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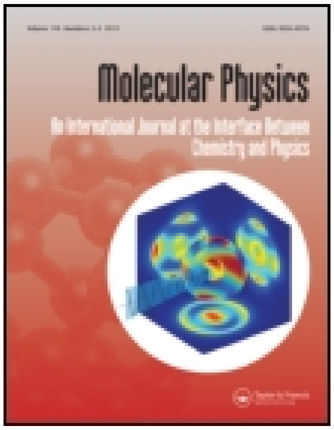

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Surface phase transitions of multiple-site associating fluids

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INVITED ARTICLE

Surface phase transitions of multiple-site associating fluids

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Surface phase transitions of Lennard–Jones (LJ) based two- and four-site associating fluids have been studied for various associating strengths using grand-canonical transition matrix Monte Carlo simulations. Our results suggest that, in the case of a smooth surface, represented by a LJ 9-3-type potential, multiple-site associating fluids display a prewetting transition within a certain temperature range. However, the range of the prewetting transition decreases with increasing associating strength and increasing number of sites on the fluid molecules. With the addition of associating sites on the surface, a quasi-2D vapor–liquid transition may appear, which is observed at a higher surface site density for weaker associating fluids. The prewetting transition at lower associating strength is found to shift towards the quasi-2D vapor–liquid transition with increasing surface site density. However, for highly associating fluids, the prewetting transition is still intact, but shifts slightly towards the lower temperature range. Adsorption isotherms, chemical potentials and density profiles are used to characterize surface phase transitions.

Keywords: surface phase transition; prewetting transition; quasi-2D vapor–liquid; associating fluids; Monte Carlo simulation

1. Introduction

Surface phase transitions are mainly due to the relative interactions of fluid–fluid and fluid–substrate molecules. The addition of sites on fluid molecules as well as on the surface can lead to different energetically or entropically favorable surface phase transitions such as layering transitions, prewetting transitions, capillary condensation, percolation, etc. The presence of surface sites can improve the structure of the adsorbed film through network-like bridging across adjacent layers which propagates towards the bulk of the system depending on the density or the special distribution or orientation of the surface sites. For example, with increasing hydroxyl group density on the silica surface, water adsorption on the surface increases significantly. Hydroxyl groups attached to the surface promote hydrogen bonds with interfacial water molecules, which compensates for the hydrogen bond loss in the bulk and induces different kinds of surface phase transitions. The arrangement of bond ordering in the proximity of the surface increases the stability of the adsorbed layer [1–4]. Similarly, water adsorption on activated carbons is significantly enhanced due to the presence of oxygenated surface groups [5–7]. With increasing surface polarity, the water adsorption isotherm shifts towards the low-pressure region. Eventually, small localized chemical groups such as hydroxyl or carboxyl on the graphene surface can induce water cluster formation around the group, which is sufficient to change the structure and dynamics of the adsorbed layer and can even lead to ice formation on the surface [8–10]. An ice-like structure is also found in a two-dimensional hydrogen-bond network on the hydrophilic mica surface due to the presence of K^+ ions [11–13]. Several studies have been performed on the adsorption of different polar molecules on different functionalized surfaces [14–17].

However, the role of surface sites in the phase behavior of polar molecules has not been well studied for molecular systems using molecular simulations due to the lack of adequate knowledge of real systems in terms of the atomistic representation of the system as well as force-field parameters and is also computationally expensive. Most studies are performed on surface wettability in terms of the contact angle of a droplet of molecular fluid on the surface to study the effect of surface polarity [18–20]. It has been shown that the wettability of the surface can be tuned by changing the surface polarity with the introduction of functional groups with varying site density. However, precise control of the adsorption of these molecular fluids is extremely difficult to study for other surface phase transitions. In this context, associating models are used extensively to study the surface phase

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transition of polar molecules and to predict various surface phase transitions such as interfacial percolation [21], layering transitions [22,23], prewetting transitions [24], dewetting transitions [25], etc. Several attempts have been made with multiple-site associating fluids with surface sites in the context of real systems such as water on activated carbon, etc., to study the different surface phase transitions and the results are in good agreement with experimental observations [6,26,27]. However, very few investigations have been performed to study the effect of surface sites and the number of fluid molecule sites on the surface phase transition [24,28]. To address the above, we investigate the influence of surface sites and their density on the surface phase transition of multiple-site associating fluids between the prewetting transition and the quasi-2D vapor–liquid transition. The rest of the paper is organized as follows. Section 2 describes the models and simulation methods used in the study. Simulation details are given in Section 3. Section 4 presents the results and a discussion followed by the conclusions in Section 5.

