

# Elements of Kinetic Theory

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## 1 Introduction

Kinetic theory treats gases as collections of small, perfectly elastic, particles in motion. Note that the assumption of perfect elasticity means that kinetic theory in its simplest form will not allow interchange of energy between the kinetic

energy of the translation motion of the particle (atom or molecule) and its internal degrees of freedom. This is not a good assumption as far as internal molecular vibrations are concerned (energies of order 0.1 eV, comparable with  $kT$ ), but is reasonable, except in extreme conditions tending towards plasmas, for electronic excitations (energies several eV).

## 2 Basic Kinetic Theory

In the simplest model, the following assumptions are made:

1. the gas consists of identical molecules, each of mass  $m$ ;
2. the molecules have zero size, and do not collide with one another;
3. the molecules do not exert any forces on one another;
4. the molecules move at random within the gas and collide elastically with the walls of their containment.

### 2.1 Gas pressure

The pressure is most easily evaluated by imagining the gas to comprise  $N$  molecules contained in a cubic box of side  $L$ , with the total velocity  $\mathbf{v} = (v_x, v_y, v_z)$ . When a molecule strikes a wall, it rebounds with its components of velocity parallel to the wall unchanged and its velocity perpendicular to the wall reversed. Thus a molecule  $i$  with an  $x$  component of velocity  $v_x^{(i)}$  will make  $v_x^{(i)}/2L$  impacts per second on each wall perpendicular to  $x$ , in each of which the change of momentum will be  $2mv_x^{(i)}$ . Thus the change in momentum per unit time, or force, is  $mv_x^{(i)}/L$ , arising from this molecule. If we now sum over all the molecules, noting that  $\sum_i v_x^{(i)2} = N\overline{v_x^2}$ , we find the total force on each wall to be  $Nm\overline{v_x^2}/L$ , corresponding to a pressure  $Nm\overline{v_x^2}/L^3$ , or if we write the number density  $N/L^3$  as  $n$ ,  $n\overline{mv_x^2}$ .

Now we may invoke the isotropy of the system, which tells us that there is no preferred direction and thus

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} (\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \overline{v^2} \quad (1)$$

for the average over all the molecules, and so we have for the pressure

$$p = \frac{1}{3} n m \overline{v^2}. \quad (2)$$

## 2.2 Temperature

Immediately, we may write  $L^3$  as the volume  $V$ , and write  $pV = \frac{1}{3}Nm\overline{v^2}$  and hence, for a perfect gas in which  $pV = NkT$ , we may deduce that the mean square velocity is proportional to temperature.

## 3 Distribution functions

It is not intellectually very satisfying to have to introduce an empirical equation such as  $pV = NkT$ . A better approach is through the Boltzmann distribution. The key element of this approach is that if the energy of a system may be written in terms of positions and momenta of the constituents,  $\{\mathbf{q}\} = \mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$  and  $\{\mathbf{p}\} = \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$  respectively, and the corresponding energy is  $E(\{\mathbf{p}\}, \{\mathbf{q}\})$ , then the probability that the system is in the state between  $\{\mathbf{p}\}$  and  $\{\mathbf{p}\} + d\{\mathbf{p}\}$ ,  $\{\mathbf{q}\}$  and  $\{\mathbf{q}\} + d\{\mathbf{q}\}$  is

$$dw = Ae^{-E(\{\mathbf{p}\}, \{\mathbf{q}\})/kT} d\{\mathbf{p}\} d\{\mathbf{q}\}, \quad (3)$$

where  $A$  is a normalising constant.

### 3.1 Factorisation of the probability

Now we may note that, for the non-interacting gas, the energy may be separated into separate kinetic energy terms  $K$  for each molecule, and internal potential energy terms  $U$  for each molecule, so that  $dw$  factors into a product

$$\begin{aligned} dw &= Ae^{-K(\mathbf{p}^{(1)}/kT} d\mathbf{p}^{(1)} e^{-U(\mathbf{q}^{(1)}/kT} d\mathbf{q}^{(1)} \dots e^{-K(\mathbf{p}^{(N)}/kT} d\mathbf{p}^{(N)} e^{-U(\mathbf{q}^{(N)}/kT} d\mathbf{q}^{(N)} \\ &= dw^{(1)} dw^{(2)} \dots dw^{(N)} \\ &= dw_K^{(1)} dw_U^{(1)} dw_K^{(2)} dw_U^{(2)} \dots dw_K^{(N)} dw_U^{(N)}. \end{aligned} \quad (5)$$

