Lesson 6 : Weakly interacting gases, heat, and work

Notes from Prof. Susskind video lectures publicly available on YouTube

Introduction

Last lesson ended on a question : when does the ideal gas law break down ? Remember that for an ideal gas we assumed that the particles where point-like particles, not interacting with each other, not colliding into each other, with no potential energy, in other words no forces between them.

We are now going to study the case where there are forces between the molecules.

So let's consider a gas of particles that are weakly interacting. Why weakly interacting ? Because we have done the problem of the non interacting gas molecules. And we want to take little steps.

Little steps are usually easy. We start from a known solved problem, and change it a little bit. More specifically, we take some of the parameters, change them a little bit and then try to expand the expressions in the small changes.

That is the usual trick. We have some problem that we solved for some quantity ϵ equal to zero. Then we reformulate the problem with ϵ not being zero and generally it is too hard to solve. But if we are lucky we might be able to expand in a power series in ϵ. Then we check if the succeeding orders are as big as the thing we started with, or if each one is an order of magnitude lower than the preceding one when ϵ is small.

That is the test to tell whether a series like that breaks down. It breaks down when the second term is as big as the first term.

Of course, the gas we are going to study is weakly interacting because it is dilute, because the molecules are on the average rather far from each other.

We will assume the range of the forces is small by comparison with the distance between the particles. We will assume that the potential energy between particles, or the forces, are small.

We will first do a calculation. Then we will look at the results and ask : Where does this break down ? Where does the correction term become as large as the uncorrected term ?

We will check and find out. It is going to depend on the density. The bigger the density, the more likely molecules are going to crash into each other. And if they crash into each other, they are going to experience the fact that they are interacting.

If we make the density too high, they are all jumbled in, squeezed on top of each other. And the ideal gas is a very bad approximation.

On the other hand, we could keep the density low, but still, if the range of the forces is long, if particles were to interact with each other when they were six feet apart, that would also be a problem. Considering for instance the molecules in this room, even if the interaction was pretty weak, if they interacted with molecules far away, that would still be a very serious modification of the ideal gas law.

So we start by assuming that we can make an expansion in

the small parameters. We will make the expansion – mathematically expand our formulas. And then we will check how the first correction term compares with the term is it correcting. Is it as big, or is it an order of magnitude smaller?

Let's set up that problem. As usual we will calculate the partition function. Our system now is made of molecules whose total energy is not just the sum of the kinetic energies. There are forces now. Forces means of a potential energy.

We start with the formula for the energy of a set of molecules with fixed positions and momenta. In other words it is *one state* of the system.

$$E(x, p) = \sum_n \frac{p_n^2}{2M} + \sum_{n>m} U(|x_n - x_m|) \qquad (1)$$

How to read this equation :

- The notation $E(x, p)$ means the energy for a given set of x's and p's.
- The first sum on the right-hand side we already met in the ideal gas case. It is the kinetic energy of all the molecules.
- M stands for the mass of one molecule.
- There are N molecules. In the first sum they are indexed by n. We haven't noted it explicitly, but n runs from 1 to N.
- The second sum is the potential energy of all the pairs of molecules.

- To track the pairs of molecules, we index the first molecule by n and the second by m.
- What is the meaning of $n > m$ under the sign sum? We don't want to count n and n as a pair. And we don't want to count pairs twice. So the indexing of the pairs uses the two letters n and m and we sum over all the indices such that $n > m$.
- A pair of molecules has a potential energy U which depends on the distance between the two molecules.
- x_n is a vector. So is $x_n - x_m$. And the vertical bars mean that we take the length of $x_n - x_m$, in other words the distance between the n-th and the m-th molecules.
- Hence we use the notation $U(|x_n - x_m|)$ to mean the potential energy due to that pair.

Now what is going to be the small quantity? It is going to be U. The potential energy between molecules will be assumed to be a good deal smaller than their kinetic energies.

In other words, we start with the ideal gas. And then we turn a knob which jacks up the potential energy of the configuration. But we keep that knob set to a very small value, so that, at least at first, the potential energy stored by these pairs of molecules is much smaller than the kinetic energy of either of them. That is our approximation, and where we are going to begin.

There is actually only one number regarding the potential energy which is going to be important. It will appear in the calculation of the following integral concerning one pair of particles, when we will integrate over all their possible

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positions, say particle 1 and particle 2. It doesn't matter which pair, we just call them 1 and 2 for convenience. When we calculate the partition function, we will have to deal with

$$\int d^3x_1 \ d^3x_2 \ U(|x_1 - x_2|) \qquad (2)$$

The notation d^3x_1 is there to remind us that x_1 is a three-dimensional vector, and the differential element is actually a small volume. Same comment for x_2.

So what we are doing in expression (2) is taking the two particles and integrating over all possible positions of the pair of particles [1].

The integral in expression (2) is actually a double integral. We can decompose its calculation into two steps. First of all we keep x_1 fixed, and look at the simple integral when x_2 ranges over its domain :

$$\int d^3x \ U(|x|) \qquad (3)$$

This term in a number. Now to complete the double integral, we integrate over the position of x_1. That gives us simply, as a multiplicative factor, in front of expression (3) the volume V. So we can write

$$\int d^3x_1 \ d^3x_2 \ U(|x_1 - x_2|) \ = \ V \int d^3x \ U(|x|) \qquad (4)$$

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1. In some manual of mathematics, this double integral would be written

$$\iint d^3x_1 \ d^3x_2 \ U(|x_1 - x_2|)$$

What are the units of the last integral on the right-hand side? Volume times energy. So this last integral is telling us how important the energy is, because it is both telling us how strong the potential energy is and on how big a volume does U act – in other words how spread out it is.

The integral $\int d^3x\, U(|x|)$ is going to be our important numerical quantity which determines the strength of the potential. As said, it is a combination of how strong the potential is and how widely spread it is distributed. So let's give it a name. We call it U_0 (read *u zero*, or *u naught*)

$$U_0 = \int d^3x\, U(|x|) \tag{5}$$

It is the only parameter that will come into our calculation. We don't know offhand whether it is big or small. It depends on the function U and the volume over which it is integrated. It could be big, even if U is never very big, because it is integrated over a wide volume, like a large thin puddle can contain a lot of water. Or the integration could be over a small volume, but where U is sufficiently big to make U_0 big.

One way or another U_0 is the quantity which will determine everything else.

Finally, as explained, when we do the double integration in expression (2), we end up with

$$\int d^3x_1\, d^3x_2\, U(|x_1 - x_2|) \;=\; V U_0 \tag{6}$$

This is the potential energy for *one pair* of particules, when

integrated over all the possible positions of the pair.

To get a feel for what U_0 is, think for a moment of x_1 and x_2 as one-dimensional variables. Then fixing $x_1 = 0$ and letting x_2 vary, $U(|x_1 - x_2|)$ is the following function, figure 1.
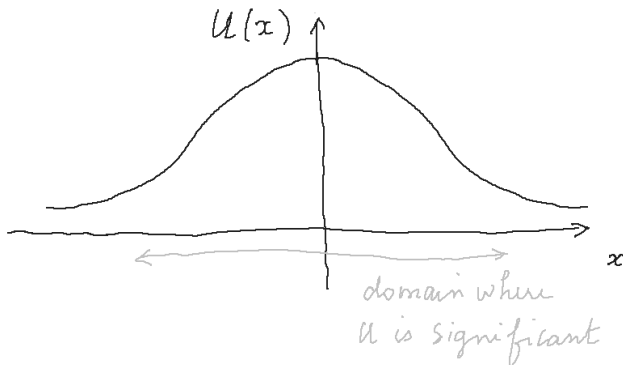

Figure 1 : Function $U(x)$. U_0 is the area under the curve.

Of course, in truth x_1 and x_2 are three-dimensional. And the integration producing U_0 is the integral of $U(x)$ over the whole *volume* of the gas.

The integral U_0 converges if $U(x)$ falls off sufficiently rapidly when the distance between the molecules grows. In practive, for a weakly interacting gas, the function $U(x)$ will become negligible when x is larger than a couple times the diameter of a molecule.

We can say that U_0 is "qualitatively equal" to $U\mathcal{V}$, meaning by that the height U of the function $U(x)$ near zero, times the volume $\mathcal{V}$ over which the function $U(x)$ is significant, figure 1. The volume $\mathcal{V}$ is a couple of time the volume of a

molecule basically.

