# Thermodynamic quantities of a Bose-Einstein condensate 

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#### Abstract

In the following pages, we will examine the most relevant thermodynamic quantities of a Bose-


 Einstein condensate.
## BOSE-EINSTEIN CONDENSATION OF AN IDEAL GAS

## A. Derivation of Bose-Einstein distribution

Bose-Einstein distribution belongs to Quantum Statistics and applies to bosons, which are particles with integer spin. Let us consider the $i$-th domain in the phase space: it is generally subdivided in $g_{i}$ cells and contains $N_{i}$ bosons. Now, let us construct the configuration of thermodynamic equilibrium according to Boltzmann's definition, which is that the macroscopic state is the one that is realized by the highest number of microscopic configurations. In this sense, the number of ways it is possible to ordinate $N_{i}$ bosons in $g_{i}$ cells is

$$
\begin{equation*}
W_{i}=\frac{\left(N_{i}+g_{i}-1\right)!}{N_{i}!\left(g_{1}-1\right)!} \tag{1}
\end{equation*}
$$

where the factor $\left(N_{i}+g_{i}-1\right)$ ! represents all the possible permutations of the $N_{i}$ bosons and of the $g_{1}-1$ walls[? ], while the factors $N_{i}$ ! and $\left(g_{i}-1\right)$ ! take account of the indistinguishability of bosons and walls. The total probability (over all of the domains) is given by

$$
\begin{equation*}
W=\frac{1}{C} \prod_{i} \frac{\left(N_{i}+g_{1}-1\right)!}{N_{i}!\left(g_{i}-1\right)!} \tag{2}
\end{equation*}
$$

where $C$ is a normalization constant. In order to find the macroscopic state, we need to maximize $W$. However, noticing that the function logarithm is an injective function, we can maximize $\ln W$ :

$$
\begin{align*}
\ln W= & \sum_{i} \ln \left(N_{i}+g_{i}-1\right)!-\sum_{i} \ln N_{i}! \\
& -\sum_{i} \ln \left(g_{i}-1\right)!-\ln C \tag{3}
\end{align*}
$$

[^0]Using Stirling approximation[?] we obtain

$$
\begin{align*}
\ln W= & \sum_{i}\left(N_{i}+g_{i}-1\right) \ln \left(N_{i}+g_{i}-1\right)-\ln C \\
& -\sum_{i} N_{i} \ln N_{i}-\sum_{i}\left(g_{i}-1\right) \ln \left(g_{i}-1\right) \tag{4}
\end{align*}
$$

Typically we deal with systems in which $g_{i} \gg 1$. Therefore, we can assume that $g_{i}-1 \simeq g_{i}$ and write[? ]

$$
\begin{equation*}
\ln W \simeq \sum_{i} N_{i} \ln \frac{N_{i}+g_{i}}{N_{i}}+\sum_{i} g_{i} \ln \frac{N_{i}+g_{i}}{g_{i}} \tag{5}
\end{equation*}
$$

Now we differentiate this last expression with respect to $N_{i}$. After a few simple algebraic steps we finally obtain the following expression:

$$
\begin{equation*}
\mathrm{d}(\ln W)=\sum_{i} \mathrm{~d} N_{i} \ln \frac{N_{i}+g_{i}}{N_{i}} \tag{6}
\end{equation*}
$$

The maximum is though bounded by the relations

$$
\begin{align*}
& \sum_{i} \mathrm{~d} N_{i}=0  \tag{7}\\
& \sum_{i} u_{i} \mathrm{~d} N_{i}=0 \tag{8}
\end{align*}
$$

since in the canonical ensemble the total number of particles $N=\sum_{i} N_{i}$ and the total energy $U=$ $\sum_{i} u_{i} N_{i}$ are both constant. Introducing Lagrange multipliers $\alpha, \beta$ we obtain for the bounded maximum the equation

$$
\begin{array}{r}
\mathrm{d}(\ln W)-\alpha \sum_{i} \mathrm{~d} N_{i}-\beta \sum_{i} u_{i} \mathrm{~d} N_{i}=0 \\
\mathrm{~d}(\ln W)+\beta \mu \sum_{i} \mathrm{~d} N_{i}-\beta \sum_{i} u_{i} \mathrm{~d} N_{i}=0
\end{array}
$$

where we put $\alpha=-\beta \mu$ for convenience. After factoring out, we have:

$$
\begin{equation*}
\sum_{i} \mathrm{~d} N_{i}\left[\ln \frac{N_{i}+g_{i}}{N_{i}}+\beta \mu-\beta u_{i}\right]=0 \tag{9}
\end{equation*}
$$

