Thermodynamic behaviour of an ideal Bose gas

Equation of state

Consider a gas of non-interacting bosons in volume V at temperature T and chemical potential μ. The system is allowed to interchange particles and energy with the surroundings. The appropriate ensemble to treat this is many - body system is the grand canonical ensemble.

Non - relativistic Bosons

Our Bosons are non - relativistic particles with spin S, whose one particle energies $\epsilon(k)$.

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

$$\epsilon_0 = \epsilon(0) = 0$$

Include only the kinetic energy term.

Negative chemical potential

Chemical potential obeys $-\infty < \mu < \mu_0$

A chemical potential larger than the lowest energy state would lead to nonphysical level occupation.

$$n(\epsilon_r) = \langle \widehat{n_r} \rangle = \frac{1}{e^{\beta(\epsilon_r - \mu)}}$$

Approaching the thermodynamic limit

We consider a situation when the gas is in a box with volume $V = L_x L_y L_z$ and subject to periodic boundary conditions. In the thermodynamic limit ($N \to \infty$, $V \to \infty$, with $n = N/V$), the sums over the wavevector $\vec{k}$ can be replaced by integrals as in the case of the Fermi gas.

However, here we have to be careful when μ happens to approach the value 0. in order to see what kind of trouble we then might into, let us calculate ground state occupation.

Occupation of the lowest energy state

We consider the expectation value of the ground state for μ approaching zero from below, viz when $-\beta\mu \ll 1$

$$n\,(\epsilon_0)= \frac{1}{e^{-\beta\mu}-1} = \frac{1}{(1-\beta\mu+\ldots)} \approx -\frac{1}{\beta\mu} \qquad \epsilon_0 = 0$$

Which means $n(\epsilon_0) = \langle \widehat{n_{r=0}} \rangle$ diverges. The lowest energy state may hence by occupied macroscopically . this is the case when

$$\frac{1}{\beta|\mu|} \sim N \qquad |\mu| \sim \frac{k_B T}{N} \qquad 1-z \sim \frac{1}{N}$$

Density of states

The density of states D(E), which has the same expression as Fermionic systems

$$D(E) \sim \sqrt{E} \qquad \lim_{E\to 0} D(E) = 0$$

Vanishes E→0. this is where we are going to encounter a problem; if we replace

$$\frac{1}{V}\sum_i \to \int dE\, D(E)$$

We will get the ground state has zero weight even though, as we have just shown that it can be macroscopically occupied. Fermionic systems do not encounter this problem due to the Pauli principle, which imposes that $\langle \widehat{n_r} \rangle \in [0,1]$

Special treatment for ground state

The problem with the potentially macroscopic occupation of the ground state can be solved using

$$\beta\Omega\,(T, V, z) = \sum_r ln\,[1 - e^{-\beta(\epsilon_r-\mu)}]$$

$$= (2s+1)\frac{V}{(2\pi)^3}\, 4\pi \int_0^\infty dk\, k^2 \ln\,(1 - z e^{\beta\epsilon(k)})$$

$$+ (2s+1)\ln\,(1-z)$$

Irrelevence of condensate

The ground state contribution to the grand canonical potential Ω formally irrelevant in the thermodynamic limit as a consequence of the scaling of the chemical potential:

$$\lim_{V\to 0} ln\frac{1}{Z-V} \approx \lim_{V\to 0} \frac{-ln(N)}{V} \to 0$$

We note, however, that the size of the*condensate*, that is the number of particles occupying the ground state, determines how many particles occupy energiers$E > E_0$, viz thedensity of the *normalfluid*

ENTRI

Dimensionless variables

With the dimensionless variable x , and the thermal de Brogile wavelength λ,

$$x = \hbar k \sqrt{\frac{\beta}{2m}} \quad , \lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

Then $$\beta\Omega\,(T, V, z) = \frac{2s+1}{\lambda^3} \frac{4V}{\pi} \int_0^\infty dx\, x^2 ln\,(1 - ze^{-x^2})$$

all in parallel to the transformations performed for the Fermi gas.

