1 Introduction

Statistical mechanics is a very important branch of physics, it deals with the behaviour of many particles and tries to use mathematics in order to control and estimate the global behaviour of a great number of independent objects (molecules, particles, charges... you name it !). For example, if we consider the movement of a single molecule in a gas, we can imagine that its movement is chaotic, that the particle will act like a ball colliding randomly with other molecules or other objects around it. Of course we know very well the basic physics of such movements. A straight line, a collision and another straight line again. This is easy Newtonian physics! But, the problem is that it is clearly too complex to use standard physics to describe an ensemble of a great number of molecules. If we wanted to do so, we would need a number of equations equal to the number of molecules involved. This means, for just a mole of gas, about 10^{23} equations ! Clearly this is absurd. Then how can we explain collective molecular phenomena like the temperature, the pressure of a gas, or other collective phenomena like diffusion, Brownian motion or electric conduction ? These are the problems that statistical mechanics approaches and solves with very good approximations in many cases.

In this book we try to explain the fundamentals of Statistical Mechanics. Especially we want to make the student to understand how some solutions are achieved. We want to give the student the method to reach a solution in order that he can derive it again by him/herself without the need of the book. Or better, we hope this book will give students a new "way of thinking" and to develop his/her own ability to derive statistical mechanical solution for general and even new problems.

The book is based on the "Thermodynamics" course (this course is named also "Micro phenomena") in Yokohama City University that accepts both Japanese and International students. English vocabulary is simplified and we tried to avoid complex phrases in order to be more easily understood by international readers. A full translation with rephrasing and comments about English expressions is also provided on the opposite side of each page for the Japanese student.

2 First Experiments with gases

Since many years ago people studied the properties of gases. Even in the late 1600, Mr. Boyle discovered that the product Pressure by Volume PV is always a constant, if the amount of gas and its temperature do not change.

The experimentalist at the time of Boyle (1650), could measure the expansion with an apparatus that is represented in principle in the figure 1:

A fixed amount of air was trapped inside this J shaped tube. Boyle changed the amount of mercury in the tube in order to exert more or less pressure on the air. With this simple system he could measure both the air volume and the pressure exerted by the mercury on it.

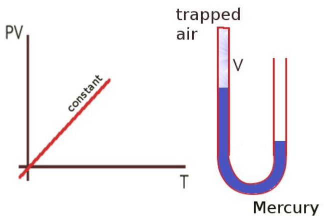

Figure 1: A schematics of the apparatus used by Boyle in 1662. In the graph it is represented the linear behaviour with temperature, however Boyle didn't know that PV=nkT at that time. He only new that the product PV was a constant, independently by Gas composition or nature.

At constant temperature, he was surprised to find the famous relation $PV = constant$. More surprisingly he discovered that this was true for any kind of gas he put inside his J shaped tube !

There was a linear relation between the product PV and the temperature T. Boyle noticed that the inclination of the line was approximately the same, for any gas, if he inserted about the same number of molecules. And this was true for ANY gas they tried ! Why this was happening ?

This fact, now called "Boyle law", it is amazing. Why it is amazing? Because of its simplicity! This result is so simple that it is easy to miss what is quite remarkable about it. Gases come in many different forms. We might have a very light gas like helium, the gas used to lift balloons, whose molecules are little spheres. Or we might have a denser gas like the oxygen of the air, whose molecules are dumbbell shaped. Or we might have a vaporized liquid, like water vapour, whose molecules are shaped something like the letter "Y". In every case, the same law holds, even if the oxygen or water vapour are mixed up with another gas like nitrogen in the air. Yet nothing in the law takes note of all these differences, but still this law works...!

Later in the 1700 century J. Charles and J.L. Gay-Lussac discovered that there was some kind of linear dependence with temperature, now we call these laws the Charles law ($V/T = constant$) and the Gay-Lussac law ($P/T = constant$).

Example:

Suppose you are Boyle in 1662. You trap in the "J" shaped tube a fixed amount of air. Changing the amount of mercury, you change the amount of pressure that is exerted on the gas (air). You first measure pressure and volume and you obtain these values:

$$V_1 = 1\ cm^2 (10^{-4} m^3)$$

$$P_1 = 0.1Pa \tag{1}$$

Then you add more mercury in the column. The weight of the column is now the equivalent of 380 mm of mercury over the atmospheric pressure, about 0.05 Pascal, so you have:

$$P_2 = 0.15Pa \tag{2}$$

can you calculate the volume you expect in this case ? Please use MKS units, Pascal is already in MKS units (1 Pa = 1 Newton per one square meter).

Answer: $V_2 \approx 6.66\ 10^{-5} \mathrm{m}^3$

3 The law of Ideal Gases

To put together all these relations found by these researchers, we have to understand one of the oldest mystery of science: what is the physical meaning of temperature? We know that material can be hot or cold at touch. But what does that means in physical terms? How to determine the real nature of the temperature ?

Well, we consider a cylinder full of gas, like in figure **??**. If we suppose that inside this piston there are N particles, what is the force exerted on the piston ? Well, the answer is easy. By definition, if the piston has an area A, the pressure on it is

$$P = \frac{< F >}{A} \tag{3}$$

where the symbolism $< F >$ means *the average force F*.

Now, for sure we can measure the average force on the piston $< F >$, but how much it is the *single* force of a single molecule hitting the piston ? Let's consider the *momentum* of a particle, it is

$$p = mv_x \tag{4}$$

we indicate v_x instead of v because we now consider only the component of the force orthogonal to the piston surface. We call this orthogonal direction x.

What is the net force acting on the piston ? Naturally, it is the force of a single particle multiplied by the total number of particles hitting the piston, lets call this number N^*, so : $< F >= N^* F$. Let's now estimate this force. We remember from basic physics that the impulse $p = mv_x$ is related to the force by

$$F = \frac{p}{t} = \frac{mv_x}{t} \tag{5}$$

where t is time. This is the force of a single hit, a collision of a molecule on the piston. Let's find how many hit will occur in a small amount of time t. Well, only the particles *near enough* to the piston will hit it, these particles are those at a distance less than $v_x t$. All the others they do not have enough time to reach it (!) These particles are enclosed in a volume $V^* = Av_x t$, where A is the area of the piston wall. Now, if we think with proportion in our mind, of course the ratio of the number of particle hitting the piston against the total particle, and the ratio between the volume that enclose them against the total volume, should be the same…so this relation must be true:

$$\frac{N^*}{N} = \frac{V^*}{V} = \frac{Av_x t}{V} \tag{6}$$

so the total number of particles hitting the piston in the time t is :

$$N^* = N\frac{Av_x t}{V} \tag{7}$$

Now using the fact that $< F >= N^* F$ and equation 5, we can calculate:

$$< F >= N\frac{Av_x t}{V}\frac{mv_x}{t} \tag{8}$$

now we simplify t and divide by the area A, we obtain immediately that :

$$PV = Nmv_x^2 \tag{9}$$

Now we notice that we have a term $mv_x^2 \ldots$, this is twice the kinetic energy $1/2mv^2$. Let's try to substitute this kinetic energy in our equation (9). To do so, we must be careful. Until now we considered the sole x direction, however for general random and uniform velocities, the kinetic energy is distributed equally in all directions, so it is

$$< v^2 >= \frac{1}{3} < v_x^2 > + \frac{1}{3} < v_y^2 > + \frac{1}{3} < v_z^2 > \tag{10}$$

this means that the total kinetic energy is three times $\frac{1}{2}mv_x^2$. So finally we can write:

$$PV = \frac{2}{3}N < E_k > \tag{11}$$

where $< E_K >= 1/2mv^2$. Again we should remember that the brackets $<>$ represent the *average* value. Coming back to our experiments, we know that the product PV is proportional to the temperature multiplied by some constant. Very interestingly if we look well at equation (11), and compare it with $PV = constant * T$, it is clear: the temperature seems to be something proportional to he kinetic energy of our gas! This is a great result, we solved one historical question: *what is the nature of temperature?*Temperature is a physiological sensation due to the kinetic energy of the molecules that collide and hit our body. More energy we feel hot, less energy we feel cold.

Now we need only to clean up a little equation (11). We define

$$< E_k >= \frac{3}{2}kT \tag{12}$$

where we call k the Boltzmann constant, we have the nice and famous expression:

$$PV = NkT \tag{13}$$

This equation is called usually *the ideal gas law.* Experimentally k results to be equal to $k = 1.38 \;\; 10^{-23}$ Joule per degree Kelvin. (if we want to use another constant, instead of the number of molecules N, we can use the number of *moles* n. Then the eq. 13 becomes $PV = nRT$ with R the *universal gas* constant $R = 8.31$ J/(mol K))

Remember that we choose eq (12) just because it is convenient to not have the number 3 or 2 in the final formula eq. (13). However, this was just a choice that was made years ago, any other definition would have been good as well.

Example:

Suppose we have a rubber balloon full of Air. We are at room temperature $T = 300K$, its volume is one litre and its pressure is a little more than the atmospheric pressure, let's say 1.5 atmospheres. Can we estimate the total number of molecules N that are inside the balloon ?

Yes it is possible, we simply use the equation $PV = NkT$, and extract N from that. In these basic calculations we must be careful not to make mistakes with dimensions. Let's do it together putting all dimensions between square brackets [].

We use MKS. First we consider that 1 litre is $10^{-3}m^3$ and that 1 atmosphere is 0.10 Pa. Now we write

$$N = \frac{PV}{kT} = \frac{0.15[Pa] * 10^{-3}[m^3]}{1.38 \;\; 10^{-23}[J]/[K] * 300[K]} \tag{14}$$

we have to be careful with units: considering that the unity $[J]$ is in MKS $[J] = [m^2 * Kg/Sec^2]$ and that $[Pa] = [Kg]/([Sec^2][m])$, we can rewrite:

$$N = \frac{PV}{kT} = \frac{0.15\frac{[Kg]}{[Sec^2][m]} * 10^{-3}[m^3]}{1.38 \;\; 10^{-23}[m^2] * \frac{[Kg]}{[Sec^2]*[K]} * 300[K]} \tag{15}$$

you note that all dimensions disappear, so at the end we have

$$N = \frac{PV}{kT} = \frac{0.1510^{-3}}{1.38 \;\; 10^{-23} * 300} \approx 3.6 \;\; 10^{16} \tag{16}$$

This is the number of molecules in the balloon! Can we estimate also the weight of this thing ? Yes, why not? If we know how many molecules are there, we can estimate also the total weight. If we assume that Air is roughly 80% of Nitrogen, from the chemical tables we know that one mole of Nitrogen (that is about $6\ \ 10^{23}$ molecules) weights 14 grams. So a mole of air roughly speaking should be about $0.014[Kg]/0.8$, that is $0.017[Kg]$ of 17 grams. Our total number of molecules is not a mole, but much less $N = 3.610^{16}$. How much less ? The fraction of moles of air we have in the balloon N_{mol} is

$$N_{mol} = \frac{3.6\ 10^{16}}{6\ 10^{23}} = 6\ 10^{-8}$$

so the total weight of the balloon is 17 grams multiplied by N_{mol}, that is

$$weight = 17[g] * 610^{-8} \approx 1 \mu g$$

As you noticed we did very rough assumptions during this calculation. However, you may agree that - very roughly speaking - this value can approximate the weight of our balloon, at least in the order of magnitude. You can devise a more fine estimation of the weight by yourself as an exercise.

3.1 Isotermal compression/expansion

We will see later that equation (13) is also called the equation of isothermal compression, because in the mathematical space PV (where PV are the variables, as XY are variables in the Cartesian space) if temperature is constant we have the relation $PV = const.$ (k is obviously a constant and N is the number of molecules in the box, so it is a constant too). We can plot this curve in the PV space (figure 2). This is called an *isothermal compression* because it represent the relation between pressure and volume of a gas when its temperature is not changing.

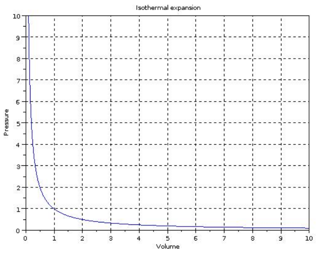

Figure 2: The isothermal expansion of a gas in the PV space. Please notice that this behaviour is valid for any time of gas or mixture of gases!

