

# Chapter 1

## Does Slip Exist?

A theory of effective slip could be treated as a purely mathematical result, with the slip length being simply a parameter in the model. However, a theory of effective slip has practical value only if the slip length parameter has some physical meaning: quantifying the slip effect for flow over a homogeneous physical surface. Establishing that a slip effect exists on clean, atomically flat surfaces is far from trivial. Therefore, in this chapter we will examine the literature on the experimental and theoretical evidence for slip.

This cannot be a comprehensive review of all available literature, but rather will be a sample of some high-profile papers. An exhaustive review of the experimental literature is available in the 2005 review article by Neto *et al* [16]. Other comprehensive reviews are by Vinogradova in 1999 [23] and Lauga, Brenner and Stone in 2006 [14]. A reasonable introduction is the progress article of Granick *et al* from 2003 [10].

### 1.1 Types of Slip

So far, we have discussed slip within a mathematical model of fluid flow; this is deliberate: in such a model the concepts of slip and slip length are straightforward and intuitive. However, we now need to tackle slip in the real world, disentangling a partially-ordered hierarchy of concepts.

### 1.1.1 Definitions in the Literature

The 2006 review article by Lauga, Brenner and Stone [14] proposes the following definitions (some paraphrased):

- **Phenomenon of slip:** A fluid dynamics system behaving as if the fluid velocity at the wall differs from the wall velocity.
- **Molecular slip** (also intrinsic slip): ‘Refers to the possibility of using hydrodynamics to force liquid molecules to slip against solid molecules.’
- **Apparent slip:** The case when the no-slip condition holds on the surface, but at larger length scales, the no-slip condition appears not to be valid.
- **Effective slip:** ‘Refers to the case where molecular or apparent slip is estimated by averaging an appropriate measurement over the length scale of an experimental apparatus.’

These definitions are a good place to start. But they make no mention of *mixed-slip* surfaces. We shall accept these definitions, but modify and extend them to deal cleanly with the separate cases of pure *and* mixed-slip surfaces.

The first modification is to separate molecular slip from intrinsic slip.

- **Intrinsic Slip:** When a clean, atomically flat homogeneous surface behaves as if the no-slip condition does not hold.

With this definition, Intrinsic Slip may be due to Molecular Slip or Apparent Slip.

The second modification is to take Lauga *et al*’s concept of ‘Effective Slip’ and simplify it, then relabel it as simply ‘Measured Slip’.

- **Measured Slip:** A slip effect measured with some experimental apparatus.

This allows us to use the phrase ‘Effective Slip’ to emphasize the possible heterogeneity of the surface:

- **Effective Slip:** A slip effect imputed to liquid-solid interface, where the surface is not known to be homogeneous and atomically flat.

We shall discuss some of these concepts in more depth.

### 1.1.2 Measured Slip

As we shall see shortly, all measurements are to some extent indirect: Experiments cannot yet directly probe the fluid velocity in the region within a few nanometers of the surface. A measurement of a slip effect may be measuring molecular slip, apparent slip, or, for a heterogeneous surface, any combination of the two.

There are no direct measurements of slip; if there were, they would be measuring molecular slip.

### 1.1.3 Intrinsic Slip

Suppose we can prepare a perfectly clean, atomically flat sample of some material. Further, suppose we can experimentally test the sample for slip effects with some pure liquid. If a slip effect appears, and can be consistently replicated, then the implied slip length is a meaningful, reliable parameter of the fluid-solid system. It is reasonable to label this the *intrinsic* slip length.

Intrinsic slip may be due to molecular slip or apparent slip.

### 1.1.4 Molecular Slip

‘True slip’ means that the fluid *at the boundary* has a non-zero velocity. At the smallest scale, the fluid velocity at a point is the average velocity of an ensemble of molecules. Thus, ‘true’ slip means that the average velocity of the molecules in contact with the wall is non-zero. This implies that the

molecules in contact with the wall are *not* all sticking to the wall all the time. If (some) fluid molecules at the surface are slipping along the surface, this is termed molecular slip.

There are no direct observations of molecular slip, though (as explained later) it is observed in molecular dynamics computer simulations.

A hypothetical mechanism for molecular slip in liquids could be one similar to the (known) mechanism for slip in gases – Knudsen Slip:

### **Molecular Slip in Gases – Knudsen Slip**

In a gas, the mean free path is many times larger than the gas molecule size, so an interaction with the wall will almost certainly not involve another gas particle. Therefore, the interaction can be treated as a simple reflection.

A gas particle has some momentum in the direction tangent to the wall. If an incident gas particle simply *sticks* to the wall, then all of its tangential momentum is transferred to the wall. This is the case of ‘stick’ or the no-slip condition. If the particle subsequently detaches with a velocity in a random direction, *on average* its tangential momentum will still be zero – the same as the wall.

At the other extreme, suppose that an incident particle undergoes specular reflection, bouncing off the wall with no change in its tangential momentum. With no momentum loss, there is no ‘friction’, and the gas experiences perfect slip.

While specular reflection is defined as the equality of well-defined angles of incidence and reflection, the key aspect of the interaction is that the wall-particle force is always perpendicular to the wall, so the wall cannot change the tangential momentum of the colliding particle. This will always be the case if the wall is perfectly flat and rigid, although this is an idealised limiting case. In real systems exhibiting Knudsen slip, only some fraction of gas particles will undergo specular or close-to-specular reflection.

An effect similar to Knudsen slip may occur in fluids, although the mean free path in a liquid is generally less than the molecular diameter, so angles

of incidence and reflection become difficult to define. However, particle-wall collisions in which the particle loses no tangential momentum may still occur. A computer simulation where the wall is defined as perfectly flat and rigid would allow this.

### 1.1.5 Apparent Slip

Perhaps the simplest alternative to molecular slip to explain slip effects is apparent slip. The idea is that there exists a *boundary layer* of reduced viscosity at the solid surface. As a consequence of the lower viscosity, the velocity gradient in the boundary layer is *steeper* than in the bulk. Thus, the velocity gradient ‘turns a corner’ at the interface between boundary layer and bulk. The no-slip condition holds at the solid-liquid interface, but the velocity gradient in the bulk can be extrapolated to generate a slip length, as shown in Figure (1.1).

