Lateral Pressure Tensor of Confined Fluids in Nanoslit Pores

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Abstract: We report here a general molecular-based analytic equation for the lateral pressure tensor profile, P_{xy} , of confined fluids in nanoslit pores with structureless, purely repulsive, parallel walls in xy plane at $z = 0$ and $z = H$, in equilibrium with a bulk fluid at the same temperature and chemical potential. The analytic expression for the lateral pressure tensor of the confined inhomogeneous fluid in nanoslit pore is derived as the following:

$$P_{xy} = kT\rho(z) - \frac{1}{2} \int \Phi'(\bar{r}_{12}) \rho^{(2)}(\bar{r}_{12}, \bar{r}_1) \frac{(r_{12y})^2}{\bar{r}_{12}} d\bar{r}_{12}$$

where $\bar{r}_{12} \equiv \bar{r}_1 - \bar{r}_2$ is the intermolecular position vector of molecule 2 with respect to molecule 1 and $r_{12y} = |\bar{r}_{12}|_y$ is the projection of distance of molecule 1 from molecule 2 in the y -direction. $\rho(z)kT$ is the kinetic contribution part of the lateral pressure tensor and $\rho(z) = \rho(\bar{r}_1)$ the local density. This general equation may be solved for any fluid possessing a defined intermolecular pair-potential energy function, $\Phi(\bar{r}_{12})$, confined in a nanoslit pore.

We also report the solution of the resulting equation for the hard-sphere (HS) and Lennard-Jones (LJ) nanoconfined fluid models. Our calculations show the lateral pressure has an oscillatory behavior in the z -direction, perpendicular to the walls, but its value is identical for all points on the xy -planes parallel to the walls at every fixed value of z . We report the result of our investigation of the effects of density, temperature and pore-width on the lateral pressure tensor profile. It is shown that as the bulk fluid density (HS and LJ) increases at constant temperature and pore-width, the height and depth of the lateral pressure tensor profile oscillations are also increased. The number of oscillations of the lateral pressure tensor increases with increasing pore-width at constant temperature and bulk density. In the case of the LJ nanoconfined fluid, the depth and height of the oscillations of the attractive energy contribution to lateral pressure tensor increase with increasing the bulk density. Our analytic integral equations for the lateral pressure tensor reduce to the statistical mechanical pressure expressions of macroscopic systems when the width of the confinement approaches infinity.

Keywords: Lateral pressure tensor, transverse pressure tensor, nanoslit pore, nanoconfined fluid, hard-sphere confined fluid, Lennard-Jones confined fluid.

1. INTRODUCTION

Molecular systems confined within narrow pores with size of a few molecular diameters in at least one of three (x , y , z) directions exhibit physical properties which differ significantly from those in the bulk [1-3]. Liquids, confined between two surfaces or walls, become ordered into layers which have lateral ordering although the normal ordering is also exists between layers. Fluids behavior in various confined geometries, such as cylindrical and slit-like pores, is a subject of numerous theoretical studies using computational simulation, integral equation and density functional theory approaches [4-11].

System walls may have two effects on the thermodynamic properties of a fluid which contains energy and entropy effects. The energy effect appears in two forms. The first form is the cutting of the intermolecular interactions by the walls, which appears for example in the integrals for calculation of the thermodynamic properties. The second one is direct walls effect which involves the walls-molecules interactions. However in the absence of any long-range

forces, its thermodynamic properties show a significant difference with those of the bulk fluids. This is because of the tendency of the system to maximize its entropy which leads to these changes in the behavior of the system and can be called entropy effects [12].

One of the important properties of a confined fluid is the pressure which determines its mechanical stability. In nanoconfined systems, as well as in inhomogeneous macroscopic fluid systems, local pressure is important for calculation of interfacial tension and the analysis of mechanical response to strain and heat, photo excitation and phase transformations [13]. In nanoconfined fluids the pressure has the tensorial nature with directional and positional anisotropy with P_{ij} components, where $i, j = x, y, z$ [14-16]. In nanoslits with structureless walls containing a stationary confined fluid, the off-diagonal components of the local pressure tensor (P_{ij} with $i \neq j$) are zero. So in such systems pressure is a diagonal tensor with P_{ii} ($i = x, y, z$) components. The normal component, P_{zz} , is exerted on a xy -plane parallel to the walls and the lateral (transverse) components of pressure, P_{xx} , P_{yy} , are exerted on the yz - and xz -planes of fluid (perpendicular to the walls). It is clear that, in our case P_{xx} and P_{yy} are identical to each other ($P_{xx} = P_{yy}$) but different from the normal component P_{zz} . It should be

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noted that the pressure which has been imposed on all parallel zx - and zy -planes, perpendicular surfaces to the walls, are the same but the pressure on each point on the zx - and zy -surfaces depends on the location on the z -coordinate.

