

# **PHY 341/641 Thermodynamics and Statistical Mechanics**

**MWF: Online at 12 PM & FTF at 2 PM**

**Record!!!**

## **Discussion for Lecture 31:**

**Quantum effects in statistical mechanics**

**Reading: Chapter 7 (mostly 7.5)**

- 1. Statistical mechanics of Bose systems**
- 2. Liquid  $^4\text{He}$**
- 3. Bose condensate**

21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	<a href="#">#18</a>	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions	<a href="#">#20</a>	03/31/2021
25	Wed: 03/31/2021	App. A & Chap. 7.1	Quantum mechanical effects	<a href="#">#21</a>	04/02/2021
26	Fri: 04/02/2021	Chap. 7.1-7.2	Quantum mechanical effects		
27	Mon: 04/05/2021	Chap. 7.3	Bose and Fermi statistics	<a href="#">#22</a>	04/09/2021
	Wed: 04/07/2021	No class	<i>Holiday</i>		
28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	<a href="#">#23</a>	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	<a href="#">#24</a>	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 8.1	Interacting particles		
33	Wed: 04/21/2021	Chap. 8.2	Spin magnetism		
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

## Your questions –

**From Kristen --** 1. Why must the ground state of the energy be equal to the chemical potential at  $T=0$ , wouldn't this make the denominator of equation 7.121 be zero? 2. At temperatures higher than  $T_c$ , why is it that the chemical potential is negative? 3. Could you reinforce why Bose-Einstein Condensation doesn't happen in all systems?

**From Mike --** Can you further elaborate on how the ground state for bose particles is more favorable if they are indistinguishable rather than distinguishable?

**From Chao --** how is the factor  $\pi$  included in the formula below?

$$n_{\max} = \left( \frac{6N}{\pi} \right)^{1/3}. \quad (7.107)$$

Comment -- This comes from the discussion of the Debye temperature

$$\int dn_x \int dn_y \int dn_z \rightarrow 4\pi \int_0^{n_{\max}} n^2 dn \quad \text{using spherical polar coordinates}$$

## Grand canonical partition function and Grand potential for non interacting Bose particles:

In terms of single particle states  $\epsilon_s$  :

$$\ln(Z_{GrandBose}(T, \mu)) = -\sum_s \ln(1 - e^{-\beta(\epsilon_s - \mu)})$$

$$\Omega_{GrandBose}(T, \mu) = -kT \ln(Z_{GrandBose}(T, \mu)) = kT \sum_s \ln(1 - e^{-\beta(\epsilon_s - \mu)})$$

Constraint consistent with particle number: 
$$\sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} = N$$

Expressed in terms of the density of states: 
$$g(\epsilon) = \sum_s \delta(\epsilon - \epsilon_s)$$

$$\Omega_{GrandBose}(T, \mu) = kT \int d\epsilon g(\epsilon) \ln(1 - e^{-\beta(\epsilon - \mu)})$$

$$N = \int d\epsilon g(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

## Evaluating the chemical potential --

$$N = \int d\epsilon \, g(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

If our Bose particle has spin  $s = 0$  and mass  $m$ , and is contained in a box of volume  $V$ , from previous analysis:

$$g(\epsilon) = 2\pi V \left( \frac{2m}{h^2} \right)^{3/2} \sqrt{\epsilon}$$

$$N = 2\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^{\infty} d\epsilon \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon - \mu)} - 1}$$

Integral to evaluate:

$$N = 2\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^{\infty} d\epsilon \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)} - 1}$$

Note that for  $\epsilon < \mu$ , the integrand is unphysical (negative)  
Deduce that  $\mu \leq 0$ .

Also recall that at high temperature, we expect that the chemical potential should take the value that we previously found for a classical ideal gas --

$$\mu = -kT \ln \left( \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right) \quad \rightarrow \text{negative value}$$

**$\rightarrow$  As  $T \rightarrow 0$  and quantum effects dominate, we expect  $\mu$  to increase to its limiting value of 0.**

## Back to our integral

$$\begin{aligned} N &= 2\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\infty d\epsilon \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)} - 1} \\ &= 2\pi V \left( \frac{2mkT}{h^2} \right)^{3/2} \int_0^\infty dx \frac{\sqrt{x}}{e^{-\beta\mu} e^x - 1} \end{aligned}$$

Now assume that as  $T$  is lowered, there may be a critical temperature  $T_c$  at which  $\mu=0$  so that

$$\begin{aligned} \frac{N}{V} &= 2\pi \left( \frac{2mkT_c}{h^2} \right)^{3/2} \int_0^\infty dx \frac{\sqrt{x}}{e^x - 1} = 2\pi \left( \frac{2mkT_c}{h^2} \right)^{3/2} \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) \\ &= \left( \frac{2\pi mkT_c}{h^2} \right)^{3/2} \zeta\left(\frac{3}{2}\right) = \left( \frac{2\pi mkT_c}{h^2} \right)^{3/2} 2.612375349 \end{aligned}$$



Riemann zeta function



Significance of this result --

$$\frac{N}{V} = \left( \frac{2\pi m k T_c}{h^2} \right)^{3/2} 2.612375349$$

Critical temperature:  $kT_c = \frac{h^2}{2\pi m} \left( \frac{N/V}{2.612375349} \right)^{2/3}$

➔ It is possible for a macroscopic number of Bose particles to occupy the lowest energy state of the system.