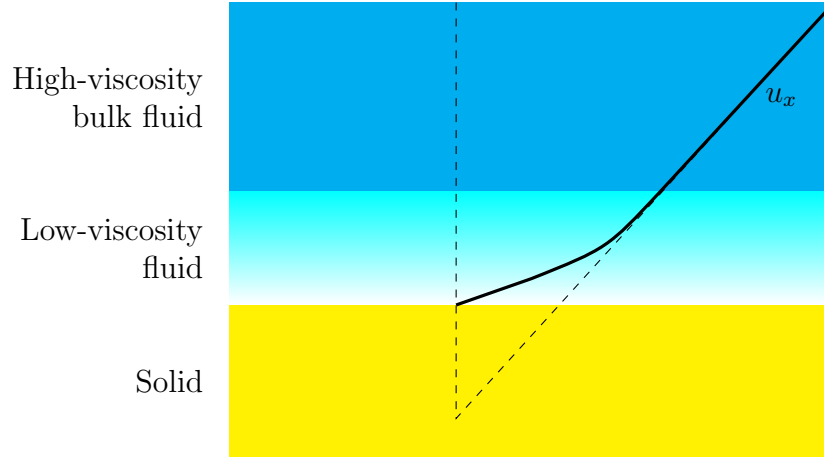


Figure 1.1: Apparent slip caused by a depletion layer with lower-than-bulk viscosity.

If the boundary layer has sufficiently low density, then only a very thin layer is required to explain observed effects: de Gennes notes that observed slip effects are explainable by a *gas* layer, only 1 or 2 atoms thick [9].

### 1.1.6 Types of Slip Redux

We summarize the hierarchy of slip concepts in Figure (1.2) below:

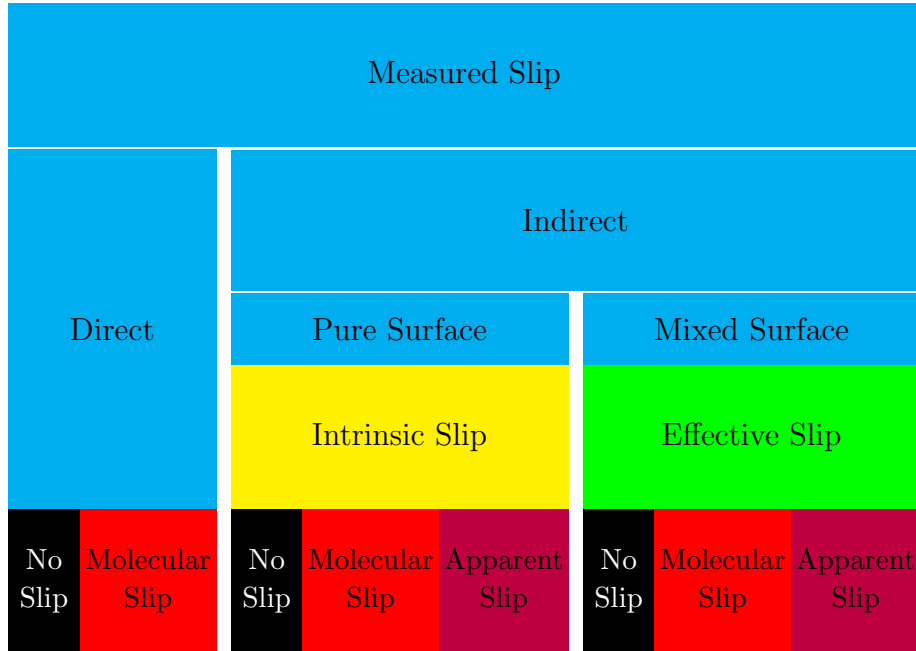


Figure 1.2: Hierarchy of slip concepts.

Note that the ‘Direct Measurement’ category is there just for completeness – as mentioned, experiments cannot presently verify molecular slip.

## 1.2 Experimental Intrinsic Slip

Probably the first credible experiments showing a slip effect are those by Erhard Schnell in 1956 [18]. In a series of careful experiments, Schnell treated glass capillaries with dimethyldichlorosilane to make them hydrophobic. The silicone layer decreased the capillary diameter by 0.01% to 0.04%. Nevertheless, at sub-turbulent velocities, the hydrophobic capillaries flowed 0% - 5% more water than otherwise-identical untreated capillaries. He attributed this excess flow to slip: “...this can only be explained by the slippage of water over the non-wettable surface.”

After Schnell, various experiments that illustrated slip were reported. But, it is fair to say that it wasn't until the 21st century that truly believable evidence appeared. Modern experimental techniques on slip progressed rapidly, starting from the 1990s, particularly after the widespread availability of the Atomic Force Microscope and its derivatives. The first of these new experiments exposed a large host of subtle errors and competing interpretations. See for example [17], [8], [3], [26], [6], [15].

Hence, there is little benefit in examining the complete history of slip experiments. Instead, we shall focus on more recent results, obtained with mature experimental techniques.

There are three common experimental techniques used to study slip: Capillary flow, drainage force, and particle velocimetry.

### Capillary Flow

In this self-explanatory technique, the volumetric flow rates through capillaries are compared to standard theory. The standard theory for flow in a straight circular pipe with no-slip boundary conditions is Poiseuille flow. There is another analytic solution for the same pipe with Navier slip on the boundary. This solution is fitted to the experimental data; the parameter in question is the slip length. Thus, an imputed slip length is found.

### Drainage Force

In this technique, a tiny sphere is repeatedly pushed towards the test surface. As the sphere nears the surface, the fluid is squeezed out of the way. The force required to squeeze the fluid depends on the boundary condition at the test surface. A theoretical model due to Vinogradova [22] is used to predict the force, with slip length as the adjustable parameter; by fitting the model to the data, a slip length is inferred. In practice, the sphere is mounted on a cantilever, and driven in an oscillatory fashion, with force being calculated by the deflection of the cantilever.

An Atomic Force Microscope (AFM) in tapping mode is often used, as well as a similar purpose-built apparatus known as the Surface Force Apparatus (SFA). This technique is very sensitive to inaccuracies in the position of the sphere relative to the surface. Recent results use sophisticated techniques to determine this accurately.

