

Today

- I. Last Time
- II. Entropy of an Ideal Gas
- III. Free Expansion
- IV. Entropy of Mixing
- V. Work and Heat
- VI. Temperature Anew

I. Talked about the width of multiplicity functions:

Considered $\Omega(N, q)$ of Einstein solid in the high temperature limit. We were able to approximate it by a gaussian centered on equal energy between two copies of the Einstein solid. We found that the gaussian is super narrowly peaked around its central value

$$\sigma = \frac{q}{2\sqrt{2N}}.$$

I. Why does the sharpness of the multiplicity matter?

Systems tend to be in the equilibrium and their fluctuations away from it are very small.

This led us to a new law of thermodynamics, the 2nd law of thermodynamics, which states that systems tend to evolve towards the largest multiplicity state. Why? Well, the largest multiplicity state is far, far, vastly, more probable than other states. So, this is just a statement of probabilities. Nonetheless from this point forward in the course, we'll treat this as fundamental law. We get away with this because the multiplicity is so narrowly peaked.

We can also formulate this in terms of entropy $S = k \ln \Omega$, where we say

$$\Delta S \geq 0.$$

II. The idea gas entropy we found was

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right], \text{ (Sackur-Tetrode Eqn).}$$

Let's find a case where the entropy of an ideal gas increases. We could hold the number of particles fixed and don't change the internal energy, we can increase entropy by increasing the volume.

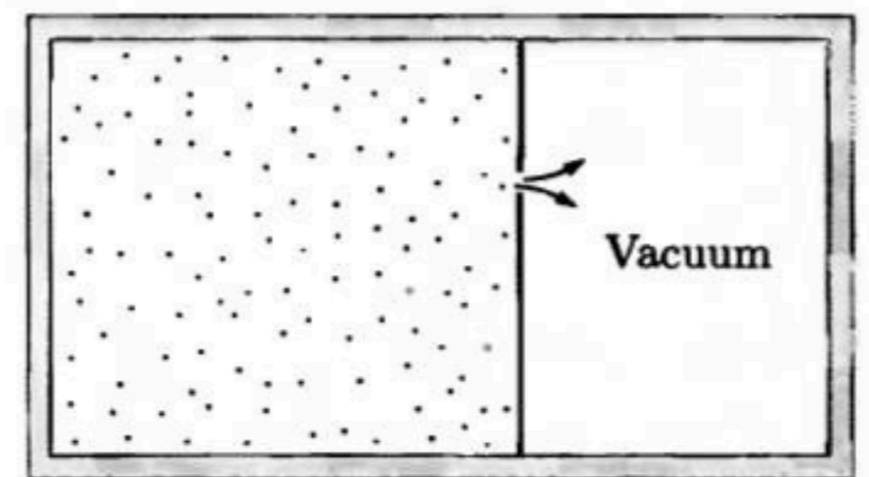
Then

$$\Delta S = Nk \ln \left(\frac{V_f}{V_i} \right) \text{ (fixed } N, U).$$

We added heat into the system in this process and heat is always accompanied by entropy.

III. Let's consider another type of process.

At some time we pierce the barrier and the gas is free to expand.