The $N_{i}^{0}$ which maximize the probability $W$ then satisfy

$$
\ln \frac{N_{i}^{0}+g_{i}}{N_{i}^{0}}=\beta u_{i}-\beta \mu
$$

which means

$$
\begin{equation*}
N_{i}^{0}=\frac{g_{i}}{e^{\beta\left(u_{i}-\mu\right)}-1} \tag{10}
\end{equation*}
$$

If we consider a single cell in the $i$-th domain, we have

$$
\bar{n}_{i}=\frac{1}{e^{\beta\left(u_{i}-\mu\right)-1}}
$$

A comparison with Thermodynamics allows us to say that $\beta=1 / k T$, where $k$ is Boltzmann constant and $T$ is the absolute temperature, and that $\mu$ is the chemical potential of the system. At last, we obtain the famous expression for Bose-Einstein distribution:

$$
\begin{equation*}
\bar{n}_{i}=\frac{1}{e^{\left(u_{i}-\mu\right) / k T}-1} \tag{11}
\end{equation*}
$$

We notice that the chemical potential $\mu$ must satisfy $\mu \leq 0$ in order to grant the condition $\bar{n}_{i} \geq 0$. In the limit $e^{\left(u_{i}-\mu\right) / k T} \gg 1$, we can write

$$
\begin{equation*}
\bar{n}_{i} \simeq e^{\mu / k T} e^{-u_{i} / k T} \tag{12}
\end{equation*}
$$

which is actually the Boltzmann distribution; therefore, Classical Statistics is valid if $\bar{n}_{i} \ll 1$ for every domain. In particular, it is sufficient that $\bar{n}_{0} \ll 1$ for the state at $u_{0}=0$ (it will follow immediately for the other states).
We can conclude that necessary and sufficient condition for which it is possible to apply Classical Statistics is that

$$
\begin{equation*}
\bar{n}_{0} \equiv a \ll 1 \tag{13}
\end{equation*}
$$

The parameter $a$ is called degeneration parameter. For non-interacting particles, $u=\mathbf{p}^{2} / 2 m$, we know that the partition function $\mathcal{Z}$ may be written as

$$
\begin{equation*}
\mathcal{Z}=\frac{V(2 \pi m k T)^{3 / 2}}{\Delta}=\frac{V(2 \pi m k T)^{3 / 2}}{h^{3}} \tag{14}
\end{equation*}
$$

Here $V$ is the accessible volume and $\Delta=h^{3}$ is the volume of a cell in the phase space ( $h$ is Planck constant). So we have

$$
\begin{equation*}
a=\frac{N}{\mathcal{Z}}=\frac{N}{V} \frac{h^{3}}{(2 \pi m k T)^{3 / 2}} \tag{15}
\end{equation*}
$$

Introducing the thermal de Broglie wavelenght:

$$
\begin{equation*}
\lambda_{\mathrm{dB}}=\frac{h}{(2 \pi m k T)^{1 / 2}} \tag{16}
\end{equation*}
$$

the parameter $a$ may be written in the form

$$
\begin{equation*}
a=\frac{N}{V} \lambda_{\mathrm{dB}}^{3} \tag{17}
\end{equation*}
$$

## B. BEC critical temperature

For the ground state $\left(i=0, u_{0}=0\right)$ the average occupation is

$$
\begin{equation*}
\bar{n}_{0}=\frac{1}{e^{-\mu / k T}-1} \tag{18}
\end{equation*}
$$

We see that for $\mu \rightarrow 0 \bar{n}_{0}$ becomes increasingly large. The number of occupied cells in the phase space is given by

$$
\begin{equation*}
g(p) \mathrm{d} p=\frac{4 \pi V p^{2} \mathrm{~d} p}{h^{3}}+\delta(p) \mathrm{d} p \tag{19}
\end{equation*}
$$

