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Adsorption and phase transitions in a two-site associating Lennard-Jones fluid confined to energetically heterogeneous slit-like pores; application of the density functional method

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Abstract

A density functional approach is used to study adsorption and phase behaviour of the two-bonding-site associating Lennard-Jones (LJ) fluid in slit-like pores with energetically heterogeneous walls. Phase behaviour of strongly and weakly associating, polymerizing fluid in the pores with a periodic surface potential, characterized by different strengths and the spacings between adjacent minima, as well as different pore widths is discussed. A comparison of the results obtained for strongly and weakly associating fluids elucidates the role of bonding between fluid species in the pore-filling mechanism. An interplay between layering transitions, the formation of an intermediate 'bridge' phase and the final capillary condensation in the pores with energetically corrugated walls is discussed in detail.

1. Introduction

Our recent work in this journal [1], referred to hereafter as I, was devoted to the study of adsorption and phase transitions in associating Lennard-Jones fluids confined to micropores. In particular, we have investigated a two-site, associating fluid confined to narrow cylindrical capillaries and have compared the results with those for the same fluid, but under a slit-like confinement. Our principal conclusions have concerned the effects of the shape of the micropores on the adsorption and the phase transitions, such as the layering transitions and the capillary condensation and evaporation.

The model of the external potential for the slit-like and the cylindrical pores used in I assumed that the pore walls were uniform, i.e. the external field was a function only of the distance of a fluid particle from the pore wall. Obviously, it is a highly idealized model. In reality microporous adsorbents are heterogeneous and to model such materials one must

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inevitably try to incorporate the effects of heterogeneity. However, in order to make theoretical equations solvable, one is usually forced to introduce assumptions concerning the form of the adsorbing potential. A simple model of energetically nonuniform pore walls can be developed by assuming that the adsorbing potential changes along one of the axes parallel to the pore walls. Such an approach has been successfully used in some recent simulational and theoretical works, which focus on the study of adsorption of simple fluids in micropores and on the changes in surface phase transitions due to energetic heterogeneity of confinements [2–8]. In particular, it has been shown that the capillary condensation of a simple fluid in slit-like pores with a periodic adsorbing potential occurs in two steps. The first step leads to the formation of an intermediate phase via the first-order phase transition in a part of the pore. The formation of this intermediate phase precedes capillary condensation for the entire pore. Triple-type points may appear in the phase diagram as a manifestation of a possible coexistence between the intermediate phase and the capillary condensation. The knowledge of the conditions under which the intermediate phase can form remains limited. We know that the pore width, strength and periodicity of the adsorbing field all are important factors, which influence the stability of different phases. In particular, the existence of an intermediate phase is directly associated with surface heterogeneity.

The objective of the present study, part of a larger project focused on inhomogeneous associating fluids, is to elucidate the effects of periodic energetic corrugation and the confinement on adsorption and phase behaviour of associating fluids in slit-like pores. For convenience, but without loss of much generality, we restrict our attention to the two-bonding-site model, described in I. Also, the theoretical tool of this study is the density functional approach, used in I.

The paper is organized as follows. In the following section we briefly outline the model and report the final equation for the density profile. The main section of this work, namely section 3, is divided into several subsections; each of them discusses the influence of distinct parameters on the phase behaviour of strongly associating and weakly associating fluids confined to pores with energetically nonuniform walls. The paper concludes in section 4, which summarizes our study and contains the final remarks.

2. Theory

The model of associating fluid and the density functional theory applied in the present study are identical to those described in I (see also [9]). Therefore, we do not need to present them again. We just recall some basic assumptions and define the interaction potentials.

Like in our previous works [10–12], we consider an associating Lennard-Jones fluid with the angle-dependent pair potential

$$u(\mathbf{r}_{12}, \omega_1, \omega_2) = u_{non}(r_{12}) + \sum_A \sum_{A'} u_{AA'}(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (1)$$

where r_{12} is the length of the vector \mathbf{r}_{12} connecting the centres of molecules 1 and 2, and ω_i , $i = 1, 2$, are the orientations of molecules 1 and 2, relative to the vector \mathbf{r}_{12} . The nonassociative interaction, $u_{non}(r_{12})$, is given by the truncated Lennard-Jones potential

$$u_{non}(r) = \begin{cases} \varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] & r < r_{cut} \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

where the cut-off distance r_{cut} is set at 2.5σ . The parameters ε and σ are taken as the energy and the length units, respectively, so all other energies and all distances are dimensionless.

The association force acting between a site A on molecule 1 and a site A' on molecule 2 is a square-well attraction with a cone geometry, and can be represented by the potential

$$u_{AA'}(\mathbf{r}_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = \begin{cases} -\varepsilon_{as} & r_{12} < r_{ca}, \theta_{A1} < \theta_c, \theta_{A'2} < \theta_c \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

where θ_{Xi} , $X = A, A'$, $i = 1, 2$, is the angle made by the vector pointing from the centre of molecule i to the site A and the vector \mathbf{r}_{12} , ε_{as} represents the energy of association, r_{ca} is the range of the association potential and θ_c is the upper limit of the angle θ_{Xi} allowing for association. Here, we set $\theta_c = 27^\circ$, $r_{ca} = 1.05$, while the energy of association, ε_{as} , assumes different values, which will be specified later. We assume the presence of two bonding sites, $M = 2$, $A, A' = S_1, S_2$, at each molecule, and only S_1S_2 bonding is allowed [1].

The fluid particles are confined between the walls of a slit-like pore of width H . The fluid-wall potential is similar to the one employed by Röcken *et al* [7]. The total adsorbing field felt by a particle located at the point (x, y, z) is the sum of contributions from two pore walls, located in the xy -plane at $z = 0$ and $z = H$, respectively:

$$v_{fw}(x, y, z) = v_1(x, y, z) + v_2(x, y, H - z). \quad (4)$$

Each of the wall-particle potentials is assumed to have the following form:

$$v_i(x, y, z) = v^{(1)}(z) + A_i(x)v^{(2)}(z) \quad (5)$$

where $v^{(1)}(z)$ is the homogeneous part of the potential, and the remaining part describes the lateral changes of the adsorbing field along the x -axis. Thus, we assume that the surface potential is periodic in one dimension only and is uniform with respect to the coordinate y . The two functions, $v^{(1)}(z)$ and $v^{(2)}(z)$, have identical forms, namely,

$$v^{(\alpha)}(z) = \begin{cases} \infty & z < 1/2 \\ \varepsilon_{gs}^{(\alpha)} \exp[-\lambda^{(\alpha)}(z - 1/2)] & z > 1/2 \end{cases} \quad (6)$$

for $\alpha = 1, 2$, and depend on the parameters $\varepsilon_{gs}^{(\alpha)}$ and λ_{α} . The periodic function $A_i(x)$ (where i is the wall index, $A_i(x) \equiv A(x)$) is given by

$$A(x) = \cos(2\pi x/l) \quad (7)$$

where l defines the period of the function $A(x)$.

