

PY 251 - Principles of Physics

Lecture notes - November 29, 2005.

Copyright by Claudio Rebbi - Boston University - November 2005.

Probability and probability density.

Given a set of events which we consider equally likely the probability of a definite outcome is the ratio between the number of events that produce that outcome and the total number of events. For example, if we throw dice the probability P_5 of getting a five is

$$P_5 = \frac{4}{36} = \frac{1}{9} \quad (1)$$

because the number of possible events is 36, with six possibilities 1, 2, . . . 6 for each of the two faces, and the number of events producing a 5 is 4, with the two faces showing (1,4), (2,3), (3,2) or (4,1). Note that if the outcomes, which we index by i , $1 \leq i \leq N$, are mutually exclusive we must have

$$\sum_i P_i = 1 \quad (2)$$

Experience shows that if we define the frequency f_i of a certain outcome i in some number of tries as the ratio between the number of occurrences of this outcome and the total number of tries, then $f_i \rightarrow P_i$ in the limit where the number of tries goes to infinity.

There are many events which do not form a discrete set, but rather have a continuous distribution. Consider for example two numbers x and y which can take values between 0 and 10 with the assumption that any value in this range is equally likely for both x and y . Then it would not make sense to ask what is the probability that the sum $z = x + y$ takes, for example, value 8, because there is a doubly continuous infinity of possible values for x and y and only a singly continuous infinity of ways by which $z = x + y$ can take value 8. If we were to define that probability still as the ratio between the doubly infinite number of total events and the singly infinite number of outcomes $z = 8$, (with some suitable definition of infinity) we would get zero. Rather, we could ask what is the probability that the sum takes a value between $z = 8$ and $z + \Delta z = 9$. On intuitive grounds, this probability will

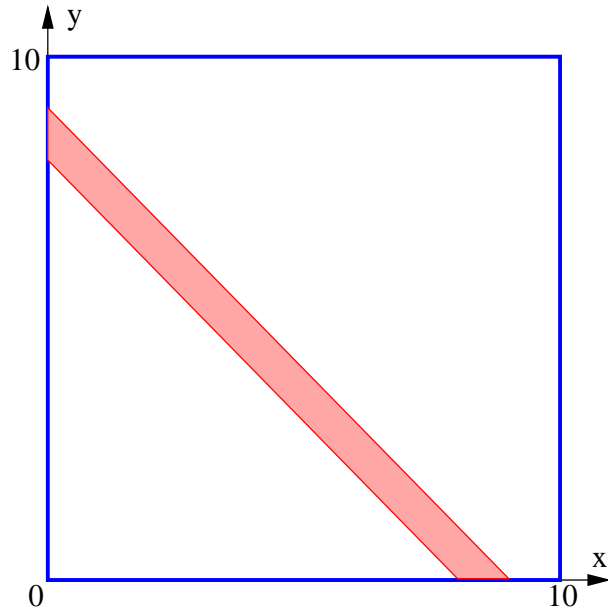


Figure 1: Illustration of probability with continuous events.

be the ratio between the shaded area in figure 1 and the area of the square $0 \leq x, y \leq 10$. If we take the z interval to be infinitesimal, i.e. if we look for a sum $z \leq x + y \leq z + dz$, the probability of the outcome will also be an infinitesimal probability dP and will be proportional to dz . Thus it will be of the form

$$dP = p(z) dz \quad (3)$$

where $p(z)$ is some function of z . $p(z)$ is called the “probability density” of z . The probability P that z takes a value between z_0 and z_1 will then be given by

$$P = \int_{z_0}^{z_1} p(z) dz \quad (4)$$

(Note that we use upper case P for probability and lower case $p(z)$ for probability density.) The probability density $p(z)$ for $z = x + y$ is shown in Fig. 2. It is proportional to the length of the segment of the line $x + y = z$ contained within the square $0 \leq x, y \leq 10$. This length is in turn proportional to z for $0 \leq z \leq 10$ and to $20 - z$ for $10 \leq z \leq 20$ (with the same constant of proportionality). Thus we can write

$$p(z) = \frac{1}{Z} z, \quad 0 \leq z \leq 10$$

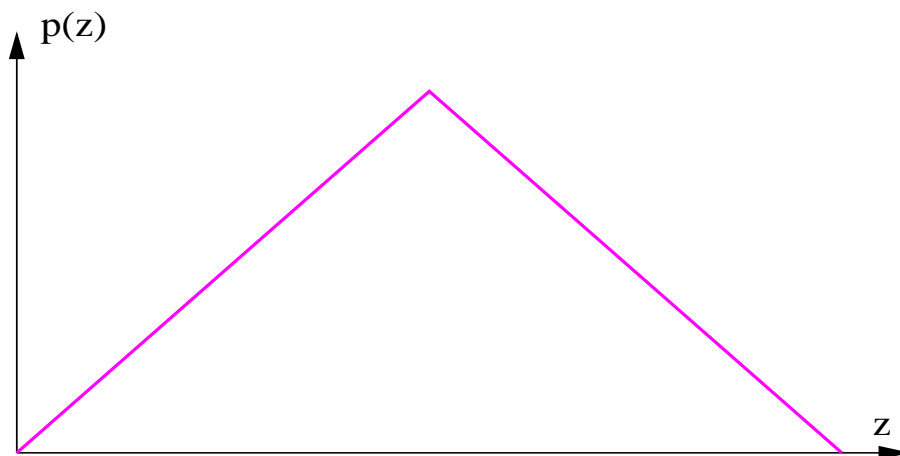


Figure 2: Probability density.

$$p(z) = \frac{1}{Z}(20 - z), \quad 10 \leq z \leq 20 \quad (5)$$

$1/Z$ being a suitable constant of proportionality. Z can be found from the requirement that the total probability must equal 1. This gives us

$$\frac{1}{Z} \left(\int_0^{10} z dz + \int_{10}^{20} (20 - z) dz \right) = 1 \quad (6)$$

or

$$Z = \left(\int_0^{10} z dz + \int_{10}^{20} (20 - z) dz \right) = 100 \quad (7)$$

In statistical applications to thermodynamics the normalizing factor Z is an important quantity called the “partition function”.

The Maxwell-Boltzmann probability distribution.

In thermodynamics we study phenomena associated with the motion of an extremely large number of molecules. Keeping track of the positions and velocities of the individual molecules is impossible and unnecessary. Thermodynamical observables are related to the average properties of the molecules’ motion. The quantity that matters is the probability density for the velocity and position of the molecules.

A crucial result due to Maxwell and Boltzmann, which we will state without proof, is that when a system is in thermal equilibrium at a temperature

T , the probability density for finding the system in a state of energy E is proportional to the exponential of $-E/kT$, where k is the Boltzmann constant. Including into the expression also the normalizing factor, which we denote again by $1/Z$, we have

$$p(\vec{r}_i, \vec{v}_i) = \frac{1}{Z} e^{-E/kT} \quad (8)$$

where \vec{r}_i and \vec{v}_i stand for the position and velocity of the i^{th} molecule.

This probability density is called the ‘‘Maxwell-Boltzmann probability distribution’’.

Let us make an application of the Maxwell-Boltzmann distribution to the calculation of the average squared velocity of the molecules of a gas. Since all molecules have the same average properties, it is sufficient to calculate the average squared velocity of a single molecule $\langle \vec{v}^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle$. (We use bracket notation $\langle \rangle$ to indicate the average value of a quantity.) Also, since because of rotational symmetry $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, we only need to calculate $\langle v_x^2 \rangle$. This is obtained multiplying v_x^2 by the velocity probability density and integrating over all possible values of the velocity components. Thus

$$\langle v_x^2 \rangle = \int dv_x \int dv_y \int dv_z v_x^2 p(v_x, v_y, v_z) \quad (9)$$

where, according to Eq. 8

$$p(v_x, v_y, v_z) = \frac{1}{Z} e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT + E'/kT]} \quad (10)$$

and E' stands for all the terms in the total energy which do not depend on the velocity components v_x, v_y, v_z of the molecule under consideration.

