

# Appendix A

## Some results from the kinetic theory of gases

### A.1 Distribution of molecular velocities in a gas

#### A.1.1 The distribution derived from the barometric formula

In Chapter 2 the variation of gas density in the atmosphere was derived. In the upper atmosphere where the gas temperature is approximately constant

$$\frac{\rho(z+h)}{\rho(z)} = e^{-\frac{\gamma g h}{a_0^2}}. \quad (\text{A.1})$$

Rewrite (B.1) in terms of molecular parameters

$$\frac{n(z+h)}{n(z)} = e^{-\frac{mgh}{kT}} \quad (\text{A.2})$$

where  $n(z)$  is the number of molecules per unit volume at the height  $z$ ,  $m = M_w/N$ , is the mass of each molecule (or the average mass in the case of a mixture like air). The Boltzmann's constant

$$k = 1.38 \times 10^{-23} \text{ Joules/K} \quad (\text{A.3})$$

is related to the gas constant and Avagadros number  $N$  by

$$k = \frac{R_u}{N}. \quad (\text{A.4})$$

Equation (B.2) expresses the distribution of molecules in any system at constant temperature subject to a body force. The fraction of molecules per unit area above a given altitude  $z + h$  is also given by the distribution (B.2). That is

$$\frac{\int_{z+h}^{\infty} n(z) dz}{\int_z^{\infty} n(z) dz} = e^{-\frac{mgh}{kT}} \quad (\text{A.5})$$

which is a basic property of an exponential distribution. The distribution of molecules under the downward pull of gravity given by (B.5) can be used to infer how the velocities of gas molecules are distributed. Consider molecules that pass through some reference height  $z$  on their way to height  $z + h$ .

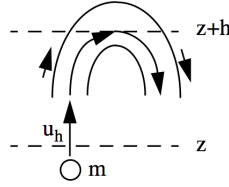


Figure A.1: *Trajectory of an upward moving molecule*

The upward velocity component  $u_h$  of a molecule whose kinetic energy at  $z$  is equal to its potential energy when it arrives at  $z + h$  satisfies

$$mgh = \frac{1}{2}mu_h^2. \quad (\text{A.6})$$

This is the minimum positive velocity needed for a molecule starting at  $z$  to reach the height  $z + h$ .

Let  $J_{u>u_h}(z)$  be the flux of molecules (number of molecules/area-sec) passing through the plane  $z$  that possess a vertical velocity component greater than  $u_h$  and let  $J_{u>0}(z)$  be the flux of molecules passing through the plane  $z$  with any positive upward velocity. The fraction of molecules passing upward through  $z$  with the requisite velocity is  $J_{u>u_h}(z) / J_{u>0}(z)$ . This ratio should be the same as the fraction of molecules above the height  $z + h$ . Therefore one can infer the equality

$$\frac{J_{u>u_h}(z)}{J_{u>0}(z)} = \frac{\int_{z+h}^{\infty} n(z) dz}{\int_z^{\infty} n(z) dz}. \quad (\text{A.7})$$

Using (B.5) we deduce that

$$\frac{J_{u>u_h}(z)}{J_{u>0}(z)} = e^{-\frac{mgh}{kT}} = e^{-\frac{mu_h^2}{2kT}} \quad (\text{A.8})$$

which is plotted in Figure B.2.

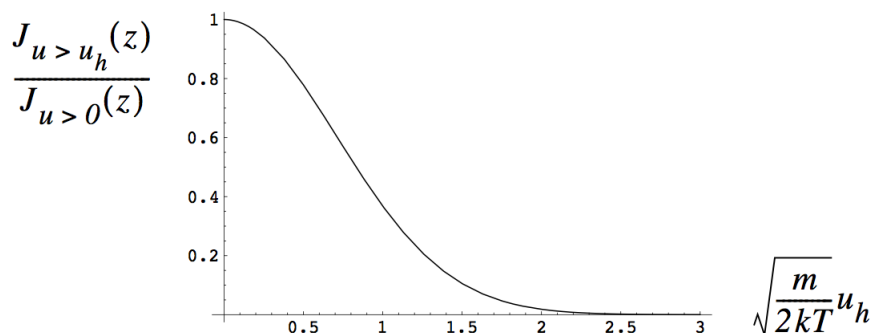


Figure A.2: *Fraction of molecules at any reference height with positive vertical velocity component exceeding  $u_h$ .*

Now use (B.7) to generate a probability density function (pdf)  $g(u_h)$  for the velocities. The pdf is defined such that, at any height  $z$ ,  $g(u_h) du_h$  equals the fraction of molecules per unit volume with velocity between  $u_h$  and  $u_h + du_h$ . The pdf we are seeking would look something like Figure A.3.

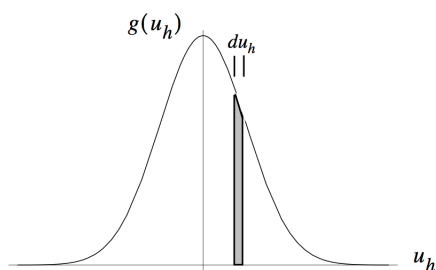


Figure A.3: *Probability density function of one velocity component. The shaded area divided by the whole area (which is one) is the fraction of molecules with velocity between  $u_h$  and  $u_h + du_h$ .*

The desired pdf is normalized so that

$$\int_{-\infty}^{\infty} g(u_h) du_h = 1. \quad (\text{A.9})$$

Note that  $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$ .

The number of molecules that pass through a unit area of the plane  $z$  in unit time (the flux of molecules) with vertical velocity component  $u_h$  is  $u_h g(u_h) du_h$ . In terms of the velocity pdf

$$\frac{J_{u>u_h}(z)}{J_{u>0}(z)} = \int_{u_h}^{\infty} u_h g(u_h) du_h = e^{-\frac{mu_h^2}{2kT}}. \quad (\text{A.10})$$

Differentiate both sides of (B.10).

$$-u_h g(u_h) = -\frac{mu_h}{kT} e^{-\frac{mu_h^2}{2kT}} \quad (\text{A.11})$$

Thus far

$$g(u_h) = -\frac{m}{kT} e^{-\frac{mu_h^2}{2kT}}. \quad (\text{A.12})$$

Apply the normalization condition (B.9) to (B.12).

$$\int_{-\infty}^{\infty} \frac{m}{kT} e^{-\frac{mu_h^2}{2kT}} du_h = \left( \frac{2\pi m}{kT} \right)^{1/2} \quad (\text{A.13})$$

Finally, the normalized 1-dimensional velocity pdf is

$$g(u_h) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{mu_h^2}{2kT}}. \quad (\text{A.14})$$

We arrived at this result using a model of particles with random vertical velocity components moving in a gravitational field. In a gas in thermodynamic equilibrium at a temperature  $T$ , the molecules constantly undergo collisions leading to chaotic motion with a wide range of molecular velocities in all three directions. The randomness is so strong that at any point no one direction is actually preferred over another and one can expect that the probability density function for a velocity component in any direction at a given height  $z$  will have the same form as (B.14).