The density functional theory provides an approximation for the grand thermodynamic potential:

$$\Omega = F + \int \rho(\mathbf{r})[v(z) - \mu] d\mathbf{r} \quad (8)$$

as a functional of the local density of a fluid, $\rho(\mathbf{r})$, at a given value of the configurational chemical potential μ and at a given temperature T . We follow the theory, described in our previous works [10–12], and write the Helmholtz free energy, F , as the sum of an ideal and the excess term. The former is just given by

$$F^{id} = \int d\mathbf{r} \rho(\mathbf{r})[\ln \rho(\mathbf{r}) - 1]$$

whereas the latter is approximated as follows:

$$F^{ex} = \int \rho(\mathbf{r}) f_{hs}^{ex}[\tilde{\rho}(\mathbf{r})] d\mathbf{r} + \int \rho(\mathbf{r}) f_{as}^{ex}[\tilde{\rho}(\mathbf{r})] d\mathbf{r} + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u_a(r_{12}) \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \quad (9)$$

where f_{as}^{ex} and f_{hs}^{ex} are the excess free energies per particle arising from hard spheres and associative interaction, respectively. The expression defining f_{hs}^{ex} follows from the Carnahan–Starling equation of state; however, the expression for the associative interaction results from first-order thermodynamic perturbation theory [10–12, 15, 16]:

$$f_{as}^{ex}(\tilde{\rho})/kT = \sum_{A=1,M} [\ln \chi_A(\tilde{\rho}) - \chi_A(\tilde{\rho})/2 + 0.5]. \quad (10)$$

Both f_{as}^{ex} and f_{hs}^{ex} are evaluated [10–12] by using the smoothed-density ($\tilde{\rho}(\mathbf{r})$) approximation. The smoothed density is given by the Tarazona recipe; its definition is given in reference [13]. Moreover, the last term in equation (9) takes into account the attractive, nonassociative interactions between fluid particles; they are considered by invoking the mean-field approximation. For this purpose the nonassociative potential, $u_{non}(r_{12})$, is decomposed into a reference and an attractive part, $u_a(r_{12})$, according to the Weeks–Chandler–Andersen scheme [14]:

$$u_a(r) = \begin{cases} -\varepsilon & r < 2^{1/6} \\ u_{non}(r) & \text{otherwise.} \end{cases} \quad (11)$$

However, the quantity χ_A entering equation (10) is the fraction of molecules not bonded at a site A. According to the approach outlined in I, χ_A follows from the solution of the algebraic equation

$$\chi_A(\tilde{\rho}) = \frac{1}{1 + 2\chi_A(\tilde{\rho})\tilde{\rho}g^{HS}(1; \tilde{\rho})K_{AA'}f_{AA'}} \quad (12)$$

where $f_{AA'} = \exp[-\varepsilon_{ass}/kT] - 1$, $K_{AA'} = 0.25(1 - \cos \theta_c)^2(r_c - 1)$ is the bonding volume and $g^{HS}(1, \tilde{\rho})$ is the contact value of the pair distribution function of a hard-sphere fluid at density $\tilde{\rho}$.

At equilibrium, $\delta\Omega/\delta\rho(\mathbf{r}) = 0$, and hence the equation for the density profile becomes

$$\begin{aligned} -kT \ln[\rho(\mathbf{r})] &= v(\mathbf{r}) + f^{ex}[\tilde{\rho}(\mathbf{r})] - f^{ex}(\rho_b) + \int \frac{\delta\tilde{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})} f^{ex'}[\tilde{\rho}(\mathbf{r}')] \rho(\mathbf{r}') d\mathbf{r}' \\ &\quad - \rho_b f^{ex'}(\rho_b) + \int u_a(|\mathbf{r} - \mathbf{r}'|) [\rho(\mathbf{r}') - \rho_b] d\mathbf{r}' \end{aligned} \quad (13)$$

where $f^{ex'}$ denotes the derivative of the excess free-energy density with respect to the fluid density and ρ_b is the bulk density, corresponding to the configurational chemical potential μ .

3. Results and discussion

Before the presentation of results and their discussion, we provide some technical details concerning the method of solution of the density profile equation (13). The fluid–wall potential is periodic along the x -axis and is uniform along the y -axis. Thus, we calculate the two-dimensional local density $\rho(x, z)$ in a unit cell, which is next periodically replicated along the x -axis. The length of the unit cell, however, depends only on the parameter l (cf. equation (7)). We have solved the density profile equation (13) on a two-dimensional grid with the mesh size 0.05×0.05 , by using a standard iteration procedure. After determining the density profile, we have evaluated the average fluid density in the pore:

$$\langle \rho \rangle = \int_C d\mathbf{r} \rho(x, z) / \int_C d\mathbf{r} \quad (14)$$

where the integration is carried out over the unit cell, C . The averaging of the profile along the x -axis has been performed from 0 to l , and the averaging along z -axis from 0 to H .

The locations of phase transitions have been found by analysing the dependence of the grand thermodynamic potential, Ω , on the configurational chemical potential, as described in I.

The systems studied by us are characterized by two values of the energy of association, namely by $\varepsilon_{as} = 20$ and $\varepsilon_{as} = 8$. The first fluid is called the strongly associating fluid (SAF). Its critical temperature is quite high, $T_c^* = kT/\varepsilon \approx 2.4$, in comparison to that of the nonassociating LJ fluid ($T_c^* \approx 1.3$). On the other hand, the weakly associating fluid (WAF), with $\varepsilon_{as} = 8$, has the critical temperature $T_c^* \approx 1.5$, which is close to the critical temperature of a pure LJ fluid. Our intention is to compare the results for the strongly associating system with those obtained for a system in which the effect of bonding on its critical properties is weak.

We have studied a set of systems, characterized by two values for the homogeneous term of attraction, $\varepsilon_{gs}^{(1)} = 6$, and a two-times-weaker attraction, $\varepsilon_{gs}^{(1)} = 3$, at a fixed value of the heterogeneous term, $\varepsilon_{gs}^{(2)} = 3$. The ranges of attraction for the homogeneous and heterogeneous terms have been fixed throughout this study: $\lambda^{(1)} = 2$ and $\lambda^{(2)} = 1$. In other words, the heterogeneous term is longer ranged as compared with the homogeneous attraction.

In the following parts of this section, we present the results obtained for different classes of systems and try to elucidate the effects of surface heterogeneity, association and confinement on their phase behaviour.

3.1. Phase behaviour of confined SAF subject to a periodic surface potential

In this part, we focus on the influence of periodicity of the fluid–wall potential (along the x -axis) on the phase transitions in strongly associating fluid, $\varepsilon_{as} = 20$, confined in a narrow pore, $H = 5$.

In figure 1, which consists of two panels, we have collected the phase diagrams obtained for a series of systems with different periods of the fluid–wall potential l , ranging from 5 to 9. Figure 1(a) presents the phase diagrams in the density–temperature plane, while figure 1(b) gives the corresponding phase diagrams in the temperature–chemical potential plane. The bulk liquid–vapour coexistence curve serves as a reference, so the temperature is scaled with respect to the bulk critical temperature (T_c^*) and the chemical potential values are given as the differences between the chemical potentials at the transition points of the confined and bulk systems at the same temperature (μ_s). Figure 1 includes also the phase diagram for the SAF confined in the pore with homogeneous walls ($\varepsilon_{gs}^{(2)} = 0$). Throughout this subsection, the homogeneous part of the fluid–wall attraction is assumed to be quite strong ($\varepsilon_{gs}^{(1)} = 6$, $\lambda^{(1)} = 2$). In such systems, we observe a layering transition before the subsequent capillary condensation transition, both in the homogeneous and the heterogeneous walls. The heterogeneous part of the fluid–wall potential is two times weaker than the homogeneous ‘background’, $\varepsilon_{gs}^{(2)} = 3$; however, the decay of the homogeneous potential is faster, because $\lambda^{(2)} = 1$.

Our principal findings are the following. In the absence of energetic heterogeneity ($\varepsilon_{gs}^{(2)} = 0$), the phase diagram consists of two branches. The first corresponds to the layering transition, whereas the second branch describes capillary condensation. Obviously, the critical temperature of capillary condensation in the pore is lower than the critical temperature of the bulk fluid. The two branches of the phase diagram may join together at the triple-point temperature.

