A multiscale approach to interpret and predict the apparent slip velocity at liquid-liquid interfaces

P Poesio\textsuperscript{1}, A Damone\textsuperscript{1} and O K Matar\textsuperscript{2}

\textsuperscript{1} Università degli Studi di Brescia, Department of Mechanical and Industrial Engineering, Via Branze 38, 25123 Brescia, IT
\textsuperscript{2} Imperial College London, Department of Chemical Engineering, South Kensington Campus, London SW7 2AZ, UK
E-mail: pietro.poesio@unibs.it

Abstract. The classical boundary conditions at flat liquid-liquid interfaces are continuity of the velocity and of the tangential component of stress; for curved interfaces, one also demands that the jump in the normal stress at the interface is balanced by the product of the interfacial tension and curvature. While these conditions are widely accepted, and are often used at the macro scale, the recent interest in micro and nano-fluidics challenges their validity. At molten polymer-polymer interfaces, for instance, it has been consistently shown by direct and indirect measurements that, apparent, velocity jumps exist and can be modelled effectively via a Navier slip condition (NSC). Here, we discuss that if a viscosity, which accounts for the density and mole fraction distributions, is included in the Navier-Stokes equations, we can describe, naturally, and without recourse to \textit{ad-hoc} models such as the NSC, the velocity profile in the interfacial region separating two fluids. This approach is supported by the observation that there is a relation between apparent slip and density distribution across the interface.

1. Introduction

Liquid-Liquid Interfaces (LLI) characterise and influence the behaviours of several macro- and micro-systems. For instance, in biology, interfaces between two immiscible liquid electrolyte solutions are of great importance as they occur in tissues and cells of all living organisms. In oil and gas industry, the balance between break-up and coalescence (both interfacial phenomena) determine the occurrence of phase inversion, a process that can lead to the blockage of the entire pipeline. Furthermore, in recent lab-on-a-chip technology, liquid droplets, moving through an immiscible liquid, are used as chemical (and biological) reactors, where reactions are carried out while the droplet is transported along micro-channels. The proper understanding and modelling of liquid-liquid interface dynamics is not only a challenging problem from a fundamental viewpoint, but it is of great significance to many industries. Experiments at liquid-liquid interfaces are difficult to perform due to the presence of thermal and hydrodynamic fluctuations and direct visualisations are carried out only at very particular conditions. One of the problems
when dealing with flows in micro- and nano-scales is the proper formulation of boundary conditions. The classical boundary conditions at liquid-liquid interfaces are continuity of the velocity and of the tangential component of stress and jump in the normal stress at the interface is balanced by the product of the interfacial tension and curvature [1]. However, the recent interest in micro-[2] and nano-fluidics [3] challenges their validity. At molten polymer-polymer interfaces, for instance, it has been shown by direct and indirect measurements [4] that, apparent, velocity jumps exist and can be modelled effectively via a Navier slip condition. In this paper, we show that if a viscosity profile is included in the Navier-Stokes equations, we can describe, the velocity profile in the interfacial region separating two fluids. This approach is supported by the observation that there is a relation between apparent slip and the viscosity profile across the interface [5]. For simple fluids, only few recent MD simulations pinpoint the presence of an apparent slip velocity, i.e. a region, whose thickness is of the molecular size, close to the interface where the velocity changes very rapidly. Similarly to solid-liquid interfaces [6], this rapid change is replaced by a velocity jump, $\Delta u$, and described by a NSC [5], $\Delta u = \alpha \tau$, where $\Delta u$ is proportional to the shear stress, $\tau$, through a slip length, $\alpha$. Another possibility is the introduction of an interfacial viscosity [7] within a layer (whose thickness must be determined by previous MD simulations) across the interface. While both strategies prove effective in describing the velocity profile far from the interface, they require case-specific information: a MD simulation must be carried out to extract, for instance, the slip length, which is, then, used as an interfacial condition for the solution of the Navier-Stokes equations.

These approaches lack generality and cannot describe the very rapid velocity transition across the interface, which is simply replaced by an unphysical discontinuity in the velocity profile. These difficulties can in principle be alleviated by full MD simulations, which are, however, computationally impossible in large scale geometries.

