Lecture 17

13.03.2018

Ideal Bose gas

Bose Einstein Condensation

Bose-Einstein statistics

Generic system of $N = \sum_j n_j$ free bosons with occupation number $n_j = 0,1,2\cdots$ corresponding to energy state ϵ_j

A microstate (E_s, N_s) is described by a specific distribution of bosons over the energy states

$$E_s = \sum_j \epsilon_j n_j \,, \qquad N_s = \sum_j n_j$$

Grand-canonical partition function: *unconditioned* weighted sum over all microstates, i.e. over all particle distributions $\{n_j\}$ corresponding to energy levels $\{\epsilon_j\}$

$$\Xi(T,V,\mu) = \sum_{\{n_j\}} e^{-\beta \sum_j (\epsilon_j - \mu) n_j} = \prod_j \sum_{n_j=0}^{\infty} e^{-\beta(\epsilon_j-\mu)n_j} = \prod_j \frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}}$$

Landau free energy:

$$\Omega(\mathrm{T},\mathrm{V},\mu) = -kT \ln \Xi(T,V,\mu) = kT \sum_j \ln\left[1 - e^{-\beta(\epsilon_j-\mu)}\right] = kT \int d\epsilon D_\epsilon(\epsilon) \ln\left[1 - e^{-\beta(\epsilon-\mu)}\right]$$

Density of states $\quad D_\epsilon(\epsilon)$- number of quantum states per energy interval

Bose-Einstein gas: Thermodynamic properties

Average number of particles:

$$\langle N \rangle = \sum_j \frac{1}{e^{\beta(\epsilon_j-\mu)}-1} = \int d\epsilon D_\epsilon(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

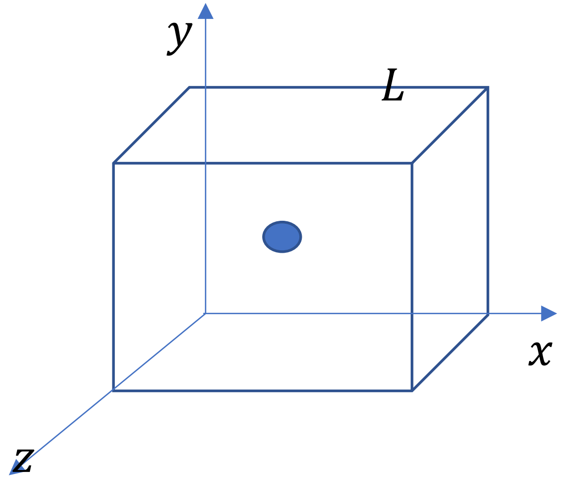
Average energy:

$$U = \sum_j \frac{\epsilon_j}{e^{\beta(\epsilon_j-\mu)}-1} = \int d\epsilon D_\epsilon(\epsilon)\frac{\epsilon}{e^{\beta(\epsilon-\mu)}-1}$$

Pressure: $\Omega = U - TS - \mu N = -PV$

$$PV = -kT\sum_j \log\left(1-e^{-\beta(\epsilon_j-\mu)}\right) = -kT\int d\epsilon D_\epsilon(\epsilon)\ln\left[1-e^{-\beta(\epsilon-\mu)}\right]$$

Ideal Bose gas: Density of states in 3D

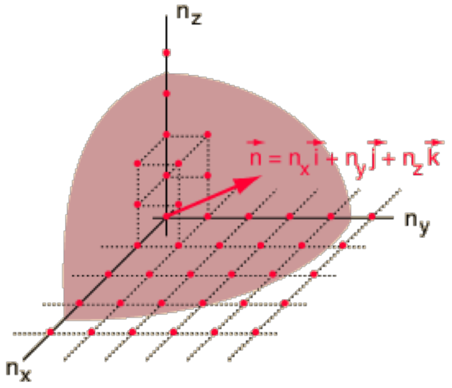


Ideal gas of Bose atoms (interactions between atoms are negligible)

- Energy levels for a particle in a box with periodic boundary conditions:

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |\vec{n}|^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2, \qquad \vec{n} = (n_x, n_y, n_z), \quad n_{x,y,z} \text{ integers}$$

- Quantum state of the particle is described by its wavefunction $\psi_1 = e^{\frac{2\pi i}{L}\vec{n}\cdot\vec{r}}$, which is determined by $\vec{n}$



Number of available states between modes with n and $n + dn$ *in 3D*

$$D(n)dn = 4\pi n^2 dn$$

Density of states corresponding to energy ϵ:

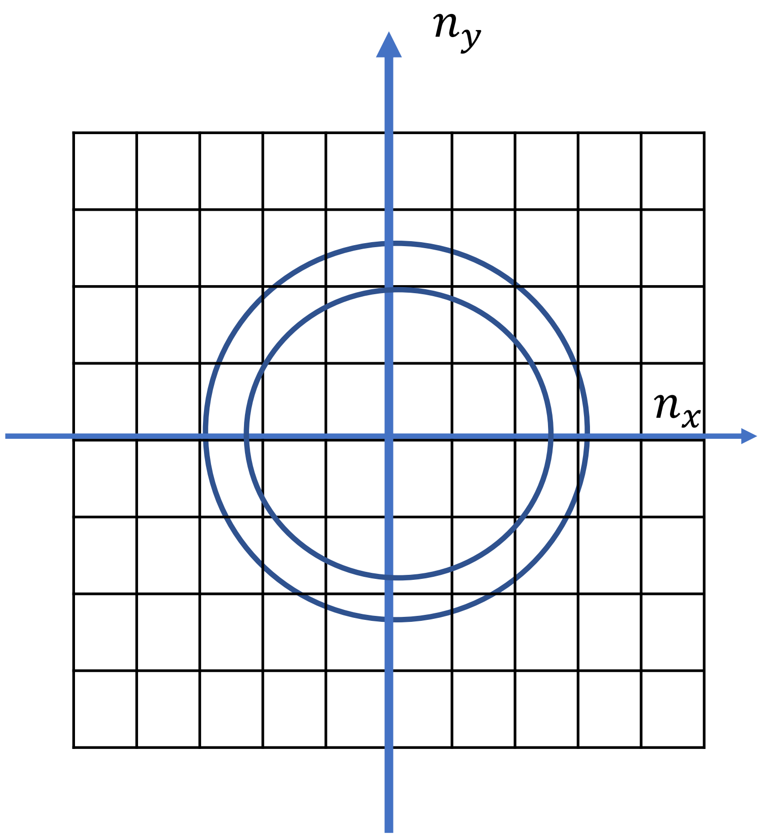
$$D_\epsilon(\epsilon) = D(n)\frac{dn}{d\epsilon} \rightarrow D_\epsilon(\epsilon) = \frac{V}{\sqrt{2}\pi^2}\frac{m^{3/2}}{\hbar^3}\epsilon^{\frac{1}{2}}$$

