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Freezing of Mixtures Confined in a Slit Nanopore

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Abstract. We report a Grand Canonical Monte Carlo study of the freezing/melting of Lennard-Jones A/B mixtures confined in a slit pore ($H = 1.44$ nm). The fluid/fluid interactions are chosen to model A = Ar and B = Kr. Fluid/wall interaction parameters are chosen so that the ratio of the wall/fluid to the fluid/fluid interactions for Kr and Ar is larger and smaller than 1, respectively. We find that the phase diagram of the confined mixture is of the same type than that for the bulk. The freezing temperature of confined mixtures rich in Kr is larger than the bulk. In contrast, we observe a decrease of the freezing temperature for mixtures rich in Ar. The confined crystal has a hexagonal structure (triangular symmetry), except for pure Ar where a square structure is observed.

Keywords: freezing, mixture, molecular simulation, confinement, solid–liquid phase diagram

1. Introduction

The freezing and melting of pure fluids confined in nanoporous materials have been extensively studied using both experiments and simulations (for reviews see Gelb et al., 1999; Christenson, 2001; Alba-Simionesco et al., 2004). This effort is relevant (i) to the fundamental understanding of phase transitions in confined geometry and (ii) to many applications that involve confined systems (lubrication, preparation of nanostructured materials, etc). Of practical interest is the understanding of confinement effects on the lubricating properties of thin films in nanotechnologies (magnetic hard disks, for instance). Freezing in narrow pores is also of importance in frost heaving and the distribution of pollutants in soils. Despite a few studies of molten salts (Meyer et al., 2000; Wilson, 2002) and colloidal mixtures (Cui et al., 2003), there seems to have been no studies on freezing and melting of confined mixture of simple fluids. In a recent work, we studied the confinement effect on freezing/melting of Ar/Kr mixtures confined in a slit graphite nanopore, by means of Grand Canonical Monte Carlo (GCMC) simulations (Coasne et al., 2004). We found that the phase diagram for the confined mixture was of the same type as that for the bulk, but the solid/liquid coexistence lines were located at higher temperatures. This result was expected since previous experiments and simulations have shown that the freezing temperature of pure fluids confined in strongly attractive pore

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is larger than the bulk (Radhakrishnan et al., 2000, 2002a).

In this paper, we explore the effect of the fluid/wall interaction on the solid/liquid phase diagram of the confined mixture. Interaction parameters are chosen so that the ratio of the wall/fluid to the fluid/fluid interactions is larger than 1 for Kr and smaller than 1 for Ar. The structure of the confined phase is studied by calculating 2D bond order parameters and both positional and bond orientational pair correlation functions. We determine the freezing temperature of the confined mixture and its dependence on the molar composition. We also report the solid/liquid phase diagram of the confined system and compare the results with data available for the bulk mixture (Hitchcock and Hall, 1999).

2. Computational Details

The GCMC technique consists of determining the properties of a system having a constant volume V (the pore with the confined phase) in equilibrium with an infinite fictitious reservoir of particles imposing its chemical potential for each species μ_{Ar}, μ_{Kr} and its temperature T (Frenkel and Smit, 2002). In order to improve the sampling of the phase space, we included in the GCMC simulations a parallel tempering technique (Yan and de Pablo, 1999). The constant parameters $\mu_{\mathrm{Ar}}(T)$ and $\mu_{\mathrm{Kr}}(T)$ of the simulations were extracted from the bulk solid/liquid phase diagram at $P = 1$ atm (Hitchcock and Hall, 1999). The freezing process was studied by starting with a liquid configuration of the system (300–400 particles) and decreasing the temperature by steps of 2 K. The final solid configuration at the lowest temperature was then used as the starting point for the study of the melting process, which proceeds in an analogous way. Full details of the simulation method have been given elsewhere (Coasne et al., 2004).

