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Effect of repulsive and attractive interactions in the adsorption of confined polydisperse fluids

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Abstract. A density functional perturbative approximation, which is based on the pair distribution function, has been developed to investigate the influence of attractive and repulsive interactions on the density behaviour of a confined polydisperse fluid. The calculated result shows that the attractive and repulsive interactions in the model potential are strongly affected on the adsorption of a confined polydisperse fluid as well as the cavity size and particle size ratio. The attractive interaction in a polydisperse square-well system increases the pore average mole fraction for small particles in a circular cavity. Whereas a repulsive interaction in a polydisperse square-shoulder system decreases the pore average mole fraction for small particles. The local relative concentration oscillates with a spatial period close to the diameter of a large particle as well as the equilibrium density distribution does.

1. Introduction

One of the important subjects in the study of fluid structure is to clarify the roles of the strong short-range repulsive part and the attraction part of the intermolecular potential in determining structural features of fluids [1–4]. Such investigations have been done for a system of particles interacting with each other via the square-well potential and the square-shoulder potential. Actually, the addition of short-range attractive and repulsive interactions beyond the hard core can profoundly influence the structural properties of a confined model fluid. One example is the local relative concentration and size selectivity in the adsorption of a confined model fluid. The other is the isostructural solid–solid transition in model fluids with sufficiently narrow attractive (square-well) or repulsive (square-shoulder) potentials [3–5]. For a purely repulsive shoulder potential, the atomic localization is found to increase with increasing temperature in contrast to the attractive square-well potential.

Lang *et al* [4] have recently investigated the structure and thermodynamics of the square-well and square-shoulder fluids using two different theoretical frameworks, i.e. the optimized random-phase approximation and the Rogers–Young equation. More recently, Lee *et al* [6] have applied the density functional perturbative approximation to study the influence of the potential well and the potential barrier on the density distribution of confined model fluids. They showed that at lower densities the density distribution is strongly affected by the barrier height and the well depth of the model potential, a contribution from the short-range repulsive part being especially important, while the effect of the barrier height and the well depth of a model potential decreases with increasing the bulk density. As for the two-dimensional fluid system, Németh and Löwen [7] have studied the freezing problem of a hard-disk fluid

in circular cavities. Takamiya and Nakanishi [8] have applied the two-dimensional weighted-density approximation to calculate the structural properties of a two-dimensional Lennard–Jones fluid confined in the system with a special symmetry. However, for the structural properties of the two-dimensional polydisperse fluids they are much less well understood than systems compared with one-component hard-disk fluids. Thus, we develop here the density functional perturbative approximation to a study of the influence of repulsive–attractive interactions in the adsorption of a confined polydisperse fluid which is generally characterized by a continuous distribution of the particle diameters. Actually, the polydisperse fluid is of great importance for the investigation of the physical properties of an emulsion interacting strongly with each other in two dimensions [9]. In this case, the crystallization is driven by a depletion attraction between the large spheres, due to the smaller spheres

In section 2, we will derive the density profile equation, which is based on the density functional perturbative approximation, for a confined polydisperse fluid. In section 3, the influence of attractive and repulsive interactions on the structural properties of a polydisperse fluid confined in a hard circular cavity is studied in detail. The local size segregation and size selectivity for a confined polydisperse fluid are investigated. Finally, the pore size and particle size ratio dependences for a confined polydisperse fluid are discussed.

2. Density functional perturbative approximation

The polydisperse bulk fluid is generally characterized by a continuous distribution of the particle diameters, $F(\sigma)$, which fulfills the normalization condition

$$\int d\sigma F(\sigma) = 1 \quad (1)$$

where $F(\sigma)$ is defined such that the probability of finding a particle of size between σ and $\sigma + d\sigma$ is given by $F(\sigma) d\sigma$. The bulk number of density equal to $\rho_0 = N/V$, where N is the number of all the particles and V is the volume of the system. The density of particles of diameter σ is $\rho(\sigma) = \rho_0 F(\sigma)$ [10].

