Pressure Calculations in Nanochannel Gas Flows

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Abstract. In this research, pressure driven flow within a nanochannel is studied for argon in rarefied gas states. A Molecular Dynamics simulation is used to resolve the density and stress variations. Normal stress calculations are based on Irving-Kirkwood method, which divides the stress tensor into its kinetic and virial parts. The kinetic component recovers pressure based on the ideal-gas law. The particle-particle virial increases with increased density. The kinetic part and the virial part of the pressure is studied from \( Kn = 0.1 \) to \( Kn = 0.5 \) at 300 K. This pressure calculation was also compared with a simulation for a static fluid. Pressure driven gas flow gives a different result compared to static situation, which has a uniform particle distribution across the system. For a flow situation, the virial part is no longer the same. This can also be predicted from the virial equation and by the fact that the compressible fluid flow causes a temperature and density difference along the flow direction. The relation between the virial and distribution of particles has been studied further to understand the nature of virial component along the flow direction in compressible flows.

1. Introduction

The development of new technologies in micro- and nano engineering has a major impact on many disciplines including fluid dynamics and transport phenomena. When dealing with flows in the scale of microns or smaller, many phenomena such as velocity slip and temperature jumps have been observed [1]. The flow characteristics at the macro and micro levels are not the same and the features of micromechanics require additional basic and applied research work.

The Knudsen number is used to characterize the gas flow regimes. The Knudsen number is defined as \( Kn = \frac{\lambda}{L} \), where \( L \) is the characteristic length scale of the physical system, and \( \lambda \) is the molecular mean free-path. Mean free path \( \lambda \) is defined as \( \lambda = \frac{1}{n \sqrt{2 \pi \kappa n}} \), where \( n = \frac{N}{Vol} \). \( N \) is number of particles and \( Vol \) is the volume of the system. It is commonly assumed that failure of continuum approach occurs at Knudsen number around 0.01 [2]. In most cases, gas flows on the nano level have been studied by direct simulation Monte Carlo (DSMC) or Molecular Dynamics (MD).

Local pressures are important in analysing micromechanical behaviour. The local pressure in the DSMC method may be evaluated from the ideal gas law or by explicitly evaluating the pressure tensor for calculating the pressure near the wall. However, the ideal-gas law is known to fail as the pressure increases. Unlike the ideal-gas law, MD simulations can predict a pressure using the Irving-Kirkwood method [3]. Less than 10% difference from experimental results are even shown for the liquid state, while ideal-gas law gives an error larger than 100% near the liquid state [4].

According to the Irving Kirkwood method the contribution of each particle to the pressure tensor consists of two parts, a configuration part and a kinetic part:

\[
P_{kl} = \frac{1}{Vol} \left( \sum_{i}^{N} m_i \left( v_{ki}^l - \overline{v}_k^l \right) \left( v_{ki}^l - \overline{v}_l^l \right) - W_{kl} \right)
\]

\[
W_{kl} = \frac{1}{2} \sum_{i,j}^{N} \left( r_{ki}^l - r_{kj}^l \right) f_{i,j}^{kl}
\]

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where the first term on the right-hand side of equation 1 represents the kinetic component and the $W_{kl}$ term represents the virial component. In the kinetic part, $m^i$ is the atomic mass of particle $i$, whereas subscripts $k$ and $l$ are the axes of the Cartesian coordinate system, $V^i_k$ and $V^i_l$ are the peculiar velocity component of particle $i$ in the $k$ and $l$ directions, and $\bar{V}_k^i$ and $\bar{V}_l^i$ are the local average streaming velocities at the position of particle $i$, in the $k$ and $l$ directions, respectively. The term $(r_k^i - r_k^j)$ in Equation 2 is $k^{th}$ component of the distance vector between particles $i$ and $j$, and $f_k^{ij}$ is the $l^{th}$ component of the intermolecular force exerted on particle $i$ by particle $j$.

The first term, $\sum^N m^i (V_k^i - \bar{V}_k^i) (V_l^i - \bar{V}_l^i)$, in the Irving-Kirkwood expression is related to the ideal-gas law. It calculates ideal gas pressure exactly by considering the momentum resulting from the particle velocities, whereas the second term, $W_{kl}$, the virial component are the corrections to the ideal-gas law because of the interaction of particles having non-zero volumes and force field.

For flow situations, the virial part is no longer isotropic. It will have a different virial component in the flow direction compared to other axial components. This can also be predicted from equation 2 and by the fact that the compressible fluid flow causes a density difference along the flow direction. Therefore, investigation of the pressure of a gaseous flow requires careful consideration of the density gradient along the channel.

