Shear-induced phase transitions in confined lattice gases

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Abstract. The phase behaviour of a fluid confined between two plane-parallel solid substrates is investigated within the framework of lattice-gas calculations where the mean-field intrinsic free energy is employed. By minimizing the grand potential numerically, phase diagrams are constructed. Substrates are composed of alternating strips of weakly and strongly adsorbing material. The lattice gas may consist of a high-density region stabilized by the strongly adsorbing portion of the substrate while a low-density region exists over the weakly adsorbing ones (the 'bridge' phase). The 'bridge' phases coexist with either a liquidlike or a gaslike phase occupying the entire space between the substrates. All three phases join at a triple point, and two critical points exist at which the 'bridge' and gaslike phases or 'bridge' and liquidlike phases become (separately) indistinguishable. By misaligning the substrates in the x-direction, the lattice gas can be exposed to a shear strain which causes the width of the one-phase region for the 'bridge' phases to vary and the triple-point location to alter.

1. Introduction

If fluids are confined to spaces of mesoscopic dimensions, their phase behaviour is altered markedly. One of the most prominent features in this regard concerns the location of the critical point which is shifted to increasingly lower temperatures as the degree of confinement increases. This effect has been predicted theoretically [1] and verified experimentally [2]. At the mean-field level of description a perturbational treatment of the free energy of a confined fluid has recently shown that the confinement-induced reduction of the net attraction between fluid molecules is the cause of the depression of the critical temperature with respect to its bulk value [3].

However, most previous studies of confined fluids are concerned with substrates composed of a single chemical species. Röcken and Tarazona [4] were the first to demonstrate the complexity of phases coexisting in fluids confined between chemically corrugated substrates by employing a mean-field lattice-gas model similar to the one used below. One of the main results of their work was revealing the existence of new phases caused by the corrugation of the substrate. In a later study they extended their original study, utilizing a more realistic density functional approach [5]. The impact of confinement by chemically corrugated substrates on the phase behaviour, materials properties, and microscopic structure of a 'simple' fluid has

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been investigated by Schoen and Diestler [6, 7]. In [6, 7] the substrate consisted of alternating strips of weakly and strongly adsorbing solid. By varying the widths of these strips the degree of chemical corrugation can be altered, which has a distinct influence on the phase behaviour of a confined fluid film as was recently demonstrated by Bock and Schoen on the basis of grand-canonical-ensemble Monte Carlo simulations and parallel mean-field lattice-gas calculations [8].

Because of the chemical corrugation, the substrate model used in [6–8] offers the possibility to expose a confined film to a shear strain by misaligning the substrates in the x-direction orthogonal to the boundary separating weakly and strongly adsorbing strips. Here we demonstrate that imposing such a shear strain has important consequences for the phase behaviour of a confined fluid. We employ a mean-field lattice-gas model similar to the one in [8]. The lattice-gas model is introduced in section 2. Its usefulness is illustrated by comparison with recent computer simulation results (see section 3) and we also discuss the impact of shear on the phase behaviour of a confined fluid.

2. The lattice gas

The grand potential Ω is a key quantity in the context of transitions between various phases. In an inhomogeneous confined fluid, $\Omega[\rho(\vec{r})]$ is a functional of the local density $\rho(\vec{r})$. A pair of coexisting phases is characterized by $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ minimizing Ω such that for a given temperature T and chemical potential μ, $\Omega[\rho_1(\vec{r})] = \Omega[\rho_2(\vec{r})]$. To determine $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ we discretize Ω by employing a lattice-gas model. For such a lattice gas one may write

$$\Omega[\rho(\vec{r})] = \mathcal{F}[\rho(\vec{r})] + \sum_{\vec{r}} (\Phi(\vec{r}) - \mu)\rho(\vec{r}) \tag{1}$$