The exponential factorizes

$$e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT + E'/kT]} = e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT]} e^{-E'/kT} \quad (11)$$

and we can absorb the term $\exp(-E'/kT)$, which does not depend on the variables of integration, in the normalization factor $1/Z$. We are thus left with

$$\langle v_x^2 \rangle = \frac{1}{Z'} \int dv_x \int dv_y \int dv_z v_x^2 e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT]} \quad (12)$$

where the normalization constant Z' is fixed by the requirement

$$\frac{1}{Z'} \int dv_x \int dv_y \int dv_z e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT]} = 1 \quad (13)$$

and is thus given by

$$Z' = \int dv_x \int dv_y \int dv_z e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT]} \quad (14)$$

The exponential $\exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT]$ also factorizes

$$e^{-[m(v_x^2 + v_y^2 + v_z^2)/2kT]} = e^{-mv_x^2/2kT} e^{-mv_y^2/2kT} e^{-mv_z^2/2kT} \quad (15)$$

and therefore the integrals in Eqs. 12, 14 can also be written in factorized form

$$\langle v_x^2 \rangle = \frac{1}{Z'} \int dv_x v_x^2 e^{-mv_x^2/2kT} \int dv_y e^{-mv_y^2/2kT} \int dv_z e^{-mv_z^2/2kT} \quad (16)$$

$$Z' = \int dv_x e^{-mv_x^2/2kT} \int dv_y e^{-mv_y^2/2kT} \int dv_z e^{-mv_z^2/2kT} \quad (17)$$

But in Eq. 16 the integrals over v_y and v_z are the same at numerator and denominator and simplify. We are thus left with

$$\langle v_x^2 \rangle = \frac{\int dv_x v_x^2 e^{-mv_x^2/2kT}}{\int dv_x e^{-mv_x^2/2kT}} \quad (18)$$

The integrals in this last equations can be done without too much difficulty starting from the identity $\int \exp(-x^2) dx = \sqrt{\pi}$, but we can avoid doing the integrals altogether by proceeding as follows. We introduce the notation (which is of common use in statistical mechanics)

$$\beta = \frac{1}{kT} \quad (19)$$

We note that β has dimensions of energy⁻¹. With this notation the integral at denominator in Eq. 18 takes the form

$$I(\beta) = \int dv_x e^{-\beta m v_x^2/2} \quad (20)$$

This integral has dimension of velocity and the only way we can form a quantity with dimensions of v starting from β and m (the only two dimensionful quantities at our disposal) is by the combination $(m\beta)^{-1/2}$. Thus we must have

$$I(\beta) = c(m\beta)^{-1/2} \quad (21)$$

where c is a numerical constant which will turn out to be irrelevant.

The integral in the numerator of Eq. 18 can be written as

$$\begin{aligned} \int dv_x v_x^2 e^{-\beta m v_x^2/2} &= - \int dv_x \frac{2}{m} \frac{d}{d\beta} e^{-\beta m v_x^2/2} = -\frac{2}{m} \frac{d}{d\beta} \int dv_x e^{-\beta m v_x^2/2} \\ &= -\frac{2}{m} \frac{d}{d\beta} I(\beta) \end{aligned} \quad (22)$$

Combining this equation with Eqs. 20 and 21 we get

$$\begin{aligned} \langle v_x^2 \rangle &= -\frac{2}{m} \frac{1}{I(\beta)} \frac{d}{d\beta} I(\beta) = -\frac{2}{m} \frac{d}{d\beta} \log I(\beta) = -\frac{2}{m} \frac{d}{d\beta} [\log(c(m\beta)^{-1/2})] \\ &= -\frac{2}{m} \frac{d}{d\beta} [(-1/2) \log(\beta) + \text{const}] = \frac{1}{m} \frac{1}{\beta} = \frac{kT}{m} \end{aligned} \quad (23)$$

We have thus found that the average value of v_x^2 is kT/m . The average value of the square of the velocity of the individual molecules is thus

$$\langle \vec{v}^2 \rangle = 3 \langle v_x^2 \rangle = \frac{3kT}{m} \quad (24)$$

and the average kinetic energy of the individual molecules due to their translational motion is

$$\langle E_{K,\text{tr}} \rangle = \frac{m}{2} \langle \vec{v}^2 \rangle = \frac{3kT}{2} \quad (25)$$

It is very important to observe that if instead of integrating the Maxwell-Boltzmann probability distribution over the components of the velocity we had integrated directly over the energy, we would have obtained a wrong result. Indeed, proceeding in this erroneous way we would have calculated

$$\langle E_{K,\text{tr}} \rangle = \frac{\int_0^\infty dE E e^{-\beta E}}{\int_0^\infty dE e^{-\beta E}} = \frac{1}{\beta} = kT \quad (26)$$

which is off by a factor of $3/2$. The reason why we must not integrate directly over the energy is that a probability density is defined assuming that some basic variables have a uniform distribution. For example, when in the previous section we looked for the probability distribution of the sum of the two variables x and y , we assumed that all values of x and y between 0 and 10 are equally likely to occur. In the study of thermodynamical phenomena at the molecular level one finds that the variables which must be considered as basic

variables are the components of the positions and momenta of all the atoms that make the system. This is another fact which we quote without proof. Since momenta and velocities are proportional, it is all right to integrate over the velocity components instead, as we have done above. But more properly one should integrate over positions and momenta. The space spanned by all positions and momenta is called “phase space”. Thermodynamical averages should be computed by integrating over phase space. If a system is made of N atoms, the dimensionality of its phase space is $6N$. Let us conclude

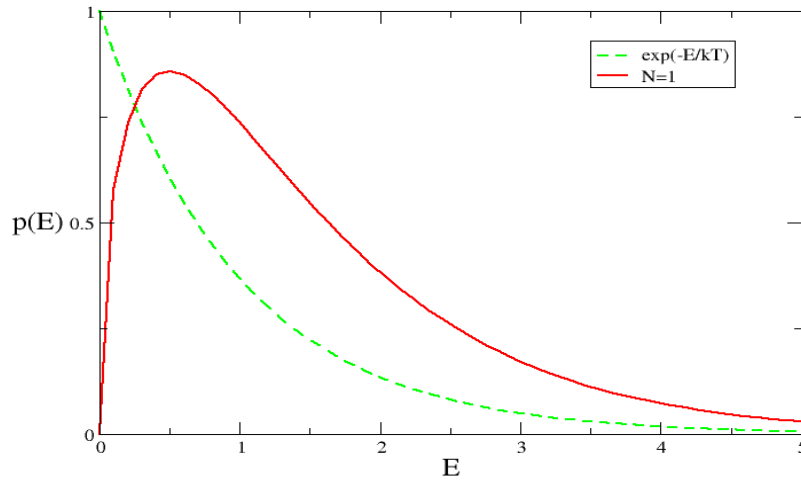


Figure 3: Maxwell-Boltzmann distribution function and probability density for the energy of a single atom.

applying these considerations to the calculation of the probability density for the kinetic energy of a single atom or of a group of several atoms. Just to simplify the notation, let us take the kinetic energy of the atoms to be their total energy, as in the case of an ideal gas made of monoatomic molecules. The Maxwell-Boltzmann distribution function $\exp(-E/kT)$ is plotted with $kT = 1$ in Fig. 3. The probability density $p_1(E)$ for the energy of a single atom is not proportional to $\exp(-E/kT)$ because the basic integration variables are the three components of the momentum of the atom. Thus, to calculate what is the probability that the atom energy be between E and $E + dE$, we first note that this range of energy corresponds to a range

between p and $p + dp$, with $p = \sqrt{2mE}$ and $dp = \sqrt{m/(2E)} dE$, for the magnitude of the momentum. In the three-dimensional space of momentum components, the spherical shell with radius between p and $p + dp$ has volume $4\pi p^2 dp \propto \sqrt{E} dE$. Thus the probability of finding the atom with energy between E and $E + dE$ will be proportional to this volume times the Maxwell-Boltzmann distribution function $\exp(-E/kT)$. On the other hand, by definition, this probability is $p_1(E) dE$. Therefore

$$p_1(E) dE \propto \sqrt{E} e^{-E/kT} dE \quad (27)$$

or

$$p_1(E) \propto \sqrt{E} e^{-E/kT} \quad (28)$$

$p_1(E)$, rescaled for a better fit into the frame of the figure, is also plotted in Fig. 3. We can generalize the argument to find the probability density

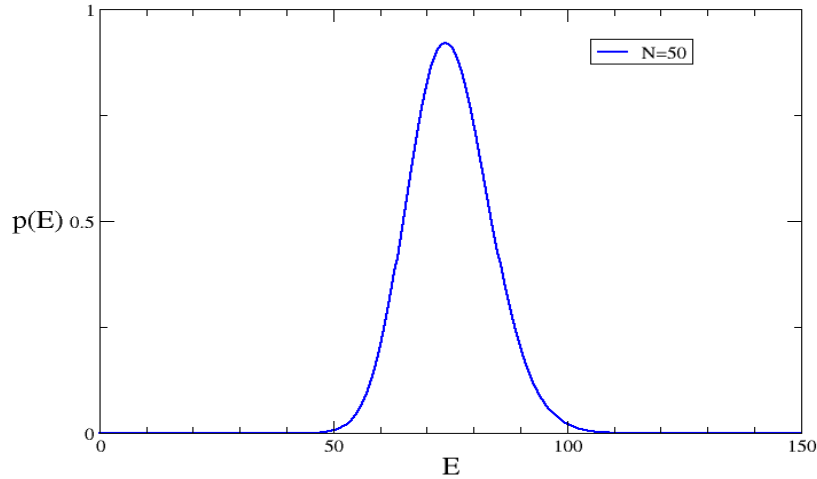


Figure 4: Probability density for the energy of a group of 50 atoms.