There exist methods to calculate the local pressure such as the Irving-Kirkwood method, the method of plane and the virial theorem [17] [Irving and Kirkwood 1950]. For homogeneous fluids the standard Irving-Kirkwood method is well suited but it is not valid for strongly inhomogeneous fluids. The virial theorem is routinely used to compute the average, but not the local, pressure over the entire volume of a closed box. Method of plane is valid for systems with planner geometry and flow in one direction. The approach we present here is a simple, efficient and general technique for calculating the lateral pressure tensor.

In fact, an analytic model for nanoconfined fluids phase transition with applications for confined fluids in nanotubes and nanoslits was developed in 2006 along with the proof of the validity of the bulk-system's van der Waals equation of state for small systems [9]. Also recently our group developed the theory for prediction of the normal pressure tensor, P_{zz} , of confined fluids in nanoslit pores [10, 11] [Keshavarzi *et al.* 2010; Heidari *et al.* 2011]. Our studies resulted in general analytic equations for the normal pressure tensor of confined fluids in nanoslit pores.

In the present report a general integral equation theory for the lateral pressure tensor, $P_{xy} = P_{yx}$, of fluids confined in nanoslit pores is presented. At first, the lateral pressure tensor integral equation is analytically solved for hard-sphere fluids confined between two parallel structureless hard walls. Then through the application of the perturbation theory of statistical mechanics, the contribution of the attractive intermolecular potential energy on the lateral pressure tensor is formulated. Then, as an example, the lateral pressure tensor of the confined the Lennard-Jones fluid in nanoslit pores is calculated and reported here.

2. THE THEORY

Analogues to Keshavarzi *et al.* [10] we assume the confined fluid in the nanoslit pore is in equilibrium with a bulk fluid at the same temperature and chemical potential. In Fig. (1) we show a nanoslit pore in the z -direction and an arbitrary zx plane with a surface area s , perpendicular to the walls. We also show there a small volume element ($d\vec{r}_1 = ds_y \times dy$) crossing this zx -plane.

Like in Keshavarzi *et al.* [10] we need to calculate the forces in the y -direction per unit area to obtain the lateral pressure tensor. The force on the surface s in an arbitrary direction of b is [18],

$$\vec{F}_b = \oint \vec{\tau}_{ab} \cdot \vec{n}_a ds_a \quad (1)$$

where subscript b is referred to direction of force component and subscript a refers to the normal direction to surface s . $\vec{\tau}_{ab}$ is the stress tensor and $\vec{n}_b$ is the vector perpendicular to

Fig. (1). Demonstration of a small volume element, v , within our system of a fluid confined in a nanoslit pore consisting of two structureless and parallel walls in the xy -plane located at $z = 0$ and $z = H$.

the surface s . For a nanoslit pore to obtain the lateral pressure tensor we need to calculate the forces in the y -direction per unit area. Therefore for the total force exerted on surface s Eq. (1) assumes the following form:

$$\vec{F}_y = \oint \vec{\tau}_{xy} \cdot \vec{n}_x ds_x \quad (2)$$

To calculate $\vec{F}_y$, the force on the y -direction, and the lateral pressure, which is the force per unit area we must obtain the total momentum, which is transferred at a unit time due to entering and leaving of fluid molecules through the surface s perpendicular to the wall. The total momentum consists of two parts: (i). Kinetic contribution; (ii). Fluid-fluid molecular interaction contribution. It must be mentioned that there is no fluid-walls contribution to momentum since that is only a function of the z -direction. In the following sections we develop the theory to calculate these contributions.

2.1. The Kinetic Contribution to Lateral Pressure Tensor

To calculate the kinetic contribution of the lateral pressure tensor we use the same method as in Keshavarzi *et al.* [10] by taking into account all the momentum transferred through the surface s . That is, the momentum transfer at unit time, dt , through surface element ds_y , by fluid molecules with momentum p_y passing through point $\vec{r}_1$ is:

$$\frac{p_y \rho^{(1)}(\vec{r}_1) dv(p_y)}{dt} d\vec{r}_1 \quad (3)$$

where $dv(p_y)$ is the momentum distribution function in the y -direction and $\rho^{(1)}(\vec{r}_1)$ is the probability density. Then we

use the relation between momentum, velocity, and time as $dt = \frac{dy}{v_y} = \frac{m dy}{p_y}$ and $ds_y \equiv \frac{d\vec{r}_1}{dy}$, in Eq. (3). Where m is mass, t is time and v_y is of velocity in the y -direction.

