Structure effects and phase equilibria of Lennard-Jones mixtures in a cylindrical pore. A non-local density-functional theory

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The effect of fluid confinement in a narrow cylindrical pore is studied by means of a density-functional approach. An extension of the smoothed-density approximation to the two-component case is employed to explore the structure and phase behaviour of a mixture in a cylindrical pore. Contact is made with the previous local-density treatment and with the macroscopic thermodynamic approach.

1. Introduction

Owing to their large mobility, fluids composed of different chemical species can come into contact and mix. Surfaces, on the other hand, have the ability to select one or more components from a mixture by adsorbing some more strongly than others. The converse may also be true, i.e. two components not easily miscible in a normal environment can be mixed in the presence of an adsorbing interface.

Whereas a great number of statistical-mechanical studies have been devoted to the bulk properties of mixtures (see e.g. [1]), the understanding of their non-uniform properties is still in its infancy.

Recently several groups [2-4] have embarked upon the theoretical study of the behaviour of mixtures at fluid-fluid and solid-fluid interfaces and have clarified some aspects of their wetting properties. These studies have accounted for the observed values of the liquid-vapour surface tension and also how these change with thermodynamic variables such as pressure, temperature and bulk concentration. Also, in the last four years pores and slits have attracted a great deal of attention because of their theoretical and industrial importance. In practice most separation processes require the use of adsorbents of high surface area, and these requirements are commonly met by means of porous materials. In these systems fluids are under extreme conditions of non-uniformity, as a result of the presence of strong external fields due to solid substrates. The phase diagrams of pure simple fluids in capillaries have been recently elucidated by employing a variety of approaches such as density-functional methods (DF) (see e.g. [5-8], and grand canonical Monte Carlo (GCMC) (see e.g. [8-11], molecular-dynamics (MD) [8, 12] and 'Gibbs-ensemble' [10] simulations. In particular, the last generation of DF theories, namely the smoothed-density approximation (SDA), developed in its present form by Tarazona [13, 14], has been shown in a thorough comparative study [8] to be in good quantitative agreement with the simulation results.

At present, the only available information on the structure and thermodynamics of confined mixtures is represented by the recent work of Tan *et al.* [3], who applied the local-density approximation (LDA) to the modelling of an argon-krypton mixture in a cylindrical carbon dioxide pore. Although their results await further testing against computer simulation, one might anticipate, on the grounds of previous experience with pure fluids [7, 8], that the calculated structure and phase boundaries will be poorly represented by the LDA, especially for the smaller pores. Some preliminary MD simulations for binary mixtures in cylindrical pores have recently been performed, and these have been compared directly with DF-theory results. To date, no systematic studies of mixtures in contact with planar walls have appeared; but some preliminary calculations have been performed by Piotrovskaya and Smirnova [15], who report density profiles for an Ar-Kr mixture near a graphite wall.

The aim of the present paper is to investigate the influence of fluid structure on phase equilibria in very narrow pores. To do this, we need a detailed description of the short-range interactions of the fluid, and this is achieved by means of a suitable generalization of the SDA to the two-component case. In view of the small difference in the atomic radii of argon (species 1) and krypton (species 2), we have assumed a common diameter $\sigma_{11} = \sigma_{22} = \sigma$, but have kept the Lennard-Jones attractive parameters ε_1 and ε_2 different.

The paper is organized as follows. In section 2 we give a brief outline of the theory; in section 3 we obtain the asymptotic equation that describes the liquid-vapour equilibrium in a large pore, by means of a very simple approximate analysis. We also give the conditions for the occurrence of critical points, analogous to those stated for confined pure fluids. In section 4 we present the results for the surface tension at a free liquid-vapour interface within the SDA and compare with the LDA predictions. In section 5 we present the results for the structure of mixtures in pores for a variety of bulk compositions and we discuss the numerical findings. We give our conclusions in section 6.

