Investigation of linear relationship between interfacial tension and excess adsorption of confined fluids in nanospherical pores

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ABSTRACT

The modified fundamental measure theory is applied to investigate the interfacial tension and excess adsorption of confined fluids in nanospherical cavities. Results show that the curvature direction and wall–fluid interactions play important roles in the behavior of interfacial tension and excess adsorption, but only wall–fluid interactions determine their sign. The interfacial tension of hard sphere and two Yukawa fluids in contact with the inside (interfacial tension of confined fluids) and outside of the hard spherical cavities are both positive; but the former increases while the latter decreases with cavity size. For an attractive cavity, the signs may be negative or positive depending on both the wall–fluid interactions and the thermodynamic state of the fluid. The behavioral trend of the interfacial tension, with respect to cavity size, of a fluid in contact with an attractive wall is opposite to that of a fluid in contact with a hard wall. Therefore, the wall–fluid interaction and the curvature direction of the wall determine this trend. Investigation of the excess adsorption of fluids with cavity size led to a linear relationship established between excess adsorption and curvature. Also, linear relationships were found between the interfacial tensions of fluids inside and outside nanocavities, between interfacial tension and excess adsorption of the fluid inside nanocavities, and also between excess adsorption of a fluid in contact with the concave and convex sides of the cavity wall.

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1. Introduction

Adsorption, interfacial tension, and wetting of fluids near planar or curved walls have been the subject of much research because of their potential industrial applications in membrane transport, chromatography, and lubrication [1–4]. Interfacial tension has found numerous engineering applications in mass transfer operations, filtration, thermal conductivity of nanofluids, and cluster formation, among others [5]. It is well known that these properties are strongly dependent on wall curvature and geometry [4,6–10] and that they will, therefore, be different for planar and curved surfaces [11]. It has also been shown that the density profile of a fluid around a concave wall is significantly different from that of a fluid around a convex wall [12], which causes differences in the wetting behavior of the fluid in contact with the concavo-convex wall of a nanospherical pore.

Different approaches might be taken to the study of confined fluids, such as experimental designs, computer simulation, or density functional theory [13]. However, the difficulties associated with the experimental study of these systems have led to a growing interest in computer simulation and statistical–mechanical theory that have been

extensively employed in recent years. The density functional theory (DFT) is one of the precipitate tools used for the investigation of confined systems as it yields data analogous to those obtained from molecular dynamic simulation [14]. In the present work, among the different versions of DFT, the modified fundamental measure theory (MFMT) has been adopted as the theoretical tool, which gives improved contact density for hard sphere fluids [14].

Despite the complications underlying the investigation of liquid and dense fluids in the molecular scale, one can generally find a number of simple regularities in their different properties [15–17]. For example, in bulk fluids, the linear relationship between bulk modulus and pressure, the intersection of the isotherms of the reduced bulk modulus as a function of composition, and the intersection of the isobars of internal pressure of a liquid as a function of temperature have been already known, some of which remain completely empirical without any theoretical basis [18]. Over the past few years, the regularities in the thermodynamic properties of confined fluids have been the subject of many theoretical studies due to their importance for engineering applications. Recently, the relationship between interfacial tension and adsorption for different sizes of droplets and bubbles has been investigated by Castellanos et al. who observed a certain regularity in the interfacial tension and adsorption of droplets and bubbles of different sizes [19]. Finally, the behavior of interfacial tension and adsorption of fluids in contact with spherical nanocavities have also been investigated by Keshavarzi and Taghizade [20]. Although studies

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have been reported on the effect of curvature on such fluid properties as interfacial tension [20–23], no study seems to have been devoted to the effect of curvature on the behavior of interfacial tension inside a spherical pore.

The present study focuses on the investigation and interpretation of the behavior of the interfacial tension and excess adsorption fluids inside a nanospherical cavity (i.e., the concave side of the wall). The study also undertakes a comparison of the results with those of fluids around a spherical nanocavity (i.e., the convex side of the wall). A final aspect of the study is certain linear regularities found in these properties. The nanospherical cavity has been chosen because of its industrial and biological applications as in zeolites, clathrates, and fullerenes which are used as the substrate in separation processes [10,24]. In this work, we chose the spherical pore with radius R_s which its wall has a hard core. In fact when the wall of the pore has a hard core, the fluid in contact with concave side of the wall, confined fluid, cannot see the fluid outside of the wall, means fluid in contact with the convex side of the wall. Therefore our results are valid for the two kinds of abovementioned and different systems: the first the properties of confined fluid in the spherical pore with radius equal to R_s, and the other is for fluid surrounding the spherical particle, with the same radius.

The rest of the article is organized as follows: In Section 2, a brief review of the MFMT is presented. Section 3 explores the behavior of the interfacial tension of a hard sphere and two Yukawa fluids inside and outside a nanospherical cavity with curvature as well as the relationship between them. Section 4 investigates the excess adsorptions of inside and outside the cavity and their changes with variations in curvature. Section 5 is dedicated to the investigation of a linear relationship between interfacial tension and excess adsorption of a fluid inside a nanospherical cavity. Finally, conclusions are presented in Section 6.

