# Lesson 5 : Pressure of an ideal gas and fluctuations

*Notes from Prof. Susskind video lectures publicly available on YouTube*

### Introduction

Over the last four lessons, the reader has seen how subtle statistical mechanics can be. It is full of all these fancy calculus tricks, with sometimes very little intuition about what is really going on. It is all in the calculus tricks then.

In this lesson we are going to study the problem of pressure of an ideal gas. Intuitively we know where the pressure comes from. It comes from the molecules bouncing against the walls of a system. We could calculate it by just using the average energy of every molecule. We already found that $E_{particle} = 3/2 \ kT$.

So we know how fast they are moving on the average. We can estimate how many of them are moving in each direction because they are pretty isotropic. And that leads to a calculation of the force exerted on a wall using Newton's law in its form $F\Delta t = m\Delta v$.

We might wonder, incidentally, if the molecules near the wall are isotropic. After all the presence of the wall influences what is going on near it. And we might think : well, maybe there are more going horizontally to the wall than going vertically, that is parallel to the wall, and then going horizontally the other way.

It turns out not to be true. Even very close to the wall, the distribution of velocities is still pretty isotropic. But we might wonder whether that is a principle or just an accident.

We might also wonder whether the velocities near the wall happen to be different than the velocities in the interior far

from the wall – in which case we would be making a mistake by just taking the good old $3/2$ $kT$ for every molecule no matter where they are.

It turns out we are not making a mistake. But how do we know we are not making a mistake?

We know from statistical mechanics. We know from an honest set of principles, which don't use intuitive pictures of molecules hitting the wall and so forth, but which really use the basic foundations of statistical mechanics.

The foundations of statistical mechanics are mathematical. They are not complicated. They are not hard. But they are very mathematical.

So we emphasized over and over that in situations where we purposefully give up intuitions because we are not sure they are correct, such as for example whether the velocity distribution near the wall is the same as in the interior of the box, then we rely on the mathematics.

When we are writing the mathematics, we are sort of on autopilot using the rules. We first figure out what we want. Then we just start cranking, using here and there whatever tricks we have, until we suddenly run across a formula that we recognize as meaningful, interesting and important.

That is just the way statistical mechanics is. You get good at it after a while. The great physicists that I have known all were very good at it. I don't mean people who just studied statistical mechanics, I mean all the very good physicists somehow love thermodynamics. Why? It is fun and full of

surprises. It abounds with surprising relationships which suddenly fit together, and tell you some physics.

That is the attraction of statistical mechanics for many of us. Einstein was the grandmaster of thermodynamics [1]. Feynman was a grandmaster of it. I am a grandmaster of it. Well, maybe, maybe. And it is good stuff.

Question : Once we have done the mathematics of a problem, can't we check them with our intuition ?

Answer : Yes we can, but what we are really doing is checking our intuition not the mathematics.

For instance, it could conceivably have been wrong that the distribution of velocities near the wall was the same as in the interior. We don't want to rely on that. We want to use a set of fundamental principles, and then rules and mathematics to calculate the pressure.

You don't want to go through all the mathematics, then say : Well, I think I proved that the rules of calculus work out ok, because they agree with my naïve intuitions about the way molecules behave near the wall. It is the other way. You are checking your intuitions from the mathematics.

So we could calculate the pressure on the walls as follows. Let's not even talk about averages. Let's say the room is filled with molecules, all moving with the same velocity $v$ satisfying

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1. Statistical mechanics is also called statistical thermodynamics.

$$\frac{1}{2}\, mv^2 = \frac{3}{2}\, T \qquad\qquad (1)$$

using our favorite units such that temperature doesn't carry Boltzmann constant with it.

We know the mass of every molecule and we know the temperature. Therefore we know the velocity of every molecule.

When we know the velocity of every molecule, we can compute the force on the wall by asking how many molecules per unit time hit the wall – if indeed they are distributed uniformly, which we don't know for sure.

If we know that the directions of their velocities are isotropic, we can calculate the number of collisions on the wall per unit time and the momentum delivered by each particle to the wall.

Particles bounce off the wall and the perpendicular component of momentum which was originally going to the wall is now going away from the wall. We can calculate the change in momentum. It corresponds to a force exerted by the wall on the particles, and therefore by the particles on the wall too.

Of course force is rate of change of momentum[2]. And so we can calculate the force on the wall. Pressure is the force per unit area.

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2. In fact that defines the *average force over time*. Indeed, everybody knows that hail does not feel the same as rain.

And so we can calculate that. It is fun. We have done it in volume 5, in the collection *The Theoretical Minimum*, on cosmology.
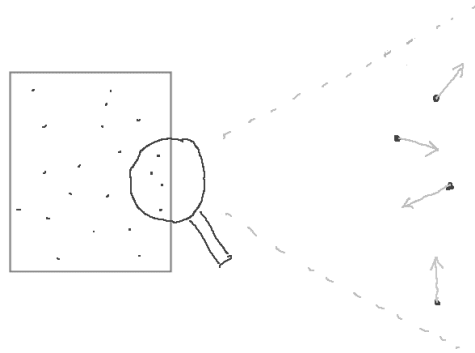


Figure 1 : Box filled with molecules exerting pressure on the walls. And view with a magnifier.

The reader can try to do it himself or herself. The method, when the molecules are assumed to be point masses isotropically distributed in position and velocity and completely free – no potential energy, no collisions between molecules, and so forth –, yields the right answer.

**Exercise 1 : Consider a volume filled with molecules, figure 1. The mass, velocity, and density of the molecules are given parameters, $m$, $v$ and $\rho$.**

**Using the formula $F\Delta t = m\Delta v$, calculate the pressure on the wall.**

> **Express it in terms of the density and the temperature.**

But that is not really good enough. We really want a set of rules which are good enough that they can take into account collisions between the molecules. Collisions between the molecules can upset the whole thing a lot. And they do.

We want a set of rules which is robust, which doesn't depend on the detailed oversimplified model of a free gas. Free gas means a gas of particles where the particles are not interacting with each other, that is an ideal gas

So the ideal gas is a model that is easy. It is easy to do things with. But it is not very general.

The rules of statistical mechanics are very general. And they would be sufficient – if you can do the calculations – to calculate the relationship between the pressure and other variables very generally.

What is it that we want? We want something called the *equation of state*.

It will relate the pressure to other thermodynamical variables. To establish that equation we need some preliminary concepts and results.

## Control parameters

We would like to calculate or know what the pressure is as a function of temperature, volume, and possibly other relevant thermodynamics variables.

What is it that determines the pressure of the gas in the room where we are? Basically the temperature and the volume. That is about it.

If we consider that the number of molecules in the room is fixed, if we don't let it vary, then the pressure is a function of the temperature and the volume.

We would like to calculate the pressure in terms of those variables. So we need a theory. We need a set of principles.

We are going to describe those principles and work out the pressure of an ideal gas, with no intuition whatever, no picture in our minds of what we are doing.

I'm not saying that pictures in our mind aren't good things for understanding physics. But there are times when you want to suppress the pictures and simply go with the principles and the mathematics.

And statistical mechanics is such a theory, because we want the rules to be general.

Let's recall a few statistical thermodynamics facts and formulas that we worked out before and that we will use. The first one has to do with entropy. Whatever the system and the model are, we have

$$S = -\sum_i P_i \ \log P_i \tag{2}$$

And if the distribution is the Boltzmann distribution, then

$$P_i = \frac{1}{Z} \ e^{-\beta E_i} \tag{3}$$

In that case equation (2) rewrites

$$S = -\sum_i \frac{1}{Z} \ e^{-\beta E_i} \ (-\beta E_i - \log Z) \tag{4}$$

The minus signs cancel, so this is also

$$S = \sum_i \frac{1}{Z} \ e^{-\beta E_i} \ (\beta E_i + \log Z) \tag{5}$$

Because of the two terms in the parentheses, this is a sum of two sums. Pulling $\beta$, the first sum is the expression of the average energy. So we get

$$S = \beta E + \sum_i \frac{1}{Z} \ e^{-\beta E_i} \ \log Z \tag{6}$$

Then in the remaining sum, the $1/Z$ and $\log Z$ can be pulled out of the sum too.

$$S = \beta E + \frac{\log Z}{Z} \ \sum_i e^{-\beta E_i} \tag{7}$$

Finally the last sum is the definition of $Z$ itself. It cancels with the $Z$ in the denominator. We arrive at

$$S = \beta E + \log Z \qquad (8)$$

Now there is another standard way to write this. We note that $\beta$ is the inverse of temperature. We multiply both sides by $T$. Then we put on one side $E - TS$, and on the other side what it is equal to.

$$E - TS = -T \log Z \qquad (9)$$

The left-hand side has a name. It is called the *Helmholtz free energy*. It occurs over and over in physics. For us it is only important because it appears in equation (9) which is in another guise equation (8), and we are going to use it a lot.