3.2 Adiabatic compression/expansion

Now let's do a last effort and make some more considerations: what happens if we strongly compress a gas in a piston? Of course, the temperature of the gas will increase. So these kind of compressions cannot be *isothermal* as the one above. How will be the dependence of Pressure and Volume in this case ?

As we know energy and temperature are related accordingly to equation 12. Using (11) and (12) we can write

$$PV = N\frac{2}{3} < \frac{1}{2}mv^2 > \tag{17}$$

let's consider now the total kinetic energy of the system $U = N < \frac{1}{2}mv^2 >$, this U is generally called the total *internal* energy of a gas. It is the multiplication of all the molecules present, N, by their average kinetic energy.

$$PV = \frac{2}{3}U \tag{18}$$

This equation is valid if all the energy is only kinetic energy. In other words if there is not other forms of *internal* energies, like for example molecule rotation, molecule bending, molecule vibration or other form of molecular energy. If our gas is for example a monoatomic gas, then all these other form of energies are negligible and the internal energy U is a good approximation of the total energy within the gas. For historical reasons, let's modify equation (18) as

$$PV = (\gamma - 1)U \tag{19}$$

this of course can be always done. It just means that the parameter γ is equal to 5/3 in the case of an ideal mono-atomic gas. Now let's suppose we want to calculate an expression for the work of the system. We know from basic physics that Fdx is the work, multiplying and dividing by the area of the piston (figure **??**), it is straightforward that

$$\frac{F}{A} * Adx = work \tag{20}$$

The pressure is F/A and Adx is the the small variation of volume dV due to the expansion of the piston. This is the mechanical work exerted to the gas by the compression. Where this mechanical energy (mechanical work is energy!) is going to end up? If there are no losses outside, this work will correspond to an equal and opposite variation of internal energy of the gas! If so, we can write $PdV = -dU$. We said above that $U = PV/(\gamma - 1)$, so we have only to differentiate equation (19):

$$dU = (PdV + VdP)/(\gamma - 1) \tag{21}$$

Now we substitute $PdV = -dU$ and we have:

$$\begin{aligned}(\gamma-1)dU &= (PdV+VdP)\\ -(\gamma-1)PdV &= (PdV+VdP)\end{aligned} \tag{22}$$

Now eliminating PdV we have:

$$\begin{aligned}\gamma PdV &= -VdP\\ \gamma\frac{dV}{V}+\frac{dP}{P} &= 0\end{aligned} \tag{23}$$

Now we integrate and we have:

$$\gamma\int\frac{dV}{V}+\int\frac{dP}{P}=\int 0 \tag{24}$$

remembering that the integral of zero is a constant and that $\int dx/x$ is $ln(x/x_0)$ we have:

$$\gamma lnV + lnP = const. \tag{25}$$

if you remember the properties of logarithms, this means that:

$$PV^{\gamma} = const. \tag{26}$$

This is a very important relation because it express the behaviour of pressure and volume in the case we have an expansion or compression that actually changes the temperature of the gas and there are not external losses of heat. Equation 26 it is also called the equation for an *adiabatic expansion* (or compression). Please notice that the exponent γ is beautifully at the exponent of the volume. Now you understand why in equation 19 we used this parameter instead of the usual 2/3. Actually, we can *measure* γ experimentally, just making an adiabatic expansion and measuring P and V. We find that for mono-atomic gases γ is about 5/3 as expected. Instead for more complex gases, because of vibrational and other spurious phenomena that make the gas a non-ideal one, we can measure different values of γ. The isothermal and adiabatic expansions look different on a PV plot as shown schematically in figure 3.

Example:

Let's suppose that a gas is kept in a box at constant temperature and at a pressure of $P_1 = 1$Atm, volume $V_1 = 1$ liter. We let expand the gas to 1.2 liter keeping the temperature constant, what happens to the pressure ? Using

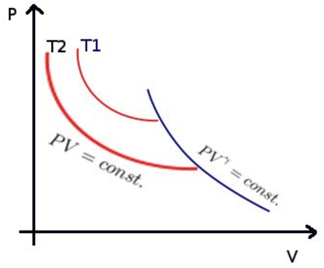

Figure 3: A scheme of isothermal and adiabatic expansions of a gas in the PV space.

what we understood above, the product PV^γ must be constant. So we simply calculate the pressure with this expression

$$P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma}$$

Let's convert this to real numbers, we again pay attention to units, we must use MKS always, so we remember that 1 Atm is about $10^5[N/m^2]$:

$$P_2 = \frac{10^5[N/m^2] * 0.001^{5/3}[m^3]}{0.0012^{5/3}[m^3]} = 73.7[N/m^2]$$

This show how a small difference in volume can result on a big drop of pressure in the adiabatic expansion.

4 A mathematic exercise: the physical meaning of differentials

In this course it is very important to understand differential models of the processes we study. For this reason it is of paramount importance to grasp the philosophy of differentiation and integration of a variable. For this purpose let's play around with few basic problems. Trying to solve these, will help us to understand the principles of differentiations from the physicist point of view.

In the real world, physical variable are related in complex way. Differentiate means to consider very small differences of variables in order reduce *curves* in *straigh lines*. In other words, we *think small* and reduce complexity.

Any curved path, can be considered as the sum of many small linear segments. For very small differences, any complex relation can be considered like a linear one. The key point is that these difference should be really small.

For example let's consider the relation $PV = NkT$ as we studied in the previous chapter. We have three variables (P, V and T) that are related by a defined mathematical relation. If V changes, the other two variables must change accordingly along a certain *curve*. Let's study the small differences between two points of this equation, point one will be (P_1, V_1, T_1) and point two (P_2, V_2, T_2). For example:

$$P_1V_1 = NkT_1 \tag{27}$$

$$P_2V_2 = NkT_2 \tag{28}$$

$$\tag{29}$$

let's take the difference:

$$P_2V_2 - P_1V_1 = Nk(T_2 - T_1) \tag{30}$$

now, let's add $+P_2V_1 - P_2V_1$, this term is zero so we can do that:

$$P_2V_2 + P_2V_1 - P_2V_1 - P_1V_1 = Nk(T_2 - T_1) \tag{31}$$

now, we collect P_2 and V_1:

$$P_2(V_2 - V_1) + V_1(P_2 - P_1) = Nk(T_2 - T_1) \tag{32}$$

$$P_2\Delta V + V_1\Delta P = Nk\Delta T \tag{33}$$

Untill now we didn't do anything special, we just used basic algebra and called the difference of two points with the symbol Δ. Now think about the fact that these two points are very near each other: if the differences between the point 1 and point 2 are really, really small, then this means that the value of P_1 and that of P_2 are almost the same. They are so similar that they can be confused. So why to write P_1 or V_2 if they are practically the same ? If so, let's call them just $P \approx P_1 \approx P_2$ and $V \approx V_1 \approx V_2$ and write again our equation (33):

$$PdV + VdP = NkdT \tag{34}$$

You see? We obtained, with only few algebra and some simple thinking, that the differential equation of $PV = NkT$ is $PdV + VdP = NkdT$. The symbol d in dV or dP is sometime called *infinitesimal*. We knew that from mathematics. But now we gave to the differentiation process a *physical meaning*. We learned that to remember how to differentiate complex physical equation, you only need to take two points of the equation and *think small* !
Any differential equation, though, is valid only for points so near each other, that almost coincide... so they do not have so much use in practical applications. To be useful they must be *integrated*.

Clearly you know how to integrate. But again, to understand the physical meaning of integration in a practical physical problem, let's do some more exercise. Let's consider a simple application problem: what is the circumference of a circle of radius R ? Of course we all know it is $l = 2\pi R$, but let's pretend we do not know that. Let's *think small* and concentrate on a very small angle, like in the figure **??**. The angle should be so small, that the curvature of the vertical arc can be neglected. We consider the arc as a straight segment of length dl.

[Cerchio.eps]

We have then a triangle, we know from trigonometry that

$$R \sin d\alpha = dl$$

We call the angle $d\alpha$ because it is as well so small, almost zero, as dl. At this point we have also the advantage that for small angles it is valid the relation $\sin d\alpha \approx d\alpha$. So if we *thought small* enough, we can write with very good approximation

$$dl = Rd\alpha$$

But this is not the circumference of our circle, it is just the very small *infinitesimal* part of it !

We have to *integrate* on all the angles and we will have our circumference.

$$\int dl = \int_0^{2\pi} Rd\alpha$$

From basic mathematics we know that R can go out of the integral because it does not depend on α, we finally have our circumference:

$$l = \int_0^{2\pi} Rd\alpha \tag{35}$$

$$l = R\int_0^{2\pi} d\alpha \tag{36}$$

$$l = 2\pi R \tag{37}$$

This is exactly what we expected! How we did this ? We simply found the correct relation for the variables in case of very small differences and then integrated. This is a principle that is very often used in making physical models in statistical mechanics and in other fields.

Just to have fun in the same way we can calculate now the area of a Sphere. This time we are in two dimensions, we must use another angle ϕ that runs vertically. We start from our previous result, the length of the circumference is $l = 2\pi R$. We *think small* again, and we construct a very small surface on our circumference in the vertical direction. To do so, we just multiply the circumference by the small length $dl = Rd\phi$, exactly in the same fashion as before (see figure **??**).

[areaSph12.eps]

$$dS = \quad (2\pi R)dl \tag{38}$$

But what is the circumference ? Is it really $(2\pi R)$ as written above ? Well, it is not ! If we look at figure **??**, we notice that while we go up with angle ϕ, the radius R" gets smaller and smaller. From trigonometry again, we know that $R" = R\cos(\phi)$, so the correct relation for the circumference is $2\pi R\cos(\phi)$, then we have

$$dS = \quad (2\pi R\cos\phi)dl \tag{39}$$

$$dS = \quad (2\pi R\cos\phi)(Rd\phi) \tag{40}$$

$$dS = \quad 2\pi R^2\cos\phi d\phi \tag{41}$$

the we integrate and we have:

$$\int_0^S dS = \quad \int_0^{\pi/2}(2\pi R)(R\cos\phi d\phi) \tag{42}$$

$$S = \quad 2\pi R^2\int_0^{\pi/2}\cos\phi d\phi) \tag{43}$$

$$S = \quad 2\pi R^2[\sin(\pi/2) - 0] \tag{44}$$

$$S = \quad 2\pi R^2 \tag{45}$$

If we look again well at the figure, integrating from 0 to $\pi/2$ we covered only the top hemisphere, so we have to multiply by two, and at the end we have what they thought us at elementary school:

$$S = 4\pi R^2$$

Now, the volume of a sphere is $V = \frac{4}{3}\pi R^3$ can you calculate it yourself ?

5 Thermodynamics

What is thermodynamics ? In few words we can say that is the science of studying the relation of between mechanical energy and thermal energy. Thermodynamics is an older theory, and it goes back to the time of Sadi Carnot the beginning of 1800 century, when the molecular theory of matter was not know well. So what we studied up to here, was not know yet, and we are going back in time a little when we study thermodynamics now.

First law: the heat engine

The theory of thermodynamics being so old is based on simple observations, more than rigorous molecular models. At the beginning of the 1800th, the heat was considered to be a kind of fluid that flows in materials, and even the principle of conservation of energy was not established. Let's consider as an example a rubber band. If we expand it, we can observe an increase in the temperature of the band. If we put it between the lips, we can clearly feel that it gets warmer. On the contrary, if we relax it quickly, we can feel that the rubber gets cooler.

These observations made the people of that years to make the following considerations about heat and mechanical force. When a rubber band is holding a weight it is well extended, it is stronger and if we measure the temperature it is hot. On the contrary, when we relax the band, for sure is not holding any weight, it is then not strong, and we observe it is cool.

People also observed that heating up a rubber band that was holding a weight, actually lifted the weight a little more. Whereas, cooling it down caused the extension of the rubber band, and released the down a weight attached to it. So the first conclusion is: if we put heat into a material we can have mechanical work for it. In our example for *mechanical work* of course we mean the product Fdx that we obtain if an object attached to our rubber band is moved up of dx by the force F of the rubber.