2. Model and methodology

2.1. *Model*

In this work, we study the surface phase transition of two-site and four-site Lennard–Jones (LJ) based associating fluids on a surface with active sites. Associating fluids are modeled as LJ potentials for isotropic van der Waals interactions between fluid molecules along with orientationally dependent square-well potentials to represent the off-center associating sites. These sites mimic the strong and short-range directional attraction of real associating fluids. In the case of the two-site associating fluid, sites are located opposite each other, and for the four-site associating fluid, sites are arranged in tetrahedral form similar in spirit to water models. The complete potential model [29] for the fluid–fluid interaction is

$$u_{ff}(r_{ij},\theta_i,\theta_j) = u_{LJ-tr}(r_{ij}) + u_{af}(r_{ij},\theta_i,\theta_j),$$

$$u_{af}(r_{ij},\theta_i,\theta_j) = \begin{cases} -\varepsilon_{af} & \text{if } \sigma < r_{ij} < r_c, \theta_i < \theta_c \text{ and } \theta_j < \theta_c, \\ 0 & \text{otherwise} \end{cases}$$

$$u_{LJ-tr}(r_{ij}) = \begin{cases} 4\varepsilon\left[\left(\frac{r_{ij}}{\sigma}\right)^{12} - \left(\frac{r_{ij}}{\sigma}\right)^{6}\right] & \text{if } r_{ij} \le r_{cut}, \\ 0 & \text{otherwise} \end{cases} \qquad (1)$$

where θ_i and θ_j are the angles between the center-to-center vector and the center-to-site vector of molecules *i* and *j*, respectively, ε_{af} is the association well depth, r_c is the range of the associating potential, σ and ε are the molecular size and energy parameter of the LJ potential, and r_{cut} is the cutoff diameter for the LJ potential. We adopt units such that σ and ε are unity. In this study, θ_c, r_c and r_{cut} are fixed at 27°, 1.00 and 2.5, respectively.

In this work, a structureless substrate with active sites is used similar to that used in our earlier work [28]. Sites are distributed uniformly on a rectangular grid on the surface as shown in Figure 1. The special distribution of surface sites depends on the surface site density (ρ_s). The substrate–fluid molecular interaction at distance *z* is specified by the following expression:

$$u_{wf} = u_{LJ-93}(z) + u_{aw}(r_{ij},\theta_i,\theta_j),$$

$$u_{LJ-93}(z) = \frac{2\pi}{3}\rho_w\sigma_w^3\varepsilon_w\left[\frac{2}{15}\left(\frac{\sigma_w}{z}\right)^9 - \left(\frac{\sigma_w}{z}\right)^3\right],$$

$$u_{aw}(r_{ij},\theta_i,\theta_j) = \begin{cases} -\varepsilon_{aw} & \text{if } \sigma < r_{ij} < r_c, \theta_i < \theta_c \text{ and } \theta_j < \theta_c, \\ 0 & \text{otherwise} \end{cases} \qquad (2)$$

where $\rho_w\sigma_w^3$, $\varepsilon_w/\varepsilon$ and σ_w/σ are set to 0.988, 1.2771 and 1.0962, respectively, which corresponds to the argon–solid CO_2 system [30]. The surface site–fluid associating interaction is also represented by a square-well potential with $r_c = 1.2$ and associating strength $\varepsilon_{aw} = 20$. In this study, the surface is placed at $z = 0$ and active sites are placed on the top of the virtual surface molecules. The centers of virtual molecules are located at $z = -0.5$. We have kept the surface particle radius the same as that of the fluid molecules. In this work, the site density, ρ_s, represents the number of associating surface sites per unit area. ρ_s is fixed at 1.0 unless otherwise stated.