2. Theory

The grand potential Ω of a non-uniform two-component fluid mixture is the minimum of the grand potential functional [4]

$$\Omega_{v}[\{\rho_{i}\}] = F[\{\rho_{i}\}] + \sum_{i=1}^{2} \int d\mathbf{r} [V_{i}(\mathbf{r}) - \mu] \rho_{i}(\mathbf{r}), \qquad (1)$$

where $\{\rho_i(\mathbf{r})\}\$ denotes the density profiles in the presence of external potentials $V_i(\mathbf{r})$, and μ_i is the equilibrium chemical potential of species *i*. In (1), \mathbf{r} is the position coordinate and the Helmholtz free-energy functional $F[\{\rho_i\}]$ is a unique functional of the densities. We shall divide the latter into two parts:

$$F[\{\rho_i(\mathbf{r})\}] = F_{rep}[\{\rho_i(\mathbf{r})\}] + F_{att}[\{\rho_i(\mathbf{r})\}].$$

$$(2)$$

The first term on the right-hand side represents the free energy arising from the repulsive forces between atoms, while the second represents the contribution from the attactive forces. Within the mean-field approximation we write for the latter

$$F_{\text{att}} = \frac{1}{2} \sum_{i,j} \int \int d\mathbf{r} \, d\mathbf{r}' \, u_{ij}(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}'), \qquad (3)$$

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where u_{ij} is the attractive part of the pairwise potential between molecules of species *i* and *j*. The equilibrium density profiles $\rho_i(\mathbf{r})$ are obtained by solving the coupled integral equations that result from minimizing Ω_v with respect to $\rho_i(\mathbf{r})$:

$$\frac{\delta \Omega_{\mathbf{v}}}{\delta \rho_i(\mathbf{r})} = 0 \quad (i = 1, 2). \tag{4}$$

The pair potential between molecules of types *i* and *j* was chosen to be a cut and shifted Lennard-Jones (LJ) potential characterized by a well depth ε_{ij} and collision diameter σ_{ij} :

$$\Phi_{ij}(r) = \begin{cases}
\Phi_{ij}^{LJ}(r) - \Phi_{ij}^{LJ}(r_{c}) & (r \leq r_{c}), \\
0 & (r > r_{c}), \\
\Phi_{ij}^{LJ}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right],$$
(5)

while $u_{ij}(r)$, the attractive part of the fluid-fluid potential, follows from a WCA division [16] of the cut and shifted LJ potential and is given by

$$u_{ij}(2) = \begin{cases} -[\varepsilon_{ij} + \Phi_{ij}(r_{c})] & (r \leq 2^{1/6}\sigma_{ij}), \\ \Phi_{ij}(r) - \Phi_{ij}(r_{c}) & (2^{1/6}\sigma_{ij} \leq r \leq r_{c}), \\ 0 & (r \leq r_{c}). \end{cases}$$
(6)

Following the WCA perturbation theory [16], we replace F_{rep} by the free-energy functional of an equivalent hard-sphere mixture. Our choice of the reference hard-sphere diameters sets $d_i = \sigma_{ii}$, i.e. d_i is taken to be temperature-independent (cf. [8, 17]). Thus we have

$$F_{\rm rep}[\rho_1, \rho_2; \sigma_{11}/\sigma_{22}] = F_{\rm HS}(\rho_1, \rho_2; \sigma_{11}/\sigma_{22}). \tag{7}$$

The hard sphere system itself is well described by the Mansoori equation of state [18]. $F_{\rm HS}$ consists of an ideal-gas contribution, which contains an entropy-of-mixing term plus a configurational term:

$$F_{\rm HS}[\{\rho_i\}] = kT \sum_{i=1}^2 \int d\mathbf{r} \,\rho_i(\mathbf{r}) \left\{ \ln\left[\frac{\rho_i(\mathbf{r})}{\Lambda_i^3}\right] - 1 \right\} + \Delta F_{\rm HS}[\{\rho_i(\mathbf{r})\}], \qquad (8)$$

where k is the Boltzmann constant and Λ_i is the de Broglie wavelength. In the LDA ΔF_{HS} the hard-sphere excess free-energy functional is written as

$$\Delta F_{\rm HS} = \int d\mathbf{r} \, \Delta f^{\rm HS}(\rho_1(\mathbf{r}), \, \rho_2(\mathbf{r})), \qquad (9)$$

where Δf^{HS} is the excess free energy per unit volume of a uniform hard-sphere fluid. This approximation has already been employed by several authors in the study of inhomogeneous mixtures [2-4]. One of the shortcomings of this approximation is the failure to describe the oscillatory density profiles that are usually observed for fluids at high pressures near solid substrates (see figures 2 and 3). Some years ago, Tarazona [13, 14] proposed a simple free-energy functional for ΔF_{HS} that does reproduce oscillatory profiles in the case of a pure fluid. In addition, Tarazona's functional has the merit of being fully thermodynamically consistent and can describe interfacial phenomena such as the growth of a wetting film on the approach to bulk coexistence [19]. This is in marked contrast with the traditional integral-equation theories [20]. In treating phenomena such as condensation in pores, thermodynamic consistency is a necessary condition if one wishes to extract any meaningful information.