Furthermore, the form of the translational kinetic energy being as it is,  $K(\mathbf{p}) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$ , and the phase space volume element  $d\mathbf{p}$  being  $dp_x dp_y dp_z$ , each kinetic energy term factorizes as

$$dw_{\mathbf{p}}^{(i)} = A^{(i)} e^{p_x^{(i)2}/2mkT} dp_x^{(i)} e^{p_y^{(i)2}/2mkT} dp_y^{(i)} e^{p_z^{(i)2}/2mkT} dp_z^{(i)}, \quad (7)$$

and knowing that if we integrate over all momenta from  $-\infty$  to  $\infty$  we cover all possibilities, so the the integral must equal unity, we have

$$A^{(i)} = (2\pi mkT)^{-3/2}. \quad (8)$$

The most significant feature of this factorisation is that if one wishes to ask about the behaviour of one variable, say the  $x$  component of velocity of one particle irrespective of the behaviour of the other particles and the other velocity components of the same particle, this may be done by integrating over all the redundant variables.

### 3.1.1 Maxwell's distribution

This gives us the Maxwellian distribution, more familiar in the form obtained by writing  $p_x = mv_x$  etc.,

$$dw_{\mathbf{v}} = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} dv_x dv_y dv_z, \quad (9)$$

or for each component

$$dw_{v_x} = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT} dv_x. \quad (10)$$

For some purposes, the directions of motion of the molecules are not important, and only the speeds matter. Then we may write

$$(v_x, v_y, v_z) = v(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (11)$$

and

$$dv_x dv_y dv_z = v^2 \sin \theta d\theta d\phi dv \quad (12)$$

and then integrate over the two angles to obtain

$$dw_v = 4\pi \left( \frac{m}{2\pi kT} \right) v^2 e^{-mv^2/2kT} dv \quad (13)$$

as the probability of finding a molecule with speed between  $v$  and  $v + dv$ . It immediately follows that the mean square speed is

$$\overline{v^2} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2kT} dv \quad (14)$$

$$= \frac{3kT}{m}, \quad (15)$$

and that for each component

$$\overline{v_x^2} = \left( \frac{m}{2\pi kT} \right)^{1/2} \int_0^\infty v_x^2 e^{-mv^2/2kT} dv_x \quad (16)$$

$$= \frac{kT}{m}. \quad (17)$$

With equal facility we may evaluate the mean speed (as opposed to the root mean square speed) for the Maxwellian distribution, which is

$$\bar{v} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT} dv \quad (18)$$

$$= \frac{2}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}}, \quad (19)$$

and the most probable speed

$$\hat{v} = \sqrt{\frac{2kT}{m}}. \quad (20)$$

All these characteristic speeds lie in the range  $10^2$  to  $10^3$  m/s under ambient conditions, comparable with the speed of sound in the gas.

### 3.1.2 Verification of Maxwell distribution

The Maxwellian expression for the distribution of molecular speeds may be verified in several fairly direct ways:

**spectral broadening** The Doppler effect shifts the wavelength of light emitted by an atom moving with a velocity  $v_x$  in the line of sight of an observer from a reference wavelength  $\lambda_0$  to  $\lambda$  where

$$\frac{\lambda - \lambda_0}{\lambda_0} = \frac{v_x}{c}, \quad (21)$$

$c$  being the speed of light. This leads immediately to a distribution of wavelengths, and hence a characteristic spectral lineshape

$$I(\lambda)d\lambda = I_0 e^{-mc^2(\lambda - \lambda_0)^2 / 2\lambda_0^2 kT} d\lambda. \quad (22)$$

**Lammert's experiment** Mercury heated in an oven was allowed to escape as a molecular beam which was fed through a pair of slotted wheels before condensing on a cold surface. Only molecules with a velocity which is matched to the separation of the wheels and the speed with which they are turned will pass through the two slits and reach the plate. Note that the distribution function of the atoms in the beam is  $v^3 e^{-mv^2/2kT}$  rather than the Maxwellian distribution (see section 3.4).

