Statistical mechanics

Lecture note: 5

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Topics Covered:

1. Thermodynamic functions of ideal BE gas.
2. To calculate E,P,$C_{V,}$S for two different cases.

   2.1 when $T<T_c$

   2.2 when $T>T_c$

Revision

A. Bose Einstein Distribution Formula

1. Bosons are indistinguishable integral spin particles such as photons, 4He atom, phonons, magnons, π-mesons.
2. Bosons have symmetric wave function
3. The occupation no. for the i^{th} energy level is given as

$$f = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1}$$

4. 'n' is called occupation number.

B. Bose Einstein Condensation:

$$T_c = \frac{h^2}{2\pi mk}\left[\frac{N}{V * \xi\left(\frac{3}{2}\right)}\right]^{2/3} \quad (1)$$

Below Tc, the particles will condense into ground state.

Thermodynamic functions of ideal BE gas

1. Properties of ideal bose gase above and below T_c are vastly different, so will calculate the physical quantites E,P,C_V,S by taking two different cases of above and below Tc.

2. P = $\frac{2}{3} * \frac{E}{V}$

3. S = $\int \frac{C_V dt}{T}$

4. $C_V = (\frac{dE}{dT})$

5. If we find E, we can easily calculate the other quantities.

Case 1: $T<T_c$

A. To find the expression for energy

For, BE gas,

$$n(\varepsilon) = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1}$$

No. of quantum states for energy ε = G* $d^3r\ d^3p/h^3$, where G is intrinsic angular momentum.

No. of quantum states: $g(\varepsilon)d\varepsilon = \frac{G*2\pi V*(2m)^{\frac{3}{2}}*\varepsilon^{1/2}d\varepsilon}{h^3}$

Thus no. of particles in phase space $d^3r\ d^3p$ is

$$dN = \frac{G * 2\pi V * (2m)^{\frac{3}{2}} * \varepsilon^{\frac{1}{2}} * d\varepsilon}{h^3} \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1}$$

$$dN = CV \frac{\varepsilon^{\frac{1}{2}} * d\varepsilon}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1} \qquad (1.1)$$

Where C = $\frac{G*2\pi*(2m)^{\frac{3}{2}}}{h^3}$

Energy of the system E = $\int \text{no. of particles in phase space d3r d3p} * \varepsilon$

$$E = \int_0^\infty CV \frac{\varepsilon^{\frac{3}{2}} * d\varepsilon}{e^{\frac{\varepsilon_i - \mu}{kT}} - 1}$$

$$E = \int_0^\infty CV \frac{\varepsilon^{\frac{3}{2}} * d\varepsilon}{\left(\frac{1}{A}\right) * e^{\frac{\varepsilon_i}{kT}} - 1}$$

To evaluate the above integral, we change the variable to x as:

Let ε/KT = x, then dε= (KT)*dx thus $E = CV * (kT)^{\frac{5}{2}} * \int_0^\infty \frac{x^{\frac{3}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1}$

For $T<T_c$, A =1, thus above equation becomes $E = CV * (kT)^{\frac{5}{2}} * \int_0^\infty \frac{x^{\frac{3}{2}} * dx}{e^x - 1}$

$$E = CV * (kT)^{\frac{5}{2}} * \Gamma\left(\frac{5}{2}\right) * \xi(5/2)$$

Where, Γ and ξ are gamma function and Riemann zeta function.

$$E = \frac{G * 2\pi * (2m)^{\frac{3}{2}}}{h^3} * V * (kT)^{\frac{5}{2}} * \Gamma\left(\frac{5}{2}\right) * \xi(5/2)$$

Considering G=1, we get, $E = \frac{2\pi * (2m)^{\frac{3}{2}}}{h^3} * V * (kT)^{\frac{5}{2}} * \frac{3\sqrt{\pi}}{4} * \xi(5/2)$ for $T<T_c$

$$E = \frac{(2\pi m)^{\frac{3}{2}}}{h^3} * V * (kT)^{\frac{5}{2}} * \frac{3}{2} * \xi(5/2) \quad \text{for } T<T_c \quad (2)$$

B. To convert E in terms of T_c

Using eqn 1, into eqn 2,

$$E = \frac{3Nk}{2} * \frac{T^{\frac{5}{2}}}{T_C^{\frac{3}{2}}} * \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{3}{2}\right)} \quad (2.1)$$

$$E = 0.7762Nk * \frac{T^{\frac{5}{2}}}{T_C^{\frac{3}{2}}} \quad \text{for } T<T_c \quad (3)$$

This means that E is proportional to $T^{5/2}$, and as T goes to 0, E goes to 0. This means when $T<T_C$, the particles in condense phase settle down into ground state.

