Structural Properties of the Fluid Mixture Confined by a Semipermeable Membrane: A Density Functional Study

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Abstract: Classical density functional theory (DFT) is employed to study the structural properties of a binary fluid mixture confined by a semipermeable membrane. The influences of volume fraction and size asymmetry on three characteristic densities and excess adsorption are investigated in detail. In addition, some of our results are calculated by the analytical method, which agree well with those from the DFT calculations. These results may provide helpful clues to understand the structural properties of other complex fluids or mixture confined by semipermeable membrane.

Keywords: structural properties; semipermeable membrane; binary fluid mixture; density functional theory

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1. Introduction

Recently, considerable attention has been attracted by confined fluid and their mixture, whose structures and phase behaviors are drastically different from the corresponding bulk system [1]. In such systems, interactions between fluid-pore and fluid-fluid lead usually to interesting phenomena including laying [2], wetting [3,4], capillary condensation [5] and so on. Actually, among various confining geometries, the semipermeable membrane (SPM) has particular importance due to its ability to model the natural biological membranes and synthetic membranes [6,7]. For instance, the Donnan equilibrium can be conveniently constructed by utilizing of the SPM, across which there exists density difference. Besides, it is also a satisfactory tool to investigate the process of ion exchange or transport in the ion channels [8].

On the theoretical side, substantial works on the SPM have been reported in the past decades. Employing the Ornstein-Zernike (OZ) integral equation with the Percus-Yevick (PY) or hypernetted chain (HNC) closure, Stell and Joslin studied the structure of the hard sphere fluids and charged fluids near a SPM [9,10]. However, the method based on OZ integral equation fails in the description of the fluid structure near the adsorbing surfaces and is not able to predict the surface phase transitions.

Actually, the DFT approach is free of the above mentioned drawbacks, because it can provide a microscopic description of the structure of the system. In DFT [11,12], the Helmholtz free energy is the only required input, and the density profile can be obtained by minimizing the grand potential functional. In addition, the DFT method has obvious advantages of saving computer time, in its comparison with other theoretical methods, including OZ integral equation and computer simulation.
Using density functional theory, Bryk et al. investigated the equilibrium density of the hard sphere mixture and Lennard-Jones fluids confined by a SPM \[13,14\]. They have also studied the phase behaviors \[15\] and depletion potential \[16\] of the fluids confined by permeable walls. Using weighted-density approximation for hard-sphere interaction and the mean-field approximation for the long-ranged dispersion, Yang et al. investigated the density profiles of binary attractive and binary repulsive hard-core Yukawa fluid mixtures near a SPM \[17\].

In recent years, synthetic and biological membranes have found their applications in the field water purification \[18\], dialysis \[19\] and targeted gene and drug delivery \[20\]. Especially in biomedical researches, the interaction of motile particles with biological membranes should be fully understood to explain the delivery of cargo to the interior of the cells \[21,22\]. Moreover, the mechanism for the penetration of active particles through the membrane remains an open question \[23–26\]. To a large extent, the fluid structure near the membrane influences the penetration of the particles \[27–30\]. Therefore, it is necessary to investigate the structural properties of the fluid mixtures that are confined by semipermeable membranes.

Actually, there are several specific densities, which can be used to characterize the structural properties of the system, including the bulk densities on each side of the membrane, the contact density of the non-penetrating component and the cross density of the penetrating component. Moreover, some of them can be described through the analytical method. Thus, in this paper, we concentrate on these characteristic densities, and study their dependence on the volume fraction and size asymmetry.

### 2. Theory and Model

In the present work, we consider a binary hard sphere fluid mixture confined by a SPM, which supplies different external potential to different components, that is:

$$V_{b}^{ext}(z) = \begin{cases} 0, & \text{if } z < z_m; \\ +\infty, & \text{otherwise} \end{cases}$$

for the big component, while $V_s^{ext}(z) = 0$ for the small component. In Eq.(1), $z_m = 0$ denotes the position of the SPM. According to the classical DFT \[11,12\], the grand potential functional $\Omega[\rho_\nu(r)]$ is formally expressed as:

$$\Omega[\rho_\nu(r)] = F[\rho_\nu(r)] + \sum_{\nu=s,b} \int \rho_\nu(r)[V_{\nu}^{ext}(r) - \mu_\nu]dr.$$ (2)

Here $\mu_\nu$ is chemical potential of a particle in the corresponding bulk phase, $F[\rho_\nu(r)] = F_{id} + F_{ex}$ is the intrinsic Helmholtz free energy, where the ideal gas contribution $F_{id} = k_B T \sum_\nu \int \rho_\nu(r)[\ln(\lambda^3 \rho_\nu(r))] - 1]dr$ is known exactly, with $\lambda$, $k_B$ and $T$ denoting respectively the thermal wavelenght, the Boltzmann constant and absolute temperature. $F_{ex}$ is the excess Helmholtz free energy, whose exact expression is unkown for most systems of practical interest. According to the variational principle, the grand potential functional $\Omega[\rho_\nu(r)]$ is minimized at equilibrium, and the equilibrium density profile $\rho_\nu(r)$ satisfies the variation principle:

$$\frac{\delta \Omega[\rho_\nu(r)]}{\delta \rho_\nu(r)} = 0.$$ (3)

