Chapter 1

Kinetics

1.1 Big numbers and probability

1.1.1 Big numbers

Take a number like Avogadro's number, $N_A = 6 \times 10^{23}$. The number of rearrangements is of Avogadro's number $N_A!$ is exponentially big, meaning the logarithm is also big. We proved the Stirling approximation[1]

$$\log(N!) \simeq N \log N - N \tag{1.1}$$

The Stirling approximation can also be written

$$\log(N!) \simeq N \log(N/e) \qquad \text{or} \qquad N! \simeq \left(\frac{N}{e}\right)^N \tag{1.2}$$

Given N objects, the number off ways I can choose r_1 objects for group 1, and the remaining r_2 objects in group 2 (with $r_2 + r_2 = N$) is given by the "binomial" coefficients [2]

$$^N C_{r_1 r_2} = \frac{N!}{r_1! r_2!} \tag{1.5}$$

You should be able to explain this formula. This generalizes – if I have N objects, and I select r_1 objects into group 1, r_2 objects into group 2, and the remaining r_3 objects into group three (with $r_1 + r_2 + r_3 = N$), the number of ways to do this is given by the "multinomial" coefficient:

$$^N C_{r_1 r_2 r_3} = \frac{N!}{r_1! r_2! r_3!} \tag{1.6}$$

You should be able to explain this formula.

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[1]$\log(x)$ is the same as $\ln(x)$ throughout this course! If we ever need the log base 10 we will write $\log_{10}(x)$.

[2]While we wont need it, the reason why its called the binomial coefficient is because the binomial $x + y$ raised to a power is

$$(x + y)^N = \underbrace{(x + y)(x + y) \ldots (x + y)}_{N \text{ factors}} \tag{1.3}$$

$$= \sum_{r_1 = 0}^{N} {}^N C_{r_1 r_2} \, x^{r_1} y^{r_2} \tag{1.4}$$

In passing to the second line I have to choose r_1 terms out of the N terms in the first line to take x and the remaining r_2 terms will take y. Try it out for $N = 2$ and $N = 3$. The multinomial coefficients are similar, and expanding $(x + y + z)^N$ will lead to a similar expansion involving $x^{r_1} y^{r_2} z^{r_3}$.

1.1.2 Probability

First consider a set of discrete outcomes $i = 1 \ldots N$, each with probability $\mathscr{P}_i$ (like a weighted six sided die). The sum of probabilities is unity

$$\sum_i \mathscr{P}_i = 1 \tag{1.7}$$

Associated with each outcome is a quantity x_i, e.g. x_3 the money you get for rolling a three. Then the mean of x (the mean money you get by rolling the die)

$$\langle x \rangle = \sum_i \mathscr{P}_i x_i \tag{1.8}$$

For a given quantity x we define the deviation from the average

$$\delta x \equiv x - \langle x \rangle \tag{1.9}$$

and the average deviation is zero $\langle \delta x \rangle = 0$. Then the *variance* is the mean of the squared deviation

$$\langle \delta x^2 \rangle = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \tag{1.10}$$

The standard deviation is

$$\sigma_x = \sqrt{\langle x^2 \rangle} \tag{1.11}$$

For continuous variable we need the concept of a probability distribution. The probability, $\mathrm{d}\mathscr{P}$, to find a particle with position in a *range* between x and $x + \mathrm{d}x$, which we denote $[x, x + \mathrm{d}x]$, is denoted

$$\mathrm{d}\mathscr{P} = P(x)\mathrm{d}x\,, \tag{1.12}$$

where the probability *density* $P(x)$ is

$$P(x) = \frac{\mathrm{d}\mathscr{P}}{\mathrm{d}x}\,. \tag{1.13}$$

A very important probability density is the Gaussian or "normal" distribution which you should try to memorize:

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}}e^{-x^2/2\sigma^2} \tag{1.14}$$

It is also called the Bell shaped curve and you should be able to sketch it. In class and in homework we showed:

$$\int_{-\infty}^{\infty} P(x)\mathrm{d}x = 1 \tag{1.15}$$

And worked out a number of integrals

$$\langle x^n \rangle = \int_{-\infty}^{\infty} P(x)x^n\mathrm{d}x = \sigma^n C_n \tag{1.16}$$

The numbers are $C_0 = 1$, $C_2 = 1$, $C_4 = 3$ with odd moments, such as $\langle x \rangle$, being zero.

1.1.3 Independence and the central limit theorem

Consider a two dimensional probability distribution

$$\mathrm{d}\mathscr{P}_{x,y} = P(x,y)\mathrm{d}x\mathrm{d}y \tag{1.17}$$

This is the probability of x in $[x, x + \mathrm{d}x]$ *and* y in $[y, y + \mathrm{d}y]$.