Taylor expansion.

We recall that the Taylor series expansion

$$\ln 1\text{-}y = -\sum_{n=1}^{\infty} \frac{y^n}{n}$$

Expressing as integral

$$\int_0^\infty dx\, x^2 ln\,(1 - ze^{-x^2}) = -\frac{\sqrt{\pi}}{4} \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}$$

In terms of

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty dx\, x^2 ln\,(1 - ze^{-x^2}) = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}$$

Note that $g_{5/2}(z)$ and $f_{5/2}(z)$ differ by a sign (-1) in the summand.

We can also define $g_{3/2}(z)$ as

$$g_{3/2}(z) = z \frac{d}{dz}\, g_{5/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}}$$

Bosonic grand canonical potential

The grand canonical potential takes the form

$$\beta\Omega\,(T, V, z) = \frac{2s+1}{\lambda^3}\, V\, g_{5/2}(z)$$

Except for the extra term on the right-hand side, and for an exchange$g_{5/2} \leftrightarrow f_{5/2}$ it hasthe same form as the expression for the Fermi gas.

ENTRI

Pressure

from Ω = - PV we get

$$\beta P = \frac{2s+1}{\lambda^3} g_{5/2}(z)$$

Particle density

For the particle density N/V

$$\frac{\langle N \rangle}{V} = \frac{1}{\beta V} [\frac{\partial}{\partial \mu} \ln Z] = \frac{z}{V} [\frac{\partial}{\partial z} \ln Z] = \frac{-\beta z}{V} \left[\frac{\partial}{\partial z} \Omega \right]$$

In this case the condensation term becomes

$$n = \frac{2s+1}{\lambda^3} g_{5/2}(z) + \frac{2s+1}{V} \frac{z}{1-z}$$

Ground state occupation

The term

$$n_0 = \frac{2s+1}{V} \frac{z}{1-z}$$

Where the n describes the contribution of the ground state to particle density n. when n_0 becomes macroscopically large on speaks of Bose - Einstein condensation.

Caloric equation of state

$$U = \frac{3}{2} PV$$

Which is identical to the one obtained for ideal Fermi gas.

Classical limit

The classical limit corresponds to low particle densities and high temperatures. The fugacity is small.

$$Z = e^{\beta \mu} \ll 1$$

With the Bose - Einstein distribution.

$$\langle \hat{n}_r \rangle = \frac{1}{z^{-1}e^{\beta r}-1} = \frac{ze^{-\beta\epsilon_r}}{1-ze^{-\beta\epsilon_r}} \approx ze^{-\beta\epsilon_r} \ll 1$$

Reducing to the Maxwell - Boltzmann distribution , just as for a Fermionic system. The differences between Bose-Fermi - and Boltzmann statistics are in next order of the order 1/Z and hence small.

Classical equation of state

The expression for the pressure reduces with $g_{5/2} \rightarrow Z^0$ to the equation of states for classical particles

$$\beta P = \frac{2s+1}{\lambda^3}\frac{n\lambda^3}{2s+1}, \qquad VP= \langle \hat{N} \rangle k_B T \quad n = \langle \hat{N} \rangle / V$$

First order correction

$$\beta P = \frac{2s+1}{\lambda^3} g_{5/2} \approx \frac{2s+1}{\lambda^3} Z^1$$

Quantum correction

$$PV = \langle \hat{N} \rangle k_B T \left[1 - \frac{n\lambda^3}{4\sqrt{2}\ (2s+1)}\right]$$

The last term in the expression are the quantum corrections.

- Equation of states for real gas, like van der waals equation, posses similar additive corrections with respect to the ideal case, which are however due to the interaction between the particles. The additive terms in the above equation originate on the other side from the indistinguishability principle and not from the interaction among the particles.
- The correction term for the ideal Fermi gas quasi - classical equation of state., is positive, contributing as a repulsion among the particles. For the Bose gas , the additive term is negative and therefore contribution as an attraction among the particles.