The Helmholtz free energy is denoted $A$.

$$A = E - TS \qquad (10)$$

Quantities are given names in physics when they occur over and over again. We are going to find out that $A$ plays a leading role in calculating the pressure, as well as all kinds of other things.

So $A$ is another thermodynamic variable. We already had the average energy $E$, the entropy $S$, the temperature $T$, etc. We now have a new variable called the Helmholtz free energy.

Remember that all these variables are dependent on each other. They are all dependent on any one of them, which can be chosen as the independent variable. At times it is in

turn $E$, or $\beta$, or $T$, etc.

We are going to introduce yet another variable into the problem. Variables of this next kind are often called *control parameters*.

Control parameters are parameters that we, as experimenters, can easily change. They are macroscopic parameters. We are not trying to change details of one molecule at a time.

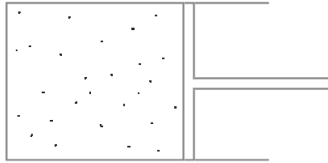An example of control parameter is the volume of the container of our gas, figure 2.



Figure 2 : Controlling the volume of the gas with a piston.

We can move the piston back and forth, and in the process change the volume of gas. So volume is a control parameter.

Other control parameters could be the magnetic field on a system, the electric field on a system. Is pressure one ? No, pressure is not a control parameter.

We shall see that variables come in pairs. One is usually called the control parameter and the other is called the *conjugate thermodynamical variable*.

Pressure and volume are closely connected. They form a conjugate pair. We can have a pressure gauge inside the volume of gas in figure 2, and by moving the piston change the pressure. But of course what we are doing is changing the volume, and the response is a change in pressure.

On the other hand, changing the number of molecules inside the box would be a control parameter.

Notice that we talk about particles of gas inside the volume, because it is easy to imagine, particularly when we compress it. But it is not a fundamental assumption. It could be anything. It could be a liquid. It could be a solid. We would be squeezing on the solid.

It doesn't have to be homogeneous either. We could have inside the box, in thermal equilibrium at the boiling temperature, a mix of steam and water simultaneously. That would be neither a gas nor a liquid. And if the box was in a gravitational field, the liquid might sit at the bottom and the gas at the top. It would still be thermal equilibrium. Same comment for a mix of two gases or anything.

That is why it is important to have general methods. You cannot use the ideal gas law for a solid inside the box!

## A mathematical result in differential calculus

We need a little mathematical theorem in differential calculus. Although totally unintuitive, it is very simple. So maybe it should only be called a lemma.

Suppose we have two functions of two variables. One function will be called $E$. Eventually it will be the energy. And the other function will be called $S$. That will be for entropy. But the mathematical theorem we are going to prove is a very general result in calculus.

The independent variables are going to be called $T$ and $V$. There again, they will have interpretations that the reader can guess. But for the moment let's just think of them as independent variables, that is, if we prefer, parameters that we can control from the outside.

If we knew the independent variables $T$ and $V$, and knew enough about the system, we could calculate the dependent variables $E$ and $S$.

The theorem says that the following relationship always holds

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T \tag{11}$$

The notations call for some comments. The left-hand side means the partial derivative of $E$ with respect to $V$ *keeping S fixed*. Usually we would talk about the partial derivative of $E$ with respect to $V$ keeping the other independent variable, namely $T$, fixed. But here it is different, in the

computation of the left-hand side the quantity being kept fixed is the other dependent variable $S$.

On the right-hand side, it begins with the more standard partial derivative of $E$ with respect to $V$ keeping $T$ fixed. And the other two partial derivatives are interpreted according to what the precise notations are, and the same explanations.

Here is the proof. It is a lovely little proof. I like it so much because I figured it out myself. You sort of fall in love with those little things that you figure out yourself when you are young.

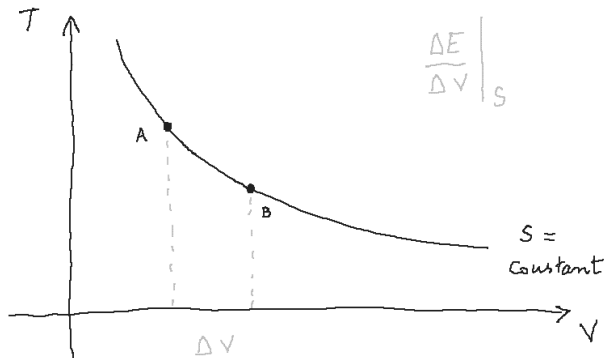On the plane of the two independent variables, $T$ and $V$, let's draw one contour line of $S$, figure 3.



Figure 3 : One contour line of $S(V, T)$. And two points at different values of $V$, on that contour line.

The contour line doesn't have to have necessarily this shape. It can be any shape. We just represented one shape to sustain the subsequent reasoning. The important point is that

$S$ has a fixed value along the contour line shown in figure 3.

Now we want to calculate the rate of change of $E$, the other dependent variable, with respect to the volume $V$, but along that line of constant $S$.

Let's begin with the following ordinary formula of calculus relating a small increase in the dependent variable $E$ to small increases in the independent variables $V$ and $T$ and the corresponding partial derivatives

$$\Delta E = \left.\frac{\partial E}{\partial V}\right|_T \Delta V + \left.\frac{\partial E}{\partial T}\right|_V \Delta T \qquad (12)$$

We use the notation $\Delta E$ instead of $dE$ only to remind ourselves that we are looking at small variations and ratios of small variations. We could use the notation $dE$, $dV$ and so forth in equation (12). And of course derivatives are *limits* of ratios.
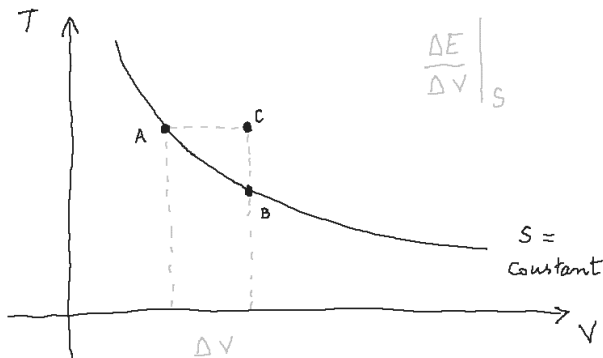


Figure 4 : $E(B) - E(A) = [\, E(C) - E(A)\, ] + [\, E(B) - E(C)\, ]$.

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Forgetting temporarily that $A$ and $B$ are points on a specific curve, equation (12) is valid for any points $A$ and $B$ nearby. It says that the variation in $E$ going from point $A$ to point $B$, namely $\Delta E$, is equal to the variation in $E$ going from $A$ to $C$, plus the variation in $E$ going from $C$ to $B$, figure 4. That is the general meaning of equation (12).

Our objective is not to prove equation (12), which is an ordinary formula of calculus that we know is true, but to prove equation (11). The first term on the right-hand side of equation (12) is the same as the first term on the right-hand side of equation (11). So it is the second term of equation (12) that we want to manipulate, and see what it is when we move on a curve of constant $S$.

For the second term on the right-hand side of equation (12), we can write

$$\left.\frac{\partial E}{\partial T}\right|_V \Delta T = \left.\frac{\partial S}{\partial T}\right|_V \left.\frac{\partial E}{\partial S}\right|_V \Delta T \qquad (13)$$

This is also true if we divide by $\Delta V$

$$\left.\frac{\partial E}{\partial T}\right|_V \frac{\Delta T}{\Delta V} = \left.\frac{\partial S}{\partial T}\right|_V \left.\frac{\partial E}{\partial S}\right|_V \frac{\Delta T}{\Delta V} \qquad (14)$$

So far, this comes from equation (12), that is, it is true for any points $A$ and $B$. Nowhere have we used yet the fact that we are moving on a line of constant $S$.

