The no-slip condition for a mixture of two liquids

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When a mixture of two viscous liquids flows past a solid wall there is an ambiguity in the use of the no-slip boundary condition. It is not obvious whether the mass-averaged velocity, the volume-averaged velocity, the individual species velocities, all or none of the above, or none of the above should exhibit no-slip. Extensive molecular dynamics simulations of the Poiseuille flow of mixtures of coexisting liquid species past an atomistic wall indicate that the velocity of each individual liquid species satisfies the no-slip condition and, therefore, so do mass and volume averages.

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The no-slip boundary condition in fluid mechanics states that the velocity of a fluid at a solid wall equals the velocity of the wall. This condition has a lengthy history and solid experimental support for the case of Newtonian liquids, but its microscopic basis has been understood only relatively recently based on molecular dynamics simulations. The validity of the no-slip condition is far from automatic, since for example gases and non-Newtonian liquids are known to exhibit slip, and in this paper we consider the question of the appropriate wall boundary condition for a mixture of two liquids. The question is relevant to any flow problem involving miscible liquids, such as double diffusive convection, where the composition is spatially varying.

Since there is no satisfactory analytic argument for the origin of no-slip even in a one-component fluid, it is not feasible to obtain a theoretical derivation here from first principles. Likewise, it is difficult to address the question experimentally because the absence of an accepted and complete theory for fluid mixtures prevents one from, for example, extracting a slip length by measuring flux vs. pressure drop in Poiseuille flow. In recent work it is common to assume that the mass-averaged velocity satisfies no-slip; see, e.g., Perera and Sekerka, and Liao and Joseph. Aside from some theoretical justification by Camacho and Brenner, and some supporting molecular dynamics simulations by Mo and Rosenberger for gases, there is some intuitive plausibility for focusing on mass-averaged velocity because in the microscopic interactions between fluid and wall atoms, the momentum is the relevant dynamical variable. On the other hand, one might say that local volume averaging is an appropriate scheme to treat mixture problems, and boundary conditions should involve this variable. Alternatively, one might be influenced by the kinetic theory arguments of Maxwell for slip in gases, and consider the momentum exchange in inter-species collisions, and conclude that the mass ratio will enter in the boundary condition. Yet another line of reasoning is to assert that a fluid molecule moves in a potential due to the nearly-fixed wall atoms and the nearly-randomly fluctuating neighboring fluid molecules, in which there is little difference between a homogeneous liquid and a mixture, and therefore the individual species velocities should satisfy no-slip. Unfortunately, none of these heuristic arguments is completely decisive in itself.

In order to provide an unbiased and fundamental calculation of the wall boundary condition for a liquid mixture, we have conducted systematic molecular dynamics (MD) calculations of the Poiseuille flow of systems of several thousand liquid atoms in a channel made of atomistic solid walls, in cases with or without a concentration gradient. Previous MD studies of this nature (see, for a general review) indicate that the continuum aspects of fluid flow are well reproduced in this way, and we have been able to obtain unambiguous numerical results for the showing that the individual species velocities satisfy the no-slip condition. We emphasize that this statement holds for liquids; in a mixture of gases one has the more difficult question of studying the variation of a non-zero slip length with the properties of the components of the mixture.

The mechanics of the MD simulations are very similar to those used by us in a study of the sliding plate problem. We first consider the channel flow of a homogeneous Newtonian liquid made of two types of atom. The simulated system consists of 8000 fluid atoms flowing between two solid plane atomic walls. The atoms interact with each other via two-body Lennard-Jones (LJ) potentials, \( V_{ij}(r) = 4\epsilon [ (r/\sigma)^{12} - (r/\sigma)^6 ] \), cutoff at separation \( r = 2.5 \), where \( c_{ij} \) (\( i,j=1,2,w \)) is an adjustable inter-species interaction strength. Hereafter, all quantities in this paper are non-dimensionalized using the energy scale \( \epsilon \), the length scale \( \sigma \), and a reference mass \( m \), giving a
natural timescale \( \tau = \sigma (m/\epsilon)^{1/2} \). The walls are tethered to fixed lattice sites by harmonic springs \( k \), and otherwise interact with all other wall and fluid atoms via an LJ potential with an appropriate \( c_{ij} \), allowing them to exchange energy and momentum with the fluid. The system is three dimensional, with the walls parallel to the \( x-z \) plane separated by a gap of width \( 18\sigma \) in the \( y \)-direction, periodic boundaries in \( x \) and \( z \), and average flow in the \( x \)-direction produced by applying a gravitation-like force \( m_ig\hat{x} \) to each fluid atom, with \( g = 0.01 \). In most cases, we extract the heat generated by viscous friction by a local Nosé-Hoover thermostat \([17]\) which couples each atom to a heat bath, providing a constant temperature system.

