Molecular Dynamics Simulations of Flow over a Nano-cylinder in a Rectangular Nano-channel

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ABSTRACT

This paper reports novel molecular dynamics simulation results obtained for flow in a rectangular nano-channel of liquid alkanes around a nano-cylinder (See Figure 1). The results reported here are obtained by using a comprehensive molecular dynamics simulation package which was developed over many years of research. One of the unique features of this computer program is to calculate the local properties of flow in nano-dimensions for a variety of systems. Spatial-temporal calculations analysis which was developed based on continuum modelling led to development of finite-element and finite volume methods which are now widely used for simulation of macroscopic phenomenon in fluid and solid mechanics problems. Such approaches when the characteristic dimensions are comparable to the size of individual atoms or molecules break down as the fundamental continuum equations, based on which these methods are founded, lose their validity.

This paper reports simulation results based on methods, which are applicable to any flow including to those encountered in the nano-fluidics and micro-fluidics application. Large scale parallel calculations are used to obtain spatial-temporal local properties of flow. The channel and cylinder have an explicit atomic structure and the liquid alkane (paraffin) is modeled by united atoms (UA) which are connected via bonded potentials to form a chain. The effects of channel and cylinder interaction energy, the size of the mesh, location of the nanocylinder on the flow are investigated.

Keywords: molecular dynamics simulations, flow in nano-channels, local properties, nano-fluidics

1 INTRODUCTION

The emergence of nanotechnology and miniaturization in the form of nano/micro electromechanical (NEMS/MEMS) devices requires a deeper understanding of flow in such small scales a necessity. The classical continuum approach such as Navier-Stokes equation has proved to be inadequate in many circumstances when length scales become comparable with the size of individual molecules, due to anisotropy and loss of continuum. In many applications such as those for heat transfer or in biological devices (e.g. lab-on-a-chip type devices) we may encounter flow situations where the size of the flow channel is only a few nanometers wide. In such channels for example, to enhance the flow circulations or to agitate the flow for more efficient heat transfer flow is passed over cylinders or spheres with sizes comparable to the width of the channel. So there are practical interests in these types of flow.

2 SIMULATION METHODS

None-equilibrium molecular dynamics simulation methods are used in this work to simulate the flow of alkanes (C_nH_{2n+2}) in a nano-channel over a nano-cylinder. In this method, simulations are usually accomplished in three stages by developing a molecular model, calculating the molecular positions, velocities and trajectories, and finally collecting the desired properties from the molecular trajectories. In molecular dynamics (MD) the molecular positions are deterministically generated from the Newtonian equations of motion and statistical mechanics are used to calculate the macroscopic properties of interest.

2.1 Modelling the fluid

The molecular model for the fluid, made of alkane molecules includes bonded valence interactions (including stretching, angle and torsion, which are given by equations (1), (2) and (3) respectively, and nonbonded van der Waals interactions , 6-12 Lennard-Jones potential which is given by equation (4). The potential model used for alkane systems here is due to Siepmann and co workers [1] and has shown to work well in predicting transport properties of these fluids.

$$\phi(r) = \frac{1}{2}k(r - r_0)^2 \tag{1}$$

$$\phi(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \tag{2}$$

$$\phi(\varphi) = \sum_i^5 C_i(\cos\varphi)^i \tag{3}$$

$$\phi_{LJ}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] - \phi_{shift}, \tag{4}$$

$$\phi_{shift} = 4\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^{6}\right]$$

The potential parameters are given elsewhere [2], [3].

2.2 Modelling the rectangular channel boundary and nano-cylinder

The channel is modelled by using an explicit atomic structure of gold.

Crystal planes of gold surfaces made from four layers of fcc (face centred cubic) lattice structure are used. Gold has a density of 19.32 g/cm^3 and an atomic weight of 196.97 amu. The interaction of the gold atoms and alkane united atoms is also governed by a 6-12 Lennard Jones potential. The interaction parameters of Au are chosen by fitting the calculated and experimental desorption data of alkanes from metal surfaces [4]. These values are (ε_w/k_B= 939 K) and σ_w=0.2655 nm, which yield energy and length parameters for the interaction of CH_2 and Au of about four times that of the fluid-fluid (CH_2-CH_2) LJ interactions. So that ε_{wf} = 1.795 kJ/mol=4.59ε_{CH2}.and σ_{wf} =0.328 nm.

