

**On the Bose-Einstein condensation**

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**Abstract**

The Bose-Einstein condensation is reviewed.

As it is well-known, the number of particles  $N$  of an ensemble of ideal bosons is given by

$$N = g \sum_{\mathbf{k}} \frac{1}{\exp[(\varepsilon - \mu)/T] - 1} \quad , \quad (1)$$

where  $g = 2s + 1$ ,  $s$  being the spin,  $\mu$  is the chemical potential and  $T$  is the temperature; the energy levels  $\varepsilon$  are given by  $\varepsilon(k) = \hbar^2 k^2 / 2m$ , where  $\hbar$  is Planck's constant and  $m$  is the particle mass;  $\mathbf{k}$  denotes the wavevectors, and we assume that the particles are confined to a cube of size  $L$ , such that the volume of the cube is  $V = L^3$ , and  $k_{1,2,3} = (2\pi/L) \cdot \text{integer}$ . Equation (1) gives the chemical potential  $\mu$  for any values of the temperature, number of particles and volume. The analysis of this equation reveals the existence of a phase transition in the Bose-Einstein ensemble of particles, *i.e.* the existence of a certain critical temperature at which the temperature slope of the specific heat is discontinuous.

First, let us note that the chemical potential in (1) can only take negative values, in order to avoid singularities in the summation over  $\mathbf{k}$ . Leaving aside, for the moment, the  $\mathbf{k} = 0$ -term in (1) the summation over  $\mathbf{k}$  may be replaced by an integral,

$$N = g \frac{V}{4\pi^2} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \int dx \cdot \frac{\sqrt{x}}{\exp(x - \mu/T) - 1} \quad ; \quad (2)$$

on decreasing the temperature  $\mu$  decreases toward small, negative values, such as (2) be satisfied. However, for a vanishing  $\mu$ , there is a certain temperature  $T_0$ , given by

$$N = g \frac{V}{4\pi^2} \left( \frac{2mT_0}{\hbar^2} \right)^{3/2} \int dx \cdot \frac{\sqrt{x}}{\exp(x) - 1} \quad , \quad (3)$$

below which equation (2) can no longer be satisfied. But, of course, the singular term  $\mathbf{k} = 0$  has to come into play around this temperature (*i.e.* for vanishing  $\mu$ ), and it is precisely this term which ensures the fulfilment of (1).

Therefore, equation (1) reads

$$N = g \frac{1}{\exp(-\mu/T) - 1} + g \frac{V}{4\pi^2} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \int dx \cdot \frac{\sqrt{x}}{\exp(x - \mu/T) - 1} \quad , \quad (4)$$

and making use of (3) one may write

$$N = g \frac{1}{\exp(-\mu/T) - 1} + N (T/T_0)^{3/2} + g \frac{V}{4\pi^2} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \int dx \cdot \sqrt{x} \cdot \left[ \frac{1}{\exp(x - \mu/T) - 1} - \frac{1}{\exp x - 1} \right] . \quad (5)$$

The integral in (5) is easily performed for small  $-\mu/T$ , and equation (5) becomes

$$N = \frac{g}{-\mu/T} + N (T/T_0)^{3/2} - g \frac{V}{4\pi} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \sqrt{-\mu/T} . \quad (6)$$

For  $T < T_0$  equation (6) can be written as

$$1 = \frac{g}{N(-\mu/T)} + (T/T_0)^{3/2} - g \frac{V}{4\pi N} \left( \frac{2mT}{\hbar^2} \right)^{3/2} \frac{\sqrt{N(-\mu/T)}}{\sqrt{N}} , \quad (7)$$

and in the thermodynamic limit we obtain

$$-\mu/T = \frac{1}{N} \frac{g}{1 - (T/T_0)^{3/2}} \rightarrow 0 , \quad N \rightarrow \infty , \quad (8)$$

*i.e.* a vanishing chemical potential. For  $T > T_0$  the first term in (6) vanishes in the thermodynamic limit and we get

$$-\mu/T = (4\pi N/gV)^2 \left( \hbar^2/2mT \right)^3 \left[ (T/T_0)^{3/2} - 1 \right]^2 ; \quad (9)$$

for  $T = T_0$  the chemical potential is zero. The existence of two distinct values of the chemical potential at a finite temperature is the origin of the phase transition mentioned above. The integral in (3) is  $I_{1/2} = \Gamma(3/2)\zeta(3/2) = (\sqrt{\pi}/2) \cdot 2.61$ , so that we can rewrite (9) as

$$-\mu/T = 0.54 \left[ 1 - (T_0/T)^{3/2} \right]^2 \quad (10)$$

for  $T$  slightly above  $T_0$ .

