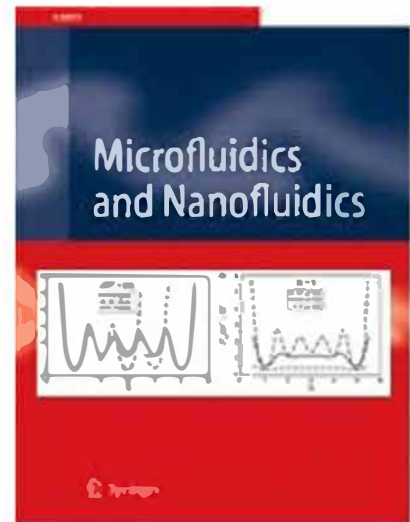


## Behavior of Confined Fluids in Nanoslit Pores: The Normal Pressure Tensor

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**Abstract** The aim of our research is to develop a theory, which can predict the behavior of confined fluids in nanoslit pores. The nanoslit pores studied in this work consist of two structureless and parallel walls in the *xy* plane located at  $z = 0$  and  $z = H$ , in equilibrium with a bulk homogeneous fluid at the same temperature and at a given uniform bulk density. We have derived the following general equation for prediction of the normal pressure tensor  $P_{zz}$  of confined inhomogeneous fluids in nanoslit pores:

$$P_{zz} = kT\rho(r_{1z}) \left[ 1 + \frac{1}{kT} \frac{\partial \phi_{ext}}{\partial r_{1z}} dr_{1z} \right] - \frac{1}{2} \int \varphi'(\vec{r}_{12}) \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) \frac{(r_{1z})^2}{\vec{r}_{12}} d\vec{r}_{12},$$

where  $\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2$  is the intermolecular position vector of molecule 2 with respect to molecule 1 and  $r_{1z} = |\vec{r}_{12}|_z$  is the projection of distance of molecule 1 from molecule 2 in the *z*-direction. This equation may be solved for any fluid possessing a defined intermolecular pair-potential energy function,  $\varphi(\vec{r}_{12})$ , confined in a nanoslit pore and with a given fluid molecules—wall interaction potential function

$\phi_{ext}$ . As an important example of its application we have solved this equation for the hard-sphere fluid confined between two parallel-structureless hard walls with different nanometer distances and at various uniform bulk densities. Our results indicate the oscillatory form of the normal pressure tensor versus distance from the wall at high densities. As the density of the nanoconfined fluid decreases, the height and depth of the normal pressure tensor oscillations are reduced.

**Keywords** Behavior of nano-confined fluid · Hard-sphere fluid · Nanoconfined fluid · Nanoslit pore · Normal pressure tensor · Stress tensor

### 1 Introduction

The knowledge about behavior of fluids confined in nanopores and nanochannels is of considerable importance in various industrial processes and scientific fields including in fluids in porous media, in lubrication, in tribology and in the emerging fields of nanoscience and nanotechnology (Ziarani and Mohamad 2006; Zhang and Li 2007; Mansoori 2005). The physics of fluids confined between two parallel walls in a nanoscale distance is quite different from their three-dimensional bulk behavior. This is because the nano-confinement drastically affects fluids molecular configuration, structural correlations, dynamical properties and phase transitions (Keshavarzi et al. 2006; Kamalvand et al. 2008). In recent years, some experimental observations and use of the molecular dynamics, the density functional theory and Monte Carlo computer simulations have somehow improved our understandings of the physics of fluids in confined geometries (Mansoori 2005; Keshavarzi et al. 2006; Kamalvand et al. 2008; Schmidt and

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Lowen 1997; Fortini and Dijkstra 2006; Brovchenko et al. 2004; Gotzelmann and Dietrich 1996; Fu 2006; Irving and Kirkwood 1950). We are now in a position to develop analytic theories for prediction of the behavior of confined fluids in nano systems, which is the emphasis of this work.

We know a fluid in a nanopore is generally inhomogeneous and anisotropic. Its pressure has a tensorial character that depends on spatial direction and position of the surface where the pressure is measured. The pressure tensor is defined through an infinitesimal force ( $df$ ) acting through an infinitesimal surface element ( $ds$ ) located at the position vector ( $\vec{r}$ ). It should be noted that any component of the pressure tensor of a confined fluid is not, in general, the same as is the pressure in a macroscopic (bulk) fluid. Irving and Kirkwood proposed a method to obtain the point-function stress tensor based on the equation of hydrodynamics (Irving and Kirkwood 1950). For homogenous fluid flows, the standard Irving–Kirkwood procedure is well suited, but for strongly inhomogeneous fluid flows (e.g. fluids confined in nanoslit pores (i.e. the slit between two parallel walls with nanoscale size) that procedure cannot be used. In this report we derive a general expression for the normal pressure tensor of the confined fluid in nanoslit pores. As an example, the resulting equation is applied for the hard-sphere fluid confined in nanoslit pores to predict its normal pressure tensor profile.