Ideal Bose gases: Density of states in 2D

- Energy levels for particles on a flat domain with area $A = L^2$:

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2,$$

The quantum state is given by $\psi_1 = e^{\frac{2\pi i}{L}\vec{n}\cdot\vec{r}}$, with $\vec{n} = (n_x, n_y)$



Number of quantum states between modes with n and $n + dn$:

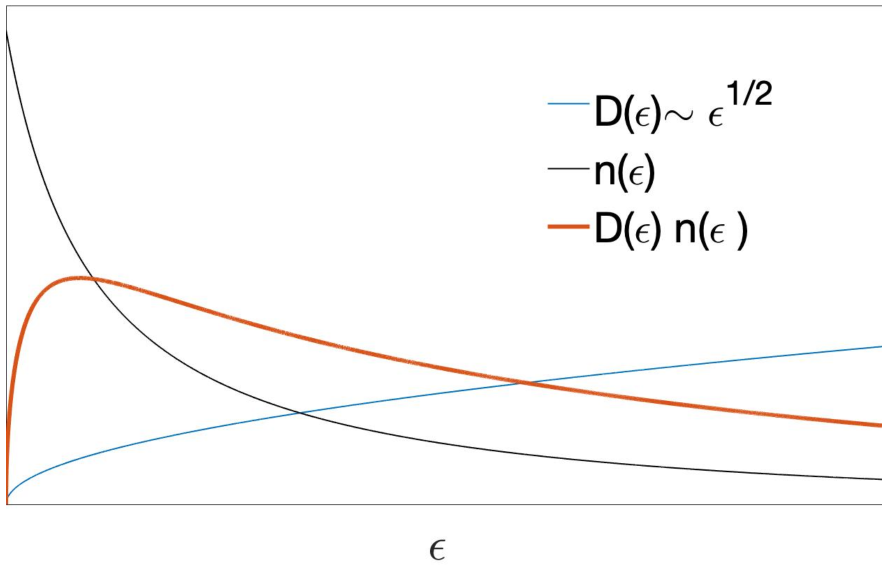
$$D(n)dn = 2\pi n dn$$

Density of states corresponding to energy ϵ, is then

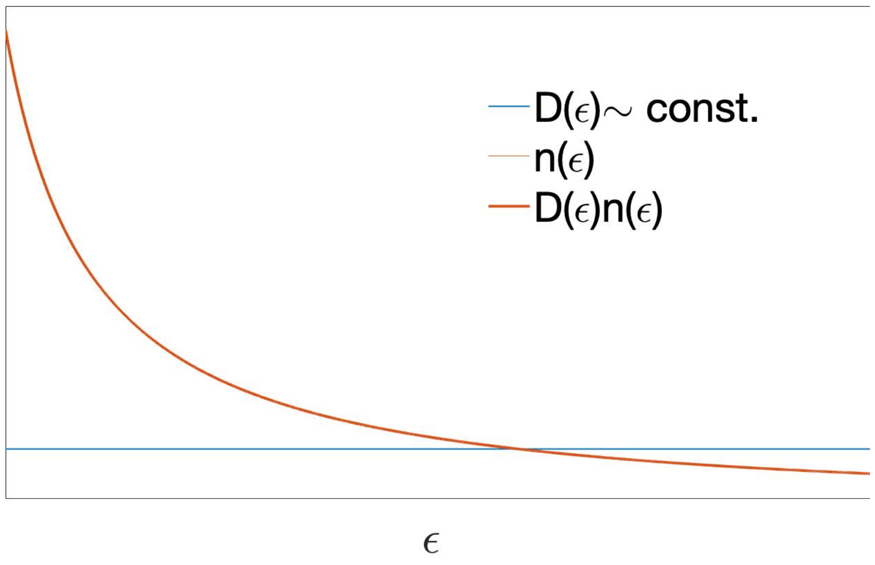
$$D_\epsilon^{(2D)}(\epsilon) = D(n)\frac{dn}{d\epsilon} \rightarrow D_\epsilon^{(2D)}(\epsilon) = \frac{Am}{2\,\pi\hbar^2}$$

In 2D, the density of states is independent of energy

3D



2D



Notice that $D_\epsilon(\epsilon)n(\epsilon) = \frac{D_\epsilon(\epsilon)}{e^{\beta(\epsilon-\mu)}-1}$ approaches zero for small ϵ in 3D. This is not the case in 2D and 1D.