$p_N(E)$ for the total energy of a group of N atoms. In this case the basic variables of integration are the $3N$ components of the momenta of the N atoms, which span a space of dimensionality $3N$. The total energy of the N atoms is proportional to the square of the radial variable in this space (the

square of the distance from the origin)

$$E = \frac{P^2}{2m} \quad (29)$$

where

$$P^2 = p_{1,x}^2 + p_{1,y}^2 + p_{1,z}^2 + p_{2,x}^2 + p_{2,y}^2 + p_{2,z}^2 + \dots + p_{N,x}^2 + p_{N,y}^2 + p_{N,z}^2 \quad (30)$$

The volume of the spherical shell between P and $P + dP$ in the space of momenta is proportional to $P^{3N-1} dP$, which in turn is proportional to $E^{3N/2-1} dE$. Thus

$$p_N(E) \propto E^{3N/2-1} e^{-E/kT} \quad (31)$$

Figure 4 shows the graph (again rescaled for a better fit into the frame) of $p_N(E)$ with $N = 50$. The graph exhibits a marked peak around the average value of the total energy of the 50 atoms $E_{\text{av}} = 3N/(2kT) = 75$ (we recall that in Figs. 3 and 4 we use $kT = 1$). The peak in the energy distribution becomes enormously sharper when the number of atoms N is of the order of Avogadro's number, as in systems of macroscopic size. It is for this reason that, although in principle one always deals with an energy distribution, in practice the energy of a macroscopic system at a fixed temperature takes a very well defined value.

Molecular theory of the ideal gas.

We would like to calculate the pressure that an ideal gas with temperature T exerts on the walls of the container. To simplify the calculation we assume that the container has the shape of a rectangular box with sides of length L_x, L_y, L_z . We introduce a set of Cartesian coordinate axes parallel to the edges of the box and origin at one of its corners, as illustrated in Fig. 5. We assume that the total internal energy of the gas is equal to the kinetic energy of the motion of its molecules, i.e. we assume that the potential energy due to the interaction among molecules is negligible. The molecules thus move without interacting, apart from elastic collisions which cause a rearrangement of their velocities. We also assume that the total volume occupied by the molecules is negligible with respect to the volume of the container. These two assumptions characterize what we call an ideal gas.

The volume of the container is $V = L_x L_y L_z$. We denote by m the mass of the molecules and by N the total number of molecules in the container.

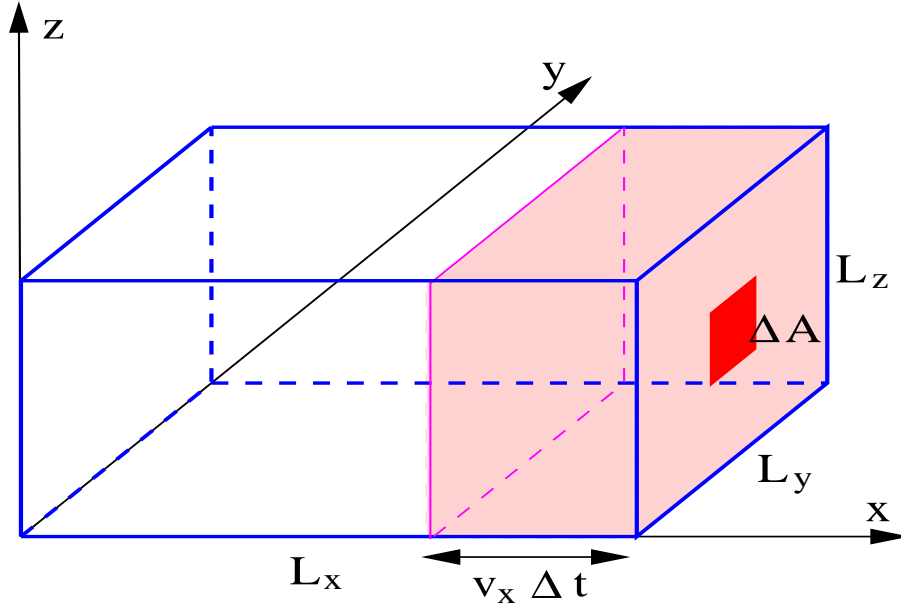


Figure 5: Calculation of the gas pressure.

The number of molecules per unit volume will be N/V . Let us calculate the pressure exerted by the gas on the wall at $x = L_x$. This pressure is due to the elastic collisions of the molecules with the wall. If a molecule hits the wall moving with velocity v_x it will bounce back with velocity $-v_x$, with a change of momentum $\Delta p_x = -2mv_x$. This change of momentum is equal to the impulse of the force that the wall exerts on the molecule during the collision. By the third principle the impulse of the force that the molecule exerts on the wall has the opposite value and thus is equal to $2mv_x$. Let us calculate the total impulse on the wall due to all the collisions that happen in an interval of time Δt . Let $p(v_x)$ be the probability density for the x component of the velocity of the molecules. This means that on the average there are $(N/V)p(v_x)dv_x$ molecules per unit volume with x component of the velocity between v_x and $v_x + dv_x$. These molecule will hit the wall at $x = L_x$ during the interval of time Δt if i) v_x is positive and ii) they are at a distance from the wall not greater than $v_x \Delta t$ (otherwise they will not reach the wall), i.e. they are contained in the shaded rectangular box in Fig. 5. Their number dN is obtained by multiplying the number of molecules per

unit volume, namely $(N/V)p(v_x) dv_x$, by the volume of the box $v_x \Delta t L_y L_z$:

$$dN = \frac{N}{V} v_x \Delta t L_y L_z p(v_x) dv_x \quad (32)$$

As we mentioned already, each of these molecules will give to the wall an impulse $2mv_x$. Thus the total impulse on the wall during Δt coming from collisions with molecules with x component of the velocity between v_x and $v_x + dv_x$ will be

$$dI = \frac{N}{V} 2m v_x^2 \Delta t L_y L_z p(v_x) dv_x \quad (33)$$

Integrating over all $v_x \geq 0$ we find that the total impulse due to the collisions with the molecules of the gas during Δt is

$$I = \frac{N}{V} 2m \Delta t L_y L_z \int_0^\infty v_x^2 p(v_x) dv_x \quad (34)$$

By symmetry

$$\int_0^\infty v_x^2 p(v_x) dv_x = \frac{1}{2} \int_{-\infty}^\infty v_x^2 p(v_x) dv_x = \frac{1}{2} \langle v_x^2 \rangle \quad (35)$$

Thus

$$I = \frac{N}{V} m \Delta t L_y L_z \langle v_x^2 \rangle \quad (36)$$

and the average force on the wall is

$$F = \frac{I}{\Delta t} = \frac{N}{V} m L_y L_z \langle v_x^2 \rangle \quad (37)$$

(The force is in the positive x direction and we denote by F its magnitude.) Dividing by the area $L_y L_z$ of the wall we find the pressure exerted by the gas on the wall

$$p = \frac{F}{L_y L_z} = \frac{N}{V} m \langle v_x^2 \rangle \quad (38)$$

With a little thought we can easily convince ourselves that if instead of considering the molecules hitting the entire wall we had considered the molecules hitting a small portion of the wall of area ΔA , such as the one shown by the filled square in Fig. 5, the force due to collisions would have been

$$F = \frac{N}{V} m \Delta A \langle v_x^2 \rangle \quad (39)$$

leading to the same pressure

$$p = \frac{F}{\Delta A} = \frac{N}{V} m \langle v_x^2 \rangle \quad (40)$$

Also, with a little further thought, one can easily realize that the result in Eqs. 38 or 40 is independent of the shape of the container.

