



Effects of fluid structure on wall pressure, interfacial tension, and surface adsorption at a spherical guest particle

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ABSTRACT

Wall pressure, interfacial tension, and surface adsorption of hard and LJ fluids at the wall of a spherical guest particle were investigated in two different media (namely, a bulk fluid and one confined in a spherical pore). The MFMT theory was exploited to determine the effects of different fluid structures on the values of the above properties. Results showed that confinement mainly caused oscillations in these parameters around their corresponding bulk values such that the amplitude of the oscillations increased with increasing density but with decreasing pore size. Maximum heights of the oscillations were observed for all the three properties at each density when the pore size was around 2 times the molecular diameter. This may be due to the structure of the confined fluid that possesses a high packing factor. It was also observed that the depths and heights of the oscillations grew smaller in response to variations in the interactions of fluid molecules from a hard sphere fluid to one of LJ. Moreover, it is found that kind of interactions of the guest particle with the fluid determine the behavior of surface adsorption and interfacial tension with guest particle size. In other words, the change of guest particle–fluid interaction from a hard to an attractive one changes the signs for the slopes of surface adsorption and interfacial tension with increasing particle size.

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1. Introduction

The last few decades have witnessed a great interest from both theoretical and technological viewpoints in the effects of very fine particles in fluids. This is reflected in the wide industrial and pharmaceutical applications of nanofluids made by nanoparticles dispersed in a base fluid [1–4], or in the extensive use of nanoparticles in catalysts, food, and cosmetic chemicals [5]. Fluid molecules are known to tend to be attracted at the surface of particles suspended in a nanofluid because of the entropy and, in cases, energy effects. Such a tendency makes the fluid structure inhomogeneous in the vicinity of these particles up to a few molecular diameters. The fluid with an inhomogeneous structure at the particle—that is, the nanolayer—exhibits a solid-like behavior to play a vital role in enhancing the thermal conductivity and viscosity of the fluid [6,7]. The range in which a fluid exhibits an inhomogeneous structure strongly depends on the kind of interaction it enters into with the nanoparticle, in addition to the nanoparticle's shape and curvature. Studies have been devoted to the investigation of the effects of nanoparticle shape and curvature on fluid structure. Ren et al. investigated the effect of the spherical nanoparticle size on the thermal conductivity of nanofluids [8]. Zhang et al. studied the effective thermal conductivity and diffusivity of nanofluids containing spherical and

cylindrical nanoparticles of difference sizes [9]. Keshavarzi and Taghizade reported a linear relationship between surface adsorption and interfacial tension at the contact of spherical particles [10].

Few studies have, however, been conducted to determine the effect of fluid structure on the interfacial tension or surface adsorption at a guest particle. The guest particle is a particle which is different from fluid particles. Keshavarzi and Namdari investigated the wall pressure, surface adsorption, and interfacial tension at the contact of a cylindrical particle in the center of a cylindrical pore and compared their results with those obtained for cylindrical particles in a bulk fluid [11]. It is known that the molecules of confined fluids also have the tendency to be attracted to the particle wall. Since confined fluids have an inhomogeneous structure, the number of their molecules accumulated at the particle will, however, be different from that of bulk fluid molecules. It is, therefore, expected that bulk fluids should exhibit a behavior at the particle wall different from that of confined fluids. As the local density of a fluid confined in a pore is different at different positions, the exact position of the insertion of the particle into the pore will, therefore, have an important role in the fluid's thermodynamic properties. Moreover, the thermodynamic properties of a confined fluid at the guest particle will be different depending on whether the guest particle is free to move within the nanopore or fixed at an exact position. For the sake of simplicity, a fixed single guest particle without the ability to move was in this work assumed at the center of a nanospherical pore, and the values for wall pressure, surface adsorption, and interfacial tension at

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its contact were accordingly determined. The results were then compared with those obtained for a guest particle inserted in a bulk fluid. It must be noted that in this second case, the location of the nanoparticle is insignificant because of the homogeneity of the bulk fluid. Moreover, the effects of nanopore size and the guest particle were investigated in addition to those of fluid temperature and density, as well as the fluid-fluid and particle-fluid interactions.

For the purposes of this study, the density functional theory (DFT) was employed because it is one of the robust methods for investigating inhomogeneous systems [12]. More specifically, the best version of the DFT—that is, the modified fundamental measure theory (MFMT)—was used in this special case as it is computationally efficient and capable of predicting certain inhomogeneous phenomena [13].

The rest of the article is organized as follows: Section 2 provides a brief review of the MFMT for fluids confined in spherical nanopores. Section 3 investigates the effects of particle curvature and confinement size on the wall pressure, surface adsorption, and interfacial tension of the fluid at the guest particle. Finally, conclusions are presented in Section 4.