Each atom on the wall is attached by a spring to its lattice position. The wall springs have a potential of the form

$$\phi_s = \frac{1}{2} k_w R^2 \qquad (5)$$

where k_w is the spring stiffness and R is the distance of the wall atom from its lattice site. Here a soft spring is used to facilitate the heat transfer between the fluid and the boundaries.

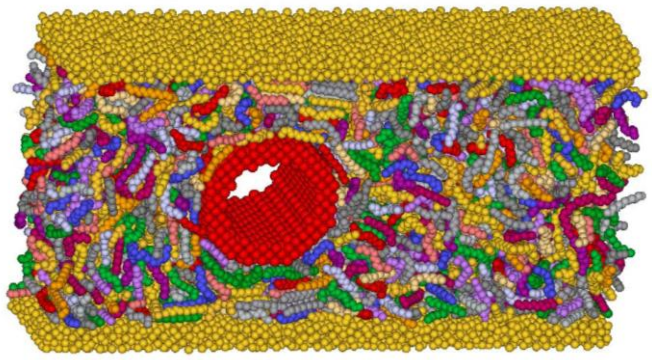

Figure 1 A snapshot taken from liquid dodecane as it flows over a nano-cylinder with a radius of 3 nm in a rectangular nano-channel 12 nm wide. The length of the simulation box, in the x direction, is 26.8 nm. Individual molecules are shown by different colours to aid visualization and the nano-cylinder and nanochannel are given red and gold colours respectively. The periodic boundary conditions are applied in the flow and lateral directions. The fluid is dodecane being simulated at 300 K and a density of 750 kg/m^3. There are 40480 atoms in the simulation box.

2.3 Creating the flow

Poiseuille flow is generated by applying a body force, similar to the gravitational force, on individual fluid united atoms. Periodic boundary conditions are applied in *x* and *y* directions only. The boundary conditions are not set as a priori and are allowed to develop as the simulation goes on. The analytical works have shown changing the boundary conditions from stick to slip have significant effects on the flow results [5].

The nano-cylinder is also modelled by fcc structure of gold. Here the fcc structure is intersected by a circular plane of a given radius and only atoms on the plane or its boundaries are retained. So the circumference is not a perfect circle. This realistically represents a crystalline material cut to the nearest circular shape, creating step defects on the surface. Only three layers of the gold atoms are retained at the surface of the nano-cylinder. This is shown in Figure 1.

2.4 Calculating the local properties

A unique binning technique is used to calculate the velocity, stresses, pressure, density and temperature contours for many different cases. In this method the average velocity is calculated from the momentum flux in each bin. The simulation box in the direction normal to the wall is sliced into a number of rectangular bins (parallel to walls). For each bin the local streaming velocity was calculated by using equation (6) where m_i and v_i are the mass and velocity of atom *i* inside the bin and N_b is the number of atoms inside the bin. So the streaming velocity in *x* direction in each bin is:

$$U_{x,b} = \frac{\sum_{i=1}^{N_b} m_i v_{i,x}}{\sum_{i=1}^{N_b} m_i} \qquad (6)$$

Other components of the streaming velocity were also calculated using analogous equations.

The same binning technique is used to calculate the local stresses. Stress tensor components were found for a microscopic system of particles by the Irving-Kirkwood [6] method. According to this method the contribution of each particle to the stress tensor is in two parts, a configuration part and a kinetic part. This can be written as

$$\sigma_{\alpha\beta} = -\frac{1}{V}\left\langle \sum_i^N \mathrm{m}_i u_{i\alpha} u_{i\beta} + \sum_i^N \sum_{j>i}^N \mathbf{r}_{ij\alpha} \mathbf{F}_{ij\beta} \right\rangle. \qquad (7)$$

The first sum in the right hand side of equation (7) denotes the kinetic contribution where m_i is the atomic mass and α and β are coordination system axes which for a Cartesian system can be simply substituted by *X*, *Y* or *Z*, and $u_{i\alpha}$ and $u_{i\beta}$ are the peculiar velocity components of particle *i* in the α and β directions. The second sum represents the configuration or potential contribution where $\mathbf{r}_{ij\alpha}$ is the α

component of the distance vector between particles *i* and *j* and $\mathbf{F}_{ij\beta}$ is the β component of the force exerted on particle *i* by particle *j*. We have to exclude the mean flow velocity ,$U_{x,i}$ is the average flow velocity at the position of particle *i*, when we consider the laboratory velocity component of a particle in the flow direction.. The angle brackets denote the time average.