The fluid/fluid interactions Ar/Ar and Kr/Kr were calculated using Lennard-Jones potentials with the following parameters: $\sigma_{\mathrm{Ar/Ar}} = 0.3336$ nm, $\sigma_{\mathrm{Kr/Kr}} = 0.3575$ nm, $\varepsilon_{\mathrm{Ar/Ar}}/k_B = 141.2$ K and $\varepsilon_{\mathrm{Ar/Ar}}/k_B = 164.4$ K. The cross-species Ar/Kr parameters were calculated using the Lorentz-Berthelot combining rules. The slit pore was described as an assembly of two structureless parallel walls. The pore width was $H = 1.44$ nm ($\sim 4.3\sigma_{\mathrm{Ar/Ar}}$) and the size of the square section was 3.6 nm × 3.6 nm ($\sim 10\sigma_{\mathrm{Ar/Ar}} \times 10\sigma_{\mathrm{Ar/Ar}}$). Periodic boundary conditions were applied in the directions (x, y) parallel to the pore walls. The interaction between the fluid and each pore wall was calculated using the Steele '10-4-3' potential (Steele, 1974):

$$U_{wf}(z) = 2\pi\rho_w\varepsilon_{wf}\sigma_{wf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{wf}}{z}\right)^{10} - \left(\frac{\sigma_{wf}}{z}\right)^4 - \left(\frac{\sigma_{wf}^4}{3\Delta(z+0.61\Delta)^3}\right)\right] \quad (1)$$

where z is the distance between the adsorbed molecule and the graphite surface. Δ is the separation between graphite layers, 0.335 nm, and ρ_{w} the atomic density of graphite layers, 114 nm^{-3}, while ε_{wf} and σ_{wf} are the wall/fluid Lennard-Jones parameters. $\varepsilon_{w/\mathrm{Kr}}$, $\sigma_{w/\mathrm{Kr}}$ and $\sigma_{w/\mathrm{Ar}}$ were determined by combining the wall/wall and fluid/fluid parameters using the Lorentz-Berthelot rules with the values $\varepsilon_{ww}/k_B = 28$ K and $\sigma_{ww} = 0.34$ nm for the carbon wall (Steele, 1974). This leads to a ratio, $\alpha = \rho_w\varepsilon_{wf}\,\sigma_{wf}^2\Delta/\varepsilon_{ff}$, of the fluid/wall to the fluid/fluid interactions larger than 1 for Kr, $\alpha_{\mathrm{Kr}} = 1.78$. In contrast, we arbitrarily chose $\varepsilon_{w/\mathrm{Ar}}/k_B = 26.1$ K so that the α parameter for Ar, $\alpha_{\mathrm{Ar}} = 0.80$, is lower than 1. This choice does not correspond to realistic Ar confined in porous carbons, but allows us to study the effect of the wall interaction on the freezing of mixtures. Comparison with our previous work for realistic Ar/Kr mixtures in a graphite pore will be discussed below (Coasne et al., 2004).

Layering was observed due to the interaction with the attractive pore walls. The structure of the confined mixture was investigated by calculating for each layer i the 2D bond order parameters $\Phi_{n,i}$ ($n = 4$ and 6 for a square and triangular structure, respectively). We determined $\Phi_{n,i}$ as the average value of the local order parameter $\Psi_{n,i}(\mathrm{r})$, which measures the hexagonal or square bond order at a position $\mathbf{r}$ of a particle located in the layer i (Nelson and Halperin, 1979; Strandburg, 1988):

$$\Phi_{n,i} = \frac{\left|\int \Psi_{n,i}(\mathbf{r})d\mathbf{r}\right|}{d\mathbf{r}}$$

$$\text{with} \quad \Psi_{n,i}(\mathbf{r}) = \frac{1}{N_b}\sum_{k=1}^{N_b}\exp(in\theta_k) \quad (2)$$

where θ_k are the bond angles between the particle and each of its N_b nearest neighbors. $\Phi_{n,i}$ is expected to be close to 1 for a crystal layer having a triangular ($n = 6$) or a square ($n = 4$) structure and close to 0 for a liquid layer.

We also monitored the 2D positional and bond orientational pair correlation functions, $g_i(r)$ and $G_{n,i}(r)$.

The latter measures for each layer i the correlations between the local bond order parameter $\Psi_{n,j}(r)$ at two positions separated by a distance r:

