§4. GRAND CANONICAL POTENTIAL

Df. Grand canonical thermodynamic potential

$$\boxed{\Phi(T,V,\mu) = U - TS - \mu \bar{N} \qquad [\bar{N} = \langle N \rangle]} \qquad (*)$$

It is given by the grand partition function

$$\boxed{\Phi(T,V,\mu) = -k_B T \ln \Xi(T,V,\mu)}$$

a small variation

$$d\Phi = \underbrace{\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}}_{-S} dT + \underbrace{\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}}_{-p} dV + \underbrace{\left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T}}_{-\bar{N}} d\mu$$

$$\bar{N} = k_B T \frac{\partial \ln \Xi}{\partial \mu}$$

$$S = +k_B \ln \Xi + \frac{1}{T}(U - \mu \bar{N})$$

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -k_B T \frac{1}{\Xi} \sum_{N E_s} e^{-\beta(E_s - \mu N)} \underbrace{\frac{\partial E_s}{\partial V}}_{p_{micro}} = -\langle p_{micro} \rangle = -p$$

hence,

$$\boxed{d\Phi = -S\,dT - p\,dV - \bar{N}\,d\mu}$$

using $(*)$
$$d\Phi = dU - T\,dS - S\,dT - \mu\,d\bar{N} - \bar{N}\,d\mu$$

we get

$$-\cancel{S\,dT} - p\,dV - \cancel{\bar N\,d\mu} = dU - T\,dS - \cancel{S\,dT} - \mu\,d\bar N - \cancel{\bar N\,d\mu}$$

$$\Rightarrow \boxed{dU = \underbrace{T\,dS}_{\text{heat in reversible processes}} - \underbrace{p\,dV}_{\text{work (mechanical)}} + \underbrace{\mu\,d\bar N}_{\text{work (chemical)}}}$$

first thermodynamical law for open systems

SUMMARY

Ensemble	micro canonical	canonical	grand canonical
physical conditions	isolated	exchange energy	exchange energy and particles
probability of i-th state	$\frac{\Omega_i}{\Omega}$	$\frac{e^{-\beta E_i}}{Z}$	$\frac{e^{-\beta(E_i - \mu N)}}{\Xi}$
normalization partition function	$\Omega = \sum_i \Omega_i$	$Z = \sum_i e^{-\beta E_i}$	$\Xi = \sum_N \sum_{E_i} e^{-\beta(E_i - \mu N)}$
independent variables	U, V, N	T, V, N	T, V, μ
Thermodynamic potential	entropy $S = k_B \ln \Omega$	free energy $F = -k_B T \ln Z$	grand therm. potential $\Phi = -k_B T \ln \Xi$

Relations between thermodynamical potentials ?

$\boxed{\text{Legendre transform}}$

$$Y = Y(\overbrace{x_1, x_2, \ldots}^{\text{independent variables}})$$

$$a_i(x_1, x_2, x_3, \ldots) = \left(\frac{\partial Y}{\partial x_i}\right)_{\{x_j,\, j \neq i\}}$$

Change independent variable x_i and a_i

From exact differential

$$dY = a_1\, dx_1 + a_2\, dx_2 + \ldots$$

and that $dY = \underbrace{d(a_1 x_1)}_{a_1 dx_1 + x_1 da_1} - x_1\, da_1 + a_2\, dx_2 + \ldots$

we get

$$d(\underbrace{Y - a_1 x_1}) = dY_1 = -x_1\, da_1 + a_2\, dx_2 + \ldots$$

$$Y_1 = Y - a_1 x_1 = Y_1(a_1, x_2, x_3, \ldots)$$

and $\frac{\partial Y_1}{\partial a_1} = -x_1$, etc. for other i

This transformation yields different state functions, thermodynamical potentials

state function	independent variables (experiments)	differential
internal energy U	S, V, N	$dU = TdS + \frac{p}{T} dV - \frac{\mu}{T} dN$
entropy S	U, V, N	$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$
Helmholtz free energy $F = U - TS$	T, V, N	available work at T=const $dF = -SdT - pdV + \mu dN$
enthalpy $H = U + pV$	S, p, N	available work at p=const $dH = TdS + Vdp + \mu dN$
Gibbs free energy $G = U - TS + pV$	T, p, N	$dG = -SdT + Vdp + \mu dN$
Grand canonical potential $\Phi = U - TS - \mu N$	T, V, μ	$d\Phi = -SdT - pdV - Nd\mu$