Prediction for the 3D ideal Bose gas:
Bose Einstein Condensation of particles in the ground state at sufficiently low temperatures

Ideal Bose gas: average gas density

Let us have a look at the average number of particles in 3D:

$$\langle N\rangle = \int_0^\infty d\epsilon \frac{D(\epsilon)}{e^{\beta(\epsilon-\mu)}-1}, \qquad \mu \leq 0,$$

Bose gas density: $\rho_{ex}(\mu, T) = \frac{\langle N\rangle}{V} = \frac{1}{\sqrt{2}\pi^2}\frac{m^{3/2}}{\hbar^3}\int_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon-\mu)}-1}$

$$(\lambda = e^{\beta\mu}, \qquad x = \beta\epsilon)$$

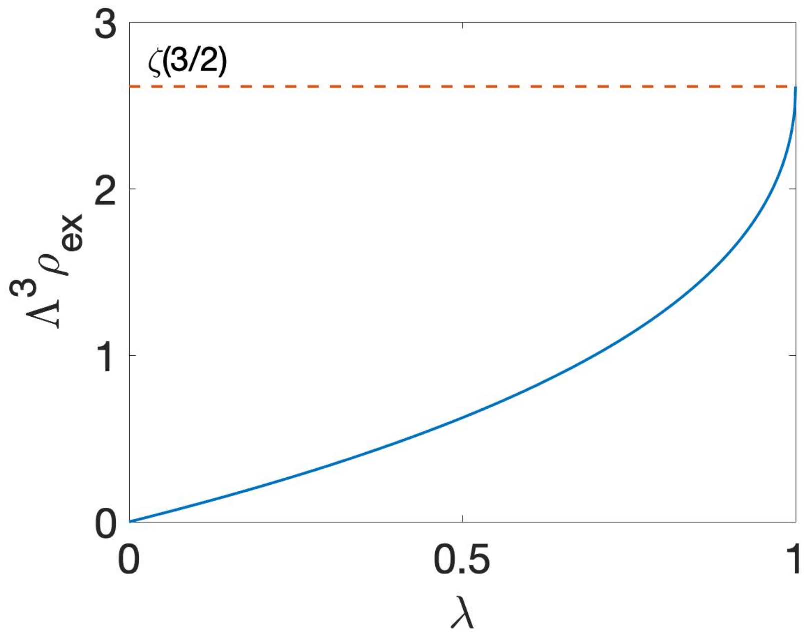
$$F(\lambda) = \frac{2}{\sqrt{\pi}}\int_0^\infty dx \frac{x^{\frac{1}{2}}}{\lambda^{-1}e^x - 1}$$

$$\rho_{ex}(\lambda, T) = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}F(\lambda)$$

$\Lambda(\mathrm{T}) = \frac{h}{\sqrt{2\pi kT}}$

$$\rho_{ex}(\lambda, T) = \Lambda^{-3}(T)F(\lambda)$$

approaches its maximum value as $\lambda \to 1$ ($\mu \nearrow 0$)



Critical average gas density $\rho_C(T)$

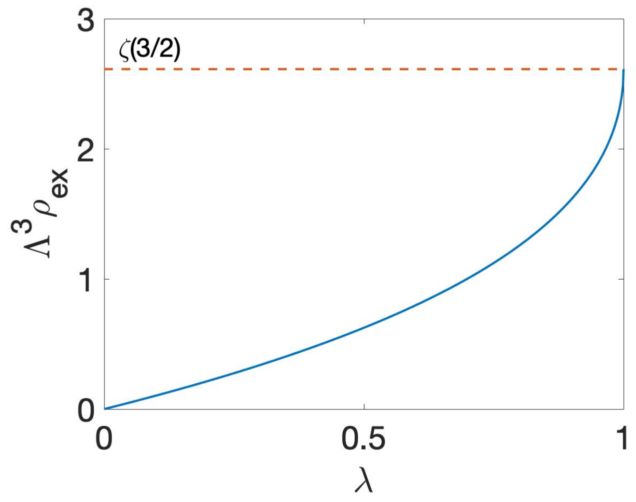
$$\rho_{ex}(\lambda, T) = \Lambda^{-3}(T)F(\lambda), \qquad (1)$$

$\rho_{ex}(\lambda, T)$ approaches its maximum value as $\lambda \to 1$ ($\mu \nearrow 0$)

For fixed T, the density ρ_{ex} increases by adding particles into the system. As the density ρ_{ex} increases, the chemical potential μ also increases according to Eq. (1). But, μ can increase up to its maximum value $\mu = 0$ corresponding to a maximal (critical) density

$$\rho_C(T) = \Lambda^{-3}(T)F(1) = \Lambda^{-3}(T)\frac{2}{\sqrt{\pi}}\int_0^\infty dx\, \frac{x^{\frac{1}{2}}}{e^x - 1}$$

$$\zeta\left(\frac{3}{2}\right) = \frac{1}{\Gamma\left(\frac{3}{2}\right)}\int_0^\infty dx\, \frac{x^{\frac{3}{2}-1}}{e^x - 1} = \sum_{n=1}^\infty \frac{1}{n^{3/2}}$$ *Riemann zeta function*



$$\rho_C(T) = \Lambda^{-3}(T)\zeta\left(\frac{3}{2}\right)$$

Average density in the ground state

$$\rho_{ex}(\lambda, T) = \Lambda^{-3}(T)F(\lambda),$$

$\rho_{ex}(\lambda, T)$ saturates at $\rho_C(T) = \Lambda^{-3}(T)\zeta\left(\frac{3}{2}\right)$ when $\lambda \to 1$ $(\mu \nearrow 0)$

Q: What happens to all the particles added to this system beyond $\rho_C(T)$ density?

