

Entropy of a Monoatomic Ideal Gas – the Sackur-Tetrode Equation

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PART I: Introduction

Entropy is a crucial concept in classical thermodynamics that measures the amount of ‘disorder’ or ‘chaos’ in a system. It is usually introduced in conjunction with the second law of thermodynamics, which states that for an isolated thermodynamic system, the total entropy S , must increase.

In 1912, physicists derived an equation for the entropy of a monoatomic ideal gas, like helium, neon and argon, called the Sackur-Tetrode equation. However, usage of the non-extensive version of this equation led to a paradox that supposedly violated the second law of thermodynamics.

PART II: Derivation of the Sackur-Tetrode Equation

We first investigate the derivation of said equation. The definition of entropy, from Ludwig Boltzmann, is

$$S = k \ln \Omega$$

where k is the Boltzmann constant, and Ω the number of microstates corresponding to the system’s macrostate.

A macrostate of a system is specified by macroscopic quantities, e.g. volume, energy, etc., here, we specify the macrostate by the gas’s internal energy U . But for a gas with given energy, there are a lot of different arrangements the molecules of gas can take such that it yields the same energy:

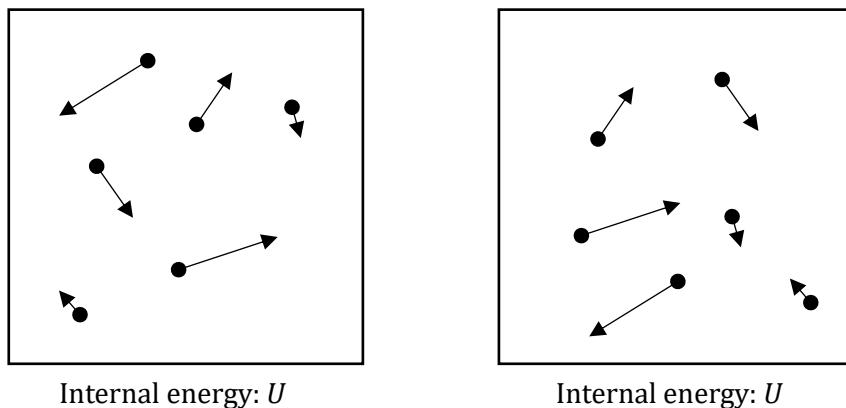


Fig. 1: Two different arrangements of a gas with the same resulting internal energy U

Figure 1 shows such an example. The same macrostate can correspond to an unthinkable amount of microstates, specified by the positions and momenta of each individual particle. Therefore, each state can be represented by a point in a $6N$ -dimensional imaginary space called the state space, where the axes are labelled by the positions and momenta of each particle in all three dimensions: $r_{1x}, r_{1y}, r_{1z}, p_{1x}, p_{1y}, p_{1z} \dots r_{Nx}, r_{Ny}, r_{Nz}, p_{Nx}, p_{Ny}, p_{Nz}$.

Now, since both position and momentum are continuous values, the total number of microstates would really be the integral rather than the sum of states over both position and momenta:

$$\Omega \sim \int d^3r_1 d^3r_2 \cdots d^3r_N d^3p_1 d^3p_2 \cdots d^3p_N$$

But notice that the units don't make sense – the left side has dimensionless units (it's just a number), and the right side has units of $m^{3N} (N s)^{3N} = (J s)^{3N}$, namely the units of action to the $3N$ power. To account for this, we must divide by a constant with such a dimension.

In fact, this constant is the Planck's constant, h . This makes sense, since according to quantum mechanics, it is impossible to be infinitely precise in the measurement of position and momentum, given by the Heisenberg uncertainty principle; it is impossible to specify a region in phase space smaller than a 'phase volume' of h^{3N} .

Hence, now we obtain the equation

$$\Omega = \frac{1}{h^{3N}} \int d^3r_1 d^3r_2 \cdots d^3r_N d^3p_1 d^3p_2 \cdots d^3p_N$$

Now, all the positional variables are limited by the coordinates of the container, which for simplicity we take to stretch from 0 to L . We can therefore evaluate the position integrals first:

$$\int d^3r_1 d^3r_2 \cdots d^3r_N = L^{3N} = V^N$$

where V is the volume of the container.

