

Calculation of friction coefficient of a solid–liquid interface via a non-equilibrium molecular dynamics simulation

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Abstract. The problem of characterizing a fluid flow near a solid surface is considered. The interface parameters are the friction coefficient and the hydrodynamic location of the interface. A method to obtain quantitatively these parameters from a non equilibrium molecular dynamics (NEMD) simulation is presented. Results for the flow of a soft sphere fluid confined between two corrugated surfaces are presented.

Keywords. Non equilibrium molecular dynamics; friction coefficient; confined fluids.

1. Introduction

The physical problem we consider is that of obtaining the boundary conditions that characterize the flow of a fluid near a solid surface (Thompson and Robbins 1990; Thompson *et al* 1992; Bocquet and Barrat 1993, 1994; Mundy *et al* 1996). This is illustrated schematically in figure 1. The geometry depicted is called planar Couette flow. The surface that we consider is atomistically corrugated. A velocity field is generated in the fluid by moving the surfaces at a constant speed in opposite directions. This would impart momentum to the fluid, and would set up a velocity gradient in the fluid. The extent of momentum transfer would be related to the interactions between the surface and the particles of the fluid. The instantaneous velocity field can be obtained by solving the Navier–Stokes equation for this geometry. This involves the specification of boundary conditions, i.e. the values of the fluid velocity at the interface has to be assumed. If the surface were ideally flat with no corrugations, the momentum transfer would be zero, and the velocity of the fluid near the interface (in fact everywhere) would be zero. Thus the velocity difference between the surface and the fluid near it would be large. This is called the no stick condition. On the contrary, if the wall–fluid interactions are strong (with respect to fluid–fluid interactions), one could expect a more robust momentum transfer, and the fluid velocity at the interface would be the same as that of the wall. This is called the no slip condition, and has been traditionally employed to obtain the velocity field of fluids in continuum mechanics. It is immediately obvious that these two limits of the condition are idealized, and real world situations would

involve an infinite spectrum of possibilities in between these two limits (Kogan 1959; de Gennes 1979). In this article, we would like to discuss a methodology to characterize the boundary condition at the interface through atomistic interactions and dynamics.

Bocquet and Barrat (Wolynes 1976; Bocquet and Barrat 1993, 1994) proposed the following boundary condition for a solid–fluid interface.

$$\left. \frac{\partial v_x(\mathbf{q}, t)}{\partial y} \right|_{y=y_{\text{wall}}} = \frac{1}{\delta_{\text{wall}}} v_x(\mathbf{q}, t) \Big|_{y=y_{\text{wall}}}, \quad (1)$$

where x is the direction of the fluid flow and y the direction of the velocity gradient. δ_{wall} and y_{wall} are the ‘slipping length’ and the ‘hydrodynamic thickness’, respectively. The former is a measure of the slip, as described above, and y_{wall} is an average position from the boundary at which hydrodynamics breaks down. In this theory, the interface need not have to be at the exact solid–liquid boundary but could be a couple of atomic layers within the fluid. The no slip condition is achieved when δ_{wall} is zero, and the no stick condition is satisfied when it is infinity. The latter is also referred to as the stress free condition, as the product of shear viscosity and the left hand side of (1), dimensionally related to stress is zero. These conditions are illustrated schematically in figure 2.

Several attempts have been made to obtain the boundary parameters via molecular dynamics simulations. A common feature of these is the exact simulation of the experimental condition, i.e. flow is induced in the fluid by moving the solid surfaces. One then obtains a velocity profile in the fluid from which one can obtain a measure of the sticky nature of the interface. An important lacunae

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of such efforts is that boundary driven flows take a long time to stabilize, particularly for interfaces with a large λ_{wall} . In addition, since the velocity profile is not known *a priori*, the simulations cannot be conducted at constant temperature conditions. This is related to the fact that only the random velocity component of the particles is to be thermostated and not the contribution from the moving boundary. In such simulations, it is not possible to distinguish between the two, as the latter is unknown. We propose to perform these simulations in an alternative manner, wherein the surfaces are stationary, but the fluid flow is induced by an external field. This is illustrated in figure 3.