The ground state has only one cell, in fact $g(0)=1$, and its average occupation will be

$$
\begin{equation*}
\bar{n}_{0}=\frac{N_{0}}{g_{0}}=N_{0} \rightarrow N \tag{20}
\end{equation*}
$$

where $N$ is the total number of particles. Generally, we can write

$$
\begin{equation*}
N=N_{0}+N_{\mathrm{exc}} \tag{21}
\end{equation*}
$$

where $N_{0}$ is the number of particles in the ground state at zero energy, and $N_{\text {exc }}=\sum_{i \neq 0} \bar{n}_{i}(T, \mu)$ is the number of particles in all the excited states, with higher energies. For a finite temperature $T$ and a large volume $V, N_{\text {exc }}$ has a smooth behavior as a function of $\mu$ and reaches its maximum $N_{c}=N_{\text {exc }}(T, \mu=0)$ asymptotically (as seen in Fig. 1.1). On the other hand, $N_{0}$ diverges as $\mu$ approaches to zero. If the value of $N_{c}$ is greater than $N$, then eq. (1.21) is always satisfied for values of $\mu$ considerably smaller then zero and $N_{0}$ is negligible compared to $N$. This situation corresponds to the point $\left(\mu_{1}, N_{1}\right)$ in Fig. 1. If $N_{c}$ is smaller than $N$, on the contrary, the occupation number $N_{0}$ of the ground state is substantial and thus it is expected the condensate is formed. This situation corresponds to the point $\left(\mu_{2}, N_{2}\right)$ in Fig. 1.1.


FIG. 1: The occupation number $N_{0}$ in the ground state and $N_{\text {exc }}$ in all excited states vs. chemical potential $\mu$. If $N>N_{c}$, the system exhibits BEC.

The critical temperature $T_{c}$ of BEC is operationally defined by the relation

$$
\begin{equation*}
N_{\mathrm{exc}}\left(T_{c}, \mu=0\right)=N \tag{22}
\end{equation*}
$$

## C. BEC threshold in a uniform system

## 1. BEC critical temperature/density

The BEC critical temperature for a uniform 3D system is given by the condition that all the particles accommodated in excited single particles state (except for a ground state) when $\mu=u_{0}=0$ are equal to the total number of particles in the system:

$$
N=\int_{0}^{+\infty} g(u) \bar{n}_{u} \mathrm{~d} u
$$

where $g(u) \mathrm{d} u$ is the density of states in terms of the energy density:

$$
\begin{equation*}
g(u) \mathrm{d} u=\frac{V}{4 \pi^{2}}\left(\frac{2 m}{\hbar^{2}}\right)^{3 / 2} \sqrt{u} \mathrm{~d} u \tag{23}
\end{equation*}
$$

Thus

$$
\begin{equation*}
N=\frac{V}{4 \pi^{2}}\left(\frac{2 m}{\hbar^{2}}\right)^{3 / 2} \int_{0}^{+\infty} \sqrt{u} \frac{\mathrm{~d} u}{e^{u / k T}-1} \tag{24}
\end{equation*}
$$

We can evaluate the energy integral using the relation $\frac{1}{e^{x}-1}=\sum_{n=1}^{\infty} e^{-n x}$, where $x=u / k T$ :

$$
\begin{align*}
\int_{0}^{\infty} \frac{\sqrt{u} \mathrm{~d} u}{e^{u / k T}-1} & =(k T)^{3 / 2} \sum_{n=1}^{\infty} \int_{0}^{\infty} e^{-n x} \sqrt{x} \mathrm{~d} x \\
& =(k T)^{3 / 2} \sum_{n=1}^{\infty} n^{-3 / 2} \int_{0}^{\infty} e^{-t} \sqrt{t} \mathrm{~d} t \\
& =(k T)^{3 / 2} \zeta\left(\frac{3}{2}\right) \Gamma\left(\frac{3}{2}\right) \tag{25}
\end{align*}
$$