A: Particles populate the ground state. This is not accounted for in the integral because of the density of states $D(\epsilon) \sim \sqrt{\epsilon} \to_{\epsilon \to 0} 0$

Corrected particle density:

The total number of particles is composed of a mixture of particles in the ground state with density ρ_0 and particles in the excited states with an excess density ρ_{ex}

$$\rho(\mu, T) = \frac{1}{V}\sum_j \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1} = \frac{1}{V}\frac{1}{\lambda^{-1} - 1} + \rho_{ex}(T, \mu)$$

Bose-Einstein condensation at T_c

At a given temperature T, density ρ and chemical potential μ are related by the following equation

$$\rho(T,\mu) = \frac{1}{V}\frac{1}{\lambda^{-1}-1} + \rho_{ex}(T,\mu) = \rho_0(T,\mu) + \rho_{ex}(T,\mu)$$

However, at and below the critical temperature T_c, the density ceases to be a function of μ, since $\mu = 0$

At the critical point, the total density ρ is determined by the maximum excess density

$$\boldsymbol{\rho(T_c) = \rho_{ex}^{max}(T_c, \mu = 0) = \Lambda^{-3}(T_c)\zeta\left(\frac{3}{2}\right)}$$

(Notice: the ground state density at the critical point is actually zero)

***Below T_c*:**

A macroscopic fraction of particles condense into the ground state with the zero momentum

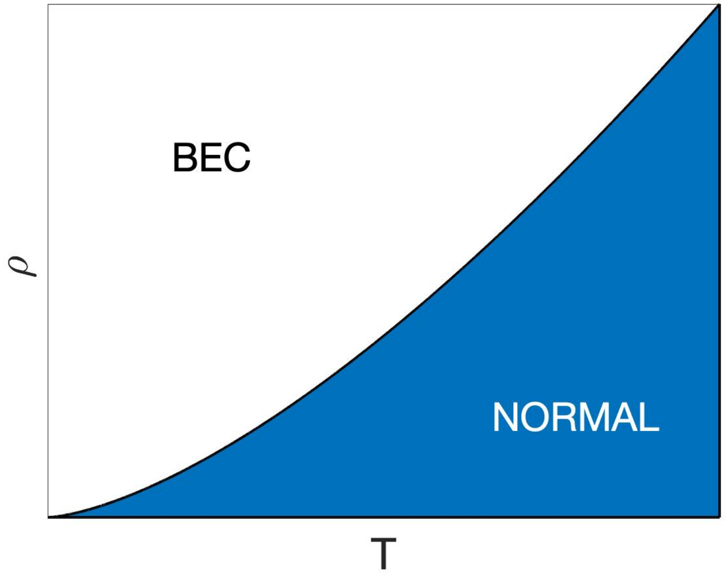
- ***Chemical potential $\mu = 0$ remains zero for all temperatures below T_c***
- ***Excess density depends only on temperature and actually decreases with decreasing temper***
- ***Ground state density becomes non-zero and increases with decreasing temperature***

Condensation in the momentum space means that particles becomes delocalized in space

Critical temperature for Bose Einstein condensation:

Determined by the density of the bose gas

$$\boldsymbol{T_c(\rho) = \frac{h^2}{2\pi m k}\left(\frac{\rho}{\zeta\left(\frac{3}{2}\right)}\right)^{\frac{2}{3}}}$$



Excess density ρ_{ex}

$$\rho_{ex}(T,\lambda) = \frac{1}{\Lambda^3(T)}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\lambda\frac{x^{1/2}e^{-x}}{1-\lambda e^{-x}}$$

$$\int_0^\infty dx\,\lambda\frac{x^{\frac{1}{2}}e^{-x}}{1-\lambda e^{-x}} =_{(\lambda<1)} \lambda\int_0^\infty dx\,x^{\frac{1}{2}}e^{-x}(1+\lambda e^{-x}+\lambda^2 e^{-2x}+\cdots) = \sum_{n=1}^{\infty}\lambda^n\left(\int_0^\infty dx\,x^{\frac{1}{2}}e^{-nx}\right)$$

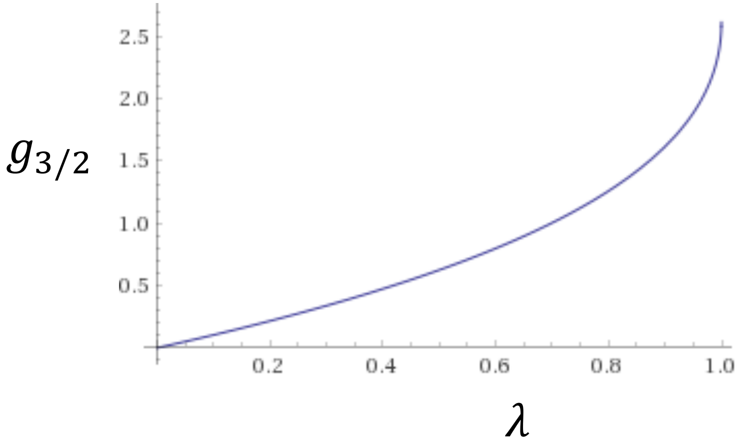
$$\int_0^\infty dx\,x^{\frac{1}{2}}e^{-nx} =_{(y=nx)} n^{-\frac{3}{2}}\int dy\,y^{\frac{3}{2}-1}e^{-y} = n^{-\frac{3}{2}}\,\Gamma\left(\frac{3}{2}\right) = n^{-\frac{3}{2}}\,\frac{\sqrt{\pi}}{2}$$

$$\rho_{ex}(T,\lambda) = \frac{1}{\Lambda^3(T)}\sum_{n=1}^{\infty}\frac{\lambda^n}{n^{3/2}}$$

$g_{3/2}(\lambda) = \sum_{n=1}^{\infty}\frac{\lambda^n}{n^{3/2}}$ polylogarithmic function convergent for $\lambda \le 1$