### A.1.2 The Maxwell velocity distribution function

We can use a slightly different, more general, argument to arrive at the velocity distribution function in three dimensions. The randomness produced by multiple collisions leads to a molecular motion that is completely independent in all three coordinate directions and so the probability of occurrence of a particular triad of velocities  $(u_x, u_y, u_z)$  is equal to the product of three one-dimensional probability distributions.

$$f(u_x, u_y, u_z) = g(u_x) g(u_y) g(u_z) \quad (\text{A.15})$$

In addition, since no direction in velocity space  $(u_x, u_y, u_z)$  is preferred over any other, then the three dimensional velocity probability distribution function must be invariant under any rotation of axes in velocity space. This means  $f(u_x, u_y, u_z)$  can only depend on the radius in velocity space.

$$f(u_x, u_y, u_z) = f(u_x^2 + u_y^2 + u_z^2) \quad (\text{A.16})$$

The only smooth function that satisfies both (B.15) and (B.16) and the requirement that the probability goes to zero at infinity is the decaying exponential.

$$f(u_x, u_y, u_z) = A e^{-B(u_x^2 + u_y^2 + u_z^2)} \quad (\text{A.17})$$

In a homogeneous gas the number density of molecules with a given velocity is accurately described by the Maxwellian velocity distribution function

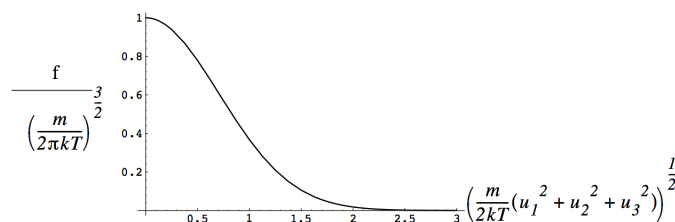
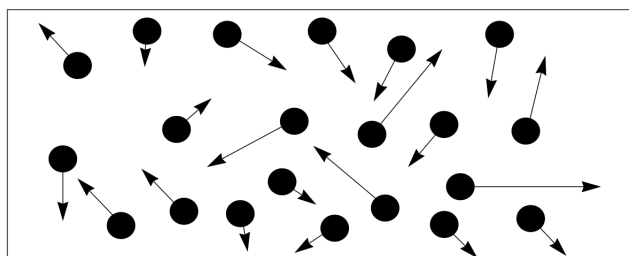
$$f(u_1, u_2, u_3) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}(u_1^2 + u_2^2 + u_3^2)} \quad (\text{A.18})$$

where the correspondence  $(u_x, u_y, u_z) \rightarrow (u_1, u_2, u_3)$  is used. The result (B.18) is consistent with the use of (B.14) in all three directions. The dimensions of  $f$  are  $\text{sec}^3/m^3$ . The pdf (B.18) is shown in figure A.4.

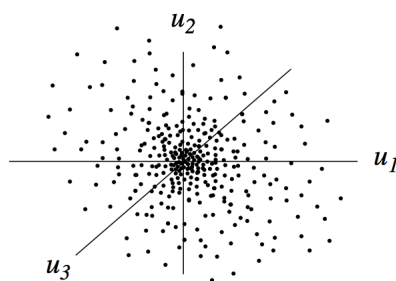
As with the 1-D pdf, the 3-D pdf is normalized so that the total probability over all velocity components is one.

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f du_1 du_2 du_3 = 1 \quad (\text{A.19})$$

To understand the distribution (B.18) imagine a volume of gas molecules at some temperature  $T$ .

Figure A.4: *Maxwellian probability density function of molecular velocities.*Figure A.5: *Colliding molecules in a box.*

At a certain instant a snapshot of the motion is made and the velocity vector of every molecule in the gas sample is measured as indicated in the sketch above. The velocity components of each molecule define a point in the space of velocity coordinates. When data for all the molecules is plotted, the result is a scatter plot with the densest distribution of points occurring near the origin in velocity space as shown in figure A.6.

Figure A.6: *Schematic of coordinates of a set of colliding molecules in velocity space.*

The probability density function (B.18) can be thought of as the density of points in figure A.4. The highest density occurs near the origin and falls off exponentially at large distances from the origin. If the gas is at rest or moving with a uniform velocity the distribution is

spherically symmetric since no one velocity direction is preferred over another.

The one-dimensional probability distribution is generated by integrating the Maxwellian in two of the three velocities.

$$f_{1D} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}(u_1^2 + u_2^2 + u_3^2)} du_2 du_3 \quad (\text{A.20})$$

which can be rearranged to read

$$f_{1D} = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mu_1^2}{2kT}} \int_{-\infty}^{\infty} e^{-\frac{mu_2^2}{2kT}} du_2 \int_{-\infty}^{\infty} e^{-\frac{mu_3^2}{2kT}} du_3. \quad (\text{A.21})$$

Carrying out the integration in (B.21) the 1-D pdf is

$$f_{1D} = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{mu_1^2}{2kT}} \quad (\text{A.22})$$

which is identical to (B.14).

## A.2 Mean molecular velocity

Any statistical property of the gas can be determined by taking the appropriate moment of the Maxwellian distribution. The mean velocity of molecules moving in the plus  $x_1$  direction is

$$\hat{u}_1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} u_1 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}(u_1^2 + u_2^2 + u_3^2)} du_1 du_2 du_3. \quad (\text{A.23})$$

Note that the integration extends only over velocities in the plus  $x$  direction. When the integral is evaluated the result is

$$\hat{u}_1 = \left( \frac{kT}{2\pi m} \right)^{1/2}. \quad (\text{A.24})$$

Let's work out the flux in the 1-direction of molecules crossing an imaginary surface in the fluid shown schematically in Figure A.7. This is the number of molecules passing through a surface of unit area in unit time.

The flux is simply

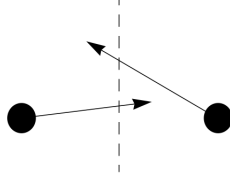


Figure A.7: *Molecules moving through an imaginary surface normal to the  $x_1$ -direction.*

$$J_1 = n\hat{u}_1 = n\left(\frac{kT}{2\pi m}\right)^{1/2}. \quad (\text{A.25})$$

At equilibrium, the number of molecules crossing per second in either direction is the same. Note that the molecular flux through a surface is the same regardless of the orientation of the surface.