Periodicity of the fluid–wall potential leads to substantial changes of the fluid phase behaviour. In such cases, the phase diagram of the confined fluid consists of either two or three branches, depending on the period of the external field, l . In the case of smaller values of $l = 5$, or, in other words, in the case of a short period of the potential variation, the

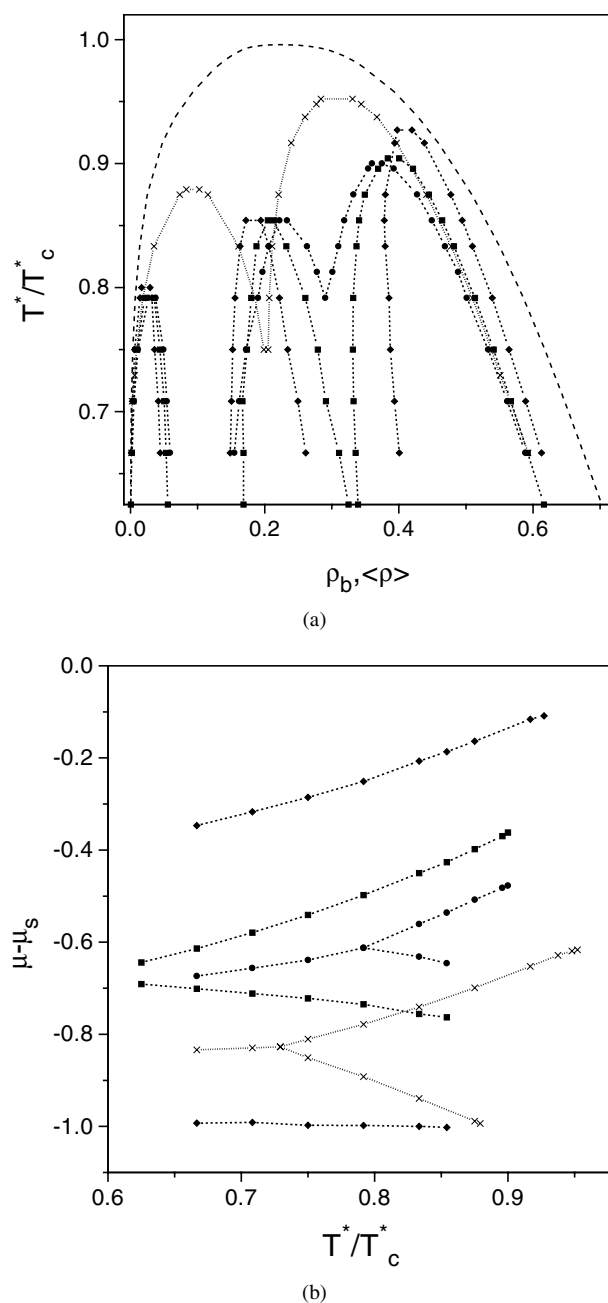


Figure 1. (a) The liquid–vapour coexistence curve of the bulk strongly associating ($\varepsilon_{as} = 20$, $T_c^* = 2.4$) model fluid (dashed line) and of confined fluid in the narrow slit-like pore, $H = 5$ (lines with symbols), in the T – ρ plane. The phase diagram of the fluid in the homogeneous pore, $\varepsilon_{gs}^{(2)} = 0$ (crosses), is compared with the phase diagrams for the heterogeneous pore with $l = 5$ (circles), $l = 6$ (squares) and $l = 9$ (rhombs). The short-dashed line in each case connects symbols to improve visualization. The parameters of the fluid–wall potential are the following: $\varepsilon_{gs}^{(1)} = 6$; $\lambda^{(1)} = 2$; $\varepsilon_{gs}^{(2)} = 3$; $\lambda^{(2)} = 1$. (b) The same as (a), but in the T – μ plane. The chemical potentials are scaled with respect to the corresponding values of the chemical potential at the bulk coexistence (μ_s) at each temperature.

phase diagram consists of a branch corresponding to the layering transition and the capillary condensation branch. In fact, the upper (high-temperature) part of the capillary condensation branch splits into two parts. This reflects the possibility of the formation of an intermediate phase, named by Röcken *et al* [7] the 'bridge' phase. The formation of this phase precedes the true capillary condensation transition, which ultimately leads to the adsorbate condensation throughout the entire pore. The part of the phase diagram which corresponds to the bridge phase is characterized by its own critical temperature and the critical density, and it can be either joined to the capillary condensation branch at a certain triple-point temperature, or may be decoupled from the capillary condensation branch. The existence of the triple point and the magnitude of the triple-point temperature are determined by the periodicity parameter l . In general, the increase of l leads to a lowering of the triple-point temperature. When l becomes high enough (cf. the results for $l = 9$ in figure 1) the two branches of the phase diagram remain separated at all temperatures investigated. We have not been able to verify the existence of triple points for the systems with large l , because the density functional technique fails at low temperatures.

We have found that the critical temperature of the bridge phase formation is only weakly dependent on the periodicity parameter, in the range of its values from $l = 5$ to $l = 9$. The critical density of the bridge phase formation decreases slightly with increasing periodicity parameter l . On the other hand, the critical temperature of the capillary condensation increases when the periodicity parameter becomes higher. Also, the branch corresponding to capillary condensation becomes substantially narrower for larger values of l . Another observation concerns the evolution of the layering transition branches with the changing periodicity of the adsorbing potential. The most striking difference between the layering transitions which take place in homogeneous and heterogeneous pores is that the density of the condensed layer is much lower in the case of heterogeneous pores (cf. figure 1(a)). This is a direct consequence of the fact that the number of particles that can be accommodated on the periodic walls is considerably reduced. On the other hand, the critical temperature of the layering transition is not very sensitive to the value of l . Nevertheless, we observe a rather large decrease of the critical temperature of layering when the fluid-wall potential becomes nonuniform along the x -axis. Although we have observed that the critical temperature is slightly higher for $l = 9$ than for the lower values of l ($=5$ or 6), it is difficult to follow these trends precisely.

Also, the distance along the density scale between the layering branch and the bridge phase formation branch of the phase diagrams in figure 1(a) slightly decreases with increasing periodicity. Another view of the effects of periodicity on the phase diagram of confined SAF gives the μ - T projection shown in figure 1(b). We will discuss this type of projection briefly below. However, it is important to mention that due to the sufficiently strong fluid-wall homogeneous attraction, all of the critical events are quite well separated from the bulk liquid coexistence line on the chemical potential scale. Only for $l = 9$ does the capillary condensation branch gradually approach the bulk coexistence line. Some of the trends discussed above have been analysed in the work of Röcken *et al* [7], though only for simple fluids confined in heterogeneous pores.

The theory of bulk associating fluids permits us to evaluate the fraction of unbonded species in the system, χ_0 ($\chi_0 = \chi_A^2$), as well as to relate this quantity to the average chain length; cf. I. The associative density functional theory involves the density profile of unbonded species as well. Therefore, one can calculate the average density of unbonded species for the entire pore and construct the phase diagram in terms of this property. Examples of the phase diagrams describing the average fraction of unbonded species for the entire heterogeneous pore along the coexistence line, according to the results shown in figure 1(a), are presented in figure 2. The branches in the right-hand part of this figure correspond to layering transitions

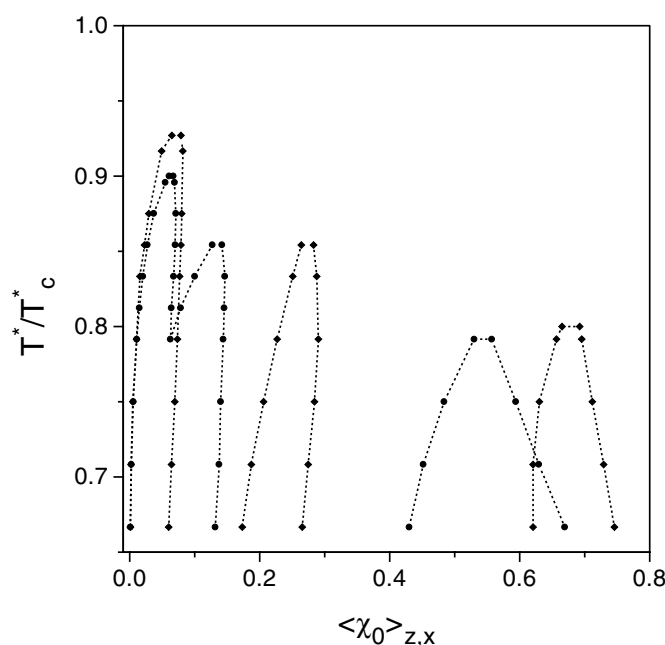


Figure 2. The dependence of the fraction of unbonded species, averaged over the entire pore, along some of the coexistence lines shown in figure 1(a). The key to the symbols is as for figure 1(a): solid circles are for $l = 5$ whereas solid rhombs are for $l = 9$.

for two values of l . The branches to the left correspond to the bridge phase and capillary condensation, respectively. One can see that the phase filling the first layer is characterized by a high, on average, fraction of unbonded species. However, the dense phases filling the pore interior consist mostly of bonded particles. Whereas the liquid phase formed in different heterogeneous pores—in effect, a capillary condensation—is characterized by similar values of the fraction of unbonded species, in less dense phases, such as in the bridge phases, the fraction of unbonded species is sensitive to the energetic heterogeneity of the pore walls. Changes of the fraction of unbonded species during phase transitions in heterogeneous pores would inevitably result in changes of the average size of complexes that can be formed in the pore via chemical association mechanisms.