We can rewrite the result of Eqs. 38 or 40 in the form

$$pV = Nm \langle v_x^2 \rangle \quad (41)$$

But in the previous section we have seen that the Maxwell-Boltzmann distribution implies $\langle v_x^2 \rangle = kT/m$. Inserting into Eq. 41 we get

$$pV = NkT \quad (42)$$

recovering the equation of state of the ideal gas.

We conclude with an important observation relative to the average energy associated to the various degrees of freedom of a molecule. If we go back to the arguments we used to prove the relation

$$E_{K,x} \equiv \frac{m}{2} \langle v_x^2 \rangle = \frac{kT}{2} \quad (43)$$

(see Eqs. 19-23) we see that the only thing we used is that the component of the energy $E_{K,x}$ associated with the translational motion in the x direction depends quadratically on the velocity v_x of the molecule, i.e. that the contribution from v_x to the total energy E is of the form $\text{const} \times v_x^2$. It follows that whenever the total energy contains a term which depends quadratically on one of the phase-space variables of integration, the average of that term in the energy will also be $kT/2$. But if a molecule has s degrees of freedom, there will be precisely s such terms in the energy, and thus the internal energy of the gas will be $NskT/2 = (s/2)nRT$, as mentioned in the previous set of lecture notes. This assumes however that the dependence of all these terms on the phase space variables is quadratic. In a real gas the potential of interaction among atoms will contain non-quadratic terms and the expression of the internal energy will be more complex.

Thermodynamical engines.

Thermodynamical engines, or simply engines, are devices which convert heat into mechanical work. One normally thinks of them as working in a cyclic fashion. A cycle is a closed set of thermodynamical transformations at whose end the state of the system goes back to the original state. In thermodynamical engines a fundamental cycle is repeated over and over, with a certain amount of work being produced at each cycle. In some cases, the engine, whether real or conceptual (i.e. a theoretical engine useful to prove some results, but very difficult if not impossible to build as a real engine), does work through cycles. More often the cycle is an idealization, which only approximates what happens in the real engine. A case in point is the engine of a car. It does work in a cyclic manner. The piston goes down allowing air and fuel to enter into the cylinder, then goes up compressing the mixture, the fuel is ignited by a spark, the gas in the cylinder expands forcing the piston to go down, finally the piston goes up again expelling the results of the combustion to the outside. However, since at every one of these cycles fresh air is let into the cylinder, the cycle does not form a closed set of thermodynamical transformations. We would have a true thermodynamical cycle if at the end of the expansion the air was kept into the cylinder, refreshed and compressed again for the next ignition. This idealized cycle actually provides a reasonably good approximation to what happens in a real automobile engine. But in other cases finding a thermodynamical cycle in a real engine requires much more of a stretch of imagination. Consider for example the turbines in the engines of a jet. Their operation is based on a continuous process, by which air is taken into the engine at a constant rate, compressed, mixed with fuel, which burns causing the air to expand and to drive the turbine. It is difficult to find cycles in this operation. Nevertheless it will be useful to think of thermodynamical engines as based on closed cycles.

Whether an engine works via a closed cycle or not, its operation is based on the conversion of some amount of the heat Q_1 it gets from suitable sources (the burning of fuel, a heat exchanger etc.) into mechanical work W . As we will see, not all of Q_1 is converted into mechanical work. Indeed, we will see that a complete conversion of heat into mechanical work is impossible. With $W < Q_1$, conservation of energy implies that some amount of heat $Q_2 = Q_1 - W$ (we measure heat in units of energy) must be returned to some

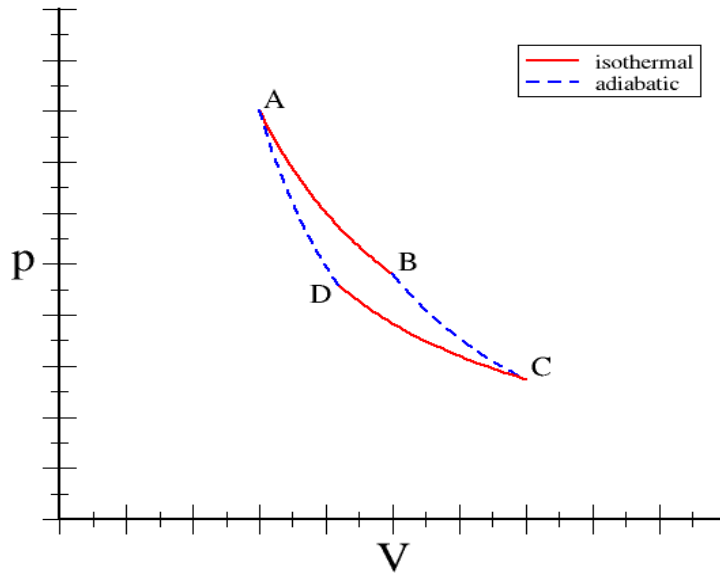


Figure 6: The Carnot cycle.

heat sink (the outside air, a heat exchanger etc.) The ratio

$$\eta = \frac{W}{Q_1} \quad (44)$$

is called the “efficiency of the engine”. We will see below that the second law of thermodynamics poses some absolute limitation on the efficiency of a thermodynamical engines.

The Carnot cycle.

The Carnot engine works by putting an ideal gas in contact with two thermal baths, at temperatures $T_A = T_B$ and $T_C = T_D$, and is based on a closed set of four transformations, which form the so-called Carnot cycle. In Fig. 6 we illustrate these transformation by means of a $V-p$ diagram. Starting at some point A on the $V-p$ diagram the gas undergoes an isothermal expansion to a new state represented by the point B . From B the expansion continues, but now adiabatically, to the point C . An isothermal compression brings the gas to point D . From here an adiabatic compression brings the gas to

the original state, at point A . The thermal bath at the higher temperature $T_A = T_B$ acts as heat source and the thermal bath at the lower temperature $T_C = T_D$ acts as heat sink.

The Carnot engine is a conceptual engine, which it would be very difficult to realize in practice, but its relevance comes from the use one makes of it to establish some fundamental results of thermodynamics. For the purpose it is important to calculate the efficiency of this engine.

The work done in the isothermal expansion $A \rightarrow B$ is (see lecture 11 Eq. 34)

$$W_{AB} = nRT_A \log\left(\frac{V_B}{V_A}\right) \quad (45)$$

where n is the number of moles of the gas. Since the internal energy $U = C_V T$ of the ideal gas does not change in an isothermal transformation, the amount of heat absorbed from the heat source must be equal to the work done by the gas

$$Q_{AB} = W_{AB} \quad (46)$$

During the adiabatic expansion $B \rightarrow C$ there is no transfer of heat and the work done by the gas is (see lecture 11 Eq. 49)

$$W_{BC} = C_V(T_B - T_C) \quad (47)$$

During the isothermal compression $C \rightarrow D$

$$W_{CD} = Q_{CD} = -nRT_C \log\left(\frac{V_C}{V_D}\right) \quad (48)$$

Finally, during the adiabatic transformation $D \rightarrow A$

$$W_{DA} = -C_V(T_A - T_D) \quad (49)$$

For the total amount of work done by the Carnot engine during a cycle we find

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = nRT_A \log\left(\frac{V_B}{V_A}\right) - nRT_C \log\left(\frac{V_C}{V_D}\right) \quad (50)$$

where we have used Eqs. 45, 48 and the fact that $W_{BC} = -W_{DA}$ since $T_B = T_A$ and $T_C = T_D$.