## 3.2 Atmospheric density

In most of what follows it is the kinetic energy term and the associated momentum or velocity distribution which will be significant. It is worth including one case in which we have to consider the potential energy term, namely the variation in the density of a gas in a variational field. According to the Boltzmann distribution, the probability of finding a molecule at a height between  $z$  and  $z + dz$ , assuming a constant gravitational field  $g$ , will be

$$w(z)dz = A' e^{-mgz/kt} dz, \quad (23)$$

and because the molecule must be *somewhere* above ground level

$$\int_0^\infty w(z)dz = 1, \quad (24)$$

whence  $A' = mg/kT$ . The gas density, then, which is proportional to the number of molecules in a given volume, varies with height according to

$$\rho(z) = \rho_0 e^{-mgz/kt}. \quad (25)$$

### 3.3 Gas pressure revisited

We are now in a position to derive the pressure of a gas without the artifice of a specially shaped (cubic) container. Consider a plane wall perpendicular to the  $x$  direction, and concentrate on the molecules with velocities in the range  $v_x$  to  $v_x + dv_x$ . Any such molecules less than  $v_x$  from the wall will hit it in one second, and if each is elastically it will impart an impulse  $2mv_x$  to the wall. The number of molecules within that distance which strike unit area is then  $nv_x w(v_x)dv_x$ , and the corresponding pressure is therefore  $2mnv_x^2 w(v_x)dv_x$ . The total pressure is found by integrating from 0 to  $\infty$  (molecules with negative  $x$  velocities are moving away from the wall)

$$p = 2mn \int_0^{\infty} v_x^2 w(v_x) dv_x \quad (26)$$

$$= 2mn \left( \frac{m}{2\pi kT} \right)^{1/2} \int_0^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x \quad (27)$$

$$= nkT. \quad (28)$$

### 3.4 Effusion

A small hole of area  $dS$  in the wall of a vessel containing gas will be the subject of

$$\frac{1}{6}n(v)v dS$$

molecular ‘collisions’ per second from molecules with speed  $v$ . Actually, see section 5.1 below, the prefactor should be  $1/4$  rather than  $1/6$ . If the hole is small, the molecules will pass straight through – this is the process of effusion. This form of the equation shows that the spectrum of the molecules which emerge will be non-Maxwellian, being weighted towards higher speeds. The total number of molecules which emerges, by integrating over all velocities, is

$$\frac{1}{6}n\bar{v}dS = \frac{p}{3\sqrt{\pi}kT} \sqrt{\frac{2kT}{m}} dS \quad (29)$$

for a perfect gas. This dependence on mass may be used as a means of separating isotopes – a lighter isotope effuses more rapidly.

Effusion is relevant when the dimensions of the hole are small enough compared with the mean free path that a molecule passes through the hole without being affected by other molecules in the hole. Under other circumstances one may have continuum choked flow, with gas flowing at the speed of sound, or viscous flow.

## 4 Transport processes

Considerations of symmetry lead us to assert that the average number of particles travelling in a given direction (that is,  $\pm x$ ,  $\pm y$  or  $\pm z$ ) will be one sixth of the total, and thus that the mean rate at which molecules cross a plane is

$$\frac{1}{6}n\bar{v} \text{ per area in unit time.} \quad (30)$$

This differs slightly from the exact result, equation 62 below, but it is a suitable form for the simplified arguments which we will use below.

This is, however, not enough to allow us to compute transport properties (such as diffusion, thermal conductivity, and viscosity). In order to find them we must know *how far* across the boundary the molecules travel – that is, how far they transport the relevant property (themselves, their kinetic energy, or their momentum). That is, we must consider intermolecular collisions.

### 4.1 Molecular collisions

In the first instance, imagine that the molecules may be represented as hard spheres with radius  $a$ . Then two molecules collide if they reach a separation of  $2a$ . Now the distance travelled by a molecule moving with speed  $v$  in time  $t$  is  $vt$ , when it ‘sweeps’ a volume  $4\pi a^2 vt$ . If the molecular density is  $n$ , and we treat all the other molecules as though they were stationary, the molecule will make  $4\pi n a^2 vt$  collisions in that time  $t$ , whence the mean distance between collisions is

$$\lambda = \frac{1}{4\pi n a^2} \quad (31)$$

or, defining the collision cross section  $\sigma$  as  $4\pi a^2$ ,

$$\lambda = \frac{1}{n\sigma}. \quad (32)$$

This simple picture needs two corrections:

- the molecules are not hard spheres – see section 4.1.1 below;
- we need to consider the relative motion of the molecules – this reduces  $\lambda$  by a factor  $1/\sqrt{2}$ .

It is useful to have some idea of how far a molecule *does* travel before colliding. A few typical values are given in the table below.

