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Effects of the confinement on wall pressure, interfacial tension, and excess adsorption at the nanocylindrical wall

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ABSTRACT

In this article, a hard sphere fluid confined between two homocentric cylinders which formed a bicylindrical pore has been investigated. Our aim is investigation of the effect of an outer cylinder on the values of wall pressure, interfacial tension, and excess adsorption of fluid at a convex nanocylindrical wall, inner wall. To investigate this effect, the modified fundamental measure theory (MFMT) used. To do so at first we presented a general solution for weighted density integrals in cylindrical coordinate which is applicable for infinite and infinite lengths of cylindrical pore, bicylindrical pore, cylindrical wall, and even truncated cone. In the second step, the wall pressures, interfacial tensions, and excess adsorptions at a convex nanocylindrical wall are obtained for confined fluids in bicylindrical pores and compared with those values for bulk fluids. Our results showed that confinement leads to an oscillatory behavior for wall pressure, interfacial tension, and excess adsorption of the fluid at the wall. The reason for these oscillations lies in structural changes that occur for a fluid as a result of confinement. Variation of the type of interaction of inner wall with fluid from hard to attractive one can reverse the behavior of interfacial tension and adsorption versus size. Also in some cases, it changes their signs while the change in the type of interaction of the outer wall only leads to an increase in amplitudes of the oscillations.

1. Introduction

Nano-confined fluids and their properties have been the focus of much research because of the significant role they play in both industrial and biological systems [1,2]. Adsorption of fluids in nanopores has important applications in protein extraction, phase separation, and chromatographic processes [3–5]. Moreover, interfacial tension plays a remarkable role in pharmaceutical production and plant nutrition. Certain phenomena such as the capillary rise in plants, ionic transfer through nanochannels in biological cells, and preparation of monodisperse emulsions in industrial processes strongly depend on interfacial tension which may exhibit different values for different nanopores [6–8].

It is expectable that the shapes and curvatures of nanopores and nanowalls should play major roles in determining the values of both fluid interfacial tension and adsorption. A number of studies have been conducted to determine the interfacial tension and excess adsorption of fluids in different geometries [9–12]. Dong Fu [13] investigated the structure, interfacial tension, and excess adsorption of a Lennard-Jones fluid confined between two planar walls for different sizes of slit-like pores. Bryk et al. [14] studied the interfacial tension of a hard sphere fluid in contact with hard spherical and cylindrical walls for a wide range of sizes and densities. Detailed investigations have also been carried out in our previous works on the structure, interfacial tension, and excess adsorption of a bulk fluid at a convex spherical wall as well as the effects of the concave and convex walls of a spherical pore on the structure of fluids [15,16]. Also, Keshavarzi and Taghizadeh studied the structure of the fluid around a nanocylindrical wall including convex and flat walls and the relevant edges [17]. Among the different nanopores, the nanocylindrical pore is the one receiving more attention in theoretical studies due to its geometry which is commonly found in nature. Moreover, it has found wide applications in industrial processes because of the lower friction it causes.

In this work, we will focus on a bicylindrical pore to investigate the wall pressure, interfacial tension, and excess adsorption of a hard sphere fluid at a convex cylindrical wall in the presence of another concave cylindrical wall. The presence of the second (concave cylindrical) wall affects the values of the above properties at the convex cylindrical wall. In our case, the fluid is confined between these two concave and convex walls which form a bicylindrical pore. Additionally, the fluid used in this study is taken to be a hard sphere one and the cylindrical wall is considered as being both a hard and an attractive wall. We will obtain

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and compare the values for wall pressure, interfacial tension, and excess adsorption for the following two different cases: one is the case of a fluid in a nanobicylindrical pore for which the radius of the outer cylinder is infinity (i.e., a bulk fluid at the contact of a convex cylindrical wall), and the second being the case of a fluid in a nanobicylindrical pore for which the radius of the outer cylinder, $R_{b,}$ is in the order of the molecular diameter (i.e., a confined fluid at the contact of the inner cylindrical wall with a radius identical to that of the first case). It should be noted that the differences observed among the properties thus obtained are directly related to the confinement effects since the inner cylinder will be the same for both cases.