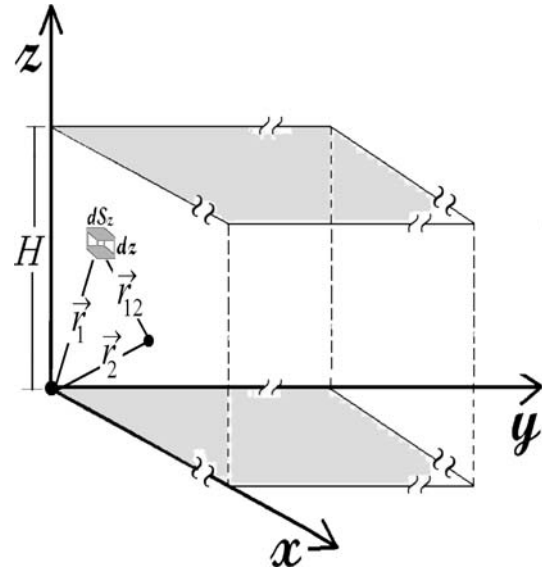
## 2 The theory

We consider a fluid confined in a nanoslit pore consisting of two structureless and parallel walls in the  $xy$  plane located at  $z = 0$  and  $z = H$ , i.e. separated by length  $H$  in the  $z$ -direction as shown in Fig. 1.

We also assume the confined fluid in the nanoslit pore is in equilibrium with a bulk fluid at the same temperature and at a given bulk density ( $\rho$ ). In this situation it is clear that fluid in such a nanopore is inhomogeneous and therefore all of its thermodynamic properties are functions of the local density. The local density is a function of  $H$ ,  $\rho$  and  $T$  and the interactions between fluid–fluid and fluid–wall molecules. Of course, in this study we are considering only the two-body intermolecular interactions. Our method is based on the molecular-based definition for pressure in a fluid system. The force on a closed surface of  $s$  in the direction of  $b$  is (Fisher and Switz 1964)

$$F_b = \oint_s \tau_{ab} n_b ds_b, \quad (1)$$

where subscript  $b$  is referred to the force component and subscript  $a$  is referred to the normal to the surface  $s$ . For a nanoslit, the normal pressure tensor in the  $z$ -direction is



**Fig. 1** Demonstration of two particles, 1 and 2, of a fluid confined in a nanoslit pore consisting of two structureless and parallel walls in the  $xy$  plane located at  $z = 0$  and  $z = H$

$-\tau_{zz}$ . Then for the confined fluid in nanoslit pore, Eq. 1, may be written as:

$$F_z = \oint \tau_{zz} n_z ds_z \quad (2)$$

To obtain the local pressure, we consider a differential volume element of  $d\vec{r}_1$  at any chosen point  $\vec{r}_1$  in a fluid ( $d\vec{r}_1 = ds_z \times dz$ ) as shown in Fig. 1. The calculations for the total momentum, which is transferred in a unit time due to the entrance and exit of particles through the surface  $s$  consist of three parts: (i) the kinetic contribution, (ii) the fluid–fluid molecules interactions contribution, (iii) the fluid–wall molecules interactions contribution. In the following sections we develop the necessary equations to calculate these three contributions.

### 2.1 The kinetic contribution

For this purpose, we consider a system with  $N$  particles in a nanoslit consisting of two structureless parallel walls in the  $xy$  plane located at  $z = 0$  and  $z = H$ , i.e. separated by length  $H$  in the  $z$  direction as shown in Fig. 1. We also assume the confined fluid in the nanoslit pore is in equilibrium with a bulk fluid at the same temperature and at a given bulk density of  $\rho$ . We consider a volume element of  $d\vec{r}_1 = ds_z \times dz$  in the nanoslit pore. Since the inhomogeneity for this system is only in the  $z$ -direction therefore if  $dz$  goes to zero, the pressure, which will be obtained for such a volume element, is only a function of  $z$ . The probability of finding the particles between points  $\vec{r}_1 \rightarrow \vec{r}_1 + d\vec{r}_1$  with momentum  $p_z$  is:

$$\rho^{(1)}(\vec{r}_1)dw(p_z)d\vec{r}_1, \quad (3)$$

where  $dw(p_z)$  is the momentum distribution function in the  $z$ -direction and  $\rho^{(1)}(\vec{r}_1)$ , the probability density, is defined by the following equation:

$$\rho^{(1)}(\vec{r}_1) = N \frac{\int \dots \int e^{-\Phi/kT} d\vec{r}_2 \dots d\vec{r}_N}{Z_N}, \quad (4)$$

where  $\Phi$  and  $Z_N$  are the total potential intermolecular potential energy function and configurational integral, respectively. Note that, we consider only the momentum that is perpendicular to the surface  $ds_z$ ,

$$dw(p_z) = \left( \frac{1}{2\pi mkT} \right)^{1/2} \exp\left(-\frac{p_z^2}{2mkT}\right). \quad (5)$$

Therefore, the momentum transfer in unit time,  $dt$ , through surface  $ds_z$ , by particles with momentum  $p_z$  passing through point  $\vec{r}_1$  is:

$$\frac{p_z \rho^{(1)}(\vec{r}_1) dw(p_z)}{dt} d\vec{r}_1. \quad (6)$$

Since  $dt = \frac{dz}{v_z} = \frac{m dz}{p_z}$ , where  $m$  is the particle mass, and  $ds_z \equiv \frac{d\vec{r}_1}{dz}$ , therefore, we can write:

$$\frac{p_z \rho^{(1)}(\vec{r}_1) dw(p_z)}{dt} d\vec{r}_1 = \frac{1}{m} \rho^{(1)}(\vec{r}_1) p_z p_z dw(p_z) ds_z. \quad (7)$$

