

## Quantum hard spheres in a slit pore

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### ABSTRACT

In this paper, the density functional theory is employed to investigate the effects of quantum correction on the structure and such thermodynamic properties of quantum-mechanical hard sphere fluids confined in nano-slit pore as excess adsorption and wall pressure. It is found that the repulsion between hard sphere molecules because of quantum effect play an important role in determining the structure and thermodynamic properties of the confined fluid. Another finding of the present study involves the key role of the excluded volume in determining the structure and thermodynamic properties of quantum mechanical hard sphere fluids. By increasing of the quantum effect  $\lambda^*$ , the periodic oscillation in the density profile becomes more obvious and the order of layers in the pore increases. Increasing the values of  $\lambda^*$  is found to lead not only to drastic changes in the structure of the fluid molecules but also, to increased excess adsorption and wall pressure of the fluid confined in slit pores.

**Keywords:** DFT; Semi-classical quantum fluid; Slit pore; Excess adsorption.

## 1. Introduction

The thermodynamic properties of confined quantum fluids are a major area of basic and applied research in nanotechnology [1]. In classical systems, quantum effects for heavy

molecules at high temperature are so small that quantum corrections are often neglected. But it should be noted that the thermodynamic properties of such quantum fluids as hydrogen, deuterium, and neon whose de Broglie's wavelengths are of the same magnitude as the mean distance between particles greatly depend on quantum corrections [1].

It is clear that in most theoretical studies, the hard sphere fluid is the one most commonly employed as a reference system to study such realistic fluids as the Lennard Jones fluid and electrolyte solutions. Hence, hard sphere fluids have attracted a lot of attention by researchers due to their importance in modeling real systems, especially confined quantum fluids.

The present work aims to investigate the effects of quantum correction on the structure and such thermodynamic properties as excess adsorption of quantum-mechanical hard sphere fluids confined in nano-scale slit pore. In this work among the different theoretical methods for studying the thermodynamic properties of fluids confined in nano-scale pores, the successful versions of the DFT, modified fundamental measure theory (MFMT), that gives improved contact density for hard sphere fluids has been used.

## 2. Experimental

### *Materials and methods*

In the density functional theory, the grand canonical potential of an inhomogeneous system is defined as [2]:

$$[\rho(\mathbf{r})] = \beta F[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) [V^{ext}(\mathbf{r}) - \mu] \quad (1)$$

where,  $\mu$  is the chemical potential and  $V^{ext}$  is the external potential for this component.

Generally, the equilibrium density profile of an inhomogeneous fluid can be obtained by minimizing the grand canonical potential as follows:

$$\rho(r') = \rho_b \exp \left[ -\beta V^{ext}(r') + \beta \mu^{ext} - \int \sum_{\alpha} dr' \frac{\partial \phi}{\partial n_{\alpha}} w_i^{(\alpha)}(r - r') \right] \quad (2)$$

where,  $\mu^{ext}$  and  $\rho_b$  are the bulk excess chemical potential and bulk fluid density, respectively. In this work, used has been made of the effective diameter method, in which the quantum-mechanical hard sphere has an effective diameter larger than that of the classical hard sphere [3].

$$\sigma_{eff} = \sigma \left( 1 + \sum_l a_l \lambda^{*l} + \sum_m \sum_n c_{mn} \rho^{*n} \lambda^{*m} \right)^{1/3} \quad (3)$$

where,  $\lambda^* = \lambda/\sigma$  and  $\rho^* = \rho\sigma^3$ . The term  $\sum_l a_l \lambda^{*l}$  is a series in the thermal wavelength, and the double summation,  $\sum_m \sum_n c_{mn} \rho^{*n} \lambda^{*m}$ , expresses the dependence of the ratio on both density and thermal wavelength. In this work, the coefficients in Table 1 were used to calculate the properties of the fluid confined in a spherical pore and in equilibrium with the bulk fluid.

**Table1.** Optimal coefficients

$a_1$	$a_2$	$a_3$	$C_{21}$	$C_{22}$
1.08016	0.752081	-0.489996	-0.471077	-1.29761

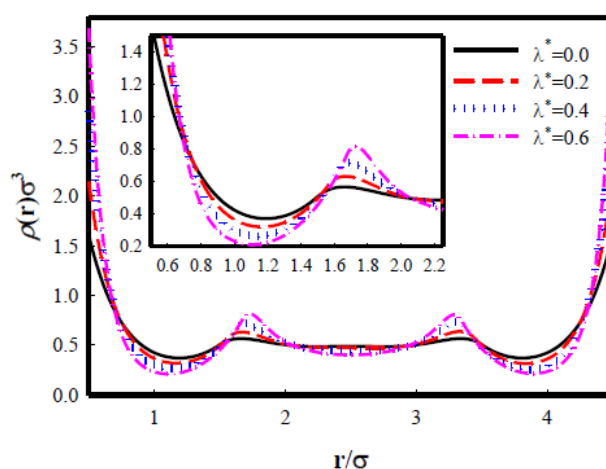
### 3. Results and discussion

In this section, we study the effects of quantum correction on the structure, adsorption and contact density of a hard sphere fluid confined in a nano-slit pore.

