Thermodynamics of Bose-Einstein Condensation
David Scheffler
Interface of Quark-Gluon Plasma and Cold Quantum Gases

from NIST/JILA/CU-Boulder
Overview

Introduction

Theory

- Partition Function of the Ideal Bose Gas
- Mean Occupation Number
- Bose - Einstein Statistics
- Total Particle Number
- Chemical Potential
- Critical Temperature
- Mean Occupation of the lowest Energy-State
- Energy
- Heat Capacity

Comparison with Experimental Results

- $\lambda$-Transition of $^4$He
- BEC of $^{23}$Na and $^{87}$Rb
- BEC of Hydrogen
# History

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1908</td>
<td>H. K. Onnes liquefies $^4$He and observes the <em>Onnes effect</em> ($T &lt; 2.17$ K)</td>
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<tr>
<td>1911</td>
<td>H. K. Onnes observes <em>superconductivity</em> in mercury at 4.2 K</td>
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<tr>
<td>1924</td>
<td>S. N. Bose sends Einstein a paper where he derives the Planck distribution law for photons by statistical arguments <em>Bose statistics</em></td>
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<tr>
<td>1924</td>
<td>Based upon Bose’s work, Einstein publishes “Quantentheorie des einatomigen idealen Gases” where he predicts a <em>phase transition</em> if total particle number is conserved</td>
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<tr>
<td>1938</td>
<td>F. London proposes that superfluidity is related to BEC</td>
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<td>1941</td>
<td>L. D. Landau publishes a phenomenological theory of superfluidity</td>
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<td>1957</td>
<td><em>BCS theory</em> explains superconductivity</td>
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<tr>
<td>1972</td>
<td>Lee, Osheroff and Richardson find superfluidity in liquid $^3$He ($T &lt; 3$ mK) which relates superfluidity and superconductivity</td>
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<tr>
<td>1995</td>
<td>Cornell and Wieman: first “real” BECs in $^{87}$Rb</td>
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<tr>
<td>1995-97</td>
<td>Ketterle at MIT: BEC of $^{23}$Na, interference, “atom laser”</td>
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</table>
Partition Function of the Ideal Bose Gas

microstate with energy $E_r$
all possible distributions of momenta that have a fixed energy $E_r$

\[ r = \{ n_p \} = (n_{p_1}, n_{p_2}, n_{p_3}, ...) \]

\[
Z(T, V, \mu) = \sum_{r} \exp\{-\beta (E_r - \mu N_r)\} \quad \beta = \frac{1}{k_B T}
\]

\[
= \sum_{n_{p_1} = 0}^{\infty} \exp\{-\beta (\epsilon_{p_1} - \mu) n_{p_1}\} \cdot \sum_{n_{p_2} = 0}^{\infty} \exp\{-\beta (\epsilon_{p_2} - \mu) n_{p_2}\} \ldots
\]

\[
= \frac{1}{1 - \exp\{-\beta (\epsilon_{p_1} - \mu)\}} \cdot \frac{1}{1 - \exp\{-\beta (\epsilon_{p_2} - \mu)\}} \cdot \ldots
\]

\[
= \prod_{p_i} \frac{1}{1 - \exp\{-\beta (\epsilon_{p_i} - \mu)\}}
\]
Mean Occupation Number $\langle n_{p_i} \rangle$

$$\langle n_{p_i} \rangle = \sum_r P_r n_{p_i}^{(r)} = \frac{1}{Z} \sum_r \exp\{-\beta(E_r - \mu N_r)\} n_{p_i}^{(r)}$$

$$= \frac{1}{Z} \cdot \sum_{n_{p_1}=0}^{\infty} \exp\{-\beta(\epsilon_{p_1} - \mu)n_{p_1}\} \cdot \ldots \cdot \sum_{n_{p_i}=0}^{\infty} n_{p_i} \exp\{-\beta(\epsilon_{p_i} - \mu)n_{p_i}\} \cdot \ldots$$

$$= \sum_{n_{p_i}=0}^{\infty} n_{p_i} \exp\{-\beta(\epsilon_{p_i} - \mu)n_{p_i}\} \cdot \left(1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}\right)$$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mu} \left( \sum_{n_{p_i}=0}^{\infty} \exp\{-\beta(\epsilon_{p_i} - \mu)n_{p_i}\} \right) \cdot \left(1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}\right)$$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mu} \left( \frac{1}{1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}} \right) \cdot \left(1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}\right)$$

$$= \frac{\exp\{-\beta(\epsilon_{p_i} - \mu)\}}{1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}} = \frac{1}{\exp\{\beta(\epsilon_{p_i} - \mu)\} - 1}$$
Bose - Einstein Statistics

\[ \langle n_{p_i} \rangle = \frac{1}{\exp\{\beta(\epsilon_{p_i} - \mu)\} - 1} \]