Now we are going to use the fact that we are moving on a line of constant entropy. Why we are interested in constant entropy ? That doesn't come from the calculus manipula-

tions we are doing. But it will come out soon enough.

We are moving from $A$ to $B$ in figure 4. They are on a curve $S = \text{constant}$. This curve is characterized by a slope between $A$ and $B$. That slope is simply $\Delta T/\Delta V$. Let's use a little bit of a calculus to see if we can work out something about $\Delta T/\Delta V$.

So let's write down the condition that we are moving on a line of constant $S$. Along that curve we have $\Delta S = 0$. But we also have the general formula that always holds

$$\Delta S = \left.\frac{\partial S}{\partial V}\right|_T \Delta V + \left.\frac{\partial S}{\partial T}\right|_V \Delta T \qquad (15)$$

So on the line of constant $S$ we have

$$0 = \left.\frac{\partial S}{\partial V}\right|_T \Delta V + \left.\frac{\partial S}{\partial T}\right|_V \Delta T \qquad (16)$$

Now we are going to be able to get a formula for $\Delta T/\Delta V$ in terms of the partial derivatives in equation (16).

Dividing by $\Delta V$ and reorganizing a bit – noting that the inverse of $\partial S/\partial T$ at constant $V$ is simply $\partial T/\partial S$ at constant $V$ – we get

$$\frac{\Delta T}{\Delta V} = -\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial T}{\partial S}\right|_V \qquad (17)$$

Now we are going to plug it into formula (14) which comes from the second part of the right-hand side of equation (12).

$$\frac{\partial E}{\partial T}\bigg|_V \frac{\Delta T}{\Delta V} = -\frac{\partial S}{\partial T}\bigg|_V \frac{\partial E}{\partial S}\bigg|_V \frac{\partial S}{\partial V}\bigg|_T \frac{\partial T}{\partial S}\bigg|_V \qquad (18)$$

By a great stroke of luck, on the right-hand side, the first and the last partial derivatives are inverse of each other. So their product is 1. And formula (18) simplifies into

$$\frac{\partial E}{\partial T}\bigg|_V \frac{\Delta T}{\Delta V} = -\frac{\partial E}{\partial S}\bigg|_V \frac{\partial S}{\partial V}\bigg|_T \qquad (19)$$

Finally, going back to equation (12), dividing both sides by $\Delta V$, we reach

$$\frac{\partial E}{\partial V}\bigg|_S = \frac{\partial E}{\partial V}\bigg|_T - \frac{\partial E}{\partial S}\bigg|_V \frac{\partial S}{\partial V}\bigg|_T \qquad (20)$$

Q.E.D. [3]

The left-hand side stipulates that we are moving on a line of constant $S$. And we used that fact on the right-hand side when we transformed equation (15) into equation (16) and then continued to turn the crank from there.

The reader may be concerned that the derivative of entropy with respect to temperature, which we eliminated in equation (18), should not be zero. For most systems in most circumstances it is true. There are some special cases where it is not true. Then we have to be more careful.

But generally speaking entropy is a monotonic function of temperature, always increasing. The reason is simple. As

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3. Abbreviation of *Quod Erat Demonstrandum*, the latin expression to mean *what was to be proved*.

you increase the temperature, the Boltzmann distribution gets broader. As you decrease the temperature it gets narrower. And entropy is just a measure of that width.

So we have established two facts : the link between Helmholtz free energy, temperature and the partition function, equation (9) ; and the above lemma.

The other facts that we need have to do with pressure.

### Pressure

First of all we would like to emphasize that pressure is just one special case of a response to a control parameter.

We need to understand what pressure really is. Going back to figure 2, we have a cylinder, gas inside it, and a piston. The molecules of gas are hitting the walls – in particular the piston, exerting pressure on it.

Supposing we move the piston a little bit, the pressure in the interior does work on the piston. If we move the piston out, the pressure pushes out in the same direction as the displacement. Then there is positive work done on the piston.

Where does that work come from ? Work is a form of energy [4].

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4. The other fundamental form of energy, in thermodynamics, is heat. In this course, we shall understand the difference between work and heat. And we shall see that heat, like entropy, is a very special characteristic of a system.

The work done on the piston is equal, with an opposite sign, to the change in energy inside the cylinder.

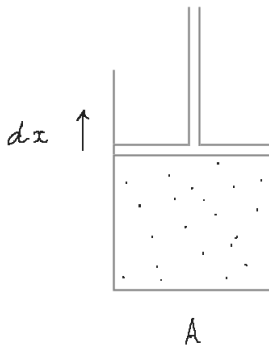For convenience, let's redraw figure 2 with the piston moving vertically, figure 3.



Figure 5 : Cylinder with a piston moving vertically. The area of the base of the cylinder is $A$.

Imagine that the piston rises a little bit, by an amount $dx$. That means, in this case, that there has been an increase in the gravitational potential energy of the piston. That is called the work done on the piston by the pressure.

And by energy conservation, any work that is done on the piston must be taken away from the gas. So energy conservation tells us that the change in energy of the gas is the opposite of the work done on the piston.

We also have to imagine something else : first of all, we have to do this slowly. Some odd things can happen if we do it fast. For example we could pull a piston out so fast that no molecule has a chance to hit the piston as it is moving.

Then, doing that operation, there would be no pressure on the piston.

That is a rather extreme situation, of course, but it does illustrate that we want to define pressure by being able to average over many collisions. So we want to slowly move the piston.

Secondly, we want to make sure that no energy comes into the system from outside. In other words we want to insulate the walls of the system.

I remember, when I was an undergraduate, I learned the word *adiabatic*. I had no idea what it meant. But my professor of engineering told me that it means that a system is insulated from heat coming into it or out of it. Then later on, when I was in graduate school, another professor told me adiabatic means slowly. Well what adiabatic means is slowly and no heat comes into or out of the system.

If you move the piston *adiabatically*, then the change in the energy of the gas is, with a minus sign, the work done on the piston.

$$dE = -PA \, dx \qquad (21)$$

$PA$ is the force exerted on the piston, that is pressure times the area of the piston. It is the elementary definition of pressure : force per unit area. Then, multiplying that force by $dx$, we obtain the work done by that force. With a minus sign, it is the change of energy $dE$ in the cylinder chamber.

Now $Adx$ is the change in the volume of the gas. So we

write $Adx$ as $dV$, and equation (21) rewrites

$$dE = -PdV \tag{22}$$

We can use this equation to define pressure [5]. We then write

$$\frac{\partial E}{\partial V} = -P \tag{23}$$

The partial derivative notation is here to remind us that other variables are kept fixed. The only question is what do we keep fixed in considering this derivative. The derivative is the rate of change of $E$ with respect to $V$ under the circumstance that we do the operation adiabatically.

There is another aspect of the notion of adiabatic change. It has to do with the second law of thermodynamics, which we will come to.

The second law of thermodynamic says that the entropy of an isolated system in evolution always increases – except when it doesn't, in which case it stays the same. But it never decreases. Well, never say never, but never mind :-)

What are the processes where the entropy of an isolated system doesn't increase? Those are the adiabatic ones.

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5. Remember that Newtonian mechanics makes much use of the notions of force and work. But then a more modern and more powerful presentation of mechanics, closer to Lagrangian mechanics, doesn't use so much force and work as it focuses on energy. That is what we do here : pressure is no longer defined as force per unit area but as the rate of change of energy with respect to volume, with a minus sign. Of course the two definitions are totally equivalent.

This requires some explanation. We shall explain it from a quantum mechanical point of view. The only aspect we are going to use of quantum mechanics is that energy levels are discrete, nothing else. In other words, the $E_i$'s of the possible states of the system are definite energy levels in a dicrete collection.

So we have our box of gas shown in figure 5, and it has a collection of energy levels. Let's plot them, figure 6.



Figure 6 : Energy levels of a box of gas.

The $E_i$'s are not a single particle energy levels, they are the possible energies of everything inside the box. There is some discrete collection of numbers, in quantum mechanics in any case.