Let us turn now to discussing the thermodynamics of the Bose-Einstein ensemble of particles. The temperature  $T_0$  given by (3) can be estimated as follows:

$$T_0 = \frac{6.64}{g^{2/3}} \left( \frac{N}{V} \right)^{2/3} \frac{\hbar^2}{2m} = \frac{6.64}{g^{2/3}} \left( \frac{m_e}{m} \right) \left( \frac{a_H}{a} \right)^2 \text{ ry} \simeq \frac{143}{g^{2/3}} \left( \frac{a_H}{a} \right)^2 \text{ K} \quad (11)$$

where we have introduced the average inter-particle spacing  $a = (V/N)^{1/3}$ , the Bohr radius  $a_H = \hbar^2/m_e e^2 = 0.53\text{\AA}$  ( $m_e = 1/1836$  and  $e$  being the electron mass and, respectively, charge), the rydberg  $e^2/2a_H = 13.6\text{eV}$  and used  $1\text{meV} \simeq 11.6\text{K}$ . For atomic (or condensed) matter, *i.e.* for  $a$  of the order of  $a_H$ , the temperature  $T_0$  is rather low. However, in the notable case of liquid helium ( $\text{He}^4$ ,  $g = 1$ , the atomic mass  $m = 4$ ), whose density is  $0.146\text{g/cm}^3$  (very low) we have

$$0.146\text{g/cm}^3 = \frac{Nm}{V} = \frac{m}{a^3} = \frac{1}{a^3} \cdot \frac{4}{6 \cdot 10^{23}} \text{ g} , \quad (12)$$

where  $m = 4/\mathcal{N}\text{g}$  is the mass of a molecule,  $\mathcal{N} = 6.022 \cdot 10^{23}$  being Avogadro's number; hence we obtain  $a \simeq 3.6\text{\AA} \simeq 6.7a_H$ , and the very low temperature  $T_0 \simeq 3.15\text{K}$ . This temperature is close to

the temperature 2.19K of the  $\lambda$ -point of the liquid helium four,[1] where an anomaly is observed in the temperature dependence of the specific heat.

Below the temperature  $T_0$ , where the chemical potential  $\mu$  vanishes, the Bose-Einstein distribution in (1) is peaked upon the zero-energy level; this is called the Bose-Einstein condensation. In this range of temperatures the energy

$$E = g \sum_{\mathbf{k}} \frac{\varepsilon}{\exp[(\varepsilon - \mu)/T] - 1} \quad (13)$$

is given by the integral

$$E_0 = g \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} T^{5/2} \int dx \cdot \frac{x^{3/2}}{\exp(x) - 1} ; \quad (14)$$

the integral in (14) is  $\Gamma(5/2)\zeta(5/2)$ , where  $\Gamma(5/2) = 3\sqrt{\pi}/4$  and  $\zeta(5/2) \simeq 1.34$ , so that we may write

$$E_0 = 0.77NT^{5/2}/T_0^{3/2} ; \quad (15)$$

hence the heat capacity at constant volume

$$c_v = 1.925N(T/T_0)^{3/2} = \frac{5}{2} \frac{E_0}{T} . \quad (16)$$

The entropy is easily obtained by integrating  $c_v/T$  with respect to the temperature; we obtain  $S_0 = (5/3)E_0/T$  and the free energy  $F_0 = E_0 - TS_0 = -2E_0/3$ ; we note that for  $\mu = 0$  the thermodynamic potentials  $\Phi$  and  $\Omega$  are given by  $F_0 = \Phi_0 - p_0V = N\mu + \Omega_0 = \Omega_0$ . The pressure  $p$  is given by  $p_0 = -(\partial F_0/\partial V)$  at constant temperature, and from (14) we obtain  $p_0 = (2/3)E_0/V$ , where we note that the pressure does not depend on the volume, as expected for particles condensed on the zero-energy level.