To obtain all the momentum transferred through the surface s we integrate Eq. (3) over the whole surface s , i.e.

$$F_y = \frac{1}{m} \oint \rho^{(1)}(\vec{r}_1) ds_y \int p_y p_y dw(p_y) \quad (4)$$

The second integral in the above equation is equal to mkT where k is Boltzmann constant and T is temperature. By comparing the result of Eq. (4) with Eq. (2), we obtain the following expression for the kinetic contribution part of the lateral pressure tensor, i.e., which is equal to the negative stress tensor:

$$\tau_{yy} = -kT \rho(\vec{r}_1) \quad (5)$$

However, since $\rho(\vec{r}_1) = \rho(z)$, the lateral pressure tensor in the y -direction has the same uniform value but it depends on the z -direction. Then we conclude,

$$P_{yy}^K = \rho(z) kT \quad (6)$$

Eq. (6) is identical with the normal pressure tensor expression as derived in Keshavarzi *et al.* [10].

2.2. Fluid-Fluid Molecules Interactions Contribution to Lateral Pressure Tensor

To calculate the fluid-fluid molecules interactions contribution to the lateral pressure tensor, we consider the interaction between a fluid molecule "1" at a location $\vec{r}_1$ with a second fluid molecule "2" at location $\vec{r}_2$. The general equation for the force acting on molecule "1" when at $\vec{r}_1$ from molecule "2" at $\vec{r}_2$ is:

$$F_{r_1} = -\nabla_{r_1} \phi(|\vec{r}_1 - \vec{r}_2|) \quad (7)$$

where $\phi(|\vec{r}_1 - \vec{r}_2|)$ is the pair-intermolecular potential energy between molecules "1" and "2". Since molecules "1" and "2" are arbitrary and their true locations are in the ranges $\vec{r}_1 \rightarrow \vec{r}_1 + d\vec{r}_1$ and $\vec{r}_2 \rightarrow \vec{r}_2 + d\vec{r}_2$, we multiply Eq. (7) with the pair-probability density of the two molecules and then take the integral on $\vec{r}_1$ over volume V and $\vec{r}_2$ over volume $V - V$. The result will be the following double-integral.

$$F_y^{FF} = - \int_{V-V} \int \nabla_{r_1} \phi(|\vec{r}_1 - \vec{r}_2|) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (8)$$

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 with respect to the former two as follows:

$$\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2, \quad \vec{R}_{12} \equiv \vec{r}_1 - \frac{1}{2} \vec{r}_{12}$$

The Jacobian of this transformation is unity and since v is very small compared to V , we assume $V - v \equiv V$. Then we have:

$$F_y^{FF} = - \int_{V-v} \int \nabla_{r_1} \phi(|\vec{r}_{12}|) \rho^{(2)}(\vec{r}_{12}, \vec{R}_{12}) d\vec{R}_{12} d\vec{r}_{12} \quad (9)$$

After using the truncated Taylor series expansion for $\rho^{(2)}(\vec{r}_{12}, \vec{R}_{12})$, i.e.

$$\rho^{(2)}(\vec{r}_{12}, \vec{R}_{12}) \approx \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) + \left(-\frac{1}{2} \vec{r}_{12}\right) \cdot \nabla_{\vec{r}_1} \rho^{(2)}(\vec{r}_{12}, \vec{r}_1),$$

we get

$$\int \rho^{(2)}(\vec{r}_{12}, \vec{R}_{12}) d\vec{R}_{12} = \int \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) d\vec{r}_1 - \frac{1}{2} \oint \vec{r}_{12} \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) n_y ds_y \quad (10)$$

The second integral in the right-hand side of Eq. (10) is transformed into a surface integral by using the Gauss's theorem. Then, by inserting Eq. (10) into Eq. (9), we get the following equation

$$F_y^{FF} = - \int_V \nabla_{r_1} \phi(|r_{12}|) \left\{ \int \rho^{(2)}(r_{12}, r_1) dr_1 - \frac{1}{2} \oint r_{12} \rho^{(2)}(r_{12}, r_1) n_y ds_y \right\} dr_{12}$$