2.2. *Methodology*

Grand canonical transition matrix Monte Carlo [31] (GC-TMMC) simulation along with histogram reweighting [32] is employed to evaluate the co-existence thermodynamic properties of thin and thick films adsorbed on the surface. Simulations are

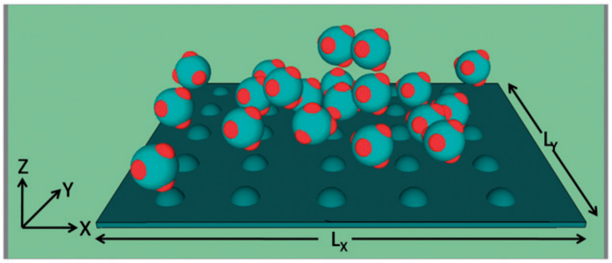

Figure 1. Schematic diagram of an associating molecule on a surface with associating sites.

performed in a grand-canonical ensemble at a constant chemical potential μ, volume V, and temperature T. In this work, four basic Monte Carlo (MC) moves are used, namely displacement, insertion and deletion, and rotation moves [33] to sample the entire phase space efficiently. The probability distribution among different density states is evaluated from the microscopic transition probability which is updated during different moves in matrix form. At regular intervals, we utilize the updated macrostate probability to bias the sampling towards low probability densities using the multicanonical sampling technique [34]. At subcritical temperature, a bimodal peak is observed in the probability distribution corresponding to coexistence phases at a given chemical potential. Histogram reweighting [32] is then used to evaluate the coexistence chemical potential and corresponding thermodynamic properties of coexistence phases. Details of GC-TMMC simulation techniques are given elsewhere [31].

3. Simulation details

To correlate the surface phase transition with the bulk phase diagram, bulk simulations are also carried out along with surface phase transition simulation for the same temperature range. Bulk simulations of a two-site and four-site associating fluid are performed in a cubic cell with cell length 8 to obtain the bulk saturation chemical potential with periodicity in three dimensions. Cell length 6 is used only for lower temperature systems. In this study, the associating strength is varied from 4 to 8 for two-site associating fluids and from 4 to 6 for four-site associating fluids. For comparison, we took the results for a one-site associating fluid from our earlier work [28,35]. Surface phase transition simulations are performed with a surface kept at the lower XY plane of the cell. The surface dimension is the same as the XY plane of the cell. The simulations in this work are conducted with $L_x = L_y = 9$. A repulsive wall is kept at a height larger than the substrate edge length. Different heights, $L_z = 20$, 40, 80 and 120, are used for lower temperatures to ensure that the hard wall has no affect on the properties. At lower temperature, the system size effect is very small (within 1–4%). However, at higher temperature, closer to the prewetting critical temperature, a substantially larger substrate area, 12×12, is used to avoid a system size effect on the phase transition.

4. Results and discussion

We start our discussion with the surface phase transition of a multiple-site associating fluid with varying site strength on a smooth surface. We observe a first-order transition of thick and thin films for different temperature ranges depending on the number of sites and the site strength of the associating fluid. The excess surface densities of thick and thin films are evaluated from the particle probability distribution at the coexistence chemical potential as described in the methodology section, and subsequently subtracted from the bulk phase density, with coexisting thin and thick films as used in our earlier work [28,35]. Figure 2 presents the excess surface density of thick and thin films, on a smooth surface, at various temperatures for different associating fluids. In general, the thin film density decreases and the thick film density increases with decreasing temperature. For comparison, Figure 2 also includes the coexisting thin and thick film density data for a non-associating fluid, which is basically the argon–solid carbon dioxide model. This system is well recognized and has been used by many investigators with different approaches [30,36–41]. It has been found that locating the locus of the prewetting line close to the bulk saturation line is very difficult when using the usual methods, as seen from earlier studies. Hence the wetting temperature (T_w) for the same system is quite diverse, varying from 0.58 to 0.96, depending on the method and the temperature range considered for evaluating T_w. For example, Finn and Monson [38] found $T_w = 0.84$ by extrapolating the locus of the prewetting line for the temperature range 0.85 to 0.92. However, the wetting temperature is found to be much lower in the work of Shi *et al.* [39], where the coexistence chemical potential difference between the bulk and the prewetting transition ($\Delta\mu$) as a function of T is used to evaluate the wetting temperature. The latter authors found that, depending on the different forms of fitting (power law or linear), T_w varied from 0.53 to 0.623. Errington [41] subsequently examined the same system using GC-TMMC, which enabled him