### Particle Velocimetry

In this technique, thousands of tiny fluorescent particles are dumped in the flow. Various methods are used to track the particles, and infer their velocity. The particles are small enough that Brownian motion is significant, so that it is necessary to average their velocity over a finite volume. This obviously reduces the resolution of the inferred velocity field, so that this technique is still not ‘direct’ enough to see molecular slip. Slip lengths are inferred by extrapolating a fitted velocity profile.

#### 1.2.1 Recent Experimental Literature

The widespread acceptance of the no-slip boundary condition of classical fluid mechanics was based on observation. But given that slip effects were not noticed until the length scale of experiments became extremely small, are we sure that the no-slip condition *really* holds? So our first order of business is to verify the no-slip condition at the smallest possible scales.



## No Slip

Two recent papers show convincing evidence that the no-slip condition holds on hydrophilic surfaces.

The first, by Vinogradova and Yakubov in 2003 [24], was a drainage force experiment, one of the earliest to use an AFM for extra sensitivity, rather than the usual SFA. A silicate glass sphere was tapped onto a hydrophilic silicon surface, both of which were molecularly smooth: rms roughness was 0.3 nanometers peak-to-peak. (For comparison, a water molecule is about the same size.) The experiment revealed no slip.

The trouble with this sort of experiment is the difficulty in determining the exact distance between sphere and surface. This concern was taken very seriously in the second paper by Honig and Ducker, from 2007 [11]. They note: “It is important to note that an error in determining the position of the solid-liquid interface ( $h = 0$ ) directly translates into an error in determining the slip length. In traditional colloidal probe measurements, the separation is not measured explicitly; the relative separation is determined from the sum of the displacement of a piezoelectric translation stage (“piezodisplacement”) and the deflection of the cantilever. The zero of separation is inferred from the shape of deflection/piezodisplacement data.” Problems include high force gradient near zero separation, thermal drift, and the fact that net separation is the small difference between two large measured displacements.

Honig and Ducker measure drainage forces with an AFM, but with what they claim is an explicit measurement of the separation between sphere and surface: “We obtain the separation from the intensity of scattering of an evanescent wave by the particle.” The particle — the glass sphere of diameter  $10\mu\text{m}$ , was hydrophilic, with an rms roughness of 0.7 nm peak-to-peak, and a typical maximum peak-trough roughness of 4.5 nm. The glass plate was also hydrophilic, with an rms roughness of 0.25 nm, and a typical peak-trough roughness of 1.5 nm. A highly-wetting sucrose solution was used, with  $\theta < 5^\circ$ .

In six experiments, no slip was found, even at shear rates of  $250,000 \text{ sec}^{-1}$ .

### Apparent or Molecular Slip

The same level (or even greater) of care was taken in drainage force experiments performed by Cecile Cottin-Bizonne *et al* in 2005 [7]. They used a SFA, but measured the distance between sphere and surface with a capacitive sensor, to a resolution of 1 Angstrom(!). The force on the plane was measured by the deflection of the cantilever on which it was mounted, with a resolution of 1 Angstrom. The sphere was hydrophilic, while the plane was rendered hydrophobic by silanization with octadecyltrichlorosilane. The plane was examined with an AFM, revealing a peak-to-peak roughness of 1 nm. Experiments were carried out in a clean and thermally isolated room.

With this setup, an implied slip of  $19 \pm 2$  nm was measured. She emphasizes that the value “does not depend on any pre-estimated values of liquid properties (viscosity, diffusivity of optical tracers) or of the geometry of solid surfaces, unlike data analysis used in AFM experiments or fluorescence measurements”. She further notes that early high-slip results were probably due to nanobubbles from cavitation or contamination with platinum nanoparticles. She finally notes that changing the environment to a clean room changed the results drastically(!).

It is worth noting that ‘conventional’ drainage force techniques continue to improve. A very recent (2011) paper by Neto *et al* [25] develops a ‘best practice experimental protocol’ for studying slip with an AFM. In a conventional AFM device, a piezoelectric element drives a small platform down towards the test surface. To the platform are mounted a laser, a photodiode and a cantilever spring. On the end of the cantilever is a small sphere — a colloid; hence the apparatus is known as a colloidal probe. When the colloid encounters hydrodynamic resistance, or hits the surface, the cantilever deflects. This deflection is optically detected by the photodiode. Thus, the raw outputs of a typical AFM are the displacement of the piezo element and the photodiode voltage.

Obviously, the colloid-surface distance is not directly measured, it is in-

ferred from raw data. This paper identifies two problems. First, the platform flexes, causing the laser and photodiode to move relative to each other, causing a spurious deflection signal. Second, when the colloid hits the surface, it scrapes sideways along the surface slightly. The resulting friction causes a deflection of the cantilever in addition to the deflection caused by the normal force. Neto *et al* quantify and correct for these effects in their processing of the raw data.

With this protocol, they study slip in di-*n*-octylphthalate, and find a reproducible slip length in the range 24 - 31 nm. The occasional slip length of  $\sim 60$  nm prompts them to inspect the surface, *after* the slip experiments. They find contamination by nanoparticles about 20 nm in diameter, and note that this causes a false value for the zero of separation, which explains the occasional anomalously high slip measurement.

Turning now to particle velocimetry techniques, Huang *et al* in 2006 [12] presented a fairly standard application of this method, but with some care taken to prevent the formation of nanobubbles: Purified water was used, which was degassed by exposure to a vacuum for 30 minutes. 200 nanometer diameter tracer particles were dispersed in the water, which flowed down channels etched in PDMS plastic. Some channels were rendered hydrophobic by silanization with octadecyltrimethylsilane. The hydrophilic surfaces had rms roughness of 0.47 nanometers, while the hydrophobic surfaces has an rms roughness of 0.35 nanometers.

Total Internal Reflection Velocimetry was used to infer slip lengths for various shear rates. Hydrophilic surfaces showed slip lengths of 26 to 57 nm. Hydrophobic surfaces showed slip lengths of 37 to 96 nm. They say “A quantitative comparison of the two cases shows a slip length attributed to surface hydrophobicity ranging from -7 nm at low shear rates to 54 nm at the highest tested shear rate, with an average value of 16 nm.” With experimental uncertainty taken into account, an upper limit of 150 nm for a

slip length is presented.