2.5 The binning mesh

The simulation box domain in the XZ plane is divided by a 100×150 mesh, that is a total of 15000 bins which are extended across the Y direction. The local properties including the velocity, stresses, temperature and density are calculated in each bin. A picture of the binning mesh is shown in Figure 2.

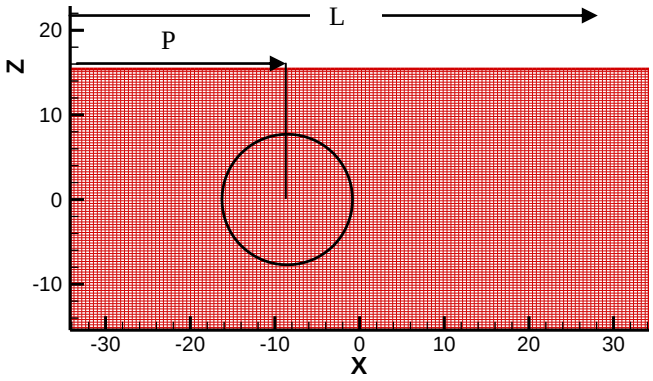

Figure 2 A 100×150 mesh for a channel of dimensions 12 nm wide. The radius of nanocylinder is 3 nm. The units on the axes are given in molecular diameter. The position of the nanocylinder is chosen so that P/L=1/3. The dimensions shown in molecular diameter of a methyl unit (σ=0.393 nm)

3 RESULTS

3.1 Streamlines

Using the X and Z components of the local velocities the streamlines were plotted which are presented in figure 3, for flow of hexadecane. The results show two distinct vortices generated as the flow is past over the cylinder. The magnitude of the vortices and their location changes by changing the size of the molecules and interaction between fluid-solid atoms. The results show increasing the wall-fluid interaction energy or using a flexible wall reduces the interfacial slip boundary and in turn affects the flow conditions. Significant layering of the molecules near the surfaces with high interaction potential can be observed. A flexible wall provides a rougher surface that results in reduction of the slip between the fluid and solid surfaces. The binning technique used to produce the local properties is analogues to meshing in discretizing schemes of continuum models. This method provides a powerful tool for studying local phenomenon in the nano-scale. Figure 3 shows the streamlines of the flow passed over a nanocylinder of 3nm radius. The two distinct vortices developed on the back of the nanocylinder, vanish and give way to a smooth laminar flow at a distance comparable to the diameter of the nanocylinder.

Figure 4 shows the streamlines when the position of the cylinder is moved to the box centre so that the P/L ratio is ½. We can see, two symmetrical vortices form in this case as well and, the vortices vanish at about the same distance from the nanocylinder. In this case the size of the mesh is 40×100 and the size of the simulation box is slightly smaller. This means the size of each bin is larger than before and the number of atoms that happen to be in the bin during sampling is larger. The larger mesh size although reduces the refinement, gives a better statistics of the results. This is reflected in the smoother streamlines that can be seen in Figure 4, as a result of having a lower statistical noise level in this case. A through study on the effect of the mesh size is not done here however these preliminary results show the importance that this might have on the results. A future study is planned to address this important factor in the results.

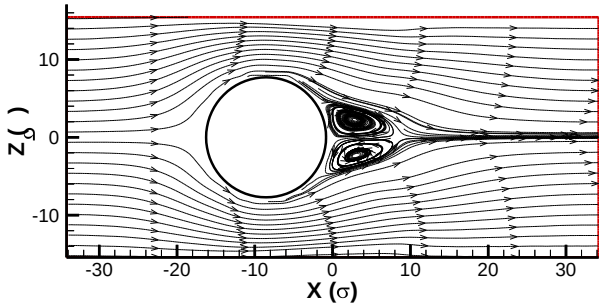

Figure 3 streamlines for flow configuration shown in Figure 2 for hexadecane, in a channel 12 nm wide over a nanocylinder of radius 3 nm. The dimensions shown in molecular diameter of a methyl unit (σ=0.393 nm)

