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

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

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

$$\langle Y\rangle = N\langle x\rangle \tag{1.22}$$

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

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 $\sigma_Y = \sqrt{\langle \delta Y^2\rangle}$. 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, which is the number of particles N in units of Avogadro's number, $n_{\mathrm{ml}} \equiv N/N_A$. The symbol $n \equiv N/V$ is reserved for the number of particles per volume:

$$n \equiv \tfrac{N}{V} \qquad \textbf{is NOT} \qquad n_{\mathrm{ml}} \equiv \tfrac{N}{N_A}\ . \tag{1.26}$$

We will work with the number of particles N instead of n_{ml} and define Boltzmann's constant k_B

$$pV = Nk_BT \qquad k_B \equiv \frac{R}{N_A} \tag{1.27}$$

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

Numerically

$$R = 8.32\,\mathrm{J}/^\circ\mathrm{K} \qquad k_B = \frac{\frac{1}{40}eV}{300^\circ\mathrm{K}} \tag{1.28}$$

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", $T \simeq 300^\circ$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

$$(1\,\mathrm{bar})\,(1\,\mathrm{L}) = 100\,\mathrm{J} \tag{1.29}$$

Standard Temperature and Pressure (STP) is one bar at 273°K (freezing). The volume of one mole of gas at STP is 22 L. Keep in mind that under STP N(particles), V(volume), and U(total energy) are Extensive which mean they will grow with the system size. While T(temperature) and P(pressure) are Intensive and are constant throughout.

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

$$U \equiv E = \frac{3}{2}NkT \tag{1.30}$$

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

$$\epsilon = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}m\vec{v}^2 \tag{1.31}$$

Technically, the equipartition theorem says that the mean energy of each independent subsystem (i.e. a single particle) is $\frac{1}{2}k_BT$ 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 $\frac{1}{2}k_{\scriptscriptstyle B}T$ so

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \tfrac{1}{2}k_{\scriptscriptstyle B}T \tag{1.32}$$

and

$$\left\langle \frac{1}{2}m\vec{v}^2 \right\rangle = \frac{3}{2}k_{\scriptscriptstyle B}T \tag{1.33}$$

The root means square velocity is

$$v_{\rm rms} = \sqrt{\langle \vec{v}^2 \rangle} = \sqrt{\frac{3k_{\scriptscriptstyle B}T}{m}} \tag{1.34}$$

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

$$\epsilon = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 \tag{1.35}$$

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 $L_x = I\omega_x$,

$$\begin{aligned} \epsilon =& \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{L_x^2}{2I} + \frac{L_y^2}{2I} & (1.36) \\ =& \frac{\vec{p}^2}{2m} + \frac{\vec{L}^2}{2I} & (1.37) \end{aligned}$$

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

$$\frac{U}{N} = \frac{5}{2}k_{\scriptscriptstyle B}T \tag{1.38}$$

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 de Broglie wavelength; typical angular velocity and angular momentum. We defined the thermal de Broglie wavelength:

$$\lambda_{\rm th} = \frac{h}{\sqrt{2\pi m k_B T}} \tag{1.39}$$

We note that $\lambda_{\rm th} \sim h/mv_{\rm rms}$. 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), e.g. a molecule in an ideal gas. Probability the subsystem will have energy ϵ is proportional to $e^{-\epsilon/k_B T}$

$$P(\epsilon) \propto e^{-\epsilon/k_B T} \tag{1.40}$$

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

$$\sum_i Ce^{-\beta\epsilon_i} = 1\,, \tag{1.41}$$

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

$$C = \frac{1}{Z} \quad \text{with} \quad Z \equiv \sum_i e^{-\beta\epsilon_i} \tag{1.42}$$

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

$$P(\epsilon) = \frac{e^{-\epsilon/k_B T}}{Z} \tag{1.43}$$

The partition function is a function of the temperature, $Z(\beta)$. The derivative of Z with respect to (minus) β determine the mean energy via the formula

$$\langle\epsilon\rangle = \frac{1}{Z(\beta)}\left(-\frac{\partial Z}{\partial\beta}\right) \tag{1.44}$$

Higher derivatives with respect to minus β determine higher moments of the energy, e.g. to find the second moment $\langle\epsilon^2\rangle$ we have

$$\langle\epsilon^2\rangle = \frac{1}{Z(\beta)}\left(-\frac{\partial}{\partial\beta}\right)^2 Z(\beta) = \frac{1}{Z(\beta)}\frac{\partial^2 Z}{\partial\beta^2} \tag{1.45}$$

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 $v_z + dv_z$.

$$\mathrm{d}\mathscr{P}_{\vec{v}} = Ce^{-mv^2/2k_B T}\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = P(v_x, v_y, v_z)\,\mathrm{d}^3v \tag{1.46}$$

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:

$$1 = \int_{\text{all }\vec{v}} \mathrm{d}\mathscr{P}_{\vec{v}} = \int_{\text{all }\vec{v}} Ce^{-m(v_x^2+v_y^2+v_z^2)/2k_B T}\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{1.47}$$

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

$$\mathrm{d}\mathscr{P}_{\vec{v}} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m\vec{v}^2/2k_B T}\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \tag{1.48}$$

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

$$\mathrm{d}\mathscr{P}_{\vec{v}} = P(v_x)\,\mathrm{d}v_x\,P(v_y)\mathrm{d}v_y\,P(v_z)\mathrm{d}v_z \tag{1.49}$$

So, the probability of finding a particle with x-component of velocity in $[v_x, v_x + \mathrm{d}v_x]$ is after integrating over v_y and v_z is

$$\mathrm{d}\mathscr{P}_{v_x} = P(v_x)\,\mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2k_B T}\,\mathrm{d}v_x \tag{1.50}$$

The book calls $P(v_x)$, the uninformative name $g(v_x)$.