We say that x and y are *independent* if $P(x,y) = P(x)P(y)$ factorizes so that the probability of finding x and y (in interval $\mathrm{d}x\,\mathrm{d}y$) is probability of x (in interval $\mathrm{d}x$) times the probability of in y (in interval $\mathrm{d}y$)

$$\mathrm{d}\mathscr{P}_{x,y} = P(x)\mathrm{d}x \times P(y)\mathrm{d}y \tag{1.18}$$

The constants can be arranged so that $P(x)$ and $P(y)$ are separately normalized, e.g.

$$\int P(x)\mathrm{d}x = 1 \quad \text{and} \quad \int P(y)\mathrm{d}y = 1 \tag{1.19}$$

When the distributions are independent

$$\langle xy \rangle = \langle x \rangle \langle y \rangle \tag{1.20}$$

For definiteness, consider a sequence of random steps in position x. Assume x_1, the step in position from step number one, is drawn from the probability distribution $P(x)$. Also assume second step x_2 is drawn from the same distribution, and that the choice of x_2 is no way dependent on x_1. Similarly, the third step x_3 is drawn from $P(x)$ and is no way dependent on x_1 or x_2; and so on for $x_4, x_5, x_6 \ldots$. Then we want to know what is the mean, variance, and probability distribution of the sum

$$Y = x_1 + x_2 + \ldots + x_N \tag{1.21}$$

The answer is for the mean and variance are

$$\langle Y \rangle = N \langle x \rangle \tag{1.22}$$
$$\langle \delta Y^2 \rangle = N \langle \delta x^2 \rangle \tag{1.23}$$

In general the probability of Y depends on $P(x)$, and nothing much can be said about $P(Y)$. However, if N is large $N \gg 1$, then, remarkably, the probability of Y takes on a universal form of a Normal distribution

$$P(Y) = \frac{1}{\sqrt{2\pi\sigma_Y^2}} \exp\left[-(Y - \langle Y \rangle)^2 / 2\sigma_Y^2\right] \tag{1.24}$$

with $\sigma_Y^2 = \langle \delta Y^2 \rangle$. We did not go over the proof, and it is enough at this level to just accept it as a statement of fact

1.2   Estimates of ideal gasses and the equipartition theorem

The pressure of an ideal gas satisfies

$$pV = n_{\mathrm{ml}}RT \tag{1.25}$$

Here n_{ml} is the number of moles, while $n \equiv N/V$ is reserved for the number of particles per volume. The number of moles is the number of particles in units of Avogadro's number, $n_{\mathrm{ml}} \equiv N/N_A$, so we define Boltzmann's constant k_B

$$pV = NkT \qquad k_B \equiv \frac{R}{N_A} \tag{1.26}$$

Sometimes we will drop the "B" and just write kT for k_BT.

Numerically

$$R = 8.32\,\mathrm{J/^\circ K} \qquad k_B = \frac{\frac{1}{40}eV}{300^\circ\mathrm{K}} \tag{1.27}$$

The reason for writing k_B like this is because this is how people (including me) remember it: e.g. typical thermal energy, $\sim k_BT$, is "one fortieth of electron volt at room temperature", $T \simeq 300^\circ\mathrm{K}$.

The typical value of pressure is $1\,\mathrm{bar} = 10^5\mathrm{N/m}^2 \simeq 1\,\mathrm{atm}$, a typical volume is a liter, $1\,\mathrm{L} = (10\mathrm{cm})^3 = 1000\,\mathrm{cm}^3 = 10^{-3}\mathrm{m}^3$. We note

$$(1\,\mathrm{bar})\,(1\,\mathrm{L}) = 100\,\mathrm{J} \tag{1.28}$$

Standard Temperature and Pressure (STP) is one bar at $273^\circ\mathrm{K}$ (freezing). The volume of one mole of gas at STP is $22\,\mathrm{L}$.

The equi-partition theorem states that mean energy per "degree of freedom (dof)" in the gas is $\frac{1}{2}kT$. We will explain what we mean here by dof using examples. Take a mono-atomic gas. Each an atom which can move in *three* ways – in the x, the y, and the z directions. Thus the number of dof is $3N$ where N is the

number of atoms in the gas. So the total mean total energy in the energy in the gas, which we call U or E (they are the same in our notation), is

$$U \equiv E = \frac{3}{2} NkT \tag{1.29}$$

The energy (or Hamiltonian) of each particle, which we typically call ϵ, is a sum of *three* quadratic forms

$$\epsilon = \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2 = \frac{1}{2} m\vec{v}^2 \tag{1.30}$$

Technically, the equipartition theorem says that the mean energy of each independent subsystem (i.e. a single particle) is $\frac{1}{2} k_B T$ per quadratic form in the classical Hamiltonian – there are three forms counting the v_x^2, v_y^2 and v_z^2 terms. Each quadratic form gives $\frac{1}{2} k_B T$ so

$$\left\langle \frac{1}{2} mv_x^2 \right\rangle = \tfrac{1}{2} k_B T \tag{1.31}$$

and

$$\left\langle \frac{1}{2} m\vec{v}^2 \right\rangle = \frac{3}{2} k_B T \tag{1.32}$$

The root means square velocity is

$$v_{\mathrm{rms}} = \sqrt{\langle \vec{v}^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \tag{1.33}$$

and is typically a couple of hundred meters a second, i.e. close to the speed of sound $c_s \simeq 330\,\mathrm{m/s}$.