number of independent variable and phase rule → see later

Example Ideal gas in grand canonical ensemble

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{s(N)} e^{-\beta \varepsilon_s} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{Z_1^N}{N!}$$

$$Z_1 = n_Q V = \left(\frac{V}{\lambda_{dB}^3}\right), \quad \lambda_{dB}^3 = \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{3/2} = \frac{1}{n_Q}$$

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} \frac{(e^{\beta\mu})^N \left(\frac{V}{\lambda_{dB}^3}\right)^N}{N!} = e^{e^{\beta\mu}\left(\frac{V}{\lambda_{dB}^3}\right)} = e^{\alpha\left(\frac{V}{\lambda_{dB}^3}\right)}$$

$\alpha = e^{\beta\mu}$ - activity

Thermodynamics:

$$\Phi = -k_B T \ln \Xi = -k_B T \alpha \frac{V}{\lambda_{dB}^3}$$

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \frac{\alpha V}{\lambda_{dB}^3} \Rightarrow \alpha = \lambda_{dB}^3 n \Rightarrow \underline{\mu = k_B T \ln(\lambda_{dB}^3 n)}$$

$$pV = -V\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -\Phi = \bar{N} k_B T$$

$$\rightarrow \mu = -k_B T \ln\left(\frac{V/\bar{N}}{\lambda_{dB}^3}\right) = -k_B T \ln\left(\frac{k_B T}{p \lambda_{dB}^3}\right)$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = k_B N\left(\frac{5}{2} + \ln\left(\frac{V/N}{\lambda_{dB}^3}\right)\right)$$

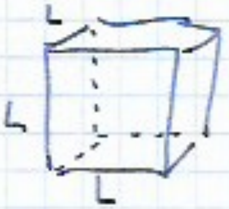
$$U = \Phi + TS + \mu\bar{N} = \bar{N} k_B T\left(-1 + \frac{5}{2}\right) = \frac{3}{2}\bar{N} k_B T$$

$\square$

V IDEAL QUANTUM GASES

§ 1. WAVE FUNCTION OF MANY PARTICLES

°) <u>one particle in a box</u>



$$\hat{H}\,\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\,\psi_{\vec{k}}(\vec{r})$$

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\Delta$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}\, e^{i\vec{k}\cdot\vec{r}} \,, \quad E_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$$

periodic boundary condition (PBC)

$$\psi_{\vec{k}}(x,y,z) = \psi_{\vec{k}}(x+L, y, z) \quad \text{etc.}$$

$$\Rightarrow \quad e^{ik_x L} = 1 = e^{2\pi i n_x} \,, \quad n_x \in \mathbb{Z}$$

$$\Rightarrow \quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

°°) <u>Two non-interacting (identical) particles</u>

$$\hat{H} = \frac{\hat{\vec{p}}_1^{\,2}}{2m} + \frac{\hat{\vec{p}}_2^{\,2}}{2m} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2$$

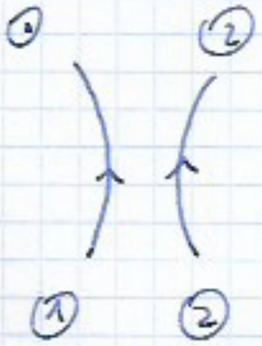
$$\psi_{\vec{k}_1\vec{k}_2}(\vec{r}_1, \vec{r}_2) = \left(\frac{1}{\sqrt{V}}\right)^2 e^{i\vec{k}_1\cdot\vec{r}_1 + i\vec{k}_2\cdot\vec{r}_2} = \psi_{\vec{k}_1}(\vec{r}_1)\,\psi_{\vec{k}_2}(\vec{r}_2)$$

$$E_{\vec{k}_1,\vec{k}_2} = \frac{\hbar^2 k_1^2}{2m} + \frac{\hbar^2 k_2^2}{2m}$$