The SDA developed by Tarazona [13, 14] is based on the use of a coarse-grained or smoothed density $\bar{\rho}(\mathbf{r})$, the density obtained by averaging the local density over an appropriately chosen local volume. This approach then accounts realistically for the repulsion between the cores. The pure-fluid case is easily generalized to a special kind of mixture for which the hard cores of the different components are equal. The more general case of arbitrary size ratios is currently being developed by the Cornell group. For the equal-sized mixture the SDA form of ΔF_{HS} is

$$\Delta F_{\rm HS} = \int d\boldsymbol{r} \left[\rho_1(\boldsymbol{r}) \,\Delta \psi_1 \,+\, \rho_2(\boldsymbol{r}) \,\Delta \psi_2 \right] \\ = \int d\boldsymbol{r} \left[\rho_1(\boldsymbol{r}) \,+\, \rho_2(\boldsymbol{r}) \right] \Delta \psi_{\rm HS}(\bar{\rho}_{\rm total}(\boldsymbol{r})), \tag{10}$$

where $\Delta \psi_i$ is the hard-sphere excess free energy per particle of species *i*, and the smoothed total density is given by

$$\bar{\rho}_{\text{total}}(\boldsymbol{r}) = \int d\boldsymbol{r}' \, w(|\boldsymbol{r} - \boldsymbol{r}'|; \, \bar{\rho}_{\text{total}}(\boldsymbol{r}))[\rho_1(\boldsymbol{r}') + \rho_2(\boldsymbol{r}')], \quad (11)$$

where w is a normalized weight function. Full details of the density expansion of w and its derivation can be found in Tarazona's original paper [13] and in [14]. The Carnahan-Starling expression for $\Delta \psi_{\text{HS}}$ is

$$\Delta\psi_{\rm HS}(\bar{\rho}_{\rm tot}) = \frac{kT(4-3\bar{\eta})}{(1-\bar{\eta})^2}$$

with

$$\bar{\eta} = \frac{1}{6}\pi \,\bar{\rho}_{\rm tot}\sigma^3$$
.

Inserting the above expressions for ΔF_{HS} into (1) and functionally differentiating with respect to $\rho_i(\mathbf{r})$, one obtains the equations for the equilibrium densities, which are then solved by a straightforward iteration procedure [3, 4].

The external field was chosen to be produced by a smooth infinitely long cylinder whose walls are infinitely thick and of uniform density:

$$V_i(s) = \pi \rho_s \varepsilon_{si} \sigma_{s1}^3 \left(\frac{\sigma_{si}}{R}\right)^3 \left[\frac{7}{32} \left(\frac{\sigma_{si}}{R}\right)^6 I_9 \left(\frac{s}{R}\right) - I_3 \left(\frac{s}{R}\right)\right], \quad (13)$$

with

$$I_n(x) = \int_0^{\pi} d\theta \left[-x \cos \theta + (1 - x^2 \sin^2 \theta)^{1/2} \right]^{-n}, \qquad (14)$$

where ρ_s is the density of the solid wall ($\rho_s \sigma_{s1}^3 = 0.988$). The Lennard-Jones parameters for the fluid mimic the Ar-Kr mixture, and the wall parameters represent CO_2 -Ar and CO_2 -Kr interactions:

$$\sigma_{11} = \sigma_{22} = 3.405 \text{ Å}, \quad \varepsilon_1/k = 119.8 \text{ K}, \\\sigma_{s1} = \frac{1}{2}(1 + 1.066)\sigma_{11}, \quad \varepsilon_2/\varepsilon_1 = 1.3614, \\\sigma_{s2} = \frac{1}{2}(1 + 1.118)\sigma_{11}, \quad \varepsilon_s/\varepsilon_1 = 1.6307. \end{cases}$$
(15)

Note that the choice $\sigma_{s1} \neq \sigma_{s2}$ indicates that the wall potentials experienced by argon and krypton have minima and zeros at different positions. The attractive interactions

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between species and also between each species and the solid are treated by using the Lorentz-Berthelot mixing rule

$$\varepsilon_{ii} = (\varepsilon_i \varepsilon_i)^{1/2} \tag{16}$$

The cut-off radius was fixed at $2.5\sigma_{11}$. In contrast, we did not truncate the fluid-wall interactions.