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)

$$d\mathscr{P}_v = \int_{\vec{v} \text{ in shell}} \mathrm{d}\mathscr{P}_{\vec{v}} \tag{1.51}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT}\, 4\pi v^2\, \mathrm{d}v \equiv P(v)\, \mathrm{d}v \tag{1.52}$$

Explicitly the probability density for speed v is

$$P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT}\, 4\pi v^2 \tag{1.53}$$

The book calls $P(v)$, the uninformative name $f(v)$.

1.5 Change of variables and solid angles

1.5.1 Change of variables in 1d

Given a variable x and its probability distribution

$$\mathrm{d}\mathscr{P}_x = P(x)\, \mathrm{d}x \tag{1.54}$$

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

$$\mathrm{d}\mathscr{P}_u = P(x(u)) \left|\frac{dx}{du}\right| \mathrm{d}u = P(x(u)) \frac{\mathrm{d}u}{|\frac{du}{dx}|} \tag{1.55}$$

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]

$$\int_R f(x)\mathrm{d}x = \int_{R_u} f(x(u)) \left|\frac{dx}{du}\right| \mathrm{d}u \tag{1.56}$$

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:

$$I = \int_1^2 \mathrm{d}x = \int_{[1,2]} \mathrm{d}x = \frac{1}{2} \tag{1.57}$$

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

$$I = \int_{-2}^{-4} \left(-\frac{1}{2}\right) \mathrm{d}u = \int_{-4}^{-2} \frac{1}{2}\mathrm{d}u = \int_{[-4,-2]} \frac{1}{2}\, \mathrm{d}u = 1 \tag{1.58}$$

1.5.2 Higher dimensions: spherical coordinates and solid angle

In higher-dimensions we have

$$\mathrm{d}\mathscr{P} = P(x, y, z)\, \underbrace{\mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z}_{\mathrm{dV}} \tag{1.59}$$

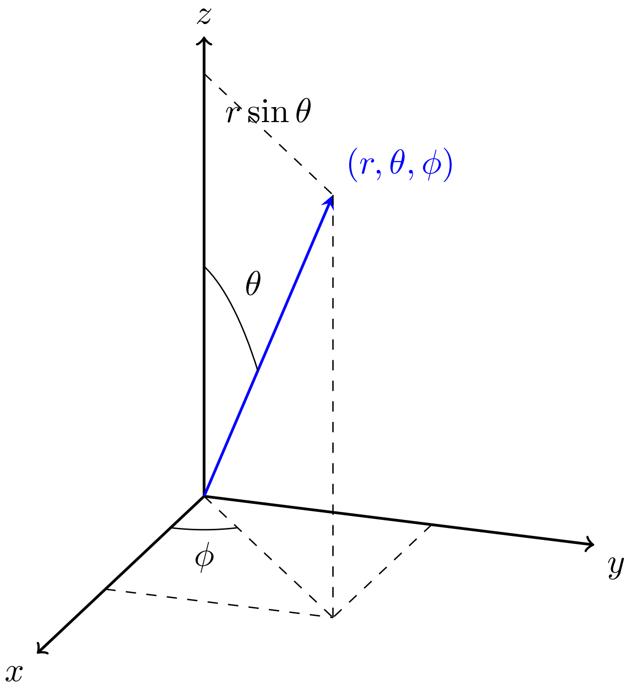
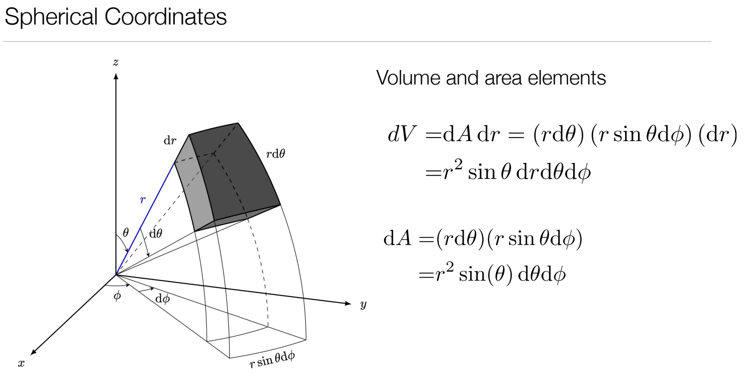


Figure 1.1: Spherical coordinates. Use the picture to justify $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$.



Spherical Coordinates

Volume and area elements

$$dV = \mathrm{d}A\,\mathrm{d}r = (r\mathrm{d}\theta)\,(r\sin\theta\mathrm{d}\phi)\,(\mathrm{d}r) = r^2\sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

$$\mathrm{d}A = (r\mathrm{d}\theta)(r\sin\theta\mathrm{d}\phi) = r^2\sin(\theta)\,\mathrm{d}\theta\mathrm{d}\phi$$

Figure 1.2: Spherical coordinates. From the figure, justify Eq. (1.60)

where $\mathrm{d}V$ is the "volume element". We will use spherical coordinates $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$ (see Fig. 1.1). A bit of geometry shows that the differential area dA and the volume element dV in spherical coordinates are (see Fig. 1.2)

$$dA = r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.60}$$

$$dV = dA\,\mathrm{d}r = r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.61}$$

So in spherical coordinates

$$\mathrm{d}\mathscr{P} = P(x,y,z)r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.62}$$

$$\equiv P(r,\theta\,\phi)\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{1.63}$$

For example, if

$$P(x,y,z) = Ce^{-(x^2+y^2+z^2)/2\sigma^2} \tag{1.64}$$

Then

$$P(r,\theta,\phi) = Ce^{-r/2\sigma^2}r^2\sin\theta \tag{1.65}$$

Rather than using geometry, we can use algebra to make the change of variables. The generalization of Eq. (1.55) is

$$\mathrm{d}\mathscr{P}_{r,\theta,\phi} = P(x,y,z)\left|\left|\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)}\right|\right|\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = P(r,\theta,\phi)\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \tag{1.66}$$

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. 1.1). 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

$$\left|\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)}\right| = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix} = \begin{vmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{vmatrix} = r^2\sin\theta \tag{1.67}$$

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

$$\Omega \equiv \frac{A}{r^2}\,. \tag{1.68}$$

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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).

