

A continuum approach applied to a strongly confined Lennard-Jones fluid.

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ABSTRACT

Results from molecular dynamics simulations are analyzed with a continuum approach. It is shown that for strongly confined fluids the Navier-Stokes equations for incompressible, Newtonian fluids are not applicable over the whole channel. Near the walls, a Knudsen layer is formed and interesting oscillatory structures are seen, the fluid behaves non-Newtonian in these regions.

1. Introduction

Molecular dynamics simulations have become an important tool for the study of microscopic fluid properties. A channel geometry is often used to study the inhomogeneous behavior of strongly confined fluids (Koplik & Banavar⁶, Bitsanis *et al.*¹, Travis & Gubbins⁷) which behave different from Newtonian fluids. Our understanding of these non-Newtonian fluids is still very limited, while gaining a deeper insight is becoming increasingly important with the rise of microfluidic and nanofluidic applications, such as lab-on-a-chip devices. Similar phenomenology (i.e. layering, anisotropy) is observed in many particle systems (van Gunsteren *et al.*³, Ghosh *et al.*²). In this study, liquid argon is confined between two walls with normal in the x -direction (Fig. 1). When an atom leaves the system in y - or z -direction, it re-enters at the opposite side due to periodic boundary conditions. Both walls consist of two layers of argon atoms (each layer containing 128 atoms) fixed in a 001-face centered cubic (fcc) lattice. The fluid-wall interaction is equal to the fluid-fluid interaction and the number density of the system is $\rho^* = 0.8$ (corresponding to a volume fraction of $\nu = 0.415$ based on atom diameter σ). Physical quantities are nondimensionalized by using the length, energy and mass scales of liquid argon, which are $\sigma = 3.405 \times 10^{-10}$ m, $\epsilon = 1.67 \times 10^{-21}$ J and $m = 6.626 \times 10^{-26}$ kg respectively. A constant body force f^* acts on the fluid in negative z -direction, causing it to flow. The mutual interaction of the neutral spherically symmetric argon atoms is modeled via a two-body Lennard-Jones (LJ) potential. From the interaction potential, the force between two atoms can be calculated:

$$F_{LJ}(r) = -\frac{\partial U}{\partial r} = 24\frac{\epsilon}{\sigma} \left(2 \left(\frac{\sigma}{r} \right)^{13} - \left(\frac{\sigma}{r} \right)^7 \right), \quad (1)$$

with r the distance between two atom centers. The force is truncated at $r_c = 2.5\sigma$ in order to reduce calculation time for pair interactions. Furthermore, the force is shifted with $F_{LJ}(r_c)$ in order to maintain a continuous force at the location of truncation $F(r) = F_{LJ}(r) - F_{LJ}(r_c)$ and $F_{LJ}(r \geq r_c) = 0$.

From the positions, velocities and interatomic forces, other physical scalar or tensorial quantities can be calculated (e.g. shear rate, stress and viscosity) (Hartkamp *et al.*⁴). The position and momentum of each atom are used to calculate the forces acting on them and then their position and velocity after an increment (Δt) in time via the Velocity Verlet algorithm. The body force

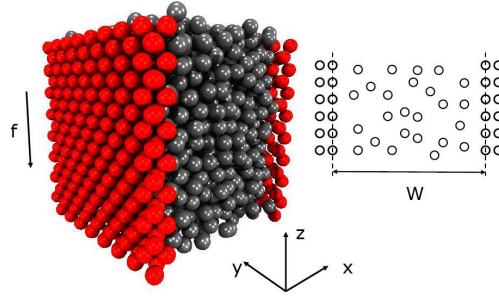


Figure 1: Liquid argon (grey, 2304 atoms) confined between solid argon walls (red, 512 atoms). The width of the channel is defined as shown on the right.

leads to an acceleration of the fluid, while viscous effects retard the flow until a steady state is reached. Local thermostats near the walls keep the energy (and thus the temperature) constant in time ($T^* = 1.0$ for the simulations presented here, which is equal to a temperature of $T = 121$ K for argon) (Ghosh *et al.*²). Atoms are initially positioned on a 001-fcc lattice. The lattice melts during the equilibration, followed by a steady state flow. The steady-state simulation results are averaged by means of 4000 snapshots over a period of time of 4000τ . Furthermore, spatial averaging is employed over the directions parallel to the solid walls, whereas, the x -direction (perpendicular to the solid walls) is divided into equally spaced bins of width $b = 0.083$. The channel is $W = 16.245\sigma$ in width and $H = 13.68\sigma$ in length and height. The fluid in the channel consists of $N = 2304$ argon atoms.