The *mean square molecular speed* is defined as the average of the squared speed over all molecules.

$$\widehat{(u^2)} = (\widehat{u_1^2} + \widehat{u_2^2} + \widehat{u_3^2}) \quad (\text{A.26})$$

From the Maxwellian

$$\widehat{u^2} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (u_1^2 + u_2^2 + u_3^2) \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(u_1^2 + u_2^2 + u_3^2)} du_1 du_2 du_3 = \frac{3kT}{m} \quad (\text{A.27})$$

where the integration is from minus infinity to plus infinity in all three directions. The root-mean-square speed is

$$u_{rms} = \sqrt{\widehat{u^2}} = \sqrt{\frac{3kT}{m}}. \quad (\text{A.28})$$

This result is consistent with the famous law of equipartition which states that, for a gas of monatomic molecules, the mean kinetic energy per molecule (the energy of the translational degrees of freedom) is

$$E = \frac{1}{2}m\widehat{u^2} = \frac{3}{2}kT. \quad (\text{A.29})$$



### A.3 Distribution of molecular speeds

The Maxwellian distribution of molecular speed is generated from the full distribution by determining the number of molecules with speed in a differential spherical shell of thickness  $du$  and radius  $u$  in velocity space. The volume of the shell is  $dV_u = 4\pi u^2 du$  and so the number of molecules in the shell is  $f dV_u = 4\pi u^2 f du$  where  $u^2 = u_1^2 + u_2^2 + u_3^2$ . The Maxwellian probability distribution for the molecular *speed* is therefore

$$f_u = 4\pi u^2 f = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 e^{-\frac{mu^2}{2kT}} \quad (\text{A.30})$$

shown in Figure A.8.

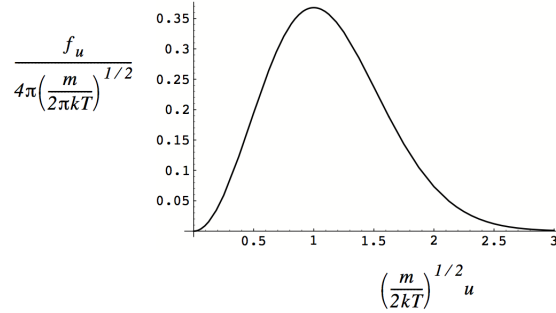


Figure A.8: *Maxwell distribution of molecular speeds.*

The mean molecular speed is

$$\hat{u} = \int_0^\infty u f_u du = \int_0^\infty 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} u^3 e^{-\frac{mu^2}{2kT}} du = \sqrt{\frac{8kT}{\pi m}}. \quad (\text{A.31})$$

In summary, the three relevant molecular speeds are

$$\begin{aligned} \hat{u}_1 &= \sqrt{\frac{kT}{2\pi m}} \\ \hat{u}_{rms} &= \sqrt{\frac{3kT}{m}} \\ \hat{u} &= \sqrt{\frac{8kT}{\pi m}}. \end{aligned} \quad (\text{A.32})$$

## A.4 Pressure

### A.4.1 Kinetic model of pressure

Before we use the Maxwellian distribution to relate the gas pressure to temperature it is instructive to derive this relation using intuitive arguments. Consider a gas molecule confined to a perfectly rigid box. The molecule is moving randomly and collides and rebounds from the wall of the container preserving its momentum in the direction normal to the wall. In doing so the molecule undergoes the change in momentum

$$\Delta p = -2mu_1 \quad (\text{A.33})$$

and imparts to the wall  $A_1$  the momentum  $2mu_1$ . Suppose the molecule reaches the opposite wall without colliding with any other molecules. The time it takes for the molecule to bounce off  $A_2$  and return to collide again with  $A_1$  is  $2L/u_1$  and so the number of collisions per second with  $A_1$  is  $u_1/2L$ .

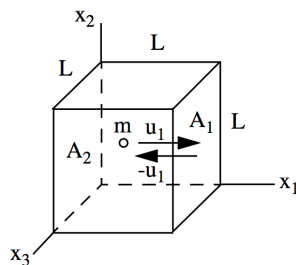


Figure A.9: A rigid box containing an ideal gas.

The momentum per unit time that the molecule transfers to  $A_1$  is

$$\text{Force on wall by one molecule} = \frac{mu_1^2}{L}. \quad (\text{A.34})$$

Let  $N_p$  be the number of molecules in the box. The total force on  $A_1$  is the pressure of the gas times the area and is equal to the sum of forces by the individual molecules

$$PL^2 = \frac{1}{L} \sum_{i=1}^{N_p} m_i u_{1_i}^2 \quad (\text{A.35})$$

where the index  $i$  refer to the  $i$ th molecule. If the molecules all have the same mass

$$P = \frac{Nm}{V} \left( \frac{1}{N_p} \sum_{i=1}^{N_p} u_{1_i}^2 \right). \quad (\text{A.36})$$

The first factor in (A.36) is the gas density  $\rho = N_p m / V$ . No one direction is preferred over another and so we would expect the average of the squares in all three directions to be the same.

$$\frac{1}{N_p} \sum_{i=1}^{N_p} u_{1_i}^2 = \frac{1}{N_p} \sum_{i=1}^{N_p} u_{2_i}^2 = \frac{1}{N_p} \sum_{i=1}^{N_p} u_{3_i}^2 \quad (\text{A.37})$$

The pressure is now written

$$P = \frac{\rho u_{rms}^2}{3} \quad (\text{A.38})$$

where

$$u_{rms}^2 = \frac{1}{N_p} \left( \sum_{i=1}^{N_p} u_{1_i}^2 + \sum_{i=1}^{N_p} u_{2_i}^2 + \sum_{i=1}^{N_p} u_{3_i}^2 \right). \quad (\text{A.39})$$

The root-mean-square velocity defined by a discrete sum in (A.39) is the same as that derived by integrating the Maxwellian pdf in (B.28). Using (B.28) and (A.38) the pressure and temperature are related by

$$P = \frac{\rho}{3} \left( \frac{3kT}{m} \right) = \rho RT. \quad (\text{A.40})$$

We arrived at this result using a model that ignored collisions between molecules. The model is really just a convenience for calculation. It works for two reasons; the time spent during collisions is negligible compared to the time spent between collisions and, in a purely elastic exchange of momentum between a very large number of molecules in statistical equilibrium, there will always be a molecule colliding with  $A_2$  with momentum  $-mu_1$  while a molecule leaves  $A_1$  with the same momentum.

### A.4.2 Pressure directly from the Maxwellian pdf

The momentum flux at any point is

$$\Pi_{ij} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} nm u_i u_j \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}(u_1^2 + u_2^2 + u_3^2)} du_1 du_2 du_3. \quad (\text{A.41})$$

For  $i \neq j$  the integral vanishes since the integrand is an odd function. For  $i = j$  the integral becomes

$$\Pi_{11} = \frac{mn}{\pi^{3/2}} \left( \frac{2kT}{m} \right) \int_{-\infty}^{\infty} u_1^2 e^{-\frac{m u_1^2}{2kT}} du_1 \int_{-\infty}^{\infty} e^{-\frac{m u_2^2}{2kT}} du_2 \int_{-\infty}^{\infty} e^{-\frac{m u_3^2}{2kT}} du_3 = nkT \quad (\text{A.42})$$

similarly  $\Pi_{22} = nkT$  and  $\Pi_{33} = nkT$ . The fluid density is

$$\rho = nm \quad (\text{A.43})$$

and the gas constant is

$$k = \frac{R_u}{N} = \frac{M_w}{N} \frac{R_u}{M_w} = mR \quad (\text{A.44})$$

where  $N$  is Avogadro's number.