Simulation methodology

The equations of motion that generate and sustain a planar Couette flow in the fluid are called the SLLOD equations. The thermostated equations of motion are

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} + \hat{\mathbf{i}} \gamma (q_{y_i} - q_0), \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \hat{\mathbf{i}} \gamma p_{y_i} - \frac{p_{\eta}}{Q} \mathbf{p}_i, \\ \dot{\eta} &= \frac{p_{\eta}}{Q}, \\ \dot{p}_{\eta} &= \sum_{i=1}^N \frac{p_i^2}{m_i} - N_f k_B T, \\ \dot{I} &= \gamma \sum_{i=1}^N (q_{y_i} - q_0) p_{x_i} \frac{p_{\eta}}{Q}.\end{aligned}\quad (2)$$

q_i and \mathbf{p}_i are the coordinates and momenta of the i th particle in the system, with corresponding mass and force

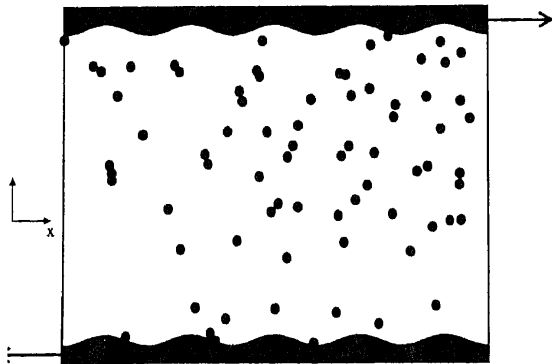


Figure 1. Schematic illustration of the planar Couette flow geometry. Flow in the fluid can be induced by moving the rugated surfaces in opposite directions.

denoted by m_i and \mathbf{F}_i , respectively. The thermostat variables are denoted by η and p_{η} with a corresponding mass parameter, $Q = N_f k_B T \tau^2$. Further details can be found elsewhere (Martyna *et al* 1996; Mundy *et al* 1996).

These equations of motion conserve the following quantity as a function of time (Tuckerman *et al* 1997).

$$H' = \sum_{i=1}^N \frac{(\mathbf{p}_i + \hat{\mathbf{i}} m_i \gamma (q_{y_i} - q_0))^2}{2m_i} + V(\mathbf{q}) + \frac{p_{\eta}^2}{2Q} + N_f k_B T \eta + I. \quad (3)$$

This quantity, H' can be used to obtain the phase space distribution function as well as a check to identify errors

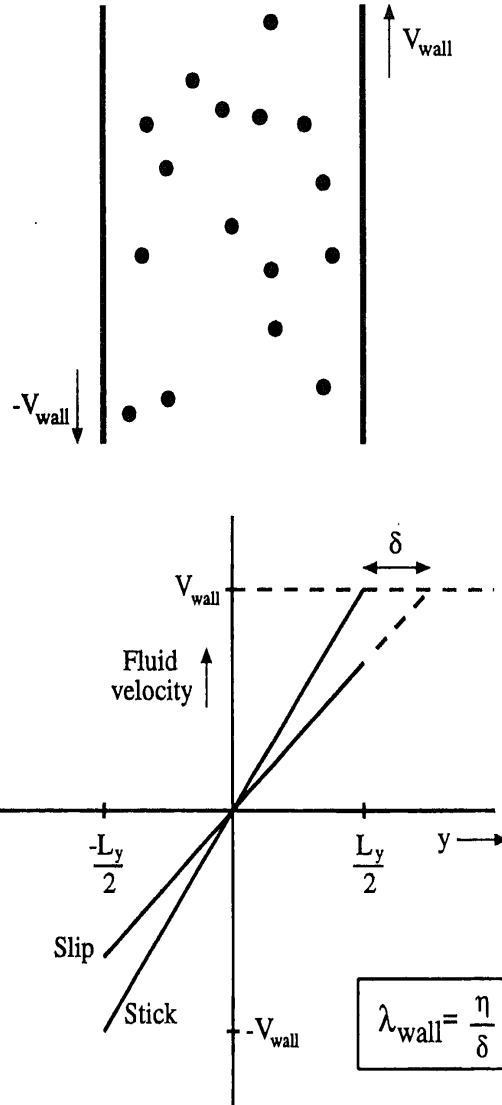


Figure 2. Illustration of the boundary parameter, slipping length, δ . The two surfaces are separated by a distance L_y , and the velocity of the walls are V_{wall} each. λ_{wall} is the friction coefficient of the interface and is dimensionally related to the slipping length through the shear viscosity of the fluid, η .

in coding the equations of motion in a molecular dynamics program.