# Physical realization of Bose condensation

$^4\text{He}$  has a phase transition at 2 K to a “superfluid” state as discovered in 1937. While it is intriguing to associate this phenomenon with Bose condensation, interactions of the He atoms in the superfluid state, modify the thermodynamics and statistical mechanics.

## ■ REPORTS

*Science* **269** (5221), 198-201.  
DOI: [10.1126/science.269.5221.198](https://doi.org/10.1126/science.269.5221.198)

### Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor

1995

M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman,\*  
E. A. Cornell

A Bose-Einstein condensate was produced in a vapor of rubidium-87 atoms that was confined by magnetic fields and evaporatively cooled. The condensate fraction first appeared near a temperature of 170 nanokelvin and a number density of  $2.5 \times 10^{12}$  per cubic centimeter and could be preserved for more than 15 seconds. Three primary signatures of Bose-Einstein condensation were seen. (i) On top of a broad thermal velocity distribution, a narrow peak appeared that was centered at zero velocity. (ii) The fraction of the atoms that were in this low-velocity peak increased abruptly as the sample temperature was lowered. (iii) The peak exhibited a nonthermal, anisotropic velocity distribution expected of the minimum-energy quantum state of the magnetic trap in contrast to the isotropic, thermal velocity distribution observed in the broad uncondensed fraction.

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$T_c = 1.7 \times 10^{-7} \text{K}$

$^{87}\text{Rb}$  atoms

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## Additional reading –

### **The Richtmyer Memorial Lecture: Bose–Einstein Condensation in an Ultracold Gas**

Carl E. Wieman

Citation: *American Journal of Physics* **64**, 847 (1996); doi: 10.1119/1.18111

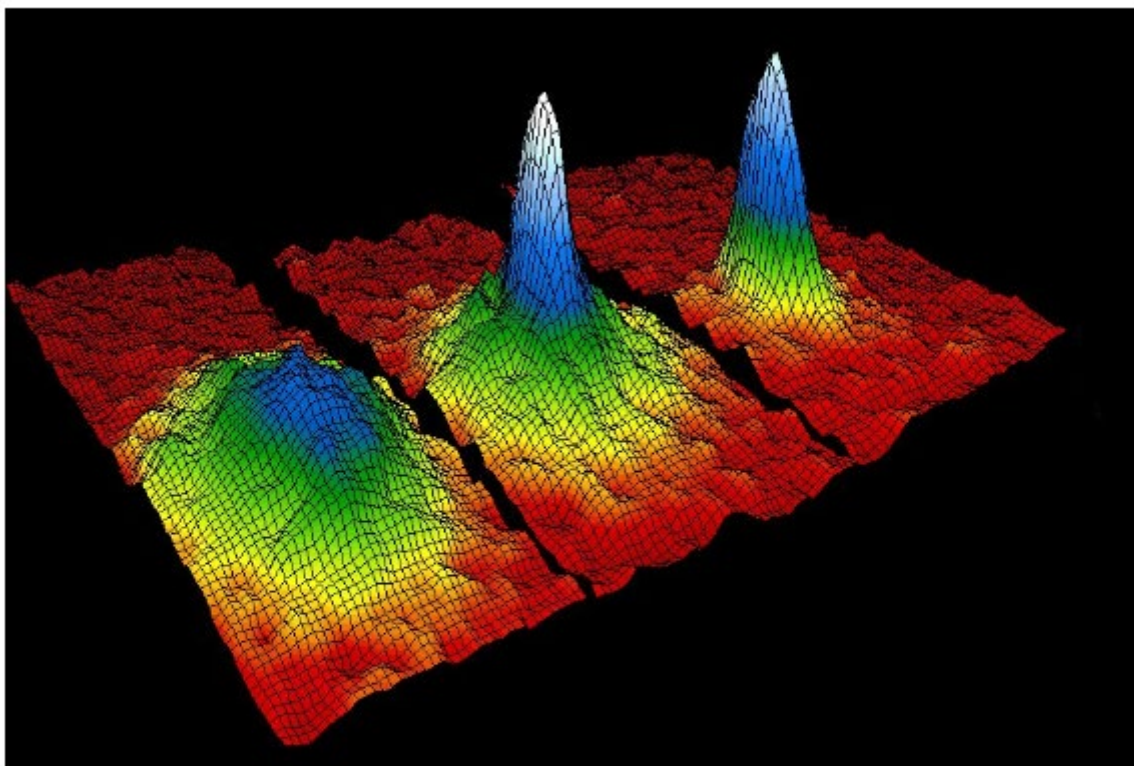
View online: <https://doi.org/10.1119/1.18111>