For a classical diatomic gas there are five degrees of freedom (quadratic forms) per molecule, since the diatomic molecule can also rotate around the x and y axis. One must include the translational and rotational kinetic energy

$$\epsilon = \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2 + \frac{1}{2} I\omega_x^2 + \frac{1}{2} I\omega_y^2 \tag{1.34}$$

We note that instead of working with the velocity and angular velocity we will increasingly work with the momentum $p_x = mv_x$ and the angular momentum $L_x = I\omega_x$,

$$\epsilon = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{L_x^2}{2I} + \frac{L_y^2}{2I} \tag{1.35}$$

$$= \frac{\vec{p}^2}{2m} + \frac{\vec{L}^2}{2I} \tag{1.36}$$

The average of each of these five quadratic forms is $\frac{1}{2} k_B T$ so the mean energy per particle is

$$\frac{U}{N} = \frac{5}{2} k_B T \tag{1.37}$$

The formulas in this section can be used to make a variety of estimates such as: the spacing between particles at room temperature; the typical speed; the typical debroglie wavelength; typical angular velocity and angular momentum. We defined the thermal deBroglie wavelength:

$$\lambda_{\mathrm{th}} = \frac{h}{\sqrt{2\pi mk_B T}} \tag{1.38}$$

We note that $\lambda_{\mathrm{th}} \sim h/mv_{\mathrm{rms}}$. The factor of $\sqrt{2\pi}$ here is purely a matter of convention.

1.3 The Boltzmann factor

A system has total energy U. If a subsystem within the system has energy ϵ, the rest of the system has energy $U - \epsilon$. The subsystem should be small and independent of the rest of the system (except in regard to energy exchange), eg. a molecule in an ideal gas. Probability the subsystem will have energy ϵ is proportional to $e^{-\epsilon/k_B T}$

$$P(\epsilon) \propto e^{-\epsilon/k_B T} \tag{1.39}$$

This is the Boltzmann factor. We can simplify $\beta = k_B T$ such as to not have to write so much. If you have a set of microscopically small states $i = 1...N$, the sum of all of these probabilities is 1, as shown below. Since $P(\epsilon) = Ce^{-\beta\epsilon}$ we have

$$\sum_i Ce^{-\beta\epsilon_i} = 1, \tag{1.40}$$

which determines the constant C which we call $1/Z$

$$C = \frac{1}{Z} \quad \text{with} \quad Z \equiv \sum_i e^{-\beta\epsilon_i} \tag{1.41}$$

Z is known as the partition function and is important in what follows. Then the probability of finding the subsystem in state r with energy ϵ_r is the following

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z} \tag{1.42}$$

1.4 The velocity and speed distributions

Consider an ideal gas. Each atom is a subsystem with velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, and v_z and $v_z + dv_z$.

$$\mathrm{d}\mathscr{P}_{\vec{v}} = Ce^{-mv^2/2k_B T} \, \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z = P(v_x, v_y, v_z) \, \mathrm{d}^3 v \tag{1.43}$$

where C is a normalizing constant and $\vec{v}^2 = v_x^2 + v_y^2 + v_z^2$. We can determine C from the normalization condition:

$$1 = \int_{\text{all } \vec{v}} \mathrm{d}\mathscr{P} = \int_{\text{all } \vec{v}} Ce^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T} \, \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z \tag{1.44}$$

Doing this integral (which factorizes into and integrals over v_x, v_y and v_z) leads to the distribution of velocities

$$\mathrm{d}\mathscr{P}_{\vec{v}} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m\vec{v}^2/2k_B T} \, \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z \tag{1.45}$$

We note that the probability for the vector $\vec{v}$ factorizes into a probability of v_x, times a probability of v_y, times a probability of v_z

$$\mathrm{d}\mathscr{P}_{\vec{v}} = P(v_x) \, \mathrm{d}v_x \, P(v_y)\mathrm{d}v_y \, P(v_z)\mathrm{d}v_z \tag{1.46}$$

So, that the probability of finding a particle with x-component of velocity in $[v_x, v_x + \mathrm{d}v_x]$ is

$$\mathrm{d}\mathscr{P}_{v_x} = P(v_x) \, \mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2k_B T} \, \mathrm{d}v_x \tag{1.47}$$