The first double integral in the above equation is zero because it has an odd integral and therefore we have:

$$F_y^{FF} = \frac{1}{2} \int_V \oint \nabla_{r_1} \phi(\vec{r}_{12}) \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) \vec{r}_{12} n_y ds_y dr_{12} \quad (11)$$

However, since we need to consider only the forces in the y -direction in the nanoslit pore, we replace $\nabla_{r_1} \phi(\vec{r}_{12})$ with $\nabla_y \phi(\vec{r}_{12})$, using the following chain rule:

$$\nabla_y \phi(\vec{r}_{12}) = \nabla_{r_1} \phi(\vec{r}_{12}) \cdot \frac{r_{12y}}{|\vec{r}_{12}|} \quad (12)$$

In Eq. (12), r_{12y} is the projection of the distance vector between molecule "1" from molecule "2" on the y -coordinate. As a result Eq. (11) will convert to the following equation:

$$\tau_{yy} = \frac{1}{2} \int_V \phi'(\vec{r}_{12}) \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) \frac{(r_{12y})^2}{|\vec{r}_{12}|} d\vec{r}_{12}$$

Therefore the fluid-fluid interactions contribution to the lateral pressure tensor $P_{yy} = -\tau_{yy}$, using Eq. (2) is:

$$P_{yy}^{FF} = -\frac{1}{2} \int_V \phi'(\vec{r}_{12}) \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) \frac{(r_{12y})^2}{|\vec{r}_{12}|} d\vec{r}_{12} \quad (13)$$

By joining Eqs (6) and (13) the analytic expression for the lateral pressure tensor of the confined fluid in nanoslit pore is derived as the following:

$$P_{yy} = P_{yy}^K + P_{yy}^{FF} = kT \rho(z) - \frac{1}{2} \int_V \phi'(\vec{r}_{12}) \rho^{(2)}(\vec{r}_{12}, \vec{r}_1) \frac{(r_{12y})^2}{|\vec{r}_{12}|} d\vec{r}_{12} \quad (14)$$

Eq. (14) is general and may be solved for any kind of fluid-fluid interactions of confined fluids in a nanoslit pore.

It should be noted that this equation may be applied for prediction of the lateral pressure of fluids in a gases and liquid states.

Also since our derivation is based on the statistical mechanical theory the behavior of the local pressure is interpretable and the role of the intermolecular interactions and kinetic term may be understood.

In the next sections we report solution of this equation for hard-sphere and Lennard-Jones confined fluids in nanoslit pores.

3. LATERAL PRESSURE TENSOR OF THE HARD-SPHERE CONFINED FLUID

Let us consider a system consisting of N hard-sphere particles with diameter d confined between two parallel hard walls with macroscopic areas and a nano-gap in between with the thickness of H . The pair intermolecular potential energy between the hard-sphere particles is given by:

$$\phi(r_{12}) = \begin{cases} 0 & r_{12} > d \\ \infty & r_{12} \leq d \end{cases}$$

Contribution of the kinetic term of lateral pressure tensor of hard-sphere fluids is equal to $\rho_H(z)kT$ as given by Eq. (6), where $\rho_H(z)$ is the local density of hard-sphere confined fluid in nanoslit pore which depends on the z position and the pore width, H .

To calculate the integral in the fluid-fluid interaction contribution of the lateral pressure tensor, Eq. (14), we use the definition of $\rho^{(2)}$ with respect to the radial distribution function (RDF), $g_{z,H}$:

$$\rho^{(2)}(r_{12}, r_1) = \rho(z_1)\rho(z_2)g_{z,H}(r_{12})$$

The subscripts z and H indicate that $g_{z,H}$ is dependent on, both H and z .

Then in the Cartesian coordinate Eq. (14) will have the following form:

$$P_{xy} = kT\rho(z_1) - \frac{1}{2} \iiint \phi'(r_{12})\rho(z_1)\rho(z_2)g_{z,H}(r_{12}) \frac{y_{12}^2}{(x_{12}^2 + y_{12}^2 + z_{12}^2)^{0.5}} dx_{12} dy_{12} dz_{12} \quad (15)$$