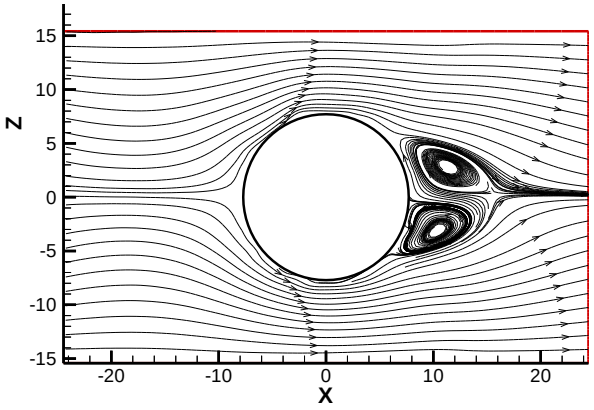

Figure 4 streamlines for flow configuration shown in Figure 2 for flow of hexadecane, in a channel 12 nm wide over a nanocylinder of radius 3 nm, where P/L=1/2. The mesh is 40×100 in this case and the box dimension in the x direction is slightly smaller. The dimensions shown in molecular diameter of a methyl unit (σ=0.393 nm)

3.2 The velocity contours

The velocity contours for the flow can also be determined using the method described in section 2.4. The contours of the X component of the velocity for the flow are shown in figure 5. We can see the maximum flow rate is achieved in the contraction between the cylinder and the boundary of the channel that is fully expected. We can detect the stagnation in front and back of the nanocylinder at the middle of the channel.

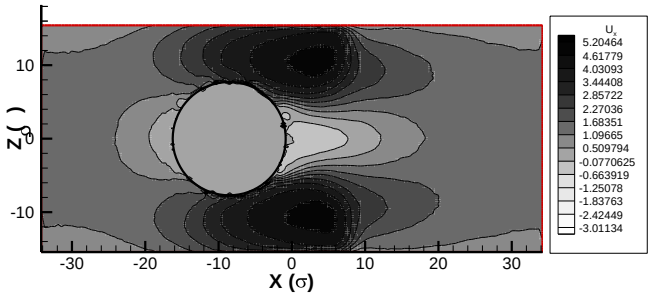

Figure 5 contours of the velocity component U_x (in the flow direction) for hexadecane flow configuration shown in Figure 2. The dimensions shown in molecular diameter of methyl unit (σ=0.393 nm). The velocities are given in reduced unites.

3.3 Pressure Contours

The local pressure values during the flow are calculated using equation (7) given in section 2.4, (note, P=-σ) and calculating the trace of the tensor, *P*=1/3 trace(P). The pressure contours are calculated and shown in Figure 6. We can see a clear pressure front developed at the inlet with a maximum pressure at the stagnation point of the nanocylinder at the inlet side of the channel. The pressure drops in the back side of the nanocylinder and at the contraction areas are evident. Away from the nanocylinder and at about the same position where the vortices disappear, the pressure front returns to constant values across the channel. The pressure contours values shown in Figure 6 are given in reduced unit. Each pressure reduced unit is approximately equals ~10.7 MPa.

CONCLUSIONS

In this paper the results of large scale molecular dynamics simulations are reported for flow in a nano-channel over a nanocylinder. A novel method is employed to calculate local properties of interest for the flow, similar to those that one might calculate for macroscopic scale flows. It is demonstrated that satisfactory results with unprecedented refinement in the nano scale may be obtained. The results obtained here are examples of the problems that can be tackled, related to nano-fluidics applications, by using novel molecular dynamics simulation methods and employing a state-of-the-art computer package developed.

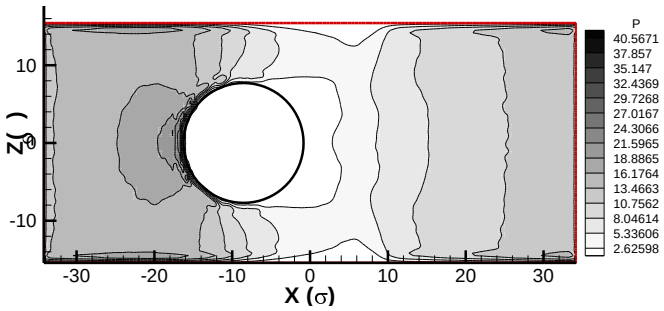

Figure 6 Pressure contours for hexadecane flow configuration shown in Figure 2. The dimensions shown in molecular diameter of a methyl unit (σ=0.393 nm)

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