where $\zeta\left(\frac{3}{2}\right)=\sum_{n=1}^{\infty} n^{-3 / 2}$ and $\Gamma\left(\frac{3}{2}\right)=\int_{0}^{\infty} e^{-t} \sqrt{t} \mathrm{~d} t$. Finally, we obtain the BEC critical density for a uniform 3D system:

$$
\begin{align*}
n_{c} \equiv \frac{N_{c}}{V} & =\frac{1}{4 \pi^{2}}\left(\frac{2 m k T}{\hbar^{2}}\right)^{3 / 2} \zeta\left(\frac{3}{2}\right) \Gamma\left(\frac{3}{2}\right) \\
& \simeq 2.612 \frac{1}{\lambda_{T_{c}}^{3}} \tag{26}
\end{align*}
$$

Here $\lambda_{T_{c}}=\sqrt{\frac{2 \pi \hbar^{2}}{m k T_{c}}}$ is the thermal de Broglie wavelenght at the critical temperature. For a generic temperature $T$, in which $\mu \neq 0$, introducing the $f u$ gacity $z \equiv e^{\mu / k T}, 0 \leq z \leq 1$, the number of particles in all the excited states is given by

$$
\begin{equation*}
N_{\mathrm{exc}}=\frac{V}{\lambda_{T}^{3}} g_{3 / 2}(z)<N \tag{27}
\end{equation*}
$$

where $g_{3 / 2}(z)=\sum_{n=1}^{\infty} \frac{z^{n}}{n^{3 / 2}}$ is a limited, positive and monotonically increasing function of $z$, which has a maximum for $z=1$ (obviously, when $\mu=0$ and the population of the excited states reaches its maximum $\left.N_{c}\right), g_{3 / 2}(1)=2.612$. Therefore, the total population can be written as

$$
\begin{equation*}
N=N_{\mathrm{exc}}+N_{0}=\frac{V}{\lambda_{T}^{3}} g_{3 / 2}(z)+N_{0} \tag{28}
\end{equation*}
$$

By imposing the constrain that the number of particles in the ground state must be positive, we obtain the condition:

$$
\begin{gathered}
\frac{\lambda_{T}^{3}}{V} N_{0}=\frac{\lambda_{T}^{3}}{V} N-g_{3 / 2}(z) \geq 0 \\
\frac{\lambda_{T}^{3}}{V} N \geq g_{3 / 2}(z)
\end{gathered}
$$

This inequality must hold for every value of $g_{3 / 2}(z)$, so it must hold for the maximum of $g_{3 / 2}(z)$ :

$$
\begin{equation*}
\frac{\lambda_{T}^{3}}{V} N \geq g_{3 / 2}(1)=2.612 \tag{29}
\end{equation*}
$$

This relation is called critical condition: if it is satisfied, then BEC can occur. For a given density $N / V$, the relation (1.29), written in terms of the temperature, defines the critical temperature $T_{c}$ :

$$
\begin{equation*}
T \leq\left[\frac{N}{2.612 V}\right]^{2 / 3} \frac{2 \pi \hbar^{2}}{m k} \equiv T_{c} \tag{30}
\end{equation*}
$$

We now notice that the number of particles in the ground state is related to the fugacity by the equation

$$
\begin{equation*}
N_{0}=\frac{1}{z^{-1}-1}=\frac{z}{1-z} \tag{31}
\end{equation*}
$$

Combining eq. (1.28) with (1.31), it is possible to determinate the chemical potential $\mu$ as a function of the temperature $T$ :

$$
\begin{equation*}
\lambda_{T}^{3} \frac{N}{V}=g_{3 / 2}(z)+\frac{\lambda_{T}^{3}}{V} \frac{z}{1-z} \tag{32}
\end{equation*}
$$

