# Ideal Bose Gas

single-particle quantum states: $i$

orthonormal: $\langle i | i' \rangle = \delta_{ii'}$

complete $\sum_i |i\rangle\langle i| = \mathbb{1}$

energy eigenstate: $H_1 |i\rangle = \varepsilon_i |i\rangle$

<u>microstates</u> for identical bosons

specify by occupation number $n_i$
for each single-particle state $i$

occupation numbers: $n_i = 0, 1, 2, \ldots$

number of bosons: $N = \sum_i n_i$

sum over single particle states

total energy: $E = \sum_i n_i \varepsilon_i$

Example: simple atoms in box

$$|i\rangle = |\vec{p}\rangle \qquad \sum_i = \frac{1}{(2\pi\hbar)^3} \int d^3r \int d^3p$$

# Grand Canonical Ensemble with temperature $T = 1/\beta$
chemical potential $\mu$

grand partition function:

$$Q = e^{-\beta\Phi} = \prod_i \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}$$

product over single-particle states

grand potential: $\Phi = U - ST - N\mu$

$$\log Q = -\beta\Phi = \sum_i \log \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}$$

sum over single-particle states

average occupation number: $\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$

average particle number: $\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$

average energy: $U = \sum_i \langle n_i \rangle \varepsilon_i = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i-\mu)}-1}$

thermodynamic relation: $d\Phi = -S\,dT - P\,dV - N\,d\mu$

entropy: $S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} = +\frac{\partial}{\partial T}\left(T\log Q\right)_{V,\mu}$

pressure: $P = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = +T\frac{\partial}{\partial V}\left(\log Q\right)_{T,\mu}$

simple bosonic atoms in volume V

single-particle energies are determined by momentum $\vec{p}$

$$\varepsilon(\vec{p}) = \frac{1}{2m}\vec{p}^{\,2}$$

sum over single-particle states

$$\sum_i = \frac{1}{(2\pi\hbar)^3}\int d^3r \int d^3p$$

$$= \frac{1}{(2\pi\hbar)^3}\, V\, 4\pi \int_0^\infty p^2\, dp$$

$$= \frac{1}{(2\pi\hbar)^3}\, V\, 2\pi (2m)^{3/2} \int_0^\infty d\varepsilon\, \varepsilon^{1/2}$$

(average) number of particles

$$N = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

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

$$= \frac{2\pi V}{(2\pi\hbar)^3}(2m)^{3/2}\frac{1}{\beta^{3/2}}\int_0^\infty dx\, \frac{x^{1/2}}{e^{-\beta\mu}e^{x} - 1} \qquad x = \beta\varepsilon$$

$$= \frac{V}{\lambda_{th}^3}\, g_{3/2}(e^{\beta\mu}) \qquad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

Bose-Einstein function: $g_\nu(z) = \dfrac{1}{\Gamma(\nu)}\displaystyle\int_0^\infty dx\, \frac{x^{\nu-1}}{\frac{1}{z}e^{x} - 1}$

Thermodynamics parametric in $z = e^{\beta\mu}$

$$N = \frac{V}{\lambda_{th}^3} g_{3/2}(z) \qquad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

$$U = \frac{3}{2} kT \frac{V}{\lambda_{th}^3} g_{5/2}(z)$$

$$P = \frac{kT}{\lambda_{th}^3} g_{5/2}(z)$$

$$S = \frac{V}{\lambda_{th}^3}\left[\frac{5}{2} g_{5/2}(z) - g_{3/2}(z) \log z\right]$$

simple relation at all temperature:

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

high-temperature limit: $\beta \to 0$, $z \to \infty$, $g_\nu(z) \to z$

$$PV = NkT$$

low-temperature limit: $\beta \to \infty$, $z \to 1$, $g_\nu(z) \to \zeta_\nu$

$$N = \zeta_{3/2} \frac{V}{\lambda_{th}^3} \qquad P = \zeta_{5/2} \frac{kT}{\lambda_{th}^3} \qquad \zeta_{3/2} = 2.612$$

$$\zeta_{5/2} = 1.341$$

$$PV = \frac{\zeta_{5/2}}{\zeta_{3/2}} NkT = 0.5135\, NkT$$

Problem at low temperature:

$$\frac{N}{V}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2} < \zeta_{5/2}$$

lower bound on temperature: $kT > \frac{2\pi\hbar^2}{m}\left(\frac{1}{\zeta_{3/2}}\frac{N}{V}\right)^{2/3}$

What happens if you decrease $T$ further?

Einstein's solution: Bose-Einstein condensation

macroscopic number $N_0$ of particle
in lowest-energy quantum state
energy $= \varepsilon_0$

must take that state into account explicitly
sum over all other single-particle states
can be expressed as integral over $\vec{r}$ and $\vec{p}$

thermodynamic variables as function of $z = e^{\beta\mu}$

$$N = \frac{1}{e^{\beta(\varepsilon_0-\mu)}-1} + \frac{V}{\lambda_{th}^3}\, g_{3/2}(z)$$

$$U = \frac{\varepsilon_0}{e^{\beta(\varepsilon_0-\mu)}-1} + \frac{3}{2}kT\frac{V}{\lambda_{th}^3}\, g_{5/2}(z)$$

$$P = \frac{1}{e^{\beta(\varepsilon_0-\mu)}-1}\left(-\frac{\partial\varepsilon_0}{\partial V}\right) + \frac{kT}{\lambda_{th}^3}\, g_{5/2}(z)$$

$$S = \frac{PV+U}{kT} - (\log z)\, N$$

lowest energy state in cubic box of length $L$

periodic boundary condition : $\varepsilon_0 = 0$

vanishing boundary condition : $\varepsilon_0 = \frac{1}{2m}\left(\frac{2\pi\hbar}{L}\right)^2(1+1+1)$

