Surface Transitions for Confined Associating Mixtures

Michael Kotelyanskii, Sanat K. Kumar

Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802.

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Abstract

Thin films of binary mixtures that interact through isotropic forces and directionally specific “hydrogen bonding” are considered through Monte Carlo simulations. We show, in good agreement with experiment, that the single phase of these mixtures can be stabilized or destabilized on confinement. These results resolve a long standing controversy, since previous theories suggest that confinement only stabilizes the single phase of fluid mixtures.
The phase behavior of mixtures in thin films can be significantly different from the bulk [3–14]. Fisher et al. theoretically considered an incompressible fluid mixture which interacted with isotropic nearest neighbor forces and showed that confinement only stabilized the single phase [4–7]. This prediction is robust, and cannot be altered by the magnitude of the interaction between the fluids and the walls.

Experiments, however, show that, depending on the surfaces, confinement can either stabilize or destabilize the single phase relative to the bulk [9–12]. Since the model of Fisher corresponds to the simplest case of a binary fluid with isotropic nearest neighbor forces, a model with more complex interactions could rationalize the experiments [7]. We have performed Monte Carlo simulations on mixtures which interact with isotropic nearest neighbor interactions and directionally specific bonds. The competition between the unfavorable dispersive interactions, and the favorable “hydrogen bonds” (HB) leads to closed loop phase diagrams in the bulk. While the bulk behavior of HB systems has been well explored [15–19], their behavior in confined geometries has not been studied theoretically. We find that, when these systems are confined between plates which only interact through HB with the molecules, both stabilization [“ordinary”] and destabilization [“surface transition”] behavior can occur depending on the specific parameters employed. To our knowledge this represents the first theoretical evidence for surface transitions for a confined binary mixture.

A binary fluid mixture with isotropic nearest neighbor interactions is isomorphic with the spin 1/2 Ising model. Consider an Ising system confined between two symmetric walls which are \( D \) layers apart. \( J \) and \( J_1 \) are the spin coupling parameters in the bulk and in the surface layers, respectively [3]. \( \Delta \equiv \frac{J_1 - J}{J} \) has a special value, \( \Delta_c \), so that when \( \Delta < \Delta_c \) the phase mixed state is stabilized in the thin film (“ordinary” behavior) [3,4]. In contrast, when
$\Delta > \Delta_c$ the surface undergoes critical ordering even when the bulk is phase mixed (“surface transition”) [20,21]. For the case of simple mixtures it has been shown that $\Delta < \Delta_c$ and hence only ordinary behavior is predicted [3–7]. We shall show here that the introduction of a new interaction, the HB, could, under certain circumstances result in $\Delta > \Delta_c$, and thus yield complex surface behavior that is consistent with experiment.

We consider a completely filled cubic lattice with its sites occupied by either $A$ or $B$ molecules. We model symmetric mixtures where the interactions between any two $A$ molecules, and any two $B$ molecules are identical. The molecules interact through isotropic nearest neighbor interactions characterized by the energy scale: $\chi \equiv (d/2k_B T)(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$. $d$ is the coordination number ($=6$), and $\epsilon_{ij}$ is the interaction energy between a nearest neighbor $i-j$ pair. Therefore, $\chi = 6/T^* \ [T^* = k_B T/((\epsilon_{AB} - \epsilon_{AA})]$.

Each molecule has one “donor” and one “acceptor” which can participate in nearest neighbor HB. Since the molecules are structureless the donors and acceptors do not have prespecified locations. The HB interactions are described by two equilibrium constants $k_{AA}$ and $k_{AB}$ for the bonds between an $A$ donor and an $A$ acceptor on different molecules, and for bonds between $A$ and $B$ particles [either one being the donor], respectively. $k_{ij} \equiv P_{ij} e^{-E_{ij}/k_B T}$ [22]. We employed $k_{AA} = 0.0275 e^{1.8/T^*}$, and $k_{AB} = 0.0134 e^{4.5/T^*}$.

While we have explored the phase behavior for a range of values of $\chi$, $k_{AA}$ and $k_{AB}$, we focus on this one set of parameters which yields closed loop phase behavior for the bulk mixture.

In simulations of the bulk [23] we employed periodic boundary conditions in all three directions. For thin films the periodic boundary conditions along the $z$ direction were replaced by two symmetric hard walls. The walls could only interact with the molecules through HB, i.e., $k_w \equiv P_w e^{-E_w/k_B T}$ independent of the identity of the molecule. The Monte
Carlo simulations utilize the symmetry of the system and locate phase coexistence through the semigrand ensemble method \cite{24} with the condition that $\Delta \mu \equiv \mu_A - \mu_B = 0$. $\mu_i$ is the chemical potential of species $i$. An elementary Monte Carlo move is to change the identity of a randomly chosen particle. The move is accepted following the standard Metropolis criterion \cite{24}. Another elementary move consists of the creation or elimination of a HB.