Following the perturbative theory which is well known in the classical liquid theory [11], the pair interaction potential $\phi_{pot}(\sigma, r)$ of model fluids can be divided by the reference part $\phi_{ref}(\sigma, r)$ plus the perturbative part $\phi_{pert}(\sigma, r)$ of model potential such as

$$\phi_{pot}(\sigma, r) = \phi_{ref}(\sigma, r) + \phi_{pert}(\sigma, r). \quad (2)$$

Then, the excess free-energy functional $F_{ex}[\rho]$ originating from the particle interaction can also be written as the reference contribution $F_{ref}[\rho]$ plus the perturbative contribution $F_{pert}[\rho]$

$$F_{ex}[\rho] = F_{ref}[\rho] + F_{pert}[\rho]. \quad (3)$$

In the density functional theory for a polydisperse system with the particle diameter σ , the equilibrium particle density distribution $\rho(\sigma, \vec{r})$ of the inhomogeneous fluid is described by the minimum of the grand canonical potential $\Omega[\rho]$ satisfying the Euler–Lagrange relation

$$\frac{\delta\beta\Omega[\rho]}{\delta\rho(\sigma, \vec{r})} = 0 \quad (4)$$

where $\beta = 1/k_B T$ is the inverse temperature and k_B is the Boltzmann’s constant [11]. If the inhomogeneous fluid is in contact with the homogeneous bulk fluid, its chemical potential $\mu(\sigma)$ is equal to that of the homogeneous bulk fluid. Then, the equilibrium density distribution function (or density profile equation), $\rho(\sigma, \vec{r})$, is given, after some manipulations, as

$$\begin{aligned} \rho(\sigma, \vec{r}) = & \rho(\sigma) \exp[-\beta u_{ext}(\sigma, \vec{r}) + c_{ref}^{(1)}(\sigma, \vec{r}; [\rho]) \\ & + c_{pert}^{(1)}(\sigma, \vec{r}; [\rho]) - c_{ref}^{(1)}(\rho(\sigma)) - c_{pert}^{(1)}(\rho(\sigma))] \end{aligned} \quad (5)$$

where $\rho(\sigma) = \rho_0 F(\sigma)$ denotes the homogeneous bulk density distribution and $u_{ext}(\sigma, \vec{r})$ is an external potential acting on species σ [11]. In (5), $c^{(1)}(\sigma, \vec{r}; [\rho])$ is the one-particle direct correlation function (DCF) of the inhomogeneous fluid, which is defined as

$$c_{ref}^{(1)}(\sigma, \vec{r}; [\rho]) = -\frac{\delta\beta F_{ref}[\rho]}{\delta\rho(\sigma, \vec{r})} \quad \text{and} \quad c_{pert}^{(1)}(\sigma, \vec{r}; [\rho]) = -\frac{\delta\beta F_{pert}[\rho]}{\delta\rho(\sigma, \vec{r})}. \quad (6)$$

As an approximation for the free-energy functional $F_{ref}[\rho]$ corresponding to the reference part of the model potential, we use the weighted-density approximation which was proposed by Rosenfeld and based on the fundamental geometric measures of particles [12]. In this case, the one-particle DCF $c_{ref}^{(1)}(\sigma, \vec{r}; [\rho])$ is simply given as

$$c_{ref}^{(1)}(\sigma, \vec{r}; [\rho]) = -\int d\vec{s} \sum_{\alpha} \frac{\partial f_{ref}[n_{\alpha}(\vec{s})]}{\partial n_{\alpha}(\vec{r})} \omega^{(\alpha)}(\sigma, |\vec{r} - \vec{s}|) \quad (7)$$

where $f_{ref}[n_{\alpha}(\vec{r})]$ is the excess free-energy per volume. Here, we choose the original free-energy model for numerical use, although some recent modifications are known to give a better description of solid phase [13]. Actually, the original free-energy model demonstrates reliable accuracy and reproduces the simulation data accurately even for a large size ratio of hard spheres. The excess free energy $f_{ref}[n_{\alpha}(\vec{r})]$ is assumed as