$$N = 6.023 \times 10^{26} \frac{\text{molecules}}{\text{kilogram} - \text{mole}}. \quad (\text{A.45})$$

The force per unit area produced by molecular collisions is

$$\Pi_{11} = \Pi_{22} = \Pi_{33} = nkT = \left( \frac{\rho}{m} \right) mRT = \rho RT = P. \quad (\text{A.46})$$

The normal stress derived by integrating the Maxwellian distribution over the molecular flux of momentum is just the thermodynamic pressure.

$$\Pi_{ij} = P \delta_{ij} = \begin{bmatrix} P & 0 & 0 \\ 0 & P & 0 \\ 0 & 0 & P \end{bmatrix} \quad (\text{A.47})$$

Recall the mean molecular speed  $\hat{u} = \sqrt{8kT/\pi m}$ . The speed of sound for a gas is  $a^2 = \gamma P/\rho$ . Accordingly, the speed of sound is directly proportional to the mean molecular speed.

$$a = \left(\frac{\gamma P}{\rho}\right)^{1/2} = \left(\frac{\gamma n k T}{n m}\right)^{1/2} = \left(\frac{\gamma \pi}{8}\right)^{1/2} \hat{u} \quad (\text{A.48})$$

## A.5 The mean free path

A molecule of effective diameter  $\sigma$  sweeps out a collision path which is of diameter  $2\sigma$ . The collision volume swept out per second is  $\pi\sigma^2\hat{u}$ . With the number of molecules per unit volume equal to  $n$ , the number of collisions per second experienced by a given molecule is  $\nu_c = n\pi\sigma^2\sqrt{8kT/\pi m}$ . The average distance that a molecule moves between collisions is

$$\lambda = \frac{\hat{u}_{rel}}{\nu_c} = \frac{\hat{u}_{rel}}{n\pi\sigma^2\hat{u}} \quad (\text{A.49})$$

where the mean relative velocity between molecules is used. This accounts for the fact that the other molecules in the volume are not static; they are in motion. When this motion is taken into account, the mean free path is estimated as

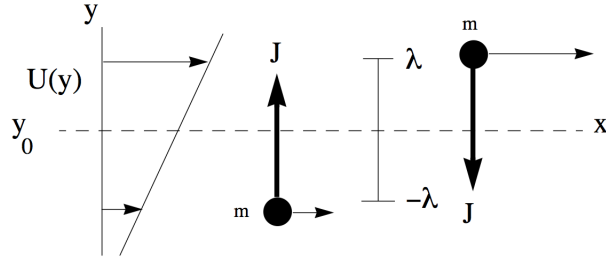
$$\lambda = \frac{1}{\sqrt{2}n\pi\sigma^2}. \quad (\text{A.50})$$

Typical values for the mean free path of a gas at room temperature and one atmosphere are on the order of 50 nanometers (roughly 10 times the mean molecular spacing).

## A.6 Viscosity

Consider the flux of momentum associated with the net particle flux across the plane  $y = y_0$  depicted in figure A.10.

On the average, a particle passing through  $y_0$  in the positive or negative direction had its last collision at  $y = y_0 - \lambda$  or  $y = y_0 + \lambda$ , where  $\lambda$  is the mean free path. Through the collision process, the particle tends to acquire the mean velocity at that position. The particle flux across  $y_0$  in either direction is  $J = n(kT/2\pi m)^{1/2}$ . The net flux of  $x_1$  - momentum in the  $x_2$ -direction is


 Figure A.10: *Momentum exchange in a shear flow.*

$$\Pi_{12} = mJU(y_0 - \lambda) - mJU(y_0 + \lambda) \cong -2mJ\lambda \frac{dU}{dy}. \quad (\text{A.51})$$

The viscosity derived from this model is

$$\mu = 2mJ\lambda = 2\rho\lambda \left( \frac{kT}{2\pi m} \right)^{1/2}. \quad (\text{A.52})$$

In terms of the mean molecular speed this can be written as

$$\mu = \frac{1}{2}\rho\lambda \left( \frac{8kT}{\pi m} \right)^{1/2} = \frac{1}{2}\rho\hat{u}\lambda. \quad (\text{A.53})$$

The viscosity can be expressed in terms of the speed of sound as follows.

$$\mu = \frac{1}{2}\rho\lambda \left( \frac{8nkT}{\pi nm} \right)^{1/2} = \left( \frac{2}{\pi\gamma} \right)^{1/2} \rho a \lambda \quad (\text{A.54})$$

This result can be used to relate the Reynolds number and Mach number of a flow

$$Re = \frac{\rho UL}{\mu} \cong \frac{UL}{a\lambda} = M \left( \frac{L}{\lambda} \right) \quad (\text{A.55})$$

where  $L$  is a characteristic length of the flow and the factor  $(2/\pi\gamma)^{1/2}$  has been dropped. The ratio of mean free path to characteristic length is called the Knudsen number of the flow.

$$K_n = \frac{\lambda}{L} \quad (\text{A.56})$$

## A.7 Heat conductivity

The same heuristic model can be used to crudely estimate the net flux of internal energy (per molecular mass) across  $y_0$ .

$$Q_2 = mJC_vT(y_0 - \lambda) - mJC_vT(y_0 + \lambda) = -2mJC_v\lambda\frac{dT}{dy} \quad (\text{A.57})$$

The heat conductivity derived from this model is

$$\kappa = \frac{1}{2}\rho\hat{u}\lambda C_v. \quad (\text{A.58})$$

The model indicates that the Prandtl number for a gas should be proportional to the ratio of specific heats.

$$P_r = \frac{\mu C_p}{\kappa} = \frac{C_p}{C_v} = \gamma \quad (\text{A.59})$$

A more precise theory gives

$$P_r = \frac{4\gamma}{9\gamma - 5} \quad (\text{A.60})$$

which puts the Prandtl number for gases in the range  $2/3 \leq P_r < 1$  depending on the number of degrees of freedom of the molecular system.

Notice that we got to these results using an imprecise model and without using the Maxwellian distribution function. In fact, a rigorous theory of the transport coefficients in a gas must consider small deviations from the Maxwellian distribution that occur when gradients of temperature or velocity are present. This is the so-called Chapman-Enskog theory of transport coefficients in gases.