The total heat absorbed by the engine from heat sources is the heat Q_{AB} it absorbs during the isothermal transformation $A \rightarrow B$. Thus the efficiency of the engine is

$$\eta = \frac{W}{Q_{AB}} = \frac{nRT_A \log(V_B/V_A) - nRT_C \log(V_C/V_D)}{nRT_A \log(V_B/V_A)} = 1 - \frac{T_C \log(V_C/V_D)}{T_A \log(V_B/V_A)} \quad (51)$$

On the other hand, in an adiabatic transformation pV^γ is a constant. (The factor γ , we recall, is equal to the ratio of specific heat at constant pressure to specific heat at constant volume, $\gamma = C_P/C_V = (C_V + nR)/C_V$.) Equivalently, since $p = nRT/V$, $TV^{\gamma-1}$ is a constant as well as $T^{1/(\gamma-1)}V$. We apply this to the transformations $B \rightarrow C$ and $D \rightarrow A$ with the results

$$V_C = V_B(T_B/T_C)^{1/(\gamma-1)}, \quad V_D = V_A(T_A/T_D)^{1/(\gamma-1)} \quad (52)$$

and

$$\frac{V_C}{V_D} = \frac{V_B}{V_A} \left[\frac{(T_B/T_C)}{(T_A/T_D)} \right]^{1/(\gamma-1)} = \frac{V_B}{V_A} \quad (53)$$

since $T_A = T_B$ and $T_C = T_D$.

With $V_C/V_D = V_B/V_A$ Eq. 51 becomes

$$\eta = 1 - \frac{T_C}{T_A} = \frac{T_A - T_C}{T_A} \quad (54)$$

i.e. the efficiency of the engine is equal to the ratio between the temperature difference of source and sink of heat and the temperature of the source.

From Eq. 54 we can derive a relation between the amounts of heat absorbed from the source and returned to the sink and the corresponding temperatures. Indeed $W = Q_{AB} - Q_{DC}$, where we denote by $Q_{DC} = -Q_{CD}$ the positive amount of heat returned to the sink, which gives

$$\eta = \frac{W}{Q_{AB}} = \frac{Q_{AB} - Q_{DC}}{Q_{AB}} = \frac{T_A - T_C}{T_A} \quad (55)$$

from which we get

$$\frac{Q_{DC}}{Q_{AB}} = \frac{T_C}{T_A} \quad (56)$$

or

$$\frac{Q_{AB}}{T_A} = \frac{Q_{DC}}{T_C} \quad (57)$$

We will make a fundamental use of this result when we introduce the notion of entropy.

A Carnot engine working in reverse direction ($D \rightarrow C \rightarrow B \rightarrow A \rightarrow D$ in Fig. 6) acts a conceptual refrigerator. It will remove an amount of heat Q_{DC} from the heat bath at lower temperature and give an amount of heat Q_{AB} to the heat bath at higher temperature. Real life refrigerators do not use an ideal gas, indeed the gas they use as coolant may liquefy during part of the cycle, and do not implement precisely the same transformations as a reverse Carnot cycle, but, contrary to most engines, they do work with closed cycles. The substance they use as coolant is kept within the refrigerator and undergoes a closed cycle of thermodynamical transformations. Typically the coolant, in gas form, is compressed adiabatically, which heats it up, and then made to surrender heat to the outside air via a heat exchanger. Then the coolant is allowed to expand adiabatically, which lowers its temperature, and finally the coolant, now cold, is made to go through a heat exchanger inside the refrigerator, where it removes further heat from the cool compartment. Although not a faithful representation of a real refrigerator, a reverse Carnot cycle gives a good idea of how an actual refrigerator works. We should take note of the fact that the ratio between the amount of heat the “Carnot refrigerator” gives to the heat bath at the higher temperature $T_A = T_B$ and the amount of heat it removes from the heat bath at the lower temperature $T_C = T_D$ is

$$\frac{Q_{AB}}{Q_{DC}} = \frac{T_A}{T_C} \quad (58)$$

or equivalently

$$\frac{Q_{AB}}{T_A} = \frac{Q_{DC}}{T_C} \quad (59)$$

This heat transfer requires work. The amount of work that must be done per cycle is $W = Q_{AB} - Q_{DC}$ and thus the ratio between the amount of work expended and the heat removed from the heat bath at lower temperature is

$$\frac{W}{Q_{DC}} = \frac{Q_{AB} - Q_{DC}}{Q_{DC}} = \frac{T_A - T_C}{T_C} = \frac{T_A}{T_C} - 1 \quad (60)$$

We see from this equation that amount of work needed to cool a system

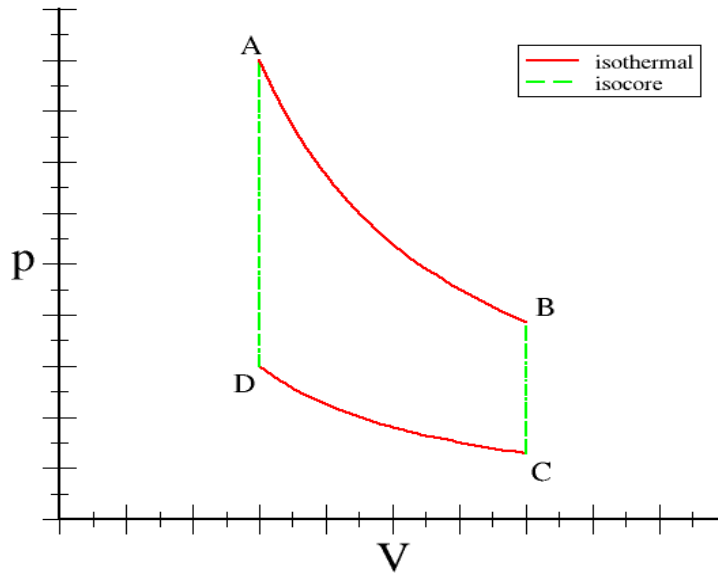


Figure 7: The Stirling cycle.

increases markedly as the temperature of the system to be refrigerated decreases, with $W/Q_{DC} \rightarrow \infty$ for $T_C/T_A \rightarrow 0$.

The Stirling cycle.

The Stirling engine is an engine based on a closed cycle which can actually be realized in practice, albeit as a demonstration model rather than for useful generation of power. The Stirling cycle, illustrated in Fig.7, consists a a set of two isothermal transformations and two isocore (constant volume) transformations. In the isothermal transformation $A \rightarrow B$ the gas expands from volume V_A to volume V_B doing an amount of work $W_{AB} = nRT_A \log(V_B/V_A)$ and absorbing an amount of heat $Q_{AB} = W_{AB}$ (see Eqs. 45, 46). During the isocore transformation $B \rightarrow C$ the gas does no work ($dV = 0$), cools down and releases an amount of heat equal to $C_V(T_B - T_C)$. During the isothermal transformation $C \rightarrow D$ the gas is compressed, with negative work $W_{CD} = -nRT_C \log(V_C/V_D)$. Finally, during the isocore transformation $D \rightarrow A$ the gas does no work and absorbs an amount of heat

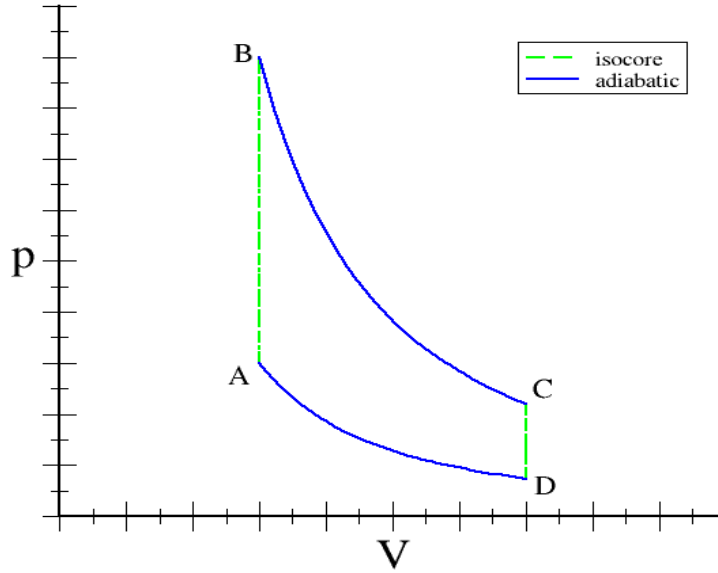


Figure 8: The Otto cycle.