To find the speed distribution we have to add up the probabilities $d\mathscr{P}_{\vec{v}}$ for all velocities with speed between v and $v + \mathrm{d}v$. This is a spherical shell of width $\mathrm{d}v$ (see lecture)

$$d\mathscr{P}_v = \int_{\vec{v} \text{ in shell}} \mathrm{d}\mathscr{P}_{\vec{v}} \tag{1.48}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_B T} \, 4\pi v^2 \, \mathrm{d}v \tag{1.49}$$

1.5   Change of variables and solid angles

1.5.1   Change of variables in 1d

Given a variable x and its probability distribution

$$\mathrm{d}\mathscr{P}_x = P(x)\,\mathrm{d}x \tag{1.50}$$

How do we find the probability of u, given a map $\varphi : x \to u$, i.e. when $u(x)$ is a function of x? Assuming that that the map is one to one we have

$$\mathrm{d}\mathscr{P}_u = P(x(u))\left|\frac{dx}{du}\right|\mathrm{d}u = P(x(u))\frac{\mathrm{d}u}{\left|\frac{du}{dx}\right|} \tag{1.51}$$

We note the absolute values here, which reflects the fact that when discussing probability we are asking whether a particle is in a bin of size $\mathrm{d}u$, and the bin size isn't like positive or negative.

The general formula for change of variables for an unoriented integral (like probability) is [3]

$$\int_R f(x)\mathrm{d}x = \int_{R_u} f(x(u))\left|\frac{dx}{du}\right|\,\mathrm{d}u \tag{1.52}$$

Here R is the region of integration for x (for example R could be interval $[1,2]$), and R_u is the image of R under the map (for example if the map is $u(x) = -2x$ then R_u is $[-4, -2]$).

To set yourself straight of this notation just make the change of variables in a simple integral, getting the signs right. For example, consider the basic integral:

$$I = \int_1^2 \mathrm{d}x = \int_{[1,2]} \mathrm{d}x = \frac{1}{2} \tag{1.53}$$

Undergoing a change of variables with $u = -2x$, giving $x = -u/2$ and $dx = -\frac{1}{2}du$, with $|dx/du| = \frac{1}{2}$. The integral then becomes

$$I = \int_{-2}^{-4} \left(-\frac{1}{2}\right)\mathrm{d}u = \int_{-4}^{-2}\frac{1}{2}\mathrm{d}u = \int_{[-4,-2]} \frac{1}{2}\,\mathrm{d}u = 1 \tag{1.54}$$

1.5.2   Higher dimensions: spherical coordinates and solid angle

In higher-dimensions we have

$$\mathrm{d}\mathscr{P} = P(x,y,z)\underbrace{\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}_{\mathrm{d}V} \tag{1.55}$$

where $\mathrm{d}V$ is the "volume element". A bit of geometry shows that the differential area dA and the volume element dV in spherical coordinates are (see Fig. 1.1)

$$dA = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.56}$$

$$dV = r^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.57}$$

So in spherical coordinates

$$\mathrm{d}\mathscr{P} = P(x,y,z)r^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.58}$$

$$\equiv P(r,\theta\,\phi)\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.59}$$

For example, if

$$P(x,y,z) = Ce^{-(x^2+y^2+z^2)/2\sigma^2} \tag{1.60}$$

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[3]The difference between oriented and unoriented integral is a matter of semantics at this level. If one replaces an integral by a sum of rectangles, you can sum them up in order from the beginning to the end (an oriented integral), or you can sum them up in any order provided they are in a specified region (an unoriented integral).
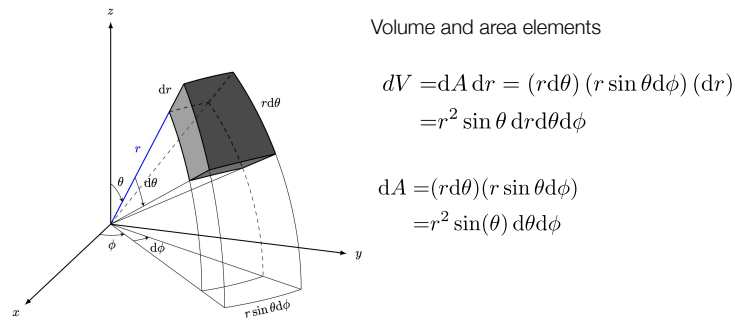
Spherical Coordinates

Volume and area elements

$$dV = dA\,dr = (rd\theta)\,(r\sin\theta d\phi)\,(dr)$$
$$= r^2\sin\theta\,drd\theta d\phi$$

$$dA = (rd\theta)(r\sin\theta d\phi)$$
$$= r^2\sin(\theta)\,d\theta d\phi$$

Figure 1.1: Spherical coordinates. From the figure, justify Eq. (1.56)