For the momenta, we realize that the total internal energy of the system can be expressed in terms of the individual momenta of all the single particles:

$$U = \frac{p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \cdots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2}{2m}$$

which upon rearranging, gives

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \cdots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2 = 2mU$$

which is the equation of a $3N$ -sphere with radius $\sqrt{2mU}$. The allowed points

$(p_{1x}, p_{1y}, p_{1z}, \cdots, p_{Nx}, p_{Ny}, p_{Nz})$ would be confined to the 'surface volume' of the $3N$ -sphere. Taking the integral over the momenta would then correspond to finding the 'surface volume' of this sphere. Deriving the equation here would be off topic, so we'll treat this as a given: it is equal to

$$\frac{2\pi^{3N/2}}{(3N/2 - 1)!} r^{3N-1}$$

Substituting in $r = \sqrt{2mU}$, we have

$$\int d^3p_1 d^3p_2 \cdots d^3p_N = \frac{2\pi^{3N/2}}{(3N/2 - 1)!} (\sqrt{2mU})^{3N-1}$$

Putting this all together, we have

$$\Omega = \frac{2\pi^{3N/2} V^N}{h^{3N} (3N/2 - 1)!} (\sqrt{2mU})^{3N-1}$$

Normally, N is a large number. We can use this fact to approximate this expression and discard some of the unimportant numbers that wouldn't affect the equation too much:

$$\begin{aligned} \Omega &\approx \frac{2\pi^{3N/2} V^N}{h^{3N} (3N/2)!} (\sqrt{2mU})^{3N} = \frac{2V^N}{h^{3N} (3N/2)!} (\sqrt{2\pi mU})^{3N} \\ \therefore \ln \Omega &\approx \ln \frac{V^N (\sqrt{2\pi mU})^{3N}}{h^{3N} (3N/2)!} = N \ln V \left(\frac{2\pi mU}{h^2} \right)^{3/2} - \ln(3N/2)! \end{aligned}$$

For the latter term of the last expression, we can use the Stirling's approximation. Using this approximation we can write

$$\ln(3N/2)! = \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2}$$

So

$$\ln \Omega \approx N \left[\ln V \left(\frac{2\pi m U}{h^2} \right)^{3/2} - \frac{3}{2} \ln \frac{3N}{2} + \frac{3}{2} \right] = N \left[\ln V \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{3}{2} \right]$$

Thus the entropy (finally!) is

$$S = k \ln \Omega = Nk \left[\ln V \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{3}{2} \right]$$

We have finally derived the Sackur-Tetrode equation, which calculates the entropy of a monoatomic ideal gas with internal energy U .

... But all is not well.

PART III: The Gibb's Paradox

Using this version of the Sackur-Tetrode equation leads to what is now known as the Gibb's paradox. This is a thought experiment that supposedly violates the second law of thermodynamics, which states that the entropy of an isolated system must increase.

Imagine we have a container filled with a monoatomic gas (helium, neon, argon, whatever), and we insert a partition that cuts the volume into exactly two halves, each with volume V , internal energy U and number of molecules N .

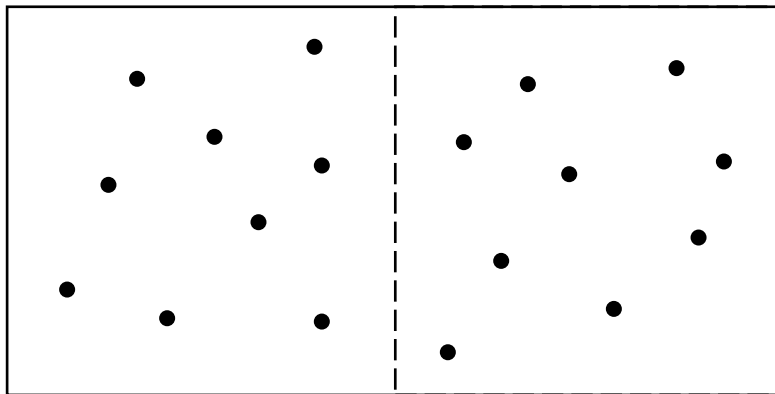


Fig. 2: A container of monoatomic gas separated by a partition (dashed line)

Each half would have entropy S , given by the Sackur-Tetrode equation,

$$S = Nk \left[\ln V \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{3}{2} \right]$$

Now, we remove the partition, the new entropy S' , would be

$$S' = 2Nk \left[\ln 2V \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{3}{2} \right]$$

The important thing to note here is that $S' > 2S$, because of the $2V$ factor inside the logarithm. Everything is well and dandy until we insert the partition back in, turning the total entropy S' back to $2S$, a decrease in entropy in violation of the second law.