The aim of this work is to further investigate this aspect and to relate the velocity discontinuity at liquid-liquid interfaces to the degree of mixing of the liquid. In particular we want to question the validity of simple potentials – such as Lennard-Jones interaction – on the few results on the slip velocity obtained so far. Different mixtures are used to show that if the effect of viscosity profile is accounted for, then the Navier-Stokes equations can predict the full velocity profile, including, crucially, the rapid change in velocity across the interface, which is often interpreted as, apparent, slip.

Our method represents a multiscale approach where pieces of information collected from MD simulation are enforced into Navier-Stokes continuum theory. In this work, we only limit ourselves to the investigation of Lennard-Jones fluids, while we leave to Ref. [8] the problem for molecular liquids.

2. Molecular dynamics simulations details

As a test geometry, we consider a simple steady Couette flow [1] between two planes at $y = \pm L$ with the streamwise component of the velocity $u (y = \pm L) = \pm V$, of two
liquids, with the interface at \( y = 0 \); here, \( y \) represents the wall-normal direction, and \( L \) and \( V \) are constants as shown in Fig. [1].

All the Molecular Dynamics simulations presented in the paper are carried out by the code LAMMPS [9]. In the following, details are provided. The simulations are performed using the properties of liquid Argon and a modified Lennard Jones potential is implemented as follow:

\[
U_{ij} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^6 - \beta_{ij} \left( \frac{\sigma}{r_{ij}} \right)^{12} \right]
\]

where the parameter \( \beta_{ij} \) allows to change the miscibility between the two fluids. \( \beta_{ij} = 1 \) if \( i = j \); if \( i \neq j \) the parameter \( \beta_{ij} \) is used to change the miscibility of the two liquids. \( \beta_{ij} = 0 \) corresponds to immiscibility, \( \beta_{ij} = 1 \) corresponds to full miscibility; \( 0 < \beta_{ij} < 1 \) corresponds the partial miscibility. The values of \( \varepsilon \) and \( \sigma \) are \( \varepsilon/k_B = 120 \) K and \( \sigma = 3.4 \) Å, where \( k_B \) is the Boltzmann constant. The mass is taken equal to \( M = 39.948 \) Kg/kmol. All the simulations are NVT thermostatted at \( T = 130 \) K using a Nosé-Hoover thermostat. A fully period box (\( L_y = 160.82 \) Å, \( L_x = L_z = 102.34 \) Å) is used in all the simulations. Each box is divided into 700 bins (\( \delta_y = 0.23 \) Å, \( \delta_x = \delta_z = L_x = L_z \)). The resulting constitutive relations are provided in Figs. [2]

2.1. Calculation of the viscosity

After stabilizing the simulation at equilibrium conditions, the viscosity is computed using the Muller-Plathe method — see Figs. [2] where the constitutive relation between the shear viscosity \( \mu \) and the density \( \rho \) and mole fraction \( \chi \) is provided, i.e. \( \mu = \mu(\rho, \chi) \).
Figure 2: Constitutive relations $\mu = \mu(\rho, \chi)$ for the Lennard-Jones fluids at different values of $\beta$. The two fluids have the same mass $M$.

The shear viscosity $\mu$ is computed using the well-known Muller-Plathe method by imposing a shear rate $\dot{\gamma}$ that induces a velocity gradient $dv/dy$ and by computing the virial stress $\sigma$ as

$$\mu = -\frac{\sigma_{yz}}{dv/dy}$$

$$\sigma_{yz} = \frac{1}{V} \sum_{i=1}^{N} \langle S_{yz}^i \rangle$$

$$S_{yz}^i = -m_i v_{iz} + \frac{1}{2} \sum_{j \neq i}^{N} \frac{\partial U(r_{ij})}{\partial r_{ij}} \frac{r_{ijz}r_{ijy}}{r_{ij}}$$

where $N$ is the total number of particles and $V$ is the volume, $v_{iz}$ and $v_{iy}$ are the z and y component of velocity vector $v_i$, $r_{ijz}$ and $r_{ijy}$ are the z and y component of vector $r_i$ and $r_j$; $m_i$ is the mass of the $i^{th}$ particle.
2.2. Simulation with imposed shear

