- HH0014 -

Bose-Einstein Condensation

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(Dec 23, 2011)

Consider a system composed of non-interaction bosons inside a box of volume $V = L^3$. It is convenient to introduce the temperature-dependent quantum concentration,

$$n_Q(\tau) = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}. \tag{1}$$

In previous lectures, we understand that quantum statistics starts to play important role when crossing the boundary $n \approx n_Q(\tau)$. Unlike the smooth crossover for non-interacting fermions from the classical regime to the quantum territory, there is a true phase transition for bosons to cross the boundary from the classical to the quantum. As will be elaborated later, the transition occurs at

$$\boxed{\frac{n}{n_Q} = \zeta(3/2) \approx 2.612} \tag{2}$$

For small density n or high temperature τ, the boson system is in the classical regime. On the other hand, by either lowering the temperature or increasing the density, it enters the condensed phase, often referred as Bose-Einstein condensate.

The existence of condensate is defined by the notion of "macroscopic occupation". For each orbital, one can define its macroscopic occupation,

$$n(\epsilon_s) \equiv \lim_{V\to\infty} \frac{f(\epsilon_s)}{V} = \lim_{V\to\infty} \frac{1}{V} \frac{1}{\exp[(\epsilon_s - \mu)/\tau] - 1}. \tag{3}$$

Except the lowest orbital, $\epsilon_s - \mu > 0$, ensuring the Bose function is always finite. In consequence, the corresponding macroscopic occupation is zero in the thermodynamic limit ($V \to \infty$). For the lowest orbital, it is possible that $\epsilon_s - \mu$ is tiny and goes to zero as $V \to \infty$. The singularity in the Bose function may cancel the $1/V$ factor and gives rise to non-zero macroscopic occupation. In general, phase transition occurs when singularity develops in thermodynamic limit, i.e. $V \to \infty$ and is usually very difficult to describe in complete details. The Bose-Einstein condensation is one of the few examples where how the singularity arises can be understood without too much mathematical difficulty.

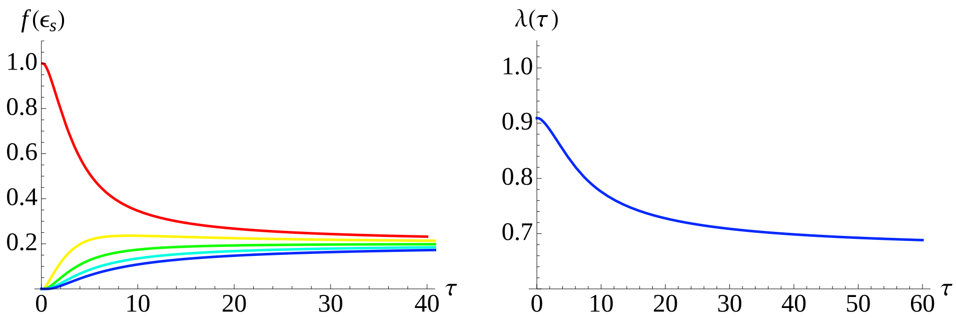

Figure 1: A boson system with $N_s = 5$ orbitals and $N = 10$ particles. For simplicity, the adjacent gap is set to unity, $\Delta = 1$.

• finite-orbital boson system

Let us start with a simple boson system with $N_s = 5$ orbitals and $N = 10$ particles. For simplicity, let's assume the orbital energies are $\epsilon_s = s\Delta$, with $s = 0, 1, 2, 3, 4$. The occupation fraction is defined as the ratio of the occupation number and the total particle number,

$$n_s \equiv \frac{1}{N} \frac{1}{(1/\lambda)\, e^{\epsilon_s/\tau} - 1}, \tag{4}$$

where $\lambda = e^{\mu/\tau}$ is the absolute activity. The conservation of particles impose the constraint on these occupation fractions,

$$\sum_{s=0}^{4} n_s = \frac{1}{N} \sum_{s=0}^{4} \frac{1}{(1/\lambda)\, e^{\epsilon_s/\tau} - 1} = 1. \tag{5}$$

The absolute activity can then by solved numerically as plotted in Figure 1. At high temperatures, it is clear that $n_s \approx 1/N_s = 1/5$. However, as the temperature cools down, the occupation fraction for the lowest orbital n_0 approaches unity, while all other occupation fractions falls down to zero.