To perform further calculations, one should firstly construct the excess Helmholtz free energy $F_{ex}$. In the existing approximations for the hard sphere contribution, one reliable choice is the Modified Fundamental Measure Theory (MFMT) \[31–33\], which gives the hard sphere contribution by:

$$\beta F_{ex} = \int \Phi[n_a(r)]dr.$$ (4)
with $\Phi[n_\alpha(r)]$ standing for the Helmholtz free energy density, which is given by:

$$
\Phi = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - n_1 n_2}{1 - n_3} + \frac{1}{36\pi} \left( n_3^3 \ln(1 - n_3) + \frac{n_3^3}{(1 - n_3)^3} \right) \left( \frac{n_3^3 - 3n_3 n_2^2}{n_3^3} \right).
$$

(5)

Here $n_\alpha(r) = \sum_v \int \rho_\nu(r') \omega_\nu^{(\alpha)}(r - r') dr'$ is the weighted densities, with $\omega_\nu^{(\alpha)}$ denoting the density independent weight functions, whose explicit forms can be found in the literatures [31–33].

The equilibrium density profiles $\rho_\nu(r)$ can be obtained from the solution of the equation which is obtained from Equation (3), that is:

$$
\rho_\nu(r) = \rho_\nu^{\text{bulk},L} \exp\left\{-\beta \frac{\partial F_{\text{ex}}[\rho(r)]}{\partial \rho_\nu(r)} + \beta [\mu_\nu - V_\nu^{\text{ext}}(r)] \right\}
$$

(6)

with $\rho_\nu^{\text{bulk},L}$ denoting the bulk density of the $\nu$ component on the left side of the SPM. Equation (6) can be numerically solved using the Picard type iterative method. Once the density profiles are obtained, it is ready to study the structural properties and the characteristic densities of the mixture, including the ratio of bulk densities for small component on right and left sides of the SPM $\rho_{\nu,R/L} \equiv \rho_{\nu,L/R}^{\text{bulk}}$, the contact density of the big component $\rho_{b,\text{con}} \equiv \rho_b^{(z_m - \frac{3}{2})} \rho_b^{\text{mix},L}$, and the cross density of the small component $\rho_{s,\text{cro}} \equiv \rho_s^{(z_m)} \rho_s^{\text{mix},L}$. Note that the above three characteristic densities have been reduced to their dimensionless forms.

Actually, besides the DFT calculation, one can also resort to the analytical methods to obtain $\rho_{b,\text{con}}$ and $\rho_{s,\text{R/L}}$. Because the system under consideration is open, the chemical potentials of the small component on both sides should be equal, that is $\mu_s(+\infty) = \mu_s(-\infty)$. According to MFMT, the chemical potential of the $\nu$ component can be given by:

$$
\beta \mu_\nu = \ln \lambda^3 \rho_\nu^{\text{bulk}} + \sum_{\alpha=0}^3 \frac{\partial \Phi_{\text{bulk}}}{\partial n_\alpha} \frac{\partial n_\alpha}{\partial \rho_\nu^{\text{bulk}}} \rho_\nu^{\text{bulk}}
$$

(7)

where $\Phi_{\text{bulk}}$ is the Helmholtz free energy density in the bulk, where the vectorial weighted densities disappear. By equating the chemical potential of small component on both sides, one can obtain the bulk density $\rho_b^{\text{bulk},L}$. It is necessary to note that in the left bulk phase, the weighted densities can be easily expressed as: $n_0 = \sum_\nu \rho_\nu^{\text{bulk},L}$, $n_1 = \sum_\nu \rho_\nu^{\text{bulk},L} \frac{\pi \sigma_\nu^2}{2}$, $n_2 = \sum_\nu \rho_\nu^{\text{bulk},L} \frac{\pi \sigma_\nu^2}{2}$, $n_3 = \sum_\nu \rho_\nu^{\text{bulk},L} \frac{\pi \sigma_\nu^2}{8}$.