where $\mathcal{F}[\rho(\vec{r})]$ is the intrinsic free energy (functional), $\Phi(\vec{r})$ is the fluid–substrate potential, and $\vec{r}$ is a site on a simple cubic lattice of $n_x \times n_y \times n_z$ nodes. Periodic boundary conditions are utilized in the x- and y-directions. If one is mainly interested in first-order phase transitions [4] one may employ a mean-field *ansatz* for the intrinsic free energy:

$$\mathcal{F}[\rho(\vec{r})] = \sum_{\vec{r}} \left[k_B T \left\{ \rho(\vec{r}) \ln \rho(\vec{r}) + [1 - \rho(\vec{r})] \ln[1 - \rho(\vec{r})] \right\} - \frac{\epsilon_{\text{ff}}}{2} \sum_{\vec{r}'} \rho(\vec{r})\rho(\vec{r}') \right]. \tag{2}$$

In (2), ϵ_{ff} determines the strength of the fluid–fluid interaction and the sum over $\vec{r}'$ extends over (the six) nearest-neighbour lattice sites of site $\vec{r}$. $\Omega[\rho(\vec{r})]$ is minimized numerically by the Jacobi–Newton method [9].

We realize various confinement scenarios through different choices for the fluid–substrate potential. In the most general case the lattice gas is confined by two parallel substrates in the x−y plane represented by $\Phi(\vec{r})$ (see below). The substrate is composed of different chemical species located in the ranges $1 \leqslant x \leqslant n_s$ and $n_s < x \leqslant n_x$ whose interaction with the lattice gas is strongly (coupling constant ϵ_{fs}) or weakly (coupling constant ϵ_{fw}) attractive, respectively. The substrates are misaligned in the x-direction; this is effected by shifting the strongly attractive portion of the upper substrate by Δn_x lattice sites in the $+x$-direction. Thus, it is convenient to introduce a parameter $\alpha := \Delta n_x/n_x$ to specify the misalignment of the substrates quantitatively. It is defined such that: $\alpha = 0$ if the substrates are 'in registry', i.e. strongly and weakly attractive portions of the two substrates are exactly opposite each other; $\alpha = \frac{1}{2}$ if the misalignment is maximum. Because of the discrete nature of the lattice, only discrete values of α can, however, be realized. Thus, α is a measure of shear strain

imposed on the confined lattice gas and

$$
\Phi(\vec{r}) \equiv \Phi^{\text{up}}(x, z) =
\begin{cases}
\infty & z > n_z \\
\begin{cases}
-\epsilon_{\text{fs}} & x - \alpha n_x \leqslant n_{\text{s}} \\
-\epsilon_{\text{fw}} & x - \alpha n_x > n_{\text{s}}
\end{cases} & z = n_z \\
0 & z < n_z
\end{cases}
\tag{3}
$$

specifies the interaction of the lattice gas with the upper substrate. Likewise

$$
\Phi(\vec{r}) \equiv \Phi^{\text{lo}}(x, z) =
\begin{cases}
\infty & z < 1 \\
\begin{cases}
-\epsilon_{\text{fs}} & x \leqslant n_{\text{s}} \\
-\epsilon_{\text{fw}} & x > n_{\text{s}}
\end{cases} & z = 1 \\
0 & z > 1
\end{cases}
\tag{4}
$$

represents the interaction with the lower substrate.

3. Results

In the bulk, $\Phi(\vec{r}) \equiv 0$ and therefore $\rho(\vec{r}) = \rho$. Thus, minima of Ω are distributed in the μ–T plane according to

$$
\mu = k_B T \ln\left(\frac{\rho}{1 - \rho}\right) - 6\epsilon_{\text{ff}}\rho
\tag{5}
$$

from which the bulk phase diagram can easily be determined analytically. A straightforward calculation yields $\mu_{\text{cb}} = -3$, $T_{\text{cb}} = \frac{3}{2}$, and $\rho_{\text{cb}} = \frac{1}{2}$ at the bulk critical point [10]. Here and throughout the remainder of this paper, we employ dimensionless units—that is, energies are given in units of ϵ_{ff}, temperatures in units of ϵ_{ff}/k_B, and lengths in units of the lattice constant ℓ. In the T–ρ projection the coexistence curve is symmetric with respect to the critical point and the critical exponent $\beta = \frac{1}{2}$ as expected for a mean-field theory.