The composition of the mixture $x = N_A/(N_A + N_B)$, where $N_i$ is the number of $i$ particles, is variable and the binodal can be determined from histograms of its distribution, $P(x)$. When the system is miscible $P(x)$ has a maximum at $x = 1/2$. In the immiscible regime two maxima are observed at $x = 1/2 \pm x_b$, corresponding to the coexisting phases.

In Figure 1 the binodals for the bulk and for three films of $D=16$ are shown. The bulk system displays closed loop phase behavior, a feature that is characteristic of many HB mixtures \cite{15-19}. If one defines the critical temperatures as the maxima of susceptibility \cite{25}, then, the upper critical solution temperature [UCST] is at $T_{ucst}^* = 1.94 \pm 0.04$, while the lower critical solution temperature [LCST] is at $T_{lcst}^* = 1.02 \pm 0.02$ [see Figure 3]. This result is obtained for system sizes of $8 \times 8 \times 8$ and $16 \times 16 \times 16$, and appears to be effectively independent of system size in this range. Note that a system with no HB interactions reduces to a standard 3-d Ising model with a critical temperature of $T_0^* = 2.25$.

We now consider this HB mixture when it is confined between two hard, non-interacting walls. The mixed state is stabilized and the film binodal lies “inside” the bulk binodal. $T_{ucst}^* = 1.80 \pm 0.05$ and $T_{lcst}^* = 1.03 \pm 0.02$. This behavior is in line with previous predictions that simple systems only show “ordinary” behavior when confined \cite{3,7,13}. When specific interactions are allowed between the molecules and the walls, the phase behavior of the film changes qualitatively. This is the essential point of our paper. The two other curves
in Figure 1 correspond to \( k_w = 0.0134e^{4.5/T^*} \) and \( k_w = 0.0134e^{10/T^*} \), respectively. In both cases the LCST is destabilized, and the UCST is stabilized on confinement. In the first case \( T_{ucst}^* = 1.90 \pm 0.05, T_{ucst}^* = 0.98 \pm 0.02 \), while \( T_{ucst}^* = 1.90 \pm 0.05, T_{lcst}^* = 0.99 \pm 0.02 \) in the second case.

To understand these issues better, in Figure 2 the composition in the surface layer, and in the center of the \( D = 16 \) films are plotted. Only composition values different from \( x = 1/2 \) are plotted for clarity. In all cases the data from the center of the film virtually coincide with the bulk binodal. When the walls are neutral, the composition in the surface layer is closer to 0.5 than in the bulk. This is consistent with the "ordinary" transition behavior observed in this case. Similar behavior is observed near the UCST with the interacting walls. In contrast, in the vicinity of the LCST the surface is "more ordered" than the bulk, a signature of "surface transition" behavior. Figure 2 shows plots of susceptibility as a function of temperature for the middle and surface layers in the \( D = 16 \) film with \( k_w = 0.0134e^{(4.5/T^*)} \). The susceptibility of the middle layer tracks the bulk behavior, consistent with trends observed in Figure 2. In the vicinity of the LCST the surface layers show a distinct peak, consistent with the notion of a "surface transition". Notice also that in the case with strongest wall interactions, the film surface remains ordered even when the middle layers becomes mixed below the LCST.

The transition from "ordinary" behavior around the UCST to the "surface transition" at the LCST occurs through the "extraordinary transition", when the surface composition equals that in the middle of the film. This occurs at \( T^* \approx 1.10 \) for \( k_w = 0.0134e^{(4.5/T^*)} \), and at \( T^* \approx 1.60 \) with \( k_w = 0.0134e^{(10.0/T^*)} \).