By assuming the position of molecule "1", fixed on the coordinate center we can replace x_{12}, y_{12} and z_{12} with x_2, y_2 , and z_2 respectively. Therefore Eq. (15) may be written as:

$$P_{xy} = kT\rho(z_1) - \frac{1}{2} \iiint \phi'(r_2)\rho(z_1)\rho(z_2)g_{z,H}(r_2) \frac{y_2^2}{(x_2^2 + y_2^2 + z_2^2)^{0.5}} dx_2 dy_2 dz_2 \quad (16)$$

$$\text{where } r_2 = \sqrt{x_2^2 + y_2^2 + z_2^2}.$$

Since the derivative of the hard-sphere potential, $\phi'_{hs}(r_2)$, is zero everywhere except at $(x_2^2 + y_2^2 + z_2^2)^{0.5} = d$ we may formulate it as:

$$\phi'(r_2) = -kT\delta\left[(x_2^2 + y_2^2 + z_2^2)^{0.5} - d\right] \exp\left(\frac{\phi_{hs}\left[(x_2^2 + y_2^2 + z_2^2)^{0.5}\right]}{kT}\right) \quad (17)$$

where $\delta\left[(x_2^2 + y_2^2 + z_2^2)^{0.5} - d\right]$ is the Dirac delta-function. By inserting Eq. (17) in Eq. (16) we get:

$$P_{xy}^{hs} = kT\rho(z_1) + \frac{kT}{2}\rho(z_1)\int \rho(z_2)g_{z,H}(r_2)dz_2 \int \frac{y_2^2}{(x_2^2 + y_2^2 + z_2^2)^{0.5}} dy_2 \int \delta\left[(x_2^2 + y_2^2 + z_2^2)^{0.5} - d\right] \exp\left(\frac{\phi_{hs}\left[(x_2^2 + y_2^2 + z_2^2)^{0.5}\right]}{kT}\right) dx_2 \quad (18)$$

Since the fluid is confined in just the z direction in the nanoslit pore (x - and y -directions are unlimited) and because we need just to consider the interaction of the molecules in one side of the xz -plane (Fig. 1) according to our definition for pressure Eq. (18) reduces to the following equation

$$P_{xy}^{hs} = kT\rho(z_1) \left[1 + \frac{\pi}{4} \int_{-d}^{+d} \rho(z_2)g_{z,H}(d)(d^2 - z_2^2) dz_2 \right] \quad (19)$$

where $\rho(z_1)$ and $\rho(z_2)$ are the local densities of the hard-sphere fluid in the nanoslit pore, $g_{z,H}(d)$ is the RDF at the contact point, and z_1 and z_2 are position of molecules "1" and "2" in the z -direction, respectively. It should be noted that when the size of confinement, H , approaches to infinity Eq. (19) becomes:

$$\frac{P}{\rho kT} = 1 + \frac{2\pi}{3} \rho d^3 g(d^*) \quad (20)$$

which is the hard-sphere pressure equation in the macroscopic systems.

In order to apply Eq. (19) for lateral pressure profile calculation we need the RDF and local density profile data. We use the local density profile of hard-sphere nanoconfined fluid as was derived by Kamalvand *et al.* (2008). The RDF, $g_{z,H}(d)$, in nano-slits is different from the bulk system RDF. It is a function of local density in the nanoslit, but due to the lack of an exact functional form for $g_{z,H}(d)$ we replace it with its average value $\langle g_{(hc)}(d) \rangle$. Then due to the lack of any information about $g_{z,H}$ we assume $\langle g_{hs}(d) \rangle \approx 1$. Considering the form of the integral appearing in the right-hand-side of Eq. 19 we do not expect this approximation to affect the lateral pressure tensor profile significantly. With these assumptions we have obtained the lateral pressure

tensor of hard-sphere confined fluid. The kinetic term of lateral pressure tensor of hard-sphere fluids is equal to $\rho_H(z)kT$. Because this term is the same as the contribution of the kinetic term for normal pressure tensor, to summarize the figures we refer the readers to our pervious work, Fig. (1a, b, c) of Heidari *et al.* [11].

In Fig. (2) we report the lateral pressure profiles of the hard-sphere confined fluid in nanoslit pore, Eq. (19), at two different reduced pore widths ($H^* = H/\sigma = 4$ and 6) and for two different reduced bulk densities ($\rho_{MAC_Bulk}^* \equiv \rho_{MAC_Bulk} \sigma^3 = 0.3$ and 0.6) and at reduced temperature $T^* = kT/\epsilon = 2$. Also plotted in this figure are the normal pressure profiles at the same state conditions as we reported in Paper 1. In defining the reduced temperature we use $\epsilon = 119.8k$ which is the Lennard-Jones energy parameter value for argon-argon interaction and k is the Boltzmann constant. According to