The problems of shear were eliminated in another particle velocimetry paper by Joly *et al* also from 2006 [13]. In this work, water containing fluorescent particles of typical diameter 200 nm was confined between two surfaces, of roughness 1 nm peak-to-peak. There was no macroscale flow, only thermal diffusion. The diffusion coefficient  $D$  was calculated by measuring the residence time of the particles in a detection volume, using fluorescence correlation spectroscopy. If the surfaces are hydrophilic, the particle mobility should be strongly reduced by the proximity of the wall. A finite element numerical solution to the Stokes equation gave a theoretical prediction for the mobility. For hydrophilic walls, the agreement between theoretical particle mobility and experimental particle mobility was “excellent”. For hydrophobic silanized walls, theory agreed with experiment if the prediction included a slip length of  $18 \pm 5$  nanometers.

These results are shear-free, ruling out flow-induced nucleation of nanobubbles.

Another complication of shear flow is that it can increase the effective diffusivity of particles — an effect known as Taylor dispersion. This complication is addressed in a 2009 paper by Vinogradova [21]. Glass capillaries, with rms roughness 0.3 nanometers, and silanized capillaries with rms roughness 0.7 nanometers were tested. Fluorescent nanoparticles were dumped in the flow, and their trajectories traced by double-focus fluorescence cross-correlation. When the predicted Taylor dispersion velocity was subtracted from the observed particle velocity, no slip was observed for hydrophilic capillaries, and a slip length of no more than 80 - 100 nanometers for hydrophobic capillaries.

Vinogradova notes “By varying the shear rate near the wall we found that it influences the value of the apparent slip. However, the true hydrophobic slip length remains the same.” Since the surface is flat and not obviously contaminated, the reported 80 - 100 nm slip lengths are candidates for be-

ing intrinsic slip lengths. Finally, she notes that particle velocimetry is not expected to be capable of detecting slip lengths of a few tens of nanometers.

### Molecular Slip?

A tantalizing glimpse of molecular slip is shown in a 2003 paper by Becker and Mugele [4] — but not with water. Rather, they do drainage force experiments with octamethylcyclotetrasiloxane (OMCTS), a much larger molecule than water. The authors were primarily interested in the layering of fluid molecules in confined geometries. Using a SFA to measure drainage force, they were able to observe discrete jumps in the force, as individual molecular layers escaped.

They model the system as consisting of  $n$  independent liquid layers and “introduce two different drag coefficients  $\mu_{ls}$  and  $\mu_{ll}$  to describe the friction between the solid substrates and the adjacent liquid layers and the mutual friction between two adjacent liquid layers, respectively”. They fit the model to their experimental data and find a best fit value of  $\mu_{ll} = (0.2 \pm 0.04) \times 10^{-13} \text{s}^{-1}$  which is “remarkably close” to the value  $0.3 \times 10^{-13} \text{s}^{-1}$  predicted by bulk viscosity. The best fit value for  $\mu_{ls}$  is  $17.9 \times \mu_{ll}$ .

Becker and Mugele do not calculate a slip length from this information, but it can be done: We adopt a similar model of  $n$  independent liquid layers, but in a steady-state shear-driven Couette flow system. Each layer experiences a force  $\mu_{ll}\Delta v$  from the layer above it, where  $\Delta v$  is the velocity difference between the two layers. Similarly for the drag force from the layer *below*. However, the bottom layer on the solid boundary is an exception. It has velocity  $v_{\text{slip}}$ , and the drag force due to moving over the stationary solid below it is  $\mu_{ls}v_{\text{slip}}$ . Therefore, in the steady state, the bottom layer experiences two forces that balance:

$$\mu_{ls}v_{\text{slip}} = \mu_{ll}\Delta v \tag{1.1}$$

The layers have thickness  $d_0$ , which Becker and Mugele measured to be  $(0.95 \pm 0.1)$  nanometers. The geometry relating  $d_0$  and the velocities to

the slip length  $b$  appears in Figure (1.3). The geometry shows two similar triangles, which means that  $v_{\text{slip}}/b = \Delta v/d_0$ .

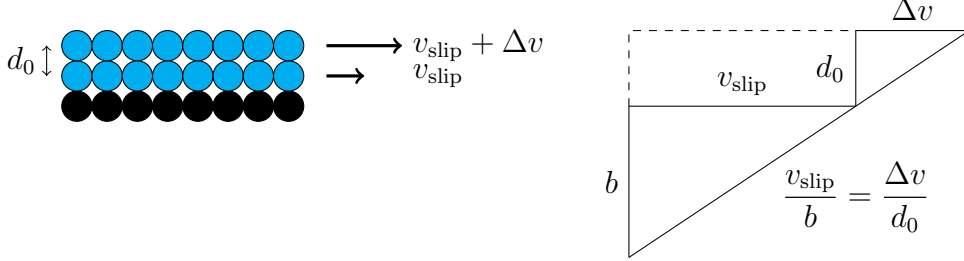


Figure 1.3: Deriving a slip length from a molecular slip experiment.

The similar triangles relation and the force balance equation give us:

$$v_{\text{slip}} = \frac{b}{d_0} \Delta v \quad \text{and} \quad v_{\text{slip}} = \frac{\mu_{ll}}{\mu_{ls}} \Delta v \quad (1.2)$$

Therefore:

$$b = \frac{\mu_{ll}}{\mu_{ls}} d_0 \quad (1.3)$$

Plugging in the numbers yields:

$$b = \frac{1}{18} 0.95 \text{ nm} = 0.05 \text{ nm} \quad (1.4)$$

If the data and model are correct, then Becker and Mugele have detected molecular slip with a slip length approximately 1/20th that of the molecule size. While small, this non-zero slip length shows that at least in the confined geometry of this experiment, the silicone molecules are not sticking to the walls.

### 1.2.2 Conclusions

These modern, sophisticated experiments investigate slip on atomically flat — rms roughness  $< 1$  nanometer — solid surfaces, with efforts made to reduce contamination by nanobubbles. They show no slip on hydrophilic surfaces. For the hydrophobic case, an undeniable intrinsic slip length is present. Two different particle velocimetry studies put an upper limit on

intrinsic slip length on the order of 100 nm. Four different techniques produce results consistent with a slip length in the range  $18 \pm 6$  nanometers, at least for moderate shear rates.