Bose Einstein condensation

We consider now limit of high particle densities and low temperatures where one finds important qualitative differences between Bosons, Fermions, and classical particles.

Particle density

Rewrite the particle density as

$$n = \int_0^\infty \frac{D(E)\, d\epsilon}{e^{\beta(\epsilon-\mu)}-1} + \frac{2s+1}{V} \frac{z}{1-z}$$

Where the density of states as

$$D(E) = A\sqrt{\epsilon}\ , \qquad A = \frac{2s+1}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$$

Dimensionless variables

The regular contribution to particle density can be evaluated for $\mu = 0$

$$\lim_{\mu\to 0} \int_0^\infty \frac{A\sqrt{E}\, d\epsilon}{e^{\beta(\epsilon-\mu)}-1} = \frac{A}{\beta^{3/2}} \int_0^\infty \frac{\sqrt{x}\, dx}{e^x-1} = \frac{A}{\beta^{3/2}}\ .\ 2.61$$

When we have used the dimensionless variable $x = \beta\epsilon$, the original expression for n becomes.

$$n = 2.61\ A(k_B T)^{3/2} + \frac{2s+1}{V} \frac{1}{e^{\beta\mu}-1}\ ,$$

This is a mixed representation where we have taken the limits $\mu \to 0$ for the regular contribution, but not for the occupation of the ground state.

Bose Einstein condensation

It is evident from the above equation there is a critical temperature T_c

$$n = 2.61\ A(k_B T)^{3/2}$$

$$n = 2.61 \frac{2}{\sqrt{\pi}} \frac{2s+1}{\lambda_c{}^3} \quad \text{where } \lambda_c{}^3 = \sqrt{\frac{h^2}{2\pi m k_B T_c}}$$

For which the regular contribution would fall below the desired particle density n. we have used that $(4\pi)^{3/2}/4\pi^2 = 2/\sqrt{\pi}$.

- T_c Is the Bose Einstein transition temperature.

- A non vanishing negative chemical potential $\mu < 0$ would lead to an even small regular term. There is no way that the regular term could account for all the particle T$< T_c$
- The transition takes place when $n\lambda^3/(2s+1) = 261.2/\sqrt{\pi}$ viz when thermal wavelength λ_c is of the order of the inter-particle distance.

Scaling of chemical potential

For $|\mu|$ we can rewrite the equation of "n"

$$n - n_c(T) \sim \frac{2s+1}{V}\frac{k_B T}{-\mu}$$

$$-\mu \sim \frac{2s+1}{V}\frac{k_B T}{n - n_c(T)}$$

Where $n_c(T)$ = 2.61 (2s+1)/λ^3. the chemical potential scales therefore like 1/V, viz it strictly vanishes only in the thermodynamic limit V→ ∞

First excited state

The energy level are quantized for a particle in a box.

$$\epsilon(k) = \frac{k_x{}^2 + k_y{}^2 + k_z{}^2}{2m}, \; k_\alpha = \frac{2\pi}{L_\alpha} n_\alpha \qquad \alpha = x, y, z$$

The volume $V = L_x L_y L_z$ the product of linear dimensions.

Diverging occupation of the first excited state

The energy ϵ_1 of one of the first excited state, corresponding to $(n_x, n_y, n_z) = (1,0,0)$ then scales

$$\epsilon_1 \sim \frac{1}{L_z{}^2} \sim V^{-2/3} \qquad \epsilon_1 \gg |\mu| \sim V^{-1}$$

The occupation n_1 of first excited state

$$n_1 = \frac{1}{e^{\beta(\epsilon_1 - \mu)} - 1} \approx \frac{1}{e^{\beta\epsilon_1} - 1} \approx \frac{1}{1 + \beta\epsilon_1 - 1} \sim V^{2/3}$$

Therefore diverges in the thermodynamic limit V→ ∞. the ground state occupation $n_0 \sim V$ diverges in contract to a macroscopic value. The Bose - Einstein condensation is characterized by divergences in occupation numbers. The ground state is however the only state with a macroscopic occupation number.