## How Bose–Einstein condensates keep revealing weird physics

Stephen Ornes, *Science Writer*

Proceedings of the National Academy of Sciences 2017

[www.pnas.org/cgi/doi/10.1073/pnas.1707804114](http://www.pnas.org/cgi/doi/10.1073/pnas.1707804114)



**Bose-Einstein Condensation at 400, 200, and 50  
nano-Kelvins**

$^{87}\text{Rb}$  atoms (~2000 atoms in condensate)



## The Nobel Prize in Physics 2001

Eric A. Cornell, Wolfgang Ketterle, Carl E. Wieman

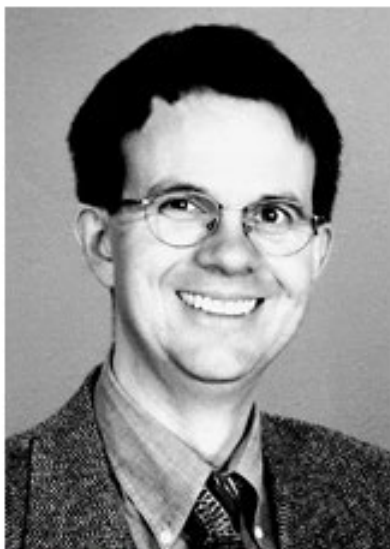
The Nobel Prize in Physics 2001 ▼

Nobel Prize Award Ceremony ▼

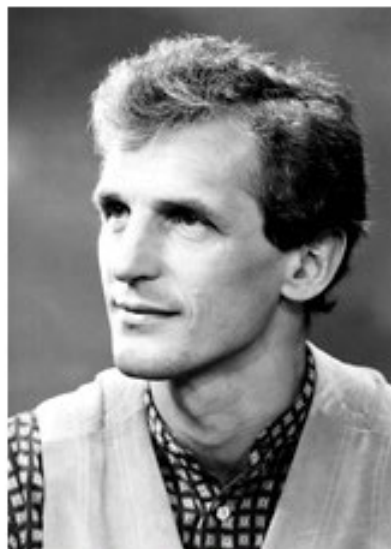
Eric A. Cornell ▼

Wolfgang Ketterle ▼

Carl E. Wieman ▼



Eric A. Cornell



Wolfgang Ketterle



Carl E. Wieman

The Nobel Prize in Physics 2001 was awarded jointly to Eric A. Cornell, Wolfgang Ketterle and Carl E. Wieman *"for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates"*.

Let  $z \equiv e^{\beta\mu}$ , noting that  $0 \leq z \leq 1$

$$N = \int d\epsilon \, g(\epsilon) \frac{z}{e^{\beta\epsilon} - z}$$

The problem is that as  $z \rightarrow 1$ , the equations become poorly defined and we need to use more careful analysis.

Note that  $z \equiv e^{\mu/(kT)}$  and  $\mu \leq 0$

Let us suppose that there are  $N_0$  particles in the ground state with

$$N_0 = \frac{z}{1-z}$$

The expectation is that both  $N_0$  and  $\frac{z}{1-z}$  may be infinite but that

$\frac{N_0}{V}$  and  $\frac{1}{V} \frac{z}{1-z}$  are well defined for a containing volume  $V$ .

Define  $g_{3/2}(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^{\infty} dx \frac{z\sqrt{x}}{e^x - z}$

Note that  $g_{3/2}(1) = \zeta(3/2) = 2.612375349$

Taking into account the more singular behavior of the functions we can write

$$\begin{aligned} N &= N_0 + 2\pi V \left( \frac{2mkT}{h^2} \right)^{3/2} \int_{0^+}^{\infty} dx \frac{\sqrt{x}z}{e^x - z} \\ &= N_0 + V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} g_{3/2}(z) \end{aligned}$$