The friction coefficient and the hydrodynamic thickness can be obtained using linear response theory for the SLLOD equations, (2). This has been developed recently (Bocquet and Barrat 1993, 1994; Mundy *et al* 1996). The result can be stated as,

$$\langle F_x^w \rangle_{\text{NE}}(t) = -S \lambda_{\text{wall}} v_x(y_{\text{wall}}). \quad (4)$$

Here, F_x^w is the sum over all particles of the force acting on the fluid, and $\langle \cdot \cdot \rangle_{\text{NE}}$ denotes an average over the non equilibrium ensemble generated by the SLLOD equations. S is the surface area, and λ_{wall} the frictional force. This is a linear relation between the response and the effect of the field, i.e. the velocity.

3. Results

We numerically integrated (2) for 300 particles interacting via a soft sphere potential model for over 100 ps. The fluid–fluid potential is described as,

$$U(r_{ij}) = \varepsilon \left(\frac{\sigma}{q_{ij}} \right)^{12}, \quad (5)$$

where ε and σ are energy and length parameters, respectively. q_{ij} denotes the distance between two particles, i and j . The fluid is confined between two walls and the wall–fluid interaction is represented as

$$U_{\text{wf}} = \varepsilon \{ [(\sigma/q_y - q_y^l(x))^{12} + (\sigma/(L_y - q_y - q_y^u(x)))^{12}] \} \quad (6)$$

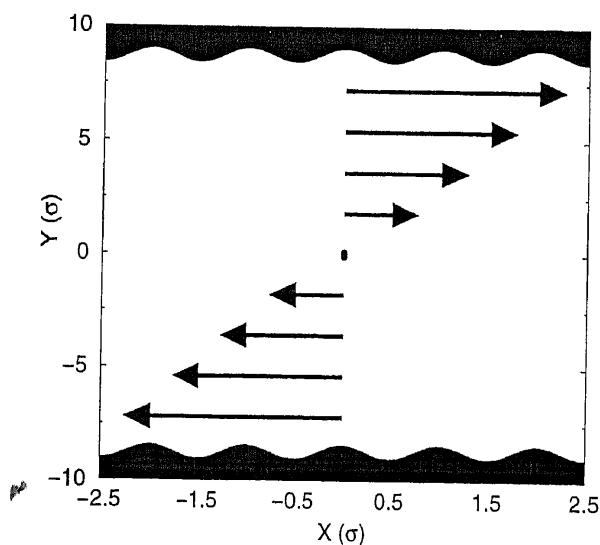


Figure 3. Illustration of the simulation methodology. The fluid flow is generated not by moving boundaries but by the application of an external field. The field sets up a velocity profile of the form shown in the fluid.

L_y is the box length in the y direction. The corrugation in U_{wf} is in the x direction and is given by $q_y^u(x) = q_y^l(x) = a \cos(kx)$, where the superscripts u and l denote the upper and lower walls, respectively, a is the corrugation amplitude, and the corrugation period is given by $2\pi/k$.

NEMD simulations were started from well equilibrated, independent, equilibrium configurations. The potential parameters ε and σ were chosen to be 480 K and 3.405 Å, respectively. The simulations were performed at a reduced temperature of $k_B T/\varepsilon = 1$ and at a density of $\rho\sigma^3 = 0.64$. The equations of motion, (2), were integrated with the additional variable I with a time step of 0.5 fs to ensure an ‘energy’ conservation (see (3)) of 1 part in 10^5 . The massive thermostating scheme, where a separate thermostat is attached to each degree of freedom was employed for temperature control and for sustaining the fluid flow.