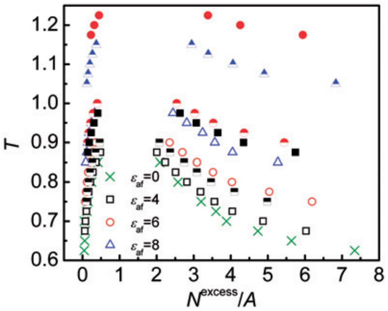

Figure 2. Surface phase coexistence curves for multiple associating fluids at $\rho_s = 0.0$ (smooth surface). The cross, open, half-open and closed symbols represent zero-site, one-site, two-site and four-site associating fluids, respectively.

to capture the coexistence thin and thick films close to the bulk saturation line and found $\Delta\mu$ to follow the power law $(T–T_w)^{3/2}$, which is also predicted by theory [42]. Recently, Errington and co-workers studied various aspects of the prewetting transition for the same system using the GC-TMMC method [43–45]. We employed the same methodology to evaluate the prewetting transition for associating fluids, and our results are in agreement with those of Errington and co-workers for the non-associating system. It is apparent that an increase in the number of sites on the fluid molecules promotes a more compact structure of adsorbed layers through association with adjacent molecules. This is clearly evident from the behavior of the thick film density with increasing number of patches on the molecules. In general, an increasing number of patches on the molecules decreases the thin film density and increases the thick film density at a constant temperature. However, the change in thick film density is quite significant compared with the thin film density due to an increase in bond formation in the thick film. For all cases, the thick film density increases with decreasing temperature and tends to diverge at lower temperature, which is a clear indication of a prewetting transition. In the case of a one-site associating fluid, the change in the thick film density with increasing associating strength at a constant temperature is quite significant in the higher association range ($\varepsilon_{af} > 6$) due to an increase in dimers in the thick film, which was also evident in our earlier work [35]. However, the change in thick film density with increasing associating strength is quite noticeably even in a lower association range ($\varepsilon_{af} > 0$) for two-site and four-site associating fluids. As the sites are located opposite to each other in the case of a two-site associating fluid, the thick film should contain linear chain clusters, as seen from the bulk liquid phase for a square-well-based associating fluid [33], and hence the reason for the enhancement in the thick film density compared with that for a one-site associating fluid with increasing associating strength. Decreasing temperature promotes two-site molecules to organize with the propensity to form a chain structure, allowing the thick film to thicken. Hence, the rate of thick film growth increases with decreasing temperature and results in shrinkage of the phase diagram. This is more pronounced in the case of a four-site associating fluid where molecules are able to form three-dimensional complex structures. For instance, increasing the associating strength from 4 to 6 in the case of a four-site associating fluid results in a significant decrease in the temperature range of the phase diagram. This suggests that the coexistence of thin and thick films beyond an associating strength of $\varepsilon_a = 6$ may be difficult to observe. This may be the reason for the lack of literature on the prewetting transition of water, whose associating strength is much higher than the values considered in this work.