- only \( \mu \leq 0 \) is possible otherwise \( \langle n_{p_i} \rangle \) has a singularity
- for \( \mu = 0 \) and \( \epsilon_{p_0} = 0 \) the mean occupation of the lowest energy diverges
- how does \( \mu(T, x) \) look like?
- what happens if \( \mu = 0 \)?

next step
derive an expression for \( \mu(T, V, N) \) from \( N(T, V, \mu) \)
Total Particle Number $N(T, V, \mu)$

\[
N(T, V, \mu) = \sum_{p_i} \langle n_{p_i} \rangle = \sum_{p_i} \frac{\exp\{-\beta(\epsilon_{p_i} - \mu)\}}{1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}}
\]

\[
= \sum_{p_i} \exp\{-\beta(\epsilon_{p_i} - \mu)\} \cdot \sum_{j=0}^{\infty} \exp\{-\beta(\epsilon_{p_i} - \mu)\}^j
\]

\[
= \sum_{p_i} \sum_{j=1}^{\infty} \exp\{-\beta(\epsilon_{p_i} - \mu)j\}
\]

\[
= \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{V}{(2\pi \hbar)^3} \int d^3 p \exp\{-\beta \frac{p^2 j}{2m}\} \quad p^2 = \frac{p'^2}{j}
\]

\[
= \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{V}{(2\pi \hbar)^3} \int \frac{d^3 p'}{j^{3/2}} \exp\{-\beta \frac{p'^2}{2m}\} \quad dp = \frac{dp'}{\sqrt{j}}
\]}
Total Particle Number \( N(T, V, \mu) \)

\[
N(T, V, \mu) = \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{V}{(2\pi \hbar)^3} \left(\frac{2m\pi}{\beta}\right)^{3/2} \int \frac{dp'}{j^{3/2}} p'^2 \exp\left\{-\beta \frac{p'^2}{2m}\right\}
\]

\[
= \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{V}{(2\pi \hbar)^3} \left(\frac{2m\pi}{\beta}\right)^{3/2} \left(\frac{\sqrt{2m\pi k_B T}}{2\pi \hbar}\right)^3
\]

\[
= \frac{V}{\lambda(T)^3} \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{1}{j^{3/2}}
\]

(1)

thermal wavelength

\[
\lambda(T) = \frac{2\pi \hbar}{\sqrt{2\pi m k_B T}} \quad \text{from} \quad E = \frac{p^2}{2m} = \pi k_B T \quad \text{and} \quad p = \frac{\hbar 2\pi}{\lambda}
\]
Intermediate Recapitulation

derived the partition function for the ideal Bose Gas

\[ Z(T, V, \mu) = \prod_{p_i} \frac{1}{1 - \exp\{-\beta(\epsilon_{p_i} - \mu)\}} \]

\[ \Downarrow \]

calculated the Bose-statistics and found \( \mu \leq 0 \)

\[ \langle n_{p_i} \rangle = \frac{1}{\exp\{\beta(\epsilon_{p_i} - \mu)\} - 1} \]

\[ \Downarrow \]

asked whether \( \mu(T, V, N) \) can be zero

\[ N(T, V, \mu) = \frac{V}{\lambda(T)^3} \sum_{j=1}^{\infty} \exp\{\beta \mu j\} \frac{1}{j^{3/2}} \]
Chemical Potential $\mu(T, V, N)$

fixed number of particles
$N(T, V, \mu) = N \quad \nu = V/N$

$$1 = \frac{\nu}{\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\frac{\mu j}{k_B T}\}}{j^{3/2}} \quad (2)$$

- $T \to \infty \quad \mu \to -\infty$
- $\mu = 0 \quad \text{at} \quad T = T_c$
- no solution for $T < T_c$

$\mu$ can indeed be zero at a critical temperature $T_c$
particles start to "condense" into the lowest energy state $\Rightarrow$ BEC
Critical Temperature $T_c$ of the Ideal Bose Gas

\[ 1 = \frac{v}{\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\beta \mu j\}}{j^{3/2}} \xrightarrow{\mu = 0} \frac{v}{\lambda(T_c)^3} \sum_{j=1}^{\infty} \frac{1}{j^{3/2}} = \frac{v}{\lambda(T_c)^3} \zeta(3/2) \] (3)