The absolute activities at low and high temperatures can be computed. In the low temperature regime, the occupation is dominated by the lowest orbital,

$$N \approx \frac{1}{(1/\lambda_0) - 1} \quad \rightarrow \quad \lambda_0 \approx \frac{N}{N+1} \approx 0.91. \tag{6}$$

At high temperatures, all occupation fractions are the same and the energy difference can be ignored,

$$N \approx N_s \frac{1}{(1/\lambda_\infty) - 1} \quad \rightarrow \quad \lambda_\infty \approx \frac{N}{N+N_s} \approx 0.67. \tag{7}$$

The above results can be checked in Figure 1. Because both N_s and N are finite here, there is no singularity.

However, for Bose gas in three dimensions, there are infinite states ($N_s \to \infty$) and the absolute activity $\lambda \to 0$ in the high temperature limit ($\tau \to \infty$). Meanwhile, it is expected that all occupation fractions vanish as $1/N_s$ at high temperatures. On the other hand, in the low-temperature regime, n_0 will be of order one, much larger than other occupation fractions. The drastic different trends in high and low temperatures imply some sort of singularity, emerging in the thermodynamic limit.

• near zero temperature

There are different ways to understand how Bose-Einstein condensation occurs. Let us follow Kittel's textbook and start with the low temperature limit first. Suppose the total particle number N is large but not infinite. Near $\tau = 0$, almost all bosons are in the ground state. The Bose-Einstein distribution simplifies,

$$N = \sum_s \frac{1}{\frac{1}{\lambda} e^{\epsilon_s/\tau} - 1} \approx \frac{\lambda}{1-\lambda}. \tag{8}$$

One can then solve for the absolute activity,

$$\boxed{\lambda \approx \frac{N}{N+1} \approx 1 - \frac{1}{N}} \tag{9}$$

In the thermodynamic limit, $\lambda = 1$. It gives rise to singularity and leads to macroscopic occupation in the lowest orbital. The chemical potential is

$$\mu = \tau \log \lambda = -\tau \log\left(1 + \frac{1}{N}\right) \approx -\frac{\tau}{N}. \tag{10}$$

The chemical potential is very close to zero but slightly less than zero. This is a very nice realization of the mathematical notion "0^-" in a physical system.

• almost-zero chemical potential

Consider an atom inside a cube of volume $V = L^3$. The energy of the single-particle orbital is

$$\epsilon = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right). \tag{11}$$

The energies of the lowest and the second lowest orbitals are

$$\epsilon_0 = \frac{\hbar^2\pi^2}{2mL^2}(1+1+1), \quad \epsilon_1 = \frac{\hbar^2\pi^2}{2mL^2}(4+1+1). \tag{12}$$

Take $m = 6.6 \times 10^{-27}$ Kg (^{4}He atom) and $L = 1$ m, it is straightforward to estimate the energy gap between the lowest two orbitals.

$$\Delta\epsilon = \epsilon_1 - \epsilon_0 \approx k_B \times 10^{-18} \text{ K}. \tag{13}$$

The energy gap is tiny for a macroscopic system. It is hard to imagine how such a tiny energy difference can play any significant role in a physical system. Well, it does and here comes the surprise!

For a Bose gas of $N = 10^{23}$ atoms at 1 mK, the chemical potential is

$$\mu \approx \epsilon_0 - \frac{\tau}{N} = \epsilon_0 - k_B \times 10^{-26} \text{ K}, \tag{14}$$

where ϵ_0 is the energy of the lowest orbital. The occupation number of the second lowest orbital is approximately

$$f(\epsilon_1) = \frac{1}{\exp[(\epsilon_1 - \mu)/\tau] - 1} \approx \frac{1}{\exp(\Delta\epsilon/\tau) - 1} \approx \frac{\tau}{\Delta\epsilon} = 10^{15}. \tag{15}$$

The number may look large at first glance but the corresponding fraction is actually very small,

$$\boxed{\frac{f(\epsilon_1)}{N} \approx \frac{\tau}{N\Delta\epsilon} \approx \frac{(\epsilon_0 - \mu)}{\epsilon_1 - \epsilon_0} \approx 10^{-8}} \tag{16}$$

That is to say, the chemical potential is much closer to the energy of the lowest orbital than the tiny energy gap $\Delta\epsilon$. For a Bose gas with constant density n, the energy gap $\Delta\epsilon \sim 1/V^{2/3}$ in the thermodynamic limit. But, $\epsilon_0 - \mu \sim 1/N \sim 1/V$ goes to zero faster. As a result, the occupation fraction of the second lowest orbital approaches zero even though its energy is extremely close to that of the lowest orbital.