We now move on to the surface phase transition of different associating fluids on functionalized surfaces. Figure 3 presents the surface phase transitions of two-site associating fluids on smooth and functionalized surfaces. The presence of surface sites encourages competition for site–site interaction between fluid–fluid and fluid–substrate. At higher associating strength, $\varepsilon_{af} > 6$, the growth of thick films is suppressed or delayed in the presence of surface sites, and this is more prominent in the case of associating strength $\varepsilon_{af} = 6$, where the site–site interaction of fluid–substrate is comparable to that of fluid–fluid. For example, the film thickness at temperature $T = 0.90$ for associating strength $\varepsilon_{af} = 6$ is significantly less than on a smooth surface, which may be due to the disruption of chain formation in the presence of surface sites. As a consequence, the thin–thick phase envelope shifts towards a lower temperature region. As a result the span of the prewetting transition for associating strength $\varepsilon_{af} = 6$ increases significantly in the presence of surface sites, which is not seen for the one-site associating fluid [28], for which thick films do not diverge at lower temperature and finally lead to a layering transition. In contrast to the higher associating fluids, the phase behavior at lower associating strength ($\varepsilon_{af} = 4$) for the two-site associating fluid on a functionalized surface is very similar to that of the one-site associating fluid [28]. Interestingly, the thick film densities at $\varepsilon_{af} = 4$ are almost the same irrespective of the number of sites, implying that the number of sites on the fluid molecules does not play any role in the phase behavior at lower associating strengths. At associating strength $\varepsilon_{af} = 4$, the thick film density initially increases and then decreases with decreasing

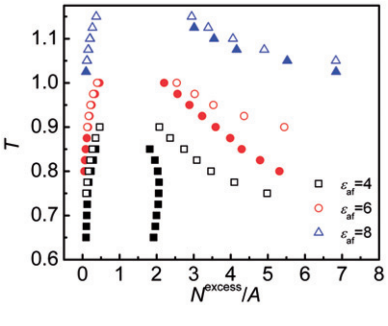

Figure 3. Surface phase coexistence curves for the two-site associating strength at $\rho_s = 0.0$ and 1.0. Open and closed symbols represent the smooth surface and a functionalized surface, respectively.

temperature, similar to the one-site associating fluid in the presence of surface sites, which is found to undergo a quasi-2D vapor–liquid transition [28]. However, the prewetting transition prevails for a smooth surface at $\varepsilon_{af} = 4$.

To locate the crossover behavior between prewetting and quasi-2D vapor–liquid transitions, we studied a two-site associating fluid with $\varepsilon_{af} = 4$ for varying surface site densities and the results are shown in Figure 4. The crossover behavior is more pronounced in the case of a two-site associating fluid than for a one-site associating fluid. At lower surface site density ($\rho_s = 0.0$ and 0.3) the thick film of the two-site associating fluid thickens with increasing temperature, indicating prewetting transitions. Interestingly, at higher surface site density ($\rho_s = 0.6$ and 1.0), the thick films are more suppressed in the case of the two-site associating fluid and display a maximum density at an intermediate temperature ($T = 0.75$). In our earlier work [28], we showed that the quasi-2D vapor–liquid transition finally split into a layering transition for a one-site associating fluid at a higher surface site density. The adsorption isotherms of the two-site associating fluid at lower temperature ($T < 0.55$) are also found to have layering-type transitions (results not shown). We resort to density profiles to understand such crossover behavior at lower associating strength.