The essence of the approach to obtain the boundary parameters is as follows: One chooses a shear rate γ and a zero shear position $q_{y_0}^l$. This sets the velocity profile $v_x^l(q_y)$. Let us assume that we would like to characterize the boundary parameters for the lower wall. After reaching steady state (which is monitored by the generation of the linear velocity profile), the total force on all the particles from the lower wall, $F_x^{l,1}$ is calculated and averaged over a hundred picosec. Since we have only one equation, (Equation (4)) from linear response theory, with two unknown parameters, two simulations with differing $v_x(y_{\text{wall}})$ have to be performed. One can change $v_x(y_{\text{wall}})$ by changing $q_{y_0}^l$. Thus, we perform another simulation with the same shear rate, γ , but with a different zero shear position, $q_{y_0}^2$. This will lead to a new average force $F_x^{l,2}$. The ratio of the forces $F_x^{l,1}$ and $F_x^{l,2}$ gives the ratio of the velocities at y_{wall} , which determines y_{wall} . The calculation of λ_{wall} is straightforward. It is to be borne in mind that not all choices of $q_{y_0}^l$ yield sensible values of the boundary parameters. Only those that obey the linearity in (4) can give values that can be compared to those obtained at equilibrium. So, it is crucial that $\langle F_x^w \rangle_{\text{NE}}$ is plotted against $v_x(y_{\text{wall}})$ to find out the values of $\{\gamma, q_{y_0}^l\}$ that fall in the linear region. y_{wall} typically is a couple of atomic layers away from the physical location of the wall. Hence, it is a good practice to choose the two values of $q_{y_0}^l$ just below and above the ‘nominal’ y_{wall} . This would lead to a sign reversal in the response, $\langle F_x^w \rangle_{\text{NE}}$ which can be used to bracket the exact value of y_{wall} .

The variation of $\langle F_x^w \rangle$ with $v_x(y_{\text{wall}})$ is shown in figure 4 for two values of the corrugation amplitude. For small values of the flow velocity, we observe a linear evolution of the frictional force, in accordance with (4). The slope of the line gives the friction coefficient in accordance with linear response. For larger values of the field, it is clear from figure 4 that linear response theory is violated. Thus, nothing can be concluded from this outlying data.

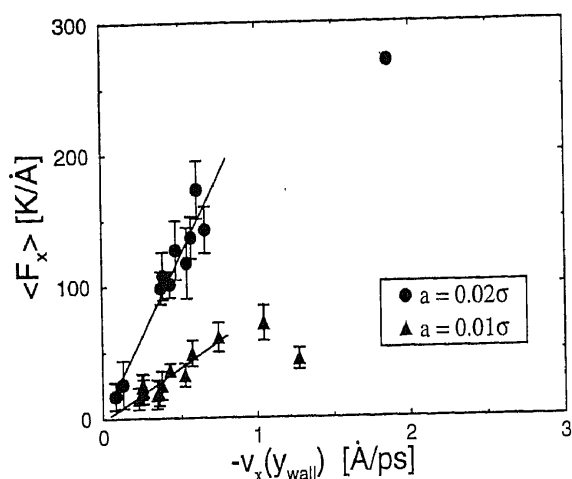


Figure 4. The non equilibrium average of the frictional force plotted against the velocity of the fluid at y_{wall} for two values of corrugation amplitude a . The slope of the lines drawn are related to the friction coefficients.

4. Conclusions

We have presented a method to determine the interface parameters for a fluid flowing near a solid surface. The method employs techniques developed to study fluid flows in bulk. The friction coefficient of the interface can be obtained by a non equilibrium molecular dynamics simulation. The friction coefficient, thus obtained is related to the atomistic corrugation of the surface. No attempts have been made to study the friction arising out

of microscopic steps, defects etc, although the formalism is general. Another caveat in the use of this method is that for fluid–solid systems that interact strongly, the velocity profile is found to be not quite linear near the interface. This would in a sense, imply that the shear rate varies within the fluid. An understanding of its origin and the consequent changes in the methodology are problems for future study.

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References

- Bocquet L and Barrat J -L 1993 *Phys. Rev. Lett.* **70** 2726
- Bocquet L and Barrat J -L 1994 *Phys. Rev.* **E49** 3079
- de Gennes P G 1979 *C. R. Acad. Sci. Paris* **B288** 219
- Kogan M K 1959 *Rarefied gas dynamics* (New York: Plenum)
- Martyna G J, Tuckerman M E, Tobias D J and Klein M L 1996 *Mol. Phys.* **87** 1117
- Mundy C J, Balasubramanian S and Klein M L 1996 *J. Chem. Phys.* **105** 3211
- Thompson P A and Robbins M O 1990 *Phys. Rev.* **A41** 6830
- Thompson P A, Grest G S and Robbins M O 1992 *Phys. Rev. Lett.* **68** 3448
- Tuckerman M E, Mundy C J, Balasubramanian S and Klein M L 1997 *J. Chem. Phys.* **106** 5615
- Wolynes P G 1976 *Phys. Rev.* **A13** 1235