MULTIPLICITY OF INTERACTING IDEAL GASES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 2.27.

We've seen that the number of microstates available to an N-molecule 2-d ideal gas with energy U contained in area A is approximately

$$\Omega\approx\frac{(\pi A)^{N}}{(N!)^{2}h^{2N}}\left(\sqrt{2mU}\right)^{2N} \tag{0.1}$$

Schroeder goes through a very similar calculation for the more realistic 3-d gas in a volume V, with the result

$$\Omega\approx\frac{V^{N}}{N!h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}(2mU)^{3N/2} \tag{0.2}$$

Separating out the factors that depend only on N, we can write this as

$$\Omega(U,V,N)=f(N)V^{N}U^{3N/2} \tag{0.3}$$

where

$$f(N)=\frac{(2\pi m)^{3N/2}}{N!(3N/2)!h^{3N}} \tag{0.4}$$

Suppose we have two such gases A and B, confined in volumes V_A and V_B and with energies U_A and U_B. We'll assume that both gases have the same number N of molecules. If the volumes are separated by a partition that allows energy (but not molecules) to be exchanged, then the total multiplicity of the combined system is just the product of the individual multiplicities:

$$\Omega_{total}=\Omega_{A}\Omega_{B}=[f(N)]^{2}(V_{A}V_{B})^{N}(U_{A}U_{B})^{3N/2} \tag{0.5}$$

The total energy is $U=U_A+U_B$ and is held constant. This is similar to the multiplicity equation for two interacting Einstein solids which had the form

$$\Omega=\left(\frac{e}{N}\right)^{2N}(q_Aq_B)^N=\left(\frac{e}{N}\right)^{2N}(q_A(q-q_A))^N \tag{0.6}$$

Here, the energy quanta in the two solids obey the relation $q_A+q_B=q=$ constant, and the calculation in Schroeder's section 2.4 showed that if we plot Ω as a function of q_A, the curve peaks very sharply about $q_A=q/2$ and can be approximated by a Gaussian of form

$$\Omega\approx\left(\frac{eq}{2N}\right)^{2N}e^{-N(2x/q)^2} \tag{0.7}$$

where $x=q_A-q/2$ is the deviation from the most probable value of $q_A=\frac{q}{2}$. The width of the peak, defined as the distance between the points where $\Omega=\Omega_{max}/e$ is

$$w=\frac{q}{\sqrt{N}} \tag{0.8}$$

For our interacting gases that can exchange energy, the $(q_A(q-q_A))^N$ factor is replaced by $(U_AU_B)^{3N/2}=(U_A(U_{total}-U_A))^{3N/2}$ and if we follow through the same steps to approximate the curve by a Gaussian around its peak, we find that the formula for the width of the peak just replaces the exponent N in the $(q_A(q-q_A))^N$ factor in 0.6 by the exponent $3N/2$ in the $(U_AU_B)^{3N/2}$ factor for the interacting gases, and the width is

$$w=\frac{U_{total}}{\sqrt{3N/2}} \tag{0.9}$$

For any macroscopic sample of gas, N is large (of the order of 10^{23}) so the width of the peak is very, very small compared to the overall scale of the graph.

Since one of the assumptions of statistical mechanics is that all microstates are equally probable, it should be possible, just by chance, to find that even if a gas has a total volume V available to it, sometimes all the molecules will clump up in some smaller portion of the volume, leaving the remaining space empty (a vacuum). How likely is this to happen?

Effectively, what we're asking is how likely is it that the volume occupied by the gas will spontaneously reduce from V to aV, where $0<a<1$. Since the volume is all that changes (both N and U are unchanged), we can look at 0.3 and find that reducing the volume reduces the multiplicity to

$$\Omega(a)=f(N)(aV)^NU^{3N/2} \tag{0.10}$$

Thus the probability that this will happen spontaeously is

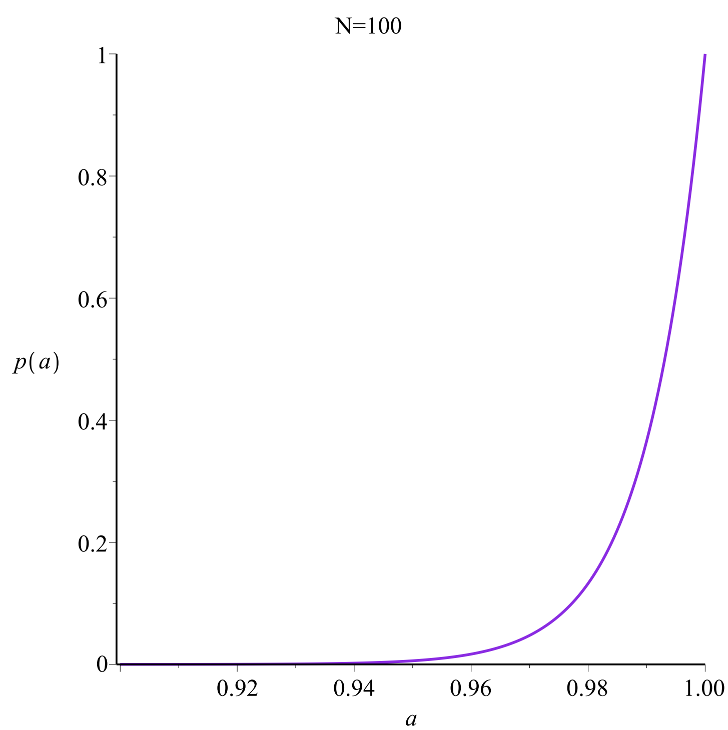
$$p(a) = \frac{\Omega(a)}{\Omega} = a^N \tag{0.11}$$

Since N is a large number, even a value of a close to 1 is still very unlikely. For example, if $a = 0.99$ we find (it's easier to work with logarithms here):

N	$p(0.99)$
100	0.366
10^4	2.25×10^{-44}
10^{23}	$\approx 10^{-4\times 10^{20}}$

With 100 molecules, we can reasonably expect to see it happen. With 10,000 molecules, we'd probably never see it within the age of the universe. With 10^{23}, that's about as close to a definition of 'impossible' as you're likely to get.

In fact, even for only 100 molecules, the chance of the gas crowding into a smaller volume is virtually zero for $a < 0.95$ as we can see from a plot (note that the horizontal axis runs from 0.9 to 1.0):



The take home message is that these sorts of events just never happen in nature.

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