$g_{3/2}(1) = \sum_{n=1}^{\infty}\frac{1}{n^{3/2}} = \zeta\left(\frac{3}{2}\right) = 2.612$ Riemann zeta function

$$\rho_{ex}(T,\lambda) = \frac{1}{\Lambda^3(T)}g_{3/2}(\lambda)$$



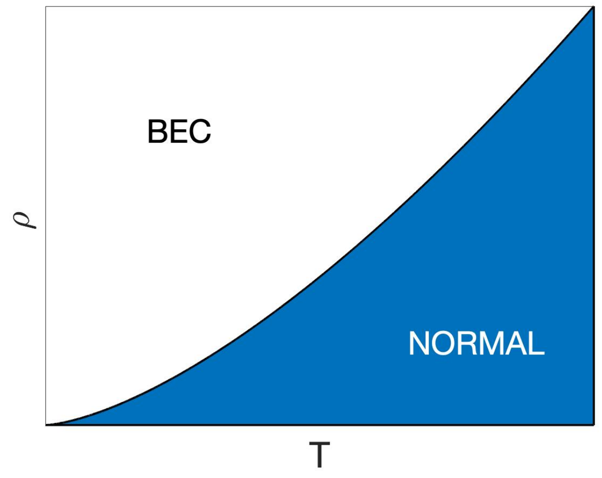
Bose-Einstein condensation (ρ, T, V)

Total density as a mixture of the density in the ground state and the density of particles in the excited states

$$\rho(T,\lambda) = \frac{1}{V}\frac{\lambda}{1-\lambda} + \frac{1}{\Lambda^3(T)} g_{3/2}(\lambda) = \rho_0(T) + \rho_{ex}(T,\lambda)$$

Critical $\boldsymbol{T_c}$: ***all the particles are in the excited state*** $\boldsymbol{\rho = \Lambda(T_c)^{-3}\zeta\left(\frac{3}{2}\right) = \Lambda^{-3}(T_c) g_{3/2}(1)}$

The temperature at which the excess particle density ρ_{ex} *reaches its maximum*



- $T \leq T_c(\lambda = 1)$

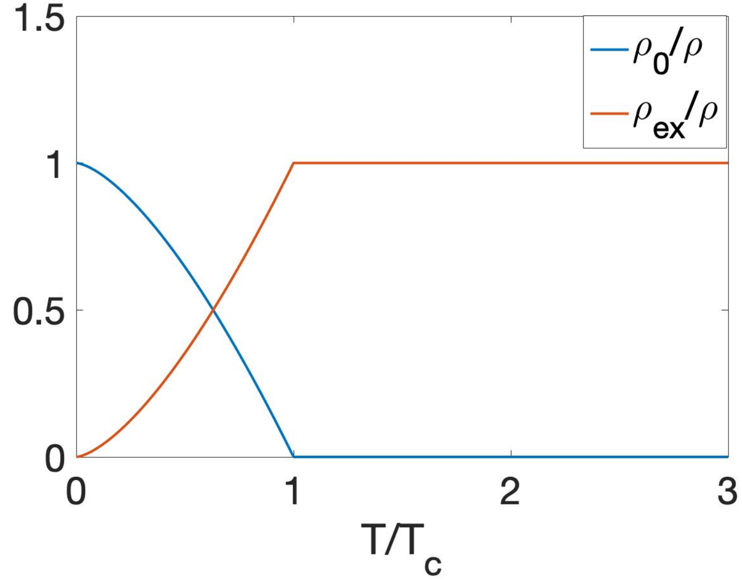
At T_c, *total density of particles is in the excited states* $\boldsymbol{\rho = \Lambda(T_c)^{-3}\zeta\left(\frac{3}{2}\right)}$

Below T_c, *only small fraction of particles are in the excited states* $\rho_{ex}(T) = \Lambda(T)^{-3}\zeta\left(\frac{3}{2}\right)$

Hence, the fraction of bosons in the ground state

$$\frac{\rho_0}{\rho} = 1 - \frac{\rho_{ex}(T)}{\rho} = 1 - \frac{\Lambda^3(T_c)}{\Lambda^3(T)} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

A macroscopic fraction of particles condense into the ground state with the zero momentum



- $T > T_c(\lambda < 1)$

$$\frac{\rho_0}{\rho} \approx 0, \qquad \rho \approx \rho_{ex} = \frac{1}{\Lambda^3(T)} g_{3/2}(\lambda)$$

Average energy

$$U(T,\mu,V) = \frac{1}{\sqrt{2}\pi^2}\frac{m^{\frac{3}{2}}}{\hbar^3}\int_0^\infty d\epsilon\,\frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)}-1}$$