$$G_{n,i}(r) = \langle \Psi^{*}_{n,i}(0)\Psi_{n,i}(r)\rangle \tag{3}$$

3. Results and Discussion

3.1. Confinement Effect on the Freezing Temperature

We first discuss the freezing of an Ar/Kr confined mixture having a high Kr mole fraction, $x_{\mathrm{Kr}} \sim 0.90$. Density profiles of the confined mixture show that the 1.44 nm slit pore accomodates two contact layers and one inner layer. We found that the confined mixture always has a larger Kr mole fraction than the bulk mixture. This result is in agreement with previous simulation (Cracknell et al., 1994) and theoretical (Tan and Gubbins, 1992) works for liquid mixtures confined in a slit graphitic pore, which have shown that the molar composition of the component having the strongest interaction with the pore wall is increased compared to the bulk. In Fig. 1, we show the in-plane pair correlation functions $g(r)$ for the contact and the inner layers of the Ar/Kr mixture with $x_{\mathrm{Kr}} \sim 0.90$. Both the contact and the inner layers have a solid-like structure at $T = 139$ K; the $g(r)$ functions exhibit the following features: (i) the minimum between the first and the second peak is close to 0, (ii) the second peak is split into two secondary peaks, and (iii) the third peak presents a shoulder on its right side. In contrast, the $g(r)$ functions at $T = 145$ K are characteristic of a liquid-like layer.

As shown in Fig. 2(a), the transition between the crystal-like and the liquid-like phases is accompanied by a sharp decrease of the Kr mole fraction. A small hysteresis loop, $\Delta T = 2$ K, was observed between the freezing and melting processes. We defined the temperature of the crystal/liquid transition, $T_f = 143$ K as the average value of the freezing temperature $T = 142$ K and the melting temperature $T = 144$ K (see Fig. 2(a)). We note that this approach gives a reasonable estimation of the transition temperature because of the very small width of the hysteresis loop. For the general case where wide hysteresis loops are observed, a free energy

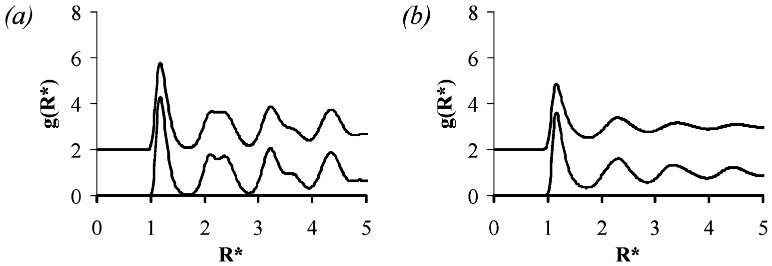


Figure 1. In-plane 2D pair correlation functions $g(r)$ for the contact and inner layers of an Ar/Kr mixture confined in the 1.44 nm slit pore at (a) $T = 139$ K, $x_{\mathrm{Kr}} = 0.93$ and (b) $T = 145$ K, $x_{\mathrm{Kr}} = 0.89$. For the sake of clarity the $g(r)$ function corresponding to the inner layer has been shifted by $+2$. R^* is the distance in reduced units with respect to $\sigma_{\mathrm{Ar/Ar}}$.

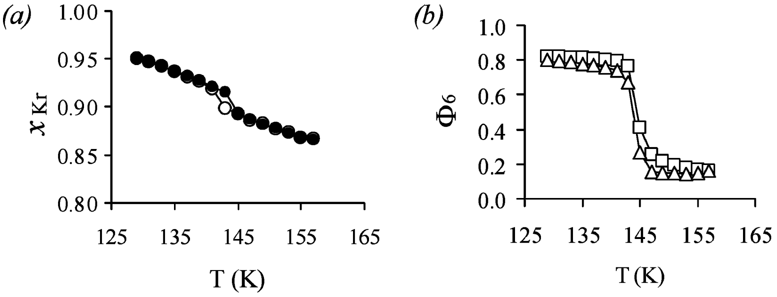


Figure 2. Ar/Kr mixture rich in Kr confined in the 1.44 nm slit pore. (a) Variations upon freezing (open circles) and upon melting (closed circles) of the molar compostion of the mixture, (b) Variations upon freezing of the hexagonal bond-order parameter Φ_6 for the contact layer (squares) and the inner layer (triangles).

calculation is required to determine accurately the location of the transition. The Kr mole fractions of the coexisting liquid, $x_{\mathrm{Kr}} \sim 0.90$, and crystal, $x_{\mathrm{Kr}} \sim 0.92$, phases were estimated from the lower and upper branch of the hysteresis loop, respectively. Interestingly, the observation of a hysteresis loop and the sharp decrease in Kr mole fraction upon melting suggests that the solid/liquid transition of the confined mixture is a first order transition.

