

# Chapter 1

## De Gennes's Gas Kinetic Theory of Slip

We seek to replicate the work of de Gennes. In his elegant little paper in *Langmuir* from 2002, entitled simply “On Fluid/Wall Slippage” [1], he presented a gas kinetic expression for slip length. However, the paper seems to contain a few typographical errors, and the result is stated in terms of the non-standard quantity  $\bar{v}_z$ , which is apparently defined as the average of the *absolute value* of the  $z$  component of velocity.

As an exercise, we derive the expression from scratch using the more standard scalar quantity of particle *speed*,  $v$ , with our final expression in terms of average speed  $\bar{v}$ . We show that our results ultimately agree with those of de Gennes.

We start by figuring out the number of gas molecules hitting a surface per second, then calculate the momentum transferred per second, yielding a shear stress, from which a slip length follows.

## 1.1 Particle Flux

Consider a gas of density  $\rho$ . If the mass of each particle is  $m$ , then the *number* density of the gas is  $\rho/m$ . This has units of number per cubic meter, and is therefore a concentration,  $C$ .

Each particle in the gas has a different velocity. The directions of motion will be uniformly distributed over all solid angles. In an ideal gas, the speeds come from the Maxwell-Boltzmann distribution. In general, the gas has some speed probability distribution  $P(v)$ , in the frequentist sense that fraction  $P(v)$  of all atoms have speed  $v$ .

Our strategy is to split the gas into separate ensembles of particles, each ensemble defined as a group of particles **all with the same speed**  $v_{\text{ens}}$ . At the end of the derivation, we will sum over all ensembles – for now we work with a single arbitrary ensemble, identified by its speed  $v_{\text{ens}}$ .

Consider a layer of gas over some area  $A$  on the surface. Let the layer width be  $l$ , where  $l$  is well under the *mean free path* in the gas. So, particles within the layer are sparsely distributed, and we can assume they do not interact.

There are  $CA l$  molecules in the layer, and fraction  $P(v_{\text{ens}})$  of them have speed  $v_{\text{ens}}$ . Thus, the ensemble indexed by  $v_{\text{ens}}$  contributes

$$CA l P(v_{\text{ens}}) \tag{1.1}$$

atoms to the layer.

We are interested in how many atoms **from the layer** hit the surface in some timeslice; during the time interval, we do not want outside atoms to enter the layer then hit the surface. To ensure this, we define an ‘isolation’ time:

First, define the layer to be the *closed* interval  $z \in [0, l]$ ; then an atom at distance  $l$  from the wall is the *outermost* atom in the layer.

Such an atom, at distance  $l$  from the wall, travelling via the shortest path to the wall, i.e. perpendicular to the wall, will hit the wall in time:

$$t_0 = \frac{l}{v_{\text{ens}}} \quad (1.2)$$

Therefore, any atom outside the layer – further than  $l$  from the wall – cannot hit the wall in time  $t_0$ . So  $t_0$  is the isolation time we need.

By construction, in time  $t_0$ , each ensemble atom travels distance  $l$  (in a random direction).

Now, we want to know what fraction of the ensemble atoms in the layer hit the wall in time interval  $t_0$ .

Consider a sphere of radius  $l$  centred on an atom. The surface of the  $l$ -sphere is the set of all possible positions of the atom after time  $t_0$ . The probability that an atom hits the wall is equal to the fraction of the area of the  $l$ -sphere that intersects the wall. This area of intersection depends on the distance  $h$  that the  $l$ -sphere protrudes into the wall. See Figure (1.1).