## 2. Condensate fraction

The BEC critical condition is usually expressed in terms of the Bose function $g_{p}(z)$, defined by

$$
\begin{align*}
g_{p}(z) & =\frac{1}{\Gamma(p)} \int_{0}^{+\infty} \mathrm{d} x x^{p-1} \frac{1}{z^{-1} e^{x}-1} \\
& =\sum_{s=1}^{\infty} \frac{z^{s}}{s^{p}} \tag{33}
\end{align*}
$$

where $z=e^{\mu / k T}$ is the fugacity and $\Gamma(p)=(p-1)$ !. The energy integral for uniform 3D, 2D and 1D systems are then reduced to the Bose functions of $z=1$ and $p=3 / 2, p=1$ and $p=1 / 2$, respectively. Among them, only $g_{3 / 2}(1)$ converges, while $g_{1}(1)$ and $g_{1 / 2}(1)$ diverge, so that a finite critical temperature $T_{c} \neq 0$ exists only for a 3D system as far as the system is uniform and infinite.
At the critical temperature $T_{c}$ in a uniform 3D system, all particles are in the thermal populations:

$$
\begin{equation*}
\frac{V}{\lambda_{T_{c}}^{3}} g_{3 / 2}(1)=N_{\mathrm{exc}}=N \tag{34}
\end{equation*}
$$

while at $T<T_{c}$, the thermal population is

$$
\begin{equation*}
\frac{V}{\lambda_{T}^{3}} g_{3 / 2}(1)=N_{\mathrm{exc}}<N \tag{35}
\end{equation*}
$$

Taking the ration of (1.29) to (1.30) we have

$$
\begin{equation*}
\frac{\lambda_{T}^{3}}{\lambda_{T_{c}}^{3}}=\frac{N}{N_{\mathrm{exc}}} \tag{36}
\end{equation*}
$$

From this expression, we obtain the number of particles in the condensate:

$$
\begin{equation*}
N_{0}=N-N_{\mathrm{exc}}=N\left[1-\left(\frac{T}{T_{c}}\right)^{3 / 2}\right] \tag{37}
\end{equation*}
$$



FIG. 2: The condensate fraction $N_{0} / N$ vs. the normalized temperature $T / T_{c}$ in a uniform 3D system.

## D. Thermodynamic functions of an ideal gas

At a generic temperature $T$, less or greater than the critical temperature $T_{c}$, the total energy $U$ of the system is

$$
\begin{align*}
U & =\sum_{i} \frac{u_{i}}{e^{\left(u_{i}-\mu\right) / k T}-1} \\
& =\frac{3}{2} k T \frac{V}{\lambda_{T}^{3}} g_{5 / 2}(z) \tag{38}
\end{align*}
$$

where $g_{5 / 2}(z)$ corresponds to Bose function (1.28) with $p=5 / 2$. The energy is therefore proportional to $T^{5 / 2}$. For $T<T_{c}, z=1$ and one has $g_{5 / 2}(1)=$ 1.342. Thus, the specific heat $C_{v}=\partial U / \partial T$ is obtained as

$$
\begin{equation*}
\frac{C_{V}}{N k}=\frac{15}{4} \frac{V}{N} \frac{1}{\lambda_{T}^{3}} g_{5 / 2}(1) \tag{39}
\end{equation*}
$$

for $T<T_{c}$, and

$$
\begin{equation*}
\frac{C_{V}}{N k}=\frac{15}{4} \frac{V}{N} \frac{g_{5 / 2}(z)}{\lambda_{T}^{3}}-\frac{9}{4} \frac{g_{3 / 2}(z)}{g_{1 / 2}(z)} \tag{40}
\end{equation*}
$$

for $T>T_{c}$. In the limit $T / T_{c} \rightarrow+\infty$, that is $z \rightarrow$ 0 , the specific heat decreases towards the classical value:

$$
\left.\frac{C_{V}(T)}{N k}\right|_{z \rightarrow 0}=\frac{15}{4}-\frac{9}{4}=\frac{3}{2}
$$

While the specific heat is a continuous function of the temperature, it presents a typical cusp at $T=$ $T_{c}$, as shown in Fig. 1.3, which is called $\lambda$-point.