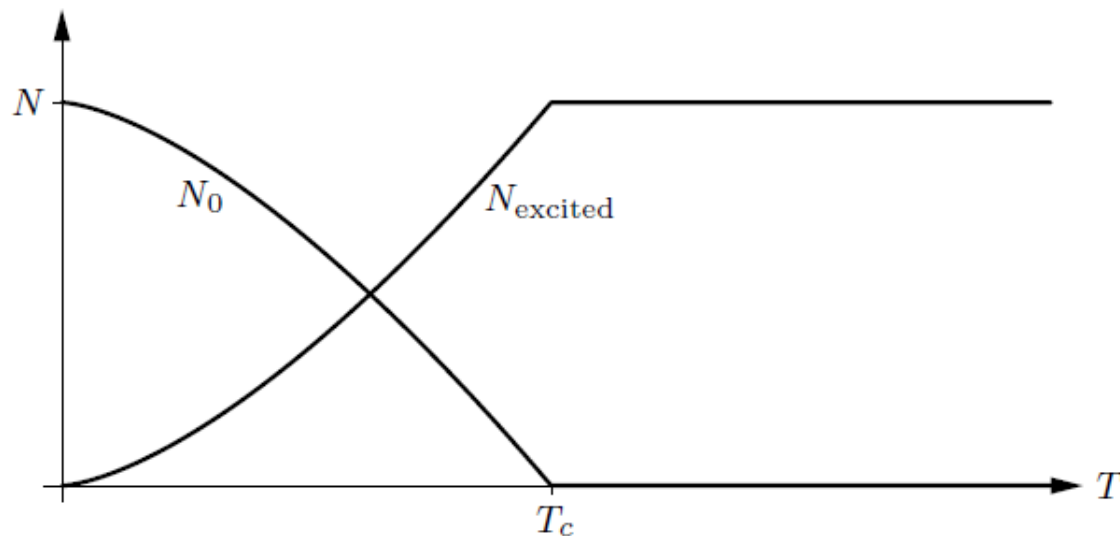
In this treatment, it is understood that the  $N_0$  term only comes into play when  $z \rightarrow 1$ . More carefully:

$$N = \begin{cases} N_0 + V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} g_{3/2}(1) & \text{for } z = 1 \\ V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} g_{3/2}(z) & \text{for } z < 1 \end{cases}$$

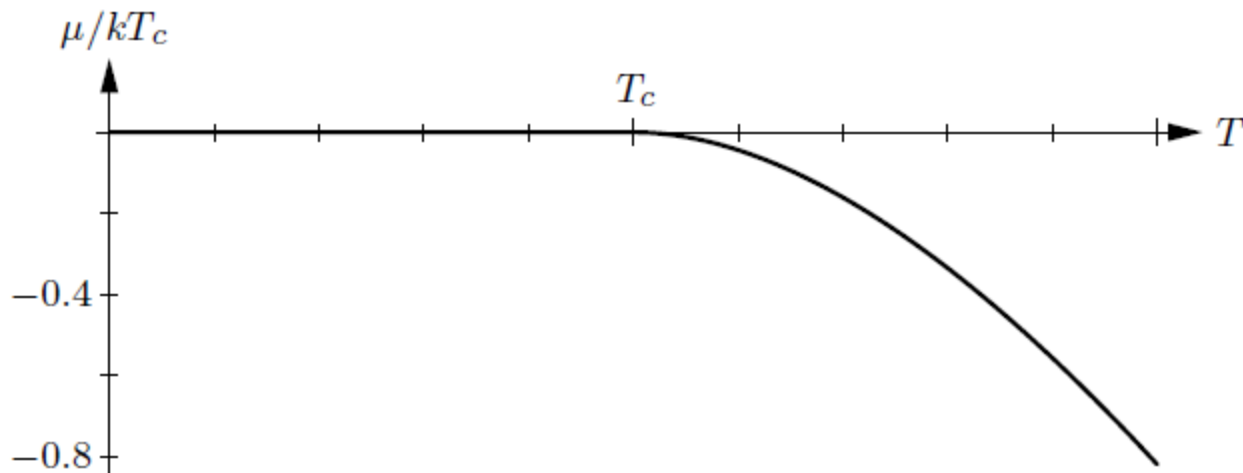


It can be shown that

$$\frac{N_0}{N} = 1 - \left( \frac{T}{T_c} \right)^{3/2} \quad \text{where} \quad kT_c = \frac{h^2}{2\pi m} \left( \frac{N/V}{g_{3/2}(1)} \right)^{2/3}$$



**Figure 7.32.** Number of atoms in the ground state ( $N_0$ ) and in excited states, for an ideal Bose gas in a three-dimensional box. Below  $T_c$  the number of atoms in excited states is proportional to  $T^{3/2}$ . Copyright ©2000, Addison-Wesley.



**Figure 7.33.** Chemical potential of an ideal Bose gas in a three-dimensional box. Below the condensation temperature,  $\mu$  differs from zero by an amount that is too small to show on this scale. Above the condensation temperature  $\mu$  becomes negative; the values plotted here were calculated numerically as described in Problem 7.69. Copyright ©2000, Addison-Wesley.