#### Effects of quantum correction on the structure

It is known that the structure of a quantum mechanical fluid in nano-pore systems depends on such parameters as pore size, intermolecular interactions, wall–fluid interactions, and the quantum effect,  $\lambda^*$ . Since the simultaneous study of these effects is complex, we consider a quantum mechanical hard sphere particles confined in a hard and structureless slit pore. Fig. 1 depict the density profiles of the hard sphere fluid with bulk density equal to 0.5 confined in a nano-slit pore with distance between the walls,  $H=5\sigma$ , for different values of the  $\lambda^*$  including

0, 0.2, 0.4 and 0.6. It is also clear that the density profile of the fluid exhibits an oscillatory behavior for different values of  $\lambda^*$  and that the number of peaks corresponds to the number of molecular layers in the nano-spherical pore. It is clear that in the absence of wall-molecule and molecule-molecule interactions, the structure of the fluid is determined by entropy effects because of the excluded volume near the walls. This excluded volume, increases with the effective diameter of the particles confined in the slit pore. The excluded volume has direct effects on the density distribution of molecules in the pore. Moreover the quantum effect causes the hard spheres to repel each other before they come into contact, while the classical ones repel each other only upon contact. This effect causes to more molecules accumulate at the wall due to the tendency of the molecules to escape from this repulsion. Also the repulsion among the molecules enhances the orderliness of the layers in the pore; which is reflected in the growing heights of the peaks and depths of the valleys in the density profiles.



**Fig. 1:** Density profiles of a quantum hard sphere fluid with bulk density equal to 0.5 confined in a slit pore with distance between the walls equal to  $5\sigma$ , in a nano-slit pore versus  $r/\sigma$  for different values of the  $\lambda^*$  including 0, 0.2, 0.4 and 0.6.

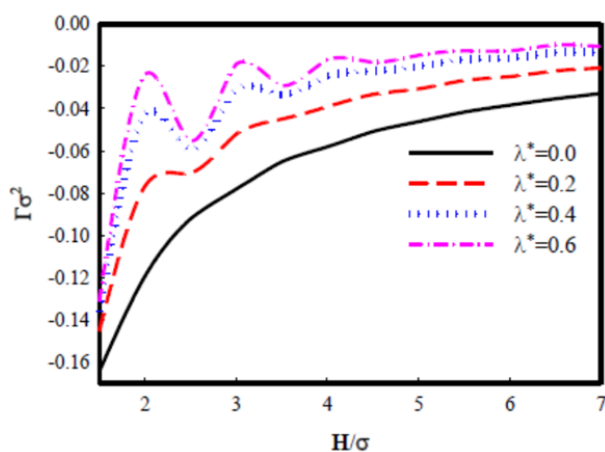
### Effects of quantum correction on the excess adsorption

As we know, the excess adsorption of fluids  $\Gamma$ , in a nano-slit pore is defined by:

$$\Gamma = 1/H \int d[\rho(\mathbf{r}) - \rho_b] \quad (4)$$

where  $\rho_b$  refers to bulk density. Fig. 2 plots the adsorption isotherm of a hard sphere fluid for different values of  $\lambda^*$  including 0, 0.2, 0.4, and 0.6 for a bulk density equal 0.6 versus  $H/\sigma$ . Based on this figure, adsorption of the fluid has an oscillatory behavior with maximum and minimum values for integral and half integral values of  $H$  respectively. It is clear that the adsorption is negative for all values of  $\lambda^*$  and  $H$ . For a fixed value of  $\lambda^*$ , adsorption increases with  $H$  and also for a fixed value of  $H$ , it increases with  $\lambda^*$ . It is also clear from these Figures that the height and depth of the oscillations increase with increasing  $\lambda^*$ .