In other words, the potential energy between molecules – and therefore the force between them [2] – is only significant when the two molecules are within a couple of molecular diameters of each other.

There are two volumes we are talking about in our analyses. The volume $\mathcal{V}$, in $U_0 = U\mathcal{V}$, is roughly the volume of a couple of molecules. The other volume, V, on the right-hand side of equation (6), is the volume of the whole sample, that is the volume of the box of gas.

The small volume $\mathcal{V}$ gets absorbed into U_0. We don't have to worry about it anymore. The quantity U_0 is the product of the small volume $\mathcal{V}$ where the potential energy between the molecules is significant, times the value U of that potential energy between the molecules. Then we have to take into account the integral in equation (6). That gives VU_0, where V is the total volume of the system.

The next steps are to calculate the partition function, and then use it. But let's first of all do a questions / answers session to clear any cloudy point that may remain before we go on.

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2. Remember that the force is minus the gradient of the potential energy.

Questions / answers session

Q. : When we calculate the potential energy of a pair of molecules, shouldn't we take into account *boundary effects* ?

A. : That is a good question. The answer is : there are boundary effects, yet they can be neglected. Let's see why.

We saw that U_0 is independent of the position x_1 where we fix the first molecule of the pair in order to compute the integral of $U(|x_1 - x_2|)$ over the position x_2 of the second molecule.

But of course that is not exactly true when x_1 is near a boundary of the box.

In all these thermodynamical problems there are always boundary effects. And we are always using the fact that for a large vessel, the total volume is much bigger than the area of the boundary times the distance of the effect, in other words much bigger than the volume where there are boudary effects.

It is because we are accustomed to these boundary effects that we didn't consider a priori that the behavior of molecules in an ideal gas was isotropic everywhere including near the walls. It turned out it is. But we established $P = \rho T$ for an ideal gas without assuming the absence of boundary effect. And that was important because, in some sense, pressure on the wall is nothing but a boudary effect !

So in general when we take the molecule x_1, and move it near the walls of the box, we make a little mistake by assuming that the other molecule x_2 can be anywhere around

it. It can be anywhere around it except when it is banging to the wall.

The mistake of neglecting the boundary effects, however, is not important as long as the total volume V of the box is much bigger than the volume $\mathcal{V}$ where the potential energy is significant around a molecule. In other words if the box is much bigger than a few molecules, even spread over the walls, then the error is negligible.

So, if the box is large enough the surface to volume ratio is very small. Then, if the forces are not long range, we can safely neglect the boundary effects. Of course, if the vessel if very small, of the order of magnitude of a few molecules, then we could not neglect boundary effects. In fact they would dominate the experiment.

Q. : The quantity $\int d^3x_1 \, d^3x_2 \, U(|x_1 - x_2|)$ is the integral of the potential energy of one pair of particles over all possible configurations of the gas in the box, is that correct ?

A. : Yes, that is perfectly correct. And as we saw it is equal to VU_0. Its units are volume squared times energy, but it is only proportional to the volume V, the proportionality factor being the important quantity U_0. We will use it in a moment.

Q. : Shall we eventually take into consideration the *collisions* between particles ?

A. : No, we shan't. Not that there are no collisions, but we won't have to introduce them specifically into our analysis. They will be taken care of automatically.

That is the power and the beauty of applying general thermodynamical principles as opposed to sticking to a mechanistic analysis – a kinetic theory analysis – of the problem.

Again, we already saw that when we studied the ideal gas. The general principles overcame the question of whether there was a boundary effect that would corrupt the simple application of $F\Delta t = m\Delta v$ onto the walls. It turned out there was none. But we didn't care.

Similarly here there will be collision effects – and this time we won't discover in the end that there aren't any – but we don't have to be concerned with them. All will be taken care of in the use of the partition function whose first brick we set with equation (1).

We are not ever going to have to think about collisions. We are never going to have to think about following the particles. We don't have to think about them.

This is the beauty of statistical mechanics : you lose all intuition about what is really going on, but you have a set of mechanical rules. You go on to autopilot. You follow the rules. And you get the answers in a completely rigorous way.

You don't have to worry about whether some assumptions that you may have made, such as whether the particles have the same average velocity, if they are near the walls or not

near the walls, near each other or not near each other. You don't have to worry about all that.

Of course, once we reach some result, it is always good to step back and ask : What really are we doing ? Are we getting the answer that we would have expected from naïve thinking ?

But if we want to really know whether we have the right answer, the best is to set up the rules, get on to autopilot, follow the equations and, at the end, look at the result and ask : Does this make sense ?

Q. : We are basing our analysis on looking at pairs of particles. Are we not losing anything by not looking at triples or other higher combinations of particles ?

A. : First of all, when we wrote that the potential energy was

$$\sum_{n>m} U(|x_n - x_m|) \tag{7}$$

there could be terms in the energy which depend on three particles at a time.

The energy between two particles conceivably could depend on the presence of a nearby third particle. So we have made an assumption when we wrote that the energy can be expressed as a sum over pairs, as in equation (7).

Now, the point is : Why was it a good approximation first of all to use the ideal gas ? And the answer is : It is a good approximation when the probability for two particles to be close enough together to feel each other is small.

When the gas is dilute, the particle spend most of the time being far enough away that they simply don't feel each other.

Some fraction of the time, two particles will get close enough together to interact. That is when they are within the little distance where $U(x)$ is not negligible – when they are in the same little volume $\mathcal{V}$. Then the forces between the two molecules become important.

Now what is the fraction of the time that three given molecules will be within the molecular distance of each other ? Much much smaller. You pick three molecules and ask what is the probability that all three of them be within a molecular diameter of each other. It is vastly smaller, than for two molecules.

It depends on the overall volume V of the gas of course. But, as said, we do assume that V is much larger than $\mathcal{V}$.

So if there were three-body forces, they would be less important not because they are weaker but because the probability of finding three particles in the neighborhood of each other for a dilute gas is even smaller than for two particles.

We are going to do an expansion. And in the expansion, there are three-body effects even if the forces are only two-body effects. The answer to the question is that we are

going to follow the expansion and see what we find. There are other terms. But they won't be important as long as the gas of particles is reasonably dilute.

Let's go on. Now we are going to go on autopilot. What do we want to calculate? We want to calculate the partition function.

Partition function

The partition function Z is the integral over the positions and the momenta of $e^{-\beta E(p,x)}$. It is the generalisation to the continuous case of equation (43b) in chapter 4 which we established in the discrete, and even finite, case.

Now the space of possible states of the system is a $6N$-dimensional phase space of positions and momenta, where N is the number of particles.

Z will be therefore calculated as a multiple integral of high dimension. dp will stand for $3N$ linear differential elements of momentum. And so will dx for positions.

Introducing, to follow the custom, the factor $N!$ downstairs, although it is not going to make any difference, here is the formula for the partition function

$$Z = \frac{1}{N!} \int dp \, dx \, e^{-\beta \sum \frac{p_n^2}{2M}} \, e^{-\beta \sum U(|x_n - x_m|)} \qquad (8)$$

The glorious and simplifying feature, that we have already seen, of this integral is that it factorizes. We can rewrite it

$$Z = \frac{1}{N!} \int dp \ e^{-\beta \sum \frac{p_n^2}{2M}} \int dx \ e^{-\beta \sum U(|x_n - x_m|)} \qquad (9)$$

The first integral, that is the momentum integral, we have already dealt with in the case of the ideal gas. It is a product of identical Gaussian integrals. We even calculated the Gaussian integral in chapter 4.

The second integral, that is the position integral, in the case of the ideal gas, was very simple. There was no potential energy. U was equal to zero. And that gave us the volume V to the power N.

So let's multiply and divide expression (9) by V^N.

$$Z = \frac{V^N}{N!} \int dp \ e^{-\beta \sum \frac{p_n^2}{2M}} \int dx \ \frac{1}{V^N} \ e^{-\beta \sum U(|x_n - x_m|)} \qquad (10)$$

The first part is just the partition function for the ideal gas. See equation (39) of chapter 5, which we wrote before introducing $N!$ downstairs. So we can call it $Z_0(\beta)$. The index 0 now stands for the calculation when U was equal to zero, that is the ideal gas case. So we write

$$Z = Z_0(\beta) \int dx \ \frac{1}{V^N} \ e^{-\beta \sum U(|x_n - x_m|)} \qquad (11)$$

The remaining integral is the new thing. It is the factor we have to work on.