Fig. (2). Reduced lateral pressure $P_{yy}^* = P_{yy} d^3 / \epsilon$ profiles of the hard-sphere confined fluid in nanoslit pores with widths $H^* = H/d = 4$ & 6, calculated using Eq.(19) with the related approximations for two different reduced bulk densities ($\rho_{MAC_Bulk}^* \equiv \rho_{MAC_Bulk} d^3 = 0.3$ & 0.6) and at the reduced temperature $T^* = kT/\epsilon = 2$. To calculate the reduced temperature ϵ is chosen as $\epsilon = 119.8k$ which is the Lennard-Jones energy parameter value for argon-argon interaction and k is the Boltzmann constant. Parameter d is the hard-sphere diameter. Also reported in these figures for comparison purposes are the reduced normal pressure profiles $P_{zz}^* = P_{zz} d^3 / \epsilon$ of the hard-sphere confined fluid as reported by Keshavarzi *et al.* [10].

Fig. (2) the lateral pressure profiles of the hard-sphere confined fluid versus distance from the walls have oscillatory forms. The height and depth of its oscillations increase with increasing the density of the bulk fluid in equilibrium with the nanoslit fluid. Also according to Fig. (2) the normal pressure profiles have similar, but more profound oscillatory forms compared to the lateral pressure profiles.

4. LATERAL PRESSURE TENSOR OF THE LENNARD-JONES (LJ) NANOCONFINED FLUID

Inhomogeneous fluids with both repulsive and attractive intermolecular potential energies have been active research subjects, because they are applied to study a variety of interesting problems such as surface adsorption, wetting, and capillary condensation. The Lennard-Jones (LJ) intermolecular potential energy function has long been a useful, but simple, model that can describe a wide variety of phenomena.

For investigation on the role of fluid-fluid interaction on lateral pressure tensor of the LJ fluid confined in nanoslit pore with structureless hard walls we assume that the system consists of N real molecules all with diameter σ confined between two parallel hard walls with macroscopic areas and with pore width equal to H . Based on the statistical mechanical perturbation theory [19, 20] the pair-potential energy may be separated in to two parts.

$$\Phi_{reference} = \Phi_{(hs)}(r_{12}) = \begin{cases} 0 & \text{for } |\vec{r}_2 - \vec{r}_1| > d \\ \infty & \text{for } |\vec{r}_2 - \vec{r}_1| \leq d \end{cases} \quad (21)$$

$$\Phi_{(perturbed)} = \begin{cases} \Phi(r_{12}) & \text{for } |\vec{r}_2 - \vec{r}_1| > d \\ 0 & \text{for } |\vec{r}_2 - \vec{r}_1| \leq d \end{cases} \quad (22)$$

Where $\Phi(r_{12})$ in our case is the pair-intermolecular potential energy function and d is the hard core effective diameter.

In the perturbation theory, with analogy to the potential energy function, thermodynamic properties may be also separated into two parts. For example for pressure of the system we have:

$$P_{yy} = P_{yy}^{hs} + P_{yy}^{perturbed} \quad (23)$$

where P_{yy}^{hs} is the lateral pressure of unperturbed hard-sphere system and $P_{yy}^{perturbed}$ is the contribution of attractive energy (perturbation) part.

Now we separate the integral appearing in the right hand side of Eq. (16) into two parts including the reference and attraction terms according to Eq. (23). The hard-sphere equation may be applied as the reference for a real fluid. Therefore the reference hard-core part of Eq. (16) will be as follows:

$$P_{yy}^{reference} = kT\rho(z_1) \left[1 + \frac{\pi}{4} \int_{-d}^{+d} \rho(z_2) (d^2 - z_2^2) dz_2 \right] \quad (24)$$

It should be noted that in Eq. (24) $\rho(z_1)$ and $\rho(z_2)$ are the local densities of the LJ fluids. To remove complications related to the choice of the hard-core diameter, d , we choose that equal to the Lennard-Jones length parameter σ .

To solve the perturbation term of Eq. (16),

$$P_{yy}^{perturb} = -\frac{1}{2} \iiint \phi'(r_2) \rho(z_1) \rho(z_2) g_{z,H}(r_2) \frac{y_2^2}{(x_2^2 + y_2^2 + z_2^2)^{0.5}} dx_2 dy_2 dz_2 \quad (25)$$

It should be noted that Eq. (25) is acceptable for thermodynamic states for which the perturbation approach is correct. We use the perturbed pair potential for $\phi(r)$ and the values of x_2, y_2, z_2 are let to vary by with the following condition:

$$r_2 = \sqrt{(x_2^2 + y_2^2 + z_2^2)} > d, \quad (26)$$

and considering the upper limit H in the z direction. To solve the perturbed part, only the interactions between the molecule "1" and those molecules which are in one side of xz -plane (Fig. 1) come into account. We consider this in the numerical solution of the integral in Eq. (25) by choosing the appropriate values of x_2, y_2 and z_2 .

