Air molecules come in different varieties: nitrogen and oxygen mostly, with smaller numbers of water, argon, and carbon dioxide molecules. As they constantly bump around, why can't they sort themselves out? In other words, why don't the lighter H_2O gas molecules form an upper layer, followed by a denser layer of nitrogen, all the way down to carbon dioxide?

Answer:

It could happen, but the likelihood is extremely small.

In liquids, especially if the attractions that a molecules has for its own kind are stronger than those it has for those of another kind, then the more dense molecules will congregate together and will be at the bottom. Otherwise less dense liquid molecules would not be able to physically support more dense ones against gravity. Mix oil and water, and except for a thin suspension layer in between them, oil ends up floating on water.

But the attractions between gas molecules are either extremely weak or virtually nonexistent for the so-called ideal gases like argon, nitrogen and oxygen. In addition there is far more empty space between gas molecules than between molecules in the liquid state. Add to that their unique translational motion, and gas molecules are fairly likely to form a random mix. But still, if they are so free to move, and if time is on their side since they are practically "immortal" (unless some are snatched up for respiration, as in the case of oxygen, or by nitrogen-fixing bacteria), why is it so unlikely to find them for a fraction of a second in a neat orderly pattern like that of layered alcoholic drink?

Such a specific horizontal pattern for our components of air would represent a single macrostate. But there are a multitude of macrostates possible for molecules: vertical, diagonal, swirl, speckled, around- the bulls eye--(all of course unlikely) and a host of other more realistic patterns, where in any reasonably sized volume you would find a representative sample of air. For each of the latter macrostates there would be almost countless microstates: exact specifications of position and velocity. To confine molecules of, say, nitrogen in a specific layer would limit their position and hence reduce the number of available microstates. These divided by the total number of all microstates possible are what gives them such a low probability of existing in that state.

W, the number of microstates for a given macrostate, is related to an important property known as entropy, *S*.

S = k log$W$, where k = Boltzman's constant = 1.38 X 10^{-23} J/K

Entropy which measures the disorder of a system will be very low when the number of microstates is low. Layered gases would represent too much order, to low an entropic state, for nature's tastes.

To make the mathematics more concrete, consider flipping three coins simultaneously. What is the likelihood of flipping three heads, in other words of

obtaining only one macrostate among the possibilities of three other microstates, two of which have a few microstates?

Macrostate	Microstate Possibilities	Number of Microstate s	Probability of occurence
3 heads	HHH	1	1/(1+3+3+1) = 0.125
2 heads, 1 tail	HHT, THH, HTH	3	0.375
1 tail, two heads	HTT, TTH, THT	3	0.375
3 tails	TTT	1	0.125

12.5% is still not too bad. But with increasing number of coins flipped, the chances keep getting smaller. (Imagine what happens with the several Avogadro number of molecules in a room!) The number of microstates for each macrostate is given by Pascal's triangle:

# of coins
flipped, *n*

```
1                                    1      1
2                                1      2      1
3                            1      3      3      1
4                        1      4      6      4    0   1
5                    1      5     10     10      5      1
6                1      6     15     20     15      6      1
7            1      7     21     35     35     21      7      1
8        1      8     28     56     70     56     28      8      1
9    1      9     36     84    126    126     84     36      9      1
```

To extend the pyramid, add a "1" at each end. Then simply add the pair of numbers to the right and left of each empty slot, and enter the result immediately below it.

The total number of microstates possible for each number of coins, n, is given by 2^n. For example for our three coins, n = 3, so we obtain $2^3 = 8 = 1 + 3 + 3 + 1$. But if we flipped eight coins, there would be 2^8 microstates = 256. The chances of flipping all heads simultaneously is reduced to 0.0039 or 0.3%. [Note that even the possibility if flipping 4 heads and 4 tails is only 70/256 = 27%.] Of course if we had a thousand coins the chances of getting all heads would be only one out $1/2^{1000} = 1$ out of 1.072×10^{301}. To be more precise it would be 1 out of
10715086071862673209484250490600018105614048117055336074437503883703510511249361224931983788156958581275946729175531468251871452856923140435984577574698574803934567774824230985421074605062371141877954182153046474983581941267398767559165543946077062914571196477686542167660429831652624386837205668069376.

Hopefully you are now convinced that gas molecules will unlikely spontaneously occupy an ordered state.

By the way if you are wondering why k's unit and therefore entropy's unit is J/K, it is because the change in entropy(ΔS) experienced by molecules as they absorb or lose energy Q at a given absolute temperature (T) is given by

$$\Delta S = Q/T$$

For example if a 10.0 g cube of ice melts at 0^oC, it absorbs 6.01 kJ /mol = 334 J/g. That implies that the water molecules experience an increase in entropy of (334 J/g)(10.0g)/(0+273)= 12.2J/K. As the heat flows into the ice, the orderly arrangement of molecules is broken up into a more chaotic pattern of rolling water molecules that have more microstates (more possible speeds and positions) than molecules in a frozen state.

Schrodinger once defined life as negative entropy. It is true that life creates more order locally within the organism. But if you consider the overall state of things, even life increases the entropy of the universe. Plants absorb sunlight extracts CO_2 from the atmosphere, protons from water, nitrates from the soil to make sugars and proteins, but they also reflect unused light and release gaseous oxygen back into the environment, increasing its entropy. As animals, we have the same effect, decreasing entropy as we build and grow, but constantly releasing waste and heat into our surroundings, leading to an overall increase in *S*.

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molecular diameter: 10^{-8} to 10^{-7} centimeters.

molecular number density: 2.7×10^{19} molecules per cubic centimeter (at STP)

total volume of gas molecules per cm^3 if they could be stacked without any space in between: 0.002 to 0.003 cm^3 (lots of empty space!)

average molecular speed: 10^4 to 10^5 centimeters per second.

average distance between molecules: 10^{-7} to 10^{-6} centimeters.

collision rate per molecule: 10^9 to 10^{10} collisions per second.

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Online
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