Figure 5(a) presents the density profile of thin and thick films for a two-site associating fluid on functionalized ($\rho_s = 1.0$) and smooth ($\rho_s = 0.0$) surfaces at different temperatures. Each peak in the density profile represents the molecular layers of thick and thin films. Away from the surface the density of each peak decreases and eventually merges with that of the bulk phase. The number of molecular layers is sensitive to the temperature in the case of a smooth surface and varies from four to six layers for thick films and from one to two layers for thin films. On the other hand, for a functionalized surface with $\rho_s = 1.0$, the number of molecular layers close to the surface is limited to four and the extent of the thick film is quite insensitive to temperature. The first layer, which is not seen for the smooth surface, is due to the interaction of surface sites with fluid molecules. Molecules in this layer are oriented towards the surface and are rather sensitive to temperature. An increase in molecules in this layer with decreasing temperature could be the reason for the shift in the nature of the phase transition. Interestingly, the location of the third peak in the density profile of thick films shifts slightly to the left side (i.e. closer to the surface) with decreasing temperature. In the case of a smooth surface (see inset of Figure 5(a)) this peak is located at $z = 2.0$, whereas for a functionalized surface at $\rho_s = 1.0$ it shifts to 1.7 at $T = 0.75$, where we observe the maximum thick film density (see Figure 3). This is in contrast to the behavior seen for the case of a smooth surface. A shift in the location of the third peak is also seen with varying surface site density at temperature $T = 0.75$, which is shown in Figure 5(b). The third peak approaches closer to the surface with increasing site density. There is a distinct crossover behavior in the nature of the third peak. As the site density increases, the third peak, which is sharp, shifts slightly towards the surface. However, at the intermediate site density of $\rho_s = 0.6$, the behavior of the third peak changes and it broadens, which perhaps indicates a change in the nature of the phase transition. The subsequent increase in site density brings back the sharpness of the third peak and also shifts the peak closer to the surface. This indicates that increasing surface site density compresses the adsorbed layers and, at a certain surface ($\rho_s < 0.6$), the surface phase transition changes from a prewetting type to a quasi-2D vapor–liquid transition. It is evident that the nature of the density (or density profiles), as a function of temperature and surface sites, provides an indication of two different types of phase transition. However, for better accuracy, a more rigorous calculation, as shown below, can be done to identify the surface phase transition.

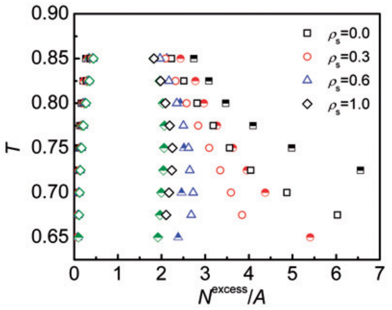

Figure 4. Surface phase coexistence curves for $\varepsilon_{af} = 4$ at different surface site densities for associating fluid. Open and half open symbols represent one-site and two-site associating fluid, respectively.

In the case of a prewetting transition, $\Delta\mu$ (difference between the bulk and prewetting chemical potentials) decreases with decreasing temperature and finally vanishes at the wetting temperature (T_w) where the thickness of the adsorbed layer diverges [35], whereas in the case of a quasi-2D vapor–liquid transition, $\Delta\mu$ increases with decreasing temperature [28,46]. We use this relation to resolve the type of phase transition with different surface site densities. Figure 6 shows $\Delta\mu$ as a function of temperature for a two-site associating fluid at different surface site densities. It clearly shows that $\Delta\mu$ approaches zero in the case of $\rho_s = 0.0$ and $\rho_s = 0.3$ and should wet the surface at a certain temperature.

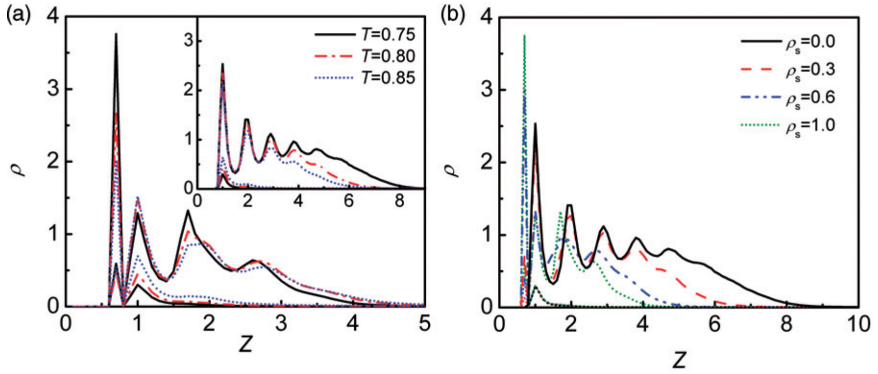

Figure 5. Local number density profile for coexistence phases for $\varepsilon_{af} = 4.0$, (a) at $\rho_s = 1.0$ and $\rho_s = 0.0$ (inset) and (b) at $T = 0.75$.

