

The Gibbs paradox

In this article, we will calculate the partition function of an ideal gas in a “naive” wrong way, and calculate the various thermodynamic quantities. Then, we will notice that the partition function gives all the correct answers except for entropy. Finally, we will fix our mistake, and obtain the correct partition function.

Let’s say that an ideal gas has N particles in volume V . Then, the energy is given by

$$E = \frac{1}{2m} \sum_{i=1}^N p_i^2 \quad (1)$$

where p_i is the momentum of i th particle. Of course, we have

$$p_i^2 = p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \quad (2)$$

Then, the density of state is given by

$$\left(\frac{dp_{1x} dx_1}{h} \right) \left(\frac{dp_{1y} dy_1}{h} \right) \left(\frac{dp_{1z} dz_1}{h} \right) \dots \left(\frac{dp_{Nx} dx_N}{h} \right) \left(\frac{dp_{Ny} dy_N}{h} \right) \left(\frac{dp_{Nz} dz_N}{h} \right) \quad (3)$$

We can now calculate the partition function. It is given by

$$Z = \frac{1}{h^{3N}} \int dx_1 \dots dz_N \int dp_{1x} \dots dp_{Nz} e^{-\beta(p_{1x}^2 + \dots + p_{Nz}^2)/2m} \quad (4)$$

$$Z = \frac{V^N}{h^{3N}} \int dp_{1x} e^{-\beta p_{1x}^2/2m} \int dp_{1y} e^{-\beta p_{1y}^2/2m} \dots \int dp_{Nz} e^{-\beta p_{Nz}^2/2m} \quad (5)$$

$$= \frac{V^N}{h^{3N}} \left(\sqrt{\frac{2\pi m}{\beta}} \right)^{3N} = \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \quad (6)$$

Problem 3. Show that

$$U = \frac{3}{2} kT \quad (7)$$

We immediately see that the heat capacity at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} Nk \quad (8)$$

which agrees with our earlier result in “Specific heats of gases.”

Problem 4. Show that

$$P = \frac{NkT}{V} \quad (9)$$

which is exactly Boyle-Charles law.

Problem 5. Show that the “naive” wrong entropy is given by

$$S_{\text{naive}}(N, V, T) = Nk \ln V + \frac{3}{2} Nk \left[\ln \left(\frac{2\pi mkT}{h^2} \right) + 1 \right] \quad (10)$$

Problem 6. Calculate the change for entropy (10) from the state $V = V_i, T = T_i$ to the state $V = V_f, T = T_f$, and confirm that it agrees with our earlier result in “Entropy as a state function.”

So, what is the problem? It doesn’t seem to have any problems so far. But, suppose you prepare an identical set of gas with the same kind of particle, the same temperature, and the same number of particles. Then, the entropy of this identical set should also be given by (10). Thus, the total entropy should be $S + S = 2S$. However, notice that the combined set now has $2N$ particles, the volume of $2V$, and the temperature of T . Thus, if we plug in these values to (10) we must get $2S$ but we don’t!

We can understand this point better by Gibbs paradox proposed by the American physicist, Josiah Gibbs. Suppose you have two compartments in a container separated by a door. The left compartment has volume V_1 and the right V_2 . On the left compartment, we have N_1 particles called “A” with temperature T . On the right, we have N_2 particles called “B.” If you remove the door, the temperature will remain the same, as they both have the same temperature but the entropy will increase, because particles A and particles B are being mixed. The particles A will be spread over a bigger volume, and the particles B as well. The total entropy increase is given by the sum of the entropy increase of the particles A and the entropy increase of the particles B as follows:

$$\Delta S_{\text{naive}} = k \left(N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right) \quad (11)$$

So far so good. Suppose now the same situation, but, instead of two different kinds of particles, we now have the same kind of particles at both compartments, and the number density at both compartments were same, i.e., $N_1/V_1 = N_2/V_2$. Then, removing the door will change nothing. The new number density is $(N_1 + N_2)/(V_1 + V_2) = N_1/V_1 = N_2/V_2$ as before. Thus, the total entropy change ΔS must be zero. However, if we follow the above logic, we still get (11), which is not zero!

The resolution of Gibbs paradox lies in the indistinguishability of identical particles. Notice that we didn’t take this into account when calculating the density of states in (3). Let me clarify. For $N = 3$, the following $N!$ configurations are all same configurations:

$$\left(\vec{p}_1 = \vec{a}, \quad \vec{p}_2 = \vec{b}, \quad \vec{p}_3 = \vec{c} \right), \quad \left(\vec{p}_1 = \vec{a}, \quad \vec{p}_2 = \vec{c}, \quad \vec{p}_3 = \vec{b} \right) \quad (12)$$

$$\left(\vec{p}_1 = \vec{b}, \quad \vec{p}_2 = \vec{a}, \quad \vec{p}_3 = \vec{c} \right), \quad \left(\vec{p}_1 = \vec{b}, \quad \vec{p}_2 = \vec{c}, \quad \vec{p}_3 = \vec{a} \right) \quad (13)$$

$$\left(\vec{p}_1 = \vec{c}, \quad \vec{p}_2 = \vec{a}, \quad \vec{p}_3 = \vec{b} \right), \quad \left(\vec{p}_1 = \vec{c}, \quad \vec{p}_2 = \vec{b}, \quad \vec{p}_3 = \vec{a} \right) \quad (14)$$

Thus, we see that (3) is redundant by $N!$ factor. Thus, the correct density of state is (3) divided by $N!$. Thus, the correct partition function is given by (6) divided by $N!$, namely,

$$Z = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \quad (15)$$

Then, we can easily check

$$S(N, V, T) = S_{\text{naive}}(N, V, T) - \ln N! \quad (16)$$

If you remember $S = k \ln W$, we see that the number of states W is reduced by $N!$ times. This is expected, as we overcounted $N!$ times earlier by not considering the indistinguishability of identical particles. Given this, let's check that $\Delta S = 0$. As the first step, notice that (11) can be re-expressed as

$$\begin{aligned} \Delta S_{\text{naive}} &= k \left(N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right) \\ &= k ((N_1 + N_2) \ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2) \end{aligned} \quad (17)$$

Problem 7. Using Stirling's approximation $\ln N! = N \ln N - N$, show that $\Delta S = 0$.

Problem 8. Using Stirling's approximation, show that the correct entropy is given by

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} + \frac{5}{2} \right) \right] \quad (18)$$

Problem 9. Repeat **Problems 3, 4, and 6** for the corrected partition function, and check that the answers do not change. Check also

$$S(\gamma N, \gamma V, T) = \gamma S(N, V, T) \quad (19)$$

Summary

- When calculating the entropy, we get a wrong value if we do not consider the indistinguishability of identical particles.
- Only when we consider the indistinguishability do we get the following desired result:

$$S(\gamma N, \gamma V, T) = \gamma S(N, V, T)$$