$Q_{DA} = C_V(T_A - T_D)$. The efficiency of the engine is

$$\eta = \frac{W_{AB} + W_{CD}}{Q_{AB} + Q_{DA}} = \frac{nRT_A \log(V_B/V_A) - nRT_C \log(V_C/V_D)}{nRT_A \log(V_B/V_A) + C_V(T_A - T_D)} \quad (61)$$

or, using $V_C = V_B, V_D = V_A$,

$$\begin{aligned} \eta &= \frac{nR(T_A - T_C) \log(V_B/V_A)}{nRT_A \log(V_B/V_A) + C_V(T_A - T_D)} \\ &= \frac{T_A - T_C}{T_A + C_V(T_A - T_D)/[nR \log(V_B/V_A)]} \end{aligned} \quad (62)$$

Since the last term at denominator $C_V(T_A - T_D)/[nR \log(V_B/V_A)]$ is positive, $\eta < (T_A - T_C)/T_A$ and we see that the efficiency of the Stirling engine is less than the efficiency $(T_A - T_C)/T_A$ of a Carnot engine operating over the same range of temperature.

The internal combustion engine. The Otto cycle.

We conclude the section on thermodynamical engines with a description of the gasoline internal combustion engine, used in most cars, and of a cycle, the Otto cycle, which approximates its operation.

Often one hears the term four-cycle engine in reference to a car engine, but one should more properly talk of four strokes, which all together form a cycle. The four strokes are the intake, compression, power and exhaust strokes. During the intake stroke one or two valves (two for better efficiency) open at the top or head of the cylinder and the piston moves downward drawing air into the cylinder. At the same time some amount of fuel (gasoline) is sprayed into the cylinder by an injector also placed at the top of the cylinder head. During the compression stroke that immediately follows the intake valves are closed and the piston moves upward, compressing the admixture of gasoline and air. At the end of the compression stroke a spark from a spark-plug ignites the fuel mixture, which burns increasing the temperature of the gas inside the cylinder. This starts the third stroke, the power stroke, during which the piston descends down the cylinder pushed by the pressure of the hot gas. In the final stroke, the exhaust stroke, one or two exhaust valves open at the top of the cylinder head and the piston moves up, expelling the air and the residuals of the combustion into the exhaust pipes.

We can approximate this set of processes with a closed thermodynamical cycle by collapsing the exhaust stroke and the intake stroke. That is, we imagine that after the piston has completed the power stroke, the remnants of the combustion are magically removed from the cylinder chamber which is replenished with fresh air, and we can thus proceed with the compression stroke. The cycle, which is known as Otto cycle, works then as follows. For convenience we start the cycle at the moment when the fuel is ignited (point A in Fig. 8). The fuel burns very rapidly and the gas inside the cylinder head increases its temperature and pressure practically at constant volume (isocore transformation $A \rightarrow B$). At this point the piston begins its descent and the gas expands adiabatically from B to C . With the piston at the lowest point, through the collapse of the exhaust and intake strokes, the gas inside the cylinder is cooled at constant volume in the isocore transformation $C \rightarrow D$. The piston moves up and the gas (air plus injected fuel) is compressed adiabatically from D to A . At this point the spark ignites the fuel and the cycle begins again.

Let us calculate the efficiency of the Otto cycle. In the transformation $A \rightarrow B$

the gas gets an amount of heat

$$Q_{AB} = C_V(T_B - T_A) \quad (63)$$

In the transformation $C \rightarrow D$ the gas loses an amount of heat

$$Q_{DC} = C_V(T_C - T_D) \quad (64)$$

(We denote by $Q_{DC} = -Q_{CD}$ the positive amount of heat lost by the gas.) During the adiabatic transformations $B \rightarrow C$ and $D \rightarrow A$ the gas does work $W_{BC} = C_V(T_B - T_C)$ (positive) and $W_{DA} = C_V(T_D - T_A)$ (negative), respectively. The total work done by the gas during the cycle is

$$W = C_V(T_B - T_C + T_D - T_A) \quad (65)$$

(Of course, $W = Q_{AB} - Q_{DC}$, in agreement with energy conservation.) The efficiency of the Otto engine is therefore, rearranging some terms,

$$\eta_O = \frac{W}{Q_{AB}} = \frac{T_B - T_A - T_C + T_D}{T_B - T_A} = 1 - \frac{T_C - T_D}{T_B - T_A} \quad (66)$$

where we simplified a common factor of C_V . On the other hand, in an adiabatic transformation $TV^{\gamma-1} = \text{const}$. Thus

$$T_B = T_C(V_C/V_B)^{\gamma-1} = T_C\rho^{\gamma-1} \quad (67)$$

where we denoted by $\rho = V_C/V_B = V_D/V_A$ the compression ratio, i.e. the ratio between the volume in the cylinder when the piston is at the bottom of its course and the volume when the piston is at the top. Similarly

$$T_A = T_D(V_D/V_A)^{\gamma-1} = T_D\rho^{\gamma-1} \quad (68)$$

Substituting Eqs. 67, 68 into Eq. 66 we get

$$\eta_O = 1 - \frac{T_C - T_D}{(T_C - T_D)\rho^{\gamma-1}} = 1 - \frac{1}{\rho^{\gamma-1}} \quad (69)$$

This shows that the larger is the compression ratio, the higher will be the efficiency of the cycle. (We recall that $\gamma = C_P/C_V > 1$.)

It is also interesting to compare the efficiency of the Otto cycle with that of a Carnot cycle operating over the same range of temperatures $T_D - T_B$. The efficiency of a Carnot cycle over this range of temperatures

$$\eta_C = 1 - \frac{T_D}{T_B} \quad (70)$$

On the other hand, using $\rho^{\gamma-1} = T_B/T_C$ (see Eq. 67) the result for η_O of Eq. 69 can be rewritten as

$$\eta_O = 1 - \frac{T_C}{T_B} \quad (71)$$

Since $T_C > T_D$, $\eta_O < \eta_C$ i.e. the efficiency of the Otto cycle is always less than the efficiency of a Carnot cycle operating over the same range of temperatures.

The second law of thermodynamics.

Thermal phenomena are associated with the disordered motion of a large number of atoms. The probability that the “amount of disorder” decreases spontaneously is zero to all practical purposes. We put “amount of disorder” in quotes because, without further specifications, the term is rather vague. Still we have an intuitive notion that a disordered system does not order itself without some external agent. The second law of thermodynamics captures this fact. It was developed, however, without reference to the microscopic theory of thermal phenomena, but rather as the result of empirical observations about the limitations we face when we try to convert heat into work. The second law of thermodynamics has two equivalent formulations, due to Kelvin and Clausius.

Kelvin’s formulation: no thermodynamical process can have as its only effect the conversion into work of heat from sources all at the same temperature.

Clausius formulation: no thermodynamical process can have as its only result the transfer of heat from a heat bath at lower temperature to a heat bath at higher temperature.

The word only is paramount in both formulations. For example, the Carnot engine produces work from heat taken from a heat source at some definite temperature, but at the same time it releases some heat to a heat sink at lower temperature, so it does not have the conversion of heat from the source as its only effect. Similarly, by working a Carnot engine in reverse we can transfer heat from a heat bath at lower temperature to a heat bath at higher temperature, but at the same time we must expend work to do so. Thus the transfer of heat is not the only result of the process, there is also the expenditure of some amount of work.

The two formulations of the second law are equivalent. Indeed, if it were

possible to produce an amount of work W from a heat bath at a definite temperature T_0 , violating Kelvin's formulation of the second law, then we could use exactly this amount of work to run a reverse Carnot engine operating between the heat bath at temperature T_0 and a heat bath at higher temperature T_1 . At the end of the process, no work would have been expended and we would have accomplished a transfer of heat from the heat bath at lower temperature to the one at higher temperature, violating Clausius's formulation. Thus the Clausius formulation of the second law implies the one given by Kelvin. Vice versa, if we could violate Clausius's formulation by transferring an amount of heat Q from a heat bath at lower temperature T_0 to a heat bath at higher temperature T_1 , then we could run a Carnot engine between the two heat baths in such a way as to take precisely the amount of heat Q from the heat bath at temperature T_1 . As we have shown above, the Carnot engine would transform a fraction $Q \times (T_1 - T_0)/T_1$ of that heat into work and give the rest back to the heat bath at temperature T_0 . The net results of the process would be that an amount of heat $Q \times (T_1 - T_0)/T_1$ taken solely from the heat bath at temperature T_0 has been converted into work, violating Kelvin's formulation of the second law. Thus the Kelvin formulation of the second law implies the one given by Clausius.

Entropy.

Using the second law of thermodynamics we can prove a very important result which will allow us to introduce a new thermodynamical quantity, called "entropy".