In general, no experiment provides direct evidence of molecular slip in water, but these experiments eliminate various confounding factors, leaving molecular slip as a distinct possibility.

## 1.3 Theoretical Intrinsic Slip

Theoretical arguments for or against slip are somewhat thin on the ground. Computer experiments, in the form of molecular dynamics (MD) simulations, form the backbone of theoretical work.

### Molecular Dynamics

Molecular Dynamics simulations involve the computer simulation of systems of particles governed by Newtonian mechanics. Each particle has a position and momentum, and a net force on it due to the interaction with neighbouring particles. Time is sliced into discrete timesteps. At each timestep, the force on each particle is calculated, then the (instantaneous) acceleration, then the resulting translation. Then the position of each and every particle is updated simultaneously, using the calculated translations. The process is then repeated at the next timestep.

The technique is rightly called a computer *experiment*, since the global behaviour is not predictable in advance. Emergent phenomena such as melting, crystallization, annealing, etc. have been very successfully studied with MD.

Molecular Dynamics simulations differ in their choice of interaction. A very popular choice is the Lennard-Jones interaction, because it is computationally cheap and physically sound: the interaction features an equilibrium distance  $\sigma$  between the particles, a strong repulsion at shorter distances, and

a weak attraction at longer distances. This models dipole-dipole Van der Waals forces quite well.

Since the power of MD studies depends on Moore's Law, the first serious MD study of the fluid boundary condition appeared in 1990, a paper by Thompson and Robbins [19]. This featured a Lennard-Jones fluid under Couette shear, in conditions equivalent to a compressed fluid about 30% above melting temperature. This was a qualitative study of the effects of varying two parameters: the wall-fluid interaction strength,  $\epsilon_{wf}$ , and the wall *density*.

The wall is composed of stationary atoms. The separation between them can be arbitrarily set to any fraction or multiple of  $\sigma$ . The wall density is the inverse of separation distance. As the wall density tends to infinity, (separation diminishes to zero), the wall structure asymptotes to a flat plane. In this case, the force between fluid atom and wall is always *perpendicular* to the wall. With no tangential component, the force cannot change the tangential momentum of an incident particle. This is the case of perfect slip, as shown in Figure (1.4). Thompson & Robbins confirm that perfect slip holds, regardless of the strength of  $\epsilon_{wf}$ .

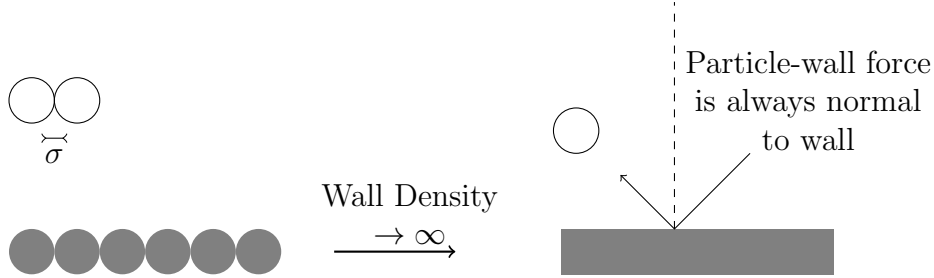


Figure 1.4: Infinite density of wall atoms leads to perfect slip.



As the wall density decreases, the wall gains some ‘texture’, and fluid atoms can be given a sideways kick by the peaks of the wall. Momentum transfer is now possible, and perfect slip no longer holds. When the wall density is equal to fluid density, (wall atom separation is  $\sigma$ ), Thompson & Robbins observe the no-slip condition. At equal density, fluid atoms can attach epitaxially to the wall. If  $\epsilon_{wf}$  is strong enough, one or two layers of fluid atoms lock to the wall. This is illustrated in Figure (1.5).

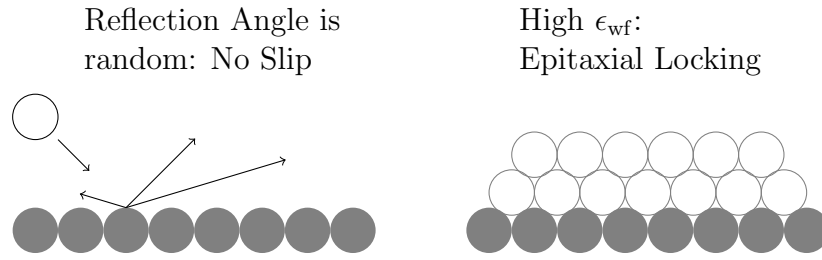


Figure 1.5: Wall atom separation equal to fluid atom diameter.

At a wall density of 2.52 times the fluid density (solid atom separation is  $0.397 \sigma$ ), Thompson & Robbins found that fluid layering was reduced, and slip increased. At higher  $\epsilon_{wf}$ , however, the fluid atoms again formed a close-packed layer, but with a periodic structure that was a harmonic of the wall structure. At the highest  $\epsilon_{wf}$ , the fluid atoms locked epitaxially to the wall, in a state of elastic strain. See Figure (1.6).

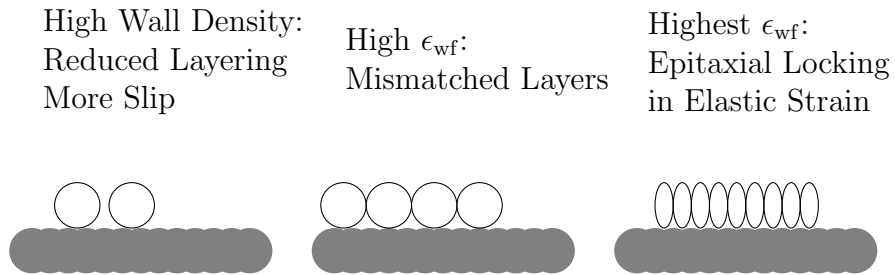


Figure 1.6: Wall atom separation  $0.4 \times$  fluid atom diameter.