A more detailed insight into the distribution of density throughout the entire pore is necessary to identify the phases formed in the pore due to the changes of the chemical potential of the bulk fluid and/or of temperature. Therefore it is inevitable that we have to discuss the density profiles of particles. To avoid a lengthy presentation, we focus on some representative examples only. In the first three panels of figure 3, we plot the density profiles of fluid species along the normal to the pore walls. Part (a) shows the profiles averaged over the periodicity interval along the x -axis. Parts (b) and (c) of figure 3 present the density profiles along normals to the walls at the maximum- and minimum-attraction points. Finally, the density profile along the x -axis at fixed $z = H/2$ (part (d)) shows changes of the density distribution at the centre of the pore. All of the curves correspond to the state, at $T^*/T_c^* = 0.792$, before the formation of the bridge phase, i.e. when $\langle \rho \rangle = 0.181$; at the triple point, $\langle \rho \rangle = 0.287$; and after the capillary condensation, $\langle \rho \rangle = 0.501$.

It is convenient to analyse the profiles together with the phase diagram represented by filled circles in figure 1(a). In general, the density profiles averaged over x demonstrate pronounced

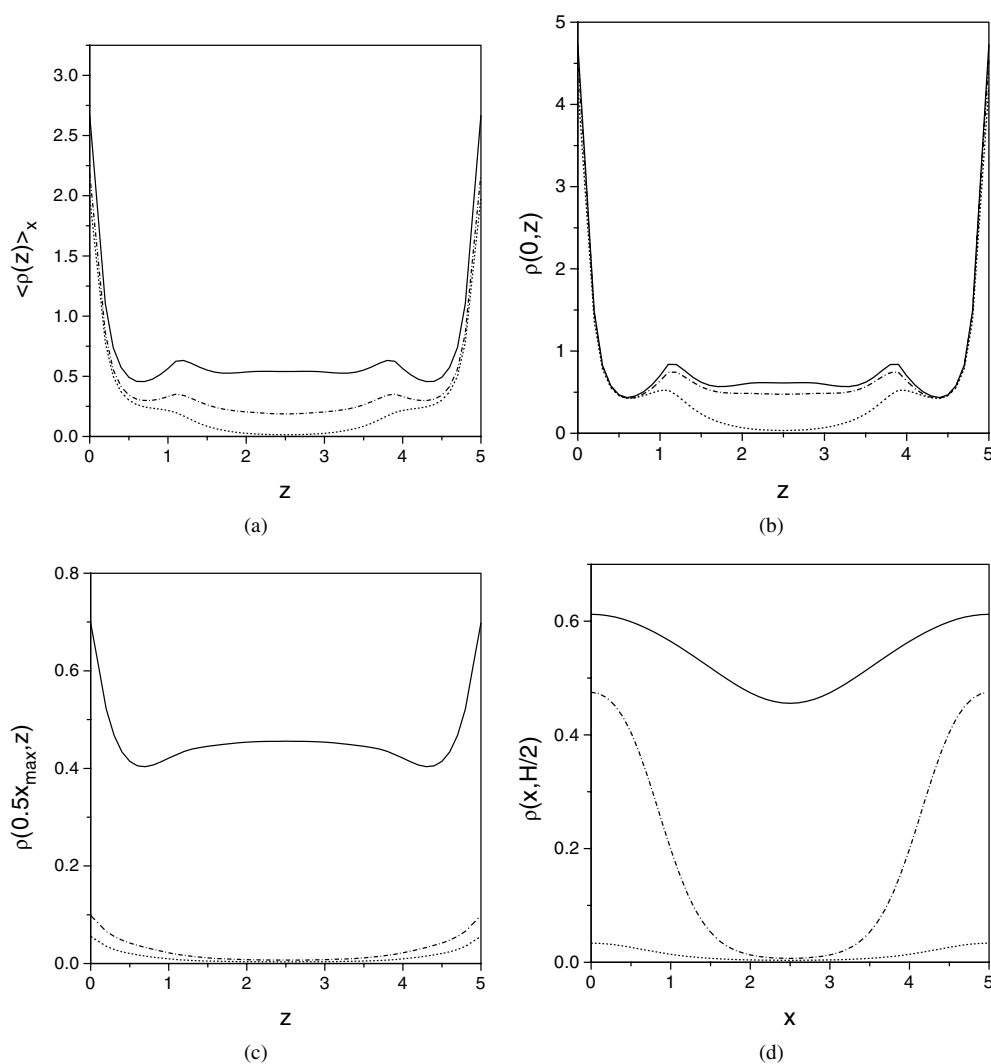


Figure 3. Examples of the behaviour of the density profiles for the fluid model in the heterogeneous pore. The fluid–wall interaction parameters are like in figure 1. The density profiles in each panel are for the state before the bridge phase formation (short-dashed line), at the triple point (dash-dotted line) and after the capillary condensation (solid line). The profiles relate to the system for which the phase diagram is shown by circles in figure 1(a). The projections describing fluid density averaged over the x -direction throughout the entire pore; at the point of maximum attraction; at the point of minimum attraction; and the profile along the x -axis and at the pore centre, $z = H/2$, are shown in parts (a), (b), (c), and (d), respectively.

changes in the central part of the pore (part (a)). These changes during transitions result from changes of density in both the maximum- and minimum-attraction regions. The changes of density in the region of minimum attraction are negligible when the bridge phase is formed. It is interesting to observe changes of density during transitions in the central part of the pore. The formation of the bridge phase results in a drastic increase of the fluid density in the region of the pore characterized by the maximum attraction, while in the region of minimum attraction there is almost no change of density. When the capillary condensation occurs, the fluid density

becomes high throughout the entire pore. Nevertheless, the density is inhomogeneous along the x -axis at the centre of the pore.

We would like to characterize the bonding structure of the adsorbed fluid. The appropriate projections of the profiles of the fractions of unbonded particles corresponding to the density profiles shown in figure 3(b), figure 3(c) and figure 3(d) are given in figures 4(a), 4(b) and 4(c), respectively. We observe that the distribution of density governs the fraction of unbonded particles. Condensed liquid which is formed during the capillary condensation is characterized by a small fraction of unbonded species throughout the entire pore. On the other hand, the bridge phase is characterized by inhomogeneous distribution of unbonded species; they are mostly concentrated in the region of the pore where the potential describing the attraction between fluid species and pore walls reaches its minimum.