More subtle effects are observed if the lattice gas is confined by solid substrates, as plots in figure 1 show. For sufficiently large n_z, chemical corrugation of the substrate does not matter but confinement effects are already present. For example, for $n_z = 13$ the critical point is shifted to lower T and lower μ compared with the bulk and the coexistence curve $\mu(T)$ is not parallel with the temperature axis. Thus, in the T–ρ projection the coexistence curve is shifted to lower T and higher ρ (compared with the bulk) in accord with experimental observations (see figure 7 in [11]). From a theoretical perspective, $\mu(T)$ can be viewed as a line of first-order phase transitions terminating at the critical point.

If n_z decreases, a bifurcation appears at some T_{tr}. Below $T = T_{\text{tr}}$ only (inhomogeneous) liquidlike and gaslike phases coexist. At $T = T_{\text{tr}}$ the latter two coexist with a 'bridge' phase characterized by a lower density over the weakly attractive portion and a higher density over the strongly attractive portion of the substrate (see (3), for $\alpha = 0$). Above $T = T_{\text{tr}}$ the coexistence curve consists of two branches. The upper one can be interpreted as a line of first-order phase transitions involving liquidlike phases and 'bridge' phases whereas the lower one corresponds to 'bridge' phases and gaslike phases, respectively. Both branches terminate at their respective critical points $\{\mu_{\text{cp}}^{\text{lb}}, T_{\text{cp}}^{\text{lb}}\}$ and $\{\mu_{\text{cp}}^{\text{bg}}, T_{\text{cp}}^{\text{bg}}\}$.

Comparing in figure 1 coexistence curves for $n_z = 8$ and 7, it is evident that the triple point shifts further to lower T_{tr} the more severe the confinement is. At the same time, $\mu_{\text{cp}}^{\text{lb}}$ increases whereas $\mu_{\text{cp}}^{\text{bg}}$ decreases, such that the one-phase region for the 'bridge' phases widens. Because of these rather complex variations of $\mu(T)$ with n_z, it is conceivable that an initially gaslike
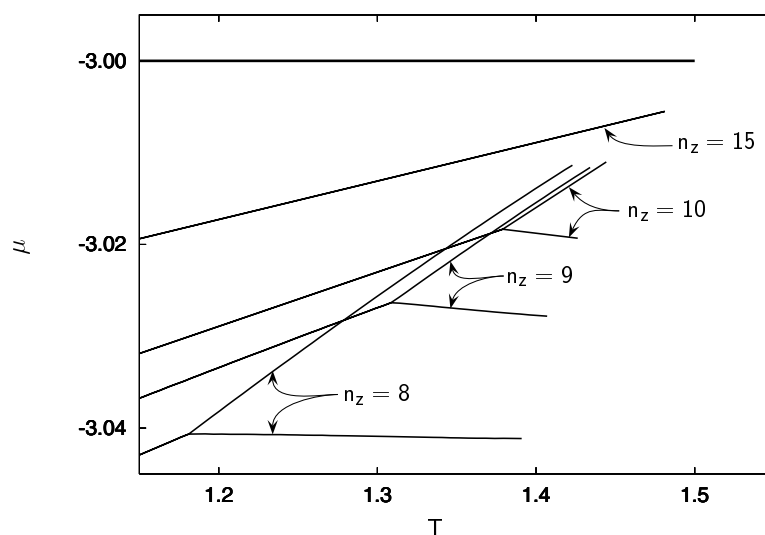
Figure 1. The chemical potential μ as a function of temperature T for lattice gases confined by chemically corrugated substrates ($n_x = 14$, $n_s = 8$, $\alpha = 0$). Substrate separations n_z are indicated in the figure. Along solid lines, two or three phases coexist. Coexistence lines terminate at critical point(s).

thermodynamic state undergoes a phase transition to a liquidlike phase at some $T < T_{tr}(n_z)$ and eventually to a 'bridge' phase at $T > T_{tr}(n_z)$ upon lowering n_z.