$$f_{ref}[n_{\alpha}(\vec{r})] = -n_0(\vec{r}) \ln[1 - n_2(\vec{r})] + \frac{n_1(\vec{r})n_1(\vec{r}) - \vec{n}_{v1}(\vec{r}) \cdot \vec{n}_{v1}(\vec{r})}{4\pi[1 - n_2(\vec{r})]} \quad (8)$$

with a function of only the system-averaged fundamental geometric measure of the particles

$$n_{\alpha}(\vec{r}) = \int d\sigma \int d\vec{s} \rho(\sigma, \vec{s}) \omega^{(\alpha)}(\sigma, |\vec{r} - \vec{s}|) \quad (9)$$

where $\omega^{(\alpha)}(\sigma, r)$ are four weight functions, selected such that the Percus–Yevick equation is recovered for a homogeneous polydisperse fluid [14].

For the homogeneous state, (7) simply becomes

$$c_{ref}^{(1)}(\rho(\sigma)) = \ln(1 - n_2) - \frac{n_0}{1 - n_2} - \frac{2n_1}{4\pi(1 - n_2)} - \frac{n_1^2}{4\pi(1 - n_2)^2} \quad (10)$$

with $n_0 = \int d\sigma \rho(\sigma)$, $n_1 = \pi \int d\sigma \sigma \rho(\sigma)$ and $n_2 = \pi \int d\sigma \sigma^2 \rho(\sigma)/4$, since $\omega^{(\alpha)}(\sigma) \propto \sigma^{\alpha}$ for a homogeneous polydisperse hard-disk fluid.

As a next step, we consider an approximation for the perturbative free energy $F_{pert}[\rho]$. The free-energy functional corresponding to the perturbative contribution is given exactly by

$$\beta F_{pert}[\rho] = \frac{1}{2} \int_0^1 d\gamma \int d\vec{r} \int d\sigma \int d\vec{s} \int d\sigma' \rho^{(2)}(\vec{r}, \vec{s}; \phi_{pert}(\gamma)) \beta \phi_{pert}(\sigma, \sigma', |\vec{r} - \vec{s}|) \quad (11)$$

where $\rho^{(2)}(\vec{r}, \vec{s}; \phi_{pert}(\gamma))$ is the pair distribution function which is related to the radial distribution function $g(\vec{r}, \vec{s}; \phi_{pert}(\gamma))$ and γ is the charging parameter [11]. Since the radial distribution function is little known for a polydisperse fluid, we introduce the mean field approximation which is based on the simple approximation to the pair distribution function

$$\rho^{(2)}(\vec{r}, \vec{s}; \phi_{pert}(\gamma)) = \rho(\sigma, \vec{r}) \rho(\sigma', \vec{s}) g(\vec{r}, \vec{s}; \phi_{pert}(\gamma)) \approx \rho(\sigma, \vec{r}) \rho(\sigma', \vec{s}). \quad (12)$$

Then, the perturbative free energy becomes, from (11) and (12),

$$\beta F_{pert}[\rho] = \frac{1}{2} \int d\vec{r} \int d\sigma \rho(\sigma, \vec{r}) \int d\vec{s} \int d\sigma' \rho(\sigma', \vec{s}) \beta \phi_{pert}[(\sigma + \sigma')/2, |\vec{r} - \vec{s}|] \quad (13)$$

where the Lorentz–Berthelot mixing rule has been used to determine the length parameter; for example, for a binary mixture the length parameter is given as $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$,

where $i, j = 1, 2$. The one-particle DCF $c_{pert}^{(1)}(\sigma, \vec{r}; [\rho])$ corresponding to the perturbative contribution becomes, from (6) and (13),

$$c_{pert}^{(1)}(\sigma, \vec{r}; [\rho]) = - \int d\vec{s} \int d\sigma' \rho(\sigma', \vec{s}) \beta \phi_{pert}[(\sigma + \sigma')/2, |\vec{r} - \vec{s}|]. \quad (14)$$

For the homogeneous state, (14) becomes

$$c_{pert}^{(1)}(\rho(\sigma)) = - \int d\sigma' \rho(\sigma') \int d\vec{s} \beta \phi_{pert}[(\sigma + \sigma')/2, s] \quad (15)$$

since $\rho(\sigma, \vec{r}) = \rho(\sigma)$. Taken together, (5), (7), (10), (14) and (15), constitute the density functional perturbative approximation for a confined polydisperse fluid.