Thanks to its higher accuracy, the modified fundamental measure theory (MFMT), which is the most successful version of the DFT approach, is used in this study to determine the structure of the fluid in the bicylindrical pore. Bryk and co-workers [18] studied the adsorption and phase behavior of fluids in pores confined between two uniaxial cylinders; however, the radius of the inner cylinder in their work was larger than the molecular size. To overcome this problem, Tarazona proposed the cavity fundamental measure theory (CFMT) based on his definition of a new free energy density proposed for this kind of nanopore [19,20]. Gonzalez and co-workers used Fourier technique to solve the weighted densities in the original FMT of Rosenfeld (OFMT) for cylindrical and spherical pores [21]. Kong et al. applied a solution for weighted density integrals in a narrow cylinder with infinity length [22]. Malijevsky solved the integration of the weighted densities in an effective one-fold numerical integration that ends up with elliptic functions [23]. Recently, a solution for spherical geometries was presented by Keshavarzi and Helmi [24]. In this study, we will initially present the solution of weighted density integrals in cylindrical coordinate for a cylindrical geometry before we proceed to deal with our main objective of investigating the effects of fluid confining on contact density, interfacial tension, and adsorption of fluid around a cylindrical wall. Although there are some reports for weighted density integrals in MFMT in the literature, our solution has some advantages. We present a general solution which is applicable for cylindrical geometries with finite or infinite lengths including cylindrical pores, bicylindrical pores, cylindrical walls, and even for truncated cone. While some of the reported solution are only applicable for their studied case. It will also be shown that this solution is easier than the two Fourier and Tarazona techniques and also using elliptic functions so far presented elsewhere.

The rest of the paper is organized as follows. Section 2 presents a brief review of the MFMT. The solution of weighted density integrals for cylindrical geometries will be presented in Section 3. Section 4 investigates the effects of confinement on the values of wall pressure, interfacial tension, and excess adsorption of a fluid at a cylindrical wall. Finally, conclusions will be provided in Section 5.

2. Modified fundamental measure theory (MFMT)

The grand canonical free energy, $\Omega[\rho(\mathbf{r})]$, of an inhomogeneous fluid is a functional of the one-body distribution function, $\rho(\mathbf{r})$, which can be defined as [25]:

$$\Omega[\rho(\mathbf{r})] = F_{\text{int}}[\rho(\mathbf{r})] + \int d\mathbf{r}\rho(\mathbf{r})[V_{\text{ext}}(\mathbf{r}) - \mu] \tag{1}$$

where, $V_{\text{ext}}(\mathbf{r})$ is the external potential, μ is the chemical potential of the inhomogeneous fluid, and $F_{\text{int}}[\rho(\mathbf{r})]$ is the intrinsic Helmholtz free energy. The functional $F_{\text{int}}[\rho(\mathbf{r})]$ is expressed as:

$$F_{\text{int}}[\rho(\mathbf{r})] = F_{\text{id}}[\rho(\mathbf{r})] + F_{\text{ex}}[\rho(\mathbf{r})] \tag{2}$$

where, $F_{\text{ex}}[\rho(\mathbf{r})]$ and $F_{\text{id}}[\rho(\mathbf{r})]$ are excess and ideal contributions to the intrinsic Helmholtz free energy, respectively. The ideal contribution is given by the exact equation as:

$$F_{\text{id}}[\rho(\mathbf{r})] = kT\int d\mathbf{r}\rho(\mathbf{r})\left[\ln\left(\rho(\mathbf{r})\Lambda^3\right) - 1\right] \tag{3}$$

where, k is the Boltzmann constant, T is absolute temperature, and Λ is the de Broglie wavelength. According to MFMT for a hard sphere fluid, the excess part of the Helmholtz free energy is expressed as follows:

$$F_{\text{ex}}[\rho(\mathbf{r})] = kT\int d\mathbf{r}[\Phi_{\text{hs}}(n_\alpha(\mathbf{r}))] \tag{4}$$