Notice that although the calculations may seem heavy, what we have done is really simple. Starting from the ideal gas case, we added a potential energy term to the energy $E(x, p)$ of one configuration, equation (1). Then we used this new $E(x, p)$ to write the partition function. The sum in $E(x, p)$ becomes a product of exponentials under the integral sign in the expression of Z. Because, as in the ideal gas case, the integral involves separately positions and momenta, it factorizes. The first term, after multiplication by V^N, is the good old partition function of the ideal gas. And the second term now is the new one due to the potential.

This remaining factor in equation (11) is an integral over all the x_n and all the x_m forming pairs, with $n > m$. Let's write it temporarily

$$\int \frac{dx}{V^N}\, e^{-\beta W(x)} \tag{12}$$

What is the small quantity in our calculation, in terms of which we are going to expand? It is the potential term $W(x)$.

The potential energy is the quantity which is assumed to be small. We are starting with an ideal gas. Then imagine turning a knob which creates a potential energy. We turn it slowly until we just reach a weak potential energy.

Then, in expression (12), having a weak potential energy, we can expand the exponential in a Taylor series in the strength of W [3]. It is very simple. It is just equal to $1 - \beta W(x)$. Those

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3. Then as usual using an approximation *under* the integral sign to obtain an approximation of the integral can in this case easily be justified mathematically.

are the first two terms of the general expansion

$$e^s = 1 + s + \frac{s^2}{2!} + \frac{s^3}{3!} + \frac{s^4}{4!} + \ldots \qquad (13)$$

This is the most famous power series. It converges for all s's positive or negative, real or complex. The reason is that the factorials force a rapid decrease to zero after a while.

The power series (13) yields useful approximations of e^s when s is small. First of all, when s is sufficient small we can ignore everything but the 1. The next approximation is $1 + s$, that is in many cases adequate for small s.

In equation (12) we want to keep track of the correction term due to potential, so we keep the 1 and the first term

$$e^{-\beta W(x)} \approx 1 - \beta W(x) \qquad (14)$$

Let's plug that in equation (12). We get rid of the exponential and replace it by the approximation

$$\int \frac{dx}{V^N} \, [\, 1 - \beta W(x) \,] \qquad (15)$$

What does the integral over 1 give us? It gives V^N. So we get

$$1 - \beta \int \frac{dx}{V^N} \, W(x) \qquad (16)$$

Now let's go back to the messy sum that we had temporarily replaced by $W(x)$. There are N choose 2 pairs $x_n \, x_m$. The factor multiplying Z_0, in equation (11), due to the potential energy between molecules can therefore be rewritten

$$1 - \beta \binom{N}{2} \int \frac{1}{V^N} \, dx_1 \, dx_2 \, U(|x_1 - x_2|) \, dx_3 \, ... \, dx_N \quad (17)$$

Once we have put the factor $\binom{N}{2}$ in front, we don't have to sum anymore. All the pairs playing the same role, we can integrate simply $U(|x_1 - x_2|)$.

The integrals over $dx_3 \, dx_4 \, ... \, dx_N$ give V^{N-2}. So, spelling also out the formula for $\binom{N}{2}$, we get

$$1 - \beta \, \frac{N(N-1)}{2} \, \frac{1}{V^2} \int dx_1 \, dx_2 \, U(|x_1 - x_2|) \quad (18)$$

Now remember, see equation (6) [4], that we have

$$\int dx_1 \, dx_2 \, U(|x_1 - x_2|) \; = \; V U_0 \quad (19)$$

So, approximating $N(N-1)$ by N^2, the factor in the partition function due to potential can be written

$$1 - \beta \, \frac{N^2}{2} \, \frac{U_0}{V} \quad (20)$$

Finally we reached the partition function for the weakly interacting gas. It is the partition function of the free gas times the factor we just calculated. This gives

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4. In equation (6) the notations had stressed that each infinitesimal element dx was actually an infinitesimal volume which we had denoted d^3x. But equation (6) and equation (19) are the same.

$$Z \;=\; Z_0 \left[1 - \frac{\beta N^2}{2V} U_0 \right] \tag{21}$$

What do we want to do with it? Well, again we go on to autopilot. Everybody knows that what we do first with a partition function is to take its logarithm. All the interesting formulas use the logarithm of the partition function.

$$\log Z \;=\; \log Z_0 \;+\; \log \left[1 - \frac{\beta N^2}{2V} U_0 \right] \tag{22}$$

Since we are considering a weakly interacting gas, U_0 is small. So we can expand in U_0. U_0 is our expansion parameter.

Above we saw the Taylor series expansion of e^s, that was formula (13). Now we want to use the Taylor series expansion of $\log(1+s)$. It is [5]

$$\log(1+s) = s - \frac{s^2}{2} + \frac{s^3}{3} - \frac{s^4}{4} + \dots \tag{23}$$

Notice that it starts with s, the signs alternate, and there are no more factorials. Unlike the power series of e^s, this one doesn't converge for all s. Its radius of convergence is one. That is to say, it is a meaningful series only for $|s| \leq 1$.

We are interested in only the first term in the expansion of $\log(1+s)$. So the log of the partition function rewrites

$$\log Z \;=\; \log Z_0 \;-\; \frac{\beta N^2}{2V} U_0 \tag{24}$$

5. By log we mean here the natural logarithm, also called Neperian logarithm.

Now, is this what we want? No, we are never really interested in the log of the partition function itself. We are interested in what we can get from it.

Let's pick something interesting that we can get from the log of the partition function. For instance, energy. Let's calculate the energy of the gas.

$$E = -\frac{\partial \log Z}{\partial \beta} \tag{25}$$

Using equation (24), this becomes

$$E = \frac{3}{2}NT + \frac{\partial}{\partial \beta}\left[\frac{\beta N^2}{2V} U_0\right] \tag{26}$$

This first term is the good old formula of Maxwell and Boltzmann for the energy of an ideal gas of N particles in thermal equilibrium at temperature T. Each particle has energy $3/2\ T$, and that is multiplied by N.

The second term is minus the derivative with respect to β of the potential term in equation (24). The minus signs cancel, and, the only term depending on β being β itself, we get

$$E = \frac{3}{2}NT + \frac{N^2}{2V}U_0 \tag{27}$$

Now of course we always expect in a situation like this that the total energy should be proportional to the number of particles. So the first term is alright. But the second term is weird. It is quadratic in the number of particles.

A priori to have an N^2 is crazy. If I have 10^{23} particles, I get an energy of 10^{46}. I don't care what units are used, 10^{46} is just too big. But that is alright, because there is a V downstairs that is also big. So let's keep one N over the volume V and pull the other one in front.

N/V is the density, which we denote ρ. Hence equation (27) becomes

$$E = \frac{3}{2}NT + N\frac{\rho}{2}U_0 \qquad (28)$$

The density is neither big nor small. It is what it is. Well, it may be on the small side because we are talking about a dilute gas. But equation (28) is the formula we obtain for the energy of a weakly interacting gas.

Let's examine this formula. It has two terms. One coming from the ideal gas. It doesn't depend on the density at all. Of course it is proportional to the number of particles.

And there is the other term that is also proportional to N. It depends on the potential energy between particles. And it also depends explicitly on the density.

Why does it depend on the factor of the density ? In formula (28) the density appears, with the factor $U_0/2$, as an energy per particle. But there shouldn't really be an energy per particle. There should be an energy per particle only if there is another particle nearby. So if we focused on one particle and ask : What is the probability that there is another particle nearby ? It would be proportional to the density.

The higher the density, the more probable is that there is a

neighboring particle. Hence the correction term in formula (28), in addition to the ideal gas term. It can also be viewed in formula (27) in the fact that there is an N^2. N^2 is the number of pairs of particles roughly [6].

We may also express formula (28) factorizing N in front of the energy per particle

$$E = N \left[\frac{3}{2}T + \frac{\rho}{2}U_0 \right] \qquad (29)$$

The energy per particle has a first term which is just proportional to the temperature. And a second term is proportional to the potential energy between pairs of particles times another factor of the density.

