Thermodynamics of Bose–Einstein Condensation*
A Simple Numerical Approach

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We present a simple method to numerically evaluate different thermodynamic quantities of non-interacting Bose gas confined in a 3D box. This method only requires the knowledge of statistical mechanics and numerical integration at the undergraduate level. Thus the proposed technique is very much appropriate for the undergraduate class.

Introduction

In 1995, the Bose–Einstein condensation (BEC) was experimentally observed [1] for the first time in a harmonically trapped dilute gas of rubidium atoms. This experimental achievement stimulated tremendous interest both in the experimental and theoretical research of quantum gases. BEC is now one of the most active research areas in physics. The phenomenon of BEC, however, was first predicted by Einstein in 1925, shortly after Satyendranath Bose, a Reader of physics at the Dacca University, brought to his attention a simple derivation of Planck’s law of radiation. Unlike Planck and Einstein, Bose [2, 3] derived the Planck distribution law independently without using classical electrodynamics in 1923. Bose treated photons as indistinguishable particles obeying some counting principles that are now called Bose–Einstein statistics and obtained Planck’s result. He submitted a paper based on this new approach to the derivation of Planck’s law to the Philosophical Magazine, and unfortunately, it was rejected. Bose, however, sent the rejected manuscript directly to Einstein in Berlin, together with a handwritten cover letter [5] dated 04 June 1924.

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“Respected Sir:

I have ventured to send you the accompanying article for your perusal and opinion. I am anxious to know what you think of it. You will see that I have tried to deduce the coefficient \( \frac{\pi n^2}{c^3} \) Planck’s Law independent of the classical electrodynamics, only assuming that the ultimate elementary regions in the phase-space has the content \( h^3 \). I do not know sufficient German to translate the paper. If you think the paper worth publication I shall be grateful if you arrange its publication in Zeitschrift für Physik.

Though a complete stranger to you, I do not hesitate in making such a request. Because we are all your pupils though profiting only from your teachings through your writings ...”

Realizing the importance of the idistinguishable principle introduced by S. N. Bose, Einstein set to translate the manuscript immediately and sent it to the Zeitschrift für Physik for publication within a week. He also made a parenthetical remark at the end of the German version of Bose’s paper:

“Bose’s derivation of Planck’s formula constitutes, in my opinion, an important step forward. The method used here also yields the quantum theory of the ideal gas, as I will explain in detail elsewhere.”

Following the work of Bose, Einstein published another paper [6] within a few days, entitled ‘Quantum theory of the monoatomic ideal gas’. He concluded that in a system of a fixed number of particles obeying Bose statistics, there should be a critical temperature below which a finite fraction of the total number of particles ‘condense’ into the lowest energy state. This macroscopic population of noninteracting bosons in the ground state is generally known as the Bose–Einstein condensation.

A key point in understanding BEC is that this condensation is entirely a consequence of quantum statistics (BE statistics) and occurs for ideal non-interacting bosons. In any normal gas, the attractive forces between the molecules cause condensation. The effect of these molecular interactions cannot be completely turned...
off but can be minimized only if the particles are kept far away from each other. This implies that to observe BEC, the system must be sufficiently dilute [7] so that the interparticle separation is larger than the range of interaction. At room temperature and atmospheric pressure, air has a molecular density of about $10^{19}/\text{cm}^3$. To be very weakly interacting [7], the density of the gas is about $10^{15}/\text{cm}^3$. Also, the effect of the quantum statistics manifests itself when the thermal de Broglie wavelength of the particles is of the same order of magnitude as the interparticle separation:

$$\lambda^3 \approx \frac{1}{n},$$

(1)

where $\lambda = \frac{\hbar}{\sqrt{2\pi mk_B T}}$ and $n = \frac{N}{V}$ being the number density of the gas. Thus a rough estimation of the temperature at which BEC occurs may be obtained from

$$T = \left(\frac{\hbar^2}{2\pi mk_B}\right)n^{2/3}.$$  

(2)

The very low density ($n \sim 10^{15}/\text{cm}^3$) makes $T$ very low. Such a low temperature ($\sim nK$) is extremely difficult to attain in reality, and that is why it took 70 years to observe BEC experimentally.