$$U =_{\lambda\leq 1} \frac{3}{2}kT\,\frac{V}{\Lambda^3(T)}\,g_{5/2}(\lambda)$$

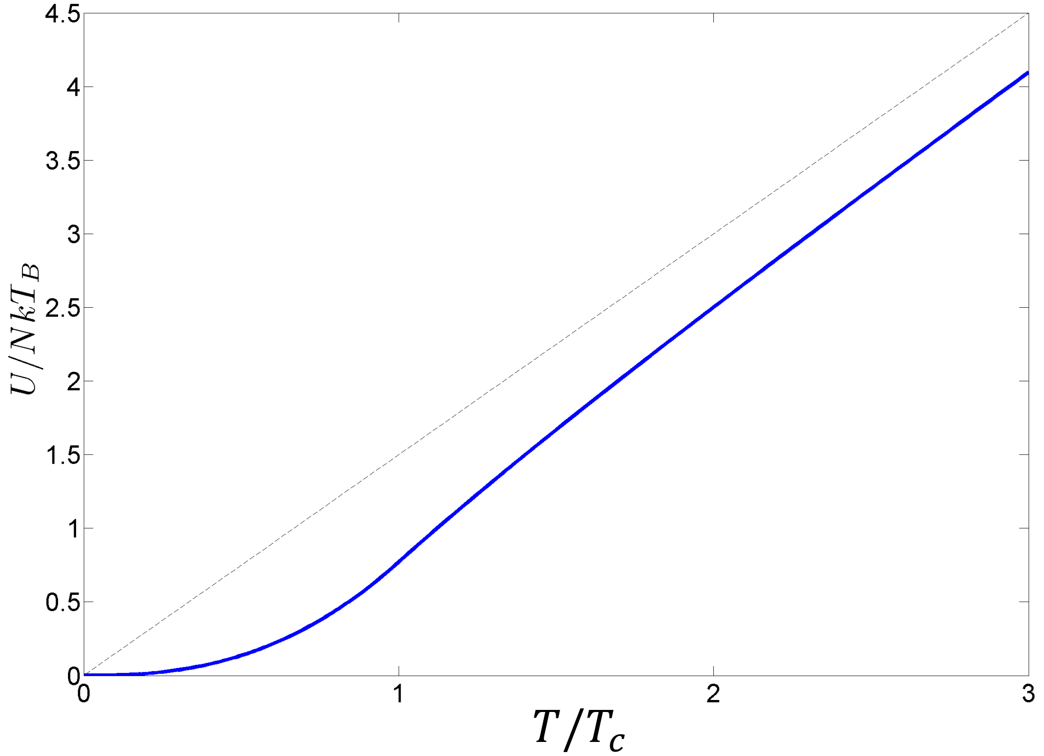
$$U = \frac{3}{2}NkT\;\rho^{-1}\Lambda^{-3}(T)g_{5/2}(\lambda)$$

- $T \leq T_c$

Using that the total density determine the critical temperature

$\rho = \Lambda^{-3}(T_c)\zeta(3/2)$,

$$U = \frac{3}{2}NkT\;\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\frac{g_{\frac{5}{2}}(\lambda)}{\zeta\left(\frac{3}{2}\right)}$$



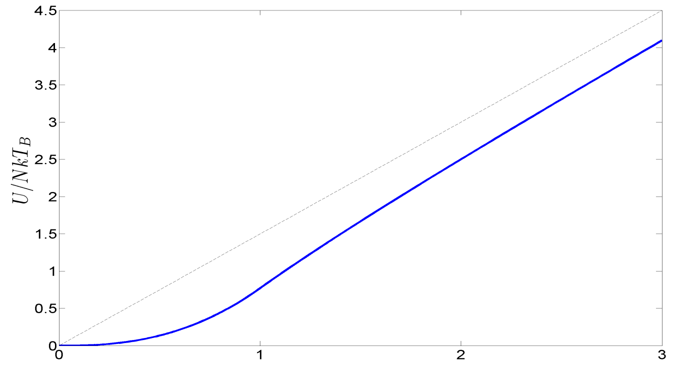
Heat capacity

Heat capacity

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V$$

$T \leq T_c(\lambda = 1)$

$$U = \frac{3}{2}NkT\left(\frac{T}{T_c}\right)^{3/2}\frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \sim T^{\frac{5}{2}} \rightarrow C_V = \frac{15}{4}Nk\left(\frac{T}{T_c}\right)^{3/2}\frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)}$$



T
$/T_c$

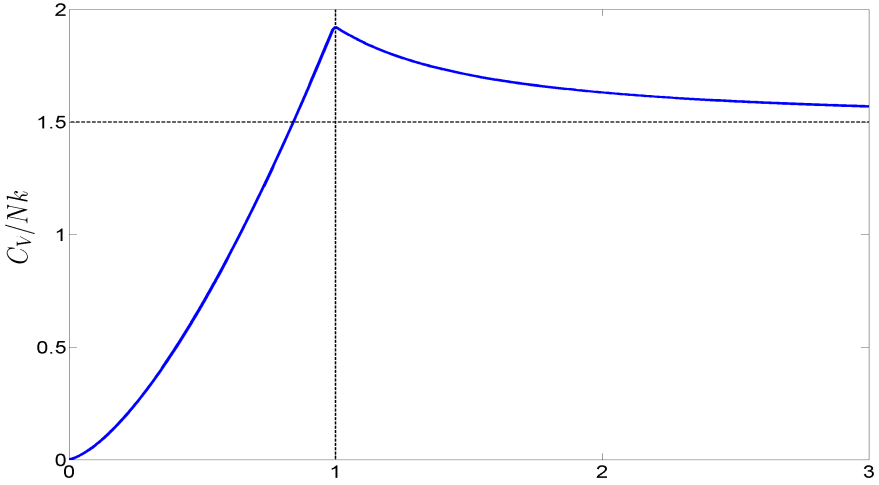
$T > T_c(\lambda < 1)$: $\rho = \Lambda^{-3}(T)g_{\frac{3}{2}}(\lambda)$

$$U = \frac{3}{2}NkT\,\rho^{-1}\Lambda^{-3}(T)g_{5/2}(\lambda) = \frac{3}{2}NkT\frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)}$$

$$C_V(T) = Nk\left[-\frac{15}{4}\frac{g_{5/2}(\lambda)}{g_{5/2}(\lambda)} + \frac{9}{2}\frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)}\right]$$