Of course this can be confirmed for a weakly interacting gas. However, despite the fact that we once in a while talked about measuring not only the average energy E but even the precise level of energy E_i of a gas, one doesn't easily measure the energy of a gas. So this is not the way to confirm it.

What is an interesting quantity that is easy to measure? I'm not alluding to the temperature. Temperature is an input in formula (29). Notice by the way that the correction term doesn't depend on the temperature.

The other interesting quantity that is easy to measure, beside temperature, is the pressure. So what does our calculation say about the pressure?

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6. In fact it is we who changed $N(N-1)/2$ into $N^2/2$ for simplicity.

We have everything we need to calculate the pressure. We built our tools in chapter 5. Remember that we defined pressure as

$$P = -\frac{\partial E}{\partial V}\bigg|_S \tag{30}$$

Then, since it is impractical to measure something at fixed entropy, we used a small result in calculus to reexpress the pressure as the derivative, with a minus sign, of the Helmholtz free energy A with respect to the volume at fixed temperature.

$$P = -\frac{\partial A}{\partial V}\bigg|_T \tag{31}$$

Helmoltz free energy is $A = E - TS = -T\log Z$. So formula (31) can be rewritten

$$P = T\frac{\partial \log Z}{\partial V}\bigg|_T \tag{32}$$

We then applied this formula to the ideal gas, see formula (46) in chapter 5.

But formula (32) is true in general. Now let's apply it to the weakly interacting gas.

In the weakly interacting gas case, we established, in formula (24), that

$$\log Z = \log Z_0 - \frac{\beta N^2}{2V}U_0 \tag{33}$$

To obtain P, we want to calculate at fixed temperature

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$$T \, \frac{\partial \log Z_0}{\partial V} - T \, \frac{\partial}{\partial V} \left(\frac{\beta N^2}{2V} \, U_0 \right) \tag{34}$$

When we differentiate $\log Z_0$, what do we get, when multiplied by T in front? We get the pressure of the ideal gas that we calculated in formula (46) of last chapter. That is ρT.

Then let's differentiate the second term in expression (34). But first of all, notice that we have the factor T in front, and the factor β inside. Those two are inverse of each other and cancel. So formula (34) yields the equation

$$P = \rho T - \frac{\partial}{\partial V} \left(\frac{N^2}{2V} \, U_0 \right) \tag{35}$$

This is

$$P = \rho T + \frac{1}{2} \frac{N^2}{V^2} \, U_0 \tag{36}$$

And finally

$$P = \rho T + \frac{1}{2} \, \rho^2 \, U_0 \tag{37}$$

That is the generalization to a weakly interacting gas of the formula we had for an ideal gas.

Notice, among other things, that we are expanding in powers of the density. If the density is zero there is no pressure.

Indeed there is no particle, no temperature, no pressure, no nothing.

Then if the density is very low, the quadratic term is negligible and we are in the ideal gas case. In that case the pressure is proportional to the density and to the temperature. That makes sense. If the temperature is zero, the molecules aren't moving at all. They don't bounce off the walls at all.

And if the temperature is not zero, the linearity with the density also makes sense, as long as the density is small. Indeed in that case the particles essentially don't interact with each other, so if we put twice as many in the same volume the pressure on the walls must double.

Then, as the density gets higher, a quadratic term appears. It represents the effect of the interaction between molecules on the pressure.

The correction term is proportional to ρ^2. That makes sense : when ρ is small, the correction term is a lot smaller than ρT.

Interestingly enough, the correction term doesn't depend on the temperature [7]. But it depends on the potential energy between molecules, or more precisely on the parameter U_0 defined as

$$U_0 = \int dx \, U(x) \qquad (38)$$

---

7. It requires a bit of physical intuition to feel that. But don't overlook that it is only the *correction term* to the pressure that is of course function of the temperature, i.e. the agitation of the molecules.

where $U(x)$ is the function of potential between two molecules with their distance as the independent variable. And integrating $U(x)$ over the entire volume around one molecule gives U_0, which has units energy times volume.

The correction term in the pressure is proportional to U_0, which – remember – we assumed to be small, enabling us to approximate e^s as $1 + s$, and $\log(1 + s)$ as s, where s was essentially proportional to U_0.

In other words, the correction term depends on the fundamental parameter U_0 which governs the strength of the interaction. And it has got ρ^2 as a factor in front.

Laboratory experiments can confirm equation (37), and even produce a numerical measure of U_0. We take a gas in a vessel, measure its temperature, its pressure and its density. Then we change for instance the density. We can change the density either by changing the volume or by introducing more matter into the vessel. And we can keep the temperature fixed, if we like, by keeping the box in equilibrium with a heat bath. Or we can also change the temperature.

If we do the experiment for several triplets (P, ρ, T), which we can all control or measure, we shall not only be able to compute U_0 but we shall also be able to verify equation (37). We will see that when the density remains reasonably low, the pressure varies according to equation (37) which we reproduce below

$$P = \rho T + \frac{1}{2} \, \rho^2 \, U_0 \qquad (39)$$

with a linear term in the temperature and the density, and a quadratic term in the density times $U_0/2$. Of course the factor $1/2$ won't show explicitely. It is a matter of definition of U_0.

Question : How would the formula for the pressure change if we took into account the 3-body interactions between molecules ?

Answer : If we assume that the energy scale for the 3-body interactions between molecules is about the same as for the 2-body interaction, then there would be a further term in ρ^3 in formula (39), with a factor depending on U_0 and also on T. You will have to look up what the cubic coefficient is exactly.

In any case $1/2\ \rho^2 U_0$ is the first correction term, for a dilute gas, to the formula $P = \rho T$, when we want to take into account weak interactions between molecules. It provides a good approximation for a dilute gas.

When

$$\rho^2 U_0\ <<\ \rho T \qquad (40)$$

the sign $<<$ meaning "much smaller than", then we can use the ideal gas formula for the pressure.

Dividing by ρ, condition (40) can be rewritten

$$\rho U_0\ <<\ T \qquad (41)$$

So when the temperature is much bigger that ρU_0, then we

can use the ideal gas model to evaluate the pressure.

Temperature is a measure of the kinetic energy of *each* particle. Remember, it is not related to the number of particles. A unique particle has a temperature. Furthermore in a vessel in thermal equilibrium, all the particles have the same kinetic energy, therefore the same temperature. They don't have to be all the same particles. You can have a mix of two gases, with different molecular masses. The particles of one type will have one speed, and the particles of the other type will have another speed.

We pointed out that we can even plunge a bowling ball into the gas in the vessel. When thermal equilibrium is reached, the ball will also have the same kinetic energy as the other molecules – which means of course that it will remain essentially still.

Remember that the units of U_0 are energy times volume. And the units of ρ are 1 over volume [8]. So the units of ρU_0 are energy. Therefore in condition (41), we are comparing energy on the left with energy on the right.

ρU_0 is the potential energy per particle. So if the potential energy per particle is much less than the kinetic energy per particle, then the ideal gas formula $P = \rho T$ is a good approximation.

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8. We are accustomed in physics to think of the density as a mass per volume, or an energy per volume. That is for instance how we defined the various parameters ρ in the course in Cosmology, that is volume 5 of the collection *The Theoretical Minimum*. But in statistical mechanics ρ is most often defined as a number of particles per volume. And that is indeed how we defined it in the previous chapters and here.

That is what we are doing when we use the ideal gas model. We are really studying the gas in the range where the potential energy is much smaller than the kinetic energy.

The purpose of what we explained so far in this chapter was to show how the rules work, to show that we are not limited to the ideal gas, and finally to show that we reached a nice and simple formula, $P = \rho T + 1/2 \; \rho^2 U_0$, that would have been difficult to guess from intuition.

Could we have guessed the correction term? We might have guessed that it was proportional to ρ^2 because it involved pairs of particles. We might have guessed that it involved the potential energy.

It would not have been so obvious, though, that it involved exactly the integral $\int U(x) \; dx$. But it is plausible that U times the volume is there. See figure 1 and the subsequent comments for what we mean by U times the volume.

Would we have guessed the factor $1/2$? May be if we are really smart, we might have guessed the $1/2$. Would we have been sure in the end that $1/2 \; \rho^2 U_0$ was right? Probably not.