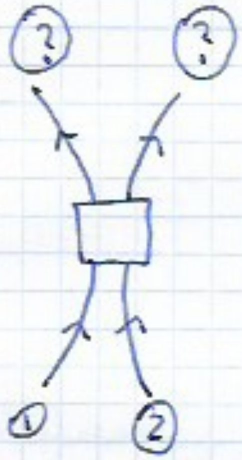
particle 1 has momentum $p_1 = \hbar k_1$

particle 2 has momentum $p_2 = \hbar k_2$

Are you sure?



Classical balls



quantum balls

$$\Delta x \, \Delta p \geq \frac{\hbar}{2}$$

Heisenberg principle

→ Identical particles in quantum mechanics are indistinguishable

Władysław Natanson (1911)

Satyendra Nath Bose (1924)

Albert Einstein (1925)

Wolfgang Pauli (1924)

Enrico Fermi (1926)

Paul Dirac (1926)

$\boxed{\text{Indistinguishability} \Rightarrow \text{exchanging two particles does not change any physics}}$

$$|\psi_{\bar{k}_1,\bar{k}_2}(\bar{r}_1,\bar{r}_2)|^2 = |\psi_{\bar{k}_1,\bar{k}_2}(\bar{r}_2,\bar{r}_1)|^2$$

probability density is invariant under a permutation of particles

$$\Rightarrow \quad \psi_{\bar{k}_1\bar{k}_2}(\bar{r}_2,\bar{r}_1) = e^{i\varphi}\,\psi_{\bar{k}_1,\bar{k}_2}(\bar{r}_1,\bar{r}_2)$$

permutation of particles leads to an arbitrary (global) phase in a wave function

Repeting twice the exchange of two particles

$$\psi(\bar{r}_1,\bar{r}_2) \leftrightarrow \psi(\bar{r}_2,\bar{r}_1) \leftrightarrow \psi(\bar{r}_1,\bar{r}_2)$$

therefore. $\quad (e^{i\varphi})^2 = 1$

or $\quad \underline{e^{i\varphi} = \pm 1}$

$$\boxed{\psi_{\bar{k}_1,\bar{k}_2}(\bar{r}_2,\bar{r}_1) = \pm\,\psi_{\bar{k}_1,\bar{k}_2}(\bar{r}_1,\bar{r}_2)}$$

A solution for two particles without interaction

$$\boxed{\psi_{\vec{k}_1\vec{k}_2}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{\vec{k}_1}(\vec{r}_1)\,\psi_{\vec{k}_2}(\vec{r}_2) \pm \psi_{\vec{k}_1}(\vec{r}_2)\,\psi_{\vec{k}_2}(\vec{r}_1)\right]}$$

Observation (Pauli)

let $\vec{k}_1 = \vec{k}_2 = \vec{k}$ $\qquad E_{\vec{k}\vec{k}} = 2\,\frac{\hbar^2 \vec{k}^2}{2m}$

$$\psi_{\vec{k}\vec{k}}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{\vec{k}}(\vec{r}_1)\,\psi_{\vec{k}}(\vec{r}_2) \pm \psi_{\vec{k}}(\vec{r}_2)\,\psi_{\vec{k}}(\vec{r}_1)\right] =$$

$$= \begin{cases} \frac{2}{\sqrt{2}}\,\psi_{\vec{k}}(\vec{r}_1)\,\psi_{\vec{k}}(\vec{r}_2) & \text{for "+"} \\ 0 & \text{for "−"} \end{cases}$$

