

Bose–Einstein Condensation

Birds of a Feather Flock Together

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In 1924 Bose introduced a counting rule for the states of a gas of photons which explained Planck's law for thermal radiation at one stroke. Einstein not only recognised the importance of this idea but immediately applied it to a more conventional gas like helium. In this case, unlike that of radiation, the number of particles is held fixed. He derived the stunning conclusion that a finite fraction of the particles could settle in the lowest energy state even above absolute zero. These ideas had to wait fourteen years for their first application. Seventy years later they are being used in atomic physics laboratories all over the world.

Everybody is talking about Bose–Einstein condensation. This discovery made in 1924 seems to have exploded like a time bomb seventy years later. How did these two names come together? S N Bose was a teacher of physics in Dacca, as far from the mainstream as one could imagine. Einstein was, of course, the giant who had already given the world special and general relativity, the light quantum, Brownian motion. The story is an extraordinary one, and it has been told earlier in these pages when the central figure was Bose [1]. Now let us look at it from Einstein's point of view. He struggled for 20 years with the concept of the light quantum and Planck's radiation formula [2]. Suddenly, a bolt from the blue arrived. Someone he had never heard of was proposing a new derivation of Planck's formula for the intensity of blackbody radiation. It made no reference to waves whatsoever, being stated entirely in the language of photons. Many times in the history of mathematics and physics, such letters have been ignored. The idea is too revolutionary and the author too unknown. Let us salute Einstein for not taking that easy path. He read the paper, recognised its



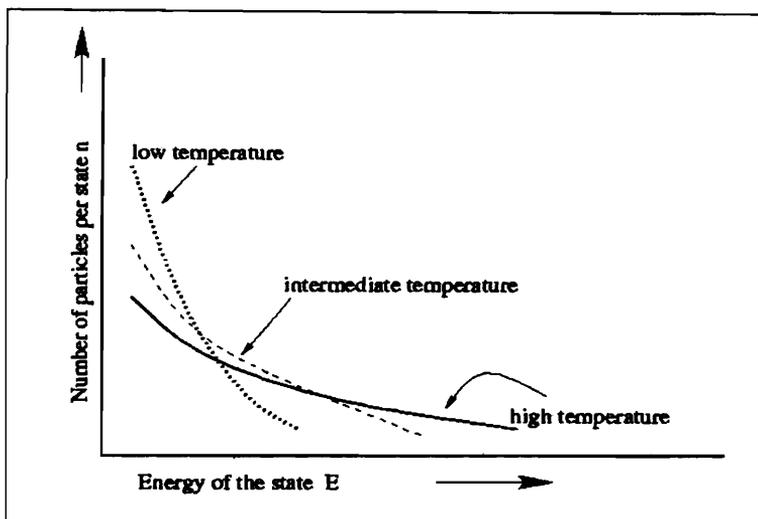
deep originality, translated it into German, wrote a covering note on its importance and forwarded it for publication.

Superficially, the mathematical steps in Bose's discussion of a gas of photons resembled what Boltzmann had gone through fifty years earlier, in the discussion of ordinary gases. We describe the basic idea here. Common observation shows that a gas fills its container uniformly. In other words, the probability distribution of the position of any particle in the gas is a constant function within the container. A more difficult experiment is needed if we want to find the probability distribution of the x -component of the velocity of the molecules (for example). This is found to be the famous bell shaped curve known as the Gaussian distribution. As a function of velocity it is $e^{(-\text{const} \times v^2_x)}$ and similarly for the y and z components. In terms of the energy E of a state, this translates into a number of particles per state, n proportional to $e^{(-\beta E)}$. The science of statistical physics tries to understand why these particular distributions, for the position and for the velocity, are special. After all, nothing in the laws of physics prevents all the molecules being on one side of the container, at least for some time. Likewise, nothing forbids a situation where all the molecules have the same speed, half going to the left and half to the right. Again, this situation could occur at some time and change because of collisions.

Boltzmann took two approaches to the problem, both of them deep and fruitful. One was to ask how any such initial state would evolve with time. Clearly, not even Boltzmann could say with certainty what the precise outcome of a huge number of molecular collisions would be. So he made a guess about what was the *most probable* number of collisions changing the velocities of the molecules in various ways. This led to the famous distribution law named after him and is sketched in *Figure 1*. The probability of finding a molecule in a single state of a given energy is proportional to an exponential function of the energy. But this method of collisions is not the whole story. One can – and Boltzmann did – look at the matter in a different way. Take a coin tossed ten times. To say that five heads turned up is not a



Figure 1. The Boltzmann distribution of particles over energy states.