All these observation led to general considerations: if a system has a certain *internal* energy U, then any variation of this internal energy must be equal to any external heat Q plus any mechanical work we give to this system. In mathematical terms:

$$\Delta U = \Delta Q + \Delta W \tag{46}$$

this is called *the first law of thermodynamics*. In the case the internal energy does not change, we can of course write:

$$\begin{aligned} \Delta Q &= \Delta W \\ Q_2 - Q_1 &= \Delta W \end{aligned} \tag{47}$$

But what is the physical nature of this *internal energy* U, and what is the nature of the *heat* Q?. In 1800, it was not clear!

5.1 The second law: order and disorder

In the times of Sadi Carnot, that was the son of a famous military leader, the steam engine was popular and under production, however there was not a proper theory to explain its working principle. So you can understand the importance of the principle of thermodynamics at that time. Carnot was very interested in these machines, and he was able to state a very important principle, the so called second principle of thermodynamics. This principle can be expressed by this phrase:

The heat flows spontaneously from a hot body to a cold one. The inverse process is not possible unless we introduce external work.

There is another way to express the same thing, is with the introduction of the concept of *disorder*. The other way to express the second principle of thermodynamics is then:

In a system any process can only increase the total disorder, unless we introduce external work.

These two phrases express the same things we can observe from real experience. The fact that a hot body put aside a colder one transfer its energy to the cold one and not the opposite. Why we introduce the concept of *disorder* ? Well, we know what is heat. It is something proportional to the molecular speed (remember eq. 12). A cold body is a body where the molecules have less speed, so are characterized by a degree of *order* which is higher of a hot body. In a hot body the molecules are moving more chaotically, so there is more disorder.

To clarify this in your mind just think to a cube of ice, a drop of water and a cloud of water vapour. These systems are just the same material at different temperature, what of these systems contains more order ? For sure the cube of ice has more order than the other two. Because the molecules of it are well organize in a cubic crystal. Instead water and vapour molecules move chaotically around each other in all directions. If we want to compare the level of order of these two who wins ? Of course water ! Why ? Because at least water molecules are bind at a certain distance between each other. They move around, but they do not go too far away of each other like in the gaseous water vapour. So the level of order is inversely proportional to the level of temperature. More temperature, less order. So if we leave a cube of ice alone he can melt or sublimate, if we want a droplet of water to become a cube of ice, we have to add external work. These observational statements are the key of the second law of thermodynamics.

The second law of thermodynamics is somehow related not solely to purely thermal process, it has a more general significance. For example let's think of another process, a drop of ink in a glass of water. What happens with time ? At first the droplet of ink is very well visible in the middle of the glass. It has a precise position within the glass, it has a certain radius, a certain shape and a certain color. So to describe it we a great amount of *information.* If we need informations to describe a systems, it means we have a certain level of order in it.

Please remember that a completely disordered system, contains very low information. Or in other words, we need very few information to describe it. Just think about white noise. What info you need to describe, if not that is white noise at a certain volume? Instead think about another sound, the sound of an instrument. How much information you need to describe it. . . ? More than before ! You need to say which tone (frequency), what kind of instrument (its timber, its spectrum) and this itself is a very complex set of information. So more information, more order, less information less order.

Coming back to our example of the ink in the glass, after time passes the droplet of ink gets bigger and bigger and at the end it dissolve in the water. What we have after some time, is a glass of water with no apparent droplet of ink, just a glass of water. The color of the water has changed a bit, it is somewhat darker than before. How much information we need to describe this system compared to before? More or less information? Less information ! Now to describe our system we have just to say the color of the water. . . that's it! The information in the system has spontaneously reduced, this means that the total disorder has increased. So this again is in agreement with the second principle, as stated above.

5.2 Entropy:

We know now that it is impossible -in a macroscopic system- to reverse the process thermodinamical processes, the disorder will always increase. However, what will happen if we *think small*? If we imagine to have a very small system with few molecules, and we increase the temperature just a little (δT), is it possible that energy flows also from cold to hot? Well, if we remember that the temperature represents the average velocity of the molecules, if the physical system is small, with very few molecules... maybe! When the system is very very small, and the two bodies have almost the same temperature, of course we can imagine that the temperature always fluctuates from the cold body to the hotter and vice-versa freely.

So, from the point of view of *differentials* the second law of thermodynamics is not valid and we can speak of *reversible engines.* A reversible heat transfer is equivalent to frictionless motion in mechanics.

Please remember PV plot in figure 3 in the first chapter. Let's consider two points a and b at the same temperature. The work done of course is

$$W = \int_a^b p dV \tag{48}$$

Since we are along an *isothermal*, we know that

$$p = \frac{NkT_1}{V_a} \tag{49}$$

so using eq (47)

$$Q_1 = \int_a^b NkT_1 \frac{dV}{V} = NkT_1 ln \frac{V_b}{V_a} \tag{50}$$

If we move along another isothermal of course we can write an equivalent equation

$$Q_2 = \int_c^d NkT_2 \frac{dV}{V} = NkT_2 ln \frac{V_d}{V_c} \tag{51}$$

Now if we connect the points b and c, d and a with *adiabatic* curves in the PV plot, we know from what we already studied that $P_1 V_1^\gamma = P_2 V_2^\gamma$. Using $PV = NkT$ we have:

$$\begin{aligned} P_1 V_1^\gamma &= P_2 V_2^\gamma && (52) \\ P_1 V_1 V_1^{\gamma-1} &= P_2 V_2 V_2^{\gamma-1} && (53) \\ N_k T_1 V_1^{\gamma-1} &= N_k T_2 V_2^{\gamma-1} && (54) \end{aligned}$$

this is equivalent to

$$TV^{\gamma-1} = constant \tag{55}$$

This lead to this two equations:

$$\begin{aligned} T_1 V_b^{\gamma-1} &= T_2 V_c^{\gamma-1} \\ T_1 V_a^{\gamma-1} &= T_2 V_d^{\gamma-1} && (56) \end{aligned}$$

just dividing these two equations we understand that

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \tag{57}$$

This means that the logarithms in eq (50) and eq(51) are identical, so dividing the two by T_1 and T_2 respectively, we obtain this very important final equation:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{58}$$

This is the equation expressing the *entropy* of a system. The value Q/T of two bodies never changes in a reversible engine. We can also write eq (58) this way

$$\frac{Q_1}{T_1} = S = \frac{Q_2}{T_2} \tag{59}$$

where S is called the entropy of the system. In a real case, of course, the entropy will increase, and will be given by this integral relation

$$S_b - S_a = \int_a^b \frac{dQ}{T} \tag{60}$$

So another way to express the two laws of thermodynamics is as the following:

first law: the energy of the universe is constant
second law: the entropy of the universe is always increasing

Thermodynamics is a complex discipline that involve deep study and we do not want to go too in details here, however please try to consider the philosophical implication of the few concept that we have given here.

6 The linear thermal behaviour of an air column

We would like to know if our theory developed up to here, is able to explain some everyday observation. If we climb a mountain, we observe a regular linear drop in temperature, can we explain it somehow? Let's again use differentials, in simple words we *think small* and consider a column of air of small section. What is the difference of pressure between two slices of the column *very near* each other?

We call p_1 the pressure in the upper slice and p_0 the one on the lower one. Since the pressure diminishes with hight we can write

$$\begin{aligned} p_1 &= p_0 + \rho g dh \qquad (61) \\ dP &= -\rho g dh \end{aligned}$$

where ρ is the density of the air (mass over volume), g the gravity and dh the vertical distance between the two slices. We notice also that from the ideal gas law the density is immediately expressed as $\rho = mP/kT$, where m is the mass of one single molecule of gas (just multiply $PV = NkT$ by the mass of a single molecule and divide by the volume V to obtain the density $\rho = mN/V$). We can rewrite the above as:

$$dP = -\frac{mP}{kT} g dh \qquad (62)$$

Now, we consider that the main reason of temperature drop at high elevations is due to the continuous convection movement of air from bottom (hot air) to top (cold air). This rise of air produce a variation of pressure and temperature. Since air is a bad temperature conductor and since the rise is slow we can approximate this variation as *adiabatic*. This means we suppose that there is no exchange of heat with other air layer, the temperature drop we will calculate will be due only to the air expansion.

$$PV^{\gamma} = const$$

We need a relation with temperature, so we use the ideal gas formula $PV = NkT$ and extract V $V = \frac{NkT}{P}$ and substitute in the above, we obtain

$$\begin{aligned} P\left(\frac{NkT}{P}\right)^{\gamma} &= const \qquad (63) \\ \frac{T^{\gamma}}{P^{\gamma-1}} &= const \end{aligned}$$

$$\frac{T}{P^{\frac{\gamma-1}{\gamma}}} = const$$
$$T = const * P^{\frac{\gamma-1}{\gamma}}$$

notice that constant values were included in *const* and that we extracted the root to the γ. Now we want to differentiate, to do that we fist use logarithms on both side to get rid of exponential, then we differentiate the last of equation 63:

$$\log T = \log const + \frac{\gamma-1}{\gamma}\log P \tag{64}$$
$$\frac{dT}{T} = \frac{\gamma-1}{\gamma}\frac{dP}{P}$$

so in conclusion, we now that

$$dP = \frac{\gamma-1}{\gamma}\frac{P}{T}dT \tag{65}$$

If we substitute this in equation 62, we eliminate dP and obtain a linear relation between the variation of temperature and the variation of height.

$$dT = \frac{\gamma-1}{\gamma}\frac{mg}{k}dh \tag{66}$$

Actually, putting in this equation reasonable MKS values, like $\gamma = 7/5$ (biatomic gas), molecular mass of air $m = 510^{-26}$ Kg (28.8 grams over the Avogadro number $6 * 10^{23}$), and $k = 1.3810^{-23}$ we obtain

$$\frac{dT}{dh} \approx \frac{0.01\,\mathrm{deg}}{meter}$$

about 10 degree per Km, the value observed experimentally ! This was one of the first self-evident proof of the success of Kinetic theory.

7 The distribution density in an air column

Let's consider a gas that is inside a big container. This gas is an ensemble of molecules, that are freely moving around. Each molecule have its own weight. This weight is surely affecting how the molecules behave. The molecules at the bottom of the room will feel the pressure of all the molecules that are above.

What is the effect of the weight? Can we deduce a mathematical relation to describe the effect of the weight on the gas? To answer we can imagine to have two parallel layer of area A that are separated by a very small *infinitesimal* distance dh. We consider that the *differential* force acting on a single layer is:

$$dF = N < F > \tag{67}$$

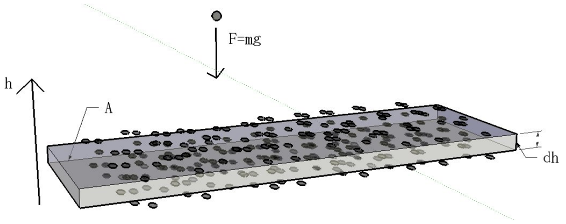

Figure 4: The molecules of gas are indicated by dots. We consider the forces acting on two imaginary planes of area A. Each molecule weight is $F = mg$ and the distance between layer is an *infinitesimal* (dh).

where $< F >$ represent the average force of a single molecule and N the number of molecules enclosed in the box between the two layers (see figure 4). Please do not forget that this box is very small and its thickness is infinitesimal.

We know that the number of molecules can be calculated if we know the *molecular density* of the gas. This value is usually known and it is indicated by the letter n, $n = N/V$, where the volume V is in our case the area of the imaginary box: A multiplied by its infinitesimal thickness dh.