Mean free paths for ideal gas		
pressure	temperature	mean free path
1 atmosphere	300 K	$7 \times 10^{-8}$ m (200 diameters)
$10^{-4}$ atmosphere	300 K	$7 \times 10^{-4}$ m
$10^{-8}$ atmosphere	300 K	7m

### 4.1.1 Intermolecular interactions

Molecules are not, of course, hard spheres. A glance at a typical intermolecular potential curve shows two significant differences. At large separations, there is an attractive interaction between molecules: thus the trajectories of molecules are distorted and collisions are more frequent than a hard sphere model would suggest. This is particularly important at low temperatures, when the interaction energy is a significant fraction of the kinetic energy of the molecules, and the collision cross-section increases quite rapidly at low temperature. At high temperatures, it becomes important that the short-range repulsion is softer than the hard-sphere model would suggest. The molecules are thus able to come closer together than the hard-sphere diameter, reducing the cross-section slightly at high temperature.

Another effect which has so far been ignored is that molecules, as opposed to atoms, may have internal degrees of freedom (vibration and rotation). In collisions there is the possibility that kinetic energy of translation may be exchanged with internal energy – indeed, it is necessary that this exchange should take place in order to maintain thermal equilibrium between the various degrees of freedom.

### 4.1.2 Scattering times - apparent paradoxes

It is worth digressing at this point to discuss an apparent paradox associated with scattering times, and hence mean free paths, as encountered in the transport theory of metals and semiconductors. The definition of scattering time  $\tau$  is that the probability of a scattering event in time interval  $dt$  is  $dt/\tau$ . This is *not* the same as saying that, if we observe a particle at random, we will find it mid-way between collisions so that the average velocity arising from constant acceleration  $a$  would be  $a\tau/2$ . The point is that if we select a sample of free times at random points in time we automatically weight the result in favour of long free times, and the average turns out to be  $2\tau$ .

To see how this works out for velocity, compute the change in velocity in time interval  $dt$ :

$$dv_{\langle} = a dt \quad (33)$$

where  $\langle \rangle$  denotes the average over all particles. In the same time interval, a fraction  $dt/\tau$  of the particles will be scattered into random directions, each particle thus losing its own fraction of  $v_{\langle}$ , contributing

$$dv_{\langle} = -v_{\langle} \frac{dt}{\tau}. \quad (34)$$

In a steady state,

$$a dt - v_{\langle} \frac{dt}{\tau} = 0 \quad (35)$$

so that  $v_{\langle} = a\tau$ .



From a statistical viewpoint, let us seek the time variation of  $p(t)$ , the fraction of the particles that have not collided for a time  $t$ . We know the probability of a collision in time  $dt$  is  $dt/\tau$ , so

$$dp(t) = -p(t)dt/\tau \quad (36)$$

whence

$$p(t) = Ae^{-t/\tau}. \quad (37)$$

Since  $p$  must be normalised,  $A = 1/\tau$ .

Hence we may evaluate the mean time between collisions,  $\bar{t}$ ,

$$\bar{t} = \int_0^\infty (t/\tau) \exp(-t/\tau) dt = \tau \quad (38)$$

as we hoped. The confusing thing, though, is that if we ask for the mean time since the last collision of a particular particle, it is also  $\tau$ , as is the mean time to the next collision.

## 4.2 Diffusion

Consider a gas in which there is a concentration gradient, either of one species in another or of a radioactive isotope in a nonradioactive background. Suppose the concentration at  $x$  is  $n$ , and those at  $x + \lambda$  and  $x - \lambda$  are  $n + (dn/dx)\lambda$ ,  $n - (dn/dx)\lambda$  respectively. Then the number of molecules per second per area moving in the positive  $x$  direction will be

$$\frac{1}{6} \left( n - \frac{dn}{dx} \lambda \right) \bar{v} \quad (39)$$

per unit area and the number per second per area moving in the negative  $x$  direction will be

$$\frac{1}{6} \left( n + \frac{dn}{dx} \lambda \right) \bar{v} \quad (40)$$

leading to a net current of molecules in the positive direction

$$J = -\frac{1}{3} \lambda \bar{v} \frac{dn}{dx} \quad (41)$$

$$\equiv -D \frac{dn}{dx} \quad (42)$$

which defines the diffusion constant  $D = \frac{1}{3} \lambda \bar{v}$ .

This result may be used to discuss the diffusion of a material as a vapour through air. If one imagines an open pool of liquid, and a condensing surface a height  $h$  above it, then in a steady state there will be a constant concentration gradient in the vapour from saturation just above the liquid to the condensing plate.