3. Results and discussion

To investigate the effect of attractive and repulsive interactions in adsorption of a confined polydisperse fluid, we consider two simple model systems with attractive and repulsive interactions. One is a polydisperse square-well system, consisting of a hard core of range σ and a square-well depth. The other is a polydisperse square-shoulder system with a barrier (a hard-sphere potential augmented with a repulsive plateau), which is believed to be due to the softness of the pair interaction potential associated with a pressure-induced change in the electronic state of the metal ions. The pair interaction potential $\beta \phi_{pot}(\sigma, r)$ of the polydisperse square-well and square-shoulder systems is given by

$$\begin{aligned} \beta \phi_{pot}(\sigma, r) &= \infty & 0 < r < \sigma \\ &= \beta \epsilon & \sigma < r < \lambda \sigma \\ &= 0 & \lambda \sigma < r \end{aligned} \quad (16)$$

where the negative well depth $\beta \epsilon$ represents an attractive square-well potential, while a positive $\beta \epsilon$ produces a repulsive square-shoulder interaction. The λ is the well (or, shoulder) range.

Following the perturbative theory, we divide the model potential into a hard-core part $\phi_{ref}(\sigma, r)$ and a perturbative part $\phi_{pert}(\sigma, r)$. Then, (16) becomes

$$\begin{aligned} \beta \phi_{ref}(\sigma, r) &= \infty & 0 < r < \sigma \\ &= 0 & r > \sigma \end{aligned} \quad (17)$$

and

$$\begin{aligned} \beta \phi_{pert}(\sigma, r) &= 0 & 0 < r < \sigma \\ &= \beta \epsilon & \sigma < r < \lambda \sigma \\ &= 0 & \lambda \sigma < r. \end{aligned} \quad (18)$$

We consider the polydisperse square-well and square-shoulder fluids within a structureless hard circular cavity. For a hard circular cavity, the external potential $\beta u^{ext}(\sigma, r)$ is simply given as

$$\begin{aligned} \beta u^{ext}(\sigma, r) &= \infty & r > R - \sigma/2 \\ &= 0 & r < R - \sigma/2 \end{aligned} \quad (19)$$

where R and r are the radius and distance to the centre of a hard circular cavity, respectively. For the numerical calculation, the Hankel transform (two-dimensional Fourier transform) has been used to calculate the weighted densities $n_\alpha(r)$ and density profile $\rho(\sigma, r)$ [15]. Through this calculation, the well (or shoulder) range has been chosen as $\lambda \sigma = 1.5 \sigma$ and the average

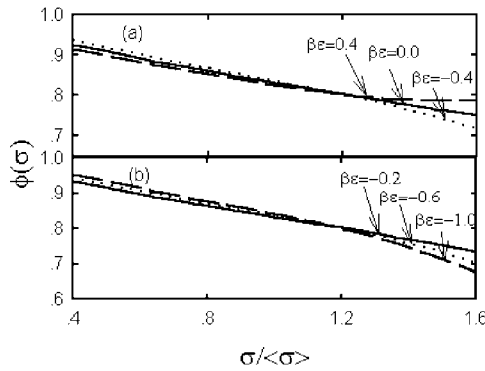


Figure 1. (a) $\phi(\sigma)$ for polydisperse fluids ($R = 3.6\langle\sigma\rangle$, $\sigma_l = 0.4\langle\sigma\rangle$, $\sigma_u = 1.6\langle\sigma\rangle$, and $\eta = 0.450$); (b) $\phi(\sigma)$ for a polydisperse square-well fluid with different well depths.

diameter of particles $\langle\sigma\rangle$ has been taken as the unit of length. The distribution function of the diameter of the molecules $F(\sigma)$ has, for simplicity, been chosen as a stepwise function

$$F(\sigma) = \begin{cases} \frac{1}{\sigma_u - \sigma_l} & \sigma_l < \sigma < \sigma_u \\ 0 & \text{otherwise} \end{cases} \quad (20)$$

where σ_u and σ_l are the minimum and maximum size of the particles, respectively. This distribution function is very simple and provides a restriction for the maximum size heterogeneity of fluid particles with respect to the average particle diameter $\langle\sigma\rangle$ [10]. Of course, other choices of $F(\sigma)$ such as the log-normal distribution which is defined by the mean diameter $\langle\sigma\rangle$ and the standard deviation in units of $\langle\sigma\rangle$ are possible [9].

