

Modelling of Boundary Layer at Nanoscale

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Abstract: Boundary layer behaviour at nanometre scale is very different than at millimetre scale. It is not possible to perform continuum simulations, as the underlying molecular structure starts to become visible to the simulation, which contradicts the continuum assumption. We therefore investigate the use of molecular simulations as a tool for predicting boundary layers at meso-scales.

1. INTRODUCTION

Computer simulations play a vital role in science and engineering today, by providing a framework on which to investigate theories and solutions in a relatively low risk and low cost environment. However, current trends are leading technology towards engineering on an incredibly small scale. The ability to accurately predict boundary layers is of great importance as they are present in a wide variety of applications, from microfluidic devices to fluid flow through porous media, cooling, and lubrication. For example, the study by Gosh et al[1], who looked at the electrical properties of liquid flowing through bundles of carbon nanotubes. Devices such as these are to be used for many applications, such as to power pacemakers from the flow of blood, or to control the blood flow to a heart-lung machine. These devices are measured in millimetres and inserted into the bulk blood flow. However, the scale of the geometry through which the liquid passes is too small to be considered by continuum mechanics, but the behaviour of the fluid near the solid boundaries plays a substantial role in the operation of the device. The behaviour of a fluid on a millimetre scale is very different to the behaviour of the same fluid viewed on a nanometre scale, and therefore continuum scale physics are not applicable at such small scales.

2. THE LIMITS OF CONTINUUM MECHANICS

Continuum simulations rely on two main approximations about the medium they represent. The first specified that there must be a sufficient number of molecules within any region under consideration for there to be thermal equilibrium. If this condition is satisfied, there are enough inter-molecular interactions/collisions within the time and length scales to smooth out any fluctuations in macroscopic quantities and the system is able to react faster than its surroundings can change. The thermodynamic equilibrium condition holds true, as long as the scale of the flow is much greater than the molecular time and length scale. As the flow scale is reduced towards the molecular scale, this assumption starts to fail. As it breaks down, the flow loses its linear relationship of stress to rate of strain, and heat flux to temperature gradient, indicating the onset of molecular behaviour.

The second approximation is of a similar nature, specifying that there must be sufficient molecules present for the system to be considered as continuous and infinitely divisible. This means that there are no discontinuities in mass, energy, or indeed any property defined throughout the domain and has a finite derivative with respect to space or time.

These conditions describe the theory of the basic limits of the continuum approximation, beyond which the continuum quantities used to define the flow become inaccurate as the molecular scale effects of the fluid start to dominate. Under some conditions that often occur

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in micro devices, the molecular dynamics of the system starts to have an effect before the continuum limit is reached and can be seen as a breakdown of the no-slip velocity and no-temperature jump conditions at solid boundaries.

2.1. Boundary Flows at small scale. Fluids flowing over solid boundaries at a molecular length scale (nanometre-angstrom) do not exhibit the same no-slip condition that is often assumed in continuum mechanics. Although the fluid particles collide with the boundary and experience a friction-like effect, due to the long-range interactions from the solid particles, the molecules are free to slide over the surface[2]. Similarly, the temperature gradient between the fluid and the solid may be discontinuous at the boundary, with a sudden jump in temperature. These effects, although caused by molecular scale interactions, can be present in systems that would otherwise still be within the continuum and thermodynamic limits[3]. Although the breakdown of the no-slip/jump conditions is an indication of the start of the degradation of thermodynamic equilibrium, it is possible to continue using continuum approximations with some modifications[3]. However, the continuum/thermodynamic limit and the point at which the boundary modifications are applied, is well documented for gas, but not for liquid flows. When considering gas flows, it is convenient to work in terms of the Knudsen number (Kn) of the gas, $Kn = \frac{\ell}{L}$. Where ℓ is the mean free path of the gas, and L is the characteristic length of the flow. This gives a measure of the rarefaction of the gas at the scale of the flow being considered, providing a scale on which to determine if the system is in the continuum regime[4]. As the Knudsen number tends to zero, the number of particles within the system are enough for it to reach an equilibrium point, based around the Maxwell form for the current conditions and satisfy the thermal equilibrium and continuum conditions. However if Kn exceeds 10, the system is fully within the molecular regime and the thermal equilibrium and continuum assumptions are not satisfied. Navier-Stokes simulations can be used up to a Kn of around 1 with modified slip/jump boundary conditions but between Kn of 1 and 10, higher order methods such as Burnett or particle methods must be used to cover the transition[5]. However, when considering liquid flows, there is no such useful measure, as the concept of mean free path cannot be defined when the particles are closely packed, and in a constant state of collision. The molecular theory for liquids is not as well advanced as for dilute gases, but Loose and Hess[6, 3] showed that thermal equilibrium, and therefore Newtonian behaviour, stops as the strain rate $\dot{\gamma}$ exceeds twice the molecular frequency scale, τ .