A Couette flow, with a given shear rate \( \dot{\gamma} \) is obtained by applying opposing velocities \( \pm V \) along the y-axis. The velocity \( V \) is enforced by applying an additional body force \( F_V \) in the \( y \) direction of each atom within the two external bins and within the central bin. Further details can be found in Ref. [10]. The application of the force \( F_V \) is based on the following (leap-frog) scheme. For a system on \( n \) particles, the center of mass velocity along one dimension is given as

\[
\frac{t}{2} \frac{v_{\text{com}}}{n} = \frac{1}{n} \sum_{i=1}^{n} \frac{t}{2} v_i;
\]

if the total force at step \( t \) is \( F_{\text{com}}^t = \sum_{i=1}^{n} F_i^t \), then we look for an additional body force \( F_V^t \) to be uniformly applied to each atom so to drive the flow with a velocity \( u_c \). By setting \( v_{\text{com}}^t = V \), we get

\[
V = v_{\text{com}}^t + \delta t \frac{F_{\text{com}}^t}{nM} + \delta t \frac{nM}{n} \sum_{i=1}^{n} F_V^t
\]

where \( nM \) is the total mass of the system and \( \delta t \) is the imposed time step. Solving for the total mass force, we obtain:

\[
\sum_{i=1}^{n} F_V^t = \left[ V - v_{\text{com}}^t \right] \frac{\delta t}{nM} - F_{\text{com}}^t
\]

that translates into a force to be applied to each particle

\[
F_V^t = \left[ V - v_{\text{com}}^t \right] \frac{\delta t}{nM} - \frac{F_{\text{com}}^t}{n}.
\]

3. Navier-Stokes – continuum scale – solution

A plane Couette flow, with non uniform viscosity, is described by the following equation

\[
\frac{d}{dy} \left[ \mu(\rho, \chi) \left( \frac{du}{dy} \right) \right] = 0.
\]

A constitutive relation to describe how viscosity changes as function of density and composition, \( \mu = \mu(\rho, \chi) \), is needed to solve this equation. Here we assume that the conditions are laminar, and therefore \( Re << 1 \). Such a relation is obtained, in our case, by MD simulations \( \mu = \mu(\rho, \chi) \).

4. Results

The first example is given by two identical immiscible atomic fluids. This simplified case allows us to compute the density and mole fraction profiles across the interface using DFT (see Fig. [3]); the viscosity distribution is then computed using a theoretical approach developed for a strongly inhomogeneous Lennard-Jones fluid [11]. Substitution
Figure 3: Close-up of the normalized streamwise velocity component in the interfacial region, obtained via MD simulations (orange line), and solution of the Navier-Stokes equations with \( \mu(\rho) \) calculated using DFT (blue line) and MD (red line) for the case of two immiscible, symmetrical Lennard-Jones fluids (\( V = 25 \text{ m/s} \), \( L = 46.65 \text{ Å} \), \( L_x = L_z = 108.34 \text{ Å} \)). The density (see insert, \( \rho_0 = 1.1705 \text{ g/ml} \)) used to solve the NS equations was obtained from DFT [12] (blue line) and MD simulations (red line). The MD simulation uses 17248 particles for each fluid.

of the relation \( \mu = \mu(\rho, \chi) \) into the Navier-Stokes equations, and their subsequent numerical solution yields the results shown in Fig. [3]. As can be seen, the agreement with the predictions [12] of the full MD simulations is very good.

The viscosity distribution \( \mu = \mu(\rho, \chi) \) is obtained using the distribution of \( \rho(y) \) and \( \chi(y) \) at equilibrium conditions and, therefore, does not depend upon the specific state. This is in contrast with the other approaches where the non-equilibrium properties, such as slip length [13] and interfacial viscosity [14], depend upon the specific state, characterised, for instance, by the imposed shear rate \( \dot{\gamma} \). As the fluid structure and the intermolecular interactions become more complex, however, the required information can not be obtained via a purely theoretical approach and MD becomes the only feasible option. If we extract from the MD simulations the relation \( \mu = \mu(\rho, \chi) \) for the case we have just described, we can see from Fig. [3] that the results compare very well in this case as well; here, the constitutive relation \( \mu = \mu(\rho, \chi) \) is computed through equilibrium MD simulations. The constitutive relation here is characteristic for this type of fluids, while is other fluid will be characterised by other relations. The density distribution across the interface is computed by equilibrium simulation, namely without any shear velocity imposed at the boundary.