The result is the following:

We consider a closed thermodynamical process which we describe in terms of infinitesimal steps during which the system absorbs heat dQ (positive or negative, negative dQ means that heat is released) while its temperature is T . Then

$$\oint \frac{dQ}{T} \leq 0 \tag{72}$$

and

$$\oint \frac{dQ}{T} = 0 \tag{73}$$

if the process is reversible.

Note that T is the temperature of the system while it absorbs the infinitesimal amount of heat dQ . It is immaterial how that heat is given to the system. It could be transferred for example by putting it in thermal contact with a heat bath at much higher temperature T' . It is the system's temperature T and not T' which enters into the equation.

Let us now prove the results stated in Eqs. 72 and 73. Precisely because it is not important how the heat dQ has been given to the system, we can imagine that it has been given by running a Carnot engine between a temperature T_0 , higher than all the temperatures appearing in Eq. 72 or 73, and the temperature T . This Carnot engine takes an amount of heat dQ_0 from the heat bath at temperature T_0 and gives back an amount of heat dQ to our system. We run a similar Carnot cycle for all the infinitesimal steps of the process. At the end of the closed process the situation is the following: the system has gone back to its original state and an amount of heat equal to the integral ΔQ_0 of dQ_0 has been taken from the heat bath at temperature T_0 . Energy conservation implies that $\Delta Q_0 = W$, where W is the total work, positive or negative, done by the system and the Carnot cycles. But W cannot be positive, otherwise the process would have violated the second law, in Kelvin's formulation: heat ΔQ_0 , taken from the heat bath at temperature T_0 , would have been converted into work W as the only result of the process. Thus $W \leq 0$ and therefore also $\Delta Q_0 \leq 0$. On the other hand for a Carnot engine running between temperatures T and T_0 (see Eq. 59)

$$\frac{dQ}{T} = \frac{dQ_0}{T_0} \quad (74)$$

This implies

$$\oint \frac{dQ}{T} = \oint \frac{dQ_0}{T_0} = \frac{1}{T_0} \oint dQ_0 = \frac{1}{T_0} \Delta Q_0 \quad (75)$$

Since, as we have just argued, $\Delta Q_0 \leq 0$, so also $\oint dQ/T \leq 0$, proving Eq. 72.

If the process is reversible, we can run it the other way around, which changes the sign to all exchanges of heat $dQ \rightarrow -dQ$. Then we must also have $\oint -dQ/T \leq 0$ or $\oint dQ/T \geq 0$. The two equations $\oint dQ/T \leq 0$ and $\oint dQ/T \geq 0$ together imply $\oint dQ/T = 0$, proving that with a reversible process the strict equality of Eq. 73 is satisfied.

Let us verify Eq. 73 in two examples. The first one, almost trivial, is a Carnot cycle. Transfer of heat only occurs during the isothermal transformations,

i.e. between the states A and B and C and D in Fig. 6 (the other two transformations are adiabatic transformations with $\Delta Q = 0$.) We have

$$\oint \frac{dQ}{T} = \frac{Q_{AB}}{T_A} - \frac{Q_{DC}}{T_C} \quad (76)$$

which vanishes on account of Eq. 59.

As a second example let us consider the Otto cycle. Again, transfer of heat occurs only during the two isocore transformations in the cycle (the other two are adiabatic transformations), namely the transformations between the states A and B and C and D in Fig. 8. We have

$$\begin{aligned} \oint \frac{dQ}{T} &= \int_A^B \frac{dQ}{T} + \int_C^D \frac{dQ}{T} = \int_A^B \frac{C_V dT}{T} + \int_C^D \frac{C_V dT}{T} \\ &= C_V [\log T_B - \log T_A + \log T_D - \log T_C] \\ &= C_V [\log(T_B/T_C) - \log(T_A/T_D)] \end{aligned} \quad (77)$$

But we have already observed, when studying the Otto cycle, that $T_B/T_C = T_A/T_D = (V_C/V_B)^{\gamma-1}$ (see Eqs. 67, 68). Thus $\log(T_B/T_C) = \log(T_A/T_D)$ and $\oint dQ/T = 0$.

As an application of Eq. 72 let us prove that the efficiency of an engine running between a maximum temperature T_{\max} and a minimum temperature T_{\min} can never exceed the efficiency of a Carnot engine running between the same temperatures. For the purpose let us denote by dQ' the infinitesimal amounts of heat absorbed by the engine during a cycle while at temperature T' and by dQ'' the infinitesimal amounts of heat released by the engine at temperature T'' . We have

$$\oint \frac{dQ}{T} = \int \frac{dQ'}{T'} - \int \frac{dQ''}{T''} \leq 0 \quad (78)$$

or

$$\int \frac{dQ'}{T'} \leq \int \frac{dQ''}{T''} \quad (79)$$

But, by assumption, $T' \leq T_{\max}$ and thus $\int dQ'/T_{\max} \leq \int dQ'/T'$. Similarly, from $T'' \geq T_{\min}$ we get $\int dQ''/T_{\min} \geq \int dQ''/T''$. It follows

$$\begin{aligned} \int \frac{dQ'}{T_{\max}} &= \frac{1}{T_{\max}} \int dQ' = \frac{Q'}{T_{\max}} \leq \int \frac{dQ'}{T'} \leq \\ &\leq \int \frac{dQ''}{T''} \leq \int \frac{dQ''}{T_{\min}} = \frac{1}{T_{\min}} \int dQ'' = \frac{Q''}{T_{\min}} \end{aligned} \quad (80)$$

where Q' and Q'' are the total amounts of heat absorbed and released, respectively, by the engine. From the inequality in Eq. 80 we get $Q''/Q' \geq T_{\min}/T_{\max}$ and for the efficiency

$$\eta = 1 - \frac{Q''}{Q'} \leq 1 - \frac{T_{\min}}{T_{\max}} = \eta_C \quad (81)$$

where $\eta_C = 1 - T_{\min}/T_{\max}$ is the efficiency of a Carnot engine working between the temperatures T_{\min} and T_{\max} .

A consequence of Eq. 73 is that the integral of dQ/T along any reversible transformation between two states A and B depends only on the initial and final states and is independent of the transformation. Indeed, if γ and γ' are two reversible transformations between A and B , the process obtained by going from A to B via γ and returning to A by following the reverse of γ' is a closed reversible process. Thus

$$\oint \frac{dQ}{T} = \int_{A,\gamma}^B \frac{dQ}{T} + \int_{B,\gamma'}^A \frac{dQ}{T} = 0 \quad (82)$$

But $\int_{B,\gamma'}^A dQ/T = -\int_{A,\gamma'}^B dQ/T$. Thus $\int_{B,\gamma'}^A dQ/T = -\int_{A,\gamma'}^B dQ/T = 0$ and

$$\int_{A,\gamma}^B \frac{dQ}{T} = \int_{A,\gamma'}^B \frac{dQ}{T} \quad (83)$$

as we wanted to prove.

This property of reversible transformations allows us to define a new thermodynamical variable, called “entropy” and denoted by S , as follows:

Starting from an arbitrary reference state which we denote by O and to which we assign entropy value S_O , the entropy of the system in any other state A is defined by

$$S(A) = S(O) + \int_O^A \frac{dQ}{T} \quad (84)$$

where the integral is taken along any reversible transformation joining the states O and A . (Notice the analogy with the way we defined the potential energy in a system with conservative forces.)

If a system consists of several components, possibly at different temperatures, the entropy of the system is taken as the sum of the entropies of the individual components. The results of Eqs. 72, 73 generalize to systems with many

components, in which case the integrals must be replaced with sum of the corresponding integrals over the various components of the system.

An interesting consequence of Eq. 72 is obtained by considering a process formed by an arbitrary transformation γ , not necessarily reversible, between two states A and B , followed by a reversible transformation γ' between B and A . $\gamma + \gamma'$ form a closed process and thus

$$\oint \frac{dQ}{T} = \int_{A,\gamma}^B \frac{dQ}{T} + \int_{B,\gamma'}^A \frac{dQ}{T} \leq 0 \quad (85)$$

On the other hand, according to the definition of entropy, $\int_{B,\gamma'}^A \frac{dQ}{T} = S(A) - S(B)$. Inserting this into Eq. 85 we get $\int_{A,\gamma}^B \frac{dQ}{T} + S(A) - S(B) \leq 0$ or

$$\int_{A,\gamma}^B \frac{dQ}{T} \leq S(B) - S(A) \quad (86)$$

i.e. the difference in entropy of two states joined by a transformation γ is always greater or equal to the integral of dQ/T taken along γ . In particular, if a system is isolated, $dQ = 0$ and therefore

$$S(B) - S(A) \geq 0 \quad (87)$$

i.e. the entropy of an isolated system never decreases.