Now, the force exerted by a single molecule is just its weight, that is $< F >= -mg$. Let's put all these things together:

$$\begin{aligned} F = &\quad -mg \\ n = &\quad \frac{N}{Adh} \end{aligned} \tag{68}$$

If we substitute these in eq (67), we have

$$dF = nAdh(-mg) \tag{69}$$

If we remember that the pressure is the force per unity of area, then we have:

$$dP = ndh(-mg) \tag{70}$$

Now, dP is the difference in pressure between the two surfaces, we know that for an *ideal* gas:

$$\begin{aligned} PV = &\quad NkT \\ P = &\quad nkT \end{aligned} \tag{71}$$

We use the concept of *differentiation* and we obtain from the above eq (71)

$$dP = dnkT$$

We now substitute that on eq (70) and we have:

$$dnkT = ndh(-mg) \tag{72}$$

To integrate we simply put together the differential variables dn and dh:

$$\frac{dn}{n} = -\frac{mg}{kT}dh \tag{73}$$

Taking in account that kT and mg are constant values (they do not change with the hight h), it is very easy to integrate this differential equation:

$$\int \frac{dn}{n} = -\frac{mg}{kT} \int dh \tag{74}$$

that results in

$$log(\frac{n}{n_0}) = -\frac{mg}{kT}\Delta h$$

applying the exponential function to both sides:

$$n = n_0 e^{-\frac{mg}{kT}\Delta h} \tag{75}$$

here n_0 is the density at h_0 ($\Delta h = h - h_0$). What this equation tells us ? First of all, we understand that the gas density varies with the hight h. So, if we have a very big volume, the density of the gas in it will change with hight. Equation 75 shows an exponential decay, so the gas at the bottom (Δh near to zero) will have a higher density than gas at the top (Δh higher). If the gas is air, we immediately understand why if we are at sea level the air density is higher than up hill.

You can notice something more. The exponential in eq (75) is modulated by the coefficient mg, the weight of the molecules. We know that Oxygen (atomic mass 16) is heavier than Nitrogen (atomic mass 14), so if the air is a mixture of the two, equation 75 tells us that Oxygen should diminish earlier than Nitrogen. This is exactly what happens if we climb an high mountain. Not only the whole air gets thinner, but also the Oxygen drops faster than Nitrogen, so the relative ratio of Oxygen in the air drops.

Amazingly all these real life facts are deducible by the equation 75 that we just found by simple elementary calculations based on the ideal gas law !

Example:

Lets calculate how much the ration Oxygen/Nitrogen in air changes with hight. Suppose you are hiking uphill and measure the Oxygen/Nitrogen ratio at a starting point and this result to be R_1. When you climb 2000 meters and measure again obtain R_2. Use what learned here to deduce the variation of R of this Δh=2000 meters hight difference.

We simply have to apply equation 75 several times. First of all, lets consider the variation of concentration of Oxygen for a rise of 2000 meters we have:

$$n^o = n_0^o e^{-\frac{m_o g}{kT}\Delta h} \tag{76}$$

and for the Nitrogen at same hight we have:

$$n^N = n_0^N e^{-\frac{m_N g}{kT}\Delta h} \tag{77}$$

here m_o and m_N represent the mass in grams of one atom of Oxygen and Nitrogen respectively. Similarly n^o represents the density of Oxygen atoms and so on. Now we divide the last two equation by each other and obtain:

$$\frac{n^o}{n^N} = \frac{n_0^o}{n_0^N}(e^{-\frac{m_o g}{kT}\Delta h} + e^{-\frac{m_N g}{kT}\Delta h}) \tag{78}$$

this is:

$$\frac{n^o}{n^N} = \frac{n_0^o}{n_0^N} e^{-\frac{g\Delta h}{kT}(m_o - m_N)} \tag{79}$$

Now we simply have to rewrite our equation and put the correct numbers (we assume that the mass of an atom is its atomic weight divided the Avogadro number NA=610^{23}, T=300, g=10, k=1.38 10^{-23} and m_o=16g, m_N=14g)

$$R = R_0 e^{-\frac{g\Delta h}{kT}\frac{(m_o - m_N)}{NA}} \tag{80}$$

$$R = R_0 e^{-\frac{10*2000}{300*1.38*10^{-23}*6*10^{23}}(16-14)*10^{-3}} \tag{81}$$

$$R = R_0 e^{-0.0161} = 0.984 * R_0 \tag{82}$$

so the ration of Oxygen diminishes of about 1.6%, which is in the order of magnitude correct.

8 The Boltzmann Law

Now let's consider what we learned in the previous chapter more generally. Let's consider a force F between any particles of a gas. In the previous chapter the only force acting on the particles were the own particle weight. Now this force can be ANY force, for example energy potential between the gas particles, due to mutual attraction... or anything else. The gravity on the previous chapter example was acting only on the Z axis (the vertical direction). Instead, the more general force we choose here acts simultaneously on the three dimensions. For example: the attraction between molecules is a force that has no privilege direction. Any molecule feels a force coming from other nearby molecules on any direction in space.

However, now for simplicity we choose one arbitrary direction and we consider what is happening on our system of molecules along this single direction. Let's call this direction x and consider two parallel plane surfaces of area A between the gas. These surfaces are normal to the direction x as shown in figure 5.

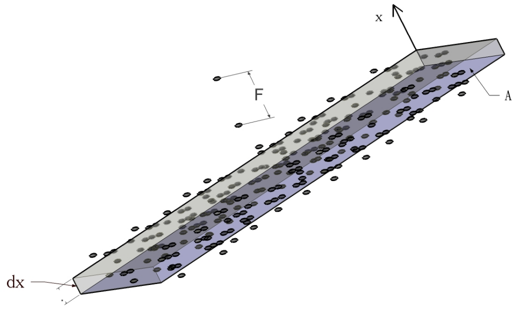

Figure 5: A generic force F is acting between particles. The force is arbitrary and acts along all the directions in space, however we consider only the effects of the force along an arbitrary axis x as represented in this sketch.

Exactly as we did on the previous chapter, the difference of force dF acting between these planes can be modelled as the net total force acting on every single particle, multiplied by the number of particles in the volume between the two surfaces. We can write this total force as:

$$dF = < F > * n * dV$$

where $< F >$ is the average force for a single gas molecule. The $n * dV$ is the gas density n $(= N/V)$ multiplied by the volume between the two surfaces (again

$dV = A * dx$ where dx is the distance between them). So we have:

$$\begin{aligned} dF = & \quad < F > ndV \\ dF = & \quad < F > nAdx \\ dP = & \quad < F > ndx \end{aligned} \tag{83}$$

P is the difference in pressure between the two surfaces dF/A, we know that for an *ideal* gas:

$$\begin{aligned} PV = & \quad NkT \\ P = & \quad nkT \end{aligned} \tag{84}$$

With n we mean the *gas density* $n = N/V$, in other words: the number of molecules per unity of volume. Due to the variation of pressure the density varies. We use again the concept of *differentiation* and we have from the above eq (85)

$$dP = dnkT$$

Substituting in eq (83) we have:

$$< F > ndx = kTdn$$

This is an easy differential equation. We know that for any product $< F > dx$ corresponds an equal and opposite *work* $-dW$, we gather the relevant variables dx and dn:

$$\overbrace{< F > dx}^{-dW} = kT\frac{dn}{n}$$

then we take the integral, we remember that kT are constants:

$$-\int dW = kT\int\frac{dn}{n}$$

$$-\Delta W = kTlog(\frac{n}{n_0})$$

$$\frac{-\Delta W}{kT} = log(\frac{n}{n_0})$$

we suppose $\Delta W = W$ (the zero potential is set to zero), then apply the exponential function to left and right of the equation and we have:

$$\frac{n}{n_0} = e^{-\frac{W}{kT}}$$

$$n = n_0\, e^{-W/kT} \tag{85}$$

this is the dependence of the gas density, for **any potential force** acting on the molecules. The generality of this relation, that is usually called *Boltzmann law*, is something awesome. It says that the gas density of an ideal gas is related in a negative exponential dependence with the potential energy relative to the forces acting on these particles. Please remember that the relation we obtained above is correct even if the force F is a realistic force that act on the three dimensions. Eq (85) limits the dependence of the density n along the one dimensional direction x. However, the force F that causes the dependence can be a general force acting an all three dimensions.

Now let's do the last generalization: can we represent the gas density $n = N/V$ in another way? Clearly, n it is something proportional to the **probability to find a gas molecule** in a given volume V. More molecules in a volume, higher probability to find a molecule, less molecules, lower probability. So, if we like, we can rewrite the Boltzmann law like this:

$$f = const\, e^{-P.E./kT} \tag{86}$$

where f is the *distribution* probability of finding a gas particle, P.E. represents a general *potential energy* and *const* is any constant. In many textbooks the Boltzmann law is written in this more general form. You can read eq (86) as: *the distribution of a certain physical property f decays exponentially with speed proportional to the energy potential relating the physical property and inversely proportional to the system temperature.* Amazingly enough, equation (86) is applicable in a multitude of real physical systems !

9 The concept of distribution of a general potential

The force acting on a particle is in general the derivative of a potential energy. For every force there must be a potential energy that generates this force. This force is the derivative of this potential, multiplied to a minus sign to indicate that the potential is always opposite to the force. So if we know the mathematical expression of the potential we can calculate the expression of the force. This is one of the great principles of nature that is at the basis of physics.

In the example of the air column that we discussed above, the potential energy is

$$dW = -(mg)dh$$

where dh is an infinitesimal variation of height, m the average particle mass and g the gravitational constant $g = 9.81 m/sec^2$. In this case the force F is then

$$F = -\frac{dW}{dh} = mg$$

This is true in the simplest case of an air column where molecules are subject only to the force of their own weight. But what happens if we consider a more complex case? For example let's suppose that each molecule has a slight attraction to the next one. This is actually true. Even gas molecules, if they are placed very near each other they feel a small force of attraction. That's why if we remove the kinetic energy (reduce temperature) the gas tends to transform to a liquid. Then, let's ask ourselves: what is usually the potential energy responsible of the forces between two molecules of gas ? Of course we do not know this answer exactly. However, we can firstly consider a very simple case: two masses (our molecules) connected by an ideal spring. We choose this, because we know how a spring works. The system we imagine looks like a simple bi-atomic molecule...!

We know that for the *Hook law*, a spring gives a force $F = -kx$ where x is the extension of the spring respect to a *rest* position x_0. In our case if we call the distance connecting the two molecules as R and the rest position as r_0, then the force between them is

$$F = -k(R - r_0)$$

.

Let's remember that in general $dW = -Fds$ where ds is the displacement along the direction of the force. Then, we multiply our dW by a small displacement dR, we obtain the infinitesimal potential energy that generate the force

$$dW = FdR = k(R - r_0)dR$$

As we said, if we integrate this we obtain the potential energy (P.E.):

$$P.E. = \frac{1}{2}R^2k - r_0Rk \tag{87}$$

We can plot this potential and its relative force, see figure 6.

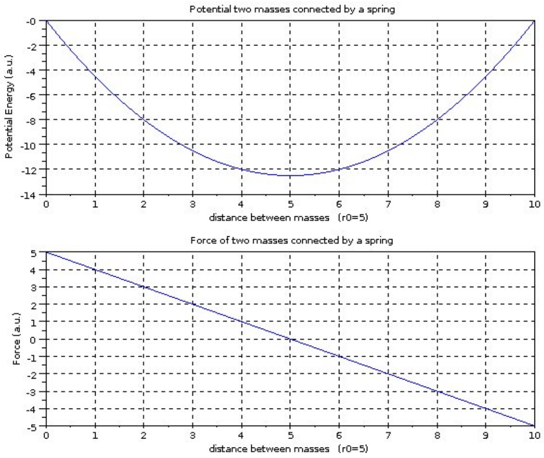

Figure 6: The potential of an ideal force connecting two molecules: a perfectly elastic spring. On the top we see the potential, at the bottom the force.

This was an ideal case, however, in reality the potential between two gas molecules usually has a shape similar to that in figure 7 (near: repulsion, far: attraction, very far: no-effect). In a gas system we do not have only two molecules, but many of them. So using the same integration methods, it is possible to derive the total potential energy W just summing up all the contributions, like this:

$$W = \sum_{ij} V_{ij} \tag{88}$$

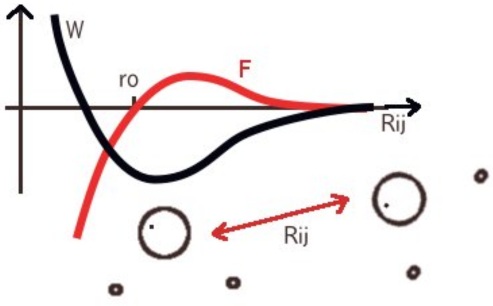

Figure 7: A schematic representation of the potential shape of two molecules attracting each other (dark line) and the corresponding force (red line).

Now let's do some consideration using the general Boltzmann law. From eq(88) the probability to find a molecule will be:

$$f = const. * e^{-\sum_{ij} V_{ij}/kT} \tag{89}$$

What will happen if the temperature changes? If the temperature decreases to low values then the term $W = \sum_{ij} V_{ij}$ will be dominant. So the probability to find particles at the minimum potential r_0 will be higher (because in that point W is minimum, so the exponential is maximum).