[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", $\mathrm{d}\Omega = \sin\theta\mathrm{d}\theta\mathrm{d}\phi$, is parametrized by two angles, θ and ϕ

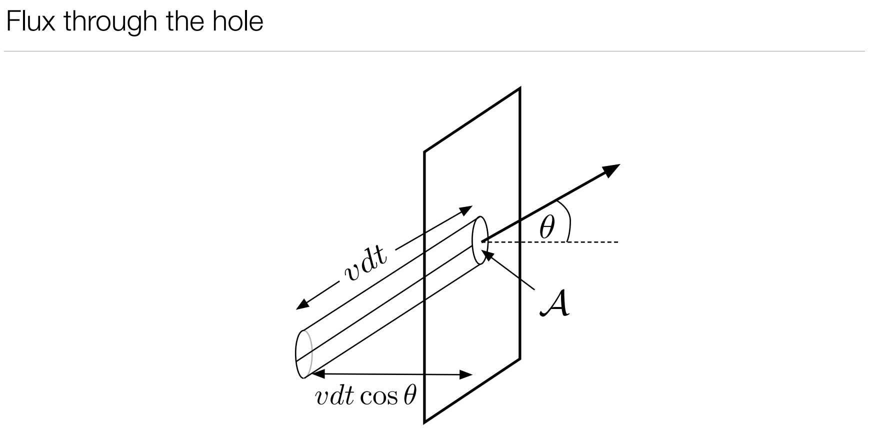

Figure 1.3: In each dt a volume $\mathcal{A}h = \mathcal{A}vdt\cos\theta$ passes through the hole

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 subtended by $\mathrm{d}\theta$ and $\mathrm{d}\phi$ (at angles θ, ϕ) we have from the geometry:

$$\mathrm{d}\Omega \equiv \frac{dA}{r^2} = \sin\theta \mathrm{d}\theta \mathrm{d}\phi \tag{1.69}$$

If a particle's position is distributed uniformly over the sphere, the probability distribution is

$$\mathrm{d}\mathscr{P} = \frac{\mathrm{d}A}{4\pi r^2} = \frac{\mathrm{d}\Omega}{4\pi} = \frac{\sin\theta \mathrm{d}\theta \mathrm{d}\phi}{4\pi} \tag{1.70}$$

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:

$$\mathrm{d}\mathscr{P}_{v,\theta,\phi} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT}\; v^2 \sin\theta\; \mathrm{d}v\mathrm{d}\theta\mathrm{d}\phi \tag{1.71}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2k_BT} 4\pi v^2 \mathrm{d}v\; \frac{\sin\theta \mathrm{d}\theta \mathrm{d}\phi}{4\pi} \tag{1.72}$$

$$=P(v)\mathrm{d}v\, \frac{\mathrm{d}\Omega}{4\pi} \tag{1.73}$$

where we have recalled Eq. (1.53) 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. $\mathrm{d}\mathscr{P}_\Omega/\mathrm{d}\Omega = 1/4\pi$. The number of particles per volume with speed in $[v, v+dv]$ and angles in $[\theta, \theta+\mathrm{d}\theta]$ and $[\phi, \phi+\mathrm{d}\phi]$ is given by the probability in Eq. (1.73) multiplied by the the number of particles per volume $n \equiv N/V$.

$$dn = nP(v)\mathrm{d}v\, \frac{\mathrm{d}\Omega}{4\pi} \tag{1.74}$$

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

$$\Phi \equiv \frac{1}{\mathcal{A}} \frac{dN_{\mathrm{cross}}}{dt} \equiv \text{number of particles crossing the hole per area per second} \tag{1.75}$$

From tube geometry in Fig. 1.3, the number of particles flying through the area $\mathcal{A}$ in time dt with speed in

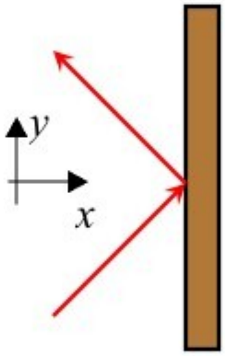

Figure 1.4: Momentum transfer to the wall is

$[v, v + \mathrm{d}v]$ and angles in $[\theta, \theta + \mathrm{d}\theta]$ and $[\phi, \phi + \mathrm{d}\phi]$ is $dN_{\mathrm{cross}} = dn\,\mathcal{A}h$, where $\mathcal{A}h$ is the volume of the tube and $h = vdt\cos\theta$ is the height of the tube. Dividing by $\mathcal{A}$ and dt we find the differential flux:

$$\mathrm{d}\Phi = nP(v)v\cos\theta\mathrm{d}v\,\frac{\mathrm{d}\Omega}{4\pi}\,. \tag{1.76}$$

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

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

$$\Phi = \int \mathrm{d}\Phi = n\int_0^\infty dvP(v)v\int_0^{\pi/2}\frac{1}{2}\sin\theta\cos\theta d\theta\int_0^{2\pi}\frac{d\phi}{2\pi} \quad =\frac{1}{4}n\left\langle v\right\rangle \tag{1.77}$$

$$=n\sqrt{\frac{kT}{2\pi m}} \tag{1.78}$$

We discussed an application or two of Eq. (1.77)