It is known that the excluded volume plays the key role in determining the structure and thermodynamic properties of classical and quantum mechanical hard sphere fluids. In fact, the excluded volume increases with increasing quantum effect,  $\lambda^*$ . This will lead to increases in the periodic oscillations of excess adsorption in nano slit pore. In fact, when  $\lambda^*$  increases, the quantum hard sphere fluid exhibits a rising tendency for being adsorbed onto the nanopore as a result of both the entropy effect and the breaking up of the repulsion between the molecules at the pore walls. From the figure, it is easy to realize that excess adsorption is become nearly uniform by increasing of the distance between the walls,  $H$ .



**Fig.2:** Adsorption isotherm of a hard sphere fluid for different values of  $\lambda^*$  including 0, 0.2, 0.4, and 0.6 for a bulk density equal 0.6.

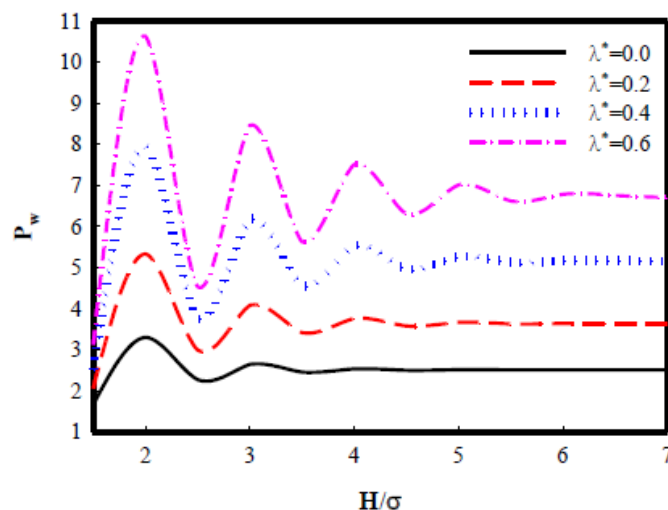
### Effects of quantum correction on the wall pressure

To investigate the effect of the distance between the walls,  $H$ , on the contact density of the fluid at the walls, we used the contact theorem directly set the contact density of the fluids at the walls equal to wall pressure,  $P_w = \rho(0)$ , and plotted it versus  $H$ , for different values of  $\lambda^*$ , as shown in Figure 3. In this figure, the wall pressure, of a hard sphere fluid with a bulk density of 0.6 confined in a pore between two flat walls for different values of  $\lambda^*$  including 0, 0.2, 0.4, and 0.6 has been plotted versus the  $H$ .

The wall pressure of the fluid at the pore walls versus  $H/\sigma$  clearly exhibits an oscillatory behavior. This oscillatory behavior increases with  $\lambda^*$ . In fact the height and depth of the wall pressure oscillations increase with increasing  $\lambda^*$ . According to this figure for a fixed value of  $H$ , wall pressure increases with  $\lambda^*$ .

As mentioned the excluded volume plays the key role in determining the structure and thermodynamic properties of quantum mechanical hard sphere fluids. In fact, the excluded volume increases with increasing  $\lambda^*$ . This will lead to increases in the periodic oscillations of wall pressure.

In the classical hard-sphere system, pressure arises due to the direct contact collisions but that quantum mechanical pressure arises from the collisions without any direct contact, that is, from inter-particle repulsions due to quantum effects. This is because the periodic oscillation in the wall pressure becomes more obvious and wall pressure grows larger with increasing values of  $\lambda^*$ . Once the repulsion between fluid molecules is increased, the wall pressure increases as result of the enhanced quantum effect,  $\lambda^*$ . The increased quantum effect,  $\lambda^*$ , then causes the hard spheres to repel each other before they come into contact; the repulsion is then broken at the wall and the molecules escaping the repulsion have a greater tendency to accumulate at the pore wall.



**Fig. 3:** The wall pressure of the hard sphere fluid with a bulk density of 0.6 confined in a pore between two flat walls versus the  $H$  for different values of  $\lambda^*$  including 0, 0.2, 0.4, and 0.6.

#### 4. Conclusions

The effective diameter method was used, in which the quantum-mechanical hard sphere has an effective diameter larger than that of the classical hard sphere. Results showed that the excluded volume increases by quantum effect in slit pore. This excluded volume causes the hard spheres to repel each other before they come into contact, while the classical ones repel each other only upon contact. This effect causes to more molecules accumulate of the molecules at the wall due to the tendency of the molecules to escape from this repulsion.

Our results also showed that, due to the effective diameter of hard molecules, Synergy's entropy effect and the broken repulsion between molecules at the pore wall causes the quantum-mechanical hard sphere fluid exhibits an increasing tendency to be adsorbed onto the nano-slit pore with increasing values of  $\lambda^*$ .

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