Following this qualitative work, Thompson and Troian report some quantitative results from very similar Lennard-Jones simulations in 1997 [20]. Again they vary the wall density  $\rho_{\text{wf}}$  and  $\epsilon_{\text{wf}}$ , (as a fraction of  $\epsilon$ , the fluid-fluid interaction strength) as well as  $\sigma_{\text{wf}}$ , the equilibrium distance of wall and fluid atoms. Slip lengths in units of  $\sigma$  are calculated for various regimes, and appear in Table (1.1).

Table 1.1: Slip lengths (units of  $\sigma$ ) for various simulation parameters.

| $\epsilon_{\text{wf}}$ | $\sigma_{\text{wf}}$ | $\rho_{\text{wf}}$ | $b$ |
|------------------------|----------------------|--------------------|-----|
| 0.6                    | 1.0                  | 1                  | 0   |
| 0.1                    | 1.0                  | 1                  | 2   |
| 0.6                    | 0.75                 | 4                  | 4   |
| 0.4                    | 0.75                 | 4                  | 8   |
| 0.2                    | 0.75                 | 4                  | 18  |

Now,  $\epsilon_{\text{wf}} < \epsilon$  means that a fluid atom is more attracted to other fluid atoms than to the wall. This could imply hydrophobicity; in general, hydrophobicity increases as  $\epsilon_{\text{wf}}$  decreases. The top line of Table (1.1) describes the case where the fluid-solid and solid-solid equilibrium distances are equal to the fluid-fluid equilibrium distance. In this case, the fluid can lock epitaxially to the solid with absolutely no elastic strain. Here, no slip is recorded ( $b = 0$ ) even though the fluid-wall interaction  $\epsilon_{\text{wf}} = 0.6$  suggests a mildly hydrophobic surface. Table (1.1) also shows that if the density of stable attachment sites is too high for epitaxial locking ( $\rho_{\text{wf}} > 1$ ), then slip results.

But the real story is the shear dependence of slip. The fluid is in a Couette flow regime, with top and bottom surfaces moving with equal and opposite velocities. At low shear rates, the slip length is a constant plateau, but at some critical shear rate, the slip length diverges. The critical shear rate depends on the regime. Interestingly, if the shear rates are normalised to their critical shear rate, and the slip lengths normalised to their plateau value, then the slip length versus shear rate data for all regimes lie *on a single curve*.

Thompson & Troian attempt to explain this “remarkable collapse of the data” with a single parameter  $R$  describing the roughness of the potential surface. A test particle at a fixed height experiences a potential  $\phi(x, y)$ . Define  $A$  as the area integral of  $\phi(x, y)$ , and  $A_\infty$  as the area integral of the limiting case of a flat plane (infinite atom density). Then

$$R = \frac{A}{A_\infty} - 1 \quad (1.5)$$

With a wall moving at velocity  $v$ , a test particle experiences perfect slip for  $v > v_c$ , some critical velocity. They find that  $v_c$  scales as  $R^{1/2}$  for a wide range of parameters. In the real fluid (with hundreds of particles) they find  $v_c$  scales as a power of  $R$  with an exponent close to  $3/4$ .

Thompson & Troian think it is reasonable to assume that  $v_c$  is set by the liquid-solid interaction timescale, so that increasing density should lead to larger  $v_c$ . They are surprised to find the reverse.

But this is an odd expectation. Assuming that the average approach velocity of impacting particles remains the same, a faster-moving or more dense surface increases the probability that the particle will interact with a peak. Since the peaks are the ‘flattest’ parts of the surface, the particle has a greater chance of being deflected by a force that is closer-to-normal to the surface plane, which will not change the tangential momentum of the particle as much. This implies increased slip.

Barrat and Bocquet [2] study flow in both Poiseuille and Couette regimes, using a Lennard-Jones fluid with an additional  $c_{ij}$  parameter:

$$v_{ij} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - c_{ij} \left( \frac{\sigma}{r} \right)^6 \right] \quad (1.6)$$

They use  $c_{FF} = 1.2$  for fluid-fluid interactions, making the fluid more cohesive than the usual Lennard-Jones fluid. They tweak the wetting properties via the  $c_{FS}$  fluid-solid parameter. There are several ways to calculate the contact angle from this parameter. The most accurate way gives  $c_{FS} = 0.5 \rightarrow \theta = 140^\circ$  and  $c_{FS} = 1.0 \rightarrow \theta = 90^\circ$ .

A hydrophobic liquid ( $\theta = 140^\circ$ ) requires a pressure  $P_0$  to pump it down the pipe. At high pressure,  $P/P_0 = 16.4$ , the fluid exhibited the same higher-density layering at the wall as seen in hydrophilic liquids. At a lower pressure, the fluid showed a **strong density depletion** near the wall. The slip length varied tremendously over this pressure range: from  $b = 8\sigma$  for  $P/P_0 = 16.4$  to over  $40\sigma$  for  $P/P_0 \sim 0$ .

Less hydrophobic fluids showed less slip, and less pressure dependence. A  $c_{FS} > 0.7$  ( $\theta \leq 120^\circ$ ) gave slip lengths of a couple of  $\sigma$  only.

Note that the position of the hydrodynamic boundary was treated as an adjustable parameter. It turned out to be located one atom width into the liquid. The arbitrary nature of the boundary position was not fully appreciated by the experimental community until almost 10 years after this sort of theoretical paper.

### Correlation Function Tuned by Molecular Dynamics

In a theoretical study [5], Bocquet and Barrat start by constructing a phenomenological model of a fluid: Each infinitesimal volume of fluid has a *momentum*. This momentum field is subject to fluctuations, which quickly dissipate, obeying the diffusion equation. Further, any pressure gradient is proportional to the gradient of momentum divergence. Incorporating density  $\rho_0$ , shear viscosity  $\eta$ , bulk viscosity  $\xi$ , and dividing through by the volume element to get a momentum *density*,  $\vec{j}(\vec{r}, t)$ , in the bulk:

$$\partial_t \vec{j} + \nabla P - \frac{\xi + \eta/3}{\rho_0} \nabla[\nabla \cdot \vec{j}] - \frac{\eta}{\rho_0} \nabla^2 \vec{j} = 0 \quad (1.7)$$

And on the boundary, Navier slip holds:

$$\vec{j}_\parallel = b_{\text{wall}} \frac{\partial}{\partial \vec{n}} \vec{j}_\parallel, \quad \vec{j}_\perp = 0 \quad (1.8)$$

Bocquet & Barrat now consider a fluid contained between two  $x, y$  planes separated by distance  $h$ . Slip lengths  $b_0$  and  $b_h$  hold on the lower and upper planes, respectively.