The mechanical calculation, starting with calculating the partition function, is the way to do these things, and to be sure in the end that we are right.

So we have done a couple of problems. The next topic is heat and work. But before that I'll take a few questions.

Questions / answers session (2)

Q. : In a typical situation of temperature and pressure, like the air in the room, how big are the numbers ρ, U_0, and their product compared to temperature ?

A. : In the room where we stand, at so-called room temperature and pressure, the temperature is much bigger than ρU_0.

It is a little exercise to work out. The potential energy U between a pair of molecules is of the order of let's say one hundredth of an electron-volt. That is 1.6 x 10^{-21} Joules.

The density ρ is the number of particules per cubic meter in the room. We can take Avogadro's number per 22.4 liters. That gives $\rho = 2.7$ x 10^{25}. The units are the inverse of cubic meters.

We need something else : the volume of a few molecules. We can take for that a cube of side 10 Angströms. One Angström is 10^{-10} meters. Following the comments to figure 1, the formula $U_0 = U\mathcal{V}$ gives $U_0 = 1.6$ x 10^{-21} x 10^{-27}.

Thus $\rho U_0 = 4.3$ x 10^{-23} Joules. On the other hand 300 Kelvins is 4.1 x 10^{-21} Joules.

You have to start getting into the range where the molecules are almost butting up against each other for the condition (41) to break down. It is when they start having appreciable probability of being on top of each other that it becomes violated.

You can calculate how much you would have to shrink the room in order that the ideal gas approximation be no longer acceptable.

Q. : Is it possible for the term U_0 to be positive or negative ?

A. : Yes, it is. Consider the potential energy function $U(x)$ between a pair of molecules. It can look like figure 2a or figure 2b.
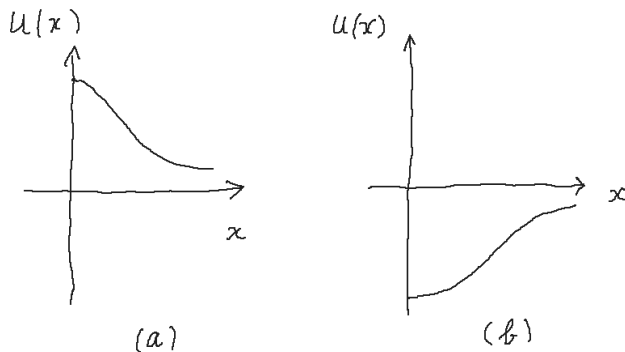

Figure 2 : Possible potential energy curve between two molecules at distance x of each other.

Which represents attraction and which represents repulsion ? Curve (b) represents attraction, because the potential energy increases as we separate the molecules. And curve (a) represents repulsion.

What should you think off hand should be the effect of repulsive forces on the pressure ? If there is repulsion bet-

ween the molecules, and you try to squeeze them to the point where they scream to each other "I don't want to get close to you, Buddy", the pressure is going to go up.

So in the repulsive situation, that is curve (2a), U_0 is positive. It corresponds to an extra bit of pressure on top of the ideal gas pressure $P = \rho T$.

If the molecules, on the other hand, attract each other that means U_0 is negative. And the actual pressure is a bit smaller than in the ideal gas case.

Q. : Can the forces between molecules be repulsive over a range of distances, and attractive over another range ? And can there be gravitational forces ?

A. : Forget gravitation. It is totally negligible for a gas in a laboratory vessel.

Then yes the intermolecular forces can be repulsive at first and then attractive after a certain distance.

To know what the forces between two molecules are, you will have to know something about molecular and atomic physics.

The potential energy $U(x)$ between two molecules as a function of distance is given by the Lennard-Jones [9] law. A typical shape is shown in figure 3. The forces are repulsive at

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9. John Edward Lennard-Jones (1894 - 1954), British theoretical physicist.

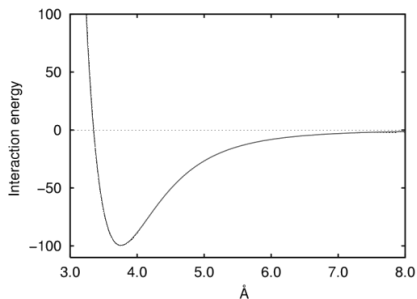short distances, and then there is an attractive tail.

Figure 3 : Typical real life $U(x)$. Lennard-Jones law.

The figure doesn't show it clearly, but usually the average force is repulsive. Therefore in most molecular situations U_0 is positive. And the actual pressure is a bit higher than in the ideal gas model.

But we are not doing molecular physics. So I'm not going to tell you how to calculate the curve. You need a handbook of physics or chemistry to learn what the actual potential energy is between a pair of molecules in various kinds of situations.

You will learn, for instance, what is the curve for a pair of hydrogen molecules, or a pair of helium molecules. Helium is usually the first example presented, because helium is not reactive.

Q. : What are the forces when we have a dipole ?

A. : Don't mix up the forces of chemical bonds, called co-valent forces, between atoms, which involve sharing electrons, and the forces between atoms or molecules resulting from other kinds of interactions, which are those that concern us here. In other words, we are not concerned by dipoles in the chemical sense.

The forces we are considering are called the Van der Waals [10] forces. And the curve $U(x)$ is sometimes called the six-twelve potential because it involves an attractive force in x^{-6} and a repulsive force in x^{-12} which are competing to form the resulting curve in figure 3.

This is not the point though. The point is, given the dynamics, given the formula for the energy, how do you proceed ?

Getting the formula for the potential energy is not a problem in statistical mechanics. It is a problem in quantum mechanics, in molecular structure, in atomic physics, or whatever.

For us the potential energy is a given we start from to think about statistical mechanics.

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10. Johannes Diderik van der Waals (1837 - 1923), Dutch theoretical physicist and thermodynamicist.

Beware that the term Van der Waals forces is used differently by different authors. Sometimes they refer to all the non covalent forces, attractive and repulsive, and sometimes only to the attractive ones. They are then used to explain for instance how geckos can walk on ceilings.

That is not subtle. It is very straightforward. As I said, it is blind navigation. Just write down the energy formula. Start doing the integrals. Here and there of course there are tricks. But with experience, you know the tricks. You know to multiply and divide by the volume to the n-th power, and things like that. It doesn't take a hell of a lot of insight. It is blind manipulation of the symbols.

Now at the end of the calculations, it takes some insight to check whether the results make sense. We can ask the question : Am I getting a sensible result ? Looking for instance at the equation

$$P = \rho T + \frac{1}{2}\,\rho^2\,U_0$$

what does this equation mean ? Has the correction term the right sign ? Does it make sense to say that, if the forces are repulsive, it increases the pressure between things ? Is it reasonable that the correction be proportional to ρ squared ?

Why the factor of $1/2$? Well, we know where that came from. It came from the $n(n-1)/2$. So you might in hindsight say : Yeah, there should be a $1/2$ there. We would overcount if we counted that 1 and 2 is different than 2 and 1. And so that is the half.

Now we arrive at something that is much less straightforward. I remember it really was confusing me when I learned thermodynamics. Unfortunately the professor was more confused than I was and couldn't straighten me out. It had to do with heat and work and something called exact diffe-

rentials. So let's take a little mathematical interlude to talk about exact and inexact differentials.

Exact and inexact differentials

Exact and inexact in this context have nothing to do with precise versus imprecise. Exact is a technical mathematical term which probably predates homology theory [11] and other fancy things like that. But it may have first turned up in thermodynamics.
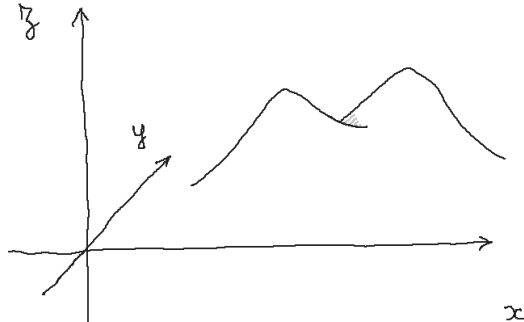
Take a function of two variables $z = F(x, y)$, figure 4.

Figure 4 : Function of two variables. It is a surface.