3. Phase equilibria in a wide pore

In order to gain some insight into the phase behaviour of fluid mixtures in pores, we shall start by making some general observations based on surface thermodynamics.

The model pore is schematized by an infinitely long open cylinder of radius R. The true equilibrium configuration of the confined fluid is the one that minimizes the thermodynamic grand potential functional (1).

In the limit when the radius becomes large we can separate Ω into a bulk and a surface contribution:

$$\Omega^{\alpha} = \omega^{\alpha} V + \gamma^{\alpha}_{\rm sf} A_{\rm sf}, \qquad (17)$$

where ω^{α} is the grand potential per unit volume of a *uniform* phase α , γ_{sf}^{α} its solid-fluid interfacial tension, and V (not to be confused with V_i of (13)) and A are respectively the volume occupied by the fluid in the pore and the solid-fluid interfacial area. Equilibrium between two distinct phases α and β implies equality of their grand potentials: $\Omega^{\alpha} = \Omega^{\beta}$, or

$$\omega^{\beta} - \omega^{\alpha} = (\gamma^{\alpha}_{sf} - \gamma^{\beta}_{sf}) \frac{A_{sf}}{V}.$$
 (18)

The difference on the right-hand side of (18) can be related to the surface tension $\gamma_{\alpha\beta}$ of the free $\alpha\beta$ interface using Young's equation:

$$\gamma_{\alpha\beta}\cos\theta = \gamma_{\rm sf}^{\alpha} - \gamma_{\rm sf}^{\beta}, \qquad (19)$$

which defines the so-called contact angle θ . If we set the geometrical ratio in (18), $A_{\rm sf}/V = 2/R_{\rm c}$, we arrive at the following equation:

$$\omega^{\beta} - \omega^{\alpha} = \frac{2\gamma_{\alpha\beta}\cos\theta}{R_{\rm c}}.$$
 (20)

A quite different situation is encountered when the phase β completely wets the solid substrate and forms an annulus of thickness *t* on the internal wall of the cylinder while the α phase occupies the remaining space in the pore. In this case one must account not only for a different geometrical ratio, but also for the presence of long-range attractive forces in the system. In physically relevant situations these forces decay as the inverse third power of the distance from the wall. Retarded forces are probably not relevant in the study of mesoporous media. The contribution of dispersion forces to the grand potential of the β phase exhibiting the wetting layers is proportional to $1/t^2$ (also called the disjoining pressure, by the Russian school). Since *t* itself grows upon approaching bulk α - β coexistence as $(\omega^{\beta} - \omega^{\alpha})^{-1/3}$, one obtains the following equation of state [2]:

$$\omega^{\beta} - \omega^{\alpha} = \frac{2\gamma_{\alpha\beta}}{R_{\rm c} - \frac{3}{2}t}.$$
 (21)

Thermodynamic relations can be applied to express the differences $\omega^{\beta} - \omega^{\alpha}$ as a function of ordinary intensive variables. We shall consider only two cases.

(a) The concentration of species 1 in the reservoir that is in contact with the pore is kept constant and the pressure P of the fluid in the reservoir is varied. Thus we obtain from (20)

$$\omega^{\beta} - \omega^{\alpha} = P_{\alpha} - P_{\beta} = \frac{2\gamma_{\alpha\beta}}{R_{\text{eff}}}, \qquad (22)$$

where P_{β} is the pressure of the metastable β phase having the same chemical potential as the α phase and R_{eff} is a suitably chosen effective radius. For small deviations from bulk coexistence we can expand the pressures of the two phases about their value at coexistence to obtain

$$P_{\alpha} - P_{\beta} = \sum_{i=1}^{2} \left(\rho_{i}^{\alpha} - \rho_{i}^{\beta} \right) \Delta \mu_{i}$$
(23)