On the other hand, the contact density $\rho_b(z_m - \frac{3}{2})$ can be calculated through the sum rule [1]:

$$
\beta [p_{\text{bulk}}(+\infty) - p_{\text{bulk}}(-\infty)] = \rho_b(z_m - \frac{\sigma_b}{2})
$$

(8)

with $p_{\text{bulk}}$ the bulk pressure, which can be given by the Mansoori-Carnahan-Starling-Leland equation of state [34]:

$$
\beta p_{\text{MCSL}} = \frac{n_0}{1 - n_3} + \frac{n_1 n_2}{(1 - n_3)^2} - \frac{(n_3 - 3)n_2^3}{36\pi(1 - n_3)^3}.
$$

(9)

Note that in the calculation for $p_{\text{bulk}}(-\infty)$, both components contribute to the weighted densities $n_\alpha$, while for $p_{\text{bulk}}(+\infty)$, only the small component contributes. Note also that in the following calculations, we have defined the dimensionless parameters $x = \frac{n_1}{n_\text{tot}}$ and $R = \sigma_b / \sigma_\nu$. Here $n_\text{tot} = \sum_\nu n_\nu$ with $n_\nu = \frac{\pi}{8} \rho_\nu^{\text{bulk}} \sigma_\nu^3$ and $\sigma_\nu$ the diameter of the $\nu$ component.
3. Results and Discussions

To evaluate our calculation, we firstly compare our DFT results with those from the Monte Carlo (MC) simulation, which is carried out by Bryk et al. [15]. The results for a binary mixture with equal diameter are shown in Figure 1a. In the calculation, we have chosen the same parameters as those in the MC simulation. That is, $\rho_{\text{bulk}, R} = 0.7695$, $\rho_{\text{bulk}, L} = 0.0641$. The comparison suggests that on both sides of the membrane, our results agree well with those from the MC simulation. Moreover, we have also compared our analytical results with those from the Ornstein-Zernike integral equation calculation, which is carried out by Zhou et al. [9]. The comparison in Figure 1b suggests that when $R = 1$, the analytical results agree with those from the HNC closure, while when $R = 10$, they agree with those from the PY closure.

**Figure 1.** (a) Comparison of our density functional results for binary mixture with those from the MC simulation carried out by Bryk et al. [15]. (b) Comparison of our analytical results for $\rho_{s, R/L}$ with those from the Ornstein-Zernike integral equation calculation which is carried out by Zhou et al. [9]. Note that the analytical calculation is performed with $\eta_{\text{tot}} = \frac{2}{15} \pi$.

In the following, some further calculations are performed to achieve richer information about the structural properties of the fluid mixture confined by the SPM. In Figure 2, the density profiles and the structural properties of the mixture are calculated under different conditions of $x$ and $R$. The results in Figure 2a suggest that when the magnitude of $x$ is small, the difference in densities on the right and left side of the SPM is rather large, while it is suppressed as $x$ increases. This can also be found in Figure 2c, which plots $\rho_{s, R/L}$ with the variation of $x$ in different cases of total volume fraction $\eta_{\text{tot}}$. This can be understood by the equality of the $\mu_i$ on both sides of the SPM, which indicates that for a smaller magnitude of $x$, a larger density difference is required to maintain the chemical equilibrium on both sides of the SPM.

Figure 2b suggests that for the given $\eta_{\text{tot}}$ and $x$, a smaller magnitude of $R$ corresponds to a larger difference between $\rho_{b, R}^{\text{bulk}}$ and $\rho_{s}^{\text{bulk}}$, while as $R$ is increased, the difference is reduced, as is also shown in Figure 2d. This may arise from the diminished contribution of the chemical potential from the big component because larger $R$ leads to a smaller $\rho_{b}^{\text{bulk}}$. Moreover, comparison between the curves in Figure 2d suggests that for a larger $x$, the influence of the size asymmetry is reduced. Besides the DFT results shown in Figure 2c,d, the analytical results for $\rho_{s, R/L}$ are also plotted to make comparison. It is obvious that the results from the two routes agree rather well with each other.
Figure 2. (a, b): Density profiles of the mixture under different conditions of $x$ and $R$. (c, d): $\rho_{s,R/L}$ under different conditions. (e, f): $\rho_{b,con}$ under different conditions. Note that in (a), the results for $x = 0.2, 0.4, 0.6$ have been consecutively shifted upward by 0.2, and that in both (a, b), the solid and dashed lines correspond respectively to the results for the small and big components. In (c, f), the solid lines is the results from the DFT calculations, while the symbols from the analytical method.
The contact density of the big component, say $\rho_{b,con}$, is another important structural property in the system. Therefore, it has also been calculated by employing both DFT and analytical methods, which is plotted in Figure 2e,f. It is obvious that for the given $\eta_{tot}$ and $R$, $\rho_{b,con}$ decreases with the increase of $x$. In contrast, for the given $\eta_{tot}$ and $x$, its value increases with $R$. This can be understood by the depletion mechanism, which ascribes the layering of big particles near the SPM to the depletion from the small particles. When $\eta_{tot}$ and $R$ are fixed, a larger value of $x$ corresponds to less big particles in the bulk, which leads to the decrease of $\rho_{b,con}$. On the contrary, the increase of $\eta_b$ and $R$ benefits the depletion, which enhances the layering of the big component, and then results in the increase of $\rho_{b,con}$.