C. Pressure

$P = \frac{2}{3} * \frac{E}{V}$, thus from equation (2),

$$P(T) = \frac{(2\pi m)^{\frac{3}{2}}}{h^3} * (kT)^{\frac{5}{2}} * \xi(5/2) \quad (4)$$

We, know that from kinetic theory of gases, pressure is directly proportional to number density, but pressure of BE condensed phase is proportional to $T^{5/2}$ and is completely independent of volume and number density. This situation is analogous to coexistence of liquid vapor state where addition of any no. of particles at constant temperature does not lead to increase in pressure.

At the transition point, when $T=T_{C,}$

$$P(T_C) = \frac{(2\pi m)^{\frac{3}{2}}}{h^3} * (kT_C)^{5/2} * \xi(5/2) \qquad (5)$$

From equation, 2 and 5,

$$P(T_C) = \frac{NkT}{2.612V} * \xi(5/2)$$

$$P(T_C) = \frac{0.5134*NkT}{V}$$

Ideal boson gas at the transition temperature exert pressure which is nearly one-half of what a classical would gas exert under similar conditions. Dividing eqn. 4 and 5 we get

$$P(T) = P(T_C)\left(\frac{T}{T_C}\right)^{5/2}$$

D. Heat capacity

$$C_V = \left(\frac{dE}{dT}\right) \qquad (6)$$

From eqn. 2.1

$$C_v = \frac{15Nk}{4}\frac{T^{\frac{3}{2}}}{T_C^{\frac{3}{2}}} * \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{3}{2}\right)} \qquad (6.1)$$

Heat capacity of boson gas tends to zero as temperature goes to zero.

E. Entropy

$$S = \int \frac{C_V dt}{T}$$

From equation 6,

$$S = 1.28Nk* \frac{T^{\frac{3}{2}}}{T_C^{\frac{3}{2}}}$$

Case 2: $T>T_C$

A. Expression for total number of particles

Following the same procedure and coming to equation (1.1)

$$dN = CV \frac{\varepsilon^{\frac{1}{2}} * d\varepsilon}{e^{\frac{\varepsilon-\mu}{kT}} - 1} \quad (1.1)$$

Replace $\alpha = -\mu$

$$dN = CV \frac{\varepsilon^{\frac{1}{2}} * d\varepsilon}{e^{\frac{\varepsilon+\alpha}{kT}} - 1}$$

Let ε/KT = x, then dε= (KT)*dx thus

N = $CV * (kT)^{\frac{3}{2}} * \int_0^{\infty} \frac{x^{\frac{1}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1},$

Where C = $\frac{G * 2\pi * (2m)^{\frac{3}{2}}}{h^3}$

Considering G = 1

$$N = \frac{V(2\pi kTm)^{\frac{3}{2}}}{h^3} * \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{\frac{1}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1},$$

$$N = \frac{V(2\pi kTm)^{\frac{3}{2}}}{h^3} * f_1(\alpha) \quad (7)$$

Where $f_1(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{\frac{1}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1}.$

B. Expression for Energy

Energy of the system E = $\int \text{no. of particles in phase space d3r d3p} * \varepsilon$

Following the same procedure E = $\frac{V(2\pi kTm)^{\frac{3}{2}} kT}{h^3} * \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{\frac{3}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1},$

$$E = \frac{3}{2} \frac{V(2\pi kTm)^{\frac{3}{2}} kT}{h^3} * \frac{4}{3\sqrt{\pi}} \int_0^{\infty} \frac{x^{\frac{3}{2}} * dx}{\left(\frac{1}{A}\right) * e^x - 1},$$

$$E = \frac{3}{2} \frac{V(2\pi kTm)^{\frac{3}{2}} kT}{h^3} * f_2(\alpha)$$

Where $f_2(\alpha) = \frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{3}{2}}*dx}{\left(\frac{1}{A}\right)*e^x-1}$,

$$f_1(\alpha) = A + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \frac{A^4}{4^{\frac{3}{2}}} + \cdots \ldots \ldots \ldots$$

$$f_2(\alpha) = A + \frac{A^2}{2^{\frac{5}{2}}} + \frac{A^3}{3^{\frac{5}{2}}} + \frac{A^4}{4^{\frac{5}{2}}} + \cdots \ldots \ldots \ldots$$

Substituting these expressions back to expression of E and N, we get,

$$N = \frac{V(2\pi kTm)^{\frac{3}{2}}}{h^3} * \left[A + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \frac{A^4}{4^{\frac{3}{2}}} + \cdots \ldots \ldots\right] \quad (8)$$

$$E = \frac{3}{2}\frac{V(2\pi kTm)^{\frac{3}{2}}kT}{h^3} * \left[A + \frac{A^2}{2^{\frac{5}{2}}} + \frac{A^3}{3^{\frac{5}{2}}} + \frac{A^4}{4^{\frac{5}{2}}} + \cdots \ldots \ldots \ldots .\right] \quad (9)$$