For macroscopic systems the radial distribution function (RDF) theory is well established [21, 22], but for nano systems we still lack any information about the theory and solution of RDF. Due to the lack of an exact analytic expression for $g_{z,H}(r_2)$ we replace it with its average value $\langle g_{z,H}(r_2) \rangle$. Then, due to the lack of any information about $\langle g_{z,H}(r_2) \rangle$ we assume $\langle g_{z,H}(r_2) \rangle = 1$.

By application of the Lennard-Jones potential energy function for $\phi(r)$,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (27)$$

and the approximation assumptions about the radial distribution function mentioned above we have calculated the lateral pressure tensor of the LJ confined fluid. The kinetic term of the lateral pressure tensor, $kT\rho(z_1)$, appearing in Eq. (24) is similar to kinetic term of the normal pressure tensor [11].

In Fig. (3) we report the contributions of the reduced lateral pressure $P_{yy}^* = P_{yy} \sigma^3 / \epsilon$ profiles of the reference (hard-core) to the lateral pressure profiles of the Lennard-Jones (LJ) confined fluid in nanoslit pores calculated using Eq.(24) with the related approximations. These results are for $H^* = H/\sigma = 4$ & 6 and for two different reduced bulk

densities ($\rho_{MAC_Bulk}^* \equiv \rho_{MAC_Bulk} \sigma^3 = 0.6$ & 0.8) and at the reduced temperature $T^* = k.T/\epsilon = 2$. Also reported in Fig. (3) for comparison purposes are the reduced normal pressure profiles $P_{zz}^* = P_{zz} \sigma^3 / \epsilon$ of the reference (hard-core) contribution to the normal pressure profiles of the LJ confined fluid as reported by Heidari *et al.* (2011).

Fig. (3). Reduced lateral pressure $P_{yy}^* = P_{yy} \sigma^3 / \epsilon$ profiles of the reference (hard-core) contribution to the lateral pressure profiles of the Lennard-Jones (LJ) confined fluid in nanoslit pores with widths $H^* = H/\sigma = 4$ & 6, calculated using Eq. (24) with the related approximations for two different reduced bulk densities ($\rho_{MAC_Bulk}^* \equiv \rho_{MAC_Bulk} \sigma^3 = 0.6$ & 0.8) and at the reduced temperature $T^* = k.T/\epsilon = 2$. Also reported in these figures for comparison purposes are the reduced normal pressure profiles $P_{zz}^* = P_{zz} \sigma^3 / \epsilon$ of the reference (hard-core) contribution to the normal pressure profiles of the LJ confined fluid as reported by [11].

According to Fig. (3) the lateral and normal pressure profiles of the reference hard-core versus distance from the walls have oscillatory forms. The height and depth of oscillations increase with increasing the density of the bulk fluid in equilibrium with the nanoslit fluid. Also according to Fig. (3) the normal pressure profiles have similar, but more profound oscillatory forms compared to the lateral pressure profiles. In comparing the results of Fig. (2) for hard-sphere confined fluid and those of Fig. (3) for reference hard-core we observe different relative amounts of lateral and normal pressures. Also the value of the lateral pressure at contact point is more than the normal pressure.

We have also calculated the contribution of the perturbation (attractive) energy term to the lateral pressure tensor. Fig. (4) show reduced lateral pressure $P_{ATT-y}^* = P_{ATT-y} \sigma^3 / \epsilon$ profiles of the perturbation contribution for nanoslit widths $H^* = 4$ & 6, calculated using Eq. (25) with the related approximations for two different reduced bulk densities ($\rho_{MAC-BULK}^* = 0.6$ & 0.8) and at the reduced temperature

Fig. (4). Reduced lateral pressure $P_{ATT-y}^* = P_{ATT-y} \sigma^3 / \epsilon$ profiles of the perturbation contribution to the lateral pressure profiles of the LJ confined fluid in nanoslit pores with widths $H^* = 4$ & 6, calculated using Eq. (25) with the related approximations for two different reduced bulk densities ($\rho_{MAC-BULK}^* \approx \rho_{MAC-BULK} \sigma^3 = 0.6$ & 0.8) and at the reduced temperature $T^* \approx kT/\epsilon = 2$. Also reported in these figures for comparison purposes are the reduced normal pressure profiles $P_{ATT-z}^* = P_{ATT-z} \sigma^3 / \epsilon$ of the perturbation contribution to the normal pressure profiles of the LJ confined fluid as reported by [11].