The topic of Bose–Einstein condensation in a non-interacting gas of bosons is treated in most textbooks on statistical mechanics [8, 9]. After a brief discussion on BEC, we present our strategy of calculating the different thermodynamic parameters of non-interacting bosons in a 3D box.

1. Bose–Einstein Condensation

The average occupation of the ground state of any system will increase with decreasing temperature irrespective of whether the particles obey Bose–Einstein (BE) or Maxwell–Boltzmann (MB) statistics. However, the phenomenon of Bose–Einstein condensation is an abrupt increase in the ground state population at a critical temperature well above the temperature at which the classical particles begin to accumulate in the ground state.

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particles begin to accumulate in the ground state. To illustrate the peculiarity of bosons at low temperatures, let us go through the following example.

### 1.1 An Example

Let us consider $N = 100$ particles distributed in three energy levels $0, \epsilon$ and $2\epsilon$. For classical particles obeying the MB statistics the average number of particles in the ground state is given by

$$\langle N_0 \rangle_{MB} = \frac{N}{1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}}. \quad (3)$$

For bosons, the canonical partition function is

$$Z = \sum_{\{n_1, n_2, n_3\}} e^{-\beta(n_1 \times 0 + n_2 \times \epsilon + n_3 \times 2\epsilon)}, \quad (n_1 + n_2 + n_3) = N, \quad (4)$$

where $n_1, n_2$ and $n_3$ are the occupation of the ground state, first excited state, and second excited states respectively. The average number of bosons in the ground state is

$$\langle N_0 \rangle_{BE} = \frac{1}{Z} \times \sum_{\{n_1, n_2, n_3\}} n_1 e^{-\beta(n_1 \times 0 + n_2 \times \epsilon + n_3 \times 2\epsilon)}. \quad (5)$$

The summation is over different values of $n_1, n_2$ and $n_3$ subject to the constraint $(n_1 + n_2 + n_3) = N$. Analytical simplification of (5) is extremely difficult. However, we may calculate it numerically and the result is presented in Figure 1.
It shows that $\frac{N_b}{N} \to 1$, as $\frac{k_B T}{\epsilon} \to 0$ both for the bosons and classical particles. However, much before $T \approx 0$, a macroscopic fraction of the total number of bosons occupies the ground state. This is basically what is known as the Bose–Einstein condensation. Here, we have considered a system with only three energy levels; hence, a sharp critical point is not obtained. We will discuss the general case in the next subsection.

1.2 Bosons in 3D Box

The average number of bosons in $i$th energy state is

$$< n_i > = \frac{1}{e^{\beta (\epsilon_i - \mu)} - 1}. \quad (6)$$

In order to guarantee a positive value of particle occupancy in any state, $\mu$ must be smaller than the ground state energy. If we assume that the ground state energy $\epsilon_0 = 0$, then to make $< n_0 >$ positive, we must have $\mu < 0$.

The total number of particles in the system can be obtained from (6) as
\[ N = \sum_i < n_i > = \sum_i \frac{1}{e^{\frac{\mu - \epsilon_i}{k_B T}} - 1}. \]  \hspace{1cm} (7)

At any given temperature, \( \mu \) is adjusted so that the sum on the right-hand side of (7) becomes equal to \( N \). Thus by normalizing \( N \) at different temperatures \( T \), the chemical potential can be determined as \( \mu = \mu(T) \).

For particles confined in large volume \( V \), the spacing between the energy levels is small, and the summation in (7) can be replaced by integration:

\[ N = \int_0^\infty g(\epsilon) \frac{de}{e^{\frac{\mu - \epsilon}{k_B T}} - 1}, \]  \hspace{1cm} (8)

where \( g(\epsilon)de \) is the density of states for a particle confined in a 3D box with an energy interval between \( \epsilon \) and \( \epsilon + d\epsilon \).