We show in Fig. 2b the 2D order parameter Φ_6 for the contact and inner layers as a function of the temperature. The sudden change of Φ_6 with temperature confirms that both the contact and inner layers undergo a liquid-like to crystal-like transition at a temperature $T_f \sim 144$ K. Φ_6 varies from ~ 0.15 in the liquid-like region up to ~ 0.80 in the crystal-like region. This latter value suggests that the contact layer has a hexagonal crystal structure (triangular symmetry) with, however, a large number of defects. This result was confirmed by calculating the bond-order pair correlation functions $G_6(r)$ for both the contact and inner layers.

We now discuss the freezing and melting of a pure Ar fluid confined in the 1.44 nm slit pore. The density of the confined fluid as a function of the temperature is shown in Fig. 3(a). Upon decreasing temperatures, the density sharply increases at the freezing temperature, $T = 85$ K, from $\rho^* \sim 0.76$ up to $\rho^* \sim 0.87$. A large hysteresis loop, $\Delta T = 12$ K, was found between the freezing and melting process. We defined the crystal/liquid transition temperature $T_f = 91$ K as the average value of the freezing and the melting temperatures. Free energy calculations are required to determine accurately the transition temperature.

The density profiles for this molar composition $x_{\mathrm{Kr}} = 0.0$ show that the pore accomodates four layers (two contact, two inner layers) in the crystal region and three layers (two contact, one inner layer) in the liquid region. Calculations of the bond-order parameters Φ_4 for the contact and the inner layer are shown in Fig. 3(b). One can see that both the contact and inner layers undergo a transition from a square crystal structure, $\Phi_4 = 0.9$, to a liquid-like structure, $\Phi_4 = 0.1$. This result was confirmed by analyzing the positional $g(r)$ and bond-order $G_4(r)$ pair correlation functions. The freezing mechanism for pure Ar strongly departs from what is observed for the mixture $x_{\mathrm{Kr}} \sim 0.90$; the increase from 3 to 4 layers and the formation of a square crystal structure was observed only for pure Ar. However, we note that freezing and melting processes involving a change in the number of layers and in the symmetry of the crystal phase have been reported in previous simulation studies for pure confined fluids (Patrykiejew et al., 2003; Vishnyakov and Neimark, 2003).

3.2. Phase Diagram of the Confined Mixture

The solid/liquid phase diagram (T_f, x_{Kr}) of the Ar/Kr mixture confined in the 1.44 nm slit pore is shown in Fig. 4(a). The different solid/liquid coexistence conditions, temperature T_f and Kr mole fractions at T_f, were determined following the analysis described in the previous section. We also report in Fig. 4(a) the phase diagram obtained in our previous work where strongly attractive pore walls were used (Coasne et al., 2004). Results are compared with the solid/liquid phase diagram obtained for bulk Lennard-Jones Ar/Kr mixtures (Hitchcock and Hall, 1999). This phase diagram is of the type "solid solution," in agreement with experiments (Jones and Fretwell, 2003). The phase

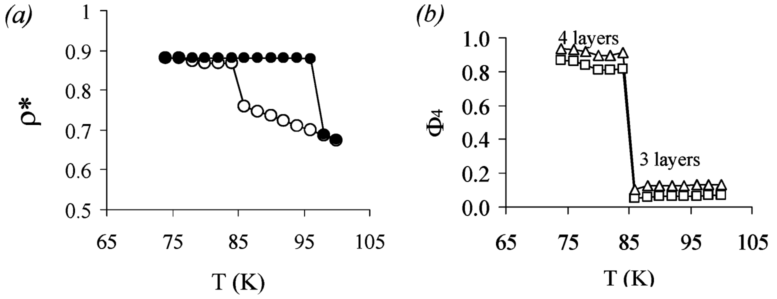
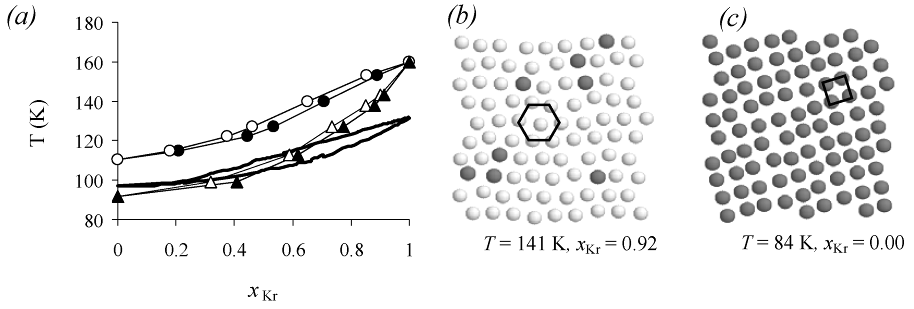


Figure 3. Pure Ar confined in the 1.44 nm slit pore. (a) Variations upon freezing (open circles) and upon melting (closed circles) of the density of the confined system, (b) Variations upon freezing of the square bond-order parameter Φ_4 for the contact layer (squares) and the inner layer (triangles).