This scenario has recently been observed in grand-canonical-ensemble Monte Carlo simulations of a closely related but more realistic model with continuous fluid–fluid and fluid–substrate interactions, namely a Lennard-Jones fluid confined between substrates chemically corrugated on mesoscopic length scales (see figure 2) [8]. Consequently, the substrate separation may also vary continuously, which we emphasize by expressing it in terms of the (continuous) variable s_z rather than the (discrete) variable n_z employed in conjunction with the lattice-gas calculations. A plot of the average pore density $\bar{\rho}$ as a function of s_z in figure 2 exhibits two discontinuities, where the one at $s_z \simeq 8.2$ (in units of the 'diameter' of a Lennard-Jones molecule) corresponds to a gas–liquid transition and the one at $s_z \simeq 7.5$ corresponds to a transition from a liquid to a 'bridge' phase (upon reducing s_z). Oscillations in $\bar{\rho}$ for small s_z reflect stratification of the confined fluid [12]. Depending on the degree of substrate corrugation, the first-order phase transition involving liquidlike and 'bridge' phases may be replaced by a continuous transition without altering the thermodynamic state of the fluid [8].

The close correspondence between computer simulation results and those obtained for the present lattice-gas model analysed in depth in [8] clearly shows that the latter is sufficiently realistic for use in investigating the interplay between molecular interactions and mesoscopic length scales and its consequences for the phase behaviour of confined fluids at little computational expense. To further elucidate the interplay between these different length scales it seems interesting to expose the lattice gas to a nonvanishing shear strain by varying α (see (3)). The coexistence curves $\mu(T)$ plotted in figure 3 show that increasing α from its initial value of zero causes the triple point to shift to higher T and μ. At the same time the one-phase region of the 'bridge' phases shrinks until it eventually vanishes for a sufficiently high shear strain.
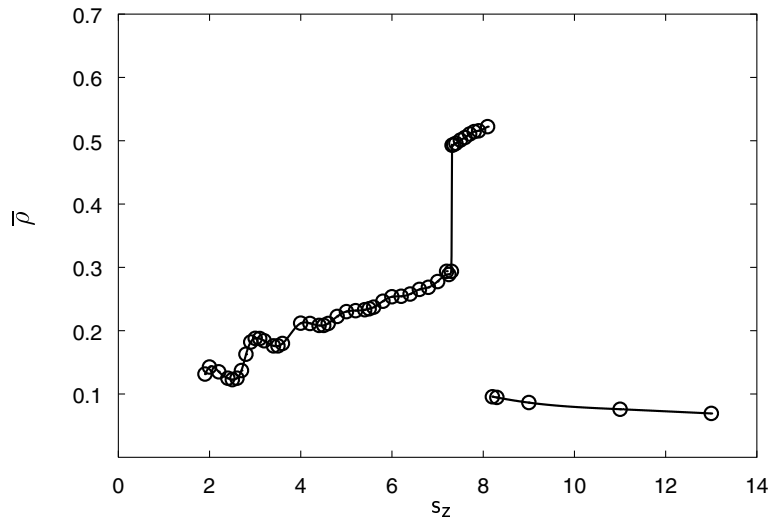
Figure 2. The average pore density $\bar{\rho}$ as a function of substrate separation s_z (see the text for the difference in notation, i.e. $n_z \leftrightarrow s_z$). Grand-canonical-ensemble Monte Carlo results were obtained for $\mu = -11.5$, $T = 1.0$ corresponding to a Lennard-Jones bulk gas.
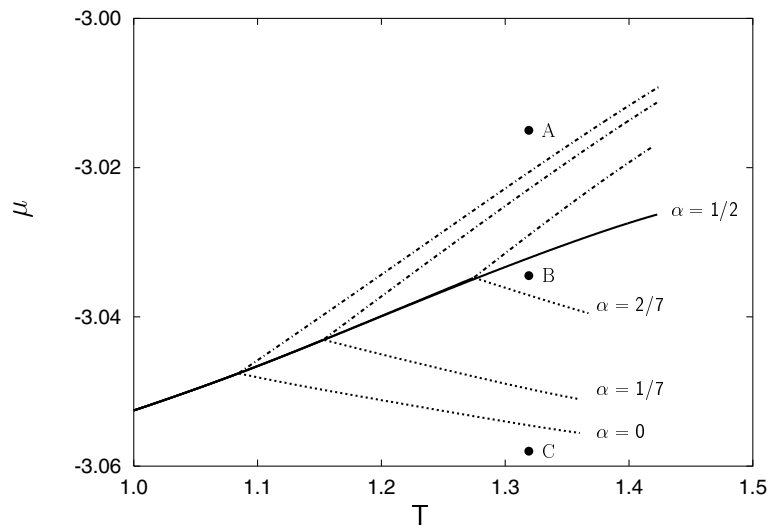