To obtain all the momentum transferred through the surface  $s$  we should integrate the right-hand side of Eq. 7 over the whole surface  $s$  and the total momentums, i.e.

$$-\frac{1}{m} \oint_s \rho^{(1)}(\vec{r}_1) ds_z \int p_z p_z dw(p_z). \quad (8)$$

The second integral in the above equation is analytically calculated as,

$$\int p_z p_z dw(p_z) = mkT. \quad (9)$$

By inserting Eq. 9 into Eq. 8 and comparing the result with Eq. 1, we obtain the following expression for the kinetic contribution part of the normal pressure tensor, i.e.

$$\tau_{zz} = -kT \rho(\vec{r}_1). \quad (10)$$

However, since we have  $\tau_{zz} = -P_{zz}$  and  $\rho(\vec{r}_1) = \rho(z)$  for the nanoslit pore, then we can write,

$$P_{zz}^K = \rho(z)kT. \quad (11)$$

This expression is the kinetic contribution of the local normal pressure tensor at any point of  $\vec{r}_1$  or  $z_1$ . For ideal systems, without interactions between its particles, this is the only contribution to the normal pressure tensor. But in real systems every particle interacts with the other

particles of the fluid and walls. Therefore, the resulting force  $F_i$  on the particle  $i$  is also due to such interactions, which we derive the related expressions in the next two sections.

## 2.2 The fluid–fluid molecules interactions contribution

Now we consider the effect of fluid particles interactions on the local pressure. To calculate this effect, we consider particle 1 at location range  $\vec{r}_1 \rightarrow \vec{r}_1 + d\vec{r}_1$  in the small volume of  $d\vec{r}_1$  and another particle, 2, at location range  $\vec{r}_2 \rightarrow \vec{r}_2 + d\vec{r}_2$ , outside volume  $d\vec{r}_1$  as shown in Fig. 1. The pair-probability density of finding particles 1 and 2 at  $\vec{r}_1 \rightarrow \vec{r}_1 + d\vec{r}_1$  and  $\vec{r}_2 \rightarrow \vec{r}_2 + d\vec{r}_2$ , respectively, is:

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \frac{\int \dots \int e^{-\Phi/kT} d\vec{r}_3 \dots d\vec{r}_N}{Z_N}. \quad (12)$$

The force acting on the particle 1 at  $\vec{r}_1$  from particle 2 at  $\vec{r}_2$  is:

$$F_{r_1} = -\nabla_{r_1} \varphi(|\vec{r}_1, \vec{r}_2|) \quad (13)$$

where  $\varphi(|\vec{r}_1, \vec{r}_2|)$  is the pair-intermolecular potential energy between particles 1 and 2. We multiply this relation to Eq. 12 and then take the integral on  $\vec{r}_1$  in the volume of  $v$  and  $\vec{r}_2$  in volume of  $V - v$ . The result will be the following double-integral:

$$-\int_{V-v} \int_v \nabla_{r_1} \varphi(|\vec{r}_1 - \vec{r}_2|) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (14)$$

We then make a change of variables from  $\vec{r}_1$  and  $\vec{r}_2$  to  $\vec{r}_{12}$  and  $\vec{R}_{12}$ , where the latter two variables are defined as follows:

$$\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2, \quad \vec{R}_{12} \equiv \frac{1}{2}(\vec{r}_1 + \vec{r}_2) = \vec{r}_1 - \frac{1}{2}\vec{r}_{12}. \quad (15)$$

Considering that the Jacobian of this transformation is unity,  $J(\vec{r}_1, \vec{r}_2, \vec{r}_{12}, \vec{R}_{12}) = 1$ , and  $V - v$  can be approximated with  $V$  (because  $v$  is very small compared to  $V$ ) we get the following equation :

$$-\int_{V-v} \int_v \nabla_{r_1} \varphi(|\vec{r}_1 - \vec{r}_2|) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = -\int_V \int_v \nabla_r \varphi(|\vec{r}_{12}|) \rho^{(2)}(\vec{r}_{12}, \vec{R}_{12}) d\vec{R}_{12} d\vec{r}_{12}. \quad (16)$$

By using the Taylor expansion for  $\rho^{(2)}(\vec{r}_{12}, \vec{r}_1)$  as:

$$\rho^{(2)}\left(\vec{r}_{12}, \vec{r}_1 - \frac{1}{2}\vec{r}_{12}\right) = \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) + \left(-\frac{1}{2}\vec{r}_{12}\right) \nabla_{\vec{r}_1} \rho^{(2)}(\vec{r}_{12}, \vec{r}_1), \quad (17)$$

we will have,

$$\int_v \rho^{(2)}(\bar{r}_{12}, \bar{R}_{12}) d\bar{R}_{12} = \int_v \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) d\bar{r}_1 - \frac{1}{2} \int_v \bar{r}_{12} \nabla_{\bar{r}_1} \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) d\bar{r}_1$$

The second integral in the right-hand side of the above equation may be transformed into a surface integral by using the Gauss's theorem, i.e.

$$\int_v \bar{r}_{12} \nabla_{\bar{r}_1} \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) d\bar{r} = \oint_S \bar{r}_{12} \rho^{(2)}(\bar{r}_{12}, \bar{r}) n_z ds_z$$