For example, we can consider the $\lambda$-phase transformation of liquid helium in its isotopic bosonic component ${ }^{4} \mathrm{He}$, which presents some characteristic typical of BEC. If we calculate the density $N / V$ at


FIG. 3: Specific heat of an ideal uniform Bose gas vs. temperature
the critical temperature using helium specific density $\rho=0.146 \mathrm{~g} / \mathrm{cm}^{3}$, the mass of ${ }^{4} \mathrm{He}, m^{4} \mathrm{He}=$ $6.4 \times 10^{-22} \mathrm{~g}$ for an Avogadro's number $N_{A}$ of particles occupying a volume $V_{A}$ and using the relation $\rho=N_{A} m_{4} \mathrm{He} / V_{A}$ we obtain

$$
\begin{aligned}
\frac{N}{V} & =\frac{N_{A}}{V_{A}}=\frac{N_{A}}{N_{A} m_{4} \mathrm{He} / \rho}=\frac{\rho}{m_{4} \mathrm{He}}= \\
& =\frac{0.146 \mathrm{~g} \mathrm{~cm}^{-3}}{6.4 \times 10^{-22} \mathrm{~g}}=2.18 \times 10^{22} \mathrm{~cm}^{-3}
\end{aligned}
$$

From this value we obtain for the critical temperature

$$
T_{c}=\left[\frac{N}{2.612 V}\right]^{2 / 3} \frac{h^{2}}{\sqrt{2 \pi m K}}=3.12 \mathrm{~K}
$$

which is quite close to the value 2.17 K measured for the temperature of the $\lambda$-transition. The difference is due to the fact that the formulas we have applied refer to an ideal gas of non-interacting particles, therefore we can't directly apply those formulas to liquid helium.

For ideal gases in three dimensions, the thermodynamic law $P=\frac{2}{3} \frac{U}{V}$ holds. In BEC, the energy $U$ increases linearly with the volume $V$, so that using (1.38) with $z=1$ for $T<T_{c}$, we obtain the equation of state for BEC:

$$
\begin{equation*}
P=\frac{k T}{\lambda_{T}^{3}} g_{5 / 2}(1) \tag{41}
\end{equation*}
$$

The pressure of the gas does not depend on the volume in a BEC regime. This means that the compressibility of the BEC phase is infinite. However,
it is possible to remedy to this problem by including the two-body interactions. At $T>T_{c}$, the pressure is given by

$$
\begin{equation*}
P=\frac{k T}{\lambda_{T}^{3}} g_{5 / 2}(z) \tag{42}
\end{equation*}
$$

Since $z=e^{\mu / k T}$ decreases toward zero with increasing the volume $V$, the pressure $P$ also decreases with $V$. Fig. 1.4 shows the equation state of the ideal Bose gas.


FIG. 4: Pressure of the ideal Bose gas vs. the specific volume $v=V / N$ for two temperatures $T_{1}>T_{2}$.

The phase transition line separating the BEC and the normal phase is obtained by substituting $\lambda_{T_{c}}^{3} N / V=g_{3 / 2}(1)$ into (1.41):

$$
\begin{equation*}
P v^{5 / 3}=\left(2 \pi \hbar^{2} m\right) \frac{g_{5 / 2}(1)}{\left[g_{3 / 2}(1)\right]^{5 / 3}} \tag{43}
\end{equation*}
$$

For $T<T_{c}$ in the limit $V / \lambda_{T}^{3} \rightarrow \infty$ with $z=1$ and $\mu=0$, the energy $U$ can be written as

$$
\begin{equation*}
U(T)=A T^{5 / 2}, \quad C_{V}=\frac{5}{2} A T^{3 / 2} \tag{44}
\end{equation*}
$$

where $A=\frac{3}{2} \frac{V}{h^{3}}\left(2 \pi m k_{B}\right)^{3 / 2} k_{B} g_{5 / 2}(1)$, therefore, in this range of temperature we have for entropy

$$
\begin{align*}
\mathrm{d} S & =\frac{\delta Q}{T}=\frac{C_{V} \mathrm{~d} T}{T}=\frac{5}{2} A T^{1 / 2} \mathrm{~d} T \\
S & =\int_{0}^{T} \mathrm{~d} S=\frac{5}{3} A T^{3 / 2}=\frac{5}{3} \frac{U}{T} \tag{45}
\end{align*}
$$

and for Helmholtz free energy

$$
\begin{equation*}
F=U-T S=A T^{5 / 2}-\frac{5}{3} A T^{5 / 2}=-\frac{2}{3} U \tag{46}
\end{equation*}
$$


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