On the contrary, if the temperature increases, and get higher than the total potential $W = \sum_{ij} V_{ij}$, exponent gets close to zero for any value of R, even the minimum point r_0 will have little influence. The exponential function becomes nearly one for every potentials. This means that the particles will be randomly distributed (same probability to find them at any distance).

What we have just described in very rough terms is the phenomena of *evaporation.* If the temperature is low, majority of particles will be located ad a rest distance to the others (like in a solid or a liquid), if temperature increases, the particles will fly away and they will be randomly separated, exactly like in a gas. Equation 88, despite its simplicity and the basic assumptions we used to derive it, it is able to explain well the phenomenon of evaporation of materials with temperature. This is already a good result, but we achieve it without knowing the real shape of the potential W. Let's try to go further and assume to know the mathematical expression of the potential.

9.1 Physical states: gas, liquid and solids

Let's consider again the hypothetical situation in which molecules are connected by a simple spring. In this case, as we said above, the potential is derived by the Hook law as in equation 87. Let's substitute it in the Boltzmann formula, we obtain the Boltzman distribution:

$$f = const. * e^{-(\frac{1}{2}R^2\bar{k} - r_0 R\bar{k})/kT} \tag{90}$$

The symbol $\bar{k}$ is used to distinguish the Hook constant from the Boltzmann one. This relation tells us the probability to find a molecule in function of the molecular distance. We use a computer and make a graph from eq (90). The simulation is done in -so called- *arbitrary units*, putting the *const.*, $\bar{k}$ and k values to one. Even if these parameters loose real meaning, the distribution shape does not change. Result is shown in figure 8. Let's try to understand its hidden physical meaning: first of all remember that in this plot there is not explicit dependence on the position of the molecules. Only their relative distance is considered here. So our graph deals about something that can be located anywhere in space.

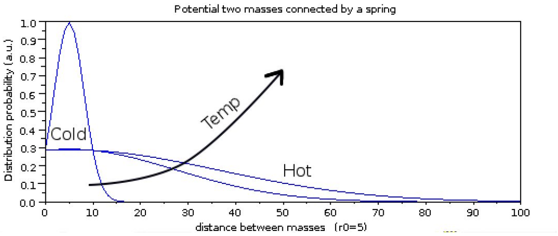

Figure 8: In this simulation of eq. (90) we run temperature $T = 10$ to $T = 1000$ (direction of temperature is indicated by the dark arrow "Temp") and set the rest position to $r_0 = 5$. Clearly, as the temperature increases the potential gets less important, because the function tends to a constant value everywhere. All molecules tend to be sparse and randomly placed far from the minimum (gas state). If temperature is low compared to the potential, the max probability to find the particles is when they are at the minimum of potential, exponential is at maximum. This can be the case of a liquid or a solid.

On the horizontal axis we have the distance between molecules R. In the case of our "Hook law" potential, the minimum potential is realized at the *rest position*, $R = r_0 = 5$ in our simulation. Let's concentrate first on the "Hot" curve, that has been plotted for high values of the parameter T ($T = 1000$). For this curve we can say that: at *any give point* in the gas, if we look at the distance between molecules (also called *intermolecular distance*), statistically we see that they have all similar probability to exist. Instead, if we are at lower temperatures, we see that the curve has a maximum. And this maximum is exactly at the rest position $r_0 = 5$! The curve goes also to zero very quickly. The physical meaning is: lower intermolecular distances are very probable, whereas higher ones are not.

Let's repeat that this specific *distribution* is valid in any given point of space. In any point of space of our gas, we find the same distribution of potential, in other words in any point of the gas the intermolecular distances have a probability to exist distributed as the Boltzmann law in figure 8. Remember: the *distribution* has always the same shape (equation 89), but the values of this distribution are different depending on temperature values and they represent different physical situations in the real world (a gas, a liquid or even a solid).

10 Speed distribution in an Ideal gas

In the previous chapters we derived the density distribution of the gas molecules for an ideal gas, in air. This time we consider about the speed of the molecules. To understand what is happening with the speeds, we have to remember these important things:

1) we are in *equilibrium*, so the velocity distribution must be the same everywhere in any point of the g
2) no forces are acting on the particles, only their own weight $-(mg)$
3) molecules *density* is known, is $n = n_0 e^{-(mgh)/kT}$

If this three conditions are true, it is intuitive to understand that the distribution of velocities should be somehow related to the term $e^{-(mg)h/kT}$. In fact, let's consider two horizontal lines $h = 0$ and $h = h$. At $h = 0$ we will have n_0 particles, instead at height $h = h$ there are n particles.

What's the ratio in number between the particles in these two levels? We know that higher up there are *less* particles (see condition "3)" !) and that the ratio is: $e^{-(mgh)/kT}$. We also know that everywhere the distribution of speed should be the same. If there are no other forces than the weight $-(mg)$, then let's go down at level $h = 0$ and consider the velocities of the particles. For sure the particles missing at the level $h = h$ should be those that do not have enough kinetic energy to reach that place. What is this energy ? It is the potential difference between the two heights, so:

$$E_k = dW = -mgh$$

Let's call u the average speed, then $\frac{mu^2}{2} = mgh$.

So we can say that all those particles that do differ in kinetic energy of $-mu^2/2$ are those that will be missing at the higher level $h = h$. If this is true we can write the ratio of kinetic energy at $h = 0$:

$$\frac{n_{v>u}(h=0)}{n_{v>0}(h=0)} = e^{-(mgh)/kT} = e^{-mu^2/2kT} \tag{91}$$

where $n_{v>u}$ means the number of particles with speed higher than u. In other words: molecules of lower speed have less energy to reach higher positions h. So,

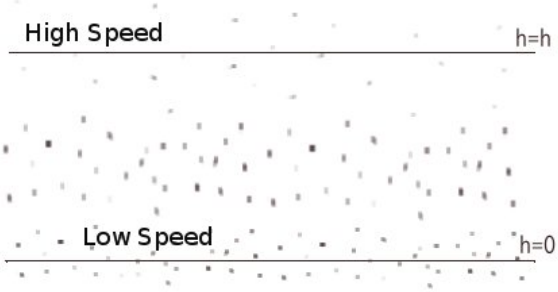

Figure 9: Scheme of the particles in motion in air. Less particles reach the higher level $h = h$ because of gravity. If we think in speed, we can say that only the particles that have speed higher than u can reach this level. In other words, only those molecules moving up at $h = 0$ with sufficient velocity can arrive at height h.

we simply obtained the *distribution of speed* within our gas. . . ! To emphasise the distribution properties of the relation, in several book you can find the general *differential* form of this equation:

$$f(u)du = Ce^{-mu^2/2kT}du \tag{92}$$

where we indicate with $f(u)$ the velocity ratio and with du the difference in average velocity. This is usually called the *Maxwell distribution* of velocities, because Maxwell derived it the first time in 1859. Notice the presence of the square on the independent variable u^2, this gives the distribution a shape of a Gaussian curve (see figure 10).

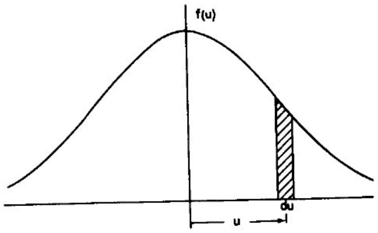

Figure 10: A graphical example of *distribution* of velocities.

Remember: eq. (92) this is the ratio of the number of particles of certain velocities in any single point of space. It is not the ratio of of velocities between $h = 0$ and $h = h$!

You may ask: "Wait a second! We know that higher up there are less particles because of the gravitational term $-mg$ in the Boltzmann distribution. So presumably higher up there is less speed too! Why you say that in any point of space the distribution is the same ?!?". If you ask yourself that, you are perfectly right. That's why higher up in mountain air is thinner (n decreases) and temperature is colder (molecular speed is reduced). However, eq. (92) represent the only the *ratio* between velocities, not the absolute value. The average velocity of gas particles can change with height, still the ratio between velocities can be maintained for every point in space accordingly to eq. (92).

11 Brownian Motion

Now we know that particles of a gas are moving around with different speeds. At any point in space we can meet a particle of lower or higher speed. Let's suppose we have a small ball immersed in a gas. This ball is a macroscopic object, so it is much bigger than the gas molecules. Let's call this particle a *pellet.* If we put the pellet in the middle of a gas, we know the gas particles move around and collide with the pellet continuously at any moment. This continuous collision is called also *bombardment.* So the pellet is bombarded from all directions by the gas molecules. The molecules, do not have all the same speed or direction. However, they have a *distribution* of speed, as we learned above.

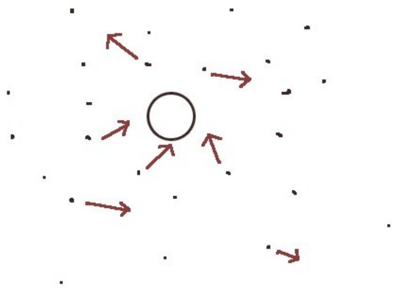

Figure 11: A graphical example of chaotic *bombardment* of a *pellet* by gas particles.

Now, let's think about this: all this collisions come homogeneously from all directions, we may think that the total force exerted on the particle is zero. Is it ? Well, not ! Let's try to calculate this and understand why. Let's imagine that the pellet is set initially in the center of our coordinates defined by the point R_0 =(0,0,0). Its position relative to this point is defined by the vector $\bar{R}$. After a single collision, the pallet moves to the left, or to the right, or up or any direction. Let's call this random movement $\bar{L}$. So the final position after $N = 1$ collision is

$$\bar{R}_1 = R_0 + \bar{L}$$

where R_0 is the start point. After two collision will be

$$\bar{R}_2 = \bar{R}_1 + \bar{L}$$

and after three

$$\bar{R}_3 = \bar{R}_2 + \bar{L}$$

Let's not forget that despite the fact that we always write $\bar{L}$, every time we have a different value. $\bar{L}$ is a it random force! In general we have

$$\bar{R}_N = \bar{R}_{N-1} + \bar{L}$$

What happens if we square right and left of this equation ? We will have

$$\bar{R}_N \cdot \bar{R}_N = (\bar{R}_{N-1} + \bar{L}) \cdot (\bar{R}_{N-1} + \bar{L})$$

so we have

$$R_N^2 = R_{N-1}^2 + L^2 + 2\bar{R}_{N-1} \cdot \bar{L}$$

this equation is impossible to solve, because every collision $\bar{L}$ is different in value and different in directions. As usual in statistical mechanics, let's consider the *average* values of these terms.

$$< R_N^2 >=< R_{N-1}^2 > + < L^2 > +2 < \bar{R}_{N-1} \cdot \bar{L} >$$

The first two terms are average of scalars (a *scalar* means a *number*, not a vector with direction and value, but only a value), so their average can be indicated for simplicity as only R_N^2, R_{N-1}^2 and L^2. Instead the remaining term $2 < \bar{R}_{N-1} \cdot \bar{L} >$ is the product of two vectors. We have to consider again that every time the collision occurs in different direction. These are random collisions, so they are spread homogeneously in all directions. The average vector $\bar{L}$ must be null. If this is the case, all the term $2 < \bar{R}_N \cdot \bar{L} >$ must be null. So at the end we have:

$$< R_N^2 >=< R_{N-1}^2 > + < L^2 > \tag{93}$$

This equation is *recursive*, it means that the value of R at the N^{th} collision is equal to the value of R at the previous collision plus the average length of the collision L. If the collision happens 10 times, we have $R = 10 * L$. So finally can write

$$R^2 = N < L^2 > \tag{94}$$

that means that the distance of the pallet from the start point $R_0 = (0, 0, 0)$ increases like the following:

$$R = \sqrt{N} < L > \tag{95}$$

So if we can estimate the average length of a free movement $< L >$, we will know the total distance after N collisions. This is called *Brownian drift.* The thing you must notice is that even if the collision are totally random, this value is not zero !