Let us calculate the entropy of an ideal gas. We have

$$dS = \frac{dQ}{T} \quad (88)$$

On the other hand $dQ = dU + pdV$. Now, for an ideal gas $dU = C_V dT$ and $p = nRT/V$. Putting everything together we get

$$dS = \frac{dU + pdV}{T} = C_V \frac{dT}{T} + nR \frac{dV}{V} = C_V d \log T + nR d \log V \quad (89)$$

Integrating we get

$$S(T, V) = C_V \log T + nR \log V + \text{const} \quad (90)$$

for the entropy of an ideal gas. The constant of integration is the entropy of the reference state, which can be taken arbitrarily.

We conclude with a simple illustration of how the entropy of an isolated system never decreases. Let us consider a system made by two equal amounts of an ideal gas at temperatures T_1 and T_2 , with $T_1 > T_2$, kept in two separate containers, which are further kept in an insulating box. There is no exchange of heat or work between the containers and the world outside the box. The system is isolated. At some point the two containers are brought in contact, always inside the insulating box, and thus there is transfer of heat from the gas at higher temperature T_1 to the gas at lower temperature T_2 . Eventually the temperature of the two gases equilibrates at $(T_1 + T_2)/2$. The volume occupied by the gases does not change and thus, for the variation of entropy of the two gases we find $\Delta S_1 = C_V \log[(T_1 + T_2)/2] - C_V \log T_1$ and $\Delta S_2 = C_V \log[(T_1 + T_2)/2] - C_V \log T_2$. The total change of entropy is

$$\begin{aligned} \Delta S &= C_V \left[2 \log \left(\frac{T_1 + T_2}{2} \right) - \log T_1 - \log T_2 \right] \\ &= C_V \left[\log \left(\frac{(T_1 + T_2)^2}{4} \right) - \log(T_1 T_2) \right] = C_V \log \left(\frac{(T_1 + T_2)^2}{4 T_1 T_2} \right) \end{aligned} \quad (91)$$

But $(T_1 + T_2)^2$ is always greater than $4T_1 T_2$ when $T_1 \neq T_2$. Proof:

$$(T_1 + T_2)^2 - 4T_1 T_2 = T_1^2 - 2T_1 T_2 + T_2^2 = (T_1 - T_2)^2 > 0 \quad (92)$$

Thus $\log[(T_1 + T_2)^2/4(T_1 T_2)] > 0$ and $\Delta S > 0$.

Microscopic interpretation of entropy and the third law of thermodynamics.

We would like to relate the entropy of an ideal gas to the number of states available to its molecules, thus establishing a relation between the macroscopic notion of entropy and a measure of the disorder of the system at a microscopic level. Let us imagine that the gas consists of N molecules and that each molecule has s degrees of freedom. In this case $C_V = (s/2)Nk$, $nR = Nk$ and the expression for the entropy of the gas becomes (cfr. Eq. 90)

$$S(T, V) = \frac{s}{2} Nk \log T + Nk \log V + \text{const} \quad (93)$$

The states of the gas are labelled by the values of the positions \vec{r}_i and momenta \vec{p}_i of all the molecules, i.e. each state is identified by a point in phase

space. These points form a continuum and thus, to count them, we must discretize phase space by dividing it into cells. We take the size of the basic interval along any coordinate axis to be Δx and along any momentum axis to be Δp . The counting of states in the space of positions become then very simple. Each molecule can be anywhere in the volume V . Since its coordinate space is divided into cells of size $(\Delta x)^3$, each molecule has $V/(\Delta x)^3$ states available in position space and the total number of states available to all N molecules is

$$\mathcal{N}_{\text{pos}} = \left[\frac{V}{(\Delta x)^3} \right]^N = V^N (\Delta x)^{-3N} \quad (94)$$

The counting of states in momentum space is a little less trivial, because this is determined by the total volume in momentum space which is available to the system at a definite energy E . We can get an estimate of this volume by reasoning as follows. We have seen that the average value of the molecules energy per degree of freedom is $kT/2$. With N molecules this gives an average total energy per degree of freedom equal to $NkT/2$. Since the energy is proportional to momentum squared, the volume available in momentum space per degree of freedom will be proportional to \sqrt{NkT} . Dividing this into cells of size Δp we find a total number of states in momentum space, per degree of freedom, proportional to $\sqrt{NkT}/\Delta p$. Since each molecule can occupy any of these states the total number of states available to all N molecules for each degree of freedom is

$$\mathcal{N}_{\text{dof}} = \left[\frac{(cNkT)^{1/2}}{\Delta p} \right]^N \quad (95)$$

where we have introduced a constant of proportionality c to account for the fact that we have not done an exact calculation of the available volume but only kept track of its dependence on the temperature T . Finally, each momentum component (degree of freedom) can occupy these states independently, so the total number of states in momentum space is

$$\mathcal{N}_{\text{mom}} = \left[\frac{(cNkT)^{1/2}}{\Delta p} \right]^{Ns} = T^{sN/2} (\Delta p)^{-sN} (cNk)^{sN/2} \quad (96)$$

The total number of states available to the system in phase space is thus

$$\mathcal{N} = \mathcal{N}_{\text{pos}} \mathcal{N}_{\text{mom}} = V^N T^{sN/2} (\Delta x)^{-3N} (\Delta p)^{-sN} (cNk)^{sN/2} \quad (97)$$

Taking the logarithm of this number we get

$$\log \mathcal{N} = N \log V + \frac{s}{2} N \log T + \text{const} \quad (98)$$

where we have put together in the constant term the logarithm of all the factors which do not depend on volume or temperature. But the r.h.s. in Eq. 98 is amazingly similar to the expression for the entropy of the gas. Indeed, leaving for the moment aside the constant, we find

$$S = k \log \mathcal{N} \quad (99)$$

i.e. the entropy of the ideal gas is, apart from an additive constant, equal to the Boltzmann constant k times the logarithm of the total number of states available to its molecules in phase-space.

This is a general result. The entropy of a system is k times the logarithm of the number of states available to it. This allows us to see the entropy as a measure of disorder and also to understand why the entropy of an isolated system never decreases. The evolution of the system will never bring it spontaneously from a configuration which has a larger number of available states to a configuration which has a smaller number of available states. Think of a deck of cards. The configuration where all the top cards are of a red seed while all of the bottom cards are of a black seed can occur in $26! \times 26!$ possible ways, whereas the configuration where all cards can occupy an arbitrary position in the deck can occur in $52!$ possible ways. $52!$ is much larger than $(26!)^2$. Indeed $52!/(26!)^2 = 52 \times 51 \dots \times 28 \times 27 / (26 \times 25 \dots \times 2 \times 1)$ is a very big number approximately equal to 496,000 billion. Thus no amount of shuffling will ever produce the configuration with separated colors.

Finally, about the constant. To some extent we do not care, since the entropy is defined with an arbitrary additive constant. In any case, the constant in Eq. 98 is the sum of two terms. One is the constant of proportionality in the evaluation of the volume in the space of momenta, which we neglected to calculate precisely since it would have been absorbed anyway in the arbitrary constant in the definition of S . But it could have been calculated. The other term is $= -3N \log(\Delta x) - sN \log(\Delta p)$ which reflects that fact that to count the number of states we had to discretize phase space by dividing it into cells. At the classical level there is nothing that can help us specify how big these cells should be, and thus we are forced to leave an arbitrary constant

in the definition of the entropy. However, in quantum mechanics the number of possible states occupied by a system does become discrete. Planck's constant h provides a fundamental quantum of volume for phase space, with $(\Delta x)(\Delta p) = h$. This gives origin to the third law of thermodynamics, also called Nernst principle, which we cannot formulate rigorously for now. Here we will just state that, according to the third law, in quantum mechanics it is possible to define the entropy of a system in an absolute way, without the need of introducing any arbitrary constant.

Read Fishbane Chapter 19 pages 548-566 and Chapter 20 pages 573-600.