Dividing eqn. 9 by eqn. 8, we get

$$\frac{E}{N} = \frac{3kT}{2}\left[A + \frac{A^2}{2^{\frac{5}{2}}} + \frac{A^3}{3^{\frac{5}{2}}} + \frac{A^4}{4^{\frac{5}{2}}} + \cdots \ldots \ldots \ldots .\right]\left[A + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \frac{A^4}{4^{\frac{3}{2}}} + \cdots \ldots \ldots \ldots\right]^{-1}$$

$$E = \frac{3NkT}{2}\left[1 - \frac{A}{2^{\frac{3}{2}}} + \frac{A}{2^{\frac{5}{2}}} - \cdots \ldots \ldots \ldots .\right]$$

C. To calculate E in terms of T_c

From eqn. 7,

$$f_1(\alpha) = \frac{N*h^3}{V(2\pi kTm)^{\frac{3}{2}}}$$

When A<<1, $f_1(\alpha) = A$

$$A = \frac{N*h^3}{V(2\pi kTm)^{\frac{3}{2}}}$$

Substitute the value of N from eqn. 1 to above eqn, we get

$$A = \frac{T_C^{\frac{3}{2}}}{T^{\frac{3}{2}}} * \xi\left(\frac{3}{2}\right)$$

So $$E = \frac{3NkT}{2}\left[1 - \frac{\frac{T_C^{\frac{3}{2}}}{T^{\frac{3}{2}}} * \xi\left(\frac{3}{2}\right)}{2^{\frac{3}{2}}} + \cdots \dots \dots \dots .\right]$$ For $T>T_c$ (10)

D. Expression for pressure:

$P = \frac{2}{3} * \frac{E}{V}$, thus from equation (10),

$$P(T) = \frac{NkT}{V}\left[1 - \frac{0.4618 * T_C^{\frac{3}{2}}}{T^{\frac{3}{2}}} + \cdots \dots \dots \dots .\right]$$

When $T>>T_c$, pressure approaches to classical value of NkT/V.

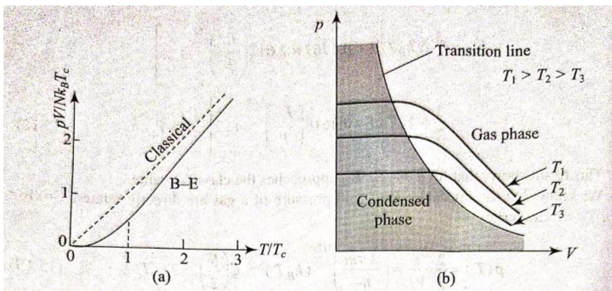

Fig. 15.3 (a) Plot of (a) pV/Nk_BT_c as a function of T/T_c, and (b) p versus V for a strongly degenerate Bose gas.

E. Heat Capacity

$$C_V = \left(\frac{dE}{dT}\right)$$

$$C_V = \frac{3Nk}{2}\left[1 + \frac{0.2309 * T_C^{\frac{3}{2}}}{T^{\frac{3}{2}}}\right] \quad (11)$$

For T>Tc, Cv tends to 3R/2. From equation 6.1 and eqn 11, we get the same value of Cv at T=Tc. This means that specific heat capacity is continuous at the condensation temperature.

F. Entropy

Integrating the above expression,

$$S(T) = S(T_C) + \frac{3Nk}{2}\left[ln\left(\frac{T}{T_C}\right) + 0.1536\left\{1 - \left(\frac{T_C}{T}\right)^{3/2}\right\}\right]$$

Entropy also shows sudden drop for T<Tc. Thus above Tc, entropy increases suddenly. Also for T tends to zero, entropy of ideal gas drops to zero, which means condensed phase has no entropy, and this result is in accordance of third law of thermodynamics.

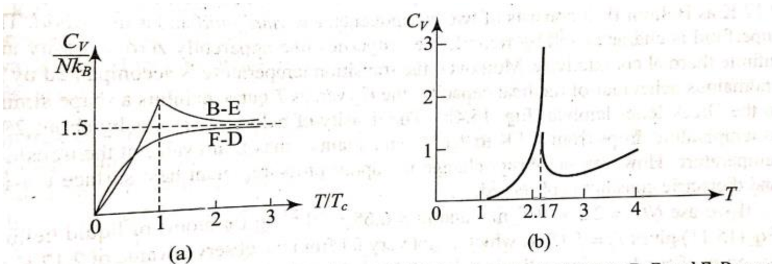

Fig. 15.4 Plot of (a) C_V/Nk_B as a function of T/T_c for strongly degenerate B–E and F–D gases and (b) C_V as a function of T for a B-E gas around the transition temperature.

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References:

1. *Thermal Physics by S.C. Garg, R.M. Bansal and C. K. Ghosh.*
2. *Statistical Physics, Berkley series volume 5.*
3. *Fundaments of Statitical Mechanics and Thermal Physics, F. Rief.*