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11. An homology in mathematics is a link between two domains that seem at first to be quite distinct, typically one belonging to geometry and the other to algebra, but which in fact have deep connections. Homology theory has been applied fruitfully to the study of differential forms

Think of $F(x, y)$ as the altitude z of the surface, at the point (x, y) on the horizontal plane. In other words, the surface F represents a hilly terrain.

Now we take a little walk *on the surface*. When projected onto the (x, y) plane, it corresponds to a dx and a dy. How much does our altitude change during the walk? The answer is given by the familiar formula

$$dF = \frac{\partial F}{\partial x} \, dx + \frac{\partial F}{\partial y} \, dy \qquad (42)$$

Our walk doesn't have to be parallel to the x-axis, or parallel to the y-axis. When projected onto (x, y), we can be moving at an angle. Formula (42) nevertheless is the answer.

Let's use the standard notation

$$dF = F_x \, dx + F_y \, dy \qquad (43)$$

Are there any restrictions on what F_x and F_y can be in order that the right-hand side really be the small change and some genuine function F? Yes there are.

There is basically one restriction. The reader may have guessed that it has to do with the cross second derivative. Consider the quantity

$$\frac{\partial^2 F}{\partial x \, \partial y} \qquad (44)$$

This is the second derivative of F where we first differentiate with respect to y and then we differentiate the result

with respect to x.

It is a theorem of calculus that within a large class of functions it doesn't matter in which order we do the derivatives. It is true for all smooth surfaces we are concerned with in physics, eliminating only teratological examples of which mathematicians have the secret.

We presented briefly partial differential calculus in the interlude 3 of volume 1, in the collection *The Theoretical Minimum*, on classical mechanics. The reader who wants to refresh his or her knowleldge of partial derivatives and their geometric interpretation is invited to go back to it.

So we have

$$\frac{\partial^2 F}{\partial x \, \partial y} = \frac{\partial^2 F}{\partial y \, \partial x} \tag{45}$$

And that translates into the statement that

$$\frac{\partial F_y}{\partial x} = \frac{\partial F_x}{\partial y} \tag{46}$$

When we look at an expression like the right-hand side of equation (43), where someone has given us a function denoted F_x and another one denoted F_y, there is clearly no guarantee that equation (46) holds.

Or said another way, given any old functions $G(x,y)$ and $H(x,y)$, clearly in general *it won't be true* that

$$\frac{\partial H}{\partial x} = \frac{\partial G}{\partial y} \tag{47}$$

The condition that G and H have to satisfy, to be respectively the partial derivative with respect to x and the partial derivative with respect to y of a unique function F, is precisely equation (47). We will see in a moment some examples.

Now take F_x and F_y which are indeed partial derivatives of F with respect to x and with respect to y. They can be seen as the components of a vector. This vector has a name. It is the *gradient* of F. If you like to think of F as a scalar field, then the gradient is a vector field, derived from the scalar field.

And if these F_x and F_y are the components of a gradient, what is the statement that $\partial F_y / \partial x = \partial F_x / \partial y$? Let's write it this way

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0 \qquad (48)$$

Notice that left-hand side is a *curl*. It is the curl of (F_x, F_y). Whether they come from a gradient, or are more general functions like G and H, doesn't matter. It is true in general. In this case (F_x, F_y) or (G, H) is only two dimensional [12].

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12. We have met and used extensively curls in three dimensions in volume 1 of the collection *The Theoretical Minimum*, when we studied electric and magnetic forces in chapter 11. For any vector field $\vec{A}$ we define a new vector field $\vec{B}$, that is called the curl of $\vec{A}$, as

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

Then, conversely, we saw that starting from any magnetic field $\vec{B}$, because its divergence is zero, there exists a vector field $\vec{A}$ such that $\vec{B}$ is the curl of $\vec{A}$. Then $\vec{A}$ is called the vector potential of $\vec{B}$. The vector potential is not uniquely defined, etc.

If we had three functions F_x, F_y and F_z, or generally speaking (G, H, K), of x, y and z, then the left-hand side of equation (48) would be only the third component of the curl of (F_x, F_y, F_z), which would be a vector. There would be other components of the curl.

Now to answer the question "Are F_x and F_y really the gradient of a function F ?", the test can be reformulated : "Is the curl

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} \tag{49}$$

equal to zero or not ?"

There is another implication of the curl being equal to zero. It is intuitively obvious. Supppose we take a walk on the hilly terrain of figure 4 or figure 5 and we come back first of all *to the same point*. How much does F change ? It doesn't change at all.
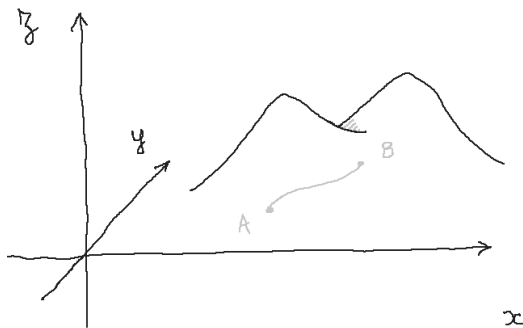

Figure 5 : Walk on the surface of F.

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Now let's ask a slightly different question : Supposing we take a walk from point A to point B, figure 5, how much does F change? Well, one answer is just the difference of F at the end point and at the starting point of the walk, that is $F(B_x, B_y) - F(A_x, A_y)$ with obvious, although heavy handed, notations.

But another answer is to add up all of the little incremental changes in F as we move from one point to another. This can be written

$$\Delta F = \int F_x dx + F_y dy \qquad (50)$$

This integral, calculated along the curve between A and B in figure 5, is the change in F.

Now what would happen if we chose another path to go from A to B? Would we get the same answer for the change of F? Yes we would, because F is just the altitude. If we go from A to B on one path or on another path, the change in the altitude is the same.

So that says that the line integral of equation (50) doesn't depend on what path we take.

Is it true in general for any F_x and F_y? In other words, if we take any function $G(x, y)$ multiplying dx and any function $H(x, y)$ multiplying dy, is the line integral

$$\int G dx + H dy \qquad (51)$$

independent of the path used to calculate the integral?

You have probably already figured out the answer. But before we explain it, let's look at an example. It is sort of a silly example but it is a concrete one.

We are going to do this operation by driving our car from one point to another along two different trajectories. And what we are interested in is not the change in the altitude but the change in the reading of the gasoline gauge. We want to know how much gasoline we use.

Does the amount of gasoline we use depend on the route that we take? Of course it does. For example, suppose A and B are at the same altitude. If we take a route from A to B that keeps us at the same altitude at all times, we will use less gasoline than if we go over a hill to reach B from A.

Another way to say this, incidentally, is that if we are going around in a closed loop, starting from one place and coming back to the same place, the net altitude won't change. But what about the gasoline in the tank? Not only will it depend on the route we take, but it certainly won't come back to the same value afterwards.

Nevertheless, the change in the fuel – now F stands for fuel [13] – can be written in the form of expression (51). From any point (x, y), how much fuel we will use to go a little distance dx and then how much fuel we will use to go a little distance dy on the terrain? It depends on the point (x, y) and can be written as a differential

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13. We should take this with a grain of salt, because now F is longer a function of (x, y). It is the reading of the gasoline gauge.

$$G(x, y) \ dx + H(x, y) \ dy \qquad\qquad (52)$$

But it is not the differential of some function.

If it were the differential of a function F, as in equation (43), then going around in a loop the total change would always have to be zero.

Another example, not using a car but walking, would be "how tired do we get, going from A to B?" Again, it would depend on the path used. We can even make the approximation for simplicity, if we like, that we don't get tired at all if we don't change altitude along the path. Then there would be some paths going from A to A consuming no energy. Yet if we climbed over a hill before coming back to the same place, we would obviously get tired. As all of us know, not only going uphill but going downhill is tiring.

Of course, if we could somehow get "untired" by going downhill, then maybe it would be possible to go around a loop, whatever path we take, and come back without net extra fatigue. That is to some extent how electric bicycles work. But then the measure of tiredness would be nothing more than the measure of potential energy according to altitude. And the potential energy is simply proportional to altitude. So we would be back in the case of looking at the function F in figure 5.

Thus in general, when $G(x, y)$ and $H(x, y)$ are not constrained in anyway, going around in a closed loop we do get a change. The line integral $\int G dx + H dy$ is not zero. Furthermore it depends on the path followed.