We introduce two quantities to study the local size segregation and size selectivity in the adsorption of a confined polydisperse fluid. One is the local relative concentration of various species, which represents the effect of the local cross correlation between particles of different species

$$\phi(\sigma, r) = \frac{\rho(\sigma, r)}{\int d\sigma \rho(\sigma, r)}. \quad (21)$$

Another is the pore average mole fraction $\phi(\sigma)$ or pore average size distribution, which represents the size selectivity in the adsorption of a confined polydisperse fluid

$$\phi(\sigma) = \frac{\int d\vec{r} \rho(\sigma, r)}{\int d\sigma \int d\vec{r} \rho(\sigma, r)}. \quad (22)$$

The pore average mole fraction $\phi(\sigma)$ for a confined polydisperse fluid is displayed in figure 1 as a function of the particle diameter σ . In this case, the bulk mole fraction x for a polydisperse fluid has been taken to be $x = \rho(\sigma)/\int d\sigma \rho(\sigma) = 1/1.2$, where $\sigma_u = 1.6\langle\sigma\rangle$ and $\sigma_l = 0.4\langle\sigma\rangle$. The packing fraction η for a polydisperse fluid is given as $\eta = \pi/4 \int d\sigma \rho(\sigma)\sigma^2 = \pi\rho_0/4 \int d\sigma F(\sigma)\sigma^2$. Since the bulk mole fraction is $x = 1/1.2$, the adsorption of particles with a size σ is preferred when the pore average mole fraction $\phi(\sigma)$ is greater than $1/1.2$. As can be seen from figure 1(a), for a confined polydisperse fluid the adsorption of small particles is generally preferred. For a polydisperse square-well fluid, the pore average mole fraction for small particles is greater than that of a polydisperse hard-sphere fluid, while the pore average mole fraction for a polydisperse square-shoulder fluid is less than that of a polydisperse hard-sphere fluid. This result shows that an attractive

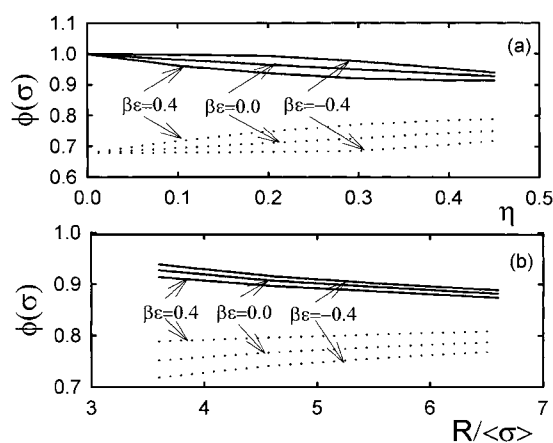


Figure 2. (a) $\phi(\sigma)$ for polydisperse fluids as a function of the bulk packing fraction ($R = 3.6\langle\sigma\rangle$, $\sigma_l = 0.4\langle\sigma\rangle$, and $\sigma_u = 1.6\langle\sigma\rangle$), (b) $\phi(\sigma)$ as a function of the radius of circular cavity $R/\langle\sigma\rangle$ ($\eta = 0.450$); full curve ($\sigma = 0.4\langle\sigma\rangle$) and dotted curve ($\sigma = 1.6\langle\sigma\rangle$).