In the present work, we mainly focus on two aspects; in the first part we investigate characteristics of the pressure from \(Kn \approx 0.1\) to \(Kn \approx 0.5\) of the gas flow inside the nanochannel since there have been no detailed study on the pressure in nanochannel gas flow. The Knudsen numbers were chosen where the transition from a CFD method to the DSMC method lies. In the second part, we investigate the effect of temperature and density gradient on virial component, so to suggest a better estimation of pressure without using a computationally expensive Irving-Kirkwood method.

In order to achieve these goals we will perform detailed 3D molecular dynamics simulations.

### 2 Three-dimensional MD simulation details

A 3D Molecular Dynamics simulation method is used to simulate the flow of argon (Ar) in a nanochannel (figure 1). Molecular Dynamics is a discrete, deterministic method that simulates the temporal and spatial dynamics of matter (solid, liquid, gases). Matter is explicitly modeled by atoms or molecules, which interact together through potentials. In this research a truncated and shifted Lennard-Jones potential, $V_{tr}$ is used to model the interaction:

$$V_{tr}(r_{ij}) = 4\varepsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right) - \left( \left( \frac{\sigma}{r_{c}} \right)^{12} - \left( \frac{\sigma}{r_{c}} \right)^{6} \right)$$

for $r_{ij} \leq r_c$, and $V_{tr}(r_{ij}) = 0$ for $r_{ij} > r_c$.

The walls are modeled by a thermal wall condition. The interaction between two argon molecules is described by the Lennard Jones potential of equation (3) with parameters as given in Table 1.

| argon particle | $\sigma_{Ar}$ | $m_{Ar}$ | $\epsilon_{Ar}/k_B$ | Cut-off Radius |
|----------------|--------------|---------|---------------------|---------------|
|                | 0.340 [nm]   | 6.63 $\cdot$ 10^{-26} [kg] | 121 [K]          | 2.5 [\sigma] |

The Molecular Dynamics code *PumMa*[6] has been used here. This code has also been used by previous researchers in the area of nano flow and heat transfer [7, 8].

In the present research, two different sets of simulations will be carried out in order to achieve two different goals of the work mentioned in the preceding section. The first simulation set (section 2.1) will be focused
on the nanochannel gas flow while the second simulation set (section 2.2) will be focused on the relationship between the virial component and density gradient.

2.1 Pressure in nanochannel gas flow
A developing flow inside a slit channel with a height $H$ has been simulated (Figure 1). The characteristic length of this system is the separation distance $H$ between the two parallel plates. In the flow direction, $x$ direction, the channel length is kept constant, $L = 100$ nm, and while $H$ is changed from 10nm to 100nm ($H = 10, 25, 50, \text{ and } 100 \text{ nm}$).

![Figure 1. Developing nanochannel flow by using gravity fed method.](image)

The simulation is started from the Maxwell-Boltzmann velocity distribution at 300 K. The walls were kept at a constant temperature $T_w = 300$ K. A thermal wall condition was applied as a boundary condition at the top and bottom plates.

The simulation box domain in the XY plane is divided by a 100x100 mesh. 10000 bins are extended across the Z direction. The local pressure properties are calculated in each bin.

Flow was induced by the gravity fed method with a gravity of $g_x = \text{m/s}^2$ in the whole domain. Time steps were chosen $\Delta t = 6.43 \text{ fs}$.

A typical computation in our simulations requires 5,000,000 time steps for flows to reach a steady flow state. We spent about 7,000,000 additional time steps for computing the averaged macroscopic properties: flow velocity, pressure, temperature, etc.

2.2 Virial vs. density & temperature gradient
In the second simulation the effect of a density and temperature gradient is investigated. Therefore a temperature gradient between two parallel walls was presented.

![Figure 2. Density gradient caused by a temperature gradient](image)
The Knudsen number of the sampling region was chosen to be 0.1, 0.2, 0.3, 0.4, and 0.5. Different numbers of particles were considered depending on the $Kn$. Number of particles varies from 1910 ($Kn = 0.5$) to 121593 ($Kn = 0.1$).

