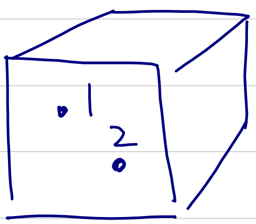
LECTURE 4: Quantum partition function for noninteracting many-particle systems

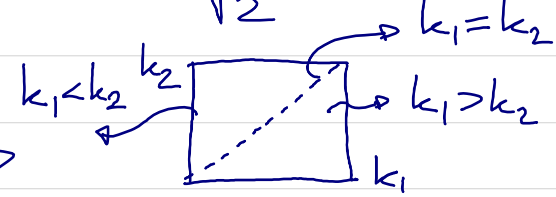
1° 2 bosons in a box



$$|\vec k_1, \vec k_2\rangle_b = \begin{cases} \frac{1}{\sqrt{2}}\left(|\vec k_1\rangle \otimes |\vec k_2\rangle + |\vec k_2\rangle \otimes |\vec k_1\rangle\right), & \vec k_1 \neq \vec k_2 \\ |\vec k\rangle \otimes |\vec k\rangle, & \vec k_1 = \vec k_2 \end{cases}$$

$$Z_b = \mathrm{Tr}\, e^{-\beta \hat H} = \sum_{\vec k_1, \vec k_2} {}_b