interaction in a polydisperse square-well system increases (or decreases) the pore average mole fraction for small (or large) particles in a circular cavity. Whereas a repulsive interaction in a polydisperse square-shoulder system decreases the pore average mole fraction for small particles. Figure 1(b) shows the pore average mole fraction for a polydisperse square-well fluid as a function of the well depth $\beta\epsilon$. With increasing the well depth ($-\beta\epsilon$) the pore average mole fraction for small (or large) particles increases (or decreases). This property can be explained by the results of competition between the Helmholtz free energy and the chemical potential [1]: the excess free energy has a large value when the densities of large disks are increased. Then, the excess free energy is more important than the chemical potential. The larger the particle size, the higher the free energy. Thus, the pore average mole fraction for small particles increases with increasing the well depth in a polydisperse square-well fluid. This explains the fact that the attractive and repulsive interactions in the model potential are affected on the adsorption of a confined polydisperse fluid.

In figure 2, the calculated pore average mole fraction has been presented as a function of the circular cavity radius $R/\langle\sigma\rangle$ and the bulk packing fraction η . At a low bulk packing fraction the adsorption of small particles is more preferred than that of large particles. With increasing the bulk packing fraction small particles are excluded for a circular cavity[†]. The pore average mole fraction for small particles decreases nearly linearly with an increase of the pore size and bulk packing fraction. This result suggests that the onset of segregation at small polydispersity is generic [14].

The local relative concentration $\phi(\sigma, r)$ and its corresponding equilibrium density distribution $\rho(\sigma, r)\langle\sigma\rangle^2$ is displayed in figures 3, 4 and 5. The calculated result shows the strong local size segregation with local cross correlation between particles of different sizes and the anti-correlated oscillations around the bulk packing fraction ($x = 1/1.2$) in the relative amounts of small and large particles. One interesting thing is that the distance between the two peaks is almost the same as the diameter of a large particle, but not the diameter of a small particle. As for the equilibrium density distribution, the distance between the two peaks is also almost the same as the diameter of a large particle. This means that the local

[†] At a very low packing fraction, the pore average mole fraction depends only on the maximum radius, $R - \sigma/2$, available to the centre of a disk; $\phi(\sigma) \approx \rho(\sigma, r)(R - \sigma/2)^2 / \int d\sigma \rho(\sigma, r)(R - \sigma/2)^2$.

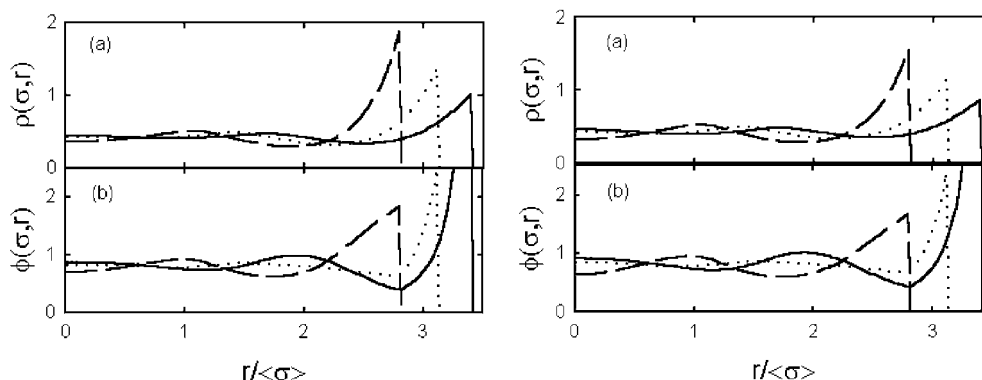


Figure 3. (a) Local relative concentration $\phi(\sigma, r)$ and (b) equilibrium density distribution $\rho(\sigma, r)\langle\sigma\rangle^2$ for a polydisperse hard-sphere fluid ($R = 3.6\langle\sigma\rangle$, $\sigma_l = 0.4\langle\sigma\rangle$, $\sigma_u = 1.6\langle\sigma\rangle$, and $\eta = 0.450$); full curve ($\sigma = 0.4\langle\sigma\rangle$), dotted curve ($\sigma = 1.0\langle\sigma\rangle$), and broken curve ($\sigma = 1.6\langle\sigma\rangle$).

Figure 4. As in figure 3, but for $\beta\epsilon = -0.4$ (a polydisperse square-well fluid).