In the simulation, the two walls are kept at a different constant temperature. The cold wall was kept at constant temperatures $T_{cold} = 60.5$ K, 121 K, 181.5 K and 242 K, and the hot wall at constant temperatures $T_{hot} = 242$ K, 301.5 K, 363 K, 424.5 K. A thermal wall condition was applied as a boundary condition.

| $T_{cold}$ [K] | $T_{hot}$ [K] |
|----------------|---------------|
| 242.0          | 242.0         |
| 181.5          | 302.5         |
| 121.0          | 363.0         |
| 60.5           | 423.5         |

Density gradient is produced by using a temperature gradient caused by the different temperature of the walls. Four different density gradients have been simulated with the same total density in the sampling region.

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3 Results and Discussion

3.1 Pressure in nanochannel gas flow

We first focus on argon gas flow at a temperature of 300 K that is developing inside the slit channel. Simulations have been carried out for 4 different channel heights $H = 10$ nm, 25 nm, 50 nm, and 100 nm. The results for the total pressure and the virial component are shown in figure 3. Figure 3a clearly shows the pressure increase when the channel height decreases for the same given Knudsen numbers. It is the same for the virial components (figure 3b). The absolute value for the virial component increases as the channel height decreases. The ideal-gas law is known to fail as the pressure increases, and understanding of the virial component becomes more important in nanochannel flows compared to microchannel flows for the same Knudsen number.

Figure 3a. Pressure of an argon gas flow inside a nanochannel

Figure 3b. Virial component of an argon gas flow inside a nanochannel

Figure 4 shows the distribution of the kinetic component and the virial component along the channel. While the kinetic term is equally distributed along the y-axis (height), the virial component shows a gradient due to the density gradient caused by the temperature gradient due to the expansion flow near the outlet.
Since the virial component is not proportional to kinetic component, it is important to understand the nature of virial component since this component can have a dominant role in the pressure calculation.

One of the situations where a virial component becomes important is a case with a low temperature. Gas channel flows often deal with an expansion flow caused by an outlet effect. Temperature drop is one of the widely known features of such expansion flow [9]. There are two reasons why the virial component becomes more important for low temperature. Equation 1 shows that the virial component takes a larger role in overall pressure at low temperature since the kinetic component is proportional to the temperature according to the Maxwell distribution. The other reason is the increase in the absolute value of the virial component at low temperature.

Density is a very important factor of understanding the nature of the virial component. In Figure 5, virial components of the simulations with different channel heights have been plotted against the number density. It shows an exponential decay in virial component of all channel heights. The result near the density 1.6 has a large error due to small number of ensembles caused by the small channel height.

**Figure 4.** Contour graph of the kinetic component (left) and virial component (right) of the pressure inside the 50nm height nanochannel

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**Figure 5.** Virial pressure component as a function of the number density.
The cut-off radius should be carefully chosen for the larger density simulations. As for example, in a 10 nm channel, different cut-off radii are used, a large difference in the virial calculation can be produced. Figure 6 shows a comparison of two different cut-off radii. For the smaller cut-off radius (2.5 \( \sigma \)), the simulation produces a smaller absolute virial component value than it should have.

![Figure 6. H = 10 nm channel simulations with a different cut-off radius. 2.5 \( \sigma \) (red) and 3.5 \( \sigma \) (orange).](image)

3.2 Static situation

To understand the nature of virial component in flow cases, it is necessary to understand non flow situation in advance. Figure 7 shows the simulation results of static situations.

![Figure 7. Virial component as function of number density in the case without any density gradient at 121 K.](image)
A 2nd order polynomial function was fitted through the data using Origin 8.5 Software [10].

\[ W_{\text{static}} = 0.080 - 17.499 \rho - 3108.418 \rho^2 \]  

where \( W_{\text{static}} \) is a virial component in the static condition, and \( \rho \) is a number density (\( \sigma^{-3} \)) of the system.

This corresponds well with the second virial coefficient. For a certain temperature, the virial expansion can be shown in the form of

\[ P = C_1 \rho - C_2 \rho^2 \]  

where \( C_1 = k_B T \) and \( C_2 = B_2(T)k_B T \). \( B_2(T) \) is the second virial coefficient. In table 2, the \( C_2 \) values are compared with other literature values [11, 12].

**Table 3.** Comparison between Irving-Kirkwood method and the second virial coefficient at 121 K. Coefficient \( C_2 \) in equation 6 is compared.

|                | \( C_2 \) [\( \sigma^6/\text{bar} \)] |
|----------------|-----------------------------------|
| This work      | -3108.418                         |
| Experiments [11] | -3111.896                     |
| Leonhard [11]  | -2972.592                         |
| Hloucha [12]    | -3222.866                         |

Our simulation results in static situation perfectly match with the literature values. This result validates our MD code while using the Irving-Kirkwood method.