A way to qualitatively understand these findings is as follows. When the walls are
non–interacting, the only effect of confinement is the loss of neighbors for molecules in the surface layer. Since this reduces the net unfavorable interaction energy of the system it stabilizes the single phase. In contrast, in the case of interacting walls, HB interactions occur between the wall and the molecules. Since each molecule has only one HB donor and one HB acceptor, the number of HBs between molecules within the surface layer is reduced due to the presence of the interacting walls. This effect is shown in Figure 4, where we plot the average number of molecule-molecule and molecule-wall HB contacts for the surface layer where $k_w = 0.0134e^{10/T^*}$. Since molecule-molecule HBs are one of the strong factors aiding the miscibility of these systems, and are primarily responsible for the LCST, it is clear that the single phase must be destabilized in the thin films. In fact, at the lowest temperatures in Figure 4 all donors and acceptors on molecules in the surface layer are occupied by the HB’s with the walls. Thus, only isotropic nearest neighbor interactions occur between these molecules, as well as with molecules in the adjacent layer (i.e., $z = 1$). Since a bulk system with isotropic nearest neighbor interactions only possesses a UCST, to a zeroth approximation, the surface will remain ordered at all low temperature conditions.

In summary, we have presented results of Monte Carlo simulations which show that the phase behavior of an associated fluid mixture in a thin film geometry can be qualitatively different from simple mixtures, which show only “ordinary” behavior. The phase behavior of such HB mixtures, which are defined by the balance of specific and dispersive interactions, can be disturbed at interfaces, leading to the occurrence of a surface transition. This finding strikingly rationalizes experimental results where surface transitions appear to be ubiquitous.

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REFERENCES

[1] e-mail address:kotelyan@plmsc.psu.edu.

[2] e-mail address:kumar@plmsc.psu.edu.

[3] H. Nakanishi and M.E. Fisher. Phys. Rev. Lett., 49:1565, 1982.

[4] M.E. Fisher. In M.S. Green, editor, Critical Phenomena, volume 51 of Proceedings of the Enrico Fermi International School of Physics, New York, 1971. Academics.

[5] M.E. Fisher and H. Nakanishi. J. Chem. Phys., 75:5857, 1981.

[6] H. Nakanishi and M. Fisher. J. Chem. Phys., 78:3279, 1983.

[7] H. Nakanishi and M.E. Fisher. J. Phys. C., 16:L95, 1983.

[8] S. Mader. Thin Solid Films, 35:195, 1976.

[9] M. R. Meadows, B. A. Scheibner, R.C. Mockler, and W.J. O’Sullivan. Phys. Rev. Lett., 43:592, 1979.

[10] B. A. Scheibner, M. R. Meadows, R.C. Mockler, and W.J. O’Sullivan. Phys. Rev. Lett., 43:590, 1979.

[11] S. Reich and Y. Cohen. J. Polym. Sci. Poly. Phys. Ed., 19:1255, 1981.

[12] V.M. Andreyeva, A.I. Dolinyy, A.B. Burdin, and Kozhevnikova Y.A. Flu. Mech. Res., 21:72, 1992.

[13] K. Binder. Phase Transitions, 8:2, 1983.

[14] T.C. Lubensky and M.H. Rubin. Phys. Rev. B, 12:3885, 1975.
In this model we have assumed that the molecules are unstructured, and consequently the donor and acceptor sites can be located at arbitrary points. Since the HB formation leads to a reduction in the entropy of the molecules, a factor which is not taken into account \textit{a – priori}, we have introduced a prefactor that accounts for this factor in the definition of the equilibrium constants.
FIG. 1. Binodals for the bulk system (thick solid line), and for the $D = 16$ film with $k_w = 0.0134 e^{10/T^*}$ (squares), $k_w = 0.0134 e^{4.5/T^*}$ (diamonds), and without specific interactions with the wall, (circles).
FIG. 2. Compositions in the surface layer (filled symbols) and middle layers (hollow symbols) of the $D = 16$ film at the same conditions as fig. [1]. Circles - neutral walls with no interactions, squares and diamonds - walls with specific interactions. Squares – $k_w = 0.0134 e^{10/T^*}$, and diamonds – $k_w = 0.0134 e^{4.5/T^*}$. Bulk binodal (thick solid line, same as fig. [1]) is shown for the reference.
FIG. 3. Susceptibilities $\chi$, obtained from the mean squared deviations of $x_A$, vs. temperature for $D = 16$ film with $k_w = 0.0134 e^{4.5/T}$. Filled diamonds – surface layers ($z = 0$, and $z = 15$), hollow symbols – middle of the film ($z = 7$, and $z = 8$). Susceptibility with no surfaces and periodic boundary conditions is plotted for the reference (thick solid line).
FIG. 4. Number of hydrogen bonds per site in the $D = 16$ film with $k_w = 0.0134e^{10/T^*}$ vs. $T^*$.

Circles– bonds between the walls and the surface layers ($z = 0$, and $z = 15$), squares–bonds within the surface layers, and diamonds– in–layer bonds in the middle layers ($z = 7$, and $z = 8$).