Then we have

$$\int_v \rho^{(2)}(\bar{r}_{12}, \bar{R}_{12}) d\bar{R}_{12} = \int_v \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) d\bar{r}_1 - \frac{1}{2} \oint_S \bar{r}_{12} \rho^{(2)}(\bar{r}_{12}, \bar{r}) n_z ds_z, \quad (18)$$

where  $\bar{r}$  is a chosen point on the surface  $S_z$ . By inserting Eq. 18 into Eq. 16, we see that the first of the two resulting integrals is an odd integral and therefore diminishes. The second integral is:

$$\frac{1}{2} \int \nabla_{\bar{r}_1} \varphi(\bar{r}_{12}) \rho^{(2)}(\bar{r}_{12}, \bar{r}) \bar{r}_{12} n_z ds_z. \quad (19)$$

However, since we only have the force in the  $z$ -direction in the nanoslit pore, we should replace  $\nabla_r \varphi(\bar{r}_{12})$  with  $\nabla_z \varphi(\bar{r}_{12})$ , using chain relations we have:

$$\nabla_z \varphi(\bar{r}_{12}) = \nabla_r \varphi(\bar{r}_{12}) \cdot \frac{r_{12z}}{|\bar{r}_{12}|},$$

therefore,

$$\tau_{zz} = \frac{1}{2} \int_v \varphi'(\bar{r}_{12}) \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) \frac{(r_{12z})^2}{|\bar{r}_{12}|} d\bar{r}_{12}. \quad (20)$$

In Eq. 20,  $r_{12z}$  is the projection of the distance of molecule 1 from molecule 2 on the  $z$ -coordinate. Therefore, the normal pressure tensor  $P_{zz} = -\tau_{zz}$  is:

$$P_{zz}^{FF} = \frac{1}{2} \int_v \varphi'(\bar{r}_{12}) \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) \frac{(r_{12z})^2}{|\bar{r}_{12}|} d\bar{r}_{12} \quad (21)$$

This expression is the fluid–fluid configurational contribution to the local normal pressure tensor at any point  $\bar{r}_1$  or  $z$ . The integral appearing in the right-hand side of Eq. 21 may be solved for a known intermolecular potential energy function. It must be pointed out that since this equation is a result of a perturbation approximation, Eq. 17, therefore, it is only valid for weakly inhomogeneous fluids in nanoslits.

In the next section we derive the fluid-wall contribution to the local normal pressure tensor.

### 2.3 The fluid–walls molecules interactions contribution

In a nanoslit pore system the particles are exposed to an external potential due to the two confining parallel walls. In this section we calculate contribution of the forces resulting from the fluid particles and the two walls particles interactions on the normal pressure tensor.

The probability of finding a particle at point  $\bar{r}_1$  in the volume element of  $d\bar{r}_1$  is:

$$\rho(\bar{r}_1) \times d\bar{r}_1 = \rho(r_{1z}) \times d\bar{r}_1 \quad (22)$$

The force from the wall to the particle at point  $\bar{r}_1$  can be defined as

$$F_{zz}^{FW} \equiv - \frac{\partial \phi_{\text{ext}}(r_{1z})}{\partial r_{1z}}, \quad (23)$$

where  $\phi_{\text{ext}}$  is the fluid particles-walls potential function and  $r_{1z}$  is the projection of the distance of molecule 1 from the wall on the  $z$ -coordinate. Therefore, the contribution of the fluid particles-walls interaction to the pressure tensor is a result of multiplying Eqs. 22 and 23 and dividing the result by  $d\bar{r}_1$ , i.e.

$$P_{zz}^{FW} = \frac{\partial \phi_{\text{ext}}(r_{1z})}{\partial r_{1z}} \rho(r_{1z}) dr_{1z} \quad (24)$$

With the availability of  $\phi_{\text{ext}}$  and the local fluid density in the nanoslit pore we can calculate  $P_{zz}^{FW}$  at any point in the nanoslit pore.

### 2.4 The sum of all the three contributions

The summation of all the three interaction contributions (kinetic, fluid-fluid and fluid-wall) to the normal pressure tensor is the sum of Eqs. 10, 21 and 24, i.e.

$$P_{zz} = P_{zz}^K + P_{zz}^{FW} + P_{zz}^{FF} = kT \rho(r_{1z}) \left[ 1 + \frac{1}{kT} \frac{\partial \phi_{\text{ext}}}{\partial r_{1z}} \right] - \frac{1}{2} \int_v \varphi'(\bar{r}_{12}) \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) \frac{(r_{12z})^2}{|\bar{r}_{12}|} d\bar{r}_{12} \quad (25)$$

As an example, in what follows, we solve this equation for the hard-sphere fluid confined in between two structureless hard walls with various nanoscale separations. This calculation is made possible since we have now available to us an accurate set of data for the density profile of hard-spheres in nano-slits which is recently produced by Kamalvand et al. (2008) through the fundamental-measure density-functional theory.