$$\dot{\gamma} = \frac{\partial u}{\partial y} \geq 2\tau^{-1}, \quad \tau = \sqrt{m\sigma^2/\epsilon} \quad (1)$$

Where u is the longitudinal velocity normal to y , σ and ϵ are the characteristic length and energy scales for molecules of mass, m . However, under standard conditions the extremely small molecular time scale for liquids such as water, puts the continuum/Newtonian limit extremely high. Therefore, to look at nanoscale boundary layers using continuum mechanics would not be possible, even with modified boundary conditions, as the continuum approximations do not hold. It is therefore necessary to turn to a method that is based on the physics on a molecular scale.

3. MOLECULAR BOUNDARY LAYERS

If a continuum simulation is performed at, or beyond the thermodynamic or continuum limits, the physics of a continuum system are not able accurately describe the properties and boundary layer behaviour at that scale. Therefore, computing the properties of a liquid in this region becomes very difficult as the details of the boundary layer must be calculated from molecular scale information. Macroscopic Flow properties such as velocity, pressure, temperature, etc, are not simply defined, but are collected via molecular simulations by considering the motion of a number of molecules, rather than just individuals. Therefore, it is possible to determine the behaviour of a boundary layer using a molecular simulation, and averaging the behaviour of regions of molecules.

Molecular simulations use a system of particles which represent atoms or molecules interacting using the basic Newton's equation [7] $F = ma$. The force on each particle is calculated from a sum of the Lennard-Jones interactions of its neighbours, which is then used to update the acceleration of the particle, which in turn leads to updated velocity and position.

$$F_i = \sum U(x_i - x_j) \quad (2)$$

Where F_i is the force on particle i , $x_i - x_j$ is the separation, r , between the two particles, and $U(x_i - x_j)$ is the Lennard-Jones interaction potential calculated as:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

When modelling fluid-solid interactions, as with boundary layer flows, it is possible to remove the solid particles from the system, and replace them with smooth continuous boundaries and appropriate boundary conditions; allowing for more fluid particles to be simulated. This was shown for nanotubes [9, 10] by Sokhan et al, where they introduced smooth boundaries with a thermalisation coefficient, to apply the effect of corrugation, or molecular roughness, of the wall on the fluid artificially.

In order to investigate the boundary layer, the velocity profile of the fluid perpendicular to the boundary needs to be calculated. In order to consider local bulk velocity, discrete points, or nodes, are placed across the direction of the flow with a moving least squares approximation used to collect a weighted average velocity of nearby molecules at each node. The theory is well established and documented, so we will summarise the theory with the basic equations on which it operates. To approximate a property, it is assumed to take the form of a basis function, P that is either linear, quadratic or possibly cubic (and in this example in one dimension, x). The objective, is then to obtain the coefficients of the basis function that will describe the property at that node. This is done by constructing a function of error between the weighted sum of the property values and the approximated function, and then minimising to find the coefficient vector, a

$$J = \sum_{i=1}^n W(x - x_i) [P^T a - U_i] \quad (4)$$

J is the error to be minimised, $W(x - x_i)$ is the weighting function of each particle and is a function of the distance from the node, P is the basis function with coefficients a , and the property values for each particle are U_i . After minimisation of this error function, we obtain equation 5.

$$Aa = Bu, \quad A = WP^T P, \quad B = WP^T \quad (5)$$

The A matrix is then inverted to obtain the coefficient vector, to complete the approximating function. This method of weighted residual, is very accurate in its own right, but errors arise from the discontinuous nature of the molecular simulations. If there are only a small number of particles included in the approximation at a node, their individual fluctuations caused by their independent velocities will have a greater effect and add to the statistical error. It is therefore preferable to have a large number of molecules within the domain of each node to smooth out the variations caused by individuals, and reveal the overall behaviour of the group. However, if the reach of the node is increased too far, neighbouring nodes will be approximating almost the same molecules giving the same or similar result.