A great simplification is to introduce the ‘transverse momentum density’:

$$j_x(z, t) = \frac{1}{L_x L_y} \int \int dx dy j_x(\vec{r}, t) \quad (1.9)$$

And similarly for  $j_y(z, t)$ .

With the pressure gradient essentially integrated out, this field obeys the diffusion equation + Navier slip conditions:

$$\left[ \partial_t - \frac{\eta}{\rho_0} \partial_z^2 \right] j_x(z, t) = 0 \quad (1.10)$$

$$j_x(z, t)|_{z=z_0} = b_0 \partial_z j_x(z, t)|_{z=z_0}, \quad j_x(z, t)|_{z=z_0+h} = -b_h \partial_z j_x(z, t)|_{z=z_0+h} \quad (1.11)$$

Work with the time-dependent correlation function:

$$C(z, z', t) = \langle j_x(z, t), j_x(z', 0) \rangle \quad (1.12)$$

where angle brackets denote a thermodynamic average.

Finally, this equilibrium correlation function also obeys the diffusion and Navier slip equations:

$$\left[ \partial_t - \frac{\eta}{\rho_0} \partial_z^2 \right] C(z, z', t) = 0 \quad : \quad 0 < z < z_0 + h \quad (1.13)$$

$$C(z, z', t)|_{z=z_0} = b_0 \partial_z C(z, z', t)|_{z=z_0} \quad (1.14)$$

$$C(z, z', t)|_{z=z_0+h} = -b_h \partial_z C(z, z', t)|_{z=z_0+h} \quad (1.15)$$

There is a general solution (details omitted):

$$C(z, z', t) = f(b_0, b_h, h) \quad (1.16)$$

That is, the correlation function is a function of *slip length* and *channel width*. The parameter ‘channel width’ is equivalent to ‘effective position of the boundary condition’. Bocquet & Barrat note that in Couette flow, the two parameters are not independent, but in general may be.

Now, one can directly observe a molecular dynamics simulation, and calculate the correlation function from the atomistic dynamics that occur in the simulation. Bocquet & Barrat carry out an equilibrium MD simulation — no shear or pressure, just thermal motion — and compute the correlation function. The parameters of the theoretical correlation function are adjusted to fit the MD correlation function.

Thus, a slip length and effective boundary position are derived from MD, without inducing and measuring velocities, therefore eliminating shear dependence from the slip effect.

The first MD experiment used a repulsive-only fluid/wall interaction – a ‘soft sphere’ model. The wall had a corrugation with wavelength of  $1\sigma$ , and a varying amplitude. Results for various amplitudes are shown in Table (1.2).

Table 1.2: Slip lengths for different amplitudes of wall corrugation.

| Amplitude | Slip Length     | BC Position |
|-----------|-----------------|-------------|
| 0 (flat)  | $\infty$        | 1.60        |
| 0.01      | $40 \pm 2.5$    | 1.60        |
| 0.02      | $7.20 \pm 0.05$ | 1.60        |
| $> 0.03$  | $0.00 \pm 0.02$ | 1.60        |

The remarkable result is that even a tiny corrugation — depth  $0.03\sigma$  — is enough to completely suppress slip. Also, the hydrodynamic BC is located about one atom width inside the fluid.

A second Lennard-Jones MD simulation with a corrugation depth of  $0.2\sigma$  was done. Particles locked epitaxially to the solid, with zero slip, and a BC located two atom widths inside the fluid.

As a final test, Bocquet & Barrat do a conventional Couette flow MD simulation, extracting velocity profiles to infer slip lengths. The results agreed with the equilibrium method.

### Depletion Layer and Drainage Force

In a landmark paper from 1995 [22], Olga Vinogradova studied the ‘drainage of a thin liquid film confined between hydrophobic surfaces’. The results are in two main parts.

#### THE BOUNDARY CONDITIONS ON THE HYDROPHOBIC SURFACE:

Vinogradova looks at the two candidates for intrinsic slip: molecular slip and apparent slip. She notes that molecular slip was first proposed by Tolstoi back in 1952; his theories were revisited by Blake in 1990, who predicted the slip effect on flow rate in a capillary. These predictions sometimes matched experiment, but Ruckenstein and Rajora in 1993 noted that the implied surface diffusion coefficients are several orders of magnitude larger than those observed even for gases.

Having found evidence for molecular slip wanting, she considers apparent slip. A ‘gas gap’ has been suggested as the cause, but this is not experimentally confirmed. Another model of apparent slip is the decrease in viscosity in a boundary layer close to the hydrophobic surface. Crucially, she states: “this fact follows from numerical simulation data, as well as from the direct experimental results obtained by the blowoff method. (Derjaguin *et al* 1993)”. From this firm foundation, Vinogradova notes that if the boundary layer of thickness  $\delta$  has an average viscosity  $\mu_{\text{slip}}$ , smaller than the bulk viscosity  $\mu_{\text{bulk}}$ , then an order of magnitude estimate of apparent slip length is:

$$b = \delta \left( \frac{\mu_{\text{bulk}}}{\mu_{\text{slip}}} - 1 \right) \quad (1.17)$$

This model covers the case of bubbles on the surface, and Vinogradova observes that much experimental slip may be due to dissolved gas, causing bubbles to form on the surface or in microcavities.

**SOLUTION OF THE DRAINAGE PROBLEM:**

Vinogradova considers two perfectly spherical (no roughness) solids being squeezed together at (instantaneous) velocity  $v$  in a Newtonian fluid of viscosity  $\mu$ . The two spheres have radii  $R_1$  and  $R_2$ , and slip lengths  $b$  and  $b(1+k)$  on their surfaces, respectively. She derives a formula for the drainage force  $F_z$  in terms of separation  $h$ :

$$F_z = -\frac{6\pi R_e^2 \mu v}{h} f^* \quad \text{where} \quad R_e = \frac{R_1 R_2}{R_1 + R_2} = \frac{R_1}{\frac{R_1}{R_2} + 1} \quad (1.18)$$

In the limiting case of a hydrophobic sphere interacting with a similar one:

$$f^* = (2) \frac{h}{6b} \left[ \left( 1 + \frac{h}{6b} \right) \ln \left( 1 + \frac{6b}{h} \right) - 1 \right] \quad (1.19)$$

Note that  $R_e = R_1$  in the case of a sphere approaching a flat plane ( $R_2 = \infty$ ).