$T \gg T_c$: $g_k(\lambda) = \sum_{n=1}^{\infty}\frac{\lambda^n}{n^k} \approx \lambda$

$$U = \frac{3}{2}NkT \rightarrow C_V = \frac{3}{2}Nk$$



T/T_c

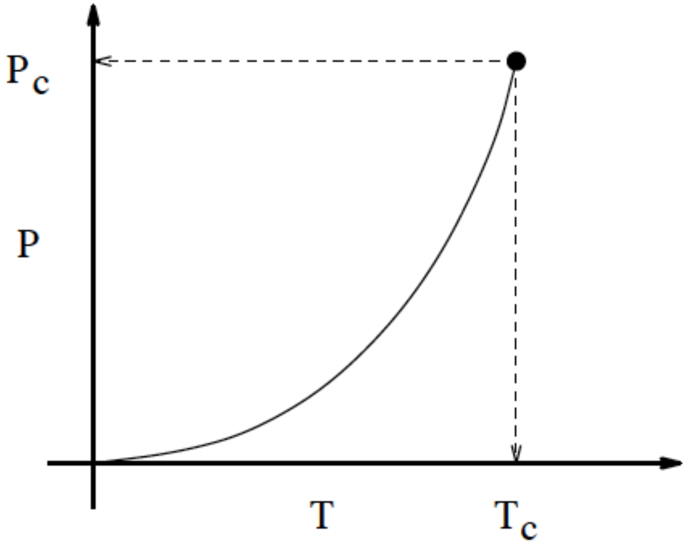
Equation of state

$$\frac{P}{kT} = -\frac{1}{V}\log(1-\lambda) - \frac{1}{\Lambda^3(T)}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\, x^{\frac{1}{2}}\log(1-\lambda e^{-x})$$

$$=_{\lambda\leq 1} -\frac{1}{V}\log(1-\lambda) + \frac{1}{\Lambda^3(T)}\sum_{n=1}^{\infty}\frac{\lambda^n}{n^{5/2}}$$

$$= \frac{1}{\Lambda^3(T)} g_{5/2}(\lambda) - \frac{1}{V}\log(1-\lambda)$$

$$\approx_{V\to\infty} \frac{1}{\Lambda^3(T)} g_{5/2}(\lambda)$$



$$T \leq T_c(\lambda = 1)$$

$$\frac{P}{kT} = \frac{1}{\Lambda^3(T)} g_{5/2}(1) \to P(T) \sim T^{\frac{5}{2}}$$

Equation of state $T > T_c$

$$\frac{P}{kT} = -\frac{1}{V}\log(1-\lambda) - \frac{1}{\Lambda^3(T)}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\, x^{\frac{1}{2}}\log(1-\lambda e^{-x})$$

$$=_{\lambda\leq 1} -\frac{1}{V}\log(1-\lambda) + \frac{1}{\Lambda^3(T)}\sum_{n=1}^{\infty}\frac{\lambda^n}{n^{5/2}}$$

$$= \frac{1}{\Lambda^3(T)} g_{5/2}(\lambda) - \frac{1}{V}\log(1-\lambda)$$

$$\approx \frac{1}{\Lambda^3(T)} g_{5/2}(\lambda)$$

$T > T_c(\lambda < 1)$

$$\frac{P}{kT} = \frac{1}{\Lambda^3(T)} g_{5/2}(\lambda), \qquad \lambda = e^{\beta\mu(\rho,T)}$$

Classical limit: Chemical potential for $T \gg T_c$

The chemical potential is determined perturbatively from the density equation above T_c.

$$\rho = \frac{1}{\Lambda^3(T)} g_{3/2}(\lambda) \to \rho = \frac{1}{\Lambda^3(T)} \sum_{n=1}^{\infty} \frac{\lambda^n}{n^{3/2}} \to \frac{1}{\Lambda^3(T_c)} \zeta\left(\frac{3}{2}\right) = \frac{1}{\Lambda^3(T)} \sum_{n=1}^{\infty} \frac{\lambda^n}{n^{3/2}} \to$$

$$\zeta\left(\frac{3}{2}\right) = \left(\frac{T}{T_c}\right)^{3/2} \sum_{n=1}^{\infty} \frac{\lambda^n}{n^{3/2}}, \qquad T > T_c, \qquad \lambda = e^{\beta\mu}$$

Inverting the equation above we can determine the fugacity $\lambda(\rho, T)$:

$$\lambda\left(1 + 2^{-3/2}\lambda + \cdots\right) = \zeta\left(\frac{3}{2}\right)\left(\frac{T}{T_c}\right)^{-3/2},$$

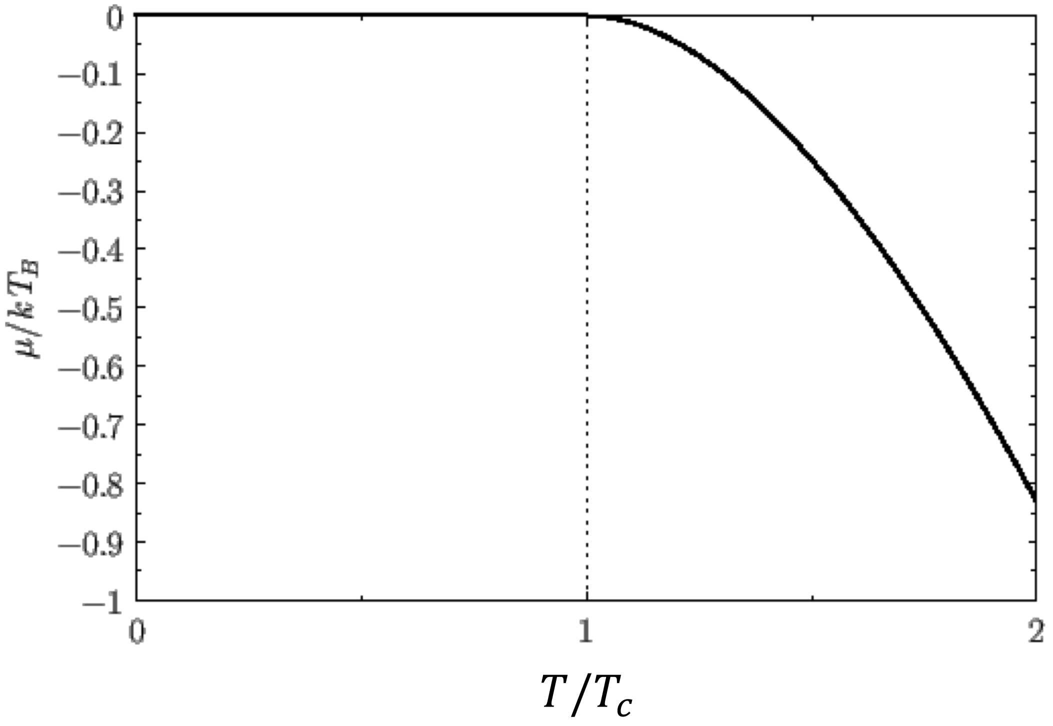
In the zeroth order, we recover the fugacity of the classical ideal gas

$$\lambda^{(0)} \approx \zeta\left(\frac{3}{2}\right)\left(\frac{T}{T_c}\right)^{-\frac{3}{2}} \to \mu = kT \ln\left[\zeta\left(\frac{3}{2}\right)\left(\frac{T}{T_c}\right)^{-\frac{3}{2}}\right]$$