In the above equation, $\Phi_{\text{hs}}(n_\alpha(\mathbf{r}))$ is the Helmholtz free energy density of a hard sphere fluid. The term $\Phi_{\text{hs}}(n_\alpha(\mathbf{r}))$ is divided up into two scalar and vector parts as follows [26,27]:

$$\begin{aligned}\Phi^{\text{S}}_{\text{hs}} &= -n_0\ln(1-n_3) + \frac{n_1 n_2}{1-n_3} \\ &\quad + \left[\frac{1}{36\pi n_3^2}\ln(1-n_3) + \frac{1}{36\pi n_3(1-n_3)^2}\right]n_2^3\end{aligned} \tag{5}$$

$$\Phi^{\text{V}}_{\text{hs}} = -\frac{n_{v1}n_{v2}}{1-n_3} - \left[\frac{1}{12\pi n_3^2}\ln(1-n_3) + \frac{1}{12\pi n_3(1-n_3)^2}\right]n_2(n_{v2}n_{v2}) \tag{6}$$

where, $n_\alpha(\mathbf{r})$ is the weighted density defined as:

$$n_\alpha(\mathbf{r}) = \int d\mathbf{r}\prime\rho(\mathbf{r}\prime)w^\alpha(\mathbf{r} - \mathbf{r}\prime) \tag{7}$$

where, w^α is the weight function that involves two vector functions, w_{v}^α, and four scalar functions, w^α, as follows:

$$\begin{aligned}w^3(\mathbf{r}) &= \theta\left(\frac{\sigma}{2} - r\right) \\ w^2(\mathbf{r}) &= 2\pi\sigma w^1 = \pi\sigma^2 w^0 = \delta\left(\frac{\sigma}{2} - r\right) \\ w_v^2(\mathbf{r}) &= 2\pi\sigma w_{\text{v}}^1 = \frac{\mathbf{r}}{|\mathbf{r}|}\delta\left(\frac{\sigma}{2} - r\right)\end{aligned} \tag{8}$$

where, $\theta(r)$ is the Heaviside step function, $\delta(r)$ represents the Dirac delta function, and r is the distance between two points in the system. By minimizing the grand canonical potential, the equilibrium local density of confined fluids obtains [28]:

$$\rho(\mathbf{r}) = \rho_{\text{b}}\exp\left(\beta\mu^{\text{hs}}_{\text{ex}} - \int d\mathbf{r}'\sum_\alpha\frac{\partial\Phi}{\partial n_\alpha}w_\alpha\left(\mathbf{r} - \mathbf{r}'\right) - \beta V_{\text{ext}}(\mathbf{r})\right) \tag{9}$$

In Eq. (9), $\mu^{\text{hs}}_{\text{ex}}$ is the hard sphere chemical potential obtained via Mansoori–Carnahan–Starling–Laland (MCSL) equation of state for the pure hard sphere fluid as [29]:

$$\beta\mu^{\text{hs}}_{\text{ex}} = \frac{\eta(8 - 9\eta + 3\eta^2)}{(1-\eta)^3} \tag{10}$$

in which, η is the packing fraction whose value is equal to $\pi\rho_{\text{b}}\sigma^3/6$. According to the above equations, the grand potential, Ω, is:

$$\begin{aligned}\Omega &= kT\int\Phi_{\text{hs}}(n_\alpha(r))dr + \int V_{\text{ext}}(r)\rho(r)dr \\ &\quad + kT\int\rho(r)ln\rho(r)dr - kT\int\rho(r)\left[1 + \ln\rho_b + \frac{\mu^{\text{b}}_{\text{ex}}}{kT}\right]dr\end{aligned} \tag{11}$$

where, $\mu^{\text{b}}_{\text{ex}}$ is the excess chemical potential of the bulk fluid. The external