This formula has been used by the experimental community in all subsequent drainage force experiments.

**Depletion Layer as a Gas Layer**

In paper from 2002 in Langmuir [9], de Gennes derives the slip length expected of a hypothetical gas layer. De Gennes finds the then-recent very high experimental slip lengths “unexpected and stimulating.” (These experiments are now suspected of being contaminated with bubbles; de Gennes is thus prescient in his gas layer theory.) “This led us to think about unusual processes which could take place near a wall. In this Letter, we discuss one (remote) possibility: the formation of a gaseous film at the solid/liquid interface.

“The source of the film is unclear: when the contact angle is large ( $\theta \rightarrow 180^\circ$ ), a type of flat bubble can form at the surface with a relatively low energy. But this energy is still high compared to the thermal energy  $k_B T$ .”

With these caveats stated, de Gennes derives the slip length expected for a bulk fluid of viscosity  $\eta$ , sliding over a gas layer of density  $\rho$ , and uniform



thickness  $h$ . Layer thickness  $h$  is assumed to be greater than the molecule size, but smaller than the mean free path in the gas.

Unfortunately, there are a few issues: there seem to be several typographical errors, and the result is stated in terms of the somewhat unfamiliar  $\bar{v}_z$ , which is defined as the mean **absolute value** of the normal component of gas particle velocity (the simple mean is zero). To resolve the inconsistencies, and restate the result in a more standard way, in Appendix A we derive the result from scratch, in terms of the mean *speed* in the gas,  $\bar{v}$ . We find:

$$b = \frac{4\eta}{\rho\bar{v}} \quad (1.20)$$

(We show that this is equivalent to the result of de Gennes.)

Note that  $b = 4\eta/\rho\bar{v}$  is the slip length parameter found in the boundary condition located at the **bottom of the fluid**. If  $b$  is instead regarded as a property of the *solid* surface, then the gas layer thickness  $h$  must be subtracted. We shall see that this is negligible:

Plugging in typical values:  $\rho = 1 \text{ kg/m}^3$ ,  $\bar{v} = 476 \text{ m/s}$ ,  $\eta = 10^{-3} \text{ kg/ms}$ , we get  $b = 8 \text{ }\mu\text{m}$ . De Gennes: “Thus, a gas film can indeed give a very large slip length. Our calculation assumed complete thermalization at each particle/boundary collision. If we had some nonzero reflectance (especially on the solid surface), this would increase  $b$  even more.”

De Gennes notes that the amount of gas required is very small, but that a “process which could generate such films remains obscure.” Serendipitously, the very next year, Andrienko *et al* proposed an abstract description of just such a process.

### Phase Separation causing a Depletion Layer

The depletion layer theory of slip was given another boost by Andrienko *et al* in a 2003 paper [1]. Rather than focusing on what the low-viscosity boundary *is*, they take an agnostic, abstract approach: They considered a toy model of a generic admixture of two different fluids, whose viscosities differ by the (arbitrary) ratio 1:3. A ‘phase field’ approach was used, in which an order parameter  $\phi$  varies over space. Here,  $\phi$  was the fraction of low-viscosity fluid in an infinitesimal volume.

The unmixing of the fluid is driven by energy. Andrienko *et al* start with a free energy functional — the semigrand potential. With this functional set up, they consider the physical case of Couette flow between two fairly close plates. Variation of the functional yields an Euler-Lagrange equation and a boundary condition.

These equations were solved numerically using the relaxation method. With the  $\phi$  field solution, the viscosity field was obtained by simply assuming that viscosity is a linear combination of the pure viscosities. Finally the Couette flow field was solved for the viscosity field.

The big result is that above a certain temperature, a layer of the low-viscosity fluid suddenly forms on the surface. Andrienko *et al* call this a ‘prewetting transition’. This causes the sudden emergence of a significant slip length. As temperature increases above this critical temperature, more mixing occurs, reducing the viscosity contrast, thus reducing slip length.

Andrienko *et al* believe this mean-field toy model to be valid for liquid-gas systems, binary mixtures, and polymer mixtures in the long wavelength approximation. Thus, large slip is predicted for those systems.

## 1.4 Conclusions

There exist a few recent experimental studies confirming intrinsic slip over hydrophobic surfaces, where the solid surface is flat – less than 1 nm rms roughness – and care has been taken to minimise contamination by nanobubbles.

The drainage force experiment of Cottin-Bizonne *et al* in 2005 [7] featured a resolution of 1 Angstrom for the probe to surface distance. They found a slip length of  $19 \pm 2$  nm. This is consistent with the particle velocimetry experiments of Joly *et al* of 2006 [13], which estimated the diffusion coefficient of unmoving water, thus eliminating issues of shear-induced bubble formation. The model fitted to the results implied a slip length of  $18 \pm 5$  nm. More conventional particle velocimetry experiments by Huang *et al* in 2006 [12] with degassed water showed a shear-dependent slip length. Given the experimental uncertainties, they present an upper limit of 150 nm for the slip length. Vinogradova in 2009 [21] noted that shear flow can increase the effective diffusivity of particles in the velocimetry experiment. Her calculations from her experimental results take this into account, yielding a slip length of no more than 80 - 100 nm for hydrophobic capillaries.

On the theoretical side, intrinsic slip is observed in molecular dynamics simulations [19], [20], [2], [5]. At sufficiently low pressure in the liquid, Barrat and Bocquet observe a depletion layer – a layer of lower-than-bulk density liquid at the solid surface [2]. The effect of a density layer was explored by de Gennes in 2002 [9]. He shows that observed slip effects are explainable by a gas layer one or two atoms thick at the surface. Andrienko *et al* in 2003 [1] presented a model of a binary mixture of high and low viscosity fluids. In the model, above a certain temperature, a depletion layer spontaneously formed on the surface.

In the next chapter, we turn to flow over mixed-slip surfaces, where the intrinsic slip length is different on different parts of the surface.



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