Now we are going to change the volume. What happens to the energy levels ? Do they stay the same ? No. Why should they ?

If we want to calculate the energy levels, we have to solve some problem, a Schrödinger equation or something like that. The Schrödinger equation will depend on the size of the box. And the energy levels will change, figure 7.
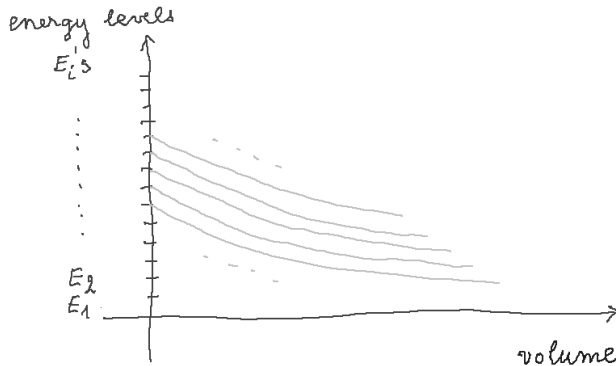


Figure 7 : Energy levels as a function of the volume of the box.

There is a theorem in quantum mechanics, called the *adiabatic theorem*, which we won't prove. It says that if a system has a definite energy, and we *slowly* change a control parameter – in this case the volume – the system will stay in the same energy level. By that we don't mean that it will keep the same energy, but it will ride along the same energy level. It won't jump from one energy level to another. It will stay on one of the lines in figure 7.

On the other hand, if you change the system rapidly this is not what happens. Then you can have jumps from one energy level to another.

That is what is special about adiabatic processes. The energy levels are remembered so to speak.

That has a beautiful mathematical consequence. If we started with a collection of probabilities $P_i$'s over the states of the system. As we change $V$ adiabatically, if we imagine the collection of energy states laid out on a vertical line which we shift to the right, that collection will slide along that vertical line. It is not a simple translation, the states may get closer to each other. But they will stay distinct and in the same order.

The crux of the argument then is that the probability distribution over the states $i$'s – which represents our incomplete knowledge of the actual state of the system – won't change. The energy levels may change, but the probabilities won't change. If you had probability $p$ to be at energy level $E_{537}$, that probability will stay the same. If $p = 1$ then at any time you will be sure to be at that same energy level. If you had probability $1/3$ to be at or above energy level $E_{129}$, it will remain $1/3$. The probability distribution doesn't care what the values of the energy levels are.

Now the entropy is just built from the $P_i$'s. The entropy of a probability distribution is $S = -\sum_i P_i \log P_i$. Therefore if, as you change some control parameter, the probabilities stay the same, then you can be sure that the entropy stays the same too.

This is in fact the general definition of an adiabatic process :

*An adiabatic process is a process in which the entropy doesn't change.*

For that reason an adiabatic process is also sometimes called an *isentropic process.*

We see that defining an adiabatic process simply as a slow one would not be good enough. If we were allowed to put heat into the system, that would corrupt it. That would change the energy and other variables via an outside intervention, and that is not what we want to do.

In summary, adiabatic means slow with no added or subtracted heat. And under those circumstances adiabatic also means constant entropy.

So now we know what to hold fixed in formula (23). It is the change in the energy with respect to volume holding the entropy fixed.

$$\left.\frac{\partial E}{\partial V}\right|_S = -P \tag{24}$$

That is the reason we spent some time on the lemma, equation (20). Formula (24) is perfectly right. But it is hard to calculate things at fixed entropy. What we are usually provided with, the easy quantities to calculate, are quantities at fixed temperature.

We stick in the temperature into the Boltzmann distribution and we calculate. And what we get out is an answer which depends on the temperature[6].

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6. Remember that at thermal equilibrium, the variables $E$, $S$, $Z$, $\beta$, $T$, and $A$, are all dependent on each other and any one of them can be chosen as the independent variable to express the others. The volume $V$ on the other hand is a control parameter.

What is easy to calculate usually is how things vary with temperature, simply because temperature directly appears in the Boltzmann distribution

$$P_i = \frac{1}{Z} \, e^{-\beta E_i} \tag{25}$$

So it is always easier to work with quantities as functions of temperature than as a functions of anything else.

Therefore what we would like to do is to convert equation (24) to something that involves derivatives with respect to temperature instead of entropy. And then we can go back and see what we can learn from the Boltzmann distribution.

From equations (24) and (20), we can write

$$\left.\frac{\partial E}{\partial V}\right|_S = -P = \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial E}{\partial S}\right|_V \tag{26}$$

Now this looks terrible. It looks too complicated.

Fortunately the last partial derivative on the right-hand side is something we have seen before. Does the reader remember what the rate of variation of the energy with respect to the entropy is ? It is the temperature.

When we hold the volume fixed, we hold the system fixed. We are not changing the control parameter. Our system is just the original system and its fixed energy levels. And we are holding those fixed. Under these circumstances $\partial E/\partial S$ is just the temperature, see equation (16) of chapter 2.

So equation (26) is not quite so bad. It rewrites

$$P = -\frac{\partial E}{\partial V}\bigg|_T + \frac{\partial S}{\partial V}\bigg|_T T \qquad (27)$$

Now the derivatives which remain are only derivatives with respect to the volume at fixed temperature. That sounds promising.

Volume and temperature can be thought of as two independent variables. And the derivatives that appear in equation (27) are sort of familiar rates of variation : how the energy changes with respect to volume at fixed temperature ; and how the entropy changes with respect to volume at fixed temperature. And $T$ is just temperature.

One more step : since the right-hand side of equation (27) involves only partial derivatives with respect to $V$ at fixed temperature, as well as temperature itself, we readily see that it can be written

$$P = -\frac{\partial}{\partial V} \left( E - TS \right)\bigg|_T \qquad (28)$$

Indeed a priori the partial derivative with respect to $V$ of the product $TS$ is a sum of two terms : the partial derivative of $S$ with respect to $V$, times $T$, plus the partial derivative of $T$ with respect to $V$, times $S$, all at fixed temperature. But what is the derivative of $T$ with respect to whatever variable, at fixed temperature ? Zero. So we can write

$$\frac{\partial}{\partial V} \left( TS \right)\bigg|_T = T \frac{\partial S}{\partial V}\bigg|_T \qquad (29)$$

Whence, equation (28).

We have reached a fundamental theorem :

*The pressure is equal to minus the derivative with respect to the volume of the Helmholtz free energy at fixed temperature.*

$$P \;=\; -\frac{\partial A}{\partial V}\bigg|_{T} \tag{30}$$

This is much simpler than anything else we could imagine for the pressure.

In fact we even know a little more. From equation (9), we know that the Helmholtz free energy is equal to $-T \log Z$. So we can also write

$$P \;=\; \frac{\partial \, ( \, T \log Z \, )}{\partial V}\bigg|_{T} \tag{31}$$

Since this is evaluated at a fixed temperature, we can pull $T$ outside the partial derivative

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

In other words, all we need to be able to calculate is how the partition function depends on the volume, at fixed temperature. Then we can calculate the pressure.

Everything we have done up to now is *completely general.* It doesn't matter if we are dealing with a liquid, a gas, a plasma or a solid. It could be a solid inside the cylinder ! It

doesn't matter what the chemical composition is either.

This is what statistical mechanics is, as opposed to the kinetic theory. Kinetic theory is the intuitive picture of molecules bouncing around. Whereas equation (32) is what statistical mechanics says : pressure is equal to temperature times the derivative of the logarithm of the partition function with respect to the volume, at fixed temperature.

Now we can carry out the same kind of derivation for basically any control parameter. We used the volume as the control parameter simply because it is familiar.

For any control parameter there is always a derivative of energy with respect to the control parameter *at fixed entropy*. That is called the *conjugate thermodynamic variable* of the control parameter.

Above, using the lemma, and doing some calculus manipulations, we then reached the pressure expressed as $T$ times the derivative of $\log Z$ with respect to $V$ *at fixed temperature.* But let's emphasize that at the start what we considered is the derivative of energy with respect to volume at fixed entropy, with a minus sign, equation (24). And that gave us the pressure.