The pressure exerted by the atoms is found by calculating how many particles bounce of the wall per area per time, and the momentum the transfer they impart to the wall. A particle striking the wall velocity $\boldsymbol{v}_i = (v_x, v_y)$, bounces off the wall with velocity $\boldsymbol{v}_f = (-v_x, v_y)$ delivering an impulse (see Fig. 1.4). The momentum transfer (or impulse) to the wall by the atom is $\boldsymbol{\Delta p} = 2mv_x\,\hat{\boldsymbol{\imath}} = 2mv\cos\theta\,\hat{\boldsymbol{\imath}}$. (The momentum transfer to the atom by the wall is $\boldsymbol{\Delta p} = \boldsymbol{p}_f - \boldsymbol{p}_i = -2mv_x\,\hat{\boldsymbol{\imath}}$.) Recall that force is $F = \Delta p/\Delta t$. The momentum transfer per area per per time, or force per area, created by the atoms with speed and angles in the ranges $[v, v + \mathrm{d}v]$, $[\theta, \theta + \mathrm{d}\theta]$, $[\phi, \phi + \mathrm{d}\phi]$ is

$$\frac{dF_x}{\mathcal{A}} = \Delta p_x\,\mathrm{d}\Phi = \mathrm{d}\Phi\,(2mv\cos\theta) \tag{1.79}$$

Integrating over v, θ, ϕ as in Eq. (1.77) gives the force per area or pressure. Of course this should give the ideal gas law $p = nk_BT$. Computing the pressure is a matter of integration

$$p = \frac{F_x}{\mathcal{A}} = \int \mathrm{d}\Phi\,(2mv\cos\theta) = nk_BT \tag{1.80}$$

Using $\mathrm{d}\Phi$ the details are similar to Eq. (1.77)

$$p = 2nm\int_0^\infty dvP(v)v^2\int_0^{\pi/2}\frac{1}{2}\sin\theta\cos^2\theta d\theta\int_0^{2\pi}\frac{d\phi}{2\pi} \quad =\frac{1}{3}n\left\langle mv^2\right\rangle \tag{1.81}$$

$$=nk_BT \tag{1.82}$$

It is satisfying how the molecular theory of gasses reproduces the ideal gas law $p = nk_BT$.

Chapter 2

The first law

2.1 Thermometers

A thermometer measures changes in mechanical properties, or changes in electrical properties, or other changes in the material at different temperature reference points. Examples include the expansion of mercury in the iconic mercury thermometer, or the platinum resistance thermometer shown in class. The values of these material properties are simply labels for the different temperature reference points.

The Boltzmann factor

$$P_m \propto e^{-\epsilon/k_B T} . \tag{2.1}$$

has a universal parameter called $k_B T$ that we want to measure[1]. To make this measurement we need a simple system where the probabilities can be translated into the material properties of the substance. We used the Boltzmann factor to calculate the pressure of an ideal gas at constant volume. This pressure is proportional to precisely the $k_B T$ parameter appearing in the Boltzmann factor. Thus a mechanical property of ideal gasses, i.e. their pressure, can be used to measure the $k_B T$ parameter. The readouts of all other thermometers were calibrated against the ideal gas pressure-thermometers[2].

2.2 The first law

The change in energy is determine by the heat added to the system $đQ$ plus the work done *on* the system by you, $đW$:

$$dU = đQ + đW \tag{2.2}$$

The work done by the system on you (or the work you get out) is $đW_{\rm out} = -đW$. So

$$dU = đQ - đW_{\rm out} \tag{2.3}$$

For a simple homogeneous substance

$$đW_{\rm out} = p(T,V)\mathrm{d}V \qquad W_{\rm out} = \int_i^f p(T,V)\,\mathrm{d}V \tag{2.4}$$

We put a bar as in $đW$ because $đW$ is *not* the change in a function called W. Rather it is a small *amount* of work. The amount of work done depends on the path taken (see lecture notes). Similarly $đQ$ is an amount of heat; it is not the change in a function which we call Q. The amount of heat added or removed from the system depends on the path.

---

[1] Later we will see that this parameter is defined as the change in the entropy with respect to energy $(\partial S/\partial E) \equiv 1/T$. The notion of entropy is independent of any particular substance or property.

[2] Today there are other systems which can provide additional absolute temperature calibrations, but the ideal gas still plays an important role.

To work with the first law we generally need to specify two functions. The first is the pressure[3] $p(T,V)$ and the second is the energy $U(T,V)$

$$P(T,V) \equiv \text{the pressure as a function of temperature and volume} \tag{2.5}$$

$$U(T,V) \equiv \text{the energy as a function of temperature and volume} \tag{2.6}$$

Often the relation pressure-temperature-volume relation is inverted expressing the volume in terms of temperature and pressure

$$V(T,P) \equiv \text{ the volume as a function of temperature an pressure} \tag{2.7}$$

2.3 Specific heats

The first law involves heat. The heat inflows are characterized by the specific heat, which is the amount heat required, $\text{đ}Q$, per change in temperature dT.