2. Theory

In the density functional theory, the intrinsic Helmholtz energy functional, $F_{int}[\rho(\mathbf{r})]$, is defined as [20]:

$$F_{int}[\rho(\mathbf{r})] = F_{id}[\rho(\mathbf{r})] + F_{ex}[\rho(\mathbf{r})] \tag{1}$$

where, $F_{ex}[\rho(\mathbf{r})]$ is the excess part of Helmholtz free energy and $F_{id}[\rho(\mathbf{r})]$ is the ideal gas contribution that can be expressed by:

$$F_{id}[\rho(\mathbf{r})] = kT \int d\mathbf{r}\rho(\mathbf{r})\left[\ln\left[\rho(\mathbf{r})\Lambda^3\right] - 1\right] \tag{2}$$

where, k, T, and Λ are the Boltzmann constant, absolute temperature, and de Broglie wavelength, respectively. The excess part of the Helmholtz free energy is expressed as [14]:

$$F_{ex}^{hs}[\rho(\mathbf{r})] = kT \int d\mathbf{r} \left\{ -n_0 \ln(1-n_3) + \frac{n_1 n_2 - n_{v1} n_{v2}}{1-n_3} + \frac{1}{36\pi}\left[n_3 \ln(1-n_3) + \frac{n_3^2}{(1-n_3)^2}\right] \right.$$
$$\left. \times \frac{\left(n_2^3 - 3n_2 n_{v2} \cdot n_{v2}\right)}{n_3^3} \right\} \tag{3}$$

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

$$n_\alpha(\mathbf{r}) = \int d\mathbf{r}'\rho(\mathbf{r}')w^{(\alpha)}(\mathbf{r}-\mathbf{r}') \tag{4}$$

and $w^{(\alpha)}(\mathbf{r}-\mathbf{r}')$ is a weight function. The long range attraction contribution of Helmholtz free energy can be expressed as:

$$F_{ex}^{att}[\rho(\mathbf{r})] = -\frac{kT}{2}\iint \rho(\mathbf{r})\rho(\mathbf{r}')c_{att}(\mathbf{r}-\mathbf{r}')d\mathbf{r}d\mathbf{r}' \tag{5}$$

where, $c_{att}(\mathbf{r}-\mathbf{r}')$ is the attractive part of the direct correlation function given by [25,26]:

$$c_{att}(\mathbf{r}-\mathbf{r}') = \begin{cases} \sum_{i=1}^{M}\beta\dfrac{\varepsilon_i \exp[-\lambda_i(r-\sigma)/\sigma]}{r/\sigma} & r>\sigma \\ \sum_{i=1}^{M}Y(r,\varepsilon_i,\lambda_i) & r\leq\sigma \end{cases} \tag{6}$$

where,

$$Y(r,\varepsilon_i,\lambda_i) = \beta\varepsilon_i\left[\frac{\sigma\exp\left[-\dfrac{\lambda_i(r-\sigma)}{\sigma}\right]}{r} - H(\lambda_i)P(r,\lambda_i)\right]$$

$$H(\lambda_i) = \left[S(t) + 12\eta L(t)e^{-t}\right]^{-2}$$

$$S(t) = \Delta^2 t^3 + 6\eta\Delta t^2 + 18\eta^2 t - 12\eta(1+2\eta),\ L(t) = \left(1+\frac{\eta}{2}\right)t + 1 + 2\eta \tag{7}$$

with $\eta = {\pi\rho_b\sigma^3}/{6}, \Delta = 1-\eta, t = \lambda_i$

$$P(r,\lambda_i)] = S^2(t)\frac{\sigma\exp\left[-\dfrac{\lambda_i(r-\sigma)}{\sigma}\right]}{r} + 144\eta^2 L^2(t)\frac{\sigma\exp\left[-\dfrac{\lambda_i(r-\sigma)}{\sigma}\right]}{r} - 12\eta^2\left[(1+2\eta)^2 t\right.$$
$$\left. + \Delta(1+2\eta)t^5\right]\frac{r^3}{\sigma^3} + 12\eta\left[S(t)L(t)t^2 - \Delta^2\left(1+\frac{\eta}{2}\right)t^6\right]\frac{r}{\sigma} - 24\eta\left[(1+2\eta)^2 t\right.$$
$$\left. + \Delta(1+2\eta)t^5\right] + 24\eta S(t)L(t)\frac{\sigma}{r}. \tag{8}$$

In our study, the hard core Yukawa potential has been employed for attractive fluids as follows:

$$u(r) = \begin{cases} \infty & r\leq\sigma \\ -\sum_{i=1}^{M}\dfrac{\varepsilon_i \exp[-\lambda_i(r-\sigma)/\sigma]}{r/\sigma} & r>\sigma \end{cases} \tag{9}$$

where, r is the center to center distance between two particles, ε_i and λ_i are the potential parameters, M is the number of tails, and σ is the molecular diameter.

The grand potential function, $\Omega[\rho(\mathbf{r})]$, is defined as [27]:

$$\Omega[\rho(\mathbf{r})] = F_{int}[\rho(\mathbf{r})] - \int \mu\rho(\mathbf{r})d\mathbf{r} + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \tag{10}$$

where, $V_{ext}(\mathbf{r})$, $\rho(\mathbf{r})$, and μ represent the external potential, equilibrium density profile, and chemical potential, respectively. The equilibrium density profile of an inhomogeneous fluid is obtained by minimizing the grand canonical potential, which yields [28]:

$$\rho(\mathbf{r}) = \rho_b \exp\left[-\beta V_{ex}(\mathbf{r}) + \beta\mu_{ex} - \int d\mathbf{r}'\sum_\alpha \frac{\partial\Phi}{\partial n_\alpha}w_\alpha(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'\rho(\mathbf{r}')c_{att}(\mathbf{r}-\mathbf{r}')\right] \tag{11}$$

where, ρ_b and μ_{ex} are the bulk fluid density and bulk excess chemical potential. The interfacial tension of a fluid in contact with a wall can be calculated by [22]:

$$\gamma = \frac{\Omega[\rho(\mathbf{r})] - \Omega_b}{A} \tag{12}$$

or

$$\gamma = \frac{F_{int}[\rho(\mathbf{r})] - \int\mu\rho(\mathbf{r})d\mathbf{r} + pV}{A} + \frac{\int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}}{A} \tag{13}$$