Volume and pressure are conjugate variables thermodynamically. There are many others, which we are not going to go into now. But anytime we have a control parameter, then we can ask : How does the energy of the system depend on the control parameter at fixed entropy ? And that defines another variable which is like pressure, which plays the role of pressure somehow.

One last point before we do a questions / answers session. Notice that in equation (32) $P$ depends on $\log Z$. As we said earlier $Z$, and more specifically $\log Z$, appears all over the place in statistical mechanics. Does the reader remember another important quantity which depends on $\log Z$? The average energy. Remember equation (43c) of chapter 4

$$E = -\frac{\partial \log Z}{\partial \beta} \qquad (33)$$

The function $\log Z$ has a lot of stuff in it. If you know $\log Z$ you know a lot of stuff.

## Questions / answers session

Question : It seems that the condition that the process we study be adiabatic is pervasive in all of thermodynamics. What happens when the process is not adiabatic?

Answer : Then it becomes a complicated non-equilibrium process. I gave you an example. If you pull the piston fast enough, no molecule will hit the wall. There won't be any pressure.

What will happen is then, if you make a very sudden change? How will the system respond? It will respond by a *shock-wave* going through the fluid.

You can change the volume in either direction. It is easier to think about it if you suddenly squeeze the fluid. You

suddenly push the piston and you make a shockwave going through the system. You will also make a shockwave if you pull it away. And very complicated things happen.

It is no longer controlled by simple statistical mechanics. It is controlled by the whole non-equilibrium dynamics. The only thing you can be sure of is that the entropy is going to increase.

Now you can actually work out the special case when you pull the piston so fast that no single molecule hits the wall. Then you know that there is no work done on the piston. And the change in the energy of the gas is absolutely zero[7].

If the change in energy is zero but the volume has changed, you can learn some things about that situation. You can do some calculations. You can figure out what the final temperature is for instance. It is solvable.

But if you were to squeeze the gas suddenly then all kinds of very complicated things would happen.

Q. : In the process you just described of pulling the piston very suddenly vertically, as in figure 5, the process is not in equilibrium. But it will return to equilibrium. The total energy is conserved. Some kinetic energy will have been transformed into potential energy as the molecules fill up the new available space, isn't it ?

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7. Of course, we have to imagine the whole system plunged into a void, so that it is isolated, and there is no external pressure from outside exerted on the piston.

A. : Yes. But the question is : What is the new temperature of the system when it has returned to equilibrium ?

That can be a very complicated problem. Generally it is not easy. Sometimes it is easy.

Q. : Concerning the lemma you proved, $E$ and $S$ are the dependent variables, and $T$ and $V$ are the independent variables. What does that mean to look at the variation of the independent variable $T$ with respect to the other independent variable $V$ ?

A. : Well, when we wrote equation (14), reproduced below,

$$\left.\frac{\partial E}{\partial T}\right|_V \frac{\Delta T}{\Delta V} = \left.\frac{\partial S}{\partial T}\right|_V \left.\frac{\partial E}{\partial S}\right|_V \frac{\Delta T}{\Delta V} \tag{34}$$

that was a pure identity, like writing

$$\frac{a}{b} = \frac{a}{c}\frac{c}{b} \tag{35}$$

Equation (34) is true for any pair of displacements $\Delta T$ and $\Delta V$ of the independent variables.

But then we looked at the ratio $\Delta T/\Delta V$, *given that we are moving along a line of constant entropy.* We calculated $\Delta T/\Delta V$ along such a line, imposing therefore $dS = 0$.

We first wrote another identity that is always true

$$\Delta S = \left.\frac{\partial S}{\partial V}\right|_T \Delta V + \left.\frac{\partial S}{\partial T}\right|_V \Delta T \qquad (36)$$

Then we imposed $\Delta S = 0$, or if you prefer $dS = 0$. That gave us an expression for $\Delta T/\Delta V$, because on an isentropy line, this ratio is no longer free. It has a value depending on the point where we are in the plane $V$, $T$, figure 4. It is the slope of the isentropy line at the point.

You can interpret it as a constraint in your calculations if you like.

Q. : In an adiabatic process, when we say slowly, is there a physical parameter that has to be lesser or greater than some value ? In other words, could we quantify what we mean by slowly ?

A. : Of course. But that will depend on the details.

Roughly speaking it means that many molecules are colliding with the piston, so that we can average over the details of the molecular collisions. We could examine specific cases.

Some questions have very general answers. And some questions depend on the details. The question of exactly what time scales constitute slow could be one that depends on the details.

On the other hand, the question of what happens if you move sufficiently slowly does not depend on details.

## Ideal gas

In the introduction we said that for the ideal gas we can use kinetic theory, plus the assumption of isotropy everywhere including near the walls, to calculate pressure from the motion of the molecules.

Rich of our new more general theory, let's go back to the ideal gas. Now we start from

$$P \;=\; T \,\left.\frac{\partial \log Z}{\partial V}\,\right|_{T} \tag{37}$$

When we work with the partition function, of course we fix the temperature. We say what $\beta$ is.

Typically when we calculate the partition function, it is $Z$ as a function of other variables at fixed temperature. We work out at fixed temperature. These other variables are not $E$, or $S$ or $A$, which are also deterministically linked to the temperature. The other variables that can still vary are control parameters.
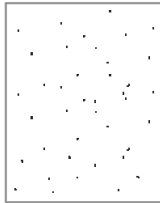


Figure 8 : Ideal gas.

So we turn to the partition function for the ideal gas. This is going to be very easy from this point on.

Figure 8 shows a box filled with an ideal gas. We saw that the partition function is the following integral

$$Z = \int dx \; dp \; e^{-\beta \sum_n \frac{p_n^2}{2M}} \tag{38}$$

We are not going to write it in great detail. Let's just recall that it is the integral over all the $x$'s and all the $p$'s of $e$ to the minus $\beta$ times the value of the energy at $(x, \; p)$, which is $\sum_n p_n^2/2M$. It depends on $p$, but not on $x$. And the parameter $M$ is the mass of one particle.

What is the actual dimensionality of $dx$? Answer : $3N$. And of $dp$? Also $3N$. Where $N$ is the number of particles in the ideal gas. The integral defining $Z$, in equation (38), factorizes into a product of identical integrals for each molecules. Its logarithm is therefore proportional to $N$.

The $x$ integration gives us the volume to the power $N$. If there was only one particle, it would indeed just be the volume. But the element, which we simply wrote $dx$, is $N$ times a differential volume So we can write

$$Z = V^N \int dp \; e^{-\beta \sum_n \frac{p_n^2}{2M}} \tag{39}$$

The $p$ integration depends on $\beta$, but doesn't depend on the volume. So whatever it is [8], we can write

$$Z = V^N f(\beta) \tag{40}$$

8. Remember that we calculated it. See equation (56) in chapter 4.

Finally, we may or may not stick in the factor $N!$.

$$Z = \frac{V^N}{N!} f(\beta) \qquad (41)$$

That doesn't make any difference. Why? Because we are going to take the logarithm of $Z$ and then differentiate with respect to the volume.

$$\log Z = N \log V + \log f(\beta) - \log N! \qquad (42)$$

When we differentiate with respect to $V$, on the right-hand side only the first term matters. The second term and the third term don't depend on $V$. So we have

$$\frac{\partial \log Z}{\partial V} = \frac{N}{V} \qquad (43)$$

Now we multiply that by the temperature, equation (37), and that gives us the pressure.

$$T \frac{\partial \log Z}{\partial V} = \frac{NT}{V} = P \qquad (44)$$

The last equality is a version of the famous Boyle–Mariotte law already known in the XVIIth century.

$$PV = NT \qquad (45)$$

Of course, if we work in laboratory units [9], $T$ is replaced by $kT$, where $k$ is the Boltzmann constant.

Notice that $N/V$ is the density $\rho$. So equation (45) can also be written

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9. That is, if we work in degrees Kelvin.

$$P = \rho T \qquad\qquad (46)$$

This particularly simple equation is the *equation of state* of an ideal gas.

This is exactly what we would have computed if we would have just used the intuitive picture of molecules bouncing off the wall – that is the kinetic theory of gas, with the assumption of isotropy everywhere, even near the walls. But here we don't need that extra assumption. It is implicitly justified [10].

Moreover, there is power in this method. Any time we can do the integrals necessary to calculate the partition function, we have a precise way then of calculating the derivative of its logarithm with respect to a control parameter.

