found that the critical end point and the critical point move closer together until they merge in a surface tricritical point [5]. Small changes in the values of $\theta$ and $\gamma$ alter the details of the phase diagram, but not its general structure.

3. Grand canonical Monte Carlo simulation studies

The system we have studied is a symmetrical binary fluid, having interparticle interactions of the Lennard-Jones (LJ) form:

$$u(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

We made the following choice of model parameters: $\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma = 1$; $\epsilon_{11} = \epsilon_{22} = \epsilon_1\epsilon_{12} = 0.7\epsilon$, i.e. interactions between similar species are treated identically, but those between unlike species are weakened. This provides for a demixing transition at some finite temperature and indeed in a previous study [4] we found a bulk phase diagram of the topology of fig.1. The inter-particle potential was truncated at a distance of $R_c = 2.5\sigma$ and no long-range correction or potential shift was applied. Monte-Carlo (MC) simulations of this system were performed using a Metropolis algorithm within the grand canonical ($\mu, V, T$) ensemble [6].

The fluid was confined within a cuboidal simulation cell having dimensions $P_x \times P_y \times D$, in the $x, y$ and $z$ coordinate directions respectively, with $P_x = P_y = P$. The simulation cell was divided into cubic sub-cells (of size the cutoff $R_c$) in order to aid identification of particle interactions. Thus $P = pR_c$ and $D = dR_c$, with $p$ and $d$ both integers. To approximate a semi-infinite geom-
etry, periodic boundary conditions were applied in the $x$ and $y$ directions, while hard walls were applied in the unique $z$ direction at $z = 0$ and $z = D$. The hard wall at $z = 0$ was made attractive, using a potential designed to mimic the long-ranged dispersion forces between the wall and the fluid [7].

$$V(z) = \epsilon_w \left[ \frac{2}{15} \left( \frac{\sigma_w}{z} \right)^9 - \left( \frac{\sigma_w}{z} \right)^3 \right]$$

Here $z$ measures the perpendicular distance from the wall, $\epsilon_w$ is a ‘well-depth’ controlling the interaction strength, and we set $\sigma_w = 1$. No cutoff was employed and the wall potential was made to act equally on both particle species.

The choice of system size was, as ever, a compromise between minimizing finite-size effects and maximizing computational throughput. Tests showed the profiles to be largely insensitive to the size of the wall area and hence $p = 7$ was used, this being the largest computationally tractable size consistent with the necessary choice of the slit width $d$. The latter must clearly be considerably larger than the film thicknesses of interest in order to prevent the liquid film directly interacting with the hard wall at $z = D$. In the results presented below, the typical slit width used was $d = 16$, corresponding to some 40 molecular diameters. For thin films a narrower slit of width $d = 8$ was used.

To determine the wetting properties at temperatures below $T_{cep}$, the number density profile $\rho(z)$ was studied along the isotherm $T = 0.988T_{cep}$ as coexistence was approached from the vapor side. The location of bulk coexistence is accurately known from a previous detailed MC study [4] and is shown in fig. 4. The critical end point is located (in LJ units [6]) at $T_{cep} = 0.958(3), \mu_{cep} = -3.017(3)$.

Coexistence was approached along the path shown in fig. 4 by incrementing the chemical potential up to its coexistence value $\mu_{ex}(T)$ in a sequence of 6-10 steps of constant size $\Delta \mu = 0.0025$. This procedure was repeated for a number of different values of the wall-fluid potential strength $\epsilon_w$, allowing the influence of this parameter on the wetting behavior to be ascertained.

For small wall strengths, we find that the film remains thin and mixed right up to bulk coexistence, although a prewetting transition from a thin mixed film to a thicker mixed film is observed [5]. The situation changes however at intermediate

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phase_diagram.png}
\caption{The phase diagram in the $\mu$-$T$ plane of the symmetrical binary Lennard-Jones fluid model described in the text. Also shown is the location of the critical end point and the isotherm along which the wetting properties were studied.}
\end{figure}
Fig. 5. (a) Density profiles for \( \epsilon_w = 3.0 \). Data are shown for 6 values of \( \mu - \mu_{eq} \) in the range \([-0.025, -1.55]\) (b) The corresponding order parameter profiles \( m(z) \).

wall strengths. Fig. 5 shows the results for \( \epsilon_w = 3.0 \). As the chemical potential increases, the thickness of the film initially increases smoothly with increasing \( \mu \). However, once the thickness reaches some 10 molecular diameters, a large jump occurs to a thickness of about 15 molecular diameters. Concomitant with this jump is a demixing of the film as a whole, as seen in the order parameter profile of fig. 5(b). A configuration snapshot of the demixed film is shown in fig. 6. The size of the jump in the layer thickness appears to reduce as the wall strength is increased to \( \epsilon_w = 4.0 \) (fig. 7, suggesting a weakening of the transition. However owing to the slowness of the interfacial fluctuations, we have been unable to determine conclusively whether continuous demixing occurs for still larger \( \epsilon_w \).

Fig. 6. Configurational snapshot of the demixed thick liquid layer

Fig. 7. Density profiles for \( \epsilon_w = 4.0 \).
4. Discussion and conclusions

The Monte Carlo simulation results at subcritical temperatures provide evidence that the mean field calculations correctly identify the qualitative wetting behavior. They show that depending on the fluid-wall interaction strength $\epsilon_w$, it is possible to have a sharp prewetting transition from a thin mixed film to a thin demixed film, the situation being very similar to that shown in figure 3. The abrupt, first order, character of this latter transition appears to weaken on further increasing $\epsilon_w$, in accord with the theoretical predictions.

Other possible wetting scenarios can be envisaged in the vicinity of the critical end point $T_{cep}$. The state of order of the film depends strongly on the boundary conditions of the two interfaces confining the liquid layer. The non-selective liquid-vapor interface always favors mixing due to the low vapor density. The liquid-substrate interface, on the other hand, can either favor mixing or demixing depending on the strength of the fluid-wall potential. For a weakly attractive wall potential, mixing is favored because the particle density at the wall is low and the presence of the wall reduces the number of interacting neighbors. For a strongly attractive wall, however, the high density at the wall can counteract the missing neighbor effect leading to an overall demixing tendency.

If the net effect favors mixing at the wall, a continuous demixing of the layer as coexistence is approached can be excluded. The film is thus always mixed close to the critical end point, and its thickness below the critical end point is finite [5]. The situation changes if the substrate favors demixing.

Then one component segregates to the surface of the film already slightly above $T_{cep}$, and the order propagates continuously into the bulk of the film at $T_{cep}$, the film remaining wet at $T_{cep}$. However, the film may still exhibit a first order wetting transition to a non-wet state at a temperature below $T_{cep}$. In such a case the first order wetting transition spawns a prewetting line of the type shown in fig. 2 which eventually switches into a second order demixing line. Finally, if the wall is strongly attractive it will be wet at all temperatures and one can speculate that the prewetting line detaches from the coexistence line and is continued by second order demixing lines both at the high and low temperature side [5].

References