There is a complete mathematical equivalent to the question of whether line integrals around closed paths give zero. It is the question of whether the curl of (G, H) is equal to 0.

The condition that, for all (x, y), the following curl

$$\frac{\partial H}{\partial x} - \frac{\partial G}{\partial y} = 0 \qquad (53)$$

is equivalent to the condition that, for any closed loop,

$$\int_{\text{loop}} G dx + H dy = 0 \qquad (54)$$

They are the same mathematical statement.

And they are equivalent to the statement : G and H are respectively the partial derivative with respect to x and the partial derivative with respect to y of some function F of x and y.
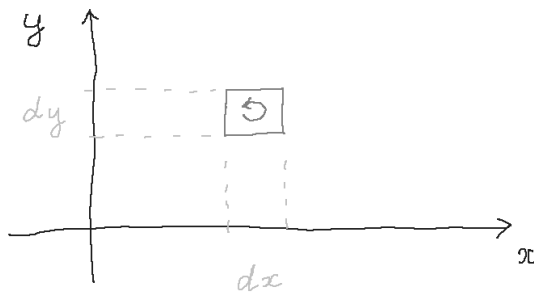

Figure 6 : Calculating the curl of (G, H) is like going around a little loop and calculating the total change in the differential given by expression (52).

In fact the curl on the left-hand side of equation (53) has to do with going around a *little loop*, figure 6, and asking how much things change. The change is the curl itself.

And the line integral on the left-hand side of equation (54) has to do with going around a *big loop*.

The whole point of this section is that not every pair of functions F_x and F_y – which we prefer to denote then G and H – enable us to define the differential of a function F.

They can always be used to define the following differential element

$$G \ dx + H \ dy \tag{55}$$

but that differential is not necessarily the differential of a function.

When G and H are the partial derivatives F_x and F_y of a function F, and therefore expression (55) is the differential of a function F, it is called an *exact differential*. It is also sometimes called a total differential.

And when the curl of (G, H) is not zero, that is when G and H are not partial derivatives of a function F, with respect to x and y, then the differential given by expression (53) is called an *inexact differential*.

Question : It this related to conservative forces ? Answer : When F_x and F_y are the components of a force field, yes, the condition that their curl be zero is equivalent to the conservativeness of the force field. But we don't want to

get into forces here. We want to concentrate on the idea that some differentials are exact and others are not.

Question : Is this related to curvature ? Answer : Yes, it is. The reader is invited to go to volume 4, in the collection *The Theoretical Minimum*, on general relativity, to study curvature and it relation to curl. But we don't want to get into curvature here either. Again we are only interested in some differential calculus concepts that we shall use in statistical mechanics, when we study heat and work.

So some $G(x, y) \ dx + H(x, y) \ dy$ are exact differentials of a function F. In that case they pass the curl test – the test being "Is the curl of (G, H) equal to zero ?", equation (53). Others are just small changes involving two functions, $G(x, y)$ multiplying dx and $H(x, y)$ multiplying dy.

The gasoline in the car is a well-defined quantity. You may be at some point (x, y) and read a certain value of the gasoline gauge. Then if you move on the hilly terrain by a small dx and a small dy (when projected onto the horizontal plane), the fuel gauge will change by the amount $G(x, y) \ dx + H(x, y) \ dy$. Yet, the reading of the gauge doesn't depend on (x, y). You may come back, after a closed trip, to the same point (x, y). The gauge will read a different value.

The gasoline in the car is a thing you carry with you. When you move along a given path, it will change in a definite way, depending on the path.

The reading of the gasoline gauge is simply not a function of where you are. It is a function of the whole path which

you took to get you where you are.

Inexact differentials usually have to do with changes that depend not only on the end points of a trajectory, but depend on the whole trajectory, like getting tired or the amount of fuel in the tank.

We now know what exact and inexact mean. Let's see some examples. To start with let's try for instance

$$F_x = y$$
$$F_y = x$$

(56)

where we could have written $H(x, y) = y$, and $G(x, y) = x$, because we don't mean that necessarily F_x and F_y are partial derivatives.

The point is precisely to check whether they are the partial derivative with respect to x and the partial derivative with respect to y of a function F. So let's do the curl test.

What is the partial derivative of F_x with respect to y? It is 1. And what is the partial derivative of F_y with respect to x? It is 1 too. So we do have

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0$$

(57)

The two functions defined by equations (56) pass the curl test.

It must mean that F_x and F_y are the partial derivatives of some function. Can the reader guess what function, F_x and

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F_y are the gradient of?

In this example F is the function xy, or the function xy plus any constant. So (F_x, F_y) is really the gradient of some function. And the line integral from A to B

$$\int_A^B ydx + xdy \qquad (58)$$

doesn't depend of the path taken.

Second example : What about the functions F_x and F_y defined below?

$$F_x = y$$
$$F_y = -x \qquad (59)$$

It would be a perfectly good rule about the small differentials of the amount of gasoline in your car[14]. But it does not define a function. How do we know that? Because it doesn't pass the curl test.

If we took a little excursion on the horizontal plane coming back to the same point, and we calculated the line integral

$$\int_{loop} ydx - xdy \qquad (60)$$

we would find that it is not zero in general.

Moreover we could not look at a corresponding round trip on a surface like in figure 5, because there is no such surface.

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14. Although a bit far-fetched.

Now we are ready to talk about heat and work.

Heat and work

Heat and work have to do with energy. And they have to do with the changes in energy. So let's define them.

For convenience we are thinking about a gas, because it is easy to imagine the particles, their positions and movements, the possible states, the velocities, the energy, the volume, the pressure, the thermodynamical state of the system, and so forth. But it doesn't have to be a gas. It could be a liquid, a solid, or other things like a plasma, etc.

So we consider the time-honored box of gas with a piston, figure 7.
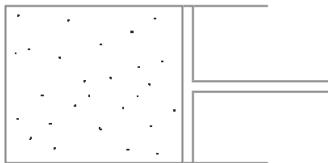

Figure 7 : Box of gas with a piston.

We can push the piston or pull it. It allows us to change the volume V of the gas, which is a control parameter.

What are the independent variables? There are two independent variables. We could take them to be the temperature and the volume. Or we could take them to be the energy of the box and the volume. In fact, beside volume, we could take any one among the variables Z, E, S, β, T or A. Take this opportunity to make sure you know what each of them are, how they are calculated, what are their basic properties.

Any pair X and V is enough to determine the thermodynamic state of the gas [15]. We are going to pick S and V as the independent variables. Knowing how much entropy the box presents, and how much volume it has, completely determines the state of the system.

Let's think about the energy. Consider the change in energy if we change the volume a little bit without changing the entropy. Do you remember how we call a process in which the entropy doesn't change? An adiabatic process.

It is also called a reversible process. But we will study the link between entropy and reversibility in chapter 7.

In an adiabatic process the following relationship holds

$$dE = -PdV \tag{61}$$

Remember that it is even how we defined pressure in general, see equation (22) of chapter 5.

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15. Not to be confused with the random states ω_i's. What we call the thermodynamic state of the system is for instance its average energy E, and its volume. It determines everything else if we look not at the molecular level but at a global level, i.e. at the human scale.

Formula (61) is the change in the energy of the gas if we change the volume slowly and without allowing any heat to flow in or out, that is with no change of entropy – reversibly if you like.

A more explicit way to write formula (61), stressing that P is the rate of variation of E with respect to V *at fixed entropy*, is

$$\left.\frac{\partial E}{\partial V}\right|_S = -P \qquad (62)$$

Now what about the change in energy if we keep the volume fixed but we add a little bit of heat ?

It doesn't matter where that extra energy comes from [16]. We have got it from somewhere and we dump it into the system whatever way. We could do it by putting a flame under the box and heating it a little bit.
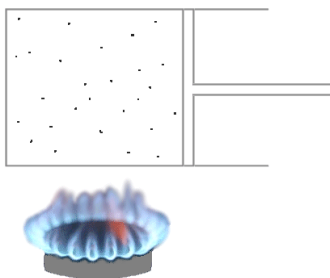

Figure 8 : Heating the gas at fixed volume.

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16. It just doesn't come from compressing the gas with the piston, since we keep V fixed.

Then what is the change in energy ?

In that case without changing the volume, it is equal to the temperature times the change in the entropy

$$dE = TdS \qquad (63)$$

That is basically the definition of temperature. Keeping all control parameters fixed, the change of energy is by definition the temperature times of change in entropy.