### 3.3 Static situation vs. flow situation

A 10nm channel was chosen to compare a static situation with a flow situation. Figure 8 shows the virial component of two flow situations (red, orange) and two static situations (green, light green). The results of two static situations are calculated based on the literature values [11].

**Figure 8.** Comparison of flow vs. static virial component in the \( H = 10 \) nm channel.
The 10nm channel gas flow simulation results with cut-off radius $3.5\sigma$ were compared to the static situation at 301.7 K. It indicates that the virial with a flow situation has a larger absolute value compared to the no-flow situation (static situation). This difference can be caused by the following effects:

1. Temperature
2. Effect of cut-off radius
3. Boundary effect (confinement effect)
4. Velocity of flow
5. Density gradient.

Since the temperature is nearly constant at 300 K for number densities ranging from $0.4 \text{ nm}^{-3}$ to $1.8 \text{ nm}^{-3}$ for this 10nm channel, this difference can hardly be caused by temperature effects. It is not due to the cut-off neither. If it was caused by the choice of the cut-off radius, it should have a smaller absolute value than literature value. This is not observed in our simulations.

For smaller nanochannels, boundary effect cannot be neglected. For our simulation, a vacuum region is modelled next to the nanochannel. This vacuum region near the channel boundaries is the one of the main cause for a smaller absolute virial component value. According to Barisik's results [4], these boundary effects last up to 0.5 nm. For 10 nm slit channel the effect will be 10% of whole channel. Table 3 indicated the importance of this boundary effect. This table shows a change in virial when the height of the channel changes from $60\sigma$ to $9\sigma$. It shows the decrease in absolute virial component value with the decrease in channel height. But this result does not also give an explanation of larger absolute virial component value compared to static situation.

### Table 3. Virial component of a static fluid inside the slit of different heights.

| Density  | $= 0.3896 \text{ nm}^{-3}$ |
|----------|---------------------------|
| $H = 60\sigma$ | -0.4040 [bar] |
| $H = 30\sigma$ | -0.3964 [bar] |
| $H = 15\sigma$ | -0.3826 [bar] |
| $H = 9\sigma$  | -0.3634 [bar] |

The velocity might also be the cause of the difference. However, the simulation has a near zero velocity near the inlet (number density $= 1.8 \text{ nm}^{-3}$). Therefore, we suspect that the density gradient plays a major role on the virial component.

### 3.4 Virial component vs. density & temperature gradient

To study this nature of the virial component and density gradient in more detail, simulations were performed for different temperature gradients as mentioned in section 2.2. Figure 9 shows the density gradient produced by this method, and figure 10 shows the temperature gradient.

We have chosen a position $X = -5\sigma$ (red transparent bar in figures 9 and 10) for a comparison. This position was chosen to ensure that the temperature effect can be neglected since it is approximately 240 K for all cases. However we can see that the number density for combination $T_{\text{cold}} = 60.5 \text{ K}$, $T_{\text{hot}} = 423.5 \text{ K}$ (indicated by the green symbols in figure 9 and 10), has a slightly lower density compared to other 3 combinations. According to the equation of state, combination $T_{\text{cold}} = 60.5 \text{ K}$, $T_{\text{hot}} = 423.5 \text{ K}$ should have approximately 0.1 bar difference with the given density difference with the other combinations. However at this position, it all had a virial near -0.3 bar.

This results indicates that steeper density gradient gives a larger absolute virial component. This founding agrees well with the definition of virial component proposed by Zhou [13]: he proposed that ‘the virial component is a stress-like measure for momentum change in space’. Density gradient in our simulation can be simply converted into the form of momentum gradient in space.
This finding can also be an opening step for the study why virial component increases with a decrease in temperature. The Irving-Kirkwood equation shows that the virial component is independent on the velocities of particles but only dependent on the positions of the particles. One of the hypothetical explanations to this contradiction is that density distribution of a given system becomes more non-uniform with lower temperature. If this hypothesis is true, density gradient of a given system will also work in the same manner as a temperature change in the system.

4. Conclusion
In this article the pressure in a nanaochannel gas flow has been studied by using MD simulation and Irving-Kirkwood method. The numerical data mainly covers the transition regime where the boundary between DSMC method and Navier Stokes Equation calculation lies. An analysis of the numerical data shows (i) the importance of virial component in the pressure calculation of a nanochannel gas flow and (ii) a relationship between the virial component and density gradient. The study suggests that steeper density gradient gives a larger absolute virial component.

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