Including the first correction to the classical limit

$$\lambda \approx \zeta\left(\frac{3}{2}\right)\left(\frac{T}{T_c}\right)^{-\frac{3}{2}}\left(1 - \zeta\left(\frac{3}{2}\right)\left(\frac{2T}{T_c}\right)^{-\frac{3}{2}}\right) \to$$

$$\mu = kT \ln\left[\zeta\left(\frac{3}{2}\right)\left(\frac{T}{T_c}\right)^{-\frac{3}{2}}\left(1 - \zeta\left(\frac{3}{2}\right)\left(\frac{2T}{T_c}\right)^{-\frac{3}{2}}\right)\right]$$



Equation of state for $T \gg T_c$

$$\frac{P}{kT} = \frac{1}{\Lambda^3(T)} g_{5/3}(\lambda) \approx \frac{1}{\Lambda^3(T)}\left(\lambda + 2^{-\frac{5}{2}}\lambda^2 + \cdots\right)$$

Using the expansion of the fugacity $\lambda \approx \rho\Lambda^3(T)\left(1 - 2^{-3/2}\rho\Lambda^3(T)\right)$

$$\frac{P}{kT} \approx \left(\rho - 2^{-\frac{3}{2}}\rho\Lambda^3(T) + 2^{-\frac{5}{2}}\rho\Lambda^3(T)\right)$$

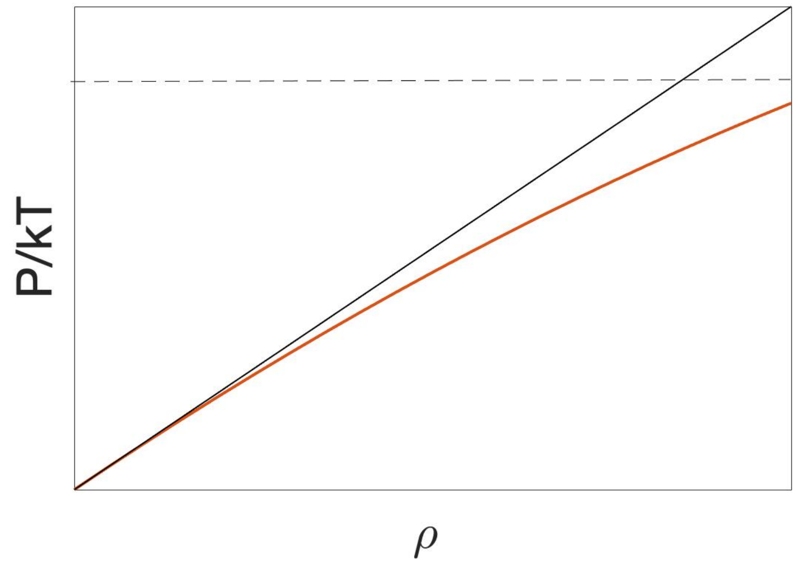
This looks like a virial expansion of the equation of state

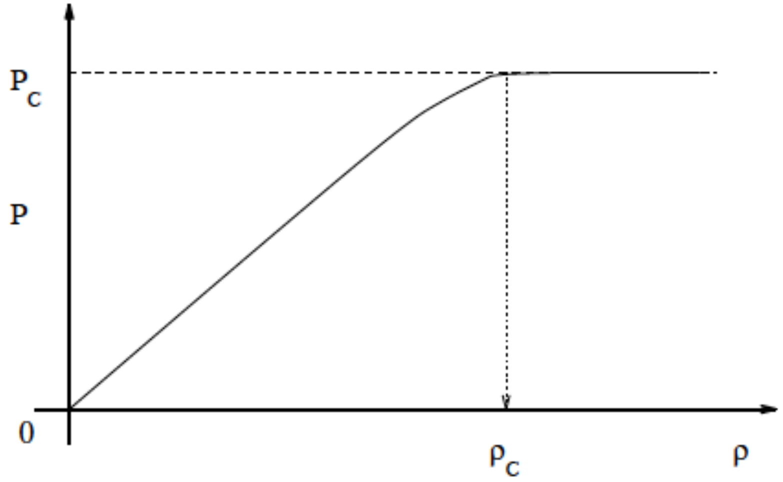
$$\frac{P}{kT} \approx \rho + B_2(T)\rho^2 + \cdots ,$$

With the second virial term

$$B_2(T) = \left(-\frac{1}{2\sqrt{2}} + \frac{1}{4\sqrt{2}}\right)\Lambda^3(T) = -\frac{1}{4\sqrt{2}}\Lambda^3(T) < 0$$

The Bose gas pressure is effectively lowered by statistical attraction forces





Bose Einstein condensation as a phase transition

- Classical ideal gas is reached is in the limit of very small density
- Pressure deviates from the classical law increasing the bose gas density
- At the critical point for the Bose-Einstein condensation (BEC), the gas density and the gas pressure have specific critical values
- Below the BEC, the gas pressure becomes independent of density.
- This is analogous to the liquid-gas phase transition, whereby the pressure becomes independent of the volume