Entropy we defined independently, probabilistically. And we showed that the temperature defined by equation (63) is also $1/\beta$, where β was one of the two Lagrange multipliers in the problem of maximising the entropy, see chapter 3.

Now supposing we change both the volume and the entropy. We could imagine the process as a sequence of little changes, each of them being a little change of the volume at fixed entropy followed by a little change of the entropy at fixed volume.

Along such a process, according to the first law of thermodynamics, we have for each little change of E

$$dE = -PdV + TdS \qquad (64)$$

So we can do a general process involving both independent variables V and S. Equation (64) gives the incremental change in E along the path we follow in the (V, S) space.

The equation giving dE just expresses energy conservation : if we inject a little bit of energy in the form of work and of

heat, the sum is the change of energy in the box.

Incidentally $-PdV$ is the work part. It is called dW. And TdS is the heat part. It is called dQ.

$$dE = dW + dQ \qquad (65)$$

Q stands for heat. Where does the Q come from? May be from the word calorie, that someone misspelled qualorie :-)

At any rate, $TdS = dQ$. And that is the definition of heat. We can change the energy by changing the entropy, at fixed volume. That is an irreversible change. It could correspond to just dumping some heat in.

And $-PdV = dW$. It is the change in energy from changing the volume at fixed entropy.

Who is doing work on whom incidentally? Is dW the work done on the gas, or is it the work done by the gas on the piston? Answer : dW is the change in the energy of the box. It is the work received by the gas. Therefore it is the work done by the piston on the gas.

Concerning equation (65), the question is whether Q is really a function. Or in other words, is dQ really an exact differential? Is there such a thing as the heat of a system?

Let's stress first of all that if we know the volume and the entropy, we know everything about the system. As said, volume and entropy is thermodynamically enough to know everything. It tells us the temperature, it tells us the energy E, it tells us everything.

Now here is the problem. If we think of going from one value of volume and entropy to another, taking a walk in a volume-entropy space, the question is whether the heat that we have to put in to go from one point to another depends on the path or doesn't depend on the path.

Another way of saying it is this : if we go around a closed loop – we put little bits of heat in, we put little bits of work in, we take little bits of work out, we take little bits of heat out –, at the end of the day, if we come back to the same point, is the total amount of heat that we put in 0 ?

Is it zero as it would be if the heat were a real function and we came back to the same point, or does it depend on the path that we took ? The answer is : *it depends on the path.*

We are going to prove that. We are going to prove that dQ is not an exact differential. Neither is dW.

What is true is that, if we take a system through a cycle, or a series of steps, and come back to the same state, then the total energy that we put into it is 0. If we bring it around and come back to the same point in the (V, S) space, the energy will come back to the same value. E is a genuine function of V and S.

But the heat that we put in, all the work that we take out, or whatever, will depend on the route that we took.

We are assuming that the path that we follow, whichever it is, is covered slowly, so that we stay in equilibrium.

Let's prove the path-dependency of Q and W. Remember that the independent variables we chose are the entropy S and the volume V. First we rewrite equation (65) as

$$dQ = dE + PdV \qquad (66)$$

Now we are going to change the independent variables from S and V to E and V.

However we move from one point to another, dQ will be equal to the small change in energy plus the pressure times the small change in volume.

Now *let's assume that Q is a real function of E and V.* That would imply that dQ is an exact differential. First of all, equation (66) would imply that

$$\frac{\partial Q}{\partial E} = 1 \qquad (67)$$

Similarly

$$\frac{\partial Q}{\partial V} = P \qquad (68)$$

That is what would hold if there really was a function Q the differential of which was equation (66).

Are equations (67) and (68) consistent? How can we test out whether there really is a function Q that satisfies this? Answer : we can test the curl.

If there is function Q, the curl of Q_E and Q_V must be zero. That is the application to Q, E and V of what we established in general in the previous section for F, x and y, see

equation (48) et seq.

So we want to calculate

$$\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial E}\right) \tag{69}$$

and

$$\frac{\partial}{\partial E}\left(\frac{\partial Q}{\partial V}\right) \tag{70}$$

and compare them.

Expression (69) is equal to 0, while expression (70) is equal to $\partial P/\partial E$.

If there really was a function Q, in other words a function that didn't depend on how you move from one place to another, it would have to say that

$$\frac{\partial P}{\partial E} = 0 \tag{71}$$

That is what would be true if the curl of Q_E and Q_V was equal to zero [17]. This equation (71) says that the partial derivative of P with respect to E when we keep the volume V constant is zero.

Would you believe that if you have a box of gas and you change the energy in the box of gas, that the pressure

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17. Q_E is the notation for $\partial Q/\partial E$ and Q_V is the notation for $\partial Q/\partial V$.

doesn't change ? No, of course it does.

Let's check it for an ideal gas. We have done the calculation for an ideal gas. We found for the pressure

$$P = \frac{NT}{V} \tag{72}$$

That is one equation. And the other equation we want is the equation for the energy

$$E = \frac{3}{2} NT \tag{73}$$

So we can write

$$P = \frac{2}{3} \frac{E}{V} \tag{74}$$

In view of this equation for P in terms of the independent variables E and V, when we change the energy at fixed volume does the pressure change ? The answer is yes. At fixed volume, the pressure is proportional to the energy. So equation (71) is simply not true.

Therefore the curl test has failed, since following a reductio ad absurdum we saw that assuming that the curl was zero lead to a false statement.

Consequently,

There is no such thing as Q being a function of where we are, or what the thermodynamic state of the system is.

It depends on how we move from one place to another in the space (E, V), or equivalently in the space (S, V), or (T, V), etc.

In other words,

The amount of heat that we have to put into the system, in order to change it from one state to another state, depends on the path that we are going to take.

That is why heat is not a good description of the system. It is as good as asking how tired you are to determine your altitude. It depends on the path you took, not just on your change of altitude. Heat is also like that. And so is work.

Only the combination of the two of them is really a function of the state of the system. A function of the state of the system means is a function of temperature and volume, or energy and volume, i.e. something that is determined by the state the system is in.

This is subtle stuff. It is tricky. It is natural to be a bit confused by it at first. Only by going over it, studying it, asking yourself many small questions and answering them, will it becomes clear.

Why should it be the case that the heat that we have to put in, versus the work, to get from one place to another should not depend on how we go there ?

This fact, that the heat Q and the work W are not functions simply depending on the state of the system, is related to all sorts of other physical concepts and facts : the operation

of steam engines, efficiency, hysteresis, memory in systems, etc.

At the end of this section on heat and work, the point to remember is that *heat is not a property of the system*, that would depend only on T and V for instance, figure 9.
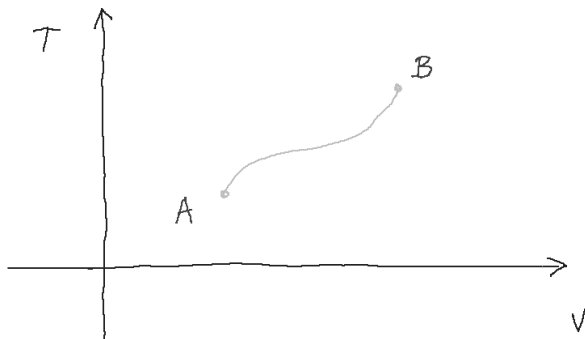

Figure 9 : Path in the (T, V) space.

The total energy E of the system depends only on where we are. But ΔQ and ΔW, when we go from A to B, depend on the the path we follow.

It is similar to the following fact : Our state of tiredness after a trek is not a property of the landscape – in the sense that it is not a property of where we stand –, it is a property of us and the trek we went over.

Let's conclude the section and the lesson with this summary. If we have a system in a state A at the beginning of an experiment, and in a state B at the end of the experiment, and in each of these two states we know everything

about the system, we certainly can know the variation in its energy. It is simply $E_B - E_A$. It is naturally the integral over the path we followed of dE.

But, if we don't know the actual path we followed, if we just know A and B, then we cannot know how much heat ΔQ we put into the system and how much work ΔW we put in it. We only know that

$$\Delta E = \Delta Q + \Delta W \qquad (75)$$

That is what makes heat and work more subtle than simply energy.