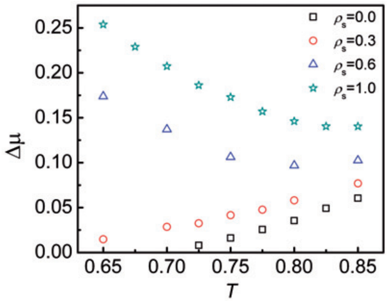

Figure 6. Difference of the bulk saturation chemical potential and the chemical potential for the surface phase transition of the two-site associating fluid vs. temperature for $\varepsilon_{af} = 4$.

Hence, at lower surface site densities the associating fluid undergoes prewetting transitions. On the other hand, at higher surface site densities ($\rho_s = 0.6$ and $\rho_s = 1.0$), $\Delta\mu$ decreases slightly and then increases with decreasing temperature. This suggests that, at higher surface site densities, the surface phase transition is of quasi-2D vapor–liquid type.

So far we have determined that the quasi-2D vapor–liquid transition is mainly due to the presence of highly dense surface sites for a lower associating fluid. Now we turn our attention to determine the wetting temperature for those systems that exhibit a prewetting transition. Theory [42] predicts that $\Delta\mu$ should scale as $(T - T_w)^{3/2}$ in the case of a prewetting transition for a surface potential with van der Waals tail $\sim 1/z^3$. To this end, we calculate $\Delta\mu$ for a series of temperatures for different associating fluids and linearly extrapolate to zero to evaluate the wetting temperature (T_w); the results are shown in Figure 7(a) for a smooth surface. For a non-associating fluid, using the aforementioned scaling relationship for the temperature range $T = 0.65$–0.725, we found $T_w = 0.5836(2)$, which is in good agreement with the value reported by Sellers and Errington [44]. However, recently, Grzelak and Errington [45] found that the locus of the prewetting line in the vicinity of the bulk saturation line is sensitive to the system size and hence can affect the estimation of the wetting temperature. In order to evaluate the system size effect in the current work, we considered a one-site model on a smooth surface as an example with $\varepsilon_{af} = 0$ and 4. The wetting temperature corresponding to $L = \infty$ is calculated by varying the system size from $L = 9$ to $L = 16$. The infinite size $T_w(L = \infty)$ values obtained for both $\varepsilon_{af} = 0$ and 4 are within 1–2% of $T_w(L = 9)$. The wetting temperature (T_w), in general, increases with increasing associating strength and number of molecular sites. To provide an idea of the complete range of the prewetting transition of each associating fluid, end data points are taken very close to the prewetting critical temperature and wetting temperature. We observe that the range of the prewetting transition shrinks as it shifts towards the right and forms a triangle-like shape. A similar observation was also made while studying the influence of substrate strength on the prewetting regime of LJ particles [44]. The range of the prewetting transition shrinks with decreasing substrate strength and vanishes at a certain substrate strength. In this work, on the contrary, the substrate strength is not changed while the fluid–fluid interaction is varied by introducing site–site interactions on fluid molecules, although the end result is the same, i.e. the relative interaction between fluid–fluid and fluid–substrate is changed. Interestingly, the prewetting regime for all associating fluids falls within this triangle. Hence, the triangle can provide a complete picture of the region of the prewetting transition for all associating fluids with variable sites (0 to 4) and associating energy (0 to 8). For example, the prewetting transition for a one-site associating fluid can be observed for a large value of