If the volume is held fixed, we have the specific heat at constant volume

$$C_V \equiv \left(\frac{\text{đ}Q}{dT}\right)_V \tag{2.8}$$

The subscript V indicates that the volume is held fixed. If the pressure is held fixed, we have the specific heat at constant pressure

$$C_p \equiv \left(\frac{\text{đ}Q}{dT}\right)_p \tag{2.9}$$

Energy and C_V:

If the volume is held fixed $dV = 0$ and $\text{đ}W = 0$. The change in energy is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \cancelto{0}{dV} \tag{2.10}$$

and so from the first law, $dU = \text{đ}Q$, and

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \tag{2.11}$$

For an diatomic gas $U = \frac{5}{2} N k_B T$, and so

$$C_V = \frac{5}{2} N k_B \qquad \text{diatomic ideal gas} \tag{2.12}$$

The specific heat grows with the number of particles in the system. For this reason we often quote the specific heat for one mole of substance, $C_V^{\rm 1ml}$. The specific for one mole of an ideal gas diatomic gas is for instance

$$C_V^{\rm 1ml} = \frac{5}{2} N_A k_B = \frac{5}{2} R \qquad \text{diatomic ideal gas} \tag{2.13}$$

We will discuss the energy $U(T,V)$ later. For any ideal gas (e.g. dilute water vapor) the energy takes the form

$$U = N e_0(T) \qquad \text{any ideal gas} \tag{2.14}$$

The specific heat takes the form

$$C_V = N e_0'(T) \qquad \text{any ideal gas} \tag{2.15}$$

---

[3] In general the pressure and energy are functions the number of particles N, but N is considered to be a constant and is not notated: $p(T,V) \equiv p(T,V,N)$

Or for one mole of substance

$$C_V^{1\text{ml}} = R\left(\frac{1}{k_B}\frac{\mathrm{d}e_0}{\mathrm{d}T}\right) \qquad \text{any ideal gas (2.16)}$$

Relating C_p and C_v:

The specific heat at constant pressure C_p is larger than C_V, because some of the heat added (per degree of temperature change) is used by the gas to do work as it gas expands at fixed pressure. By figuring how much work is done, we will show shortly that for any ideal gas (not just diatomic or monoatomic)

$$C_p = C_V + Nk_B \qquad \text{any ideal gas (2.17)}$$

Or

$$C_p^{1\text{ml}} = C_V^{1\text{ml}} + R \qquad \text{any ideal gas (2.18)}$$

In general C_p and C_V are related. We will show much later using the second law

$$C_p = C_V + \frac{VT\beta_p^2}{\kappa_T} \qquad \text{all substances (2.19)}$$

Here β_p is the volume expansion coefficient, and κ_T is the isothermal compressibility – see the next section.

The ratio of specific heats is given a name

$$\gamma \equiv \frac{C_p}{C_V} \tag{2.20}$$

The factor γ is close to unity in practice and often nearly constant. For instance for a diatomic gas where $C_V = \frac{5}{2}Nk_B$, we find using the relation in Eq. (any ideal gas (2.17)), that $\gamma = 7/5$.

2.4 The pressure

Generally the pressure is a function of temperature T, volume V, and number N, $p(T, V, N)$. Usually the dependence on N is not notated, as N is considered to be a fixed constant, i.e. $p(T, V) \equiv p(T, V, N)$.

The volume per particle is the inverse of the density

$$v_N \equiv \frac{V}{N} = \frac{1}{n} \tag{2.21}$$

The pressure is intensive. This means that if I consider twice as many particles at the same temperature and desity the pressure is unchanged.

Since the pressure is intensive, $p = p(T, V, N)$ is only a function of temperature and $v_N = V/N$, and not V and N separately, $p = p(T, v_N)$. If you prefer, you can parametrize the pressure by the temperature and density, $p = p(T, n)$. Thus, we have three parametrizations of the same physical quantity[4]:

$$p = p(T, V, N) = p(T, v_N) = p(T, n) \tag{2.25}$$

---

[4] We are using a common notation in physics, which mathematicians don't like. What we are really talking about here is three separate functions (or maps) which return the same value at corresponding arguments

$$p = p_1(T, V, N) = p_2(T, v_N) = p_3(T, n) \tag{2.22}$$

p_1 and p_2 and p_3 describe the same quantity but have different *functional forms*, since they are functions of different variables. Take the ideal gas law:

$$p_1(T, V, N) = \frac{NkT}{V} \qquad p_2(T, v_N) = \frac{kT}{v_N} \qquad p_3(T, n) = n\,kT \tag{2.23}$$

For a mathematician the *map* or *functional form* is paramount, and the name of the argument is irrelevant, e.g. :

$$p_3(T, x, y) = \frac{y}{x}\,kT \qquad p_2(T, x) = \frac{kT}{x} \qquad p_3(T, x) = x\,kT \tag{2.24}$$

Mathematicians kind of have point: $1/x$ and x are not the same function! The physics notation uses the names of the arguments, $p(T, V, N)$, $p(T, v_N)$, and $p(T, n)$, to distinguish the functions p_1, p_2, and p_3. The physics notation prevents an explosion of symbols for the same physical quantity, but if confused you should go back to the math notation.

Using the chain rule, we can relate the volume derivatives of $p(T, V, N)$ to derivatives with respect to the volume-per-particle or with respect to the density :

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{1}{N}\left(\frac{\partial p}{\partial v_N}\right)_T \qquad \text{and} \qquad \left(\frac{\partial p}{\partial V}\right)_{T,N} = -\frac{N}{V^2}\left(\frac{\partial p}{\partial n}\right)_T , \tag{2.26}$$

Thus, the derivative with respect to volume records how the pressure changes with the particle density[5]:

$$N\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial v_N}\right)_T = -n^2\left(\frac{\partial p}{\partial n}\right)_T \tag{2.27}$$

Hopefully this is clear enough.