### 4.3 Thermal conductivity

The derivation here is very similar to that for diffusion, except that the quantity which varies with position is temperature  $T$  rather than density  $n$ . Suppose the temperature at  $x$  is  $T$ , and those at  $x + \lambda$  and  $x - \lambda$  are  $T + (dT/dx)\lambda$ ,  $T - (dT/dx)\lambda$  respectively. Then nett number of molecules per second per area moving in the  $x$  direction will be zero, but if the specific heat of the gas is  $c_V$  then the rate of transport of thermal energy in the positive  $x$  direction will be

$$\frac{n\bar{v}c_V}{6} \left( T - \frac{dT}{dx}\lambda \right) \bar{v} \quad (43)$$

per unit area and that moving in the negative  $x$  direction will be

$$\frac{n\bar{v}c_V}{6} \left( T + \frac{dT}{dx}\lambda \right) \bar{v} \quad (44)$$

leading to a net flux of energy in the positive direction

$$Q = -\frac{n\bar{v}\lambda c_V}{3} \frac{dT}{dx} \quad (45)$$

$$\equiv -\kappa \frac{dT}{dx} \quad (46)$$

which defines the thermal conductivity  $\kappa = \frac{1}{3}n\lambda\bar{v}c_V$ .

If we substitute the form of  $\bar{v}$ , replace  $\lambda$  from equation 32, and recall that the specific heat  $c_V$  is a constant for a classical gas, then we find that the conductivity of a gas should increase with temperature as  $\sqrt{T}$  and be independent of pressure. Measurements of thermal conductivity in gases, however, are notoriously difficult to make. In particular, it is very hard to avoid the effect being swamped by convective heat transport.

### 4.4 Viscosity

The viscosity of a gas is governed by the rate at which momentum can be transferred between layers of the gas. We assume lamellar flow, that is, flow in which the gas may be treated as planes perpendicular to the  $x$  axis in each of which the flow velocity (that is, the drift velocity as opposed to the individual molecular velocities) is constant. Let the drift velocity be  $u(x)$ , parallel to the  $y$  axis. Suppose the velocity at  $x$  is  $u$ , and those at  $x + \lambda$  and  $x - \lambda$  are  $u + (du/dx)\lambda$ ,  $u - (du/dx)\lambda$  respectively. Then the rate of transport of momentum in the positive  $x$  direction will be

$$\frac{nm\bar{v}}{6} \left( u - \frac{du}{dx}\lambda \right) \bar{v} \quad (47)$$

per unit area and that moving in the negative  $x$  direction will be

$$\frac{nm\bar{v}}{6} \left( u + \frac{du}{dx} \lambda \right) \bar{v} \quad (48)$$

leading to a net flux of momentum in the positive  $x$  direction

$$F = -\frac{nm\bar{v}\lambda}{3} \frac{du}{dx} \quad (49)$$

$$\equiv -\eta \frac{du}{dx} \quad (50)$$

which defines the viscosity  $\eta = \frac{1}{3}nm\lambda\bar{v}$ .

Note that this result, when we substitute the form of  $\bar{v}$ , and replace  $\lambda$  from equation 32, suggests that the viscosity of a gas should increase with temperature as  $\sqrt{T}$  and be independent of pressure. This is a reasonable result – as the velocity of the molecules increases with temperature, so the rate of interchange of molecules and hence of momentum between stationary and moving layers increases. It is, of course, the opposite of what is found in liquids, where viscosity decreases with increased temperature. For a real gas, however, the cohesive forces between atoms cause the viscosity to increase more rapidly than this simple form would suggest.

#### 4.4.1 Relation of viscosity to conductivity

The equations derived above for  $\eta$  and  $\kappa$  lead us to expect

$$\frac{\kappa m}{\eta c_V} = 1. \quad (51)$$

## 4.5 Properties of rarefied gases

In the previous derivations we have assumed that the mean free path  $\lambda$  was an intrinsic property of the gas, unaffected by any confining surfaces. As long as  $\lambda$  is small compared with the dimensions of the system, this is a good approximation, but as the pressure is reduced the mean free path increases until it may be the walls which limit the molecules' travel.

#### 4.5.1 Viscosity of rarefied gases

To analyse the viscosity of rarefied gases we need to consider a typical measurement, in which we might have two plates, a distance  $L$  apart, perpendicular to the  $x$  axis, with the one at  $x = 0$  stationary and the one at  $x = L$  moving parallel to the  $y$  axis with speed  $u$ . If we imagine the molecules near the wall to strike the wall, stick briefly, and then rebound, they will emerge with the same  $y$  component of velocity as the walls. They will carry that velocity with them to