## A.8 Specific heats, the law of equipartition

Classical statistical mechanics leads to a simple expression for  $C_p$  and  $C_v$  in terms of  $\beta$ , the number of degrees of freedom of the appropriate molecular model.

$$\begin{aligned} C_p &= \frac{\beta + 2}{2} R \\ C_v &= \frac{\beta}{2} R \\ \gamma &= \frac{\beta + 2}{\beta} \end{aligned} \tag{A.61}$$

For a mass point,  $m$ , with three translational degrees of freedom,  $\beta = 3$ , the energy of the particle is

$$E = \frac{1}{2}mu^2 + \frac{1}{2}mv^2 + \frac{1}{2}mw^2 \tag{A.62}$$

where  $(u, v, w)$  are the velocities in the three coordinate directions. The law of equipartition of energy says that any term in  $E$  that is quadratic (proportional to a square) in either the position or velocity contributes  $(1/2)kT$  to the thermal energy of a large collection of such mass points. Thus the thermal energy (internal energy) per molecule of a gas composed of a large collection of mass points is

$$\tilde{e} = \frac{3}{2}kT. \tag{A.63}$$

For one mole of gas

$$N\tilde{e} = \frac{3}{2}R_uT \tag{A.64}$$

where  $R_u = Nk$  is the universal gas constant. On a per unit mass of gas basis the internal energy is

$$e = \frac{3}{2}RT \tag{A.65}$$

where



$$R = \frac{R_u}{\text{molecularweight}}. \quad (\text{A.66})$$

This is a good model of monatomic gases such as Helium, Argon, etc. Over a very wide range of temperatures

$$\begin{aligned} C_p &= \frac{5}{2}R \\ C_v &= \frac{3}{2}R \end{aligned} \quad (\text{A.67})$$

from near condensation to ionization.

## A.9 Diatomic gases

### A.9.1 Rotational degrees of freedom

The simplest classical model for a diatomic molecule is a rigid dumb bell such as that shown in figure A.11. In the classical theory for a solid object of this shape there is one rotational degree of freedom about each coordinate axis shown in the figure.

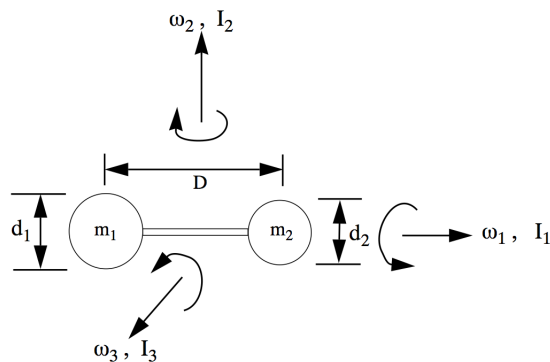


Figure A.11: *Rigid dumb bell model of a diatomic molecule.*

The energy of the rotating body is

$$E_{\text{soliddumbell}} = \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2. \quad (\text{A.68})$$

The moment of inertia about the 2 or the 3 axis is

$$I_2 = I_3 = m_r D^2 \quad (\text{A.69})$$

where

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (\text{A.70})$$

is the *reduced mass*. The moment of inertia of the connecting shaft is neglected in (A.69) where it is assumed that  $d_{1,2} \ll D$  so that the masses of the spheres can be assumed to be concentrated at the center of each sphere. In classical theory, the energy (A.68) is a continuous function of the three angular frequencies. But in the quantum world of a diatomic molecule the energies in each rotational degree of freedom are discrete. As in the classical case the energy varies inversely with the moment of inertia of the molecule about a given axis. When the Schroedinger equation is solved for a rotating diatomic molecule the energy in the two coordinate directions perpendicular to the internuclear axis is

$$E_{2,3 \text{ diatomic molecule}} = \left( \frac{h}{2\pi} \right)^2 \frac{K(K+1)}{2I_{2,3}} = \left( \frac{h}{2\pi} \right)^2 \frac{K(K+1)}{2(m_r D^2)} \quad (\text{A.71})$$

where  $h$  is Plancks constant

$$h = 6.626 \times 10^{-34} \text{ J} - \text{sec} . \quad (\text{A.72})$$

The atomic masses are assumed to be concentrated at the two atomic centers. The rotational quantum number  $K$  is a positive integer greater than or equal to zero, ( $K = 0, 1, 2, 3, \dots$ ). The law of equipartition can be used with (A.71) to roughly equate the rotational energy with an associated gas temperature. Let

$$\frac{1}{2} k \theta_r \cong E_{2,3 \text{ diatomic molecule}} . \quad (\text{A.73})$$

Equation (A.73) defines the characteristic temperature

$$\theta_r = \left( \frac{h}{2\pi} \right)^2 \frac{2}{k(m_r D^2)} \quad (\text{A.74})$$

for the onset of rotational excitation in the two degrees of freedom associated with the 2 and 3 coordinate axes. In terms of the characteristic temperature, the rotational energy is

$$E_{2,3 \text{ diatomic molecule}} = K(K+1)k\theta_r. \quad (\text{A.75})$$

Rotational parameters for several common diatomic species are given in figure A.12.

	$m_r \times 10^{27} \text{ kg}$	$D \times 10^{10} \text{ M}$	$\theta_r \text{ }^\circ\text{K}$
H <sub>2</sub>	0.8393	0.74166	87.28
N <sub>2</sub>	11.629	1.094	2.89
O <sub>2</sub>	13.284	1.207	2.08
CO	11.392	1.13	2.77

Figure A.12: *Rotational constants for several diatomic gases.*

The characteristic rotational excitation temperatures for common diatomic molecules are all cryogenic and, except for hydrogen, fall far below the temperatures at which the materials would liquefy. Thus for all practical purposes, with the exception of hydrogen at low temperature, diatomic molecules in the gas phase have both rotational degrees of freedom fully excited.

### A.9.2 Why are only two rotational degrees of freedom excited?

The discretized energy for the degree of freedom associated with rotation about the inter-nuclear axis is

$$E_{1 \text{ diatomic molecule}} = \left( \frac{h}{2\pi} \right)^2 \frac{K(K+1)}{2I_1} \quad (\text{A.76})$$

and the characteristic excitation temperature is

$$\theta_{r1} = \left( \frac{h}{2\pi} \right)^2 \frac{1}{2kI_1} \quad (\text{A.77})$$

Almost all the mass of an atom is concentrated in the nucleus. This would suggest that the appropriate length scale,  $d$ , to use in (A.76) might be some measure of the nucleus diameter.

Consider a solid sphere model for the two nuclear masses. For a homo-nuclear molecule the characteristic rotational excitation temperature for the 1-axis degree of freedom is

$$\theta_{r1_{solid\ nuclear\ sphere}} = \left(\frac{h}{2\pi}\right)^2 \frac{1}{2k(md^2/5)} \quad (\text{A.78})$$

The diameter of the nucleus is on the order of  $10^{-14}m$  four orders of magnitude small than the diameter of an atom. From this model, one would expect

$$\theta_{r1_{solid\ nuclear\ sphere}} \cong 10^8 \theta_r. \quad (\text{A.79})$$

This is an astronomically high temperature that would never be reached in a practical situation other than at the center of a star.