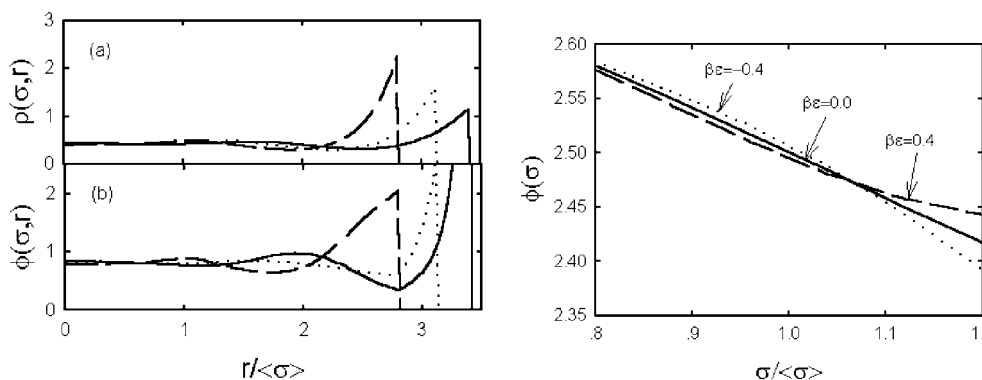


Figure 5. As in figure 3, but for $\beta\epsilon = 0.4$ (a polydisperse square-shoulder fluid).

Figure 6. As in figure 1(a), but for $\sigma_l = 0.8\langle\sigma\rangle$ and $\sigma_u = 1.2\langle\sigma\rangle$.

relative concentration oscillates with a spatial period close to the diameter of a large particle as well as the equilibrium density distribution does. As can be seen from figures 3, 4 and 5, for a polydisperse square-shoulder fluid the higher density distribution near a cavity wall can be found compared with that of the polydisperse square-well and hard-sphere fluids. For a polydisperse square-well fluid, the strong anti-correlated oscillations around the bulk packing fraction can be found compared with those of the polydisperse hard-sphere and square-shoulder fluids. Actually, at a low packing fraction the equilibrium density distribution strongly depends on the attractive (or, repulsive) part of the model potential rather than the hard-sphere potential.

The pore average mole fraction and its corresponding equilibrium density distribution for $\eta = 0.450$ are shown in figure 6, where $\sigma_u = 0.8\langle\sigma\rangle$ and $\sigma_l = 1.2\langle\sigma\rangle$. Since the bulk packing fraction is $x = 2.5$, the adsorption of particles with size σ is preferred when the pore average mole fraction $\phi(\sigma)$ is greater than 2.5. For a polydisperse square-well fluid, the pore average mole fraction for small particles is greater than that of a polydisperse square-shoulder fluid. Once again, this result shows that the attractive (or repulsive) interaction of the model potential

is affected on the adsorption of a confined polydisperse fluid. Even though we did not display the local relative concentration in the figure, the calculated results also show the anti-correlated oscillations around the mean value ($\phi(\sigma) = 2.5$). The local relative concentration oscillates with a spatial period close to the diameter of a large particle as well as the equilibrium density distribution does. A comparison of figures 1 and 6 indicates that the size selectivity of a confined polydisperse fluid depends on a particle size ratio σ_u/σ_l .

In summary, we have developed a density functional perturbative approximation to investigate the influence of attractive and repulsive interactions on the density behaviour of confined polydisperse fluids with the continuous distribution of the particle diameters. The calculated results have shown that the preferred species in a circular cavity depend on the size ratio of mixtures as well as the cavity size. The local relative concentration oscillates with a spatial period close to the diameter of the large particle as well as the equilibrium density distribution does. The attractive and repulsive interactions in the model potential are affected on the adsorption of a confined polydisperse fluid. Here, the interesting things are: (i) the role of the attractive and repulsive interaction on the adsorption of a polydisperse fluid confined in a spherical cage [16, 17]; and (ii) the adsorption of a polydisperse soft-sphere fluid in a micropore or near a hard wall [18, 19]. We will investigate these problems in the near future.

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