In Fig. 1, we show typical results for the tangential velocity \( u(y) \) and the shear stress \( s(y) \). The three sets of curves are a reference one-species system (unit mass and unit fluid-wall coupling) plotted as a solid line, and then the two distinct species for the mixture case shown as dashed or dotted lines. In this case there are an equal number of atoms of each species, and their parameters have been chosen as \( m_1 = 1.5, m_2 = 0.75, c_{12} = 0.9, c_{1w} = 0.75 \) and \( c_{2w} = 0.25 \). The \( y \)-coordinate is such that \( y=0 \) and \( 21 \) are the centers of the two innermost layers of wall atoms confining the fluid, and there are 20 sampling bins for the fluid velocity and stress, centered at integer values of \( y \). All velocity profiles are parabolas which go to zero in the vicinity of the wall. The pure liquid has a stronger wall attraction, so its extrapolated velocity vanishes slightly further away from the wall. In other mixture simulations of this type, if \( c_{iw} = 1 \) the species velocities vanish at approximately the same position as the pure liquid, while when \( c_{iw} > 1 \) the species velocities vanish further away. The difference in the height of the parabola of pure liquid compared to the mixture arises from the latter having a different effective viscosity.

The stress profiles are linear in the interior of the channel, as expected in Poiseuille flow, but the component of the mixture which is more (less) strongly attracted to the wall has a higher (lower) stress value there, accompanied by a sharp increase (decrease) in density. We have repeated this calculation for a number of uniformly mixed systems with different parameter values, and in all cases the two components have essentially the same velocity profile. When the mixture concentration is 50%, the shear stress profiles agree, but for other concentrations we observe distinct slopes: the component of higher concentration has a steeper stress gradient, and a correspondingly higher effective viscosity, and a higher pressure as well. In one test case we omitted the thermostat and allowed the system’s temperature to rise. The result is again a parabolic velocity profile which goes to zero near the walls, but with larger numerical values reflecting the decrease of viscosity with temperature.

Although we do not have a precise mathematical model to elucidate the numerical observations, the physics is reasonably clear. The molecular origin of no-slip is that fluid molecules near the wall are on the one hand dragged along in the direction of the net flow by their neighbors further away from the wall, and on the other hand are pushed up against the wall by the crowding of molecules in a dense liquid, where they interact with the effectively corrugated potential of the wall. While the molecules near the wall are not literally stuck there, their translation speed is much reduced as they interact with the almost-fixed wall atoms, and a typical trajectory \([4]\) is a random walk with a drift in the direction of the applied force and some transient localization near the wall. When the atoms are sorted by sampling bins (or averaged over position by the finite spatial resolution of any

![FIG. 1. (a) Velocity and (b) shear stress profiles for a single liquid (solid line), and for the individual species of a uniform mixture (dashed and dotted lines.](image)
realistic laboratory measurement) the average velocity decreases systematically as the wall is approached, and tends to zero near the wall. The precise value of “near” depends on the details of the wall-fluid interaction, but for reasonable choices, the distance from the nominal wall position is at most one or two atomic sizes, and zero from a macroscopic viewpoint. The key point about a mixture of liquids is that the qualitative argument just given does not depend in any way on the details of the interactions between the fluid atoms or whether there is more than one fluid species. Thus, in a dense liquid in good contact with the wall, any species should satisfy the no-slip condition. (The qualification concerning the wall contact is to distinguish Newtonian from non-Newtonian fluids or suspensions: in a polymer melt only part of a molecule adjacent to a wall need be in atomic contact, while in the case of a polymer solution or suspension there can be a depletion region near the wall.)