a distance  $\lambda$  from the wall, where the average  $y$  velocity is  $v(\lambda)$  for the plate at  $x = 0$ ,  $v(L - \lambda)$  for the other. Thus within those layers of thickness  $\lambda$  the average velocities are the average of the plate velocity and the gas velocity a distance  $\lambda$  away. This is equivalent to saying that the molecules slip over the walls with a speed equal to this average velocity. This, in turn, defines the velocity gradient by

$$\lambda \frac{dv}{dx} = \frac{v(\lambda)}{2} \quad (52)$$

and similarly near  $x = L$ . Between these slipping layers there is a layer of ‘normal’ behaviour, in which there will be a constant velocity gradient  $dv/dx$ . Thus the difference in speed between the gas near the wall at  $x = 0$  and the gas near the wall at  $x = L$  will be

$$u - 2\lambda \frac{dv}{dx}. \quad (53)$$

Thus the velocity gradient will be

$$\frac{dv}{dx} = \frac{u - 2\lambda(dv/dx)}{L} \quad (54)$$

or

$$\frac{dv}{dx} = \frac{u}{L + 2\lambda}. \quad (55)$$

Clearly, then, the apparent viscosity will be reduced by a factor  $L/(L + 2\lambda)$ .

In very confined geometries, where  $\lambda$  is larger than  $L$ , the entire argument breaks down. We may do two things

- assume that the geometry defines the mean free path;
- perform the calculation properly.

If we take the simpler approach, we would argue that the force between two plates  $L$  apart moving with a relative velocity  $u$  should be, per unit area,

$$F = \eta u/L \quad (56)$$

$$= \frac{1}{3}nm\bar{v}u \quad (57)$$

simply replacing  $\lambda$  in the formula for  $\eta$  with  $L$ . This gives a force which is independent of the plate separation.

Alternatively, we would argue that the number of molecules striking unit area per second is  $\frac{1}{6}n\bar{v}$ , and that each transfer of a molecule between one plate and the other without colliding with other molecules on the way transfers momentum of  $mu$ , leading to a force per area

$$F = \frac{1}{6}nm\bar{v}u. \quad (58)$$

Although the coefficients are different, both results agree on the conclusion that the force between the plates becomes proportional to the pressure (through  $n$ ) rather than independent of it as when the viscosity depends on the bulk gas mean free path.

#### 4.5.2 Thermal conductivity of rarefied gases

One crucial point here is the extent to which the molecules can equilibrate with the walls. If the molecules rebound elastically, that is with no change of kinetic energy, there is no transfer of thermal energy to the gas and the apparent thermal conductivity will be zero. However efficient this heat transfer, however, the thermal conductivity of a gas becomes negligible at low pressures.

## 5 More formal kinetic theory

Although the results for such quantities as viscosity, pressure, conductivity and diffusivity derived above are correct, their derivation has lacked formality. Let us now tighten up the arguments somewhat.

### 5.1 Collisions with a wall

More formally, consider a small area  $dS$ , which we may assume without loss of generality to be normal to the  $z$  axis, and seek an expression for the number of molecules which pass through  $dS$  after having their last collision in a volume element  $dV$  whose position relative to  $dS$  is, in spherical polar coordinates,  $(r, \theta, \phi)$ . Note that at this stage we are just treating  $dS$  as an arbitrary surface in the gas, so we do not mind which side of  $dS$  the volume  $dV$  is located. We will actually compute a *flux* of molecules, which counts molecules crossing from positive to negative  $z$  as positive, those crossing in the opposite direction as negative.

The number of molecules in  $dV$  is  $n dV$ , each of which collides, on average, with frequency  $\bar{v}/\lambda$ . Thus the frequency of collisions in  $dV$  is  $(n\bar{v}/\lambda)dV$ . As the collisions are assumed to randomise directions of travel, the fraction of these collisions which dispatches molecules towards  $dS$  is given by the solid angle subtended at  $dV$  by  $dS$ , that is,  $(dS \cos \theta)/(4\pi r^2)$ .

Not all the molecules which set off towards  $dS$ , however, will get there. Some will collide again, and the fraction which reach  $dS$  unscathed will be those whose mean free path exceeds  $r$ . As the probability of a mean free path being between  $r$  and  $r + dr$  is  $(1/\lambda) \exp(-r/\lambda)dr$ , the probability that it exceeds  $r$  is

$$\frac{1}{\lambda} \int_r^\infty e^{-r/\lambda} dr = e^{-r/\lambda}. \quad (59)$$