## 2.5 Normal pressure tensor of the hard-sphere fluid confined in a nanoslit pore

The investigation of the hard-sphere fluid confined in a nanoslit pore is an important step for the study of nano-confined fluids. It is also an appropriate model for the general description of the configurational behavior of other systems. This is because a hard-sphere fluid effectively resembles the major configurational properties of real fluids (Mansoori 1977; Mansoori and Kioussis 1985; Chen et al. 1987). In addition, it is known that certain colloidal particles between glass plates behave like hard-spheres in a slit as it is observed by means of video microscopy (Carbajal-Tinoco et al. 1996). Confined micelles represent another realization of the hard-sphere model system having substantial technical and biological applications (Parker et al. 1992; Kekicheff and Richetti 1992). Also within the framework of the statistical mechanics long-range interactions between the fluid particles are typically incorporated by the variational and perturbation theories (Mansoori and Canfield 1970), which needs as a prerequisite the result of the corresponding hard-sphere reference systems. Our model system consists of  $N$  hard-sphere molecules with diameter  $\sigma$  confined between two parallel hard walls with macroscopic areas  $S$  and a nano-gap with the thickness  $H$ . The pair-interaction potential energy between hard-sphere particles with position vectors  $\vec{r}_1$  and  $\vec{r}_2$  depends only on the scalar magnitude of the distance between the two hard-spheres,  $|\vec{r}_2 - \vec{r}_1|$ , and it is given by the following equation:

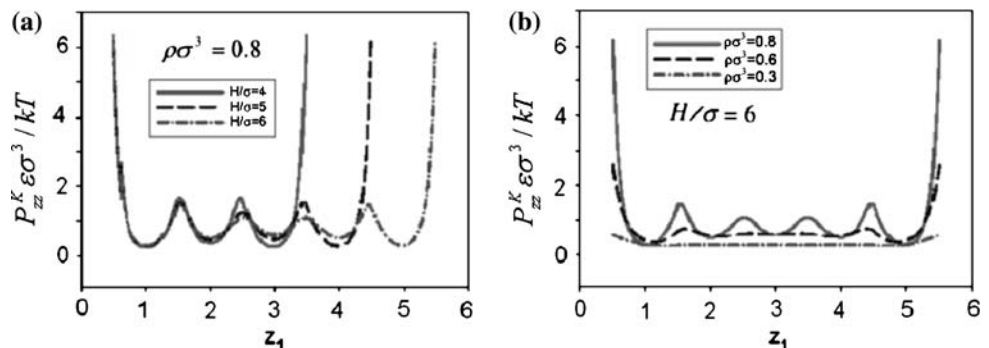
$$\phi_{hs}(r_{12}) = \begin{cases} 0 & \text{for } |\vec{r}_2 - \vec{r}_1| > \sigma \\ \infty & \text{for } |\vec{r}_2 - \vec{r}_1| \leq \sigma \end{cases} \quad (26)$$

The hard-wall-hard-sphere fluid inter particle-potential function,  $\phi_{\text{ext}}$ , will then become

$$\phi_{\text{ext}}^{hs}(r_{1z}) = \begin{cases} 0 & \text{for } \frac{\sigma}{2} < r_{1z} < H - \frac{\sigma}{2} \\ \infty & \text{for } r_{1z} \leq \frac{\sigma}{2}; r_{1z} \geq H - \frac{\sigma}{2} \end{cases} \quad (27)$$

where  $r_{1z}$  is the projection of the distance of molecule 1 from wall on the  $z$ -coordinate.

**Fig. 2** The contribution of kinetic term to the normal pressure tensor,  $P_{zz}^K \epsilon \sigma^3 / kT$ , versus  $z_1$ , the distance from the wall. **a** At dimensionless bulk density  $\rho \sigma^3 = 0.8$  but at various dimensionless nanoslit widths  $H/\sigma$  ( $H/\sigma = 4, 5, 6$ ). **b** At  $H/\sigma = 6$  but at various dimensionless bulk densities  $\rho \sigma^3$  ( $\rho \sigma^3 = 0.8, 0.6, 0.3$ )



We now proceed to calculate the kinetic, fluid-fluid, wall-fluid contributions and then the total contribution to the normal pressure tensor of a confined hard-sphere fluid in nanoslits with different widths and at various densities of the bulk hard-sphere fluid in equilibrium with the hard-sphere fluid in the nanoslit pore.

## 2.6 The kinetic contribution for nanoconfined hard-spheres

The contribution of the kinetic term in the pressure tensor for a hard-sphere fluid confined between hard walls is given by Eq. 11,  $P_{zz}^K = \rho_H(z)kT$ , where  $\rho_H(z)$  is the local density as a function of the vertical position  $z$  in the pore which depends on  $H$ . In Fig. 2 we report the contribution of the kinetic term in the pressure tensor for the hard-sphere fluids confined between hard walls using the local density data reported by Kamalvand et al. (2008) based on the fundamental-measure density functional theory.

According to Fig. 2a for  $H/\sigma = 6$  and  $\rho \sigma^3 = 0.8$  there is enough space for the hard-spheres to form six distinct layers, two sharp ones at the walls and four broader layers in the middle. The kinetic contribution of the pressure shows oscillatory behavior and has a maximum at the contact point to the walls. When the local density decreases to  $\rho \sigma^3 = 0.3$ , the layers become more diffuse and broad, therefore, the normal pressure between the walls decreases but maintains its oscillatory behavior.

Also according to Fig. 2b the contribution of kinetic part in the normal component of the pressure tensor versus position of molecules 1 ( $z_1$ ) decreases as the bulk density decreases. In fact, by reducing density the layers of molecules become broader, therefore the pressure between the walls decreases. Also, when the pore width increases, the layers of molecules in the pore increases but the height of the layers decreases.