We learned from eqn. 95 that the distance R increases with the number of collisions. But -of course- in real life, we do not know the number of collisions...! In a *real* problem, what shall we do ? What is the real variable that we can measure, instead of the number of collisions N? Clearly, on average, we have a constant number of collision per unity if time. So, N is proportional to time $N = rt$, where r is the *rate of collision* (number of collisions per unity of time).

The distance from the start point increases with time. From eq (94) we can state:

$$< R^2 >= N < L^2 >= rt < L^2 >= \alpha t \tag{96}$$

Where α is then $r < L^2 >$. As said above, the $\bar{L}$ is the average movement that the particle does after a collision. We can call this *free mean path* and indicate it with the letter λ. So $\lambda =< \bar{L} >$, it represent the average length of *free* movement the particle does between collisions. The term *free* is given because we suppose that during this movement the particle is totally free of forces, so the movement is a straight line of uniform speed.

Now, let's try to estimate this free mean path. Well, if we know the average velocity of the particle (let's call it v_o), then we can easily say:

$$\lambda = \frac{v_o}{r} \tag{97}$$

or $\lambda = v_o\tau$ if $\tau = \frac{1}{r}$ (we can call τ *free mean time*). Please notice that the velocity v_o is not the velocity of the gas molecules, but the velocity of our *pellet* macro-sized particle that is bombarded by the molecules.

If you remember the laws of ideal gas, you know that the average velocity of the gas molecules is known, it depend on the temperature and using eq. (12):

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \tag{98}$$

Gas molecules of this average velocity will collide with the particle. For the conservation of momentum, the particle -on average- will move away with this speed:

$$m_o v_o = mv \tag{99}$$

then taking in account eq. 98 we can write:

$$\begin{aligned} v_o = & \quad \tfrac{m}{m_o} v \\ \frac{3}{2}kT & = \tfrac{1}{2} m (\tfrac{m_o}{m} v_o)^2 \end{aligned} \tag{100}$$

doing the proper simplifications, you can obtain easily the expression for the average particle velocity:

$$v_o = \frac{\sqrt{3kTm}}{m_o} \tag{101}$$

If we substitute this in our previous expression for λ eq. 97, we have finally

$$\lambda = \frac{\sqrt{3kTm}}{m_o r} \tag{102}$$

Now substituting this in the expression eq. (96) that we where looking for, we have

$$R^2 = \frac{3kTm}{m_o^2 r} t \tag{103}$$

What is the rate of collision r ? For sure it is something related to the temperature of the gas. If the gas has more energy, presumably there will be more collisions. However, this parameter must be connected also to the geometrical dimensions of the particle. If the particle is bigger will receive many collision per second, if it is very small just a few. Let's suppose that the gas molecules are so small that their size can be neglected compared to the dimension of the particle. Then the probability to have a collision will depend only on the size of the particle and the molecular density per unit of volume n. If the section of the particle has an area σ (usually called *cross section*) then the number of collisions N will be

$$N = \sigma n dx \tag{104}$$

where dx is a infinitesimal displacement in space.

Now, in the dx direction, the gas has a kinetic energy $\frac{1}{2}kT$ that is equal to $\frac{1}{2}mv^2$. We can assume that the infinitesimal displacement dx correspond to the molecular movement in the same direction. So $N = \sigma n v dt$, that yields:

$$r = \frac{N}{dt} = \sigma n v \tag{105}$$

Because $\frac{1}{2}kT = \frac{1}{2}mv^2$ easily we obtain:

$$r = \frac{N}{dt} = \sigma n \sqrt{\frac{kT}{m}} \tag{106}$$

then:

$$R^2 = \frac{3\sqrt{kT} m^{3/2}}{m_o^2 \sigma n} t \tag{107}$$

This equation show how the Brownian motion depends on temperature and other important parameters. All the group of terms $\frac{3\sqrt{kT}m^{3/2}}{m_o^2\sigma n}$ represent our parameter α that was defined previously, eq (96). α simply tells us how fast is the Brownian motion; it is a kind of Brownian ”speed”. It is not a real speed because R is the distance from a center point $R_0 = (0, 0, 0)$, so α tells us how far are we from that point, but does not tell us exactly where we are! We only know that the pellet goes away in a random direction within a radius R given by eq (107). Try to imagine for example that the particle m_o becomes very heavy, or its size gets bigger (σ increases)... the total movement becomes slow because of the inertia or because the total amount of collision average out to zero. The same will happen if the molecular density increases. If instead the temperature T grows, or the gas molecules are heavier, the Brownian movements get faster and quickly the particles run away, as it is logical to be. Our simple model make sense !

12 Thermal Noise

The Brownian motion is caused by the temperature. We know that the motion of the particles is energy, and that the temperature we feel in an object is simply the kinetic energy of the molecules of that object. For this reason the Brownian motions have consequences generally, on all possible systems! For examples lets consider again our pellet immersed in a gas. We know that the kinetic energy of the gas, for simplicity we consider only one dimension x, is

$$E_{gas} = \frac{1}{2}kT$$

we know that this must equal the average kinetic energy of the pellet, so

$$\frac{1}{2}m < v_x^2 >= \frac{1}{2}kT$$

where m is the mass of the pellet. So we can say that

$$< v_x >= \pm\frac{\sqrt{kT}}{m}$$

What does this means in practice? It means that because of the thermal energy, whatever is the velocity of the pellet, there is always an average thermal velocity that adds up to the total velocity of the pellet. This velocity is very small, but it always exist. For a pellet of one gram it is (let's use MKS):

$$\begin{aligned} m = &\quad 0.001Kg \\ k = &\quad 1.3810^{-23}J/\ ^\circ K \\ T = &\quad 300\ ^\circ K \\ < v_x >= &\quad \pm 6 * 10^{-8}m/sec \end{aligned} \tag{108}$$

very small, but not zero. This fact also has implications when we want to measure the velocity of the pellet in the gas, this velocity can be big, because there will be other external forces we put on the pellet. However, our measurement of the pellet's speed will be disturbed. We cannot know the speed of the pellet, with a precision better than $< v_x >$. In mathematical terms: if the real velocity is V_0, what we actually measure is

$$V = V_0 \pm < v_x >$$

This is the effect of the *thermal noise* on our measure.

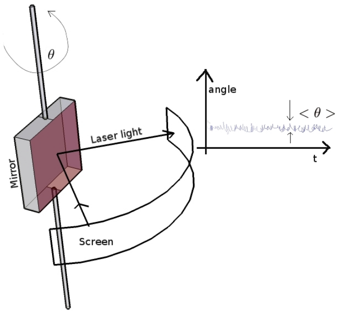

Figure 12: The scheme of a light-beam galvanometer, a Laser light is reflected by a mirror suspended on a very low friction string. The reflection at angle θ is affected by an error of $< \theta >$ due to thermal noise, as represented in the graph.

This fact applies in any system we can think of. Where there is temperature (thermal energy) there is this thermal noise that affect measurements.

For example we can consider a mirror suspended by a small string, like in figure 12. In this case the thermal energy $\frac{1}{2}kT$ will be equal to the rotational energy of the mirror. If you remember from the physics classes, this energy is $\frac{1}{2}I\omega_0^2 < \theta^2 >$, these two should be equal so we have:

$$< \theta >= \pm \frac{\sqrt{kT/I}}{\omega_0}$$

This effect of thermal noise can be verified experimentally in the laboratory! A variety of examples can be dome. We do a last one: in electric circuits. The energy accumulated in a inductance for example $\frac{1}{2}LI^2$ will be equal to $\frac{1}{2}kT$ with similar consequences. Can you think to some other examples in another field?

13 Evaporation

As you remember from previous chapters, the equation 86 express the fact that the probability to find a particles at a certain distance is related to the potential energy (P.E.).

$$f = const\, e^{-P.E./kT}$$

This consideration is usually called *kinetic theory* because, as you remember, equation above is derived from the fact that we demonstrated that the kinetic energy in one dimension (for example the dimension "x") $E_k = \frac{1}{2}m < v_x^2 >$ is equal to the thermal energy

$$\frac{1}{2}m < v_x^2 >= \frac{1}{2}kT \tag{109}$$

Now, let's consider the evaporation of a liquid, and let's try to apply the same concepts of kinetic theory, in order to find the equation of such system. Let's consider a closed box filled with liquid at a certain temperature. Because there is temperature, we know from kinetic theory that there will be molecular speed. If so, why the molecules do not fly away like a gas ? Well, because there is a force keeping them together. We do not know exactly the mathematical formula for this force, but let's assume that we know the shape of it. The force is represented in figure 13.

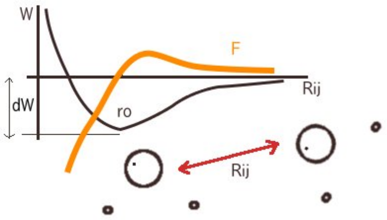

Figure 13: The potential energy between liquid molecule. We remember that force is $F = \frac{dW}{dx}$ and it is represented in clear color in the picture. dW represent the difference in potential energy, necessary to remove the particle from the attraction. This energy is often called *work function*

From the shape of the curve you can understand that if the temperature is such that $E_k < dW$ then the particles have energy *less* than dW, they seems to be trapped near each other. So they cannot escape in the gas state.

Is this really right? Well, not! We know that the distribution of velocities is an exponential decreasing curve that never reach zero (equation 85). So, for sure some particle will have a speed much higher than the average $E_k = \frac{1}{2}kT$. So -for sure- these few molecules will leave the liquid and become gas. So in our box we will have a liquid *in equilibrium* with a certain small quantity of gas. This gas is also called *vapour*. The Energy dW necessary to leave the liquid and become gas, is called *work function* and often indicated by the letter Φ.

Now, let's consider this problem: in our box of volume V_a, suppose we have a vapour with n molecules per unity of volume. How many molecules will be in the vapour phase, compared with the number that are in liquid ?

The solution is not so difficult. Lets suppose that every molecule occupies a volume V_a. Then the number of molecules per unity of volume in the liquid is $1/V_a$. So we have $n_1 = n$ molecules per unity of volume in vapour phase, and $n_2 = 1/V_a$ molecules per unity of volume in liquid phase.

Now we have to remember equation 85. Lets consider the two situations: gas phase and liquid phase. We write eq. 85 for each case:

$$n_1 = n_0\, e^{-W_1/kT} \tag{110}$$

$$n_2 = n_0\, e^{-W_2/kT} \tag{111}$$

now we simply substitute and have

$$n = n_0\, e^{-W_1/kT} \tag{112}$$

$$\frac{1}{V_a} = n_0\, e^{-W_2/kT} \tag{113}$$

n_0 is not relevant. It is simply the density of molecules for the initial potential. It is a value that we do not know, and we do not care to know. In fact, lets divide eq.112 by eq.113 and we have

$$nV_a = e^{-(W_1-W_2)/kT} \tag{114}$$

the difference in potential energy $W_1 - W2$ that we called before dW, is the work function, also called Φ, so we have finally:

$$nV_a = e^{-dW/kT} \tag{115}$$

What does it means? It means that the ratio of the density in liquid phase and in gas phase, is proportional to the exponential of some energy (the work function) divided by kT. In other words, if we have a big work function dW, this exponential is a big number, and small variations of temperature, make big variations of this ratio.

Anyways, please remember that this equation is the result of our <u>model</u>. So there are *assumptions* we made that we must remember:

1) we are in *equilibrium* so the velocity distribution must be the same everywhere. This is not true in r
temperature is assumed constant, but it is not
3) the volume occupied by one particle V_a is <u>not</u> constant !
If the temperature changes, also the volume occupied by a particle changes(the liquid *expands*).
4) The real situation is much more complicated, and we cannot obtain a formula.
We use this equation 115 because it is simple and it is demonstrated that is valid in good approxima

Lets remember a most important concept in physics. Everything we know are results of our models. Our models are <u>not</u> the true reality of physics. But, we just represent physics with our models.

Now let's try a very important test. Let's use another model, and describe again evaporation.

We have our liquid in the closed box. Some of the molecules have escaped from the liquid and become vapour (gas). Of course, some of these gas molecules will hit the surface of the liquid, and become liquid again. How many are them ? Let's think small and imagine a small volume of gas, of area dV. This small volume of gas it is located exactly adjacent to the surface of the liquid. How many molecules per unity of time, will hit the liquid in this small volume ?