Riemann's Zeta Function

\[ \zeta(x) = \sum_{j=1}^{\infty} \frac{1}{j^x} \quad \zeta(3/2) \approx 2.612 \]

critical temperature

\[ T_c = \frac{2\pi \hbar^2}{\zeta(3/2)^{2/3}mv^{2/3}k_B} \]

constraint for BEC

\[ \frac{\text{particles}}{\text{Volume}} \cdot \lambda(T)^3 \geq 2.612 \]
What happens below $T_c$? – eq. (2)

for $\mu = 0$ and $p^2 \to 0$,  
\[ \langle n_p \rangle = \frac{1}{\exp\{\beta(\frac{p^2}{2m} - \mu)\} - 1} \propto \frac{1}{p^2} \]

\[ N = \sum_p \langle n_p \rangle = \langle n_0 \rangle + \sum_{p \neq 0} \langle n_p \rangle \]

\[ N = \Delta \int_{p} \langle n_p \rangle p^2 dp = \Delta \int_{0}^{\delta p} dp + \Delta \int_{\delta p}^{\infty} \langle n_p \rangle p^2 dp \]

in contradiction to diverging $\langle n_0 \rangle$ for $\mu = 0$!

**treat $\langle n_0 \rangle$ separately below $T_c$**

\[ \sum_p \langle n_p \rangle = \langle n_0 \rangle + \sum_{p \neq 0} \langle n_p \rangle \to \langle n_0 \rangle + \frac{4\pi V}{(2\pi \hbar)^3} \int_p \langle n_p \rangle p^2 dp \]  (4)
Mean Occupation of the lowest Energy-State

\[ N(T, V, \mu) = \frac{V}{\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\beta \mu j\}}{j^{3/2}} \quad \text{for } T > T_c \quad \text{eq. (1)} \]

\[ N(T, V, \mu) = \langle n_0 \rangle + \frac{V}{\lambda(T)^3} \zeta(3/2) \quad \text{for } T \leq T_c \quad \text{eq. (4)} \]

\[ T > T_c \]

\[ \frac{\langle n_0 \rangle}{N} = O(1/N) \approx 0 \]

\[ T \leq T_c \quad \text{with eq. (3)} \]

\[ \frac{V}{\lambda^3} \zeta(3/2) = \frac{V \lambda_c^3}{V \lambda^3} = N \left( \frac{T}{T_c} \right)^{3/2} \]

\[ \frac{\langle n_0 \rangle}{N} = 1 - \frac{V}{N \lambda(T)^3} \zeta(3/2) = 1 - \left( \frac{T}{T_c} \right)^{3/2} \]
$E(T, V, \mu)$ of non-condensed particles

similar to $N(T, V, \mu)$

$$E(T, V, \mu) = \sum_p \epsilon_p \langle n_p \rangle = \ldots = \frac{3k_B TV}{2\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\beta \mu j\}}{j^{5/2}}$$

$T \leq T_c, \mu = 0$ with eq. (3) $V = \frac{N\lambda^3_c}{\zeta(3/2)}$

$$E(T, V, N) = \frac{3k_B TV}{2\lambda(T)^3} \sum_{j=1}^{\infty} \frac{1}{j^{5/2}} = \frac{3\zeta(5/2)}{2\zeta(3/2)} Nk_B T \left( \frac{T}{T_c} \right)^{3/2}$$

$T > T_c$

$$E(T, V, \mu) = \frac{3k_B TV}{2\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\beta \mu j\}}{j^{5/2}} , \quad 1 = \frac{V}{N\lambda(T)^3} \sum_{j=1}^{\infty} \frac{1}{j^{3/2}} \exp\{\beta \mu j\}$$
Expansion of $E(T, V, \mu)$ for $T > T_c$

$$E(T, V, \mu) = \frac{3k_B TV}{2\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\{\beta \mu j\}}{j^{5/2}}, \quad 1 = \frac{V}{N\lambda(T)^3} \sum_{j=1}^{\infty} \frac{1}{j^{3/2}} \exp\{\beta \mu j\}$$

$j = 1$

$$E(T, V, \mu) = \frac{3k_B TV}{2\lambda(T)^3} \exp\{\beta \mu\}, \quad 1 = \frac{V}{N\lambda(T)^3} \exp\{\beta \mu\}$$

$$E^1(T, V, N) = \frac{3}{2} k_B N T$$

$j = 2$

$$E(T, V, \mu) = \frac{3k_B TV}{2\lambda(T)^3} \frac{\exp\{\beta \mu 2\}}{2^{5/2}}, \quad (\exp\{\beta \mu\})^2 = \left(\frac{N\lambda(T)^3}{V}\right)^2$$

$$E^2(T, V, N) = \frac{3}{2} k_B N T \frac{\lambda(T)^3 N}{2^{5/2} V}$$

$$E(T, V, N) \approx E^1 + E^2 = \frac{3}{2} k_B N T \left[ 1 + \frac{\zeta(3/2)}{2^{5/2}} \left(\frac{T_c}{T}\right)^{3/2} \right] \quad \text{with} \quad \frac{V}{N} = \frac{\lambda_c^3}{\zeta(3/2)} \quad \text{eq. (2)}$$
Heat Capacity $C_V(T)$

$$C_V(T) = \left( \frac{\partial Q}{\partial T} \right)_{NV} = \left( \frac{\partial E}{\partial T} \right)_{NV} \quad \text{with} \quad dW = 0$$