Figure 3. As figure 1, but for various shear strains α indicated in the figure ($n_x = 14$, $n_s = 6$, $n_z = 7$).

One notices from figure 3 that, unlike the degree of confinement (i.e., n_z), a variation of α does not alter the position of $\mu(T)$ relative to the T-axis for $T \leqslant T_{\mathrm{tr}}(\alpha)$. It is furthermore interesting to realize that the critical temperatures $T_{\mathrm{cp}}^{\mathrm{lb}}$ and $T_{\mathrm{cp}}^{\mathrm{bg}}$ depend only negligibly on the shear strain, unlike $\mu_{\mathrm{cp}}^{\mathrm{lb}}$ and $\mu_{\mathrm{cp}}^{\mathrm{bg}}$, such that the critical points are shifted upwards and downwards, respectively, as α increases. Consider state point B in figure 3. In the unsheared lattice gas it corresponds to a 'bridge' phase. As $\alpha \to \frac{1}{2}$ the thermodynamic state B will eventually coincide with the 'bridge'–gas branch of $\mu(T)$ for $T > T_{\mathrm{tr}}$. Thus, one expects a

shear-induced first-order phase transition from a 'bridge' to a gaslike confined lattice gas. If thermodynamic conditions are such that state point B is located above the solid line in figure 3, the shear-induced first-order transition may involve liquidlike and 'bridge' phases instead. It is furthermore conceivable that the transition occurs at $T = T_{\text{tr}}$, i.e. at the triple point.

4. Discussion and conclusions

In this paper we investigate the phase behaviour of fluids confined to spaces of mesoscopic dimensions by complex-structured solid substrates. We employ a lattice gas whose intrinsic free energy is treated at the mean-field level. Comparison between lattice-gas results and recent Monte Carlo simulations for a related but more realistic model fluid indicate that a mean-field lattice gas is sufficiently realistic for use in investigating first-order phase transitions in confined fluids.

If the substrate material is chemically structured on mesoscopic length scales, it is possible to expose the confined phase to a nonvanishing shear strain by misaligning the two substrates along the x-axis. It was shown that the shear strain has profound consequences for the phase behaviour of the confined fluid related to shifts of the location of triple and critical points as functions of α, thus causing the width of the one-phase regime for the 'bridge' phases to vary accordingly.

As one would expect intuitively, only a 'bridge' phase can exhibit 'resistance' against shear deformation. Quantitatively, this resistance can be cast in terms of the dependence of Ω on α. For example, for state points A and C in figure 3, which are both located sufficiently deep in the one-phase regime of gaslike and liquidlike phases, respectively, Ω is essentially independent of α. For a 'bridge' phase, on the other hand, Ω increases substantially with α, indicating that the stability of this phase decreases as it is progressively sheared. For continuous models one can identify the derivative $(\partial\Omega/\partial\alpha)$ with the shear stress, which can be calculated from molecular expressions in computer simulations [13]. A systematic study of the shear stress in a continuous model closely parallel to the lattice-gas calculations of this work is currently under way.

Acknowledgment

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