**Density of States**: Let us consider a particle moving freely in a box of volume \( V \). For simplicity, we assume that the box is cubic, with length \( L \), so that \( V = L^3 \). The walls of the box are rigid and do not allow particles to penetrate. This requires the wavefunction to vanish at the walls. Instead of this boundary condition, we often use the periodic boundary condition, according to which the wavefunction is to repeat the same with the period of \( L \) in each direction of \( x, y, \) and \( z \)-axis:

\[ \psi(x + L, y + L, z + L) = \psi(x, y, z). \]

Applying this periodic boundary condition, we obtain

\[ \psi = A e^{i(k_x x + k_y y + k_z z)} \quad \text{with} \quad k_x = \frac{2\pi}{L} n_x, \; k_y = \frac{2\pi}{L} n_y \; \text{and} \; k_z = \frac{2\pi}{L} n_z, \]

and the energy of the particle

\[ \epsilon_n = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2), \]  \hspace{1cm} (9)

where \( n_x, n_y \) and \( n_z \) are integers \( 1, 2, 3, \ldots \).
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We may think of a number space where the state of the particle is specified by a point \((n_x, n_y, n_z)\) in that space. The density of states in the number space is easy to find. Since the density of points in the number space is one, the density of states as a function of energy \(g(\epsilon)\) can be obtained very simply from

\[
g(\epsilon) = \int_0^\infty \int_0^\infty \int_0^\infty \delta(\epsilon - \epsilon_n) \, dn_x \, dn_y \, dn_z, \tag{10}\]

where we assume that the dimension of the box is large and the energy spectrum is nearly continuous. Since the delta function is a probability distribution function, the unit of \(g(\epsilon)\) is the inverse of energy, and \(g(\epsilon) \, d\epsilon\) represents the number of states between the energy interval \(\epsilon\) and \(\epsilon + d\epsilon\). Using (9), we find

\[
g(\epsilon) = \int_0^\infty \int_0^\infty \int_0^\infty \delta(\epsilon - \frac{\hbar^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)) \, dn_x \, dn_y \, dn_z
= \frac{1}{8} \times 4\pi \int_0^\infty \delta(\epsilon - \frac{\hbar^2}{8mL^2}n^2) \, n^2 \, dn, \tag{11}\]

where the factor of \(\frac{1}{8}\) corrects for counting both positive and negative values of \(n_x, n_y,\) and \(n_z\). We have used \(n^2 = n_x^2 + n_y^2 + n_z^2\) that represents a sphere of radius \(n\) in the number space.

Substituting \(x = \frac{\hbar^2}{8mL^2}n^2\) in (11), we obtain

\[
g(\epsilon) = \frac{1}{8} \times 4\pi \left(\frac{8mL^2}{\hbar^2}\right)^{3/2} \int_0^\infty x^{1/2} \delta(\epsilon - x) \, dx
= \frac{2\pi V(2m)^{3/2}}{\hbar^3} \frac{\epsilon^{1/2}}{\epsilon^{3/2}}. \tag{12}\]

Substituting the value of the density of states from (12), (8) can be expressed as

\[
\frac{N}{V} = \frac{2\pi(2m)^{3/2}}{\hbar^3} \int_0^\infty \frac{\epsilon^{1/2} \, d\epsilon}{e^{\frac{\epsilon}{k_B T}} - 1}. \tag{13}\]

The form of (13) is vital in understanding the properties of bosons. For a fixed \(N\) and \(V,\) the left-hand side of (13) is constant and independent of temperature. Thus we expect the value of the integral on the right-hand side must also be constant and independent
of temperature. As we decrease $T$, $|\mu|$ must decrease, that is, $\mu$ must increase ($\mu$ is negative) and comes closer to zero to keep the right-hand side constant. Let us consider the case of sufficiently low temperature for which $\mu \to 0$. If $T$ is lowered further, $\mu$ cannot increase anymore ($\mu$ cannot be greater than 0).

