First-order layering and critical wetting transitions in non-additive hard sphere mixtures

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Using fundamental-measure density functional theory we investigate entropic wetting in an asymmetric binary mixture of hard spheres with positive non-additivity. We consider a general planar hard wall, where preferential adsorption is induced by a difference in closest approach of the different species and the wall. Close to bulk fluid-fluid coexistence the phase rich in the minority component adsorbs either through a series of first-order layering transitions, where an increasing number of liquid layers adsorbs sequentially, or via a critical wetting transition, where a thick film grows continuously.

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Studying the interfacial properties of liquid mixtures is of significant fundamental and technological relevance \cite{1}. Bulk liquid-liquid phase separation, which can arise at or close to room temperature, is usually associated with rich phenomenology of interfacial behaviour at a substrate. Gaining a systematic understanding of how the different types of intermolecular and of substrate-molecule interactions induce phenomena such as wetting, layering, and drying at substrates constitutes a major theoretical challenge. Relevant for surface adsorption of liquids are Coulombic and dispersion forces, but also solvent-mediated and depletion interactions which occur in complex liquids. Arguably the most important source for the emergence of structure in dense liquids is the short-ranged repulsion between the constituent particles; this may stem from the overlap of the outer electron shells in molecular systems or from screened charges or steric stabilization in colloidal dispersions.

Hard sphere fluids form invaluable reference models for investigating the behaviour of liquids at substrates. Both the pure \cite{2} \cite{3} and binary \cite{4} hard sphere fluids are relevant, the latter playing an important role when adding e.g. electrostatic interactions in order to study wetting of ionic liquids at a substrate \cite{5}. The most general binary mixture is characterized by independent hard core distances between all different pairs of species, and is referred to the non-additive hard sphere (NAHS) model. Here the cross species interaction distance can be smaller or larger than the arithmetic mean of the like-species diameters. The NAHS model gives a simplified representation of more realistic pair potentials, i.e. charge renormalisation effects in ionic mixtures in an explicit solvent induce non-additive effective interactions between the ions \cite{6}. It is also a reference model to which attractive or repulsive tails can be added \cite{7}. The Asakura-Oosawa-Vrij (AOV) model of colloids and non-adsorbing polymers \cite{8} is a special case where one of the diameters (that of the polymers) vanishes.

It is surprising that the wetting behaviour of the general NAHS model is largely unknown, given the fundamental status of the model. In this Letter we address this problem and consider the NAHS fluid at a general, non-additive hard wall. We find a rich phenomenology of interfacial phase transition, including two distinct types of surface transitions: one is layering, where the adsorption of one of the phases occurs through a number of abrupt jumps, and the other is critical wetting, where the thickness of the adsorbed film grows continuously when varying the statepoint along the bulk fluid-fluid binodal. Via changing the wall properties a crossover between these transitions occurs.

The binary NAHS model is defined by the pair potentials $v_{ij}(r)$ = $\infty$ for $r < \sigma_{ij}$ and 0 otherwise, where $i,j = s,b$ refers to the small and big species, respectively, $\sigma_{ss}$ and $\sigma_{bb}$ are the diameters of the small and big particles, respectively, and $r$ is the center-to-center distance.
The cross-species diameter is $\sigma_{sb} = \frac{1}{2}(1 + \Delta)(\sigma_{ss} + \sigma_{bb})$, where $\Delta \geq -1$ measures the degree of non-additivity, see Fig. 3 for an illustration of the length scales. The model is characterised by the size ratio, $q = \sigma_{ss}/\sigma_{bb} \leq 1$, and by $\Delta$. In this Letter we restrict ourselves to the asymmetric size ratio $q = 0.5$, and to positive non-additivity $\Delta = 0.2$, as a representative case. We relate $\Delta$ to a length scale via $d = \frac{1}{2}(\sigma_{ss} + \sigma_{bb})\Delta \equiv \sigma_{sb} - \frac{1}{2}(\sigma_{ss} + \sigma_{bb})$, where here $d = 0.3\sigma_{ss}$. The statepoint is characterised by two partial bulk packing fractions, $\eta_i = \pi\sigma_{ib}\rho_i/6$, where $\rho_i$ is the number density of species $i$. We define a general planar hard wall via the external potentials $u_i(z) = \infty$ if $z < l_i$, and 0 otherwise; here $z$ is the distance between the wall and the particle center, and $l_i$ is the minimal distance of approach of species $i = s, b$. Clearly the origin in $z$ is irrelevant, so the only further control parameter is the wall offset, $\delta l = l_b - l_s$. For additive hard sphere mixtures it is common to set $l_i = \sigma_{ii}/2$; for our model parameters this results in $\delta l = 0.5\sigma_{ss}$. Besides this ‘additive wall’, two further special cases are shown in Fig. 1(b). The $b$-type wall has properties similar to the big particles so that it sees these with their ‘intrinsic’ size $l_b = \sigma_{bb}/2$, but sees the small particles with their ‘non-additive’ size $l_s = \sigma_{ss}/2 + d$, such that $\delta l = 0.2\sigma_{ss}$. We expect that the bigger particles adsorb more strongly to this wall. Conversely, the $s$-type wall has properties similar to the small particles, so that it sees these with their ‘intrinsic’ size $l_s = \sigma_{ss}/2$, and sees the big particles with their ‘non-additive’ size $l_b = \sigma_{bb}/2 + d$, so that $\delta l = 0.8\sigma_{ss}$. Thus, one expects the small particles to adsorb more strongly.