To resolve this paradox, we must first carefully consider what exactly went wrong. Suppose we colour the molecules in each half to be red and green:

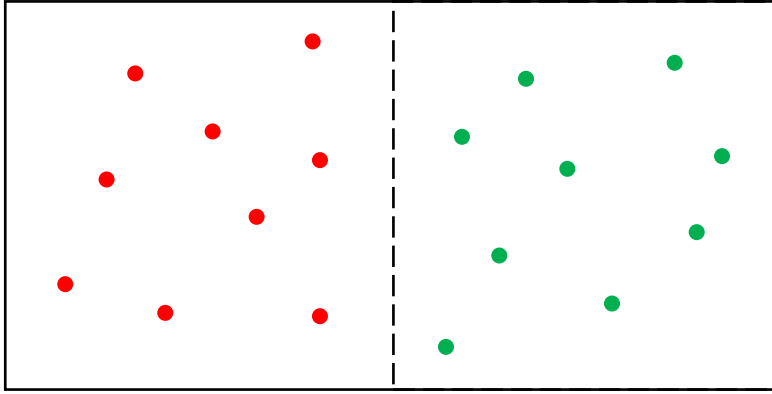


Fig. 3: Container separated into halves with a partition, with gas coloured on each side

If we remove the partition, the gases end up mixing, and if we place the divider again, the situation will most likely be in some sort of random arrangement like below:

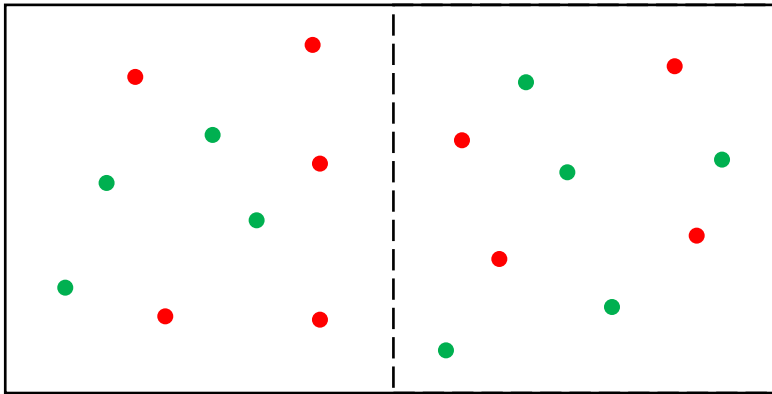


Fig. 4: Mixed gases re-divided by the partition

It is easy to see that in fact, the entropy has not decreased. The gases remain mixed even after we have placed the divider. This problem arises because we made an implicit assumption that all gas molecules are distinguishable, i.e. you can tell a molecule apart from the others. So when we removed the partition, we would have thought that the gases have 'mixed' when they are in fact still the same gas, so the entropy increased.

To account for this inconsistency, we'd have to step back and rederive it once more. If we now assume that all atoms are indistinguishable, we would have overcounted Ω by a factor of $N!$ (to verify this, simply pick a microstate and swap the molecules; you would have $N!$ arrangements). Hence,

$$\Omega = \frac{2V^N}{h^{3N}N!(3N/2)!} (\sqrt{2\pi mU})^{3N}$$

Taking the natural logarithm,

$$\begin{aligned} \therefore \ln \Omega &= N \ln V \left(\frac{2\pi mU}{h^2} \right)^{3/2} - \ln N! - \ln(3N/2)! \\ &\approx N \left[\ln V \left(\frac{2\pi mU}{h^2} \right)^{3/2} - \ln N - \frac{3}{2} \ln \frac{3N}{2} + \frac{5}{2} \right] \\ &= N \left[\ln \frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} + \frac{5}{2} \right] \end{aligned}$$

Therefore, the entropy is

$$S = k \ln \Omega = Nk \left[\ln \frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} + \frac{5}{2} \right]$$

This is the *real* Sackur-Tetrode equation.

PART IV: Conclusion

Throughout this article, we have tried to calculate the entropy of a monoatomic ideal gas, given its internal energy, volume and number of molecules. By invoking quantum mechanics, a $6N$ -dimensional phase space and Stirling's approximation, we have arrived at a version of the equation that was still not quite correct; but after assuming that all atoms are indistinguishable, we have resolved an arisen paradox.

We hope you have enjoyed this article. If you have any questions or noticed that we had made a mistake (we are after all just physics enthusiasts), feel free to email to primusmathematica1729@gmail.com. Check us out on [Youtube](#), and stay tuned at [Prime Pursuit](#) for more articles and monthly problems!