Another approach is to ignore the nuclear contribution to the moment of inertia along the 1-axis but include only the moment of inertia of the electron cloud. If we take all of the mass of the electron cloud and concentrate it in a thin shell at the atomic diameter the characteristic rotational temperature is

$$\theta_{r1_{electron\ cloud\ hollow\ sphere}} = \left(\frac{h}{2\pi}\right)^2 \frac{1}{2k((1/3)m_{electron\ cloud\ hollow\ sphere}d_{atom}^2)}. \quad (\text{A.80})$$

Most atoms are on the order of  $10^{-10}m$  in diameter which is comparable to the internuclear distances shown in figure A.12. But the mass of the proton is 1835 times larger than the electron. So the mass of the nucleus of a typical atom with the same number of neutrons and protons is roughly 3670 times the mass of the electron cloud. In this model we would expect

$$\theta_{r1_{electron\ cloud\ hollow\ sphere}} \cong 3670 \theta_r \quad (\text{A.81})$$

This puts the rotational excitation temperature along the 1-axis in the 8 to 10,000K range, well into the range where dissociation occurs. The upshot of all this is that because  $I_1 \ll I_2$  and  $I_3$  the energy spacing of this degree of freedom is so large that no excitations can occur unless the temperature is extraordinarily high, so high that the molecule is likely to be dissociated. Thus only two of the rotational degrees of freedom are excited in the range of temperatures one is likely to encounter with diatomic molecules. The energy of a diatomic molecule at modest temperatures is

$$\begin{aligned}
E &= E_T + E_R \\
E_T &= \frac{1}{2}mu^2 + \frac{1}{2}mv^2 + \frac{1}{2}mw^2 \\
E_R &= \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2.
\end{aligned}
\tag{A.82}$$

At room temperature

$$\begin{aligned}
C_p &= \frac{7}{2}R \\
C_v &= \frac{5}{2}R.
\end{aligned}
\tag{A.83}$$

From the quantum mechanical description of a diatomic molecule presented above we learn that  $C_p$  can show some decrease below  $(7/2)R$  at very low temperatures. This is because of the tendency of the rotational degrees of freedom to freeze out as the molecular kinetic energy becomes comparable to the first excited rotational mode. More complex molecules with three-dimensional structure can have all three rotational degrees of freedom excited and so one might expect  $n = 6$  for a complex molecule at room temperature.

### A.9.3 Vibrational degrees of freedom

At high temperatures  $C_p$  can increase above  $(7/2)R$  because the atoms are not rigidly bound but can vibrate around the mean internuclear distance much like two masses held together by a spring as indicated in figure A.13.

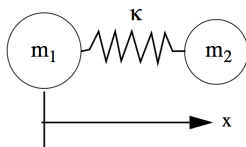


Figure A.13: *Diatomic molecule as a spring-mass system.*

The energy of a classical harmonic oscillator is

$$E_{spring-mass} = \frac{1}{2}m_r\dot{x}^2 + \frac{1}{2}\kappa x^2 \tag{A.84}$$

where  $m_r$  is the reduced mass,  $\kappa$  is the spring constant and  $x$  is the distance between the mass centers.

In the microscopic world of a molecular oscillator the vibrational energy is quantized according to

$$E_V = \left(\frac{h}{2\pi}\right) \omega_0 \left(j + \frac{1}{2}\right) \quad (\text{A.85})$$

where  $\omega_0$  is the natural frequency of the oscillator and the quantum number  $j = 0, 1, 2, 3, \dots$ . The natural frequency is related to the masses and effective spring constant by

$$\omega_0 = \sqrt{\frac{\kappa}{m_r}}. \quad (\text{A.86})$$

For a molecule, the spring constant is called the bond strength. Notice that the vibrational energy of a diatomic molecule can never be zero even at absolute zero temperature.

A characteristic vibrational temperature can be defined using the law of equipartition just as was done earlier for rotation. Let

$$\frac{1}{2}k\theta_v \cong E_V. \quad (\text{A.87})$$

Define

$$\theta_v = \left(\frac{h}{2\pi}\right) \frac{\omega_0}{k} = \left(\frac{h}{2\pi}\right) \frac{1}{k} \sqrt{\frac{\kappa}{m_r}}. \quad (\text{A.88})$$

Vibrational parameters for several common diatomic species are given in Figure A.14.

	$m_r \times 10^{27} \text{ kg}$	$\kappa(N/M)$	$\theta_v \text{ }^\circ K$
H <sub>2</sub>	0.8393	570	6297
N <sub>2</sub>	11.629	2240	3354
O <sub>2</sub>	13.284	1140	2238
CO	11.392	1860	3087

Figure A.14: *Vibrational constants for several diatomic gases.*

The characteristic vibrational excitation temperatures for common diatomic molecules are all at high combustion temperatures. At high temperature seven degrees of freedom are excited and the energy of a diatomic molecule is

$$\begin{aligned}
 E &= E_T + E_R + E_V \\
 E_T &= \frac{1}{2}mu^2 + \frac{1}{2}mv^2 + \frac{1}{2}mw^2 \\
 E_R &= \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_3\omega_3^2 \\
 E_V &= \frac{1}{2}m_r\dot{x}^2 + \frac{1}{2}\kappa x^2
 \end{aligned}
 \tag{A.89}$$

where the various energies are quantized as discussed above. At high temperatures the heat capacities approach

$$\begin{aligned}
 C_p &= \frac{9}{2}R \\
 C_v &= \frac{7}{2}R.
 \end{aligned}
 \tag{A.90}$$

Quantum statistical mechanics can be used to develop a useful theory for the onset of vibrational excitation. The specific heat of a diatomic gas over a wide range of temperatures is accurately predicted to be

$$\frac{C_p}{R} = \frac{7}{2} + \left( \frac{\theta_v/2T}{\sinh(\theta_v/2T)} \right)^2.
 \tag{A.91}$$

The enthalpy change of a diatomic gas at and above temperatures where the rotational degrees of freedom are fully excited is

$$h(T) - h(T_1) = \int_{T_1}^T C_p dT = R \int_{T_1}^T \left( \frac{7}{2} + \left( \frac{\theta_v/2T}{\sinh(\theta_v/2T)} \right)^2 \right) dT.
 \tag{A.92}$$

With  $T_1$  set (somewhat artificially) to zero, this integrates to

$$\frac{h(T)}{RT} = \frac{7}{2} + \frac{\theta_v/T}{e^{\theta_v/T} - 1}
 \tag{A.93}$$

plotted in figure A.15.