The above methods have been employed to simulate a small scale boundary layer of a fluid passing over a wall in three dimensions. The fluid was given an initial velocity of $4.5 \times 10^{-2} A/ps$ and then left to be slowed down by the collisions between the fluid particles and the wall. The Fluids response to this was monitored using moving least squares approximation at five, one dimensional nodes equally spaced, and perpendicular to the wall at 5 angstrom intervals (Figure 1b). The moving least squares approximation was performed for velocity, and used the position perpendicular to the wall for the weighting function to take advantage of the depth of the simulation cube. The results are shown in figure 1a, the wall boundary is on the

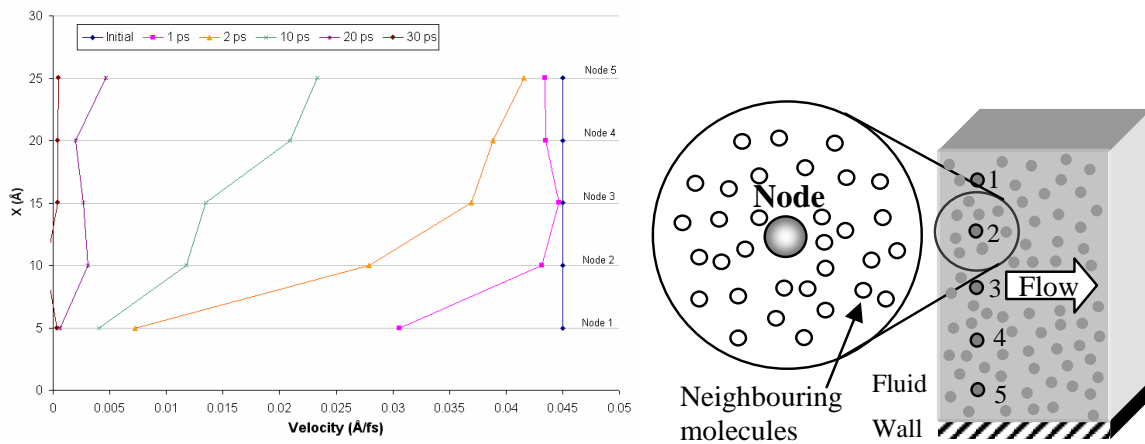


FIGURE 1. **Left: (a)** Velocity profiles at 0-30ps of 5 approximating nodes. **Right: (b)** Schematic of Nodes and boundary conditions

bottom of the graph, and the velocity profile at the five nodes is plotted at five different time steps. Despite some statistical variations, caused by the small system size, a friction like effect is clearly visible as the fluid close to the wall slows down much faster than the main body of the flow. Friction, however, is a macroscopic concept that is not defined at this scale, however fluid is slowed down by the fluid molecules close to the wall colliding with the stationary solid molecules. As the wall is not continuous, the fluid molecules that collide with the wall molecules do not rebound in a predictable way, as discussed by Sokhan[9]. These collisions slow down the fluid molecules close to the wall, which in turn slows down the next layer of molecules, and so on. This results in the fluid displaying a viscous-like effect which dissipates the original kinetic energy, throughout the fluid. This effect is originating purely from the molecular interactions, giving the viscous behaviour displayed in the results.

4. CONCLUSIONS

We have so far seen a definite need to investigate boundary layers at nano scales, as they occur in so many of today's engineering and scientific applications. However, continuum simulations are not able to capture the physics at a molecular scale. Instead, we turn to molecular simulations to predict the fluid properties and boundary layer behaviour at nano scale. The main problem faced with this method is that many macroscopic quantities, such as pressure, viscosity, and flow velocity are not defined directly by individual molecules, but are described by the behaviour of a region, or group of molecules. By averaging the behaviour of molecules using a moving least squares approximation, the macroscopic properties can be identified within a nanoscale systems. This shows, albeit on a small scale, how molecular simulations may be used to determine the properties of mesoscale systems. There are big differences between the behaviour of the boundary layer at nanometre scale and millimetre scale, so the next step is start to close the gap between them to see exactly what and where the changes occur.

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