where $\Delta \mu_i = \mu_i - \mu_i^{\text{coex}}$. If the α phase is a gas phase, we can write this difference in terms of the saturation densities: $\Delta \mu_i = kT \ln{(\rho_i/\rho_i^{\text{sat}})}$ and, since the concentration is kept constant, we have $\ln{(\rho_i/\rho_i^{\text{sat}})} = \ln{(P/P_{\text{sat}})}$. Substituting these results into (22), we obtain for a vapour-liquid equilibrium

$$kT\ln\left(\frac{P}{P_{\text{sat}}}\right) = -\frac{2\gamma_{\alpha\beta}\cos\theta}{R_{\text{eff}}\sum_{i=1}^{2}\left(\rho_{i}^{\beta}-\rho_{i}^{\alpha}\right)}.$$
 (24)

(b) An alternative way of restoring the phase equilibrium, broken by the presence of the walls, would be to keep the pressure of the α phase constant and to use the concentration variable to control the difference in the bulk contributions to the grand potential. In this case Evans and Marini Bettolo Marconi [2] derived

$$\Delta \mu_1 \rho_1^{\alpha} + \Delta \mu_2 \rho_2^{\alpha} = \frac{2\gamma_{\alpha\beta} \cos\theta}{R_{\rm eff}}.$$
 (25)

Using the Gibbs-Duhem equation, we eliminate $\Delta \mu_1$ to obtain

$$\Delta \mu_2 \left(\frac{\rho_2^{\alpha}}{\rho_1^{a}} - \frac{\rho_2^{\beta}}{\rho_1^{\beta}} \right) = \frac{2\gamma_{\alpha\beta}}{R_{\rm eff} \rho_1^{\alpha}} \cos \theta.$$

In this paper we limit our investigation to equilibria belonging to case (a) and compare the macroscopic prediction with the self-consistent microscopic calculations based on the density-functional theory. To conclude this section, we shall state the conditions for the occurrence of criticality in a confined mixture. As discussed in [2], the coexistence line for a one-component fluid in a pore ends in a capillary critical point where two phases in equilibrium become identical. This phenomenon has been termed 'capillary criticality', and for a given radius it is characterized by well-defined values of the temperature and chemical potential, which are different from the corresponding bulk critical values.

The conditions for criticality of a fluid mixture confined in a pore are directly analogous to those that describe the criticality of the pure fluid. Along a coexistence line the grand potentials of the two phases are equal. Their first derivatives with respect to the fields are not equal, but show a finite jump on going from one phase into the other. However, it may happen that as the temperature, the concentration or

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the size of the pore is varied, the two phases eventually coalesce, defining a critical point. At this point the first derivatives become continuous. In order to observe criticality in a mixture, two kinds of conditions must be satisfied. First,

$$\det\left[\frac{\partial\mu_i}{\partial\Gamma_j}\right]_{T,V,A} = 0.$$
 (26)

This condition alone is not sufficient to identify a critical point. We also require

$$\frac{\partial}{\partial \Gamma_1} \left(\det \left[\frac{\partial \mu_i}{\partial \Gamma_j} \right] \right) \left(\frac{\partial \mu_2}{\partial \Gamma_1} \right)_{T,V,A} - \frac{\partial}{\partial \Gamma_2} \left(\det \left[\frac{\partial \mu_i}{\partial \Gamma_j} \right] \right) \left(\frac{\partial \mu_1}{\partial \Gamma_1} \right)_{T,V,A} = 0, \quad (i = 1, 2),$$
(27)

$$\Gamma_i \equiv \int \mathrm{d}\boldsymbol{r} [\rho_i(\boldsymbol{r}) - \rho_i^{\text{bulk}}].$$

Unfortunately, these formally exact equations cannot be solved analytically because one does not know the functional dependence of Γ_i on the control parameters. As a result, this information has to be extracted from explicit numerical DFT calculations.

In the case of large pores, however, parametrizations of the solutions, as used in the past, might be helpful in locating the critical points [2].

4. Results and discussions

The SDA is a very attractive approximation, since it generally provides accurate descriptions of both the thermodynamics and the structure of confined fluids. The critical region forms an obvious exception, since the mean-field treatment of the attractive contribution of the free energy (3) neglects important fluctuations and therefore will not be in agreement with experiments on more advanced theoretical treatments of critical phenomena [21].