• cooling down from high temperature

Now we reverse the direction and try to understand the Bose gas from the high temperature side. The total number is expressed as the sum of Bose functions over all orbitals,

$$N = \sum_s \frac{1}{\frac{1}{\lambda} e^{\epsilon_s/\tau} - 1}. \tag{17}$$

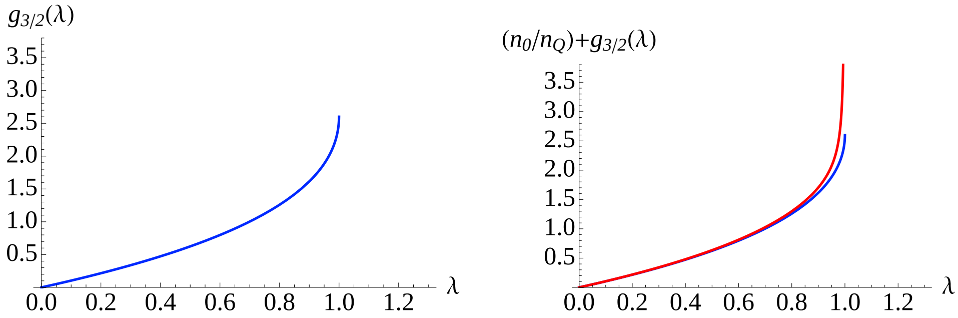

Figure 2: Polylog function $g_{\frac{3}{2}}(\lambda)$ and the same function but with lowest-orbital occupation. The quantum concentration is set to unity ($n_Q = 1$) in the right panel.

As explained in previous lecture, the summation can be converted into the integral,

$$\sum_s (\cdots) = \frac{2}{\sqrt{\pi}}(n_Q V) \int_0^\infty dx\, \sqrt{x}(\cdots), \tag{18}$$

where $x = \epsilon/\tau$ is dimensionless. Thus, the particle density is expressed by the following integral,

$$n = n_Q\, \frac{2}{\sqrt{\pi}} \int_0^\infty dx\, \frac{\sqrt{x}}{(1/\lambda)e^x - 1} \tag{19}$$

Recall the definition of the polylogarithm function,

$$g_\nu(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\nu} = \frac{z}{1^\nu} + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots\,, \tag{20}$$

and the useful integral formula,

$$\int_0^\infty dx\, \frac{x^{\nu-1}}{(1/\lambda)e^x - 1} = \Gamma(\nu) g_\nu(\lambda). \tag{21}$$

The particle density of a Bose gas can be expressed elegantly by the polylogarithm function,

$$n = n_Q\, g_{\frac{3}{2}}(\lambda) \le n_Q\, g_{\frac{3}{2}}(1). \tag{22}$$

The inequality comes from the fact that $g_{\frac{3}{2}}(\lambda)$ is a monotonically increasing function with maximum at $\lambda = 1$ as shown in Figure 2. At high temperatures,

n_Q is large and the inequality is easily satisfied. But, as the temperature cools down to the critical one,

$$n = g_{\frac{3}{2}}(1)\left(\frac{m\tau_c}{2\pi\hbar^2}\right)^{3/2} \approx 2.612\left(\frac{m\tau_c}{2\pi\hbar^2}\right)^{3/2}, \tag{23}$$

The absolute activity reaches unity, $\lambda = 1$, i.e. $\mu = 0$. This is already strange because the occupation number of the lowest orbital becomes singular. What if we further cool down the Bose gas below the critical temperature τ_c? Troubled... We don't even have a real solution for λ if the temperature is cooled below the critical one!

• macroscopic occupation of the lowest orbital

The confusions stem from the macroscopic occupation of the lowest orbital,

$$n_0 = \frac{1}{V}\frac{\lambda}{1-\lambda}. \tag{24}$$

Since the density of state at $\epsilon = 0$ vanishes, it is legal to separate the occupation number of the lowest orbital and the others. If the volume is large (but not yet infinite), the summation can again be converted into integral and the density can be expressed as

$$n = n_0 + n_Q\, g_{\frac{3}{2}}(\lambda). \tag{25}$$

Note that, if we blindly take the thermodynamic limit ($V \to \infty$),

$$n_0 = \lim_{V\to\infty}\frac{1}{V}\frac{\lambda}{1-\lambda} = 0. \tag{26}$$

We then come back to the same expression in previous paragraphs. To overcome the difficulty explained before, one needs to be cautious when taking the thermodynamic limit. For $\tau > \tau_c$, the absolute activity can be solved from $n = g_{\frac{3}{2}}(\lambda)$. For $\tau < \tau_c$, one should keep the volume large but finite momentarily. As can be seen in Figure 2, the equation $n = n_0 + n_Q g_{\frac{3}{2}}(\lambda)$ indeed has a real solution for λ,

$$\boxed{\lambda \approx 1 - \frac{1}{N}\left(\frac{n}{n_0}\right), \quad \text{when } n_0 \neq 0.} \tag{27}$$