2.4.1 Pressure, Volume, and the Equation of State

Virial Expansion: First consider gasses. At low density, we can make an expansion in the density N/V

$$p(T, V, N) = \frac{NkT}{V}\left(1 + B(T)\frac{N}{V} + C(T)\left(\frac{N}{V}\right)^2 + \ldots\right) \tag{2.28}$$

At very low density the ideal gas NkT/V is valid, while at higher density there are corrections. The $B(T)$ is known first virial coefficient. It corrects the ideal gas pressure by an amount of order $\delta p = B(T)kTn^2$. This goes like the square of the number of particles, and hence reflects the interactions between them.

Response coefficients: Now consider a general substance. Instead of working with the pressure as a function of temperature and volume, we will often work with the volume as a function of temperature and pressure, which contains the same information. The differential in volume is

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \tag{2.29}$$

The two derivatives characterize the response of the system. The first one characterizes the expansion of the system with increase in temperature

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \equiv \text{Thermal expansion coefficient} \tag{2.30}$$

The second one characterizes the increase in pressure with decrease in volume

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T \equiv \text{Isothermal compressiblity} \tag{2.31}$$

The derivatives of like $(\partial V/\partial T)_p$ are divided by V so that response coefficients, β_p and κ_T, are intensive. This means that as the number of particles is increased at fixed pressure and temperature, β_p and κ_T are unchanged. Both $(\partial V/\partial T)_p$ and $V(T, p)$ are proportional to the number of particles, but β_p, which is the ratio of these two quantities, is independent of the total number of particles.

The speed of sound and the compressibility: The first coefficient β_p has a clear everyday meaning, i.e. how much does something expand when heated. The second coefficient κ_T is inversely related to the stiffness of the material. The *isothermal bulk modulus* directly reflects the stiffness

$$B_T = -\frac{1}{V}\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{\kappa_T} \tag{2.32}$$

---

[5] More explicitly we would write

$$\left(\frac{\partial p}{\partial V}\right)_T \equiv \left(\frac{\partial p}{\partial V}\right)_{T,N}$$

At constant temperature, an increase in volume $\mathrm{d}V$ leads to a drop in pressure determined by κ_T:

$$\mathrm{d}p = -B_T \frac{\mathrm{d}V}{V} \tag{2.33}$$

Since sound is a pressure wave, it is not surprising then that κ_T is related to the speed of sound. The speed of sound is

$$c_s = \sqrt{\frac{\gamma}{\kappa_T \rho}} \tag{2.34}$$

where ρ is the mass per unit volume, and $\gamma = C_p/C_V$ is the adiabtic index.

The adiabatic compressibility and sound: The adiabatic compressibility κ_S is directly related to κ_T. κ_S is the decrease in volume with increasing pressure, with no heat flow[6]:

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{adiab} \tag{2.35}$$

Similarly there is an adiabatic bulk modulus

$$B_S = -V\left(\frac{\partial p}{\partial V}\right)_{adiab} = \frac{1}{\kappa_S} \tag{2.36}$$

We will show much later in the course that for any homogeneous substance

$$\kappa_S = \frac{\kappa_T}{\gamma} \tag{2.37}$$

and so the speed of sound is naturally expressed using the adiabatic compressibility

$$c_s = \sqrt{\frac{B_S}{\rho}} \tag{2.38}$$

2.5 Energy

The total energy of the substance is $U(T, V, N)$, and usually the N is considered fixed and not notated $U(T, V) \equiv U(T, V, N)$.

The energy is $U(T, V, N)$ is extensive. This means that if I consider twice as many particles at the same temperature and density, the energy is twice as large. The energy per particle is notated e_N:

$$e_N \equiv \frac{U}{N}$$

and is intensive. Like with the pressure, the energy per particle U/N is a function of temperature and the volume per particle, $U/N = e_N(T, v_N)$. If you prefer you may parametrize the energy per particle by the temperature and density $n \equiv N/V$, that is $U/N = e_N(T, n)$. Summarizing

$$U(T, V, N) = N e_N(T, v_N) = N e_N(T, n) \tag{2.39}$$

At low densities or large volume we can make a Taylor series expansion in powers of the density N/V, leading to the following series expansion for e_N at low densities:

$$U(T, V, N) = N e_0(T)\left[1 + C_1(T)\frac{N}{V} + \ldots\right] \tag{2.40}$$

---

[6] The "S" means at fixed entropy, and as the course progresses we will write

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S .$$

For an ideal gas, an adiabatic expansion means that $pV^\gamma = \text{const}$ (see below), which can be used to prove Eq. (2.37) for the simple case of an ideal gas. Proving Eq. (2.37) in general requires a more extensive discussion of entropy, covered later in the course

The first term, $Ne_0(T)$, is finite in the limit of infinite volume. This is the ideal gas limit. $Ne_0(T)$ represents the energy of the individual atoms, and hence is proportional to N. The next term in the series represents the interactions between the particles and is therefore proportional to N^2.

For an ideal gas, we neglect the interactions and have:

$$U(T,V,N) = Ne_0(T) \qquad \text{any ideal gas} \quad (2.41)$$

This implies that for an ideal gas[7]

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{any ideal gas} \quad (2.43)$$

As discussed above the function $e_0(T)$ determines the specific heat C_V for an ideal gas. For a classical mono-atomic or classical diatomic gas the function $e_0(T)$ is just proportional to T. For instance for a diatomic gas, where $U = \frac{5}{2}Nk_BT$, then

$$e_0 = \frac{5}{2}k_BT \qquad \text{diatomic ideal gas} \quad (2.44)$$

However, if the gas is not entirely classical, e.g. the quantum mechanical vibrations of dilute H_2O vapor, then $e_0(T)$ will have a non-trivial dependence on T. We will calculate $e_0(T)$ for some cases as the course progresses.