The method that we use requires a small amount of computation time—orders of magnitude less than the traditional simulation methods. Furthermore, if the comparison between theory and simulation is made at the reduced temperature T/T_c , the agreement is quite remarkable [8]. Here we present some results for the equally sized two-component mixture for several values of the bulk-gas composition $y = \rho_1^g(\rho_1^g + \rho_2^g)$ and the bulk pressure. The temperature was chosen to be $T^* = 1.044$. This corresponds to $T/T_c = 0.8$ for the pure component 1 (Ar) and $T/T_c = 0.588$ for the pure component 2 (Kr). The bulk critical temperature of the mixture varies smoothly with compositional changes [1].

A necessary ingredient of the macroscopic equations like the Kelvin equation (24) is knowledge of the liquid-vapour interfacial tension. To this end, we apply the SDA to the study of the planar interface between a liquid and its vapour at bulk coexistence. A systematic study of this subject is still lacking. Telo de Gama and co-workers [4] obtained some results within the LDA framework for the Ar-Kr mixture and compared them with MC simulations. They reported fair agreement between theory and simulation and observed that the LDA closely follows the prediction

$$\gamma_{\text{Ar-kr}} = x_{\text{Ar}}\gamma_{\text{Ar}} + (1 - x_{\text{Ar}})\gamma_{\text{kr}}, \qquad (28)$$

. . . .

where x_{Ar} is the mole fraction in the liquid phase. The difference between the actual value and that given by (28) defines the so-called 'surface-tension excess'. This quantity turns out to be negative in each of the approaches mentioned above [4]. We

у	x	$\gamma \sigma_{11}^2 / \varepsilon_{11}$ (SDA)	$\gamma \sigma_{11}^2 / \varepsilon_{11}$ (LDA)
1	1	0.1802	0.2063
0.925	0.7303	0.3174	0.3574
0.6	0.1723	0.6680	0.7494
0.2	0.0300	0.8156	0.9144
0	0	0.8538	0.954

Surface tensions.

have made a similar comparison between the LDA and the SDA, starting from the same form of the free energy for a uniform system. The surface tension in the LDA is always larger than the corresponding quantity in the SDA by about 15%, as has already been noted for pure fluids. In the table we present the results for a temperature $T^* = 1.044$ and different concentrations.

The partial-density profiles at a free interface are shown in figure 1 for $y_g = 0.6$ and $T^* = 1.044$.

5. Pore study

We shall start with the widest pore that we studied, i.e. $R_c^* = R_c/\sigma = 8$. This could correspond to 27 Å for argon, a typical mesoporous material size. In figure 2 we show two solutions at capillary condensation, where the grand potential function displays two separate minima of equal depth. The ratio of the bulk pressure to the pressure at coexistence (P_{sat}) is $P/P_{sat} = 0.6876$ and the bulk composition is y = 0.925. The 'gas-like' density profiles show two pronounced peaks and a shoulder in



Figure 1. SDA and LDA liquid-vapour profiles for an Ar-Kr mixture at a temperature $T/T_c^{Ar} = 0.8$ and at bulk-gas mole fraction of Ar, $y_{gas} = 0.6$: —, Kr (SDA); ---, Ar (SDA); ---, Kr (LDA); ---, Ar (LDA). The height z is measured in units of the Ar diameter ($\sigma = \sigma_{11}$).



Figure 2. Ar (species 1) and Kr (species 2) density profiles from the SDA in a cylindrical pore of radius $R = 8\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8$ ($P/P_{sat} = 0.6876$); the bulk-gas mole fraction of Ar is $y_{gas} = 0.925$: —, Ar (liquid); -..., Ar (gas); ---, Kr (liquid); -..., Kr (gas). The radial distance r is measured in units of the Ar diameter ($\sigma = \sigma_{11}$).

the more strongly adsorbed component (Ar), and a two-peak structure in the other component (Kr). The major peak of each species is very similar in height and shape to the corresponding peaks of the liquid phase, and the second peak also follows this trend. Wetting 'annuli' appear to be formed at the cylindrical wall, whereas towards the axis of the cylinder the profiles are monotonically decreasing. Note that, although Kr experiences a larger attraction towards the wall, the Ar density is larger in both phases, owing to the large difference in their chemical potentials, which favours argon.