Plugging in $\mu = 0$ in (13),

$$\frac{N}{V} = \frac{2\pi (2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{\epsilon^{1/2} - 1} \approx \left(\frac{2\pi mk_B T}{\hbar^2}\right)^{3/2} \times 2.612. \quad (14)$$

This result, (14), cannot be correct in general, as it implies that $\frac{N}{V}$ depends on temperature ($T$), which is completely absurd. In fact there exists a particular temperature ($T = T_c$) at which the (14) is correct. Thus only at $T = T_c$,

$$\frac{N}{V} = \left(\frac{2\pi mk_B T_c}{\hbar^2}\right)^{3/2} \times 2.612. \quad (15)$$

(14) is true only for $T > T_c$, but for $T < T_c$, it cannot be correct; it must have to be modified. The trouble starts from the replacement of summation in (7) by integral (8). As the temperature is lowered sufficiently, particles begin to be crowded in the ground state with zero energy. However, the occupation of this state is completely neglected in (8), since it is given zero weightage by the term $\epsilon^{1/2}$ in the density of states $g(\epsilon) d\epsilon$. At high temperatures, the number of particles in the ground state is very small, and the conversion from the summation to integration does not introduce any significant error. However, we cannot simply omit the ground state at low temperatures as it now contains an appreciable number of particles. In replacing the sum with integral, this term must be retained explicitly. Thus, in order to resolve this contradiction, we must isolate the population of the ground state from the remaining one as.
\[ N = \frac{1}{e^{-\frac{\mu}{kT}} - 1} + \frac{2\pi V(2m)^{\frac{3}{2}}}{\hbar^3} \int_0^{\infty} \frac{e^{\frac{1}{2}}d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}. \] (16)

At \( T > T_c \), the ground state population is negligible, and we may omit the 1st term. However, for \( T < T_c \), the ground state population \( (N_0) \) is quite significant. Therefore, at \( T < T_c \), \( (\mu \text{ remained } = 0) \) the (14) gives the population in excited states:

\[ N_{e>0} = V\left(\frac{2\pi mk_BT}{\hbar^2}\right)^{3/2} \times 2.612 \]
\[ = N\left(\frac{T}{T_c}\right)^{\frac{1}{2}}. \] (17)

The number of particles in ground state with zero energy is thus given by

\[ N_0 = N \left(1 - \left(\frac{T}{T_c}\right)^{\frac{1}{2}}\right). \] (18)

Equation (18) shows that \( N_0 \) increases gradually as \( T \) decreases beyond \( T_c \), and finally at \( T \to 0, N_0 \to N \). At temperature \( T < T_c \), a significant fraction of the particles in the system condense in the single-particle state with the lowest energy.

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1.3 Thermodynamics

In this section, we determine the thermodynamic properties of ideal Bose gases and calculate the energy, specific heat, entropy, and other properties of the condensed phase as well as of the normal phase. We also explore the temperature dependence of the energy fluctuation of ideal bosons in a 3D box.

1.3.1 Condensed Phase \( (T < T_c) \)

The energy of the ground state, which is macroscopically occupied, is taken to be zero, and only excited states contribute to the
total energy of the system. At $T < T_c$, the number of particles in the excited state is

$$N_{e>0} = N \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.$$  

If the energy of each particle is taken $\approx k_B T$, the energy of the system will roughly be

$$E \approx N k_B T \left( \frac{T}{T_c} \right)^{\frac{3}{2}},$$  \hspace{1cm}(19)$$

and the specific heat will be

$$C_v \approx \frac{5}{2} R \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.$$  \hspace{1cm}(20)$$

Since only the particles in an excited state contribute to the energy, the exact value of the energy may be obtained from

$$E = \frac{2\pi V (2m)^{\frac{3}{2}}}{\hbar^3} \int_0^{\infty} \frac{e^{\frac{3}{2}k_B T}}{e^{\frac{\xi(3/2)}{\xi(5/2)}} - 1}$$

or,

$$\frac{E}{N} = \frac{3k_B T^{3/2}}{2} \left( \frac{T}{T_c} \right)^{3/2} \frac{\xi(5/2)}{\xi(3/2)}$$

$$\approx 0.77k_B T \left( \frac{T}{T_c} \right)^{\frac{3}{2}},$$  \hspace{1cm}(21)$$

and the specific heat is

$$C_v \approx 0.77 \times \frac{5}{2} R \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.$$  \hspace{1cm}(22)$$

Notice that for $T = T_c$, the specific heat takes on the value of $1.925k_B$, which is greater than the classical value of $1.5k_B$ that it takes on in the limit of high temperatures.