All the above thermodynamic results are valid for  $T < T_0$ , where the chemical potential vanishes, and the particles condense gradually on the zero-energy level. What happens near  $T_0$  and beyond this temperature, where the condensate is gradually destroyed? According to the discussion above all the thermodynamic quantities are continuous functions of temperature, including the chemical potential  $\mu$  and its first derivative with respect to the temperature. In the limit of high temperature the chemical potential increases rather drastically, and the Bose-Einstein distribution becomes the Boltzmann distribution of a classical ensemble of particles; the same happens, of course, for a highly dilute ensemble of particles, in both cases the quantum correlations becoming less and less effective. As it is well-known, the nature of these correlations originates in the existence of the energy levels, and the possibility of the identical particles to occupy indiscriminately these energy levels. Using the Boltzmann distribution for high temperatures we obtain straightforwardly  $\mu \sim -(3/2)T \ln T$  from (2) and the well-known classical energy  $E = (3/2)NT$ ; hence the heat capacity at constant volume  $c_v = 3N/2$ . It is indeed remarkable how close this value is to  $1.925N$  obtained from (16) at  $T_0$ . The vanishing temperature slope of the classical heat capacity  $c_v = 3N/2$  is compared usually with the temperature slope  $2.89N/T_0$  of the heat capacity (16) at  $T = T_0^-$ , whence the conclusion that the phase transition at  $T_0$  is of third-order.[2] It is, however, worth remarking that the  $\lambda$ -anomaly of the liquid helium indicates rather a singularity in the specific heat, *i.e.* a second-order phase transition.[3]

Let us turn now to compute the energy for  $T$  slightly above  $T_0$ . The regularization procedure used in estimating the number of particles in (5) is not practicable in this case. Instead, we make use of general thermodynamic properties. As it is well-known the grand-partition potential

$$\Omega = gT \sum_{\mathbf{k}} \ln \{1 - \exp[(\mu - \varepsilon)/T]\} \quad (17)$$

may be integrated by parts and gives  $\Omega = -2E/3$ ; on the other hand,  $\partial\Omega/\partial\mu = -N$ , so that  $E = E_0 + (3/2)N\mu$ , where  $E_0$  is the energy below  $T_0$ , as given by (15), for  $\mu = 0$ . We use for  $\mu$  its value given by (10), and, in order to keep the same order of approximation as that used in deriving this  $\mu$  we should use  $N(T/T_0)^{3/2}$  for  $N$ , as follows from (6) for  $T > T_0$ . The energy for  $T > T_0$  is therefore given by

$$E = 0.77NT^{5/2}/T_0^{3/2} - 0.81N(T^{5/2}/T_0^{3/2})[1 - (T_0/T)^{3/2}]^2, \quad (18)$$

whence one can see that the heat capacity  $c_v$  is continuous at  $T_0$ , but its slope at  $T_0^+$  is  $-0.77N/T_0$ . [4]

The phase transition at  $T_0$ , with its jump in the temperature slope of the specific heat, is plagued, in addition, by the divergent fluctuations in the occupancy number of particles on the zero-energy level,  $\langle (n_{\mathbf{k}} - \langle n_{\mathbf{k}} \rangle)^2 \rangle = \langle n_{\mathbf{k}} \rangle + \langle n_{\mathbf{k}} \rangle^2$  for  $\mathbf{k} = 0$ , which shows, as expected, the inadequacy of the equilibrium statistical mechanics in treating the critical phenomena. The fact that the Bose-Einstein distribution of an ensemble of ideal bosons is not appropriate for describing the Bose-Einstein condensation does not mean, however, that the Bose-Einstein distribution is not compatible, and would not allow (and indicate), a phase transition. Indeed, suppose, for instance, as the behaviour of this distribution indicates, that there is a certain temperature  $T_c$  below which all the particles condense, more or less abruptly, on the zero-energy level. Then we get from (1)

$$N = gN \frac{1}{\exp(-\mu/T) - 1}, \quad (19)$$

whence the chemical potential

$$\mu = -T \ln(1 + g) \quad (20)$$

for this ordered state. Above  $T_c$  the particles are in a highly disordered state, as if the temperature would be extremely high; in this case the Bose-Einstein distribution becomes formally the Boltzmann distribution, and we obtain the chemical potential

$$\mu = -\frac{3}{2}T \ln T. \quad (21)$$

An estimate of  $T_c$  is obtained by equating the two expressions for the chemical potential given by (20) and (21). For liquid helium  $g = 1$  and we get  $T_c = 2^{2/3} \simeq 1.59\text{K}$ , which is close to the  $\lambda$ -point temperature  $2.19\text{K}$ . The estimate can be improved by noting that the nature of the distribution changes (from Bose-Einstein to Boltzmann) around  $\mu \sim T$ , so that  $T_c \simeq e^{2/3} \simeq 1.95\text{K}$ .

Finally, it is worth mentioning perhaps what happens in one or two dimensions. The integral in (2) is singular in this case for a vanishing chemical potential, so that (1) is satisfied for finite values of  $\mu$  (at non-zero temperatures); therefore, in one and two dimensions we have not even an indication of an anomalous behaviour, and no phase transition.

## References

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[4] See, for instance, L. Landau and E. Lifshitz, *Statistical Physics*, Mir, Moscow (1967).