Then

$$P(r,\theta,\phi) = Ce^{-r/2\sigma^2}r^2\sin\theta \tag{1.61}$$

Rather than using geometry, we can use algebra to make the change of variables. The generalization of Eq. (1.51) is

$$d\mathscr{P}_{r,\theta,\phi} = P(x,y,z)\left\|\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)}\right\|drd\theta d\phi = P(r,\theta,\phi)drd\theta d\phi \tag{1.62}$$

Here it is understood that $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$ are functions of (r,θ,ϕ) (see Fig. 1.2). The double bars denote the absolute value, of the determinant of the Jacobian matrix. The Jacobian matrix (determinant) is defined by the matrix (determinant) of the possible derivatives

$$\left|\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)}\right| = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix} = \begin{vmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{vmatrix} = r^2\sin\theta \tag{1.63}$$

Take a patch of area A on a sphere. The solid angle is defined as[4]

$$\Omega \equiv \frac{A}{r^2}\,. \tag{1.64}$$

This analogous to an angle in 1d where $\theta = s/r$. Since the area of a region on the a sphere runs from 0 up to $4\pi r^2$, we have that Ω is in the range $0\ldots 4\pi$. For a small patch of the sphere parametrized substended by $d\theta$ and $d\phi$ we have from the geometry:

$$d\Omega \equiv \frac{dA}{r^2} = \sin\theta d\theta d\phi \tag{1.65}$$

If a particles position is distributed uniformly over the sphere the probability distribution is

$$d\mathscr{P} = \frac{dA}{4\pi r^2} = \frac{d\Omega}{4\pi} = \frac{\sin\theta d\theta d\phi}{4\pi} \tag{1.66}$$

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[4]I have always found the word "angle" here problematic, since it is a two dimensional region were are talking about. Indeed, the differential solid "angle", $d\Omega = \sin\theta d\theta d\phi$, is parametrized by two angles, θ and ϕ
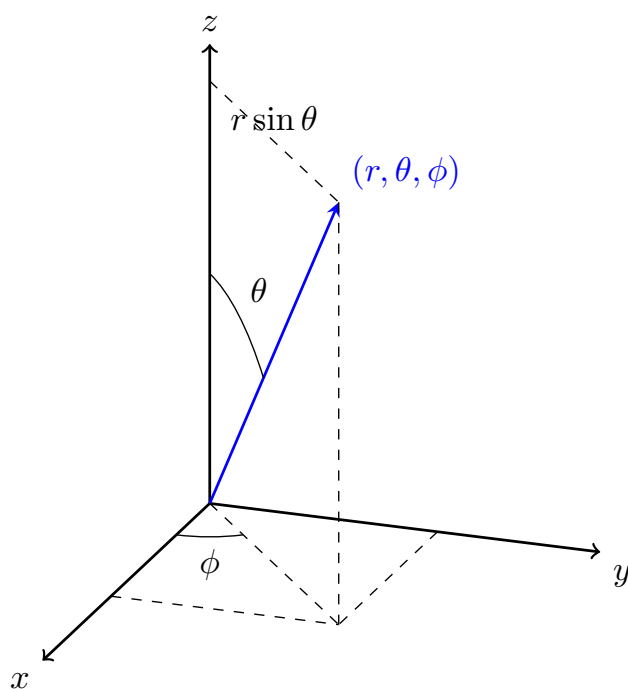
Figure 1.2:   Spherical coordinates. Use the picture to justify $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$ and $z = r \cos \theta$.
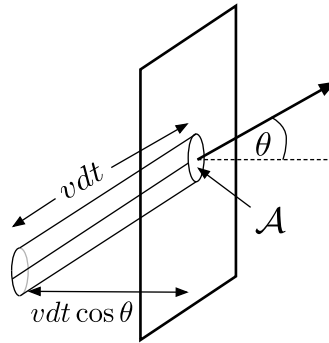
Flux through the hole

Figure 1.3: In each dt a volume $\mathcal{A}h = \mathcal{A}vdt\cos\theta$ passes through the hole

1.6 Pressure and effusion

After a change of variables the probability distribution of velocities (v_x, v_y, v_z) can be written as distribution particles with the speed v, flying with angles θ and ϕ:

$$d\mathscr{P}_{v,\theta,\phi} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT} \, v^2 \sin\theta \, dvd\theta d\phi \tag{1.67}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT} 4\pi v^2 dv \, \frac{\sin\theta d\theta d\phi}{4\pi} \tag{1.68}$$

$$= P(v)dv \, \frac{d\Omega}{4\pi} \tag{1.69}$$

where we have recalled Eq. (1.48) for the speed distribution. Thus, the probability of v, θ, ϕ in a specified range is probability of speed v in a range dv, times a probability of angles which are uniformly distributed the sphere, i.e. $d\mathscr{P}_\Omega/d\Omega = 1/4\pi$. The number of particles per volume with speed in $[v, v+dv]$ and angles in $[\theta, \theta + d\theta]$ and $[\phi, \phi + d\phi]$ is given by the probability in Eq. (1.69) multiplied by the the number of particles per volume $n = N/V$.