For comparison we present the LDA profiles in figure 3 for the same conditions used in figure 2. As has been noted previously for the case of pure fluids (see e.g. [8, 17]), the LDA does not show any liquid structure and the amount adsorbed is less than in the SDA. This is because the LDA does not allow the local density to become large at the walls.

Figure 4 shows the pure argon fluid at capillary condensation. We note that the Ar peak is higher than the corresponding peak in figure 2 owing to the lack of competition with the other component, together with the different value of the applied bulk pressure (moreover, the bulk vapour pressure decreases as the mole fraction y_g decreases). Figure 5 shows the partial-density profiles for a mixture with y = 0.6. The results for y = 0.2 (not shown) appear to be very similar. Remarkably, the structure of the gas phase is totally different from that seen in figures 2 and 4. No liquid is seen to coat the walls. Surprisingly, we re-encounter a layered structure in the pure Kr (i.e. y = 0) system, shown in figure 6. In view of the higher critical temperature of this pure component and the increased interaction with the wall, the layered structure is probably more stable as a result. Of course, the pore also appears to be slightly smaller to Kr (by about 5%), but this does not seem to have a pronounced influence. The



Figure 3. Ar (species 1) and Kr (species 2) density profiles from the LDA ($P/P_{sat} = 0.7985$) for the same conditions as in figure 2 (for key to curves see caption to figure 2.



Figure 4. Liquid and gas density profiles from the SDA for pure Ar ($y_{gas} = 1$) in a cylindrical pore of radius $R = 8\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8 (P/P_{sat} = 0.7278): ---$, liquid; _____, gas.



Figure 5. Ar (species 1) and Kr (species 2) density profiles from the SDA in a cylindrical pore of radius $R = 8\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8$ ($P/P_{sat} = 0.6483$); the bulk-gas mole fraction of Ar is $y_{gas} = 0.6$ (for key to curves see caption to figure 2).



Figure 6. Liquid and gas density profiles from the SDA for pure Kr ($y_{gas} = 0$) in a cylindrical pore of radius $R = 8\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8 (P/P_{sat} = 0.5295)$: ---, liquid;



Figure 7. Ar (species 1) and Kr (species 2) density profiles from the SDA in a cylindrical pore of radius $R = 3\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8$ ($P/P_{sat} = 0.2574$); the bulk-gas mole fraction of Ar is $y_{gas} = 0.2$ (for key to curves see caption to figure 2).

rather high value of the maximum of the first layer should also be noted. We speculate that the mechanism by which the liquid film is washed out for intermediate values of y is related to the increase of the interfacial tension, which makes the film unfavorable. As $y \rightarrow 0$, however, the interaction between the fluid and the wall becomes more effective. The first peak approximately doubles in height, and this seems to lower the energy by a sufficient amount to compensate for the accompanying increase in surface tension. As a result, the film is restored. Further work on the planar solidfluid interface is in progress to help elucidate this effect. As the pore size decreases, the structure becomes more and more pronounced at high pressures, and this is reflected in the adsorption isotherms. In figures 7 and 8 we have plotted the (SDA) gas and liquid density profiles at capillary condensation for a radius $R_c^* = 3$ and a temperature $T^* = 1.044$. The bulk concentration in figure 7 is y = 0.20, while that in figure 8 is y = 0.925. The corresponding adsorption isotherms are displayed in figures 9 (SDA) and 10 (LDA), where we have plotted the partial adsorption for both Ar and Kr. The first-order phase transition and the loops in the SDA move towards lower pressures. This is because the non-local approximation takes better account of the fact that it is energetically favorable for the liquid to be in the pore. We stress that this trend goes in the opposite direction to what one would expect from the lower SDA value of the liquid-vapour surface tension compared with the LDA value. Thus macroscopic considerations based on the use of the Kelvin equation predict

$$\frac{\ln \left(P_{\text{cond}}^{\text{SDA}}/P_{\text{sat}}\right)}{\ln \left(P_{\text{cond}}^{\text{LDA}}/P_{\text{sat}}\right)} = \frac{\gamma_{1v}^{(\text{SDA})}}{\gamma_{1v}^{(\text{LDA})}} > 1,$$



Figure 8. Ar (species 1) and Kr (species 2) density profiles from the SDA in a cylindrical pore of radius $R = 3\sigma_{11}$ at a temperature $T/T_c^{Ar} = 0.8$ ($P/P_{sat} = 0.2388$); the bulk-gas mole fraction of Ar is $y_{gas} = 0.925$ (for key to curves see caption to figure 2).