$$= 6\pi^2 \frac{\hbar^2}{m V^{2/3}}$$

$$-\frac{\partial \varepsilon_0}{\partial V} = +\frac{2}{3}\frac{\varepsilon_0}{V}$$

thermodynamic limit : $N \to \infty$, $V \to \infty$, $\frac{N}{V}$ fixed

If $N_0 = \frac{1}{e^{\beta(\varepsilon_0 - \mu)} - 1}$ has thermodynamic limit

$$\frac{\varepsilon_0}{e^{\beta(\varepsilon_0-\mu)}-1} \sim \frac{N_0}{V^{2/3}}$$

$$\frac{1}{e^{\beta(\varepsilon_0-\mu)}-1}\left(-\frac{\partial \varepsilon_0}{\partial V}\right) \sim \frac{N_0}{V^{5/3}}$$

Simplified treatment in thermodynamic limit

$T > T_c$ : ignore lowest energy state
$\mu < 0$ in $g_\nu(e^{\beta\mu})$

$T \leq T_c$ : keep lowest energy state in $N$ but not in $U, P, S$
$\mu = 0$ in $g_\nu(e^{\beta\mu})$ : $g_\nu(1) = \zeta_\nu$
treat $(T, N_0)$ as parameters instead of $(T, \mu)$

thermodynamic variables below $T_c$

$$N = N_0(T) + \zeta_{3/2} \frac{V}{\lambda_{th}^3}$$

$$U = 0 + \zeta_{5/2} \frac{3}{2} kT \frac{V}{\lambda_{th}^3}$$

$$P = 0 + \zeta_{5/2} \frac{kT}{\lambda_{th}^3}$$

$$S = 0 + \zeta_{5/2} \cdot \frac{5}{2} \frac{V}{\lambda_{th}^3}$$

critical temperature: $T_c$ $\quad N_0(T_c) = 0$

$$N = 0 + \zeta_{3/2} V \left( \frac{mkT_c}{2\pi\hbar^2} \right)^{3/2}$$

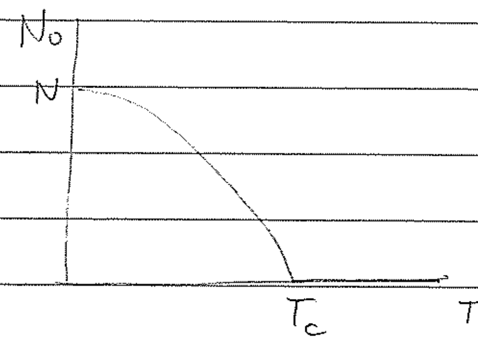
$$\Longrightarrow kT_c = \frac{2\pi\hbar^2}{m} \left( \frac{1}{\zeta_{3/2}} \frac{N}{V} \right)^{2/3}$$

eliminate $V$ in equation for $N$

$$N = N_0(T) + N \left( \frac{T}{T_c} \right)^{3/2}$$

solve for $N_0(T)$:

$$N_0(T) = N \left[ 1 - \left( \frac{T}{T_c} \right)^{3/2} \right]$$



The decrease in temperature from $T_c$ to $0$
is a phase transition

from a Bose gas with $0$ chemical potential

$$PV \simeq 0.5135\ NkT$$

$$U \simeq 0.5135 \cdot \tfrac{3}{2} NkT$$

$$S \simeq 0.5135 \cdot \tfrac{5}{2} N$$

to a condensed phase in which all the bosons
are in the same lowest energy quantum state

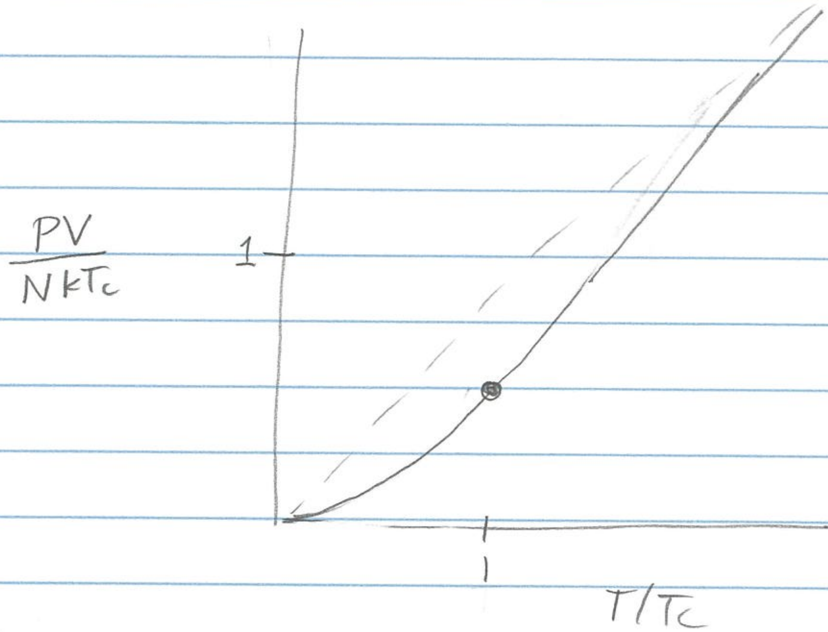
$$P=0, \quad U=0, \quad S=0$$

The region $0<T<T_c$ is a coexistence region
between the two phases

As $T$ decreases from $T_c$ to $0$,

the fraction of atoms in the condensed phase
increases from $0$ to $1$

Pressure vs. temperature




At $T=T_c$, $P, U, S$ are all continuous
and their first derivative are continuous
but they have $2^{nd}$ derivative that are discontinuous

"$2^{nd}$ order phase transition"

specific heat at constant volume