¹This can occur in 252 ways out of a total 1024 possible outcomes of ten tosses.

complete description, because we are not saying which of the tosses were heads, this can happen in many¹ ways. Similarly, to say that a gas has a certain distribution of velocities is not a complete description; this can happen in many ways. All one has to do is to count the number of ways, and this tells us the state in which the gas is most likely to be found. Boltzmann was able to show that the most probable behaviour of a gas, the one which can occur in the largest number of ways, is to fill the container uniformly, and have a gaussian distribution for each component of the velocity vector.

With this background, we can state what was revolutionary in the paper that Bose sent to Einstein. Treating the photons as a gas, he used a counting rule different from Boltzmann's. Again, we give only the basic idea here. Take two different boxes, called 1 and 2, and two balls, called A and B. Let us look at all possible states of the system. Clearly there are four of them, which we can symbolically denote as A1 B1, A2 B2, A1 B2 and A2 B1. Bose's counting rule was equivalent to saying there were only *three* states, with the last two viz. A1B2 and A2B1, counted as one. This was as if someone had rubbed off the letters A and B painted on the two balls. One says that in Bose's way of counting, the particles are *indistinguishable*. We can see what effect this has in our simple example. The two cases in which both the particles



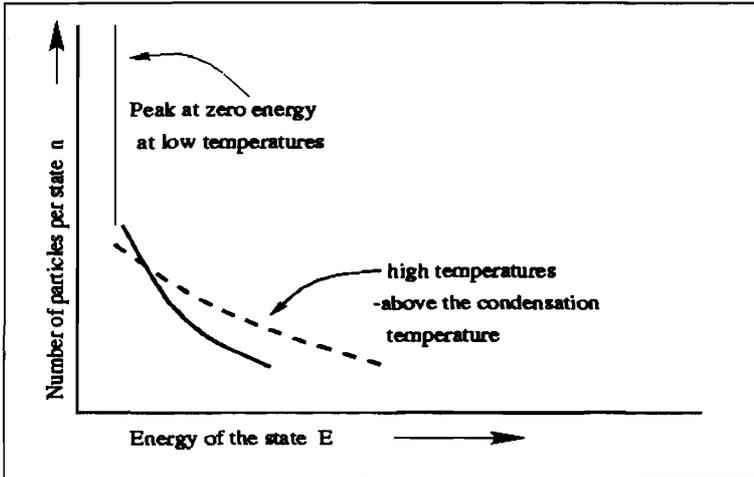


Figure 2. The Bose-Einstein distribution for a gas at a high and at a low temperature.

are in the same state (A1 B1 and A2 B2) now get two thirds of the weight, instead of half as in Boltzmann's way of counting. This result carries over in more general cases with many more boxes and balls. The example given above shows that the Bose distribution² gives more weightage to situations in which many particles occupy the same state. And this extra weightage was able to explain the observed distribution of photons over frequency in thermal radiation.

Einstein had an immediate additional deep insight into the consequences of Bose's counting rule. In the case of photons, the total number of particles actually decreases as we decrease the total energy of the system (equivalently, as we lower the temperature). In fact, the total number of photons is proportional to the cube of the absolute temperature. Since their average energy is proportional to the temperature, the total energy per unit volume is proportional to the fourth power of the temperature. However, if we apply Bose statistics to a gas of helium atoms in a box, we must obviously keep the number of atoms fixed as the temperature varies. So the precise formula for the number of atoms in a state with energy E is different from what Bose used in the case of photons. It looks very similar, but contains an additional term denoted by μ subtracted from the energy. The formula reads³

$$n = 1 / (1 + \exp(\beta(E - \mu)))$$

² The new distribution law reads $n = 1 / (\exp(\beta E) - 1)$, β is inversely proportional to the temperature $\beta = 1 / k_B T$ with k_B = Boltzmann's constant.

³ One simple way of understanding the origin of such a term is as follows. Let us imagine a "reservoir" which contains a large number of helium atoms, all having energy μ . Connect the reservoir to our box. Every time we move a particle from the reservoir into our box to a state of energy E , the total energy of the system changes by $E - \mu$. The box alone now behaves like a system with a variable number of particles, where the energy E is replaced by $E - \mu$. Clearly μ , cannot be greater than zero in this formula since n would become negative for $E < \mu$.