So this was just the simplest of many examples where people can calculate the formula for a conjugate thermodynamical variable. Here the pressure $P$, with a minus sign, is the conjugate thermodynamical variable of the volume $V$. That is the meaning of equation (24). And the formula for $P$ is as simple as it can be : $P = NT/V$.

We did this example in detail in order to see how the basic concepts fit together.

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10. Indeed in the kinetic theory, with a different assumption for the behavior of the molecules near the walls, we would not get equation (46). And now we have proved that this different assumption would be mistaken.

## Fluctuations

What is a fluctuation? If we look at a box of gas, like in figure 8, and it is in equilibrium with another system, for instance a heat bath, so that it is exchanging energy with the outside, the energy in the box won't be a definite value.

What we have called $E$ so far is the *average energy*. But the energy itself is a random variable. It will fluctuate over the energy levels $E_i$'s.

The fact that the energy fluctuates in certain ways is evidence that the system is really made up of molecules and so forth.

But we need a definition of the fluctuation of a quantity when it has a probability distribution, that is when the quantity is a random variable.

This section is pure elementary probabilities, and will be straightforward to a reader familiar with probabilities. In the next section we shall get back to physics, apply the calculation of fluctuation to the energy, relate it to specific heat, etc.

Remember that to talk about probabilities, we need to have a well-specified random experiment $\mathcal{E}$. Here the experiment is "wait until the box is in thermal equilibrium on its own and with the heat bath surrounding it", then, at a random time, and supposing that we have the adequate instruments, look at the *exact energy* of the system. It is one of the $E_i$'s, and there is a probability distribution, which is the Boltzmann distribution.

For any probability distribution, here is the general definition of fluctuation. Let's begin with a random quantity whose average is zero, figure 9.
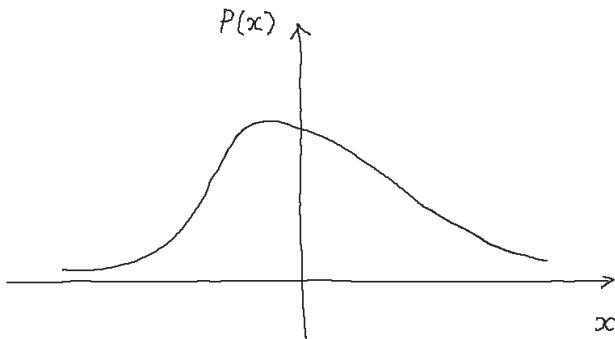


$P(x)$

$x$

Figure 9 : Probability distribution [11] of a random variable with mean zero.

For a random variable to have mean zero doesn't mean that the picture of its distribution is symmetric around zero. It means that $\sum_i x_i P_i = 0$, if we are in the discrete case, or $\int x P(x) dx = 0$, if we are in the continuous case.

Fluctuation is a precise definition and measure of the intuitive concept of *width* of the probability distribution around its mean – how broad the distribution is. For the sake of illustration, let's call the random quantity $X$, and let's denote its mean – another name for average – $< X >$. This average is not a random variable, it is a number. And we decide to talk first of all about a random variable whose

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11. We mix with the same picture the concepts of probability distribution and probability density, which we assume the reader is by now familiar with. Go to chapter 1, or to any manual on elementary probabilities, for details.

average is zero.

$$< X > = 0 \tag{47}$$

Then its fluctuation is defined as

$$\Delta X = \sqrt{< X^2 >} \tag{48}$$

It is the square root of the average of the random variable $X^2$. Probabilists call the average of $X$ its first moment, the average of $X^2$ its second moment, the average of $X^3$ its third moment, etc.

It turns out that knowing the entire collection of moments of a random variable is equivalent to knowing its whole distribution of probability.

Knowing its first two moments gives a first approximate view of its distribution, namely where is its average, and what is its width, figure 9. In fact for Gaussian distributions, the knowledge of $< X >$ and $< X^2 >$ determines completely the distribution.

We just defined the fluctuation of a random quantity $X$ when its mean was zero. Now let's gives the definition in the general case of a variable $Y$ whose mean $< Y >$ can be any value, not necessarily zero. We will shift the variable $Y$ so that its new mean is zero, and then apply the first definition.

So we define the new variable

$$X = Y - < Y > \tag{49}$$

It is easy to see again that $< X > = 0$. Then the fluctuation of $Y$ is by definition the fluctuation of its "centered" version, that is the fluctuation of $X$.

$$\Delta Y = \sqrt{< X^2 >} \qquad (50)$$

We can also write it

$$(\Delta Y)^2 = < X^2 > \qquad (51)$$

Or even more elaborately, without reference to $X$,

$$(\Delta Y)^2 = < [\, Y - < Y > \,]^2 > \qquad (52)$$

In probability theory the fluctuation $\Delta Y$ of a random quantity $Y$ is called its *standard deviation.* It is often denoted $\sigma_Y$. And the square of the fluctuation is called the *variance.*

We leave to the reader the following simple yet important exercise

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**Exercise 2 : Consider a random variable $Y$, whose mean is $< Y >$, not necessarily zero. Prove that**

$$(\Delta Y)^2 = < Y^2 > - (< Y >)^2 \qquad (53)$$

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In summary, the square of the fluctuation of a random quantity is by definition the average of the square of its departure from its mean, equation (52). And we have a simple result

saying that it can be calculated as the average of the square minus the square of the average, equation (53).

Now let's see if we can calculate the fluctuation of the energy.

## Fluctuation of energy and specific heat

Having made a detour in elementary probability theory to define fluctuation, now we go back to physics. We want to calculate the fluctuation of the energy.

We will calculate it in terms of the partition function. Generally speaking, in our problems in statistical mechanics, we are armed with one big tool : the partition function. One always goes back to it. It is the Swiss army knife of statistical mechanics.

In an honest real experiment, if we repeat it over and over again, and each time we are able to measure the exact energy inside the box, what fluctuation shall we observe ?

Why does it vary ? It varies because there is energy coming in and out of the system. It is not just a mathematical definition. The energy in our box does fluctuate if it is in equilibrium with a heat bath.

We want to calculate the fluctuation of energy. So we shall apply equation (53) to energy.

$$(\Delta E)^2 \ = \ <E^2> \ - \ (<E>)^2 \qquad (54)$$

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*Important caveat* : in the past chapters, $E$ was the average energy. Now, in the above formula, $E$ is the random variable, which can take values $E_i$'s if we use a discrete model, or a continuum of values of we use a continuous model. And its average is $< E >$.

What is $< E >$ in terms of the partition function ? We go back to formula (43c) in chapter 4. It is

$$< E > = -\frac{\partial \log Z}{\partial \beta} \tag{55}$$

Thus we have the average energy already. We don't have to do any more work on that term in equation (54).

But what about the average of the square of the energy ? To figure it out, let's remember the trick used to calculate the average energy, and see if we can use it again somehow. To calculate $< E >$, we wrote

$$< E > = \sum_i \frac{1}{Z} e^{-\beta E_i} E_i \tag{56}$$

Then we noticed that the last factor $E_i$ could be produced by taking the derivative of the exponential with respect to $\beta$. So we wrote

$$< E > \ = \ \sum_i \frac{1}{Z} \, e^{-\beta E_i} \ E_i$$

$$= \ -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} \, e^{-\beta E_i}$$

$$= \ -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} \tag{57}$$

$$= \ -\frac{1}{Z} \frac{\partial}{\partial \beta} \, Z$$

And the last equality became equation (55).

But suppose we want to calculate the average of the energy squared now. What do we do? We want to calculate

$$< E^2 > \ = \ \sum_i \frac{1}{Z} \, e^{-\beta E_i} \ E_i^2 \tag{58}$$

We will differentiate twice.

$$< E^2 > \ = \ \sum_i \frac{1}{Z} \, e^{-\beta E_i} \ E_i^2$$

$$= \ \frac{1}{Z} \sum_i \frac{\partial^2}{\partial \beta^2} \, e^{-\beta E_i}$$

$$= \ \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \sum_i e^{-\beta E_i} \tag{59}$$

$$= \ \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \, Z$$

Finally we can write the square of the fluctuation in the energy as follows

$$(\Delta E)^2 \;=\; \frac{1}{Z}\,\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 \qquad (60)$$

Let's see if we can do anything with it. But, first of all, observe that it tells us that we can calculate the fluctuation in the energy if we know $Z$. Again that shows the power of the partition function.