The Knudsen number of the flow, which is the ratio between the mean free path λ and the characteristic length scale $L_W = W/3$, is $\text{Kn} = (\sqrt{2}\pi\sigma^2\rho^*L_W)^{-1} = 0.052$. Typically, flows with a Knudsen number in the regime $0.001 \leq \text{Kn} \leq 0.1$ can be analyzed with conventional fluid dynamics equations such as the Navier-Stokes equations. However, the no-slip boundary condition does not hold if $\text{Kn} \geq 0.01$. A region forms near the wall, called the Knudsen layer, where the flow can not be analyzed by the conventional approach, an additional slip boundary condition is needed. The thickness of this layer depends on the Knudsen number, but is typically of the same order of magnitude as the mean free path.

Section 2 treats the conservation of momentum, applied to the system which is considered here. In section 3, the computational results are compared to the Newtonian theory and the results are briefly discussed.

2. Equations of fluid motion

The equations of fluid motion for an incompressible and Newtonian fluid are given by:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} + \mathbf{f}, \quad (2)$$

with ρ being the density, \mathbf{v} the velocity vector, p the pressure, μ the shear viscosity and \mathbf{f} the external force on the fluid per unit volume.

For the system discussed here, the equations of motion can be simplified considerably. The system properties are (kept) constant in the y - and z -direction and the fluid is confined in x -direction. The force vector is: $\mathbf{f} = \{0, 0, -f\}$, with $f = \rho^* f^*$, where ρ^* is the number density and f^* is the body force on each particle. The body force on the fluid causes a streaming velocity profile in the negative z -direction.

After substituting the force vector and the velocity field, all the terms in the conservation of

x - and y -momentum drop out¹, leaving only the z -component of the momentum conservation Eqn. (2), which reduces to a Poisson equation:

$$\frac{\partial^2 v_z}{\partial x^2} = \frac{f}{\mu}. \quad (3)$$

The macroscopic fields are obtained from molecular dynamics simulations in the canonical ensemble (NVT). The averaged results satisfy Eqn. (3) if the fluid in the nanochannel behaves indeed incompressible and Newtonian. Velocity is an almost parabolic function of the x -location, due to the boundary conditions, besides wall effects.

3. Results and discussion

Fig. 2 shows the streaming velocity in z -direction as function of x and the first and second derivative with respect to the x -direction. The derivatives are obtained from the velocity profile via a central difference scheme. The velocity profile is approximately quadratic in the bulk, corresponding to linear and constant first and second derivatives respectively. However, the fluid deviates from this behavior near the walls of the channel. The predicted Knudsen layer can be identified where the trend in the streaming velocity deviates from a quadratic profile. This region is especially clear from looking at the first and second derivative of the velocity profile. The apparent slip in velocity corresponds to a slow decay to a zero shear rate at the sides of the channel. In addition to the Knudsen layer, oscillatory structures are seen in each of the profiles. The magnitude of these oscillations are maximal near the walls and decay towards the bulk.