This simple extra term has profound consequences. As the temperature is lowered, more and more particles pile into the lowest energy state. (For the gas of photons, they just disappear from the system). At a low temperature, *but one which is still above absolute zero*, the answer for the number of particles in the lowest state becomes infinite because μ approaches zero from below. A lesser man might have concluded that something absurd was happening and the whole counting rule had to be abandoned. But Einstein realised that this infinite answer, though wrong, held the key to what was really happening in the gas as it was being cooled. He boldly said that one has to treat the lowest energy state as a separate entity from all the other states. All physical quantities would receive separate contributions from the lowest state, called the 'condensate', and from *all* other states. In a Boltzmann gas the contribution of any single state, even the one of lowest energy, is negligible because there are so many states which have nearby energies. But the Bose counting rule tilts the balance in favour of a *finite fraction* of the particles being in the lowest energy state, below the special value of the temperature which Einstein had calculated. The values of density N and temperature T can be described as those which give approximately one particle per thermal de Broglie wavelength λ_T . For typical energy $k_B T$, the corresponding momentum is $(2mk_B T)^{1/2}$ and the wavelength λ_T equals $h/(2mk_B T)^{1/2}$. The number of particles in a volume λ_T^3 is $N(h^3/(2mk_B T)^{3/2})$. When this exceeds 14.54, the condensation begins. This can be achieved by raising N or lowering T .

One should remember that Einstein was not motivated by any experimental fact regarding gases in his work. He was following the basic principles of statistical physics to their logical, though amazing, conclusion. He also had a deep conviction that Bose's counting rule was not just a trick to understand radiation but a new general principle. When Einstein wrote his paper, and for more than a decade later, it did not appear that there was any direct connection with known phenomena. Even fourteen years later, in 1938, the eminent quantum and statistical physicist



Fritz London could say that “In the course of time, the degeneracy of the Bose–Einstein gas has rather got the reputation of having a purely imaginary existence”. In the same paper that we have quoted, London noted that at the density of liquid helium, the temperature for Bose–Einstein condensation of an ideal gas would be about three degrees above absolute zero.⁴ Liquid helium shows new properties below 2.1 degrees Kelvin [3]. London boldly suggested that these new properties were a consequence of Bose–Einstein condensation. He was fully aware that liquid helium was very far from being an ideal gas. There is a strong repulsive force between two atoms which came too close to each other, and a weaker attractive force at larger distances. Recent experiments, sixty years after London, show that his guess regarding liquid helium was right. About ten per cent of the atoms have zero momentum at absolute zero. (In an ideal gas this would have been 100%.)

This subject took another turn in 1995, when experimenters in the US were able to produce a Bose–Einstein condensate for Rubidium atoms. In this case, the density was low enough that Einstein’s original ideas, with small modifications, could be applied [4]. This is now a very active field of experimental physics. Nowadays, a beam of atoms in the same quantum state is called an ‘atom laser’ and various ingenious schemes for producing and utilising such beams are being invented. This is expected to give rise to extremely accurate measurements of time and other physical quantities.

Statistical physics was certainly Einstein’s early love. He had written papers on the statistical basis of thermodynamics even before his relativity papers – unfortunately, they mainly rediscovered what Gibbs had already just done. His discussions of Brownian motion, of photons, of critical opalescence, are all gems of statistical thinking. And his single paper on condensation in a gas obeying Bose statistics should be counted amongst these gems. Anyone else who did just this work would have acquired a towering reputation. But Einstein the statistical physicist was ultimately eclipsed by Einstein the relativist.

⁴We should add that not all kinds of identical particles obey Bose statistics and show condensation. Electrons, for example, show Fermi statistics and behave in a completely different way at low temperatures. The same is true of ³He, the rarer isotope of helium!

Suggested Reading

- [1] *Resonance*, Vol.1, No.2, p.92, 1996.
- [2] N Mukunda, *Resonance*, Vol.5, No.3, p.35, 2000.
- [3] R Srinivasan, *Resonance*, Vol.2, No.2, p.8, 1997.
- [4] Rajaram Nityananda, *Resonance*, Vol.1, No.2, p.111, 1996.

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