Since $C_v = T \left( \frac{\partial S}{\partial T} \right)_v$, the entropy of the system can be obtained as

$$S = \int \frac{C_v dT}{T}$$

$$\approx 1.28R \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.$$  \hspace{1cm}(23)$$
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Note that below $T_c$, the energy, entropy, and specific heat do not depend on the total number of particles. This is because only particles in excited states contribute, and consequently, the number of particles in the macroscopically occupied state is irrelevant to these quantities.

For ideal gas in 3-dimension, the following relation, (24), holds irrespective of their statistics.

$$pV = \frac{2}{3}E.$$  \hspace{1cm} (24)

Equation (24) may be used to determine the pressure of the system.

As the chemical potential $\mu = 0$, below $T_c$, the Helmholtz free energy $F$ is

$$F = E - TS - \mu N = -0.51 R \left( \frac{T}{T_c} \right)^{3/2}. \hspace{1cm} (25)$$

Pressure may also be obtained from $p = -\left( \frac{\partial F}{\partial V} \right)_T$.

1.3.2 Normal Phase ($T > T_c$)

In this case, the ground state population is negligible, and the chemical potential is negative. The total number of particles is thus given by

$$N = \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^{\infty} \frac{e^{3/2}d\epsilon}{e^{\epsilon/k_BT} - 1}. \hspace{1cm} (26)$$

The total energy of the system is

$$E = \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^{\infty} \frac{e^{3/2}d\epsilon}{e^{\epsilon/k_BT} - 1}. \hspace{1cm} (27)$$

Given the chemical potential, all of the thermodynamic properties may be calculated directly from the relations explained earlier.
2. Numerical Techniques

To determine the thermodynamic quantities numerically, we have to calculate first the chemical potential \( \mu = \mu(T) \), and using this calculated value of \( \mu(T) \), we may determine the temperature dependence of different thermodynamic quantities both for \( T < T_c \) and \( T > T_c \).

2.1 Chemical Potential: \( \mu(T) \)

In evaluating the chemical potential, we have assumed that the value of the chemical potential is approximately zero for temperature \( T \leq T_c \). Since we are studying the thermodynamics of a system of bosons in the thermodynamic limit, this approximation [10] is quite reasonable.

As mentioned in earlier, the chemical potential for \( T > T_c \) is determined from the constraint of fixed \( N \), that is by normalizing the (26) for particular \( N \).

Substituting the value of \( \frac{N}{V} \) from (15) in (26) and using the dimensionless parameters

\[
\tau = \frac{T}{T_c}, \quad \mu_0 = \frac{\mu}{k_B T_c}, \quad \text{and} \quad x = \frac{\epsilon}{k_B T_c},
\]

we get

\[
\frac{2\pi(2m)^{\frac{1}{2}}}{\hbar^3} \int_0^\infty \frac{e^{\frac{1}{2}x^2} dx}{e^\frac{x^2}{2k_B T_c} - 1} = \frac{(2\pi m k_B T_c)^{\frac{1}{2}}}{\hbar^3} \times 2.612
\]

\[
\int_0^\infty \frac{x^\frac{3}{2} dx}{e^\frac{x^2}{2k_B T_c} - 1} = \frac{2.612 \times \sqrt{\pi}}{2} = 2.3148247. \quad (29)
\]

Equation (29) has been used to compute the chemical potential of the system at different temperatures. First, we select a particular temperature, say \( T = T_1 \), then we evaluate the integral, (29), by adjusting the parameter \( \mu_0 \) properly so that the value of the integral becomes equal to the right-hand side within the desired accuracy. Initially, the upper limit \( (x_m) \) of integration is chosen...
at any convenient value. By increasing the upper limit \( (x_m) \), the process is repeated to obtain a new value of \( \mu \). The upper limit is then increased in steps until the convergence in \( \mu \) is reached. The entire process is then repeated for different \( T \).