$$dn = nP(v)dv \, \frac{d\Omega}{4\pi} \tag{1.70}$$

Consider an hole of area $\mathcal{A}$ on the wall of a container containing a gas (see Fig. 1.3). The flux through the hole is

$$\Phi = \frac{1}{\mathcal{A}} \frac{dN_{\text{cross}}}{dt} = \text{number of particles crossing the hole per area per second} \tag{1.71}$$

From tube geometry in Fig. 1.3, the number of particles flying through an area $\mathcal{A}$ in time dt with speed in $[v, v+dv]$ and angles in $[\theta, \theta + d\theta]$ and $[\phi, \phi + d\phi]$ is the $dN_{\text{cross}} = dn\,\mathcal{A}h$, where $h = vdt\cos\theta$ is the height of the tube, and the tube volume is $\mathcal{A}h$. Dividing by $\mathcal{A}$ and dt we find the differential flux:

$$d\Phi = nP(v)v\cos\theta dv \, \frac{d\Omega}{4\pi} \,. \tag{1.72}$$

$d\Phi$ is the number of particles passing through the hole per area per second with speed in $[v, v + dv]$ and angles in $[\theta, \theta + d\theta]$ and $[\phi, \phi + d\phi]$.

We can integrate the flux $d\Phi$ over the velocity and over half of the sphere to find the total flux. Writing the 4π in the $d\Omega/4\pi$ as $2 \cdot 2\pi$ (see homework for motivation), we find:

$$\Phi = \int d\Phi = n \int_0^\infty dv P(v)v \int_0^{\pi/2} \frac{1}{2}\sin\theta\cos\theta d\theta \int_0^{2\pi} \frac{d\phi}{2\pi} = \frac{1}{4}n\langle v\rangle \tag{1.73}$$

$$= n\sqrt{\frac{kT}{2\pi m}} \tag{1.74}$$

We discussed an application or two of Eq. (1.73)

The pressure is computed similarly, each particle striking the wall with x component of velocity v_x, bounces off with velocity $-v_x$, and this delivers a momentum transfer (or impulse) of $\Delta p_x = m(v_x - (-v_x)) = 2mv_x = 2mv\cos\theta$ to the wall. The momentum transfer per area per time by atoms with v, θ, ϕ in a range $[\mathrm{d}v, \mathrm{d}\theta, \mathrm{d}\phi]$ is

$$\Delta p_x \, \mathrm{d}\Phi = \mathrm{d}\Phi\,(2mv\cos\theta) \tag{1.75}$$

Integrating over v, θ, ϕ as in Eq. (1.73) gives the force per area (recall that force $F_x = dp_x/dt$). We will not go through the details which are similar to Eq. (1.73)

$$p = \frac{F_x}{A} = \int \mathrm{d}\Phi\,(2mv\cos\theta) = nkT \tag{1.76}$$

You should feel comfortable completing the integration – the details are similar to Eq. (1.73). It is satisfying how the molecular theory of gasses reproduces the ideal gas law.

Appendix A

Estimates

We came across a number of physical constants that you need to know. Outside of this list, the constants will be given.

1. Giga $= 10^9$, Mega $= 10^6$, milli $= 10^{-3}$ so

$$1\,\text{meV} = 10^{-3}\,\text{eV} \quad 1\,\text{MeV} = 10^6\,\text{eV} \quad 1\,\text{GeV} = 10^9\,\text{eV} \tag{A.1}$$

2. Avogadro's number $N_A = 6 \times 10^{23}$.

3. The speed of light $c = 3 \times 10^8\,\text{m/s}$.

4. The speed of sound in air is approximately $c_s \simeq 330\,\text{m/s}$.

5. A useful unit of volume is liters. One liter is $(10\,\text{cm})^3 = 1000\,\text{cm}^3$. One mole of an ideal gas at STP has a volume of $22\,\text{L}$.

6. A useful unit of pressure is a bar. One atmosphere is approximately 1 bar. 1 bar is $10^5\,\text{N/m}^2$. A typical scale of energy is $1\,\text{bar} \times 1\,\text{L} = 100\,\text{J}$.

7. The ideal gas constant is $R = 8.32\,\text{J/}^\circ\text{K}$:

8. The Boltzmann constant k_B you can remember in two ways:

   - The macroscopic way: one Avogadro's number times k_B is R:

$$N_A k_B = R \tag{A.2}$$

   - The microscopic way: kT is "one fortieth of an eV at room temperature", $T = 300\,^\circ\text{K}$.

$$k_B = \frac{\frac{1}{40}\,\text{eV}}{300\,^\circ\text{K}} = \frac{0.025\,\text{eV}}{300\,^\circ\text{K}} \tag{A.3}$$

9. You should remember the proton (and neutron mass) in two ways:

   - The microscopic way: i.e. the rest energy in mega electron volts is

$$m_p c^2 \simeq 938\,\text{MeV} \simeq 1000\,\text{MeV} \simeq 1\,\text{GeV} \tag{A.4}$$

   - The macroscopic way: an Avogadro's number of protons weighs a gram. This is the molar mass of the proton:

$$\mathcal{M}_{\text{ml}} = m_p N_A = 1\,\text{g} \tag{A.5}$$

Protons and neutrons and weigh nearly the same thus the mass of one Avogadro's number of diatomic oxygen weighs $32\,g$, since there are eight protons and neutrons in one oxygen nucleus, and two such nuclei. The electrons are light (see below) for the mass budget.