As shown above, the impenetrability of the big particles is responsible for the density difference of small particles on both sides of the SPM, that is, $\rho_{s, L}^{bulk} < \rho_{s, R}^{bulk}$. Actually, another characteristic density, the cross density $\rho_{s, cro}$, may transfer additional information to understand the structural properties of the mixture. Therefore, in Figure 3, we have studied $\rho_{s, cro}$ under different conditions of $x$ and $R$ with the DFT calculations. Obviously, the dependence of $\rho_{s, cro}$ on $x$ and $R$ is the same as that of $\rho_{s, R/L}$. Moreover, comparing Figure 3a,b with respectively Figure 2c,d, one can always find $1 < \rho_{s, cro} < \rho_{s, R/L}$, which indicates that the cross density is between $\rho_{s}^{bulk, L}$ and $\rho_{s}^{bulk, R}$. Note that $\rho_{s, cro}$ can not obtained by the analytical method, because the required weighted densities $n_v^{(a)}(z)$ with $z \in [z_m - \frac{\sigma_s}{2}, z_m + \frac{\sigma_s}{2}]$ is unknown in an analytical route.

From Figure 2a,b, it is obvious that the density gradient of small component crosses the SPM with unequal contributions on the two sides of the membrane, which reflects indirectly the structure of the mixture. Therefore, to understand this aspect of the structural property, we define a dimensionless parameter $\Delta$:

$$\Delta = \frac{\rho_s(z_m) - \rho_{s, L}^{bulk}}{\rho_{s}^{bulk, R} - \rho_{s, L}^{bulk}}.$$  (10)

The results for $\Delta$ in Figure 3c,d show that for the chosen parameters, one can always find $\Delta > \frac{1}{2}$, which suggests that most of the density gradient distributes on the left side of the SPM. This may originate from the impenetrability of the big particles, whose direct influence on the chemical potential $\mu_s$ is restricted to the region $z < z_m$. In addition, with the increase of $x$ and $R$, the value of $\Delta$ is also increased.

Strictly speaking, in the system under consideration, only the big component is confined by the SPM because the small component can cross the membrane freely. In such a confined fluids, the excess adsorption is another fundamental quantity that reflects the influence of the confining geometry. Therefore, in Figure 4, we have calculated the excess adsorption of the big component:

$$\Gamma_{ex} = \frac{1}{A} \int [\rho_s(r) - \rho_{b}^{bulk,L}] dr,$$  (11)

where $A$ stands for the surface area of the SPM. The results show that $\Gamma_{ex}$ decreases with the value of $R$ and $x$. On one hand, this is due to the close relation of $\Gamma_{ex}$ to the bulk density of big component $\rho_{b}^{bulk,L}$. On the other hand, the density gradient of the small component leads to a depletion force on the big particles, which acts towards left, and prevents the big particles from gathering to the SPM.
Figure 3. (a, c) correspond respectively the $x$ dependence of $\rho_{s,cr}^0$ and $\Delta$ under different conditions of $\eta_{tot}$. (b, d) correspond respectively the $R$ dependence of $\rho_{s,cr}^0$ and $\Delta$ under different conditions of $x$. Note that the symbols in the figure is used to guide eyes.

Figure 4. Excess adsorption $\Gamma_{ex}$ of the binary mixture confined by a SPM. Note that the symbols in the figure is used to guide eyes.
4. Conclusions

In summary, employing the density functional theory and the analytical methods, the structural properties of a binary mixture confined by a SPM are studied. Specifically, the density difference of the small component $\rho_{s,R/L}$, the cross density of the small component $\rho_{s,cro}$ and the contact density of the big component $\rho_{b,con}$ are investigated, respectively. Our results suggest that for the given $\eta_{tot}$ and $R$, all of these three characteristic densities decrease with $x$. However, for the given $\eta_{tot}$ and $x$, their dependence on $R$ shows different pattern. That is, $\rho_{s,R/L}$ and $\rho_{s,cro}$ decrease with $R$, while $\rho_{b,con}$ increase with $R$. In addition, our calculation for the excess adsorption suggests that the increase of both $x$ and $R$ is not conducive to the gathering of the big particles to the SPM.

Note that in the text, the obtained results has been compared with those from MC simulation and OZ integral equation. However, these obtained microscopic properties, say local densities, are not compared with any experimental result, because most of the experimental measurements give only macroscopic properties. Nevertheless, the satisfying agreement shown in its comparison with MC simulation has shown the reliability of the employed method. Therefore, it is expected that our results can provide useful clues for understanding the structural properties and phase behaviors of the classical fluids and their mixtures confined by a SPM.

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