## 2.7 The fluid-fluid hard-sphere molecules interactions contribution

To calculate the integral in the fluid-fluid interaction contribution to the pressure tensor of hard-spheres,  $P_{zz}^{FF}$ ,

Eq 21, we use the cylindrical coordinate where  $d\vec{r}_{12} = r_{12}dr_{12}dz_{12}d\theta$ . We also use the definition of  $\rho^{(2)}$  with respect to the radial- (or pair-) distribution function as  $g$ . Since the radial distribution function of hard-spheres is only a function of the distance  $(r_{12}^2 + z_{12}^2)^{0.5}$  between the two molecules, then we can write

$$\rho^{(2)} = \rho(z_1)\rho(z_2)g_{hs}\left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right). \quad (28)$$

Then Eq. 21 will be in the following form,

$$P_{zz}^{FF} = -\frac{1}{2} \iiint \varphi'_{hs}\left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right) \rho_{hs}(z_1)\rho_{hs}(z_2)g_{hs} \\ \times \left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right) \frac{z_{12}^2}{(r_{12}^2 + z_{12}^2)^{\frac{1}{2}}} r_{12}dr_{12}dz_{12}d\theta, \quad (29)$$

where  $\rho_{hs}(z_i)$  is the local density of hard-spheres,  $g_{hs}\left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right)$  is the hard-sphere radial-distribution function, which is angle-independent but it depends on the distance between molecules,  $(r_{12}^2 + z_{12}^2)^{\frac{1}{2}}$ . As a result Eq. 29 reduces to

$$P_{zz}^{FF} = -\pi \iint \varphi'_{hs}\left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right) (\rho_{hs}(z_1)\rho_{hs}(z_2)g_{hs} \\ \times \left((r_{12}^2 + z_{12}^2)^{\frac{1}{2}}\right) \frac{z_{12}^2}{(r_{12}^2 + z_{12}^2)^{\frac{1}{2}}} r_{12}dr_{12}dz_{12} \quad (30)$$

We select the position of molecule 1 (fixed) on the center of coordinate, therefore the coordinates of the distance between two molecules  $z_{12}$  and  $r_{12}$  are replaced with  $z_{12} = z_2$ ,  $dz_{12} = dz_2$ ,  $r_{12} = r_2$ , and  $dr_{12} = dr_2$ . Then we can write Eq. 30 as:

$$P_{zz}^{FF} = -\pi \rho_{hs}(z_1) \iint \varphi'_{hs}\left((r_2^2 + z_2^2)^{0.5}\right) \rho_{hs}(z_1)\rho_{hs}(z_2)g_{hs} \\ \times \left((r_2^2 + z_2^2)^{0.5}\right) \frac{z_2^2}{(r_2^2 + z_2^2)^{0.5}} r_2dr_2dz_2 \quad (31)$$

For the hard-sphere potential  $\varphi'_{hs}\left((r_2^2 + z_2^2)^{0.5}\right)$  is zero everywhere except at  $(r_2^2 + z_2^2)^{0.5} = \sigma$ . Therefore, to solve Eq. 31 we use the following definition.

$$\varphi'(r) = \delta\left((r_2^2 + z_2^2)^{0.5} - \sigma\right) (-kT) \exp\left(\frac{\varphi_{hs}\left((r_2^2 + z_2^2)^{0.5}\right)}{kT}\right), \quad (32)$$

where  $\delta\left((r_2^2 + z_2^2)^{0.5} - \sigma\right)$  is the Dirac delta-function. By inserting Eq. 32 into Eq. 31 we get:

$$P_{zz}^{FF} = \pi kT \rho_{hs}(z_1) \left[ \int_{-\sigma}^{+\sigma} \rho_{hs}(z_2) \frac{z_2^2}{(r_2^2 + z_2^2)^{0.5}} g_{hs}(\sigma) dz_2 \right. \\ \left. \times \int_0^{\infty} \delta(C) \exp\left(\frac{\varphi_{hs}\left((r_2^2 + z_2^2)^{0.5}\right)}{kT}\right) r_2 dr_2 \right] \quad (33)$$

where  $C = ((r_2^2 + z_2^2)^{0.5} - \sigma)$  and  $g_{hs}(\sigma)$  is the value of the hard-sphere radial distribution function at the contact point. The second integral in Eq. 33 is equal to unity when  $C = 1$  and otherwise it is zero. Let us also change the upper limit of the first integral appearing in Eq. 33 to zero because we want just to consider the interaction of the molecules in a one side of the imaginary plate (note that the definition of the pressure is arbitrary). The result will be simplified to the following equation

$$P_{zz}^{FF} = \pi kT (\sigma)^{0.5} \rho_{hs}(z_1) \int_{-\sigma}^0 \rho_{hs}(z_2) g_{hs}(\sigma) z_2^2 dz_2$$

We do not presently have the expression for the contact hard-sphere radial distribution function  $g_{hs}(\sigma)$  in nanoslits. We expect it to be different from the bulk system contact value while it is also a function of local density in the nanoslit. If we assume  $\langle g_{hs}(\sigma) \rangle$  represents the average value of  $g_{hs}(\sigma)$  in the nanoslit we can calculate  $P_{zz}^{FF}/\langle g_{hs}(\sigma) \rangle$ , i.e.,