Response: As with the pressure we need to characterize the response

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (2.45)$$

The first law allows one to relate these derivatives to the measured specific heats and the response coefficients β_p that we have already defined.

Fixed volume: If the volume is held fixed $dV = 0$ and $đW = 0$. The change in energy at fixed volume is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT \quad (2.46)$$

and so from the first law, $dU = đQ$, and so

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V} \quad (2.47)$$

Fixed pressure: Consider a change in temperature and volume at fixed pressure. From the first law

$$dU = C_V\, dT_p + \left(\frac{\partial U}{\partial V}\right)_T dV_p = đQ_p - p dV_p \quad (2.48)$$

where we have put subscript "p" to remind ourselves that the path taken is at fixed pressure. Dividing by dT_p we see that:

$$C_V + \left(\frac{\partial U}{\partial V}\right)_T V\beta_p = C_p - pV\beta_p \quad (2.49)$$

where we have used the definition of C_p ( )and β_p Thus the second response coefficient is given by C_V and C_p

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\beta_p} - p} \quad (2.50)$$

---

[7] As is common, we are suppressing the N. More precisely the equation is written:

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = 0\,. \quad (2.42)$$

This relation gives an experimental way to determine $(\partial U/\partial V)_T$, from the measured specific heats.

For an ideal gas you should be able to show that $V\beta_p = Nk_B/p$, and recognize $(\partial U/\partial V)_T = 0$, to produce the relation between C_p and C_V given in Eq. (any ideal gas (2.17)).

2.6 Isothermal and Adiabatic Expansion for Ideal Gasses and Engine Cycles

We will consider and ideal gas with constant specific heat, so $U = C_V T$. Then $\gamma = C_p/C_V = 1 + Nk_B/C_V$ is also constant.

Isothermal Expansion: For an isothermal expansion of a gas there is no change in temperature due to influx of heat compensating the expansion. For an ideal gas you should be able to show that

$$\Delta U = 0 \qquad Q = W_{\text{out}} = \int_i^f p dV = Nk_{\scriptscriptstyle B}T \ln(V_f/V_i) \tag{2.51}$$

Adiabatic Expansion: For an adiabatic expansion $Q = 0$, and there *is* a change in temperature as the system expands.

$$\Delta U = -\int_i^f p dV \tag{2.52}$$

You should be able to show that during the expansion

$$pV^\gamma = \text{const} \qquad \text{or} \qquad \frac{p_i}{p_f} = \left(\frac{V_f}{V_i}\right)^\gamma \tag{2.53}$$

Or, since $p = Nk_{\scriptscriptstyle B}T/V$, we have

$$TV^{\gamma-1} = \text{const} \qquad \text{or} \qquad \frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{\gamma-1} \tag{2.54}$$

Using the fact that $U = C_V T$, one can use Eq. (2.54) to find the change in energy $\Delta U = C_V \Delta T$.

Engines: In a car engine we burn gasoline. This involves chemical transitions of atomic levels, each of which provide somewhat less than an electron-volt of energy. Since there are of order an Avogadro's number of such transitions we typically get

$$N_A\,(\text{eV}) \simeq 100\,\text{kJ} \tag{2.55}$$

of energy for every mole. The constant $N_A\,\text{eV}$ is known as Faraday's constant. This is a lot of energy which is why internal combustion engines have taken over.

In a given closed cycle of an engine we have

$$\cancelto{0}{\Delta U} = Q - W_{\text{out}} \tag{2.56}$$

The net heat Q involves positive inputs to the engine Q_{in}, and exhaust Q_{out} which is negative, $Q_{\text{out}} = -|Q_{\text{out}}|$. In total

$$Q = Q_{\text{in}} + Q_{\text{out}} = Q_{\text{in}} - |Q_{\text{out}}|.$$

The efficiency is

$$\eta = \frac{W_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{|Q_{\text{out}}|}{Q_{\text{in}}} \tag{2.57}$$

Chapter 3

Entropy

3.1 Basic notions

We worked a very particular example to explain the concept of entropy. Specifically we considered N quantum harmonic oscillators sharing (or partitioning) the q units of energy $E = q\hbar\omega_0$ amongst themselves. (The graphical presentation of this problem is given in the lecture notes.) The total number of ways the system can partition the available energy is $\Omega(E)$ and the entropy is

$$\Omega(E) \tag{3.1}$$

The system will evolve until all possible partitions of the energy are equally likely. The probability of a specific partition is

$$P_m = \frac{1}{\Omega(E)} \tag{3.2}$$

If there are six possible outcomes $\Omega(E) = 6$ (like a regular die) then the probability of an outcome is 1/6. Ω is an exponentially large number and is of order e^N. A precise computation done in homework gives $\Omega = e^{555}$ for $N = q = 400$. The entropy is (up to a constant) the log of the number of partitions

$$S = k_B \ln \Omega(E) = -k_B \log P_m \tag{3.3}$$

Thus the entropy is of order $\sim N k_B$.