Thus, the final expression for the number of molecules which collide within  $dV$  and travel to  $dS$  without further collision is

$$dS \cos \theta \frac{n\bar{v}}{4\pi r^2 \lambda} e^{-r/\lambda} r^2 \sin \theta dr d\theta d\phi \quad (60)$$

which we may integrate over all distances  $r$  and azimuthal angles  $\phi$  to obtain the number of molecules per second striking unit area at an angle between  $\theta$  and  $\theta + d\theta$  as

$$R(\theta)d\theta = \frac{1}{2}n\bar{v} \sin \theta \cos \theta d\theta. \quad (61)$$

If now we compute the total number of molecules striking unit area per second, by integrating over  $\theta$  from 0 to  $\pi/2$ , we find

$$\frac{1}{4}n\bar{v}. \quad (62)$$

## 5.2 Pressure

Although we have followed the above argument for the average particle, it is equally applicable to any subgroup of molecules, such as those with speeds in the range  $v$  to  $v + dv$ . If the probability of a molecule having such a speed is  $p(v)$ , then the number of molecules in that speed range striking a wall at an angle  $\theta$  is  $w(v)R(\theta)$ , and if it rebounds elastically the impulse on the wall will be  $2mv \cos \theta$ , leading to a pressure

$$p = \int_0^{\pi/2} d\theta \int_0^{\infty} dv R(\theta) 2mv \cos \theta w(v) \quad (63)$$

$$= \frac{1}{3}nm \int_0^{\infty} v^2 w(v) dv \quad (64)$$

$$= \frac{1}{3}nm\bar{v}^2. \quad (65)$$

Here we emerge with the same expression as before because the inclusion of the angular factor  $\cos \theta$  in the angular integral yields the same result as our previous treatment's use of a smaller number of impacts (factor of 1/6 instead of 1/4) but larger momentum change.

## 5.3 Viscosity, Diffusivity, Conductivity

Here we note that molecules crossing our reference plane at an angle  $\theta$  come, on average, from a distance  $\lambda \cos \theta$  from the plane. Again, on integrating over all angles  $\theta$  this provides the conversion between the factor of 1/4 and 1/6, and our previous results still hold.

## 6 A sample of Finals Questions on Kinetic Theory

**1993.IA.2.** Define the *coefficient of viscosity*  $\eta$  of a fluid. Show that, according to simple kinetic theory,  $\eta$  for a gas is given by

$$\eta = A \left( \frac{M\bar{c}}{\pi d^2} \right)$$

where  $A$  is a constant of order unity,  $M$  is the mass of an atom,  $\bar{c}$  is the mean speed and  $d$  is the diameter of an atom. [7]

Show that, for a monatomic gas, simple kinetic theory leads to the following expression relating  $\eta$  to the thermal conductivity  $\kappa$ :

$$\kappa = \frac{3k_B}{2M}\eta$$

where  $k_B$  is the Boltzmann constant. Explain why it is much easier to make reliable measurements of  $\eta$  than of  $\kappa$ . [8]

Two flat discs, each of radius 50 mm, are mounted coaxially with their adjacent surfaces 1 mm apart. They are in a chamber containing helium gas (mass number 4) at STP, and are free to rotate independently about their common axis. One of them rotates with an angular velocity of 5 rad s<sup>-1</sup>. Use the results of simple kinetic theory to estimate the couple which needs to be applied to the other to keep it stationary. Take  $\bar{c} \approx v_{\text{rms}}$ , the root mean square velocity, and assume that the diameter of a helium atom is 0.1 nm. [10]

**1992.IA.1.** The Boltzmann postulate states that in a statistical assembly of particles, the number of particles occupying a state of energy  $\epsilon$  is proportional to  $e^{-\epsilon/kT}$ . Briefly justify why the Maxwell-Boltzmann distribution of speeds  $v$  takes the form:

$$n(v)dv \propto v^2 e^{-mv^2/2kT} dv.$$

Find a formula for the average speed  $\bar{v}$  of particles in a gas. [8]

Show that for a gas with  $n$  molecules per unit volume the rate  $R(\theta)$  of particles arriving per unit area on a plane surface, between angles  $\theta$  and  $\theta + d\theta$  to the normal, is given by

$$R(\theta)d\theta = \frac{1}{2}n\bar{v} \sin \theta \cos \theta d\theta.$$

[7]

Gas molecules enter a small hole in the surface of an evacuated glass sphere, striking the inside surface of the glass and sticking there. Prove that the inside surface of the sphere becomes uniformly coated with a thin layer of the molecules. Suggest a possible application of this result. [10]

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} \quad \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

**1991.IA.1.** Justify the form of the Maxwellian distribution of speeds  $c$  for a gas of molecules of mass  $m$

$$n(c)dc = Ac^2 \exp\left(-mc^2/2kT\right) dc,$$

and obtain an expression for the constant  $A$ . [6]