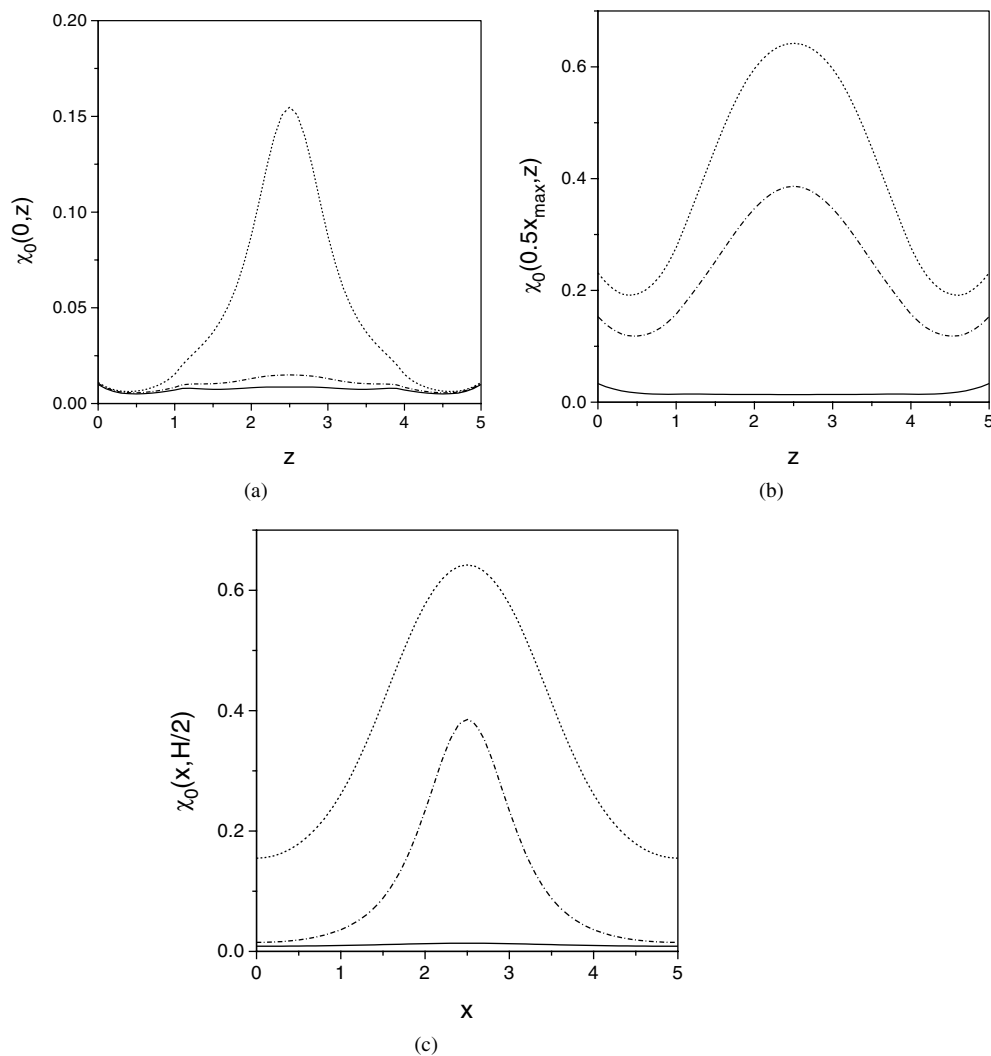


Figure 4. Examples of the behaviour of the density profiles for the fraction of unbonded particles corresponding to the profiles given in figure 3(b), figure 3(c) and figure 3(d), for the same thermodynamic states. The key to the lines is similar to that for figure 3.

3.2. Effects of pore width on the phase diagram of confined SAF

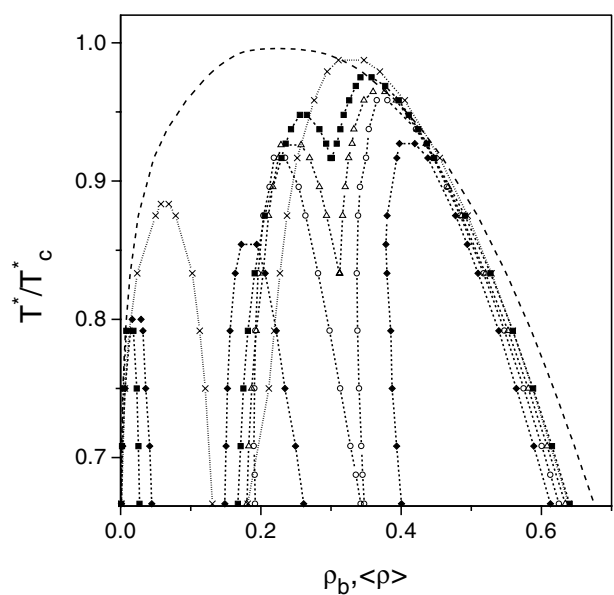
Next, we proceed to the description of the effect of the pore width on the phase behaviour of the strongly associating confined fluid. We consider the same model parameters for the fluid–wall attraction as discussed in the previous subsection for the period of the adsorbing potential equal to $l = 9$. However, the pore width varies from $H = 5$ to $H = 7$, then to $H = 8$ and, finally, to $H = 9$. Figure 5 shows the phase diagrams corresponding to all of these systems, together with the bulk phase diagram and the phase diagram for the fluid confined in the widest pore ($H = 9$) with uniform walls. In the case of a pore with energetically homogeneous walls we see that the phase diagram in the temperature–density plane consists of two well separated branches, corresponding to the layering transition and to the capillary condensation (figure 5(a)). The density change accompanying the layering transition is quite large. The critical temperature of the capillary condensation in a wide uniform pore ($H = 9$) is close to the bulk critical temperature. In the case of energetically heterogeneous pores for which $H \leq l$, we observe a substantial influence of the heterogeneity on the phase behaviour of the confined fluid. This influence is manifested by changes of the layering branch of the phase diagram and by decoupling of the capillary condensation branch into two fragments with or without the triple point. The layering branch is suppressed, its critical temperature is much lower than in the homogeneous pore and the entire layering envelope is much narrower than for the homogeneous pore. Even in the widest pore in question, the layering transition branch remains extremely narrow in comparison to the case for a homogeneous pore of the same width. This is a manifestation of the fact that the layering is a single-wall phenomenon and that the layer density is lowered by the nonuniformity of the fluid–wall potential, as already discussed in the previous subsection.

In the narrow pore, $H = 5$, the branches describing the bridge phase and the capillary condensation are well separated. In fact, one must essentially increase the chemical potential (or the bulk fluid density) to force the liquid to be condensed throughout the entire pore with respect to the chemical potential at which the intermediate (the bridge) phase between the most attractive parts of the pore walls is formed. In a wider pore a triple point joining the bridge and the capillary condensation phase is observed. The triple-point temperature exhibits large changes when the pore width is increased just by the amount equal to one fluid particle diameter. Also, the critical temperatures of the bridge phase formation and of the capillary condensation increase when the pore becomes wider. In all cases considered, the critical temperature of capillary condensation is higher than the critical temperature of the bridge phase formation. In the case of the wider pores ($H > l$) we expect the branches of the bridge phase and the capillary condensation to flow together. However, not only the pore width but also the ratio of energies and the range of homogeneous and heterogeneous contributions to the total fluid–wall attraction determine whether a separate bridge phase exists.

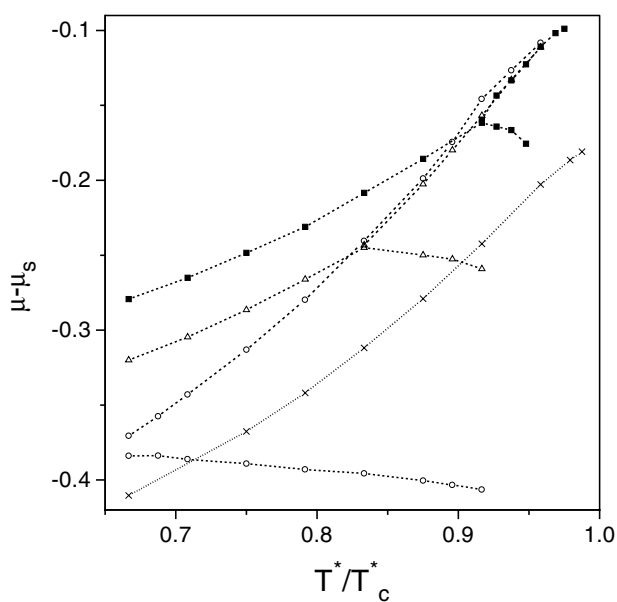
Further insight into the phase behaviour may be readily seen in figure 5(b). The branch corresponding to the capillary condensation gradually approaches the bulk fluid coexistence in its high-temperature part. In the particular case of a pore with $H = 9$, the phase diagram of the SAF in the heterogeneous pore is entirely closer to the bulk coexistence than the phase diagram for the pore with energetically homogeneous walls.