We investigate the inhomogeneous NAHS fluid using a fundamental measure density functional theory [9, 10]. Comparison of theoretical results to Monte Carlo simulation data for bulk fluid-fluid phase diagrams [9, 10], partial radial distribution functions [9, 11] and density profiles in planar slits [12] indicates very good quantitative agreement. We obtain equilibrium density distributions $\rho_i(z)$ from the grand potential functional, $\Omega[\rho_s, \rho_b]$, by numerical solution of $\delta\Omega/\delta\rho_i(z) = 0$, $i = s, b$. To calculate coexisting (bulk or surface) states we use the equality of the chemical potentials $\mu_s$, $\mu_b$, and $\Omega$ in the two phases. The NAHS functional [9] features both a large number of terms and a large number of convolutions that take account of the non-locality. Therefore the accurate calculation of density profiles close to phase coexistence, and close to interfacial transitions, is a challenging task.

For $q = 0.5$ and $\Delta = 0.2$ the DFT predicts fluid-fluid phase separation with a critical point at $\eta_s = 0.049$, $\eta_b = 0.151$ – see Fig. 2(b). We start with the $b$-type wall, which we find does indeed preferentially adsorb the bigger particles. For $b$-rich statepoints the preferred species is already at the wall and no surface transitions occur. For $s$-rich statepoints at bulk coexistence, but far from the bulk critical point, we find that the small particles dominate the region close to the wall, but that there is a small amount of adsorption of the bigger particles. To illustrate this, see the pair of density profiles, $\rho_s(z)$ and $\rho_b(z)$, furthest from the bulk critical point in Fig. 2(a). Reducing $\eta_s$ along the binodal in the direction towards the bulk critical point, there occurs a series of discontinuous jumps of the density profiles. The first jump corresponds to the big particles displacing the small particles from the wall and forming a layer at a distance $\sigma_{bb}$ away from the wall, see Fig. 2(a). Each subsequent jump corresponds to the adsorption of an extra $b$-rich liquid layer at the wall. Using the coexistence criteria we have located five distinct layering transitions. Beyond the fifth transition we find that the layer rich in the big particles becomes macroscopically thick. We discuss the possible
nature of this transition below. The inset to Fig. 2(a) shows the adsorption, $\Gamma_i = \int dz \ [\rho_i(z) - \rho_i(\infty)]$, of each species $i = s, b$ as a function of $\eta$. Each plateau represents the range of statepoints along the binodal which have a particular number of adsorbed layers. The formation of the infinitely thick layer corresponds to $\Gamma_b$ jumping to $+\infty$, and $\Gamma_s$ to $-\infty$. The layering transitions are first-order surface phase transitions, characterised by a range of coexisting states. In Fig. 2(b) we plot the coexistence lines of the first two transitions in the $(\eta_s, \eta_b)$ plane. We find that the layering transitions intersect the bulk binodal [16] and that they lie very close to the binodal on the $s$-rich side of the phase diagram. Each transition terminates at a surface critical point, where the jump in $\Gamma_s$ vanishes. The first layering transition, where the big particles strongly adsorb at the wall and form the first layer, is the largest both in terms of the change in the densities and its size on the phase diagram. Each subsequent transition is smaller than the previous one.