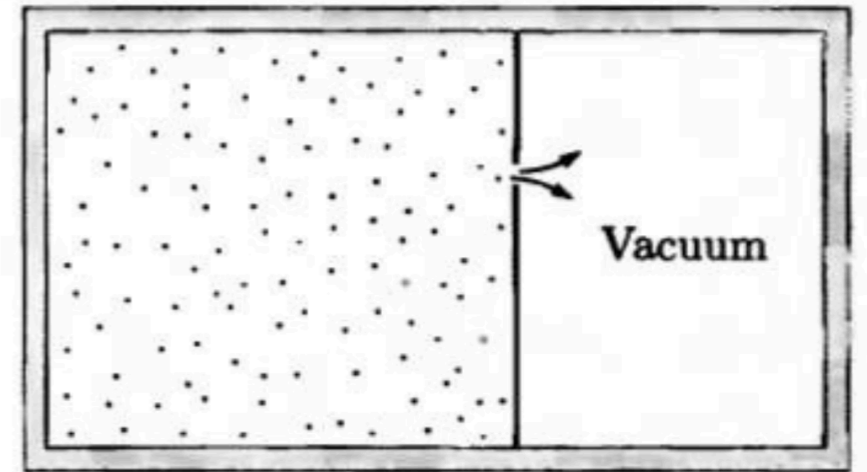


III. Let's consider another type of process. At some time we pierce the barrier and the gas is free to expand. We didn't add any heat to the system or doing any work on it, so

$$\Delta U = Q + W = 0 + 0 = 0.$$

There's also no change in number of particles, so our formula from II. applies and the change in entropy is

$$\Delta S = Nk \ln \left(\frac{V_f}{V_i} \right).$$



IV. Entropy of Mixing. Suppose I had a container divided in two and that I put different gases on each side of the division.

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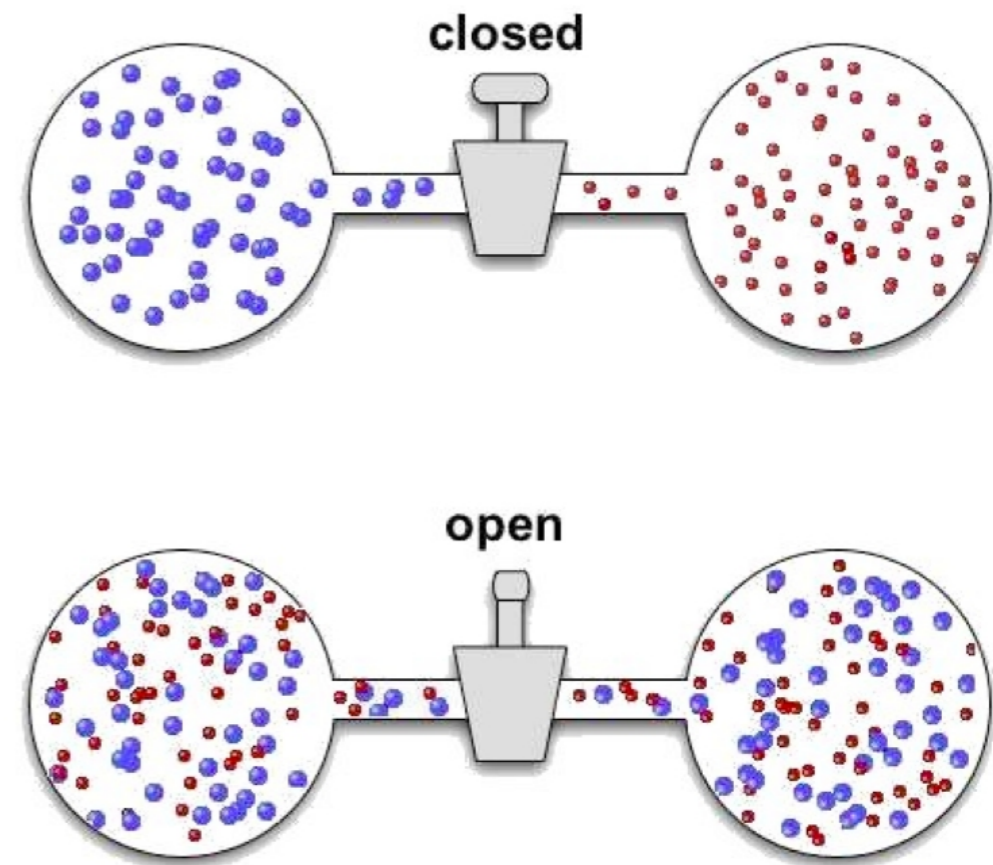
Let's begin by considering one of the gases

$$\Delta S_A = Nk \ln \frac{V_f}{V_i} = Nk \ln 2. \text{ Similarly}$$

for the second gas. Then, the total change is

$$\Delta S_{\text{total}} = \Delta S_A + \Delta S_B = 2Nk \ln 2.$$

This is called the entropy of mixing.