Well, we know that the gas density per unity of volume is n. Then we know that the total number of molecules N in this volume is -of course- $N = n * dV$. If this volume has an area A, then dV can be written also as $A * dx$, where dx is the movement toward the liquid in a small time dt. We know that the average speed of the molecules is v, so we can write

$$\begin{aligned} N = &\quad nAdx \\ N = &\quad nAvdt \end{aligned} \tag{116}$$

If we choose a unity of time (one sec) and a unity of area (one square meter) then the number of molecules that condensate on the liquid per second per square meter is:

$$N_c = nv \tag{117}$$

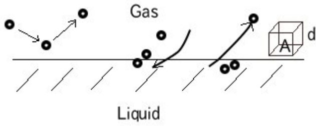

Figure 14: A scheme of the condensation-evaporation process. A liquid is in a box a temperature T. Some molecules of the liquid win enough energy to escape and become a gas. Some gas molecules, on the contrary, hit the surface and condense in the liquid.

Condensation, means a transformation of phase, from gas to liquid. What about the opposite transformation *evaporation* from liquid to gas ? Our question is: how many molecules per unity of time leave the liquid ?

If a liquid molecule acquire enough energy, it can win the energy gap dW and become a gas molecule. We know from previous kinetic theory (Boltzmann

Law, eq. 85) that the probability that this happens is $e^{-dW/kT}$. Let's do some simple considerations: we can understand that the number of molecules leaving the liquid and becoming a gas should be proportional to the number of atoms near the surface, per unity of area, divided by the time it takes to leave the surface, multiplied by the probability to leave the surface. In mathematical terms this is:

$$N_e = (\frac{N}{A})(\frac{1}{t_e})(e^{-dW/kT)} \tag{118}$$

In the case of liquid, every molecule is packed near each other, the number of atoms per unity of area is simply A/A_s, where A is the total area and A_s is the area occupied by a molecule. To know how many leaves per unity of time, we have to estimate the time it takes to leave. We know the average velocity v, and we suppose that the molecules that leave are the only ones adjacent to the surface, not the ones deep inside the liquid. So the distance they run is only one layer of molecules. If D is the thickness of one molecule layer, the time it takes is $t_e = D/v$. So the product

$$\frac{A}{A_s}\frac{v}{D} \tag{119}$$

gives us the number of molecules that leave the area A per unity of time if *all* the molecules were leaving the liquid. This is not true ! Only the fraction that has enough energy to win the work function will leave. This fraction is $e^{-dW/kT}$. In conclusion, we fix $A = 1$ (per unity of area) and we have:

$$N_e = (\frac{1}{A_s})(\frac{v}{D})\, e^{-dW/kT} \tag{120}$$

Now we notice that in situation of equilibrium, the number of molecule that condense N_c (eq. 117) and the number that evaporate (eq. 120) must be the same. So we have:

$$nv_{gas} = (\frac{1}{A_s})(\frac{v_{liq}}{D})\, e^{-dW/kT} \tag{121}$$

Now, let's consider finally two things. One is easy: the area A_s of the molecule, multiplied by its thickness D is of course the volume occupied by a molecule $V_a = DA_s$. The other is less intuitive: the velocity v_{gas} of the gas molecules, and the velocity v_{liq} of the liquid *on average* are equal ! Why ? Because we are in thermal equilibrium. We know that $1/2mv^2 = 1/2kT$, so if this was not true, we would have two different average energies and temperatures in the gas and the liquid, and this is not possible. So putting $v_{gas} = v_{liq} = v$ and $V_a = DA_s$ in the equation, we obtain again equation 115 !

$$nV_a = e^{-dW/kT} \tag{122}$$

This is a fantastic results ! Why ? Because it tell us that our approximate models work. To obtain equation 122 in the first case we started from a physical model based only on the ideal gas energies. The second time we started from a molecular mechanical model, using equilibrium and the Boltzmann law concept. We arrive to the same result. This is the power of modelling with statistical mechanics.

14 Diffusion process

Lets consider the particles of a Gas. They move in all direction, and their energy is $\frac{1}{2}kT$ as we know very well. Of course the particles will collide each other often. How often ?

Well, this depends on many things. Of course if the particles density is high, we expect to have more collisions. Each particle move straight, undisturbed for a while, then it collides elastically with another particle. The word *elastic* means that the collision preserve the kinetic energy. In other words, the kinetic energy $\frac{1}{2}mv^2$ of the particle before and after the collision remains the same. Let's suppose to have a very big box, with few gas particles in it. Let's suppose that, in this box, each particle has on average one collision every one minute. It's just a supposition. So we can call $\tau = 60\text{sec}$ the *average time* between collisions of any single gas particle.

Of course, the number of collisions that this particle is experiencing, is depending on time, and *on average* will be equal to

$$N(t) = \frac{t}{\tau} \tag{123}$$

This equation is very easy to understand: after a time $t = \tau$, *on average*, the particle will have experienced one collision. If $t = 2\tau$, two collisions and so on.

So let's as ourselves: what is the probability to have a collision ? If we know that every $\tau = 60\text{secs}$ we have a collision, after only one seconds we have $1/60th$ probability to have one, and after 30 seconds, we will have $1/2 = 50\%$ to have one. This means that dt/τ is the probability to have a collision for one particle.

Now let's think about what's happening collectively. What is the probability that *any* of *all* the particles collide ?

To understand this, let's define $N^*(t)$ as the number of gas molecules that **do not have yet** had a collision. Then we can write

$$N^*(t + dt) = N^*(t) - N^*(t)\frac{dt}{\tau} \tag{124}$$

What is this equation? This equation is very simple. It just means that the particles that do not have hit anything at $t + dt$, is given by the initial particles at t, $N^*(t)$, minus the total collisions occurred in the time dt. The total number of hits during this small interval dt is of course the current number of molecules -again $N^*(t)$- multiplied the probability dt/τ, so we obtain the above eq. 124. If we manipulate eq. 124 we easily obtain

$$\frac{N^*(t + dt) - N^*(t)}{dt} = -\frac{N^*(t)}{\tau} \tag{125}$$

if $dt \to 0$ this becomes

$$\begin{aligned}\frac{dN^*(t)}{dt} &= -\frac{N^*(t)}{\tau}\\ \frac{dN^*(t)}{N^*(t)} &= -\frac{dt}{\tau}\end{aligned} \tag{126}$$

and if we integrate we finally have this equation:

$$N^*(t) = N^*(0)e^{-t/\tau} \tag{127}$$

This means that the number of particles N^* that do **not** experience any collision, diminish in time with the equation 127 above. We can also say that *the probability of* **no** *collision* is $e^{-t/\tau}$ and that the probability of collision is then

$$P(t) \propto 1 - e^{-t/\tau} \tag{128}$$

This is the *collective* probability of collision, the probability that *any* of *all* the particles collide. If the time t tends to infinite, this probability of course tends to one. We can call the average time of collision τ *relaxation time* because it somehow represents -on average- how much time the particle can run without any collision.

Now, we know that our gas particles move with a certain speed. Every particles has its own speed, and at each collision the speed change. However, we know that -on average- the speed is given by $\frac{1}{2}mv^2 = \frac{1}{2}kT$! If this is true we can define another important parameter

$$\lambda = \tau v \tag{129}$$

this λ is called usually *mean free path.* It is the average length that the particle can run free. This parameter is as important as τ and has almost the same meaning. The mean distance the gas particle can go -on average- before it experiences a collision.

Now let's try to relate some gas parameters that we know. Let's ask ourselves, what is the probability of collision after the particle has moved a distance dx ? Similarly to what we already did when we were considering the *relaxation time*, we know the answer; this probability (for only *one particle*) is:

$$\frac{dx}{\lambda} \tag{130}$$

Now, lets consider it from another point of view. If we have a box of volume dV, with particle density n, what is the probability of collision in a small section of it of length dx ? Well, as we know the number of particles in this section is $nAdx$, where A is the area of this section (see figure 15).

If every single particle has an average area σ, then the total area occupied by the particle is $\sigma nAdx$. If we divide this area with the total area available (which of course is A), the we obtain the probability of collision within this section of length dx: σndx. But this value must be equal to eq. 130, so finally we have:

$$\frac{dx}{\lambda} = \sigma ndx \tag{131}$$

simplifying this yields this very important relation:

$$n\sigma\lambda = 1 \tag{132}$$

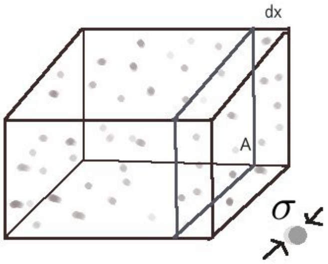

Figure 15: A scheme for the modelling of the collision probability. The *cross section* is represented by the average area of a single gas molecule.

this equation is very important because it relate the *particle density* n, their *cross section* σ and their *mean free path* λ in a gas system each other with a very simple and compact formula. These parameters are statistical molecular parameters.

14.1 The drift velocity

Now suppose we have some particles in the middle of other particles of another kind. They can be gas particles in the middle of other heavier molecules. Or they can be electrons in a metal, in the middle of the atomic ions. Suppose these particles are subject to a force, let's call it F. Let's suppose that this force will push the particles in one specific direction, but they will not influence the other kind of particles. As we know, for a small interval of time, the particles will accelerate freely under the force F. Then there will be a collision, maybe with the other kind of particles. Now, during the free time they are solely subject to the force F, they will accelerate. How much ? Of course the acceleration will be

$$a_p = \frac{F}{m} \tag{133}$$

where m is the mass of the particle.

After how much time there is a collision? We do not know exactly. However, we already defined the *average* time between collisions. We called this time *relaxation time* and used the symbol τ. If we suppose that after every collisions our speed is reset and we have to start again, then we can calculate how much is the *average* speed that the particles move. Of course it is the average speed the particles have, multiplied the average time they move freely in space. It is an *average*, *collective* speed, and usually is called *drift* speed:

$$v_{drift} = a_p \tau = \frac{F\tau}{m} \tag{134}$$

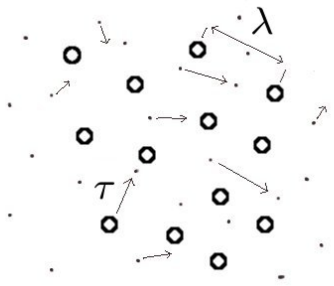

Figure 16: A scheme describing the drift process. Smaller particles in movement under a force F collide against heavier ones supposed fixed. The average relaxation time is τ and the average *mean free time* is λ. If these parameter are true on average, it results equation 134.

In general the velocity of drift is expressed under the following form:

$$v_{drift} = \mu F \tag{135}$$

The parameter μ is very important, called *mobility* and it is expressed as

$$\mu = \frac{\tau}{m} \tag{136}$$

We have to remember that drift velocity for a system particles can be defined only between some kind of particles against some other. We cannot define drift if we have only one species of particles in our box (!)