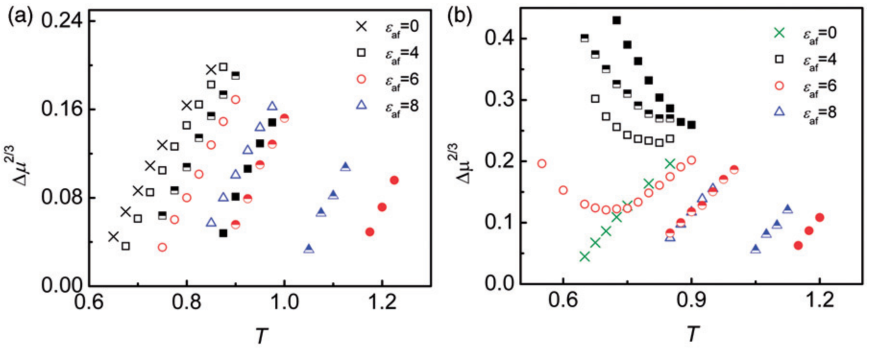

Figure 7. Difference of the bulk saturation chemical potential and the chemical potential for the surface phase transition vs. temperature for multiple-site associating fluids (a) at $\rho_s = 0.0$ and (b) at $\rho_s = 1.0$.

the associating strength, whereas for two- and four-site associating fluids the prewetting transition should be absent beyond an associating strength of 8 and 6, respectively. This suggests that the prewetting transition of multiple-site associating fluids with high associating strength would be very difficult to observe, which is evident from the very few experimental observations for polar molecules [47]. This behavior is in line with that observed for relatively weaker substrate strengths (equivalent to the case of relatively stronger fluid–fluid interactions as studied in this work) by Sellers and Errington [44]. The agreement between the prewetting regimes of two different systems suggests the existence of a generic prewetting phase region, which, with future work, particularly on complex fluids, may be confirmed.

The wetting behavior of multiple-site associating fluids on a functionalized surface, on the other hand, is relatively complicated and is shown in Figure 7(b). At a lower associating strength, $\varepsilon_{af} = 4$, all associating fluids undergo a quasi-2D vapor–liquid transition. Interestingly, at $\varepsilon_{af} = 4$, a four-site associating fluid is more prone to a quasi-2D vapor–liquid transition than a one-site associating fluid. On the other hand, at a higher associating strength ($\varepsilon_{af} = 8$), all associating fluids show a prewetting transition. However, for associating strength $\varepsilon_{af} = 6$, a one-site associating fluid still undergoes a quasi-2D vapor–liquid transition.

5. Conclusion

Molecular simulation is used to investigate the surface phase transition of multiple-site associating fluids. A prewetting transition is found for the multiple-site associating fluid on a smooth surface. The regime of the prewetting transition shifts towards a higher temperature range with increasing associating strength as well as with the number of sites on fluid molecules with shrinking of the prewetting range and forms a triangle-like shape of the prewetting regime bounded by the wetting temperature and the prewetting critical temperature. This behavior interestingly is in agreement with Ref. [44], where the substrate strength is varied, effectively changing the relative fluid–fluid interaction as also done in this work. The triangular regime suggests that the prewetting transition of one-site associating strength can be found for larger values of the associating strength, whereas for two- and four-site associating fluids it is restricted to 8 and 6, respectively. This may be one of the reasons why the prewetting transitions of multiple-site associating fluids such as hydrogen fluoride, water, etc. are sparse or not known in nature. However, the prewetting transition of a one-site fluid such as alcohol or acetone can readily be found for different surfaces, which is also evident from experimental observation [47].

We also observed that the growth of the thick film is substantially suppressed in the presence of surface sites for low associating fluids with decreasing temperature. This is a characteristic feature of the quasi-2D vapor–liquid transition where the coexistence chemical potential shifts away from the bulk saturation line with decreasing temperature and finally splits into a layering transition. In the presence of surface sites, we observed an additional fluid layer adjacent to the surface which is closely bound with surface sites. The number of molecules in that layer increases with decreasing temperature and significantly affects the subsequent layers, and is responsible for the shift in the nature of the phase transition. However, at higher associating strength, the prewetting transition, although intact, shifts slightly towards a lower temperature range.

This study provides a clear picture of the prewetting and quasi-2D vapor–liquid transitions of associating (polar) molecules with one to four sites. However, the calculations are expensive and hence it is not practical to use the current method to obtain global surface phase diagrams for real polar molecules. Nevertheless, the current work can be used to improve the ability of density functional theory in the prediction of the surface phase transition of complex molecules.

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