$T = 141$ K, $x_{\text{Kr}} = 0.92$

$T = 84$ K, $x_{\text{Kr}} = 0.00$

Figure 4. (a) (triangles): T, x_{Kr} phase diagram of the Ar/Kr mixture confined in the 1.44 nm slit pore with $\alpha_{\text{Ar}} = 0.80$, $\alpha_{\text{Kr}} = 1.78$. For each transition temperature T, open and closed symbols are the Kr mole fractions of the coexisting liquid and crystal states, respectively. The open/closed circles are the results for confined Ar/Kr mixtures with $\alpha_{\text{Ar}} = 1.93$, $\alpha_{\text{Kr}} = 1.78$ (from Coasne et al., 2004). The thick lines are the solid/liquid coexistence lines for the bulk mixture (Hitchcock and Hall, 1999). (b), (c) Triangular and square crystal structure of the contact layer of Ar/Kr mixtures confined in the 1.44 nm slit pore. Gray and white spheres correspond to Ar and Kr atoms, respectively.

diagram for the confined Ar/Kr mixture has the same shape as the bulk, but the solid/liquid coexistence lines are shifted in temperature.

For mixtures rich in Kr, we find that the freezing temperature of the confined system is larger than that for the bulk. This result is due to the α parameter for Kr that is larger than 1, $\alpha_{\text{Kr}} = 1.78$. Indeed, previous works have shown that the freezing temperature of confined fluids is increased compared to the bulk, provided that the fluid/wall interaction is larger than the fluid/fluid interaction (Radhakrishnan et al., 2000, 2002a). In the case of mixtures, we extended this result by considering Ar/Kr mixtures confined between walls that more strongly attract Ar, $\alpha_{\text{Ar}} = 1.93$ and $\alpha_{\text{Kr}} = 1.78$; the freezing temperature of the confined system is larger than the bulk freezing temperature for all molar compositions (see Fig. 4(a)). Such an increase of the freezing temperature is consistent with recent dielectric relaxation measurements performed by Sliwinska-Bartkowiak and coworkers for a carbon tetrachloride/cyclohexane mixture confined in strongly attractive slit-pores of activated carbon fibers (Sliwinska-Bartkowiak et al., 2004). The authors also found a shift of the azeotrope point towards the higher CCl_4 concentration.

In contrast to the case of mixtures rich in Kr, the freezing temperature for $x_{\text{Kr}} < 0.5$ is decreased compared to the bulk (see Fig. 4). This result was expected since the α parameter for Ar is smaller than 1, $\alpha_{\text{Ar}} = 0.80$.

Atomic configurations of the contact layer of the confined mixture are shown in Fig. 4(b) and (c). In each case, the same structure was observed for the inner layer. For all mixtures, the crystal layers have a triangular symmetry, which corresponds to a centered hexagonal structure (see Fig. 4(b)). This structure is usually observed in the case of strongly attractive pores ($\alpha > 1$) since it corresponds to a dense close-packing of the atoms at the surface of the pore wall. In contrast, the origin of the square crystal phase for pure Ar (see Fig. 4(c)) is not clear; as previously mentioned, such a symmetry is observed for particular reduced pore sizes where a change in the number of layers occurs. Our results for mixtures also suggest that weak wall/fluid interactions may favor the square symmetry since it is observed only for pure argon ($\alpha < 1$). Further study is needed to clarify this issue.

Although the use of the parallel tempering technique in simulations greatly reduces the probability of getting trapped in a metastable state, free energy calculations will allow us to check the thermodynamic stability of each of the phases present in the system in a rigorous way. Such calculations are currently in progress. Further study, including a system size scaling analysis (Radhakrishnan et al., 2002b) is also needed to check whether the confined mixture undergoes a crystal to hexatic phase transition followed by a hexatic to liquid phase transition or only a crystal to liquid phase transition.

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