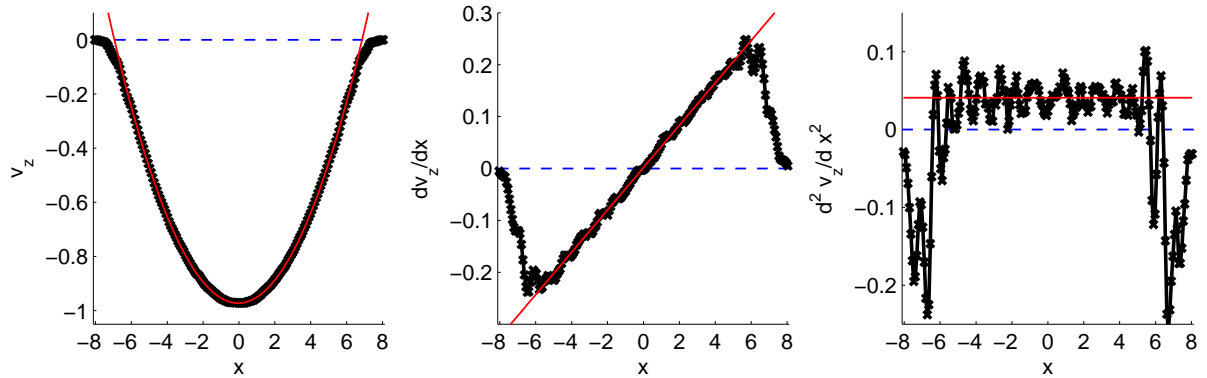


Figure 2: (left) Velocity profile in negative z -direction across the channel and (middle) first and (right) second derivatives with respect to x . The red solid lines represent the parabolic velocity profile with $f/\mu = 0.0408$ [(ms)⁻¹].

Fig. 3 shows the right-hand side of Eqn. (3) (left) and the difference between the right- and left-hand sides (right). The shear viscosity is defined as the ratio between the shear stress and the shear rate. The ratio between the force per volume and the shear viscosity (Fig. 3 (left)) forms a plateau in the bulk of the fluid and clearly deviates from this plateau near the walls of the channel. The strong oscillations in the center of the channel are an artefact due to the calculation of the shear viscosity; the shear rate is approximately zero in the center of the channel, leading to unphysical results for the shear viscosity, which should be ignored.

¹This is true for a homogeneous fluid, which is not necessarily in agreement with the outcome of the molecular dynamics simulations.

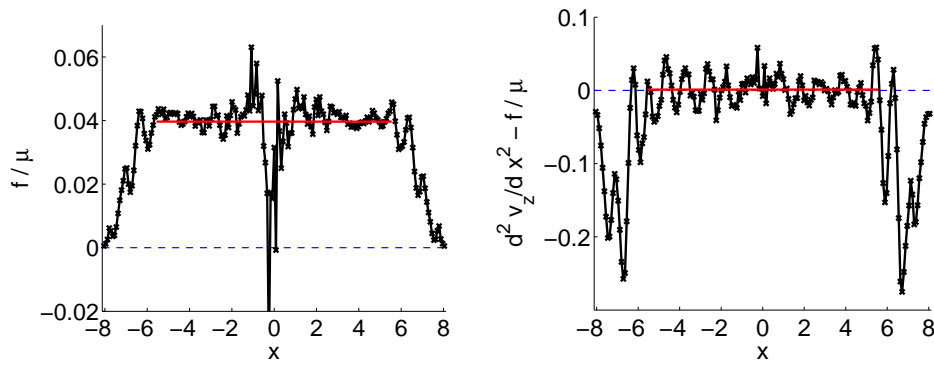


Figure 3: (left) The ratio between force and shear viscosity. (right) The difference between the left- and right-hand side of the conservation of z -momentum.

The difference between both terms in the conservation of momentum (Fig. 3 (right)) is a measure for the error that is made by treating the fluid as Newtonian. In the bulk region, the difference between both terms fluctuates around zero, which indicates that the fluid behavior is Newtonian in the bulk region, apart from statistical noise. The deviation from zero near the walls is larger in magnitude and opposite in sign compared to the average value of both individual terms in the bulk, indicating that the made assumptions do not hold in this region due to the Knudsen layer and the oscillatory structures close to the wall. The behavior of the curvature near the wall can not be compensated by a positive viscosity. This indicates that important contributions to the constitutive relation are missing, as will be studied in future work (Hartkamp *et al.*⁴). The Navier-Stokes equations with a slip boundary condition are also questionable near the walls due to the layering which extends a few σ into the fluid, see Hartkamp & Luding⁵.

Acknowledgements

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