Pauli exclusion principle

no two $\overbrace{\text{particles}}^{\text{"−"}}$ with the same quantum numbers

Conclusions

$$\boxed{\text{A many body wave function is symmetric (bosons) or antisymmetric (fermions) when two particles are exchanged.}}$$

Spin-statistic theorem

bosons: spin $S = 0, \hbar, 2\hbar, 3\hbar$ integer

fermions: spin $S = \frac{\hbar}{2}, \frac{3}{2}\hbar, \frac{5}{2}\hbar$ half-integer

Examples

bosons: photons, phonons, fluons, gravitons, Higgs bosons, ^4He isotopes

fermions: protons, neutrons (hadrons), electrons (leptons), quarks, ^3He isotopes

$$^4He = \underbrace{2p + 2n + 2e}_{6 \cdot \frac{1}{2}} \qquad ^3He = \underbrace{2p + 1n + 2e}_{5 \cdot \frac{1}{2}}$$

Pauli exclusion principle:
no two fermions in the same quantum state

§2. FERMI-DIRAC AND BOSE-EINSTEIN DISTRIBUTION FUNCTIONS

Grand partition function

$$\Xi = \sum_{N=0}^{\infty} \sum_{E_{\vec{k}}(N)} e^{-\beta\left(\sum_{\vec{k}\sigma} \varepsilon_{\vec{k}} n_{\vec{k}} - \mu N\right)}$$

since $E_{(N)} = \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}} n_{\vec{k}}$ for non-interacting particles.

$\varepsilon_{\vec{k}}$: orbital energy

$n_{\vec{k}}$: number of particles in a given orbital (indistinguishability)

$$\Xi = \sum_{N=0}^{\infty} \sum_{n_k}^{\left(\sum_{k\sigma} n_k = N\right)} e^{-\beta\left(\sum_{k\sigma} \varepsilon_k n_k - \mu \sum_{k\sigma} n_k\right)} =$$

$$= \underbrace{\sum_{N=0}^{\infty} \prod_{k\sigma}} \sum_{n_k}^{\left(\sum n_k = N\right)} e^{-\beta(\varepsilon_{\vec{k}} - \mu) n_k} =$$

$$= \prod_{k\sigma} \sum_{n_k}^{\infty} \left(e^{-\beta(\varepsilon_k - \mu)}\right)^{n_k}$$

$$\underbrace{\sigma = -s, -s+1, \dots, s-1, s}_{\rho = 2s+1 \text{ degeneracy}}$$

$$n_{\vec{k}} = \begin{cases} 0,\ 1 & \text{fermions} \\ 0, 1, 2, \dots \infty & \text{bosons} \end{cases}$$

$$\boxed{\begin{aligned} \Xi_f &= \prod_{k\sigma} \left(1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)}\right) \\ \Xi_b &= \prod_{k\sigma} \left(1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)} + \left(e^{-\beta(\varepsilon_k - \mu)}\right)^2 + \dots\right) = \prod_{k} \left(\frac{1}{1 - e^{-\beta(\varepsilon_k - \mu)}}\right) \end{aligned}}$$

converges iff

$\forall \vec{k}$ $e^{\beta(\varepsilon_{\vec{k}} - \mu)} < 1$

Taking into account g - degeneracy factor

$$\boxed{\Xi_g(T,V,\mu) = \prod_{\vec{k}} \left(1 \pm e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right)^{\pm g}}$$

(+) - fermions

(-) - bosons

Grand canonical potential

$$\boxed{\Phi_g(T,V,\mu) = -k_B T \ln \Xi_g = \mp k_B T g \sum_{\vec{k}} \ln\left(1 \pm e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right)}$$

f

b

Average number of particles

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \underset{\text{(tutorials)}}{=} g \sum_{\vec{k}} \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)} \pm 1} = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle$$