Hence calculate the mean speed and most probable speed for a molecule which has effused out of an enclosure at temperature  $T$ . [8]

The deposition in vacuo of materials in the form of thin films requires high vacuum if the necessary cleanliness of the surface is to be achieved. Given that during the deposition process a surface can be coated with a monatomic layer of film material in a time of 100 ms, estimate the greatest allowable background pressure in the vacuum vessel if the surface contamination is to be kept to 1 in  $10^5$ . [Assume the contaminant gas is nitrogen, and that all molecules that strike the deposited layer stick there.] State any further assumptions you make. [11]

**1990.IA.2.** A thermally insulating thin partition separates an ideal gas into two regions which are maintained at temperatures  $T_1$  and  $T_2$ . A hole in the partition allows gas to move between the two compartments. Explain how the relative steady state pressures,  $p_1$  and  $p_2$  respectively, in the compartments compare when the hole is (i) very large and (ii) very small. In this context, what condition must be satisfied for the hole to be considered small? [12]

A monatomic gas of relative atomic mass  $M$  at pressure  $p$  and temperature  $T$  effuses through a very small area  $S$  into a vacuum space where the effusing molecules are all trapped on a cold adsorbing surface. Calculate the power input to the surface from the kinetic energy of the molecules. [13]

$$\left[ \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \left( \frac{\pi}{a^3} \right)^{\frac{1}{2}} ; \quad \int_0^\infty x^5 e^{-ax^2} dx = \frac{1}{a^3} \right]$$

**1989.IA.2.** Derive an expression for the thermal conductivity of an ideal gas according to elementary kinetic theory, and show that it is independent of pressure. State the assumptions made in your derivation. [8]

Two flat plates at different temperatures are held a small distance apart in a gas at low pressure. Show that at sufficiently low pressures, the rate of heat transfer between the plates is a linear function of pressure, and derive an expression for it, stating any approximations you may make. [9]

This device may be used as a pressure gauge if the power required to maintain a given temperature difference is measured. Discuss the range of pressure over which useful measurements can be obtained, and estimate both the upper and lower limits for an apparatus of reasonable dimensions. Assume that the gauge is operated so that one plate is held at about 10 K above the other, and that heat transfer occurs only between the facing surfaces. [8]

**1988.IA.1.** Write down expressions for the pressure and for the number of molecules per second crossing unit area in a gas according to the kinetic theory and derive **one** of them stating clearly the assumptions you make. [7]



A sample of molten metal is maintained at a temperature  $T$  in a silica pot within an evacuated vessel. Atoms of vapour escape through a small hole in the lid of the pot and are collected on a cooled target. Show that the rate of mass deposition is given by

$$\frac{dm}{dt} = \left( \frac{M}{2\pi RT} \right)^{1/2} Sp$$

where  $p$  is the pressure of the vapour in the pot,  $S$  the area of the hole,  $R$  the molecular gas constant and  $M$  the mass of one mole of the metal. You may assume that

$$\bar{c}^2 = \frac{8}{3\pi} \overline{c^2}$$

where  $\bar{c}$  is the mean speed and  $\overline{c^2}$  is the mean square speed of molecules in the gas. [10]

Calculate the vapour pressure of lead at 600 K if it takes 10 hours to deposit 0.12 mg of metal on the target through a hole of 1 mm radius. The relative atomic mass of lead is 207. [8]

**1987.IA.1.** Define the coefficient of viscosity. Use kinetic theory to show that the coefficient of viscosity of a gas is given, with suitable approximations, by

$$\eta = K\rho\bar{c}l$$

where  $\rho$  is the density of the gas,  $l$  is the mean free path of the gas molecules,  $\bar{c}$  is their mean speed and  $K$  is a number which depends on the approximations you make. [8]

In 1660 Boyle set up a pendulum inside a vessel which was attached to a pump which could remove air from the vessel. He was surprised to find that there was no observable change in the rate of damping of the swings of the pendulum when the pump was set going. Explain this observation in terms of the above formula. [6]

Make a rough order of magnitude estimate of a lower limit to the pressure which Boyle obtained; use reasonable assumptions concerning the apparatus which Boyle might have used. [The viscosity of air at atmospheric pressure and at 293 K is  $18.2 \mu\text{N s m}^{-2}$ .] [5]

Explain why the damping is nearly independent of the pressure despite the fact that fewer molecules collide with the pendulum as the pressure is reduced. [6]

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