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

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

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

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

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

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

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

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

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
    $$m_p c^2 \simeq 938\,\mathrm{MeV} \simeq 1000\,\mathrm{MeV} \simeq 1\,\mathrm{GeV} \tag{A.4}$$
    - The macroscopic way: an Avogadro's number of protons weighs a gram. This is the molar mass of the proton:
    $$\mathcal{M}_{\mathrm{ml}} = m_p N_A = 1\,\mathrm{g} \tag{A.5}$$

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 $v_{\rm rms}$ in atomic hydrogen gas at room temperature

$$v_{\rm rms} = \sqrt{\frac{3kT}{m_p}} = c\sqrt{\frac{3kT}{m_pc^2}} = (3\times10^8{\rm m/s})\times\sqrt{\frac{(1/40){\rm eV}}{938\times10^6\,{\rm eV}}} \simeq 2700\,{\rm m/s} \tag{A.6}$$

Or if you prefer

$$v_{\rm rms} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3\,(N_Ak_B)\,T}{N_Am_p}} = \sqrt{\frac{3RT}{1g}} = \sqrt{\frac{3\times8.32\,{\rm J/^\circ K}\times300^\circ{\rm K}}{1g}} \simeq 2700\,{\rm m/s} \tag{A.7}$$

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

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

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

    $$m_ec^2 \simeq 0.511\,{\rm MeV} \tag{A.8}$$

    - In comparison to the proton mass:

    $$\frac{m_e}{m_p} \simeq \frac{1}{2000} \tag{A.9}$$

11. Planck's constant is needed to convert wavelength to energy

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

    or using $h = 2\pi\hbar$

    $$hc = 1240\,{\rm eV\,nm} \tag{A.11}$$

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

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

    Planck's constant is also useful for measuring typical de Broglie wavelength at room temperature

    $$\frac{h}{\sqrt{2\pi m_pkT}} = \frac{hc}{\sqrt{2\pi(m_pc^2)(kT)}} \simeq \frac{1240\,{\rm eVnm}}{\sqrt{2\pi\cdot10^9\,{\rm eV}\frac{1}{40}\,{\rm eV}}} \simeq 1.0\,\text{Å} \tag{A.13}$$

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

    $$a_0 = 0.53\,\text{Å} \tag{A.14}$$

    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 $1.09\,\text{Å}$)

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

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

    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 kJ of energy per mole. Burning a mole of gasoline gives roughly this amount of energy.

---

[1] We can quickly find the charge in Coulombs from this relation,

$$1eV \simeq 100\,{\rm kJ}/N_A \simeq 1.6\times10^{-19}{\rm J} \qquad \text{and so} \qquad 1e = 1.6\times10^{-19}{\rm C}. \tag{A.16}$$

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, $L = pa_0 = \hbar$. So the momentum is

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

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

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

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

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

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

13.6 eV is the Rydberg constant.

For the ground states of a quantum mechanical system it is generically the case that

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

If the system size is of order L then $p \sim \hbar/L$ and the kinetic energy is $\hbar^2/2mL^2$, and often this a good estimates for $|PE|$ and $|E|$. So the intuition from the Bohr model is often a good guess for more general quantum mechanical systems.

These facts give another way to estimate the thermal de Broglie wavelength of a *proton* at room temperature, by inserting a_0 and the electron mass, and noting that $h = 2\pi\hbar$:

$$\lambda_{\text{th}} \equiv \frac{(2\pi\hbar)}{\sqrt{2\pi m_p kT}} = 2\pi a_0 \sqrt{\frac{\hbar^2}{2m_e a_0^2}\left(\frac{1}{k_B T}\right)} \sqrt{\frac{m_e}{\pi m_p}} = 2\pi\,(0.5\text{Å})\sqrt{\frac{13.6\,\text{eV}}{0.025\,\text{eV}}}\sqrt{\frac{1}{\pi 2000}} \simeq 1\text{Å} \tag{A.25}$$

---

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

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

Multiplying this equation by $r/2$ gives

$$\frac{1}{2}mv^2 = \frac{1}{2}\frac{e^2}{4\pi\epsilon_0 r}\,.$$

Appendix B

Math

B.1 Rant on units management

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[1], 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!

---

[1] This value of c follows by a change of variables, defining $y = u^2$ in Eq. (B.4).

B.2 Basic Taylor Series

You are expected to know what a Taylor series is, but we will develop facility with them as the course develops. You are expected to have the following memorized:

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} + + \mathcal{O}(x^7) \tag{B.7}$$

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \mathcal{O}(x^6) \tag{B.8}$$

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \tag{B.9}$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \tag{B.10}$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \tag{B.11}$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \tag{B.12}$$

These get me through life.

They can be integrated, etc, so for example the expression for $\log(1+x)$ follows from the geometric series $1/(1+x)$ by integration:

$$\log(1+x) = \int_0^x \frac{\mathrm{d}x'}{1+x'} = \int_0^x \mathrm{d}x' \left[1 - x' + (x')^2 + \mathcal{O}((x')^3)\right] = x - \frac{x^2}{2} + \frac{x^3}{3} + \mathcal{O}(x^4) \tag{B.13}$$

B.3 Gaussian Integrals

We discussed the integrals

$$I_n = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, e^{-x^2/2} x^n \tag{B.14}$$

The first couple results are

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

We found these using the generating function technique.

B.4 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[2]

$$\Gamma(z) = \int_0^\infty x^{z-1} e^{-x} \mathrm{d}x \tag{B.17}$$

and has the familiar recursive relationship

$$\Gamma(z+1) = z\Gamma(z) \tag{B.18}$$

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

$$\Gamma(n) = (n-1)! \tag{B.19}$$

---

[2] I like to write $\Gamma(z)$ like this

$$\Gamma(z) = \int_0^\infty x^z e^{-x} \frac{\mathrm{d}x}{x} \tag{B.16}$$

since the measure $\mathrm{d}x/x$ is invariant under a rescaling $x' = \lambda x$, i.e. $\mathrm{d}x/x = \mathrm{d}x'/x'$. This is one reason why clever math folk defined $\Gamma(z)$ with the power $z-1$ in Eq. (B.17) instead of just z.

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,

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}. \tag{B.20}$$

So for instance, using the recursion, $\Gamma(3/2) = \frac{1}{2}\Gamma(\frac{1}{2}) = \sqrt{\pi}/2$.

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

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}\,. \tag{B.21}$$

which comes up a lot later in the course.