2. Theory

According to the density functional theory, the equilibrium density profile can be obtained by minimizing the following grand potential $\Omega[\rho(r)]$ function [13]:

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

where, $\rho(r)$ and μ are the density of molecules and the chemical potential, respectively. $V(\mathbf{r})$ is the potential of the guest particle imposed on fluid molecules. Finally, $F_{int}[\rho(r)]$ is the intrinsic Helmholtz energy function that, for a hard sphere fluid, can be defined as in Eq. (2) below:

$$F[\{\rho\}] = F^{id}[\{\rho\}] + F_{hs}^{ex}[\{\rho\}] + F^{dis}[\{\rho\}] \tag{2}$$

where, F^{id} , F_{hs}^{ex} , and F^{dis} are the free energy functionals for the ideal gas, hard-sphere repulsion, and attractive interaction, respectively. The ideal gas contribution to the Helmholtz free energy is given by:

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

where, k is the Boltzmann constant, T is absolute temperature, and Λ is the de Broglie thermal wavelength. The Helmholtz free energy functional due to the hard sphere repulsion represented by the MFMT is given by Eq. (4) below:

$$F_{hs}^{ex}[\{\rho\}] = kT \int \left\{ -n_0 \ln(1-n_3) + \frac{n_1 n_2 - \vec{n}_1 \cdot \vec{n}_2}{1-n_3} + \left[\frac{1}{36\pi n_3^2} \ln(1-n_3) + \frac{1}{36\pi n_3(1-n_3)^2} \right] (n_2^3 - 3n_2(\vec{n}_2 \cdot \vec{n}_2)) \right\} d\mathbf{r} \tag{4}$$

where, the weighted densities $n_\alpha(\mathbf{r})$ for the fluid around the guest particle confined in a spherical nanopore are as follows [14]:

$$\begin{aligned} n_2(r) &= \frac{\pi}{r} \int_{r-\sigma/2}^{r+\sigma/2} \rho(r')r'dr', n_1(r) = \frac{n_2(r)}{2\pi\sigma}, n_0(r) = \frac{n_2(r)}{\pi\sigma^2} \\ n_3(r) &= \frac{\pi}{r} \int_{r-\sigma/2}^{r+\sigma/2} \left[\frac{\sigma^2}{4} - (r-r')^2 \right] \rho(r')r'dr' \\ n_{2v}(r) &= \frac{\pi e_r}{r^2} \int_{r-\sigma/2}^{r+\sigma/2} \left[r^2 - r'^2 + \frac{\sigma^2}{4} \right] \rho(r')r'dr', n_{1v}(r) = \frac{n_{2v}(r)}{2\pi\sigma} \end{aligned} \tag{5}$$

Also, the weighted densities $n_\alpha(\mathbf{r})$ for the fluid confined in a spherical nanopore are taken from Ref. [15]. According to mentioned paper,

weighted densities do not diverge at the center of spherical pore, $r = 0$. The excess Helmholtz free energy due to the long-range attraction can be expressed by using the analytical expression of the direct correlation function via FMSA:

$$F^{dis}[\{\rho\}] = -\frac{kT}{2} \iint \rho(r)\rho(r') c^{att}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}d\mathbf{r}' \tag{6}$$

where, \mathbf{r} is a vector character and $c^{att}(|\mathbf{r}-\mathbf{r}'|)$ is the attractive part of the direct correlation function which can be given by:

$$c^{att}(|\mathbf{r}-\mathbf{r}'|) = \begin{cases} c^Y(T_i^*, z_i d, r/d) - c^Y(T_2^*, z_2 d, r/d) & r < d \\ 0 & d \leq r < \sigma \\ -\frac{4}{T^*} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] & \sigma < r < r_c \end{cases} \tag{7}$$

with

$$c^Y(T_i^*, z_i d, r/d) = \frac{\varepsilon}{T_i^*} \left[\frac{\exp[-x_i(r_{12}-1)]}{r_{12}} - Q(x_i)p(x_i) \right] \tag{8}$$

where, T^* is the reduced temperature, $T^* = KT/\varepsilon$, and ε is the dispersion energy parameter. The equations for c^Y in Eq. (8) may be found in Ref. [13]. Also, d is the effective hard-sphere diameter and obtained via:

$$d = \frac{1 + 0.2977T^*}{1 + 0.33163T^* + 0.00104771T^{*2}} \tag{9}$$

The chemical potential is defined as in [16,17]:

$$\mu = \mu^{hs} + \mu^{att} \tag{10}$$

in which, the hard sphere and attractive contribution in the chemical potential are:

$$\mu^{hs} = kT \frac{\eta(8-9\eta+3\eta^2)}{(1-\eta)^3} \tag{11}$$

and,

$$\mu^{att} = kT\rho_b \int c^{att}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r} \tag{12}$$

By inserting Eqs. (3), (6), and (10) in Eq. (1), the grand potential may be obtained from the following equation:

$$\begin{aligned} \Omega[\{\rho\}] &= \int_{R_s}^R \frac{\partial F_{hs}^{ex}}{\partial \rho(r)} d\mathbf{r} + \int_{R_s}^R V(\mathbf{r})\rho(r)d\mathbf{r} + kT \int_{R_s}^R \rho(r) \ln \rho(r) d\mathbf{r} \\ &\quad - kT \int_{R_s}^R \rho(r) \left[1 + \ln \rho_b + \frac{\mu_{ex}^b}{kT} \right] d\mathbf{r} - \frac{kT}{2} \int_{R_s}^R \int_{r-\sigma}^{r+\sigma} \rho(r)\rho(r') c^{att}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}d\mathbf{r}' \end{aligned} \tag{13}$$

where, R_s and R are the radius of the guest particle and the radius of the spherical nanopore, respectively. In this study, this potential is considered for the two hard and attractive ones as follows [11]:

$$V_1 r = \begin{cases} \infty & r < R_s + \sigma/2 \\ 0 & r \geq R_s + \sigma/2 \end{cases}$$

where r is the distance from the guest particle. And, also

$$V_2(r) = \begin{cases} \infty & r < R_s + \sigma/2 \\ -\varepsilon_w \exp \left[-\lambda_w \frac{\left(r - \left(R_s + \frac{\sigma}{2} \right) \right)}{\sigma} \right] & r \geq R_s + \sigma/2 \end{cases} \tag{14}$$

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