### 2.2 Different Thermodynamic Quantities

Once \( \mu(T) \) is found, the average energy of the system in dimensionless form can be obtained directly from (27):

$$
\frac{E}{Nk_B T_x} = \frac{1}{2.31482473} \int_0^\infty \frac{x^{3/2}}{e^x - 1} \, dx.
$$

The specific heat per particle in dimensionless form has been calculated from the relation

$$
\frac{C_v}{Nk_B} = \frac{1}{2.31482473} \int_0^\infty \frac{x^{3/2}}{e^{x/\tau} - 1} \left[ \frac{x - \mu_0}{\tau^2} + \frac{1}{\tau} \frac{d\mu_0}{dT} \right] \, dx.
$$

The entropy of the system can be computed from the relation for the Gibbs' free energy as

$$
G = E - TS + pV = \mu N
$$

or,

$$
TS = E + pV - \mu N \quad \text{where} \quad pV = \frac{2}{3} E
$$

or,

$$
\frac{S}{Nk_B} = \frac{5}{3} E - \frac{\mu}{T}.
$$

### 2.3 Condensate Fraction

Below the critical temperature, the chemical potential is zero, and the number of particles in the excited state is given by

$$
N_{e>0} = \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{e^{\frac{1}{2}d\epsilon}}{e^{\frac{\epsilon}{2\theta}} - 1}.
$$

Below the critical temperature, the chemical potential is zero.
Therefore, the number of particles in the ground state is

\[
N_0 = N - \frac{2\pi V (2m)^{3/2}}{\hbar^3} \int_0^\infty \frac{e^{\frac{1}{2}e}}{e^{\frac{1}{2}e^2} - 1} e^{\frac{1}{2}e} \, de
\]

or,

\[
\frac{N_0}{N} = 1 - \frac{2}{\sqrt{\pi} \times 2.612} \int_0^\infty \frac{x^{1/2}}{e^{x} - 1} \, dx,
\]

where we have used the dimensionless parameters defined in (28).

2.4 Energy Fluctuation

The average energy of the system in dimensionless form can be obtained directly from (30). Similarly, the average value of \( E^2 \) per particle can be expressed in dimensionless form as

\[
\frac{E^2}{Nk_B^2 T_c^2} = \frac{1}{2.31482473} \int_0^\infty \frac{x^{5/2}}{e^{x} - 1} \, dx.
\]

The fluctuation in energy is thus obtained from

\[
\frac{1}{Nk_B^2 T_c^2} (\Delta E)^2 = \frac{\langle E^2 \rangle}{Nk_B^2 T_c^2} - \frac{1}{N} \left( \frac{\langle E \rangle}{k_B T} \right)^2.
\]
We expect that $\left( \frac{T_c}{T} \right)^2 \frac{1}{Nk_B} (\Delta E)^2$ must approach its classical value $\frac{c_c}{k_B} = \frac{3}{2}$ at high temperature.

3. Results and Discussion

**Figure 3.** Condensate fraction as a function of reduced temperature ($\frac{T}{T_c}$) in dimensionless form.

**Figure 4.** Variation of average energy with reduced temperature ($\frac{T}{T_c}$) in dimensionless form.
Figure 5. Pressure as a function of reduced temperature \( \frac{T}{T_c} \) in dimensionless form.

Figure 6. Specific heat as a function of reduced temperature \( \frac{T}{T_c} \) in dimensionless form.
Figure 7. Entropy as a function of reduced temperature ($T/T_c$) in dimensionless form.

Figure 8. Energy fluctuation as a function of reduced temperature ($T/T_c$) in dimensionless form.
4. Conclusion

Finally, to conclude, we mention that the proposed method is quite helpful in studying the thermodynamic properties of BEC numerically. The same procedure may also be applied to bosons confined in a harmonic trap.

Suggested Reading