$T \leq T_c$

$$C_V(T, N) = \frac{15\zeta(5/2)}{4\zeta(3/2)} Nk_B \left( \frac{T}{T_c} \right)^{3/2}$$

$T > T_c$

$$C_V(T, N) \approx \frac{3}{2} k_B N \left[ 1 + \frac{\zeta(3/2)}{2^{7/2}} \left( \frac{T_c}{T} \right)^{3/2} \right]$$
calculated the critical temperature

\[ T_c = \frac{2\pi \hbar^2}{\zeta(3/2)^{2/3} m v^{2/3} k_B} \]

\[ \downarrow \]

observed an inconsistency in our equation for \( \mu \) for \( T < T_c \)

\[ 1 = \frac{v}{\lambda(T)^3} \sum_{j=1}^{\infty} \frac{\exp\left\{ \frac{\mu j}{k_B T} \right\}}{j^{3/2}} \]

\[ \downarrow \]

and fixed it

\[ \downarrow \]

calculated \( N(T, V, N) \rightarrow E(T, V, N) \rightarrow c_V(T, N) \)
\( \lambda \)-Transition of \(^4\text{He}\)

- In 1908 Heike Kamerlingh Onnes liquefied Helium
- In 1913 Onnes received the Nobel prize
  “for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium”
- \( \lambda \)-transition at \( T = 2.17 \text{ K} \)
- In 1962 Landau received the Nobel prize
  “for his pioneering theories for condensed matter, especially liquid helium”

**Ideal Bose Gas**

\[
T_c = \frac{2 \pi \hbar^2}{\zeta(3/2)^{2/3} m v^{2/3} k_B} \quad \text{with} \quad v \approx 46 \text{ Å}^3, \ m = 4 u \quad \Rightarrow \quad T_c = 3.11 \text{ K}
\]

Well, not bad for an ideal gas model
BEC of dilute $^{23}\text{Na}$ and $^{87}\text{Rb}$ gases

- First observation of real BEC in 1995 by Cornell and Wieman (Rb, CU-Boulder), Ketterle (Na, MIT)

- Nobel prize in 2001
  “for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates”

- $^{23}\text{Na}$: $T_{\text{exp}} \approx 2 \mu K$, $T_c = 2.2 \mu K$
- $^{87}\text{Rb}$: $T_{\text{exp}} \approx 170 \, nK$, $T_c = 34 \, nK$

lower picture: from NIST/JILA/CU-Boulder
BEC of Hydrogen

Ideal Bose gas

\[ \nu = \frac{1}{n} \quad m = 1 \text{u} \quad \Rightarrow \quad T_c = 51 \mu K \]

\[ \nu^{1/3}/r_B = \Delta r/r_B \approx 3300 \quad \lambda/r_B \approx 4600 \quad r_B : \text{Bohr radius} \]

in molecular H\(_2\) \[ \Delta r/r_B \approx 1.4 \]

→ BEC is driven by quantum statistics and not by interactions!
Thanks for your attention!
What is a BEC?

High Temperature $T$:
- Thermal velocity $v$
- Density $d^{-3}$
- "Billiard balls"

Low Temperature $T$:
- De Broglie wavelength $\lambda_{dB}$
  - $\lambda_{dB}=h/mv \propto T^{-1/2}$
  - "Wave packets"

$T=T_{crit}$: Bose-Einstein Condensation
- $\lambda_{dB} = d$
- "Matter wave overlap"

$T=0$: Pure Bose condensate
- "Giant matter wave"
Atom Laser & Interference of BECs

- interference fringes between separated parts of a BEC cloud "macroscopic matter wave" by MIT group
- coherent emission of condensed atoms "pulsed atom laser" by MIT group

more about this in

- Fermion-Fermion and Boson-Boson Interaction at low $T$
- Experimental production of BECs

upper picture from Ketterle et al., Science 275, 637 (1997)
lower picture from http://cua.mit.edu/ketterle_group/Nice_pics.htm