A more interesting case arises when the relative concentration of the species varies with position along the wall. The intuitive argument just presented is unchanged by this complication, but the numerical verification is rather more involved. If the variation is weak, one may treat a local region by the homogeneous simulation just described, using the appropriate local concentration value. More generally, we wish to consider a rapid linear concentration gradient along the direction channel; it is trivial to initialize the system in this way, but an additional ingredient is needed to prevent the gradient from diffusing away with time. To this end, we divide the channel along the \((x)\) flow direction into 40 “concentration bins”, where in bin 1 (21) the concentration of species 1 is fixed at 0.75 (0.25) at all time. These values are maintained by changing the identity of atoms chosen at random from species 1 to 2, or vice versa, until the concentration has the desired value. In these two bins a kind of Maxwell demon is operating, and the fluid and flow properties there may not be fully realistic, but the other 38 bins are untouched and presumably faithful models of two-fluid coexistence at whatever local value of concentration occurs. A more sophisticated computation \[\text{IS}\] would fix the concentration in the two reference bins by coupling them to particle reservoirs using a grand canonical Monte Carlo procedure, which has realistic fluid behavior everywhere, but the simpler method suffices here.

In the absence of net flow the procedure just described indeed produces a sawtooth concentration profile (Fig. 2, dashed line) but when motion occurs the reservoir values of concentration are convected downstream and the result is a profile which is not piecewise linear (Fig. 2, solid line). In fact, as one might expect, the observed profiles are similar to solutions of the convection-diffusion equation. One then has a numerical dilemma: in order to have a statistically significant velocity profile, it is preferable to have a strong forcing acceleration and large values for the mean velocity, but in this case the concentration profile is unsuitable. In Lennard-Jones systems a liquid freezes if the temperature is too low, corresponding to an \(O(1)\) minimum liquid thermal velocity, and if the mean velocities are much below this value they are obscured by thermal noise. However, if the mean velocities are too large, the resulting concentration profile approaches a step, with a very narrow transition region, and within each step the species concentrations are constant.

The profile shown in Fig. 2 was obtained with a rather weak forcing, \(g = 0.001\), and in order to observe a meaningful velocity profile we have simply averaged over a very long time interval of 2500\(\tau\) (and also doubled the length of the system so as to have 16000 fluid atoms). The resulting computation required about 2 months on an HP-735/125 workstation, and gave the concentration profile above and the subsequent velocity plots, which are still somewhat noisy, but clearly display no-slip velocity profiles.

In Fig. 3, we show some typical fluid 1 velocity profiles, \(u_1(x, y)\), as a function of \(y\) for selected \(x\)-bins. The concentration at each \(x\) may be found from the solid curve in Fig. 2. Each curve is roughly parabolic and tends to zero near the wall positions. Because each point involves an average of only 5-15 atoms, compared to 200 in the uniform mixture case in Fig. 1, the statistical fluctuations are much stronger. If these curves are \(\bar{}\) averaged, one finds a smooth parabola resembling Fig. 1a. The profiles of the second fluid and the other half of the channel are qualitatively the same. Note that there is no qualitative difference as a function of concentration, nor between

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**FIG. 2.** Concentration profiles for one species in a mixture at rest (dashed line) and under Poiseuille flow (solid line). The first curve is noisier because it results from a much shorter averaging interval.
bin 1, where the atoms’ identity was varied unphysically, and the other bins. This insensitivity is analogous to that found as the method of thermostatting varies, and is characteristic of MD simulations of this type.

We have shown that in a mixture of liquids the species velocities satisfy the no-slip condition and, a fortiori, so do mass and volume averages. The details of liquid-solid interactions may affect the behavior within atomic distances of the walls, but macroscopically the classical boundary condition holds. Although we have not pursued the matter here, this type of data and calculation can be used to test detailed theories of the dynamics of liquid mixtures. Channel flows of uniform mixtures are computationally efficient, although in concentration gradients the results can be noisy and time-consuming to obtain. However, molecular dynamics simulations can again provide otherwise inaccessible information.

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