Figure 9. Adsorption isotherms versus P/P_{sat} for an Ar-Kr mixture in a cylindrical pore of radius $R = 3\sigma_{11}$ as obtained from the SDA; the bulk-gas mole fraction of Ar is $y_{gas} = 0.2$: +, Ar; O, Kr. The transition is at $P/P_{sat} = 0.2574$.



Figure 10. LDA adsorption isotherms versus P/P_{sat} for an Ar-Kr mixture; the transition is at $P/P_{sat} = 0.4050$; conditions and key are as in figure 9.

in clear contradiction with what is actually observed. We have plotted the results for y = 0.925 in figure 11, where the SDA and LDA results are compared with the Kelvin equation.

One of the most immediate reasons why such considerations must fail is that the thickness of a free interface is comparable to the size of the whole system, and therefore it cannot be easily accommodated in small capillaries. However, in the limit of large radii, where the Kelvin equation becomes asymptotically correct, there should be a crossover, i.e. $P_{\text{cond}}^{\text{LDA}} < P_{\text{cond}}^{\text{SDA}}$. In figure 12 we plot the mole fraction of Ar for the two theories. In the low-pressure limit the two theories become identical, while at higher pressures the ratios agree only within 10%. The pore produces a larger extent of mixing (lower x) in the SDA than in the LDA. For comparison, the value of x in the liquid phase is x = 0.7303. Finally, in figure 13 we display the equilibrium transitions obtained for the three radii that we have investigated and for a variety of compositions. We have plotted both SDA points and the Kelvin prediction using SDA values for the surface tension. Note that for a given value of the undersaturation, condensation in wider pores occurs for mixtures richer in Kr. This is due to the increase of the surface tension with decreasing values of y. We have also located the phase transitions for the pure fluids, which serve as a reference. According to the same macroscopic arguments presented above, the position of the phase transition on the $P/P_{\rm sat}$ axis should be given by the simple mixing rule $[x\gamma_1 + (1 - x)\gamma_2]/R_{\rm eff}$. A large deviation from this 'rule' is seen for all radii that we studied. The implication is that the local structure near the wall is of dominating importance at these pore sizes, and negates the possibility of using standard surface thermodynamics (see e.g. [22]).



Figure 11. Kelvin-equation predictions using SDA (LDA) surface tensions versus SDA and LDA results; $y_{gas} = 0.925$: O, SDA; \triangle , LDA; —, Kelvin equation with LDA; —, Kelvin equation with SDA.



Figure 12. Relative absorption, defined as $\Gamma_1/(\Gamma_1 + \Gamma_2)$, versus P/P_{sat} for an Ar (species 1)-Kr (species 2) mixture along the $T/T_c^{Ar} = 0.8$ isotherm; the bulk-gas mole fraction of Ar is $y_{gas} = 0.2$ and the pore radius $R = 3\sigma_{11}$: +, SDA; O, LDA.



Figure 13. Kelvin-equation predictions (curves) versus SDA results (symbols): —, \diamond , $y_{gas} = 0; -\dots, +, 0.2; \dots, \blacksquare, 0.6; -\dots, 0, 0.925; -\dots, \Delta, 1.$

6. Conclusions

We have applied the so-called SDA to the study of a model mixture in a cylindrical pore. We find that for small capillaries the SDA and the LDA disagree quantitatively. What is completely missed by the latter approximation is the local structure at the wall, and this entails a large error in the estimate of the fluid-solid contact angle. Also, we find that macroscopic equations based on standard surface thermodynamics commonly used to describe phase equilibria in narrow pores cannot be applied to such small systems. Further work is required to investigate the role of size differences such as those found in more realistic mixtures [23]—particularly in very small pores. It might also be worthwhile to model the fluid beyond the mean-field approximation for the attractive part of the free energy. One might expect that this would lead to better agreement with the simulation results. A start has recently been made to test the SDA results against simulation [24]. Although the initial MD calculations have been performed for just two radii and one composition, the agreement found is encouraging.

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