It is worth emphasizing that the above relation is true only when $n_0 \neq 0$ and the particle number N is enormous. When the macroscopic occupation is nonzero, a finite fraction of particles stay in the lowest orbital, referred as Bose-Einstein condensate. Though we only work out the critical temperature here, it is expected that all other physical quantities in the condensate can be computed with more advanced techniques.

Meanwhile, the temperature dependence of the condensation fraction can be derived,

$$n_0 = n - n_Q g^{\frac{3}{2}}(1) = n\left[1 - \left(\frac{\tau}{\tau_c}\right)^{\frac{3}{2}}\right]. \tag{28}$$

Because N for a macroscopic system is huge (of the order 10^{23}), even for τ slightly less than the critical temperature τ_c, a large number of bosons occupy the lowest orbital. These particles in the lowest orbital form a condensate and usually give rise to superfluidity when realistic interactions are included.

• phase transition due to singularity

The emergence of a condensate marks a true phase transition from the gas phase to the condensation phase. The phase transition is associated with the nonuniform convergence so that the order of limits does not commute,

$$\lim_{\lambda\to 1}\lim_{V\to\infty}\frac{1}{V}\,\frac{\lambda}{1-\lambda} = 0 \tag{29}$$

$$\lim_{V\to\infty}\lim_{\lambda\to 1}\frac{1}{V}\,\frac{\lambda}{1-\lambda} = \infty \tag{30}$$

If the thermodynamic limit is taken first, the macroscopic occupation is always zero. However, if the absolute activity is taken to be unity first, the macroscopic occupation is divergent. None of the results are sensible and these two limits are not independent but related: $1-\lambda \approx 1/(n_0 V)$. A final comment is that the pause transition is not directly related to $\tau \to 0$ limit – the condensation occurs at finite temperature!

• occupation number fluctuations

It is interesting to study the fluctuation of the occupation number in a Bose gas. The occupation number for each orbital is

$$\langle N_s\rangle = \frac{1}{\mathcal{Z}}\sum_{m=0}^{\infty} m\, e^{-m(\epsilon_s-\mu)/\tau}, \tag{31}$$

where $\mathcal{Z}$ is the Gibbs sum. Taking derivative with respect to ϵ_s, one finds a useful identity,

$$-\tau \frac{\partial}{\partial \epsilon_s} \langle N_s \rangle = \frac{1}{\mathcal{Z}} \sum_{m=0}^{\infty} m^2 \, e^{-m\epsilon_s/\tau} + \frac{\tau}{\mathcal{Z}^2} \frac{\partial \mathcal{Z}}{\partial \epsilon_s} \sum_{m=0}^{\infty} m \, e^{-m\epsilon_s/\tau}. \tag{32}$$

After a little bit of massage, the above identity can be rewritten as

$$\langle N_s^2 \rangle - \langle N_s \rangle^2 = -\tau \frac{\partial}{\partial \epsilon_s} \langle N_s \rangle. \tag{33}$$

Since the occupation number is $\langle N_s \rangle = [e^{(\epsilon_s - \mu)/\tau} - 1]^{-1}$, it is straightforward to obtain the fluctuations in particle numbers,

$$\boxed{(\Delta N_s)^2 \equiv \langle N_s^2 \rangle - \langle N_s \rangle^2 = \frac{e^{(\epsilon_s-\mu)/\tau}}{[e^{(\epsilon_s-\mu)/\tau} - 1]^2} = \langle N_s \rangle + \langle N_s \rangle^2} \tag{34}$$

For a Bose gas, the fluctuation is always strong, $\Delta N_s / \langle N_s \rangle > 100\%$. It is important to stress that the fluctuation we discuss here is about the occupation number for each orbital, not the total particle number. It is quite interesting that the fluctuation is smaller when $\langle N_s \rangle$ is larger. As a result, in the condensation phase, the occupation fluctuation of the lowest orbital is the smallest, $\Delta N_0 / \langle N_0 \rangle = 1$ while other orbitals gave stronger fluctuations. The strong fluctuation in the occupation number reflects the nature of non-interacting bosons: they love to hang out together, known as boson bunching effects in the literature.

2011.1223
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