All of statistical mechanics is about the power of the partition function, and the power of differentiation.

To try to improve expression (60), let's take a look at

$$\frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) \qquad (61)$$

This is the derivative of the product $1/Z$ times $\partial Z/\partial \beta$. So, applying the product rule, and noting that the derivative of $1/Z$ is $-1/Z^2$ times the derivative of $Z$, expression (61) can be rewritten

$$\frac{1}{Z}\,\frac{\partial Z^2}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 \qquad (62)$$

This is exactly the right-hand side of equation (60). So we can rewrite the square of the fluctuation of energy as

$$(\Delta E)^2 \;=\; \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) \qquad (63)$$

We could write the derivative of a log inside the parentheses. But it is even simpler : inside the parentheses is minus the average energy. So we reach

$$(\Delta E)^2 \;=\; -\frac{\partial}{\partial \beta} <E> \qquad (64)$$

And what is the right-hand side of this equation ? It is, with a minus sign, the rate of change of the average energy with respect to $\beta$. Remember that $\beta$ is the inverse of the temperature.

Massaging equation (64) a bit, we get

$$(\Delta E)^2 \;=\; -\left(\frac{\partial}{\partial T} <E>\right) \frac{\partial T}{\partial \beta} \qquad (65)$$

The last derivative is

$$\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial \beta}\frac{1}{\beta}$$
$$= -\frac{1}{\beta^2} \qquad (66)$$

Therefore equation (65) is simply

$$(\Delta E)^2 \;=\; T^2 \frac{\partial}{\partial T} <E> \qquad (67)$$

What is the rate of change of the average energy of the system with respect to temperature ? It is called the *heat capacity* of the system.

How much energy you have to put into a bucket of water to increase its temperature by one degree ? That is the heat

capacity of your bucket of water. And if you look at one unit of water – meaning one kilogram – then it is called the *specific heat.*

Notice that, when writing formula (67), we keep the volume fixed. We are not varying any control parameter. We are not changing the volume. On the right-hand side, next to $T^2$, we just look at the relationship between $<E>$ and $T$, and more precisely at the rate of change of the average energy with respect to the temperature.

The heat capacity at constant volume $V$ is usually denoted $C_V$. It depends on $V$. It also depends on the number of particles in the box in figure 8. But all these are fixed control parameters in our experiment. We just look at the relationship with the temperature. And so, for the square of the fluctuation in energy we finally reach the formula

$$(\Delta E)^2 \;=\; C_V \; T^2 \qquad\qquad (68)$$

where $C_V$ is the rate of change of the average energy with respect to temperature. It is a famous formula, due to Gibbs and to Einstein.

So, if you know the heat capacity $C_V$ of your system – which can be calculated as the specific heat times the mass –, you multiply it by the temperature squared and that will tell you how much fluctuation in the exact random energy there is.

Now we left out something : the Boltzmann constant. If we work with laboratory units, in the definition of $C_V$ as $\partial <E> /\partial T$, there will be a $k_B$ downstairs, and from

$T^2$ there will be $k_B^2$ upstairs, so formula (68) in laboratory units rewrites

$$(\Delta E)^2 \;=\; k_B \; C_V \; T^2 \tag{69}$$

That means it is small. We expect fluctuations when there is a lot of particles. But they will be fairly small.

Formula (68) or (69) is the fluctuation in the energy of any system. It is not specific to a particular kind of system. Inside the box, again, it can be gas, ideal or not, liquid, solid, etc.

Notice that $C_V$ doesn't have to be constant when temperature changes. So it would be more accurate to write equation (69) as

$$(\Delta E)^2 \;=\; k_B \; C_V(T) \; T^2 \tag{70}$$

The fluctuation depends on $T$ not only because there is a $T^2$ in the formula, but also because $C_V$ may depend on $T$.

A final comment : This is again part of the beautiful structure of statistical mechanics. Formula (70) goes beyond classical thermodynamics.

Whenever there is a $k_B$ appearing in the formula like here [12], it really does depend on the fact that systems are made up out of molecules and so forth. It depends on Avogadro's number. Boltzmann's constant $k_B$ is closely related to Avogadro's number.

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12. That is, not simply replacing $T$ by $kT$.

# Questions / answers session (2)

Q. : If we set pressure constant instead of volume, and therefore work is performed when the temperature changes, would formula (68) become different ?

A. : Well, formula (68), or its variant, was the derivation of the fluctation in the energy when all the control parameters are kept fixed, and the actual energy of the system ranges randomly over the $E_i$'s, which themselves are also fixed energy levels.

We amply described the fact that, due to microexchanges with the heat bath, the actual energy inside the box fluctuates. This fluctuation – another word for the standard deviation of the actual energy – happens to depend on the temperature $T$ and on the heat capacity $C_V(T)$.

One can define the coefficient $C_P$ as

$$C_P = \frac{\partial E}{\partial T}\bigg|_P \tag{71}$$

But if you use it instead of $C_V$ in equation (68), you will get the wrong answer.

If you want to study the relationship between $\Delta E$ and $C_P$, you first of all have to describe in details what you mean. What random experiment ? The fluctuation of which random variable precisely ? Etc.

No doubt there are connections between the various coefficients of heat capacity that can be defined under various assumptions. You will have to look them up, or figure them

out by yourself.

Q. : Isn't the specific heat a constant for a given material ?

A. : Well, first of all, we don't use the specific heat in equation (68), but the heat capacity $C_V$ of the system. It is of course related to the specific heat.

What is the definition of specific heat ? It is the rate of change of energy per unit temperature per unit mass ? In other words, it is the heat capacity per unit mass of the material. For instance, for water under ordinary conditions of temperature and pressure, it is $1\ Calorie\ /\ K$ x $kg$ [13].

Therefore the coefficient $C_V$ in equation (68) is the specific heat times the mass of the sample.

Roughly speaking the heat capacity is proportional to the number of molecules in a sample.

Finally the specific heat of a given material is more or less constant over a sizable range of temperatures, but it may vary when the temperature gets very low or very high.

The important thing to note is that formula (68) and its variants don't depend on the details of what things are made out of. Once you have measured the specific heat, you know the fluctuations without having to worry about what kind of material it is or anything else.

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13. $1\ Calorie = 1000\ calories = 4184\ Joules.$

# Ideal models in physics, linearity, and measurements

Last question was refering to a thermodynamical variable – the specific heat – that is presumably constant when temperature changes. A consequence would be that heat capacity depends only on mass, linked to it by a constant proportionality factor.

Moreover for a gas at fixed density $\rho$, by definition of density the mass $m$ is proportional to the volume $V$. So heat capacity in that case would be proportional to $V$.

If the gas is ideal, we saw that the following relation holds

$$P = \rho T \qquad (72)$$

Then at fixed volume and mass, we can use the pressure to measure the temperature. In other words, we could transform a pressure gauge into a thermometer.

And since at fixed volume and density the variation in heat would be proportional to the variation in temperature, it would also be an instrument measuring the quantity of heat transfered inside.

The general point we want to address here is that all these observations are based on *linear relationships*.

In physics we often assume linear relationships between variables, at least over a limited range of the independent variable.

The case of the ideal gas is an example. It is ideal if its energy is only the kinetic energy of the molecules, if they don't collide with each other, don't interact, don't have potential energy like the Earth and the Sun, etc. So we assume that it has low density, that the particles are small, etc. This is often a fair assumption. And for many calculations on gases the ideal gas approximation is a good approximation.

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**Exercise 3 : Consider the air at room temperature and pressure. Show that if we increased scale so that one molecule would have the size of a cherry, then we would have roughly one hundred cherries per cubic meter.**

*Hint : Suppose the air is made only of nitrogen molecules $N_2$. Assimilate a molecule of nitrogen to a sphere of diameter 0.3 nanometer. Under ordinary conditions, in 22.4 liters there is Avogadro's number of molecules. Take the average diameter of cherry to be 2 cm.*

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As a matter of fact, the air in the room is far from an ideal gas. We now made a calculation to get a feel for the density. If we remember that the molecules of nitrogen move at a speed of approximately 500 meter per second – and that is before the rescaling ! – we are not suprised to know that there are plenty of collisions. Yet for some calculations the ideal gas approximation is still satisfactory.