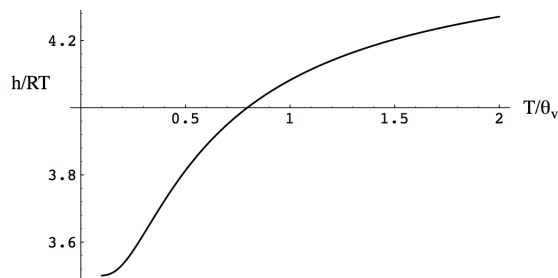


Figure A.15: *Enthalpy of a diatomic gas.*

## A.10 Energy levels in a box

We discussed the quantization of rotational and vibrational energy levels but what about translation? In fact the translational energies for particle motion in the three coordinate directions are quantized when the particle is confined to a box. The wave function for a single atom of mass  $m$  contained inside a box with sides  $L_x, L_y, L_z$  satisfies the Schroedinger equation

$$\frac{ih}{2\pi} \frac{\partial \Psi(\bar{x}, t)}{\partial t} + \frac{h^2}{8\pi^2 m} \nabla^2 \Psi(\bar{x}, t) - V(\bar{x}) \Psi(\bar{x}, t) = 0 \quad (\text{A.94})$$

where  $h = 6.626068 \times 10^{-34} \text{ m}^2 \text{ kg} / \text{ sec}$  is Plancks constant. The potential is

$$\begin{aligned} V(\bar{x}) &= 0 & 0 < x < L_x, \ 0 < y < L_y, \ 0 < z < L_z \\ V(\bar{x}) &= \infty & \text{on and outside the box.} \end{aligned} \quad (\text{A.95})$$

The solution must satisfy the condition  $\Psi = 0$  on and outside the walls of the box. For this potential (A.94) is solved by a system of standing waves.

$$\Psi(x, y, z, t) = \left( \frac{8}{L_x L_y L_z} \right)^{1/2} e^{-i \left( \frac{2\pi E}{h} |\bar{k}| \right) t} \sin \left( \frac{n_x \pi x}{L_x} \right) \sin \left( \frac{n_y \pi y}{L_y} \right) \sin \left( \frac{n_z \pi z}{L_z} \right) \quad (\text{A.96})$$

The quantized energy corresponding to the wave vector



$$\bar{k} = \left( \frac{n_x \pi}{L_x}, \frac{n_y \pi}{L_y}, \frac{n_z \pi}{L_z} \right) \quad (\text{A.97})$$

is

$$E_{|\bar{k}|} = \frac{h^2}{8\pi^2 m} (k_x^2 + k_y^2 + k_z^2) = \frac{h^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (\text{A.98})$$

The corresponding frequency is

$$\nu = \frac{E_{|\bar{k}|}}{h}. \quad (\text{A.99})$$

The volume of the box is  $V = L_x L_y L_z$ . The wave function is zero everywhere outside the box and must satisfy the normalization condition

$$\int_0^{L_x} \int_0^{L_y} \int_0^{L_z} \Psi(\bar{x}, t) \Psi^*(\bar{x}, t) dx dy dz = 1. \quad (\text{A.100})$$

on the total probability that the particle is inside the box. The implication of (A.100) and the condition  $\Psi = 0$  on the walls of the box, is that the quantum numbers  $(n_x, n_y, n_z)$  must be integers greater than zero. The energy of the particle in the box cannot be zero similar to the case of the harmonic oscillator. For a box of reasonable size, the energy levels are very closely spaced. A characteristic excitation temperature can be defined for translational motion at the lowest possible energy. Let

$$\frac{1}{2} k \theta_T \equiv E_T \quad (\text{A.101})$$

where

$$E_T = \frac{3h^2}{8mV^{2/3}}. \quad (\text{A.102})$$

The translational excitation temperature is

$$\theta_T = \frac{3h^2}{4mkV^{2/3}}. \quad (\text{A.103})$$

Take monatomic helium gas for example. The characteristic translational excitation temperature is

$$\theta_{T_{He}} = \frac{3h^2}{4m_{He}kV^{2/3}} = \frac{3(6.626 \times 10^{-34})^2}{4(6.643 \times 10^{-27})1.38 \times 10^{-23}V^{2/3}} = \frac{3.57 \times 10^{-14}}{V^{2/3}} K. \quad (\text{A.104})$$

In general, the characteristic translational temperature is far below any temperature at which a material will solidify. Clearly translational degrees of freedom are fully excited for essentially all temperatures of a gas in a box of reasonable size.

### A.10.1 Counting energy states

For simplicity let  $L_x = L_y = L_z = L$ . In this case, the energy of a quantum state is

$$E_{|\vec{k}|} = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2). \quad (\text{A.105})$$

Working out the number of possible states with translational energy of the monatomic gas less than some value  $E$  amounts to counting all possible values of the quantum numbers,  $n_x$ ,  $n_y$  and  $n_z$  that generate  $E_{|\vec{k}|} < E$ . Imagine a set of coordinate axes in the  $n_x$ ,  $n_y$  and  $n_z$  directions. According to (A.98) a surface of constant energy is approximately a sphere (with a stair-stepped surface) with its center at the origin of the  $n_x$ ,  $n_y$  and  $n_z$  coordinates. The number of possible states with energy less than the radius of the sphere is directly related to the volume of the sphere. Actually only 1/8th of the sphere is involved corresponding to the positive values of the quantum numbers. Figure A.15 illustrates the idea.

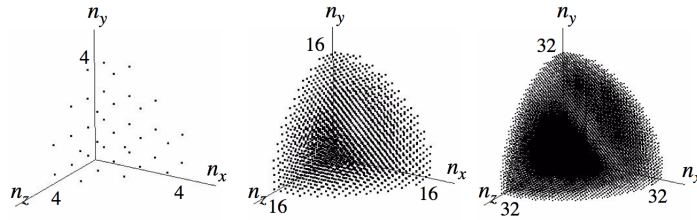


Figure A.16: Points represent quantum states in a box for energies that satisfy  $8EmV^{2/3}/h^2 \leq n_x^2 + n_y^2 + n_z^2$ . Three cases are shown where the maximum value of the quantum numbers are 4, 16 and 32.

Following Boltzmann's notation, let  $W$  be the number of states.

$$W_{oneatom}(E, V) = \frac{1}{8} \left( \frac{4\pi}{3} (n_x^2 + n_y^2 + n_z^2)^{3/2} \right) = \frac{\pi}{6} (n_x^2 + n_y^2 + n_z^2)^{3/2} \quad (\text{A.106})$$

In terms of the volume of the box and the gas kinetic energy the number of states with energy  $E_{|k|} < E$  is, according to (A.105) and (A.106)

$$W_{oneatom}(E, V) = \frac{\pi}{6} \left( \frac{8m}{h^2} \right)^{3/2} V E^{3/2}. \quad (\text{A.107})$$

Equation (A.107) gives the number of possible energy states with energy less than  $E$  for a single atom. If we add a second atom to the box then the number of possible states lies within the positive region of a six dimensional sphere of radius  $R = \sqrt{8mV^{2/3}E/h^2}$ .

$$\frac{8mV^{2/3}E}{h^2} = (n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2) \quad (\text{A.108})$$

The volume of a sphere in six dimensions is  $(\pi^3/6) R^6$ . For a box with  $N$  molecules the total number of possible energy states of the system lies within a sphere of  $3N$  dimensions with volume

$$\frac{\pi^{3N/2} R^{3N}}{\left(\frac{3N}{2}\right)!}. \quad (\text{A.109})$$

The volume of the positive region of this  $3N$  dimensional sphere is

$$\frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \left(\frac{R}{2}\right)^{3N}. \quad (\text{A.110})$$

In terms of the energy, the number of distinct states with energy less than  $E$  is

$$W(E, V, N) = \frac{\pi^{3N/2}}{N! \left(\frac{3N}{2}\right)!} \left(\frac{2m}{h^2}\right)^{3N/2} V^N E^{3N/2}. \quad (\text{A.111})$$

States with the same energy must not be counted more than once. Since the atoms are indistinguishable, the additional factor of  $N!$  in the denominator is needed to account for states that are repeated or degenerate.