3.3. Effects of the homogeneous attraction contribution to the fluid–wall interaction on the phase behaviour of SAF

All of the results discussed so far have been obtained for the following set of parameters: $\varepsilon_{gs}^{(1)} = 6$; $\lambda^{(1)} = 2$; $\varepsilon_{gs}^{(2)} = 3$; $\lambda^{(2)} = 1$. The application of a fluid–pore wall potential in the



(a)



(b)

Figure 5. (a) The liquid–vapour coexistence curve of the bulk strongly associating ($\varepsilon_{as} = 20$) model fluid (dashed line) and of confined fluid in slit-like heterogeneous pores of different widths—lines with symbols: $H = 5$ (rhombs); $H = 7$ (circles); $H = 8$ (triangles); and $H = 9$ (squares), in the T – ρ plane. The phase diagram of the fluid in the homogeneous pore, $\varepsilon_{gs}^{(2)} = 0$ (crosses), of width $H = 9$ is shown for comparison. The parameters of the fluid–wall potential are the following: $\varepsilon_{gs}^{(1)} = 6$; $\lambda^{(1)} = 2$; $\varepsilon_{gs}^{(2)} = 3$; $\lambda^{(2)} = 1$; and $l = 9$. (b) The same as (a), but in the T – μ plane. Only the results for wider pores ($H = 7, 8$ and 9) are shown, with the same notation. The chemical potential is scaled with respect to the value of the chemical potential at the bulk coexistence at each temperature. The branches corresponding to the layering transition are omitted.

form of a Yukawa interaction permits us to conveniently change the strength of attraction by changing the parameters $\varepsilon_{gs}^{(i)}$. Whereas the results of changes of $\varepsilon_{gs}^{(2)}$ can be intuitively well understood, it has not been clear to us how the value of $\varepsilon_{gs}^{(1)}$ influences the phase diagram in the presence of energetic heterogeneity. Therefore, we have undertaken the following investigation. The parameter describing homogeneous attraction, $\varepsilon_{gs}^{(1)}$, has been decreased twice, i.e. set equal to $\varepsilon_{gs}^{(1)} = 3$, so that in the region of minimum attraction to the wall, the homogeneous and heterogeneous terms of the total fluid–pore potential cancel each other. In that region of the pore, a small repulsion develops along the normal to the pore walls, due to the difference in range of decay of the homogeneous and heterogeneous terms.

The curves given in figure 6 are the phase diagrams of the SAF in the pores with different homogeneous attraction terms, plotted in the temperature–density plane. The pore width and the period of the fluid–wall potential are kept constant and equal $H = 5$ and $l = 6$, respectively. The dashed line denotes the bulk phase diagram. There are two sets of curves: squares denote the phase diagram evaluated for $\varepsilon_{gs}^{(1)} = 6$ (that has been discussed previously), whereas rhombs show the diagram for $\varepsilon_{gs}^{(1)} = 3$. We stress that while the layering is only weakly influenced by the value of $\varepsilon_{gs}^{(1)}$, the two remaining branches of the phase diagram—that is, the bridge part and the capillary condensation part—change substantially under the reduction of the value of $\varepsilon_{gs}^{(1)}$. When $\varepsilon_{gs}^{(1)} = 6$, the critical temperatures of the bridge phase formation and of the capillary condensation are different; the former is lower than the latter. If $\varepsilon_{gs}^{(1)} = 3$, these two critical temperatures become quite similar. Also, the shape of the coexistence lines suggests that the triple-point temperature for the system with $\varepsilon_{gs}^{(1)} = 3$ is significantly lower than that for the system with $\varepsilon_{gs}^{(1)} = 6$.

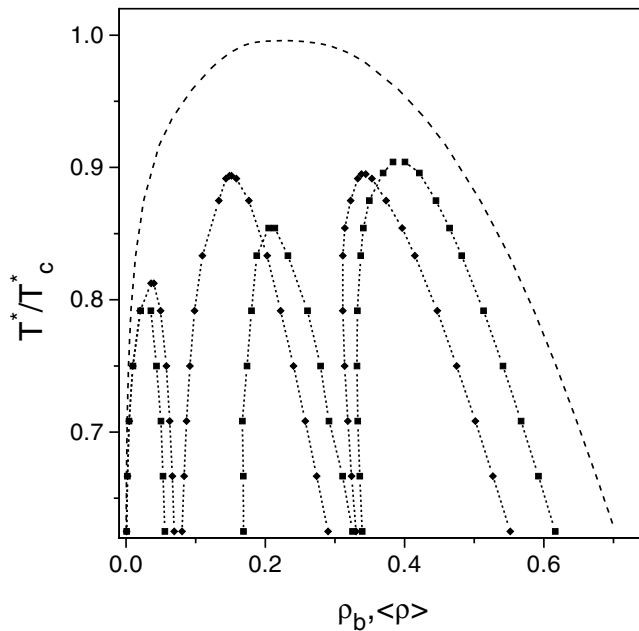


Figure 6. A comparison of the phase diagrams of the strongly associating fluid confined in a narrow slit-like pore, $H = 5$, with heterogeneous walls at a fixed periodicity of corrugation $l = 6$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$, $\lambda^{(1)} = 2$. Different curves correspond to the different strengths of homogeneous attraction: $\varepsilon_{gs}^{(1)} = 6$ (squares) and $\varepsilon_{gs}^{(1)} = 3$ (rhombs).

Figure 7 illustrates the evolution of the phase diagram in the μ - T plane under the changes of period of the corrugation potential. The pore width is $H = 5$ and the adsorbing potential contains a weak homogeneous part, i.e. $\varepsilon_{gs}^{(1)} = 3$, $\lambda^{(1)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$. We observe that with increasing period of the corrugation potential the branches corresponding to the layering transition are located at lower values of the chemical potential, i.e. they move away from the bulk coexistence curve. Similarly, the bridge phase branches also tend to move away from the bulk coexistence curve. In contrast, the capillary condensation branch approaches the bulk coexistence curve, especially at high temperatures. In particular, for $l = 6$, there exists a temperature at which the line of the capillary condensation crosses the bulk coexistence curve. We have not intended to investigate the evaporation-type phase behaviour for these pores, but evidently there exists a crossover between condensation and evaporation at high temperatures. We have verified that for the higher-periodicity range, namely for $l = 11$, the entire capillary condensation branch lies above the bulk coexistence, i.e. the capillary condensation becomes metastable with respect to the bulk fluid liquid-vapour coexistence throughout the entire range of the temperatures investigated.