We next turn to the $s$-type wall. As this preferentially adsors the smaller particles, tracing the bulk coexistence curve on its $b$-rich side is interesting. For statepoints far from the bulk critical point, we find that there is some adsorption of the small particles, but that big particles dominate the region close to the wall. The density profiles peak farther from the bulk critical point. In Fig. 3, where $\rho_i(z)$ exhibits oscillatory decay that indicates high-density packing effects. Increasing $\eta$ along the binodal in the direction of the bulk critical point, we find that the small particles start to adsorb more strongly at the wall, replacing the big particles. On moving further towards the bulk critical point, a thick film rich in the small particles grows. No jumps are observed and the thickness increases continuously and reversibly with the state point up to a wetting critical point, beyond which the film is infinitely thick, see Fig. 3. Hence we conclude that this wetting transition is critical. In such a case the adsorption can be shown [13, 14] to diverge as $\Gamma_i \propto \log(\eta_s^* - \eta_s)$. The inset to Fig. 2 compares the adsorptions to the asymptotic log-arithmetic form. The location of the wetting critical point, $\eta_s^* = 0.0043$ is shown in relation to the bulk binodal in the inset to Fig. 4.

We next vary the wall offset parameter, $\delta l$, between the two cases discussed above. Starting with the $b$-type wall, $\delta l/\sigma_{ss} = 0.2$, and increasing $\delta l$ we find the location of the layering transitions moves towards the bulk critical point. In Fig. 4, we show the value of $\eta_s$ at each of the intersections of a layering transition and the bulk binodal as a function of $\delta l$. The jump in adsorption at each layering transition becomes smaller and the extent of the line in the phase diagram becomes shorter (not shown). Decreasing $\delta l$ further, we find that at $\delta l/\sigma_{ss} \simeq 0.27$ the individual layering transitions bunch up and become indistinguishable from each other. For smaller $\delta l$ there is a single continuous wetting transition, where the thickness of the adsorbed $b$-rich layer grows logarithmically, in a similar manner to the behaviour at the $s$-type wall described above. We establish the location of the surface critical point by fitting $\Gamma_i$ to its asymptotic form and plot...
the value of $\eta^*_w$ at the wetting critical point in Fig. [1] Increasing $\delta l$ further results in the location of the wetting critical point moving further along the bulk binodal towards the bulk critical point so that at $\delta l/\sigma_{ss} \approx 0.43$ the wetting transition critical point coincides with the bulk critical point, and the wall is neutral such that neither species is preferentially adsorbed at the wall. As $\delta l$ is increased beyond 0.43 we find that the wetting transition moves to the $b$-rich side of the phase diagram. The additive wall, $\delta l/\sigma_{ss} = 0.5$, has a critical wetting transition, but located very close to the bulk critical point. As $\delta l$ is increased, the wetting critical point moves further along the bulk binodal, so that we return back to the $s$-type wall, $\delta l/\sigma_{ss} = 0.8$.

In order to ascertain the generality of our findings, we have investigated the trends upon changing the model parameters. For size ratio $q = 0.5$ and vanishing wall offset, $\delta l = 0$, we find layering transitions far from the bulk critical point for a range of non-additivity parameters $\Delta = 0.1, 0.2, 0.5$. Adjusting $\delta l$ towards the case of the additive wall, the layering transitions move towards the bulk critical point. We also investigated symmetric mixtures with $q = 1$ and $\Delta = 0.1$. Clearly, for the additive wall, $\delta = 0$, there is no preferential adsorption at the wall and hence no layering transitions. Introducing preferential adsorption via a non-vanishing wall offset, $\delta l = 0.1, 0.2, 0.3$, layering transitions occur, and these move away from the bulk critical point upon increasing $\delta l$.

In summary, we have shown that the NAHS model exhibits both layering and critical wetting transitions depending on the hard wall offset parameter. We expect this wetting scenario to be general and to occur in a large variety of systems where steric exclusion is relevant. A set of layering transitions had been previously found in the AOV model at a hard wall [5]. In these studies the wall parameter is equivalent to the $b$-type wall. As in these previous papers the existence of an infinite number of layering transitions is a possibility within our mean-field DFT treatment. The effects of fluctuations would be to smear out the higher-order layering transitions to produce a final ‘wetting’ transition as found here. A change from a first-order to a critical wetting transition is not uncommon [14]. What is remarkable here is that tri-critical behaviour can be induced in a purely entropic system by merely changing a non-additive wall parameter, $\delta l$. Moreover, the NAHS model is much less special than the AO model, as here both species (not only the AO colloids) display short-ranged repulsion and hence packing effects. In future work, it would be interesting to see the effects of non-additivity on wetting in charged systems where first-order and critical wetting transitions occur [5].

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[16] For a quantitative comparison of the bulk fluid-fluid demixing phase diagram from DFT to simulation results for $q = 0.1$ and 1, see Fig. 3 of Ref. [12] (location of the critical point) and Fig. 4 of Ref. [11] (binodals).