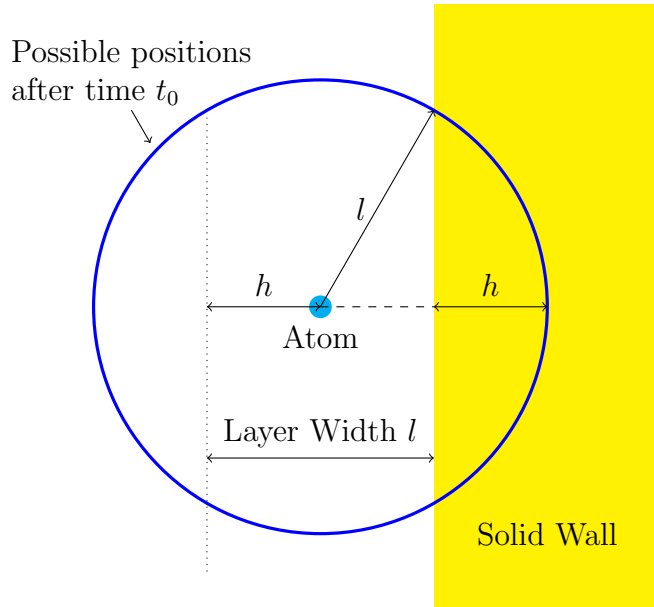


Figure 1.1: Some fraction of the  $l$ -sphere intersects the wall.

Area of sphere:  $4\pi l^2$

Area of spherical cap:  $2\pi lh$

$\therefore$  fraction of spherical surface inside solid is:

$$\phi(h) = \frac{2\pi lh}{4\pi l^2} = \frac{h}{2l} \quad (1.3)$$

The distance  $h$  that the sphere penetrates into the wall is equal to the distance from the layer boundary to the atom's starting position. So,  $h$  varies from 0 to  $l$ , as the starting position of the atom may be anywhere between the layer boundary and the solid wall.

For a group of atoms with starting position a distance  $h$  inside the layer, we know what fraction of them hit the wall. To find the fraction for *all* atoms in the layer, we *average* over all positions in the layer. That is, we integrate  $\phi(h)$  over the layer, and divide by domain size  $l$ :

$$\phi = \frac{1}{l} \int_0^l \frac{h}{2l} dh = \frac{1}{2l^2} \int_0^l h dh = \frac{1}{2l^2} \left[ \frac{1}{2} h^2 \right]_0^l = \frac{1}{4l^2} [l^2 - 0] = \frac{1}{4} \quad (1.4)$$

So, in time interval  $t_0$ ,  $1/4$  of ensemble atoms within the layer hit the wall.

Recall that the number of *ensemble* atoms in the layer is  $CAlP(v_{\text{ens}})$ , thus, the number hitting area  $A$  per second is:

$$\frac{\frac{1}{4}CAlP(v_{\text{ens}})}{t_0} = \frac{\frac{1}{4}CAlP(v_{\text{ens}})}{\frac{l}{v_{\text{ens}}}} = \frac{1}{4}CAP(v_{\text{ens}})v_{\text{ens}} \quad (1.5)$$

Note that layer width  $l$  has cancelled out.

Define the 'ensemble flux' as the number of particles with given speed  $v_{\text{ens}}$  hitting the wall per second per unit area:

$$F(v_{\text{ens}}) = \frac{1}{4}CP(v_{\text{ens}})v_{\text{ens}} \quad (1.6)$$

To find the *total* number of atoms hitting of *all* speeds, we simply need to integrate over all speeds. In other words, sum over all possible ensembles:

$$F = \int_0^\infty F(v) dv = \int_0^\infty \frac{1}{4} C P(v_{\text{ens}}) v_{\text{ens}} dv = \frac{C}{4} \int_0^\infty P(v_{\text{ens}}) v_{\text{ens}} dv \quad (1.7)$$

Now – here’s the cunning bit – the construction  $\int P(v_{\text{ens}}) v_{\text{ens}} dv$  is just the *average* of  $v$ , denoted  $\bar{v}$ . Hence:

$$F = \frac{1}{4} C \bar{v} \quad (1.8)$$

Note that we did *not* need to know the specific statistical mechanical probability distribution for the particle speeds.