You might want to use either of these methods to evaluate v_{rms} in atomic hydrogen gas at room temperature

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m_p}} = c\sqrt{\frac{3kT}{m_pc^2}} = (3\times 10^8 \mathrm{m/s}) \times \sqrt{\frac{(1/40)\mathrm{eV}}{938\times 10^6\,\mathrm{eV}}} \simeq 2700\,\mathrm{m/s} \tag{A.6}$$

Or if you prefer

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\,(N_Ak_B)\,T}{N_Am_p}} = \sqrt{\frac{3RT}{1g}} = \sqrt{\frac{3\times 8.32\,\mathrm{J/^\circ K}\times 300^\circ\mathrm{K}}{1g}} \simeq 2700\,\mathrm{m/s} \tag{A.7}$$

This is almost a factor of 10 faster than the speed of sound $c_s \simeq 330\,\mathrm{m/s}$, because hydrogen is so light.

10. You should remember the electron mass in two ways:

   - The microscopic way: the mass is "half an MeV"

   $$m_e \simeq 0.5\,\mathrm{MeV} \tag{A.8}$$

   - In comparison to the proton mass:
   $$\frac{m_e}{m_p} \simeq \frac{1}{2000} \tag{A.9}$$

11. Plancks constant is needed to convert wavelength to energy

   $$\hbar c = 197\,\mathrm{eV\,nm} \tag{A.10}$$

   or using $h = 2\pi\hbar$
   $$hc = 1240\,\mathrm{eV\,nm} \tag{A.11}$$

   Thus the energy of a photon of yellow light with $\lambda = 550\,\mathrm{nm}$ (emitted by sodium) is

   $$E = \frac{hc}{\lambda} = \frac{1240\,\mathrm{eV\,nm}}{550\,\mathrm{nm}} \simeq 2.3\,\mathrm{eV} \tag{A.12}$$

   Plancks constant is also useful for measuring typical de Broglie wavelength at room temperature

   $$\frac{h}{\sqrt{m_pkT}} = \frac{hc}{\sqrt{(m_pc^2)(kT)}} \simeq \frac{1240\,\mathrm{eVnm}}{\sqrt{10^9\,\mathrm{eV}\frac{1}{40}\,\mathrm{eV}}} \simeq 2.5\,\mathrm{\mathring{A}} \tag{A.13}$$

12. A useful unit of distance in atomic physics is angstroms, $1\,\mathrm{\mathring{A}} = 0.1\,\mathrm{nm}$. The Bohr radius

   $$a_0 = 0.53\,\mathrm{\mathring{A}} \tag{A.14}$$

   is about half an Angstrom. A typical bond length is normally between 1-5 Bohr Radii. (For N_2 the distance between the two nuclei is $1.09\,\mathrm{\mathring{A}}$)

13. An electron volt is a good unit of microscopic energy. Avogadro's number times $1\,\mathrm{eV}$ is a good unit of macroscopic chemical energy and is 100 kilo Joules.

   $$N_A\,\mathrm{eV} \simeq 100\,\mathrm{kJ} \tag{A.15}$$

   This is sometimes called the Faraday constant[1]. An explosion involves roughly an Avogadro's number of atomic transitions, with each atomic transition releasing about an electron volt of energy, for approximately $100\,\mathrm{kJ}$ of energy per mole. Burning a mole of gasoline gives roughly this amount of energy.

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   [1]We can quickly find the charge in Coulombs from this relation,
   $$1eV \simeq 100\,\mathrm{kJ}/N_A \simeq 1.6\times 10^{-19}\,\mathrm{J} \qquad \text{and so} \qquad 1e = 1.6\times 10^{-19}\mathrm{C}. \tag{A.16}$$