15 Electric Resistance

Let's now apply what we know to a conduction problem. Let's suppose we have a mixture of gas between two electrodes, like in figure 17. The drifting particles are moving under a force. The other particles can be neutral atoms that do not move and oppose the drifting process. The two electrodes are under a potential V. As we know from physics this will correspond to a electric field of value $E = V/d$, where d is the separation of the two electrodes. What is the force acting on these ions ? If the charge of the ion is q, from basic physics we know it is $F = qE$. So using eq (135) we have:

$$v_{drift} = \mu F = \mu q E = \mu q \frac{V}{d} \tag{137}$$

Now let's make another physical model of the charge movement in the gas. We suppose -as we did many times- that the density of drifting particles is known and its value is n_i, we give the index i because in this case the moving particles

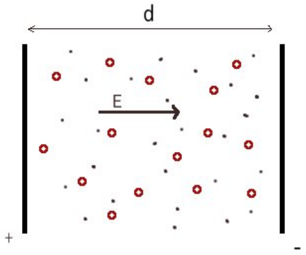

Figure 17: A scheme describing the conduction process. The bigger particles are those which are fixed and oppose the drift process, neutral atoms for example. The smeller particles represent the drifting ions.

are ions. What is the electric current at the electrodes? Current is defined in physics as the number of charges arriving at the electrode in a time t per unity of area A. We ask ourselves: how many ions are arriving at the electrode, if the velocity is v_{drift} ? In a time t the particles move on average for a distance $v_{drift}t$. If we multiply this small distance for the area of the electrodes A_e we have the volume containing all the ions that will reach the electrode within the time t. This volume multiplied by the density n_i will result in the total number N_e of ions reaching the electrode in a time t.

$$N_e = n_i A_e v_{drift} t \tag{138}$$

Now let's come back to our question: what is the electric current at the electrodes ? Well, the current is the number of charges per second per unity of area. So if multiply by the charge of every single ion q and divide by the unity of area and by the time t, we have what we want:

$$I = q n_i A_e v_{drift} \tag{139}$$

Now if we substitute the value of v_{drift} we have:

$$I = \frac{\mu q^2 n_i A_e}{d} V \tag{140}$$

Please remember that to divide by the unity of area is like to divide by one, as long as the other area (A_e, the area of the electrodes) is expressed in that unit. Now using the Ohm law $V = RI$, we immediately find the expression of Resistance R for an ionized gas under an electric field

$$R = \frac{d}{\mu q^2 n_i A_e} \tag{141}$$

Also, if we remember from any textbook the general expression of the resistance as $R = \rho l/S$ where l is the distance of the electrodes, S their area and ρ is the so call *resistivity*, then we can also find an expression of the resistivity in terms of molecular parameters:

$$\rho = \frac{1}{\mu q^2 n_i} \tag{142}$$

15.1 Diffusion

What is the difference between *drift* and *diffusion* ? First of all we have to define diffusion. You remember the definition of current ? We have an electric current if a certain amount of electric charges passes a unity of area in a certain time. Now, we can define another current, we call it *molecular current*, it is defined by the number of molecules that flow in a unity of area per unity of time, very similar to the definition of electric current. If we know the density of molecules n_a, we can easily calculate the total number of molecules in the time t, as we did usually:

$$N_{tot} = n_a * dV = n_a A v_x t \tag{143}$$

with dV representing the small volume of particles moving in the time t, A the section area we are considering and v_x the average velocity of the molecules in the direction x. So we can write tentatively that the molecular current is

$$J = n_a v_x \tag{144}$$

This could be true if there is a force pushing the molecules around. But we do not have this force in this case, otherwise we would be speaking about *drift*. We want to speak about *diffusion*, a natural movement of particles that do not require an external force.

So we need to have a reason for the molecules to move around, without any force. This reason is the difference in concentration ! So we have as usual to *think small*. Let's imagine that there are two concentrations, n_- and n_+. These are the concentration of the molecules one on the left and right of an imaginary x axis **before** the molecules begin to move. The distance of these two very near particles is of course the free mean path, a very small distance!

In this situation we have two concentration, n_+ and n_- representing the concentration of molecules near the imaginary separation axis x. Let's consider the difference (the *differential*) between these two concentrations $dn_a = (n_+ - n_-)$. We can define $J_x = dn_a v_x$, and for easy mathematical reason

$$dn_a = \frac{dn_a}{dx}\Delta x = \frac{dn_a}{dx}\lambda \tag{145}$$

where λ is the free mean path. Why we chose λ as dx? Because we are *thinking small* so we suppose a tiny variation of particle density dn_a. So our current is

$$J_x = -\lambda v_x \frac{dn_a}{dx} \tag{146}$$

this is valid in general for every other xyz direction. We remember that $\lambda = v_x \tau$ and $\tau = \mu m$ then:

$$J_x = -v_x^2 \mu m \frac{dn_a}{dx} \tag{147}$$

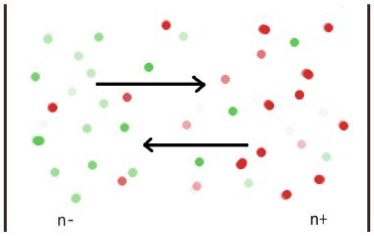

Figure 18: A scheme describing the diffusion process of two different species at different concentration. Note that there is not an external force F in this case(!)

Let's recall the fundamental equation $\frac{1}{2}mv_x^2 = \frac{1}{2}kT$ and we have

$$J_x = -\mu kT \frac{dn_a}{dx} \tag{148}$$

In conclusion, if we define the *diffusion coefficient* D as

$$J_x = -D\frac{dn_a}{dx} \tag{149}$$

we have $D = \mu kT$.

Now what will happen if we have a combination of drift and diffusion ? In this case the drift velocity should compensate the diffusion, so $J_x = -n_a v_{drift}$ (the minus appears because the two velocities are in the opposite direction).

Knowing that $v_{drift} = \mu F$, we substitute on the above eq. 149 and we have

$$D\frac{dn_a}{dx} = n_a \mu F \tag{150}$$

and because $D = \mu kT$ we have finally

$$\frac{dn_a}{dx} = \frac{n_a F}{kT} \tag{151}$$

which is a very important relation that was firstly found by A. Einstein. This relation shows that when we have an external force F, the combined effect of diffusion and drift provoke a *gradient* of concentration equal to n_aF/kT as in the equation 151. This is valid -of course- only at the equilibrium. There is something very important related to equation 151. Let's see there are two variables, n_a the particles concentration and x the spacial variable. Let's put these variables together:

$$\frac{dn_a}{n_a} = \frac{F dx}{kT} \tag{152}$$

Interestingly, Fdx is the *work* done on the molecules. Now we can integrate the two sides:

$$\int \frac{dn_a}{n_a} = \frac{1}{kT} \int F dx \tag{153}$$

We remember from basic physics that $F = -dU/dx$ which means $U = -\int F dx$, so:

$$\ln \frac{n}{n_0} = \frac{1}{-kT} U \tag{154}$$

Let's forget the index a in the gas-concentration parameter n, so for simplicity for now on $n = n_a$, applying the exponential function left and right, we have:

$$\frac{n}{n_0} = e^{-\frac{U}{kT}} \tag{155}$$

because U is the potential energy we can write finally this surprising equation:

$$n = n_0 e^{-\frac{U}{kT}} \tag{156}$$

What's so exiting now about this equation ? It is exiting the fact that we already know it ! It is exactly equation 85, the equation for *ideal gas* we found many sections above. . . ! This is very exiting ! Why..? Because all our modelling where somehow approximate. We used many simplifications and assumption, however using this approach we reached equation 151 studying the effect of diffusion and drift on particles and we discovered that this equation contains in itself the ideal gas relations we started from. This means all our reasoning make sense and that there are no contradictions in the treatment.

16 Black Body radiation

Suppose we want to study the radiation emission of a hot body. In a hot body, all the molecules vibrates. We can approximate these vibrations as elastic oscillations of a charged particle. We do not derive here the detail of the calculations, however you can imagine that the energy of the emission is of course stronger at higher temperatures ($E_k = \frac{1}{2}kT$!). If the energy is proportional to kT, what is the relation of Energy and the frequency of vibration ω ? If we consider the simplest oscillator (the *harmonic oscillator*), we can write that the energy is

$$W = \frac{1}{2}m\omega^2 x_o^2$$

The detailed calculation is complex and we skip it here, however you should not be surprised if we find in the final relation for the intensity $I(\omega)$ a direct dependence with ω^2 and the molecules kinetic energy: kT,

$$I(\omega) = \frac{\omega^2 < E_k >}{\pi^2 c^2} = \frac{\omega^2 kT}{\pi^2 c^2} \tag{157}$$

this equation is called the *Rayleigh's law* for the *black body* radiation. Interestingly enough, this equation fits very well the experimental data for low energies, however, it fail completely to predict a diminished emission at higher energies. Accordingly to eq. 157, because of the ω^2, we should observe a lot of X-Ray and other unhealthy emission from a hot body, much more UV and X-rays than other radiation! Instead, of course, in the experiments, we never observe emission over UV or X-rays, even if we heat-up a body at very high temperatures ! Even if it looks correct, there is something completely wrong in this equation, what is going on here ?!? Many researchers at that time studied the problem, and nobody was able to find an answer. The problem was called by physicists of the time *the UV catastrophe*. Max Planck also studied the problem and was getting mad at it. Until one day that he made the very fancy hypothesis that the kinetic energy cannot be a continuous value, but must be quantized in multiple steps of $h\omega$. In this way he calculated the average energy that is not any more kT as in the equation 157, but a different value that drops down very fast at higher frequencies. This supposition that Energy cannot be continuous, was defined by Planck and his colleagues as an *act of desperations* ! How it was done ?

Planck thought that for some reason, the oscillation of electrons must be *quantized*, exactly as the strings of a guitar are forced to vibrate only to multiple frequencies. This idea was not unfamiliar to physicists, in fact standing waves in musical instruments behave exactly this way: frequency is *quantized* in multiples of a base tone (see fig. **??**)

Planck thought then that the vibration of the molecules in a hot body, must behave exactly this way. So he simply calculated the average energy of such systems. The average energy is : $< E >= \frac{E_{tot}}{N_{tot}}$ where E_{tot} is the total energy of the system, and N_{tot} is the total number of available *states*.

Let's calculate first N_{tot}: lets choose one frequency ω. For this single ω, if we have many possible levels of energies E_0, E_1, E_2 etcetera, we will have N_0, N_1, N_2 molecules on each of these energy levels, right? The problem now is: "what will be the *distribution* of these energies?", in other words, how many molecules will be in N_0, N_1, N_2 etcetera? Of course, Planck wanted to be simple and he thought at the well known Boltzmann distribution that we know very well. So he said, the number of molecules in each energy states E_0, E_1, $E_2 \ldots$, will be distributed as a Boltzmann distribution, so like this :

$$\begin{aligned} &N_0 \\ N_1 &= N_0 e^{-h\omega/kT} \\ N_2 &= N_0 e^{-2h\omega/kT} \\ N_3 &= N_0 e^{-3h\omega/kT} \\ &\ldots \end{aligned} \tag{158}$$

where h is a constant. If we have an infinite number of these states, what is the total N_{tot} that we are looking for ? Well, let's simplify the equation by calling $x = e^{-h\omega/kT}$, then our eq. 159 becomes:

$$\begin{aligned} &N_0 \\ N_1 &= N_0 x \\ N_2 &= N_0 x^2 \\ N_3 &= N_0 x^3 \\ &\ldots \end{aligned} \tag{159}$$

and so on. Then the total N_{tot} is

$$N_{tot} = N_0(1 + x + x^2 + x^3 + \ldots)$$

For the theory of series it is very easy to demonstrate (simply multiply the series by x and compare it with itself) that

$$N_{tot} = N_0 \frac{1}{1-x} \tag{160}$$

At this point we only need to calculate the total energy of the system. Planck simply added up the energy for each level. The total Energy at the lowest *ground* level was for simplicity set to zero, the total energy at the fist level was $N_1 * E_1$, for the second $N_2 * E_2$ and so on... since Planck assumed that energy proceed in multiple of a base (*ground*) value $E_0 = h\omega$, then $E_1 = 2h\omega$, $E_3 = 3h\omega$. If we proceed this way, using again $x = e^{-h\omega/kT}$ the total energy is then

$$E_{tot} = h\omega(x + 2x^2 + 3x^3 + \ldots) \tag{161}$$

Again, if this series is infinite, the theory says that (again multiply the series by x and compare it with itself)

$$E_{tot} = h\omega \frac{x}{(1-x)^2} \tag{162}$$

so the average system energy that we are looking for is:

$$< E_k >= \frac{E_{tot}}{N_{tot}} = h\omega \frac{x}{1-x} \tag{163}$$

or substituting back x

$$< E_k >= \frac{h\omega}{e^{h\omega/kT} - 1} \tag{164}$$

(note that the exponent of the exponential now is positive and not negative as usual!). This formula is what we have to substitute to $< E_k >= kT$ in eq. 157, it goes down very fast for higher frequency. We obtain a curve that fits perfectly experimental data:

$$I(\omega) = \frac{\omega^2 < E_k >}{\pi^2 c^2} = \frac{h\omega^3}{\pi^2 c^2 (e^{h\omega/kT} - 1)} \tag{165}$$

This equation grows initially with ω as before, but at higher frequencies the exponential wins and everything goes to zero as it should be, the *UV catastrophe* was finally solved! This was the first *quantum* equation ever, it became very famous as the *Planck radiation law*, or Planck's blackbody equation. The problem of the ultraviolet emission of hot body of equation 157 was solved for ever and *quantum mechanics* was born.