Orbital occupation

$$\langle n_{\vec{k}} \rangle = \frac{1}{\Xi} g \sum_{n_{\vec{\ell}}} e^{-\beta(\varepsilon_{\vec{\ell}}-\mu) n_\ell} \, n_\ell \overset{\text{(tutorials)}}{=}$$

$$= g \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)} \pm 1}$$

must be non-negative

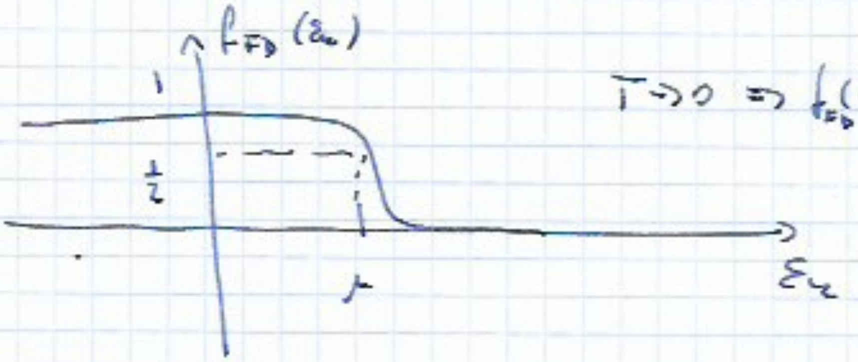
Fermi-Dirac and Bose-Einstein functions

$$\boxed{f_{\substack{FD\\BE}}(\varepsilon_{\vec{k}}) = \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)} \pm 1}}$$

(+) FD

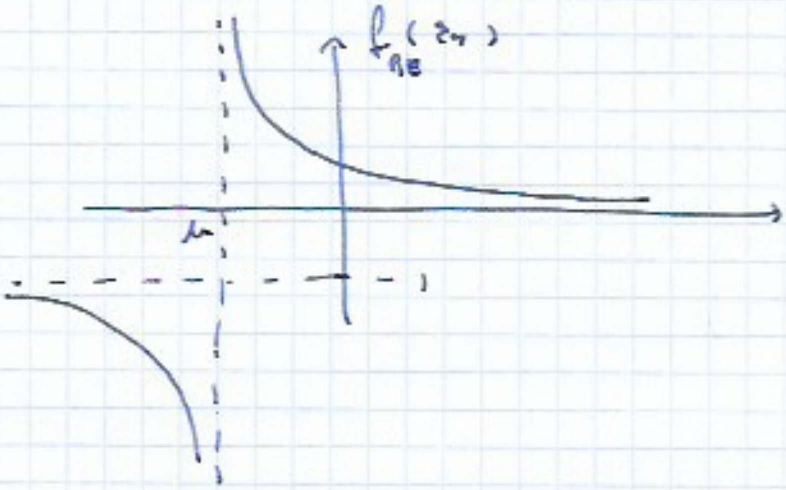
(−) BE

FD



$T \to 0 \Rightarrow f_{FD}(\varepsilon_k) = \Theta(\mu - \varepsilon_k)$

BE



only for $\varepsilon_{\vec{k}} > \mu$

$f(\varepsilon_{\vec{k}}) > 0$

geometric series converges if

$e^{\beta(\varepsilon_{\vec{k}}-\mu)} < 1$.

§3. QUANTUM CORRECTIONS TO IDEAL GAS

Classical limit $n \ll n_Q$

$$\mu = k_B T \ln\left(\frac{n}{n_Q}\right) \xrightarrow[n \ll n_Q]{} -\infty$$

and $T \to \infty$ $(\beta \to 0)$

What are quantum corrections to the ideal gas?

$$\boxed{\Phi_{f/b}(T,V,\mu) = \mp k_B T g \sum_{\vec{k}} \ln\left(1 \pm e^{-\beta(\varepsilon_{\vec{k}} - \mu)}\right)}$$