14. The Bohr model provides a lot of estimates of the microscopic world.

In the Bohr model the radius of the lowest electron orbit is $a_0 = 0.53\,\text{Å}$, and the angular momentum of the lowest orbit is discrete, $L = p a_0 = \hbar$. So the momentum is

$$\boxed{p = \frac{\hbar}{a_0}} \tag{A.17}$$

reflecting the uncertainty principle. In the lowest orbit Bohr orbit the kinetic energy is half of the potential energy in magnitude[2]. The potential energy is negative reflecting the positive charge $+e$ of the proton and negative charge $-e$ of the electron. The potential energy of the orbiting electron is

$$\text{PE} = -\frac{e^2}{4\pi\epsilon_0 a_0} \tag{A.18}$$

The binding energy of the electron to the proton

$$\text{BE} = \text{KE} + \text{PE} \tag{A.19}$$
$$= \frac{p^2}{2m} + \left(-\frac{e^2}{4\pi\epsilon_0 a_0}\right) \tag{A.20}$$
$$= -13.6\,\text{eV} \tag{A.21}$$

Thus we have for the Hydrogen atom where $p = \hbar/a_0$ and $\text{KE} = p^2/2m$

$$\text{KE} = \tfrac{1}{2}|\text{PE}| = |\text{BE}| \tag{A.22}$$

$$\boxed{\frac{\hbar^2}{2m_e a_0^2} = \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0 a_0}\right) \simeq 13.6\,\text{eV}} \tag{A.23}$$

$13.6\,\text{eV}$ is the Rydberg constant. For the ground states of a quantum mechanical system it is often the case that

$$\text{KE} \sim |\text{PE}| \sim |\text{BE}| \tag{A.24}$$

These facts give another way to estimate the thermal de Broglie wavelength of a *proton*, by inserting a_0 and the electron mass

$$\lambda_{\text{th}} \sim \frac{\hbar}{\sqrt{2m_p kT}} = a_0\sqrt{\frac{\hbar^2}{2m_e a_0^2}\left(\frac{1}{k_B T}\right)}\sqrt{\frac{m_e}{m_p}} = 0.5\,\text{Å}\,\sqrt{\frac{13.6\,\text{eV}}{k_B T}}\sqrt{\frac{1}{2000}} \tag{A.25}$$

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[2]This follows from Newton's Law for a circular orbit for an electron attracted to the proton via the Coulomb force:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Appendix B

Math

B.1 Rant on units

Prof. T and most professional physicists care a lot about units. If you have a dimensionful integral you can't do, that is bad. If you can turn the integral to something with overall units times a dimensionless integral (which is a number like $\sqrt{2}$) that isn't so bad.

Suppose, for example, the integral integral you are trying to compute is an integral over position:

$$I = \int_0^\infty \mathrm{d}x \, x^4 e^{-x^2/\ell^2} \tag{B.1}$$

where ℓ has units of length. Then $I \propto \ell^5$ times a dimensionless number, which turns out to be 0.66467. You should be able to show the ℓ^5 without doing any integrals, by simply switching the integration variable from the *dimensionful* variable x to a *dimensionless* variable $u = x/\ell$ (the position in units of ℓ). Here are the steps

$$I = \int_0^\infty dx x^4 \exp(-x^2/\ell^2) \tag{B.2}$$

$$= \ell^5 \int_0^\infty \frac{dx}{\ell} \frac{x^4}{\ell^4} \exp(-x^2/\ell^2) \tag{B.3}$$

$$= \ell^5 \times \int_0^\infty du u^4 \exp(-u^2) \tag{B.4}$$

$$= \ell^5 c \tag{B.5}$$

where c is an order one constant. I think that we can agree that

$$I = c\ell^5 \tag{B.6}$$

shows a great deal more insight than Eq. (B.1).

The fact that the proportionality constant is $c = \Gamma(5/2)/2 = 3\sqrt{\pi}/8 \simeq 0.66467$ doesn't seem so important, and I would be happy with $I = c\ell^5$ as a result. Finding c requires doing a dimensionless integral, which is the only kind of integral you should *ever* try to do!

B.2 Gaussian Integrals

We discussed the integrals

$$I_n = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \mathrm{d}x \, e^{-x^2/2} x^n \tag{B.7}$$

The first couple results are

$$I_0 = 1 \quad I_2 = 0 \quad I_4 = 3 \quad I_6 = 15 \tag{B.8}$$

We found these using the generating function technique.

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B.3   The Gamma function

The gamma function is a useful special function that extends the domain of the factorial function to non-integer values. It is defined by the integral

$$\Gamma(n) = \int_0^\infty x^{n-1} e^{-x} \mathrm{d}x \tag{B.9}$$

and has the familiar recursive relationship

$$\Gamma(n+1) = n\Gamma(n) \tag{B.10}$$

starting from $\Gamma(1) = 1$. We have

$$\Gamma(n) = (n-1)! \tag{B.11}$$

While the gamma function is defined for all complex numbers except the non-positive integers, analytical expressions are only known where n is an integer or half-integer. In particular,

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}. \tag{B.12}$$

So for instance $\Gamma(3/2) = \sqrt{\pi}/2$.

In statistical mechanics, the gamma function occurs frequently in integrals involving the Maxwell–Boltzmann distribution. In addition, the area of a sphere in d dimensions is

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} . \tag{B.13}$$

which comes up a lot later in the course.