In the next section, we deal with the momentum of gas particles, so it is expedient to express concentration as  $C = \rho/m$ , where  $m$  is the mass of a gas particle. Then the flux is:

$$F = \frac{\rho \bar{v}}{4m} \quad (1.9)$$

## 1.2 Lateral Momentum Transfer = Shear Stress

Consider a bulk of water separated from a solid surface by a very thin gas layer of thickness  $l$ . Assume  $l$  is less than the mean free path in the gas, so that the previous analysis is valid.

Assume that the water bulk is moving, and that the bottom surface (facing the gas) has a constant tangential velocity  $v_s$ .

The gas is a vapour of liquid molecules, detaching and reattaching from the bulk liquid. Each molecule detaches from the liquid in a random direction, with an *average* tangential velocity of  $v_s$ . Each atom has mass  $m$ , so has average lateral momentum  $mv_s$ . Each atom subsequently hits the solid surface, and sticks to the surface – an inelastic collision that transfers all of momentum  $mv_s$  to the surface. See Figure (1.2)

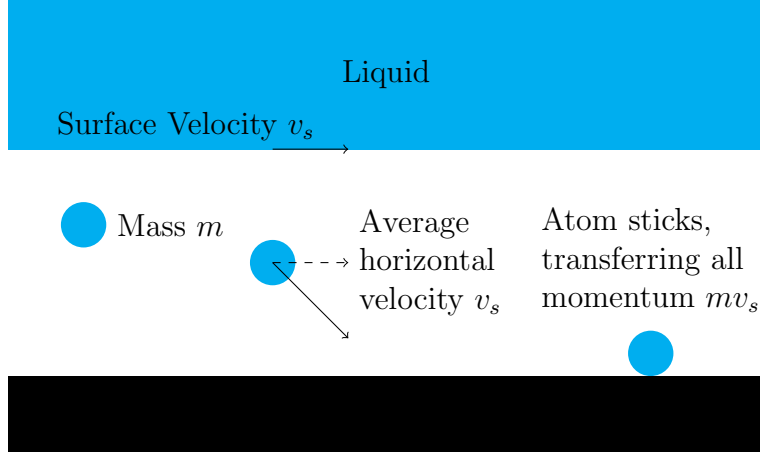


Figure 1.2: Each incident atom transfers average momentum  $mv_s$  to the solid surface.

Recall, the number of particles hitting the solid surface is  $\rho\bar{v}/4m$  per second per area.

Thus, momentum transferred to the surface per second per area:

$$\frac{1}{A} \frac{dP}{dt} = \frac{\rho\bar{v}}{4m} mv_s = \frac{1}{4} \rho\bar{v}v_s \quad (1.10)$$

This force per unit area is a *shear stress*:

$$\sigma = \frac{1}{4} \rho\bar{v}v_s \quad (1.11)$$

Now, a velocity gradient in the bulk of a *viscous* fluid of viscosity  $\eta$  causes a shear stress:

$$\sigma = \eta \left| \frac{dv(z)}{dz} \right| \quad (1.12)$$

At the surface, however,  $dv/dz$  may be infinite, so surface shear stress may be better conceptualized — by analogy with solid-solid friction — with a friction coefficient  $k$ :

$$\sigma = kv_s \quad (1.13)$$

Equating the gas kinetic shear stress with the frictive shear stress:

$$\sigma = kv_s = \frac{1}{4} \rho\bar{v}v_s \quad \Rightarrow \quad k = \frac{1}{4} \rho\bar{v} \quad (1.14)$$

Alternatively, since  $dv/dz$  is defined *above* the surface, we may extrapolate  $dv/dz$  down into the surface, getting the Navier slip condition:

$$v_s = b \left| \frac{dv(z)}{dz} \right| \quad (1.15)$$

Equating frictive and viscous shear stresses, and substituting  $v_s$ :

$$\sigma = kv_s = kb \left| \frac{dv(z)}{dz} \right| = \eta \left| \frac{dv(z)}{dz} \right| \quad (1.16)$$