If the number of molecules in the volume  $V$  is more than a few tens or so, the number of states can be represented using the Stirling approximation for the factorial.

$$\alpha! \cong \alpha^\alpha e^{-\alpha} \quad (\text{A.112})$$

Now

$$W(E, V, N) = \pi^{3N/2} e^{5N/2} \left(\frac{V}{N}\right)^N \left(\frac{4mE}{3h^2 N}\right)^{3N/2}. \quad (\text{A.113})$$

The result (A.113) is presented in Beckers Theory of Heat, page 135, equation 35.4. A more accurate version of the Stirling approximation is

$$\alpha! \cong (2\pi\alpha)^{1/2} \alpha^\alpha e^{-\alpha}$$

which would give

$$W(E, V, N) = \frac{\pi^{3N/2} e^{5N/2}}{\sqrt{6\pi N}} \left(\frac{V}{N}\right)^N \left(\frac{4mE}{3h^2 N}\right)^{3N/2}. \quad (\text{A.114})$$

Note that for values of  $N$  greater than a few hundred the number of states with energy less than  $E$  is virtually the same as the number of states with energy equal to  $E$  because of the extremely steep dependence of (A.114) on  $N$ . All of the energy states are concentrated within a membrane thin spherical shell at the energy  $E$ .

### A.10.2 Entropy of a monatomic gas in terms of the number of states

According to the Law of Equipartition and the development in the early part of this appendix, the internal energy of a monatomic gas is

$$E = \frac{1}{2} m N \widehat{u^2} = \frac{3}{2} k N T. \quad (\text{A.115})$$

The number of states can be expressed in terms of the temperature as

$$W(T, V, N) = \pi^{3N/2} e^{5N/2} \left(\frac{V}{N}\right)^N \left(\frac{2mkT}{h^2}\right)^{3N/2}. \quad (\text{A.116})$$

Take the logarithm of (A.116).

$$\text{Log}(W(T, V, N)) = N \left( \text{Log}\left(\frac{V}{N}\right) + \frac{3}{2} \text{Log}(T) + \frac{3}{2} \text{Log}\left(\frac{2\pi mk}{h^2}\right) + \frac{5}{2} \right) \quad (\text{A.117})$$

Differentiate (A.117) and multiply both sides by Boltzmanns constant,  $k$ .

$$k \frac{dW}{W} = \frac{3kN}{2} \frac{dT}{T} + kN \frac{d(V/N)}{V/N} \quad (\text{A.118})$$

Recall  $R_u = kN_a$  where  $N_a$  is Avogadros number. Equation (A.118) now becomes

$$k \frac{dW}{W} = \frac{3}{2} n R_u \frac{dT}{T} + n R_u \frac{d(V/N)}{V/N}. \quad (\text{A.119})$$

where the number of moles of gas in the box is  $n = N/N_a$ .

The model we are considering is that of a monatomic gas with only three degrees of freedom. For such a gas the constant volume molar heat capacity is  $C_v = 3R_u/2$ . Equation (A.119) now reads

$$k \frac{dW}{W} = n C_v \frac{dT}{T} + n R_u \frac{d(V/n)}{V/n}. \quad (\text{A.120})$$

Recall the Gibbs equation

$$dS = \frac{dE}{T} + \frac{P}{T} dV. \quad (\text{A.121})$$

For an ideal gas with the equation of state  $PV = nR_u T$  the Gibbs equation becomes

$$dS = n C_v \frac{dT}{T} + n R_u \frac{dV}{V}. \quad (\text{A.122})$$

Comparing (A.122) with (A.120) leads to the conclusion that

$$dS = k \frac{dW}{W}. \quad (\text{A.123})$$

Integrating (A.123) leads to the famous Boltzmann relation for the entropy

$$S = k \text{Log}(W) + \alpha. \quad (\text{A.124})$$

Substitute (A.113) into (A.124). The entropy of the gas is

$$S = kN \left( \text{Log} \left( \frac{V}{N} \left( \frac{E}{N} \right)^{3/2} \right) + \frac{5}{2} + \frac{3}{2} \text{Log} \left( \frac{4\pi m}{3h^2} \right) \right). \quad (\text{A.125})$$

The relation (A.125) is known as the Sackur-Tetrode equation after its discoverers in the early 1900s. It can be used to derive the various equations that govern a gas. In terms of the temperature, the entropy expression is equation (A.117) multiplied by  $k$

$$S = kN \left( \text{Log} \left( \frac{V}{N} (T)^{3/2} \right) + \frac{5}{2} + \frac{3}{2} \text{Log} \left( \frac{2\pi mk}{h^2} \right) \right) \quad (\text{A.126})$$

which agrees with equation 35.8 in Beckers *Theory of Heat*, page 136.

The additive constant in (A.126) is not in disagreement with the third law nor is the fact that (A.126) becomes singular at  $T = 0$ . The theory just developed is for a Boltzmann gas that necessarily implies temperatures well above absolute zero where the material is not in a condensed state and Boltzmann statistics apply. The constant is needed for the theory of condensation. The Sackur-Tetrode equation provides a remarkably accurate value of the entropy for monatomic gases. As an example, select helium at a pressure of  $10^5 \text{ N/m}^2$  and temperature of  $298.15 \text{ K}$ . At these conditions  $V/N = 4.11641 \times 10^{-26} \text{ m}^3/\text{molecule}$ . The mass of the helium atom is  $m = 6.64648 \times 10^{-27} \text{ kg}$  using these values the entropy evaluated from (A.126) is

$$\frac{S}{kN} = \text{Log} \left( e^{5/2} \left( \frac{V}{N} \right) \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right) = 15.1727 \quad (\text{A.127})$$

The value provided in tabulations of helium properties is 15.17271576. Similar results can be determined for other monatomic gases.

According to the third law  $\alpha = 0$  and

$$S = k \text{Log} (W) \quad (\text{A.128})$$

is the absolute entropy of the system. Consider the state of a single atom contained in a box in the limit  $T \rightarrow 0$ . From the solution to the Schroedinger equation, (A.98), the least energy that the atom can have is

$$E_{111} = \frac{3h^2}{8mV^{2/3}}. \quad (\text{A.129})$$

This is a tiny but finite number. In this model of a single atom gas, as the temperature goes to zero the atom in the box falls into the lowest quantum state so the entropy is  $S = k \text{Log}(1) = 0$ .

We derived (A.128) using the energy states in an ideal monatomic gas rather than follow the more general proof of Boltzmann. The remarkable thing about (A.128) is that it applies to a wide range of systems other than ideal gases including solids and liquids.