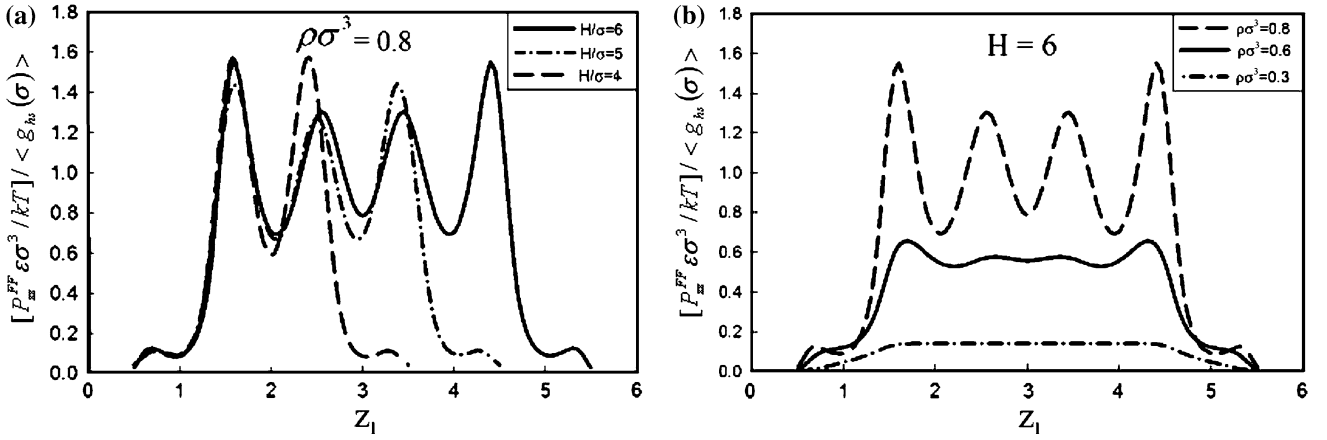
$$P_{zz}^{FF}/\langle g_{hs}(\sigma) \rangle = \pi kT (\sigma)^{0.5} \rho_{hs}(z_1) \int_{-\sigma}^0 \rho_{hs}(z_2) z_2^2 dz_2$$

at various densities and nanoslit widths. Of course  $\langle g_{hs}(\sigma) \rangle$  will be still a function of the bulk fluid density in equilibrium with the fluid in the nanoslit. Figure 3 shows the ratio  $P_{zz}^{FF}/\langle g_{hs}(\sigma) \rangle$  as a function of  $z_1$  position for various values of  $H/\sigma$  and  $\rho\sigma^3$ . Since the fluid in a nanopore is inhomogeneous, therefore, the molecules are not exposed to symmetric forces from the other molecules. According to Fig. 3 the ratio  $P_{zz}^{FF}/\langle g_{hs}(\sigma) \rangle$  has the oscillatory behavior in the nanoslit pore. The values of the  $P_{zz}^{FF}/\langle g_{hs}(\sigma) \rangle$  has a maximum and minimum (the extrema occurs at  $(z_1/2)\sigma$  where  $z_1$  is an integer). Remember that this figure shows the average force acting normal to the surface, where the forces are caused by atoms on one side of the surface interacting with atoms on the other side. If we insert the imaginary plane at  $z = 0$ , therefore no forces act though such surface from the left side.

In Fig. 3 we report the contribution of fluid-fluid interaction to the normal pressure at various pore width and at constant reduced dimensionless density  $\rho\sigma^3 = 0.8$ . We also report the contribution of the interactions between fluid-fluid molecules in the normal component of the pressure tensor at  $H/\sigma = 6$  and  $\rho\sigma^3 = 0.3, 0.6, 0.8$ . We see that when the local density decreases the pressure profile becomes smooth and the height and depth of oscillations are reduced (see Fig. 3), furthermore.

## 2.8 The normal pressure tensor for hard-sphere fluids in nanoslit pores

Considering Eq. 27 for  $\phi_{ext}^{hs}(r_{1z})$  we can conclude that the wall-fluid interaction term  $P_{zz}^{FW} = \frac{\partial \phi_{ext}(r_{1z})}{\partial r_{1z}} \rho(r_{1z})$  for



**Fig. 3** Variation of  $[P_{zz}^{FF} \epsilon \sigma^3 / kT] / \langle g_{hs}(\sigma) \rangle$  versus  $z_1$ , the distance from the wall: **a** At dimensionless bulk density  $\rho\sigma^3 = 0.8$  but at various dimensionless nanoslit widths  $H/\sigma$  ( $H/\sigma = 6, 5, 4$ ). **b** At  $H/\sigma = 6$  but at various dimensionless bulk densities  $\rho\sigma^3$  ( $\rho\sigma^3 = 0.8, 0.6, 0.3$ )

hard-sphere molecules in nanoslits is zero. This indicates that the normal pressure tensor of hard-sphere particles confined between the hard walls do not have any contribution from the walls. Therefore, the total normal pressure tensor in the confined hard-sphere system is equal to:

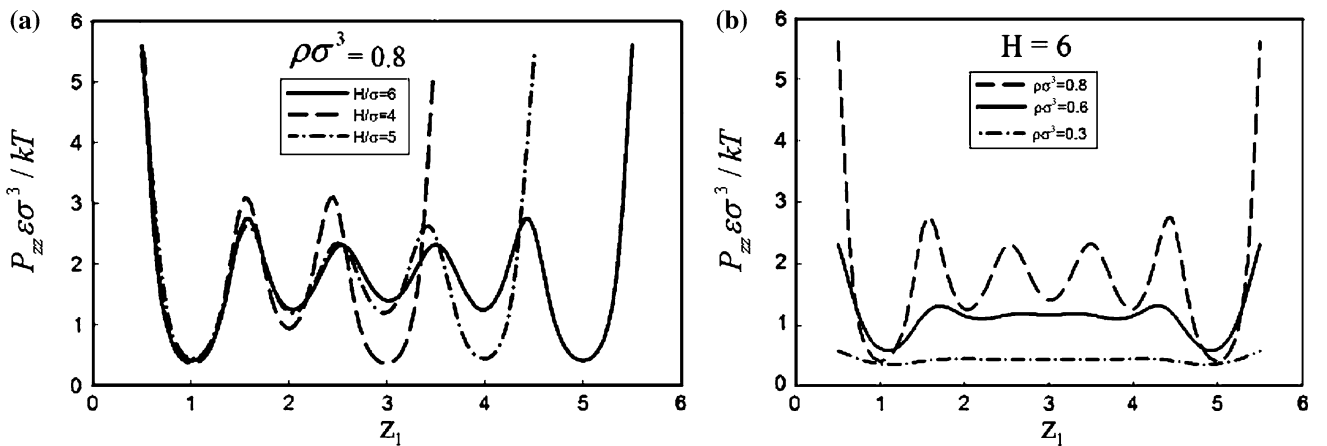
$$P_{zz}^{hs} = \rho(z_1)kT + \pi kT(\sigma)^{0.5} \rho_{hs}(z_1) \int_{-\sigma}^0 \rho_{hs}(z_2) g_{hs}(\sigma) z_2^2 dz_2 \quad (34)$$

Due to our lack of knowledge about  $g_{hs}(\sigma)$  and even  $\langle g_{hs}(\sigma) \rangle$  we are not presently able to calculate the exact value of the total normal pressure tensor for hard-spheres confined in nanoslit pores. However, considering the fact that both  $P_{zz}^K \epsilon \sigma^3 / kT$  and  $P_{zz}^{FW} \epsilon \sigma^3 / kT$  indicate the existence of six distinct layers, we expect  $P_{zz} \epsilon \sigma^3 / kT$  to possess also six distinct layers. To get an approximate idea about  $P_{zz} \epsilon \sigma^3 / kT$ , the  $z$  component of the pressure in the direction normal to

the wall, we have plotted Fig. 4 assuming  $\langle g_{hs}(\sigma) \rangle = 1$ . We see that the pressure has different values between the walls and shows the oscillatory behavior. Also, we plot the normal pressure versus position  $z_1$  for various pore width and reduced bulk density. Our result shows, the oscillatory form of the normal pressure tensor versus distance of the walls has been observed for very high densities. As the densities decreased, the height and depth of the oscillation is reduced.

### 3 Conclusions

It is well known that a confined fluid in a nanoslit pore is inhomogeneous and its thermodynamics properties are functions of the local density. We have derived an analytic equation for the local normal pressure tensor of a confined fluid in a nanoslit pore as a function of distance from the



**Fig. 4** Dimensionless normal pressure tensor  $P_{zz} \epsilon \sigma^3 / kT$  of hard sphere versus distance from the wall assuming  $\langle g_{hs}(\sigma) \rangle = 1$ . **a** At dimensionless bulk densities  $\rho\sigma^3 = 0.8$  but at various dimensionless nanoslit widths  $H/\sigma$  ( $H/\sigma = 6, 4, 5$ ). **b** At  $H/\sigma = 6$  but at various dimensionless bulk densities  $\rho\sigma^3$  ( $\rho\sigma^3 = 0.8, 0.6, 0.3$ )

wall. The confined fluid is assumed to be in equilibrium with a bulk (macroscopic) fluid system with known uniform density and temperature. The resulting normal pressure tensor equation is applicable for any fluid that is confined in a nano slit pore and with a any intermolecular pair-potential energy and fluid-wall interaction potential function.

The normal pressure tensor is composed of three parts, which include the kinetic contribution due to momentum of the particles, the contribution resulting from the force due to fluid-fluid two-body interactions and the contribution due to fluid-wall interaction.

We have calculated the normal component of the pressure tensor for the hard-sphere fluid confined between two parallel-structureless hard walls at different nanometer distances and at various uniform bulk densities. The choice of hard-sphere fluid is due to the availability of density profile data which we have generated recently and the fact that its configurational behavior is similar to other molecular confined fluids at.

Our computational results indicate that the kinetic contribution of the pressure tensor shows an oscillatory behavior and has a maximum at the contact point to the walls. When the local density decreases the layers become more diffuse and broad. Therefore, the pressure between the walls decreases but maintains its oscillatory behavior. When the pore width increases the layers of the molecules in the pore increase but the height of the layers decrease.

We also report the fluid-fluid interaction contribution to the normal component of pressure tensor at different local densities and pore widths. The results indicate that this contribution also has an oscillatory behavior inside the pore. When the local density decreases this profile becomes smooth and the height and depth of the oscillation are reduced.

There is no fluid-wall interaction contribution to the normal component of the pressure tensor of a hard-sphere confined fluid. This is because the hard-sphere particles confined between hard walls are not exposed to any force from the walls.

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