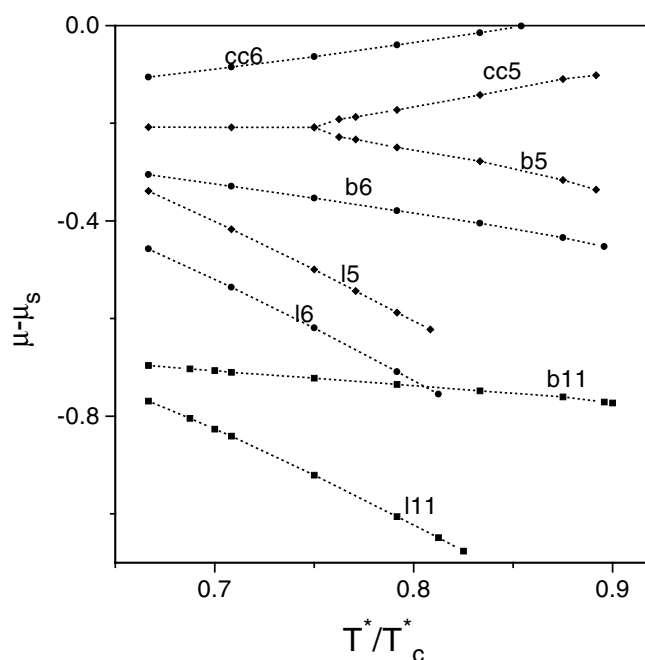


Figure 7. A comparison of the phase diagram of the strongly associating fluid confined in the narrow slit-like pore, $H = 5$, with heterogeneous walls, under the conditions of a weak homogeneous attraction ($\varepsilon_{gs}^{(1)} = 3$, $\lambda^{(1)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$) with varying periodicity of the heterogeneous term. The squares, circles and rhombs correspond to $l = 11$, $l = 6$ and $l = 5$, respectively. Note that for $l = 6$, the capillary condensation branch enters the bulk coexistence region at high temperatures, whereas for $l = 11$ this branch is located entirely inside the bulk coexistence region. The labels l (layering), b (bridge) and cc (capillary condensation) mark each branch to provide a better understanding for the reader.

Figure 8 illustrates the effect of pore width on the phase behaviour of a SAF confined to a pore with weakly attractive heterogeneous walls; $\varepsilon_{gs}^{(1)} = 3$, $\lambda^{(1)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$. The corrugation potential period has been set at $l = 6$. The important conclusion is that the effects of energetic heterogeneity are well observed in terms of the bridge phase branch of the

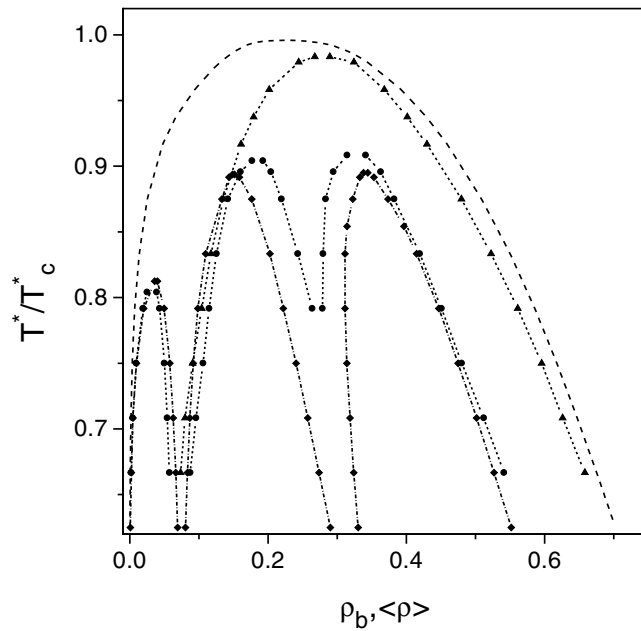


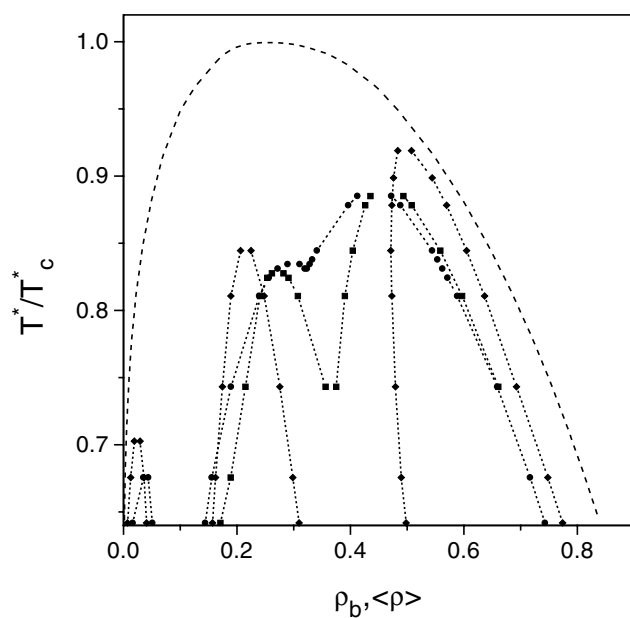
Figure 8. The effect of pore width on the phase behaviour of the strongly associating fluid confined in the slit-like pore of width $H = 5$ (rhombs), $H = 6$ (circles) or $H = 9$ (triangles), with weakly attracting walls; $\varepsilon_{gs}^{(1)} = 3$, $\lambda^{(2)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$, $l = 6$. The layering transition is shown only for $H = 5$ and $H = 6$.

phase diagram, if the pore width is less than or comparable to the corrugation period. In such a case, the critical temperature of the bridge phase formation and the capillary condensation critical temperature are quite similar. If the pore width becomes larger than the corrugation period, then the capillary condensation occurs without the formation of an intermediate phase. Note also that for weakly attractive heterogeneous walls, the branches corresponding to the layering transition lie closer to the remaining branches of the phase diagram than in the case of the phase diagrams for more strongly attractive adsorbing walls discussed in the previous subsections. In the previous cases the layering branch and the intermediate phase branch of the phase diagram were well separated in density. In the present case, however, we even observe the existence of a triple-point temperature between the layering transition and the bridge phase formation.

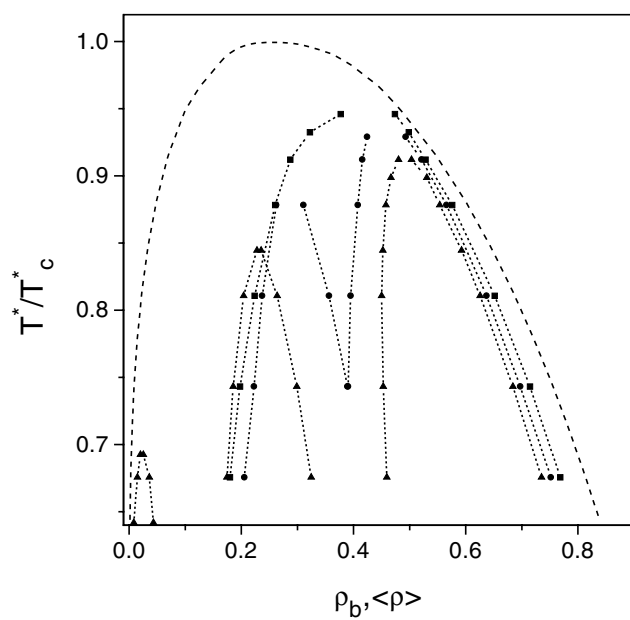
3.4. Phase diagrams of a confined WAF model; effects of the surface corrugation and the pore width

In the previous parts of this section, we have discussed how the phase behaviour of the SAF depends on the periodicity of the surface corrugation potential and on the pore width. A set of similar results has been obtained for the WAF model, and we have focused here on a comparison of effects on the phase diagrams resulting from different sources for the SAF and WAF models.