$T^* = kT/\epsilon = 2$. According to Fig. (4) at constant bulk density and temperature by increasing the pore width, the number of layers and their depths increase. At constant temperature and pore width when the bulk density increases contribution of the attractive energy decrease but its fluctuations increase. Also reported in Fig. (4) for comparison purposes are the reduced perturbation contribution to normal pressure $P_{ATT-z}^* = P_{ATT-z} \sigma^3 / \epsilon$ profiles as reported by Heidari *et al.* [11]. According to Fig. (4) lateral perturbation profiles are more negative than the normal perturbation profiles. Also there is more profound layering in lateral perturbation pressure profiles than in the normal ones.

In Fig. (5) we report the result of our calculations for the lateral pressure $P_{yy}^* = P_{yy} \sigma^3 / \epsilon$ profiles of the LJ confined fluid in nanoslit pores at $\rho^* = 0.6$ & 0.8, $H^* = 4$ & 6 and $T^* = 2$. Also reported in Fig. (5) for comparison purposes are the reduced LJ normal pressure $P_z^* = P_z \sigma^3 / \epsilon$ profiles as originally reported by Heidari *et al.* [11]. The pressure profiles in this figure are the sum of those in Figs. (3 and 4). According to Fig. (5) there are oscillatory behaviors in the lateral pressure profiles which are much less profound than the normal pressure profiles. Fig. (5) shows that the lateral pressure of the LJ fluid confined in a nanoslit pore increases with increase in the bulk density as in the case of the hard-sphere lateral pressure as shown in Fig. (2). On the other hand the oscillations become broad and smooth as the density decreased.

5. CONCLUSIONS

We have derived analytic algebraic integral equations for the lateral pressure components of the pressure tensor of hard-sphere and Lennard-Jones (LJ) confined fluids in nanoslit pores based on the statistical mechanics. The resulting lateral pressure expressions contain both, kinetic and fluid-fluid interaction terms. It is shown that the wall-fluid interactions do not contribute to the lateral pressure. The resulting expressions are solved numerically to calculate lateral pressure profiles in nanoslit pores as a function of slit width, temperature and macroscopic bulk density of a fluid in equilibrium with the nanoslit pore fluid. Our calculations contain the approximation of assuming nanoslit fluid radial distribution functions are unity. Using the mean field approximation in the perturbed part increases the attractive contributions in the local pressure. Also considering $g_{z,H}(d) = 1$ in the reference part decreases the repulsive contributions. Therefore our predicted results of lateral pressure are less than the real values. We show that the local lateral pressure in nanoslit pores has an oscillatory behavior which is a result of the layering effects of molecules in the nanoslit pore. Since the nanoslit pore is confined in the z -direction (perpendicular to walls), the lateral pressure has different value along any point of z -axis. However for surfaces parallel to the walls the normal pressure has unique value which depends on the value of z .

Fig. (5). Reduced lateral pressure ($P_{L-yz}^* = P_{L-yz} \sigma^3 / \epsilon$) profiles of the Lennard-Jones confined fluid in nanoslit pores with widths $H^* = H/\sigma = 4$ and 6 , calculated using Eq. (23) with the approximations mentioned in the text for two different reduced bulk densities ($\rho_{MAC,BULK}^* \cong \rho_{MAC,BULK} \sigma^3 = 0.6$ and 0.8) and at the reduced temperature $T^* \equiv kT/\epsilon = 2$. Also reported in these figures for comparison purposes are the reduced normal pressure profiles $P_{L-xx}^* = P_{L-xx} \sigma^3 / \epsilon$ of the LJ confined fluid as reported by [11]. The profiles reported in this figure are the sums of related profiles in Figs. (3 and 4).

For the confined hard-sphere and Lennard-Jones fluids at constant pore width when the bulk density decreases the oscillatory behaviors become more diffuse and broad. At higher densities the lateral pressure increases in all cases but maintains its oscillatory behavior. At constant bulk density when the pore width increases, the number of layers of the molecules in the pore increase but their heights decrease.

Comparison is also made between the lateral and normal pressure profiles for both hard-sphere and LJ confined fluids. It is shown that the difference between the lateral and normal pressure profiles for hard-spheres is quite small for the ranges of data compared. However, the LJ lateral pressure profiles are much less than their normal pressure profiles, but with the same number of fluctuations.

6. REFERENCES

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