Now, let's analyze this again in more detail.

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

IV. Now, let's analyze this again in more detail.

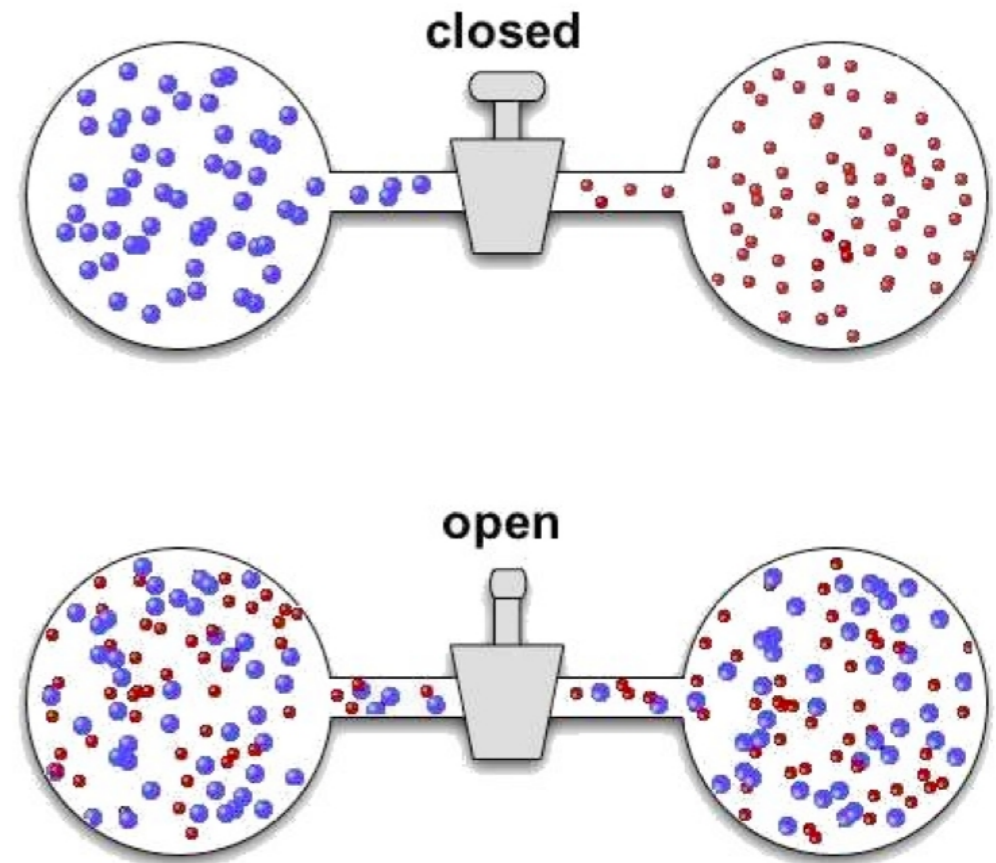
$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

The total entropy is the sum of the entropy of the two types

$$S_{\text{total}} = S_{\text{helium}} + S_{\text{argon}}$$

and this is approximately double either constituents entropy. What happens when we double N , say that of the helium, in the ST eqn.? Note

The factor of 2 in the denominator when we double N , this changes the entropy by $\Delta S = -2Nk \ln 2$. The distinction of these two formulas is evidence for the fact that fundamental particles are indistinguishable. (When you don't treat them that way you get a paradox of entropy, which is called Gibb's paradox.)



Aside on the “width” of a distribution:

I used the “standard deviation”

$$P = Ae^{-\frac{x^2}{2\sigma^2}},$$

Which is when we have fallen by $1/\sqrt{e}$.

Schroeder used the “characteristic width”: falls by $1/e$ of its maximum value.

Also be careful of full vs. half widths.