Therefore, quite generally:

$$b = \frac{\eta}{k} \quad (1.17)$$

And for our de Gennes-inspired gas kinetic theory:

$$b = \frac{4\eta}{\rho\bar{v}} \quad (1.18)$$

This is the slip length in the Navier slip boundary condition as experienced by the fluid at the **bottom of the liquid**. If we consider the slip length to be a parameter of the **solid** surface, then we must subtract the gas layer thickness  $l$ :

$$b = -l + \frac{4\eta}{\rho\bar{v}} \quad (1.19)$$

If the gas layer is only a few atom diameters thick, then  $l < 1$  nm, and is therefore negligible.

de Gennes himself says:

$$b = -l + \frac{\eta}{\rho\bar{v}_z} \simeq \frac{\eta}{\rho\bar{v}_z} \quad (1.20)$$

— Note that I have corrected what I think are typos; his original paper says:

$$b = -l + \frac{\eta}{\rho\bar{v}_x} \simeq \frac{\eta}{\rho\bar{v}_z} \quad (1.21)$$

### 1.3 Reconciling with de Gennes

We use average speed (in any direction)  $\bar{v}$ . De Gennes used average speed *in the  $z$  direction*,  $\bar{v}_z$ .

$$\text{We have shown: } b \simeq \frac{4\eta}{\rho\bar{v}}, \quad \text{de Gennes claims: } b \simeq \frac{\eta}{\rho\bar{v}_z} \quad (1.22)$$

If

$$\bar{v} = 4\bar{v}_z \quad (1.23)$$

then our analyses are in perfect agreement.

De Gennes defines  $\bar{v}_z$  like this:

$$\bar{v}_z = \int_0^\infty \frac{1}{(2\pi)^{1/2}v_{\text{th}}} v_z e^{-v_z^2/2v_{\text{th}}^2} dv_z = v_{\text{th}}/(2\pi)^{1/2} \quad (1.24)$$

where  $v_{\text{th}}^2 = kT/m$ .

That is:

$$\bar{v}_z = \int_0^\infty \sqrt{\frac{m}{2\pi kT}} v_z e^{-\frac{1}{2}\frac{mv_z^2}{kT}} dv_z = \sqrt{\frac{kT}{2\pi m}} \quad (1.25)$$

Now, in the Maxwell-Boltzmann statistics for an ideal gas, the distribution of a given *component* of velocity is:

$$f_v(v_z) = \sqrt{\frac{m}{2\pi kT}} \exp\left[\frac{-mv_z^2}{2kT}\right] \quad (1.26)$$

which is clearly what de Gennes is playing with.

This is a Gaussian distribution, therefore the average of  $v_z$ , given by  $\int_{-\infty}^\infty f_v(v_z)v_z dv_z$  is **zero**.

Hence, de Gennes's definition  $\bar{v}_z = \int_0^\infty f_v(v_z)v_z dv_z$  is the average of the **absolute value** of  $v_z$ .

So to reconcile. The Maxwell-Boltzmann statistics yield an average value of the particle speed:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad (1.27)$$



which is:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{16kT}{2\pi m}} = \sqrt{16} \sqrt{\frac{kT}{2\pi m}} = 4 \sqrt{\frac{kT}{2\pi m}} = 4\bar{v}_z \quad (1.28)$$

So we have found that  $\bar{v} = 4\bar{v}_z$ , hence our analysis and that of de Gennes reconcile perfectly. Therefore

$$b \simeq \frac{4\eta}{\rho\bar{v}} = \frac{\eta}{\rho\bar{v}_z} \quad (1.29)$$



# Bibliography

- [1] P. G. de Gennes. On fluid/wall slippage. *Langmuir*, 18:3413–3414, 2002.