$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$, $\Delta n_i = 1$, $\Delta k_i = \left(\frac{L}{2\pi}\right)^{-1} \Delta n_i$

$$\sum_{\vec{k}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} = \sum_{n_x} \Delta n_x \sum_{n_y} \Delta n_y \sum_{n_z} \Delta n_z =$$

$$= \left(\frac{L}{2\pi}\right)^3 \sum_{k_x} \Delta k_x \sum_{k_y} \Delta k_y \sum_{k_z} \Delta k_z \xrightarrow[L\to\infty]{} \left(\frac{L}{2\pi}\right)^3 \int dk_x \int dk_y \int dk_z$$

$$e^{-\beta(\varepsilon_{\vec{k}} - \mu)} \ll 1$$

expand

$$\ln(1 \pm x) = \pm x - \frac{1}{2} x^2$$

$$\Phi_{f/b}(T,V,\mu) = \mp g k_B T \frac{V}{8\pi^3} \int d^3k \left[\pm e^{-\beta(\varepsilon_{\vec{k}} - \mu)} - \frac{1}{2} e^{-2\beta(\varepsilon_{\vec{k}} - \mu)} \right] =$$

$$= - g k_B T \frac{V}{8\pi^3} \underbrace{e^{\beta\mu}}_{\alpha} \int d^3k \, e^{-\beta \frac{\hbar^2 k^2}{2m}} \pm \frac{1}{2} g k_B T \frac{V}{8\pi^3} \underbrace{(e^{\beta\mu})^2}_{\alpha^2} \int d^3k \, e^{-\beta \frac{\hbar^2 k^2}{m}} + \dots$$

activity

$\alpha = e^{\beta\mu} \ll 1$ $\to$ a formal expansion in the activity, virial expansion

$$\boxed{\Phi_{f/b}(T,V,\mu) = -g\, k_B T\, e^{\frac{\mu}{k_B T}} \frac{V}{\lambda_{dB}^3} \pm \frac{1}{2^{5/2}}\, g\, k_B T\, e^{\frac{2\mu}{k_B T}} \frac{V}{\lambda_{dB}^3} + \dots}$$

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \rightarrow \text{eliminate } \mu = \mu(T,V,n)$$

$$\boxed{\Phi_{f/b}(T,V,\mu) = -k_B T V n \mp k_B T V \frac{n^2 \lambda_{dB}^3}{2^{7/2} g} + \dots}$$

$$\boxed{pV = -V\left(\frac{\partial \Phi_{f/b}}{\partial V}\right)_{T,\mu} = k_B T \underbrace{n V}_{N} \pm k_B T V \frac{n^2 \lambda_{dB}^3}{16 g} + \dots}$$

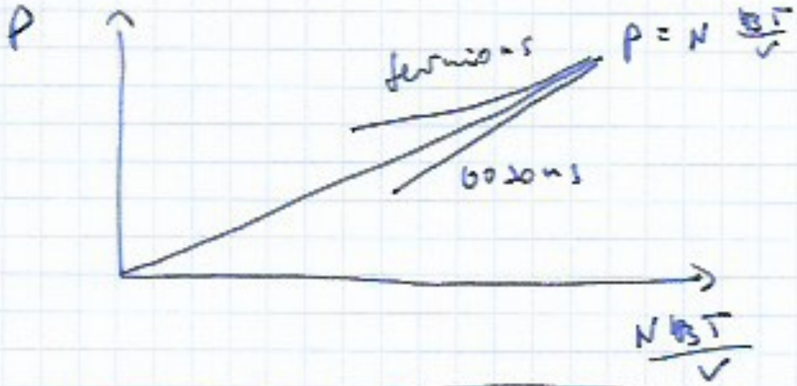
<u>Equation of state</u>

$$\boxed{pV = N k_B T \overset{f}{\underset{b}{\pm}} N k_B T \left(\frac{n \lambda_{dB}^3}{2^{5/2} g}\right)}$$

quantum virial expansion

classical — quantum correction

when $T \to \infty$, $\lambda_{dB} \to 0$ and classical gas limit



$P_{fermions} > P_{classical}$

$P_{bosons} < P_{classical}$

At low T fermions and bosons must be treated separately.