In Fig. [4], we show the same results for two identical Lennard-Jones fluids with different levels of miscibility, induced by changing the interaction parameter \( \beta \).
Changing the interaction (between the two fluids) results in different density profiles at the interface; when we move from complete immiscibility ($\beta = 0$) to full miscibility ($\beta = 1$), the density profile changes and the dip (molecular depletion region) gradually reduces to zero at full miscibility. Due to molecular depletion, the shear viscosity at the interfaces is lower than in the bulk region showing that the transport of momentum in the former region is less efficient than in the bulk; to balance the viscosity decrease, the velocity gradient increases, as shown in Fig. [4], leading to apparent slip. As the density contrast disappears, the associated variation in the velocity profile flattens and the apparent slip is not present anymore. If we introduce the corresponding density variation into the Navier-Stokes equations, numerical solutions of the latter are in excellent agreement with MD predictions.

In Fig. 5, we show that our approach is valid for different imposed shear rate ($\dot{\gamma}$), without requiring new, or ad-hoc conditions, as opposite to to approaches that rely on the use of slip models [15]. The density distribution does not depend on $\dot{\gamma}$, supporting the choice of computing at equilibrium conditions.

5. Conclusions

We have shown that the apparent slip velocity results from a molecular depletion at the interface, which is a direct consequence of the molecular interactions and, therefore, a property of the fluids not of shear rate $\dot{\gamma}$. When the two fluids are well-mixed at the interface, no apparent slip is present. This conclusion is further supported by the observation that the density distribution, which, in turn, determines the apparent slip, does not depend on the shear rate (as long as the fluids behave as Newtonian), but only on the intermolecular interactions. Furthermore, we have shown that if we account for the viscosity dependence on the density variation across the interface, the Navier-Stokes equations can be used to predict the velocity distribution throughout the domain, without the need for ad-hoc boundary conditions such as slip models, but all the properties can be independently measured.

With such a multi-scale approach, we can enforce some microscopic features into Navier-Stokes equations; the final result is therefore a better and physically sound description of liquid-liquid interactions.

Acknowledgements

All authors would like to acknowledge the support of the support of the NANO-BRIDGE project, namely “Heat and mass transport in NANO-structures by molecular dynamics, systematic model reduction, and non-equilibrium thermodynamics: An international collaborative effort to develop authentically multi-scale engineering recipes to BRIDGE the gap among scales and to validate them for carbon binders in thermal storage and carbon-based nano-filters” (PRIN 2012 call, code 2012LHPJSJC, duration 36 months), involving Politecnico di Torino and Universitá di Brescia. PP and OKM thank
Figure 4: Normalized streamwise velocity component \( (V = 50 \text{ m/s}, \ L = 40.205 \text{ Å}, \ L_x = L_z = 108.34 \text{ Å}) \) across the interface (a), obtained for different density distributions \( (\rho(\dot{\gamma} = 0) \equiv \rho_0 = 1.36 \text{ g/ml}) \), (b), calculated by varying the parameter \( \beta_{ij} \) in the intermolecular potential used in the MD simulations. The Navier-Stokes solutions that use these distributions and MD velocity predictions are shown in (a) by the solid lines and symbols, respectively. The MD simulations use 17248 particles for each fluid.
Figure 5: Streamwise velocity component calculated from the Navier-Stokes equations (solid lines) and MD simulations (symbols), obtained for different shear rates ($L = 40.205\ \text{Å}$, $L_x = L_z = 108.34\ \text{Å}$), $\dot{\gamma}$ with $\beta_{ij} = 0$. The MD simulations use 17248 particles for each fluid.

acknowledge the support of the Royal Society through their International Exchanges Scheme (2014/R3), and the Engineering and Physical Sciences Research Council, UK, through the MEMPHIS programme grant (EP/K003976/1).

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