The assumed fluid–pore wall interaction is the same as for the SAF, namely $\varepsilon_{gs}^{(1)} = 6$, $\lambda^{(1)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$. The effects of periodicity and the pore width are illustrated in figures 9(a) and 9(b), respectively. In the case of potential corrugation with a large period, the



(a)



(b)

Figure 9. (a) The liquid–vapour coexistence curve of the bulk weakly associating ($\epsilon_{as} = 8$, $T_c^* = 1.5$) model fluid (dashed line) and of confined fluid in the narrow slit-like pore, $H = 5$ (lines with symbols), in the T – ρ plane. The phase diagrams of the WAF model are shown for different periods of the corrugation potential: $l = 5$ (circles), $l = 6$ (squares) and $l = 11$ (rhombs). The parameters of the fluid–wall potential are the following: $\epsilon_{gs}^{(1)} = 6$; $\lambda^{(1)} = 2$; $\epsilon_{gs}^{(2)} = 3$; $\lambda^{(2)} = 1$. (b) The same as (a), but for a confined WAF model in slit-like pores of different widths $H = 5$ (triangles), $H = 7$ (circles) and $H = 9$ (squares). The layering branch is shown only for some selected cases as indicated by the symbols.

condensation of the WAF in the pore occurs in two stages. First the bridge phase is formed and then capillary condensation takes place throughout the entire pore. We observe that the critical temperature increases with increasing l for both of these phases. The increase of the period of the corrugation potential results in the more pronounced decoupling of the bridge phase and capillary condensation branches, so the bridge phase critical density decreases with l , whereas the critical density of the capillary condensate slightly increases with l . Also, the layering transition is influenced by the period of the corrugation potential. The density of the adlayer after the relevant transition is slightly higher if the period of the corrugation potential is smaller.

It is more difficult to investigate layering transitions in the WAF model than in the SAF one. The reason is that in the case of the WAF the layering transition occurs at much lower temperatures compared to the SAF case. We have left only one example of the layering-type branch in the phase diagram displayed in figure 9(b), to illustrate that the layering transitions occur also in the WAF model investigated. However, the important conclusion following from figure 9(b) is that for WAF the bridge phase disappears at considerably smaller pore width than has been observed for the SAF model. For a similar fluid–wall interaction and for the same pore width, $H = 9$, the phase diagram for the WAF does not exhibit the existence of a bridge phase, in contrast to that of the SAF model. Thus, it follows that association promotes the formation of a bridge phase.

Finally, we turn our attention to a comparison of the phase diagrams for the SAF ($\varepsilon_{as} = 20$) and the WAF ($\varepsilon_{as} = 8$) in a narrow pore, $H = 5$ (figures 10(a) and 10(b)), and in a wide pore, $H = 9$ (figure 10(c)). The fluid–wall potential has been assumed to be the same in all of those cases, i.e. $\varepsilon_{gs}^{(1)} = 6$, $\lambda^{(1)} = 2$, $\varepsilon_{gs}^{(2)} = 3$, $\lambda^{(2)} = 1$; and the periodicity parameter is also fixed, $l = 9$. From the results presented in figure 10(a), it clearly follows that in spite of the qualitative similarity of the phase diagrams of the two models in a narrow pore (each of them consists of three branches describing layering, bridge phase formation and capillary condensation), the critical temperatures of all transitions are higher in the SAF than in the WAF. This is an obvious effect of association. Also, the critical densities for both phases—the bridge phase and the condensed liquid—are lower for the SAF than for the WAF, again as a result of bonding.

The above-described trends are similar to in the case of bulk critical phenomena for both models of associating fluids. On the other hand, from the examination of the curves given in figures 10(b) and 10(c), it follows that stronger bonding serves as a supplement to the nonassociative fluid–fluid attraction to ‘overcome’ the fluid–wall attraction, so the branches corresponding to dense phases in the SAF model, for almost all thermodynamic states, are located closer to the relevant bulk coexistence curve in comparison to those of the WAF model. Also, the results of figure 10(c) illustrate that the capillary condensation in the pore may occur with or without the formation of the intermediate phase, depending on the bonding strength. The stronger tendency towards the formation of bonds between monomers results in the appearance of the bridge phase.

4. Conclusions

We have applied the density functional theory to investigate the adsorption of strongly and weakly associating two-site fluid models in energetically heterogeneous pores with one-dimensional periodic modulation of the adsorbing potential. The model for the heterogeneous pore considered by us is similar to that introduced by Röcken *et al* [7]. However, our discussion of the phase behaviour seems to be more comprehensive. In particular, we also study the layering-type phase transitions in addition to the formation of the bridge phase and

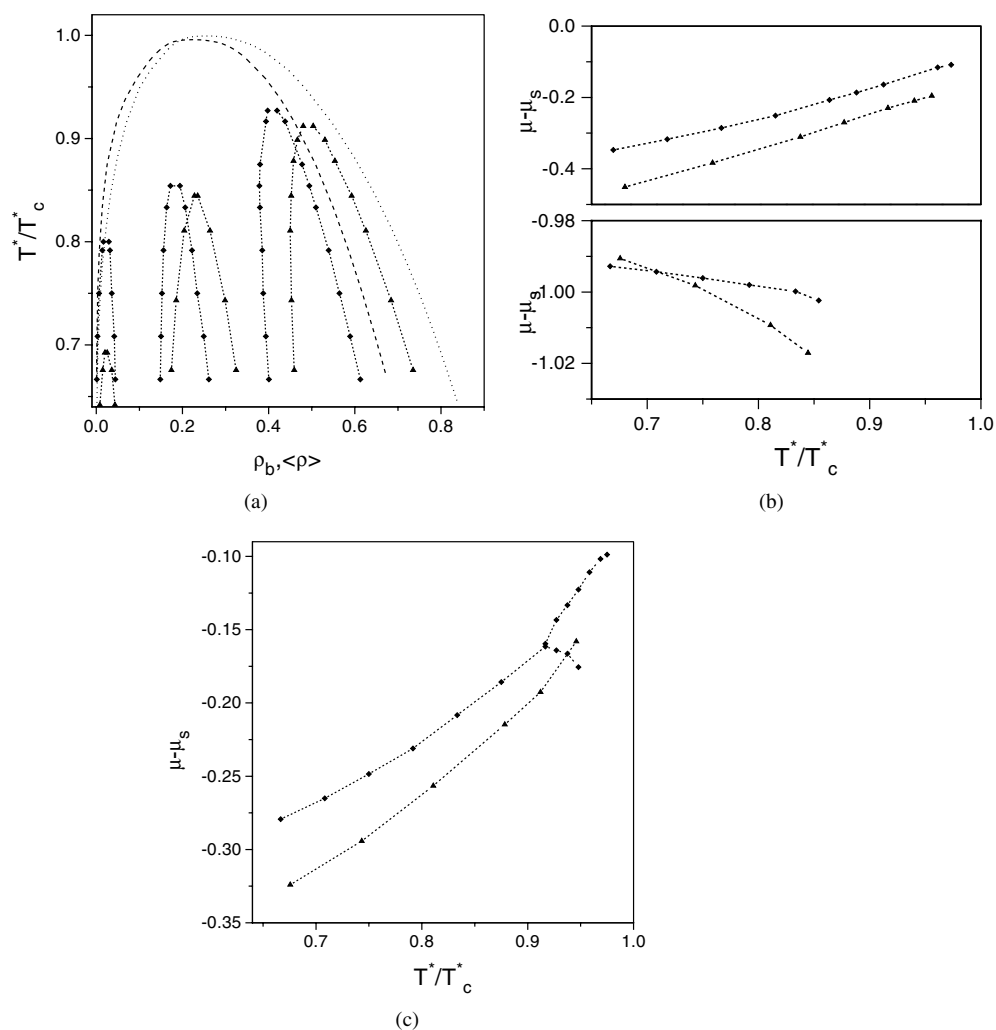


Figure 10. A comparison of the phase diagrams for a SAF model (rhombs) and for a WAF model (triangles) confined in slit-like pores, $H = 5$ (parts (a) and (b)), and in a pore with $H = 9$ (part (c)). The parameters of the fluid–wall potential are the following: $\varepsilon_{gs}^{(1)} = 6$; $\lambda^{(1)} = 2$; $\varepsilon_{gs}^{(2)} = 3$; $\lambda^{(2)} = 1$; $l = 9$. Layering branches are shown only in (a). Dashed line: bulk SAF; dotted line: bulk WAF.

the capillary condensation. Moreover, we have studied in detail the influence of the length of the periodicity of the adsorbing potential, the width of the pores and the strength of the ‘background’ homogeneous potential on the phase diagrams of confined fluids.

Acknowledgments

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