The notion of ideal device, or ideal relationship, or ideal conditions, is common in physics. It refers to a model that we know is simpler than reality, but is useful when it is not

to far off because then calculations become tractable.

Generally speaking, laboratory instruments are physical devices relying on a linear relationship between two variables. Sometimes, like in the case of analog integrators, we rely on a more complicated relationship, but that is not the rule.

In truth however, as said, no physical device ever measures what it is intended to measure – the mathematical thing it is intended to measure.

At best what is usually true is that it measures what it is supposed to measure over a limited range of the independent variable which we want to measure by reading off the dependent one.

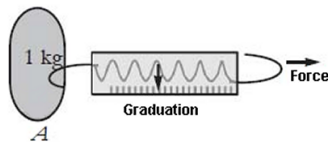For instance we can use a spring to measure force, figure 10.



Figure 10 : Dynamometer. In this contraption, it is used to measure inertia, and check Newton's law $F = ma$.

Over a limited range of forces, the elongation of the spring will be proportional to the force. Therefore we will be able to measure the force by reading off the elongation. But if we pull too hard, we will distend the spring, ruining the instrument.

So normally the situation is this : we have in the laboratory many quantities which we can measure easily. It could be the length of a stretched spring, or it could be the height of the mercury in a thermometer, or the displacement of a needle on a dial in response to some input.

And we ask ourself : What could the quantity we want to measure depend on ? Or, the other way around : What could the elongation of the spring depend on ?

It clearly depends on the force exerted on it, but it could depend on other things. It could depend on the temperature. It could depend on the air pressure. But jeez that is not terribly important. Those variations are pretty small so we ignore them. And we say it depends on the force that is pulling the spring.
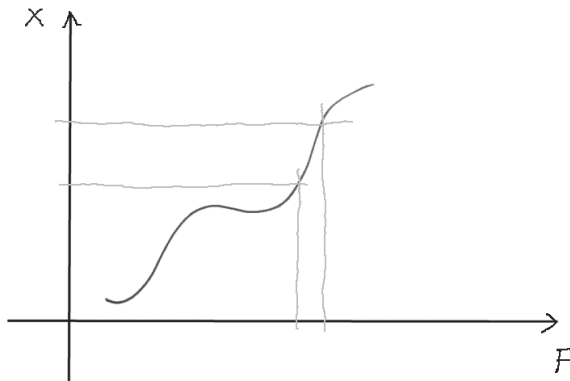


Figure 11 : Relationship between elongation $X$ and force $F$.

There is going to be some relationship between the force $F$ and the elongation $X$. It doesn't have to be a straight line.

It might be some crazy curve that looks like figure 11.

Over some limited range, if the function is smooth, it will be linear. And, as you know, any function that is smooth enough, when looked at sufficiently locally is linear. If we want to be more precise, it is like the arc of a circle. And we can be even more precise. That is the geometric interpretation of the Taylor-Maclaurin expansion.

Anyway, for any device if over some range the relationship between the two variables is linear, then you can stay over that limited range, and use your device as a measuring instrument. The relationship between the variable $y$ you can read off, and whatever the independent variable $x$ you want to measure happens to be, that relationship can be approximated by $y = ax + b$.

In the case of the spring balance it is just force and elongation. For a thermometer it is the height of mercury in a column and the temperature, figure 12. Indeed what else can the height of mercury depend on ?
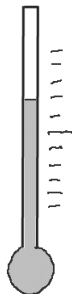
Figure 12 : Mercury thermometer.

Can it depends on the air pressure in the room ? Not much because the air pressure in the room is isolated from the mercury by the closed glass. What else can it depend on ? The local gravitational field ? Yes a tiny bit. Let's formulate it in a different way : it can depend on the direction that we hold the thermometer.

Now for a common thermometer that won't make any difference. But we could imagine a thermometer that would behave differently if we held it horizontally than if we held it vertically. That would not necessarily be a bad thermometer. We would just add, for instance, the rule that the thermometer must be held vertically. We would make it part of the definition of the thermometer.

What else ? The age of the thermometer ? Well, mercury and glass are pretty inert. So we are in pretty good shape regarding that. Of course over a very long time that is right. The protons that make up the mercury could decay. But the order of magnitude of their half-life is $10^{35}$ years, so we are on the safe side here too.

We think about it for a while, and eventually we conclude : Gee, to a very very good approximation, the only thing that the height of the column is going to depend on is the temperature.

Or, equivalently, the energy that the mercury has absorbed from the thermal environment that it is in is proportional to the temperature. That assumes of course that the thermometer is in thermal equilibrium with its environment. Of course if the thermometer is not in equilibrium with the environement, it is not measuring the temperature of

the environment. It is only if enough time has been left for the environment to come to equilibrium with the mercury. Then the only variable around is the temperature.
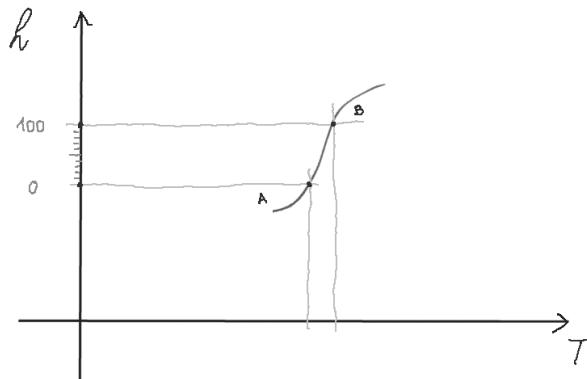


Figure 13 : Relationship between mercury height and temperature.

At equilibrium the height of the column depends on the temperature in some way. Suppose it is the curve in figure 13.

Suppose that $A$ is the point of freezing water, $B$ the point of boiling water, and between $A$ and $B$ the curve looks pretty straight [14]. Then we can arbitrarily call the ordinate of $A$ zero, and the ordinate of $B$ one-hundred. We then divide the corresponding interval on the $h$-axis into a hundred little segments. And we say that each segment is one degree – one rung, so to speak – on a centigrade scale.

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14. Remember that we already have a definition of temperature as the rate of variation of energy with respect to entropy, and that we know, at least in theory, the relationship between $E$ and $T$. So we can check that the curve is straight between $A$ and $B$, and we can do this calibration.

Is the thermometer measuring temperature ? Yes. It is measuring temperature to a high accuracy.

However it is not measuring temperature in the absolute sense. We have called the point $A$ temperature zero. It is not the absolute zero. When you go out in the winter time and it says 0 degrees on your Celsius thermometer, it doesn't mean you are going out into absolute zero. So there is a convention about where we put the zero.

But small incremental changes in the temperature will be proportional to small incremental changes in the height of the column.

## Questions / answers session (3)

Q. : When we use a thermometer to measure the temperature, you said that we need to wait until it is in thermal equilibrium with the environment. When do we know that equilibrium has been reached ?

A. : The answer is simple : when the height of the thermometer has stopped changing. Depending on the heat conductivity of the glass that may take more or less time. Typically, in ordinary conditions, a minutes or so is sufficient.

But that also depends on the density of the environment. It is possible that the density be very low but the temperature be very high. There is no reason why that can't

happen. High temperature just means the kinetic energy of the molecules is high. That doesn't say anything about their number. There may be very few molecules in the room. If you bring the thermometer into the room, it is not going to equilibrate very rapidly because very few molecules are going to hit it.

Q. : Can't there be a difference between the radiation temperature and the air temperature?

A. : Yes, there can be. Usually there is. The air and the radiations are usually not in equilibrium.

It is rather hard to bring radiation in the room in thermal equilibrium with the air. The molecules of gases making up the air are neutral. They don't interact much with photons. They don't radiate much.

I can assure you that the optical radiation in the room is nowhere being in equilibrium with the air.

On the other hand there are very few photons in the room compared with the air molecules. And so they really don't count very much.

Q. : When does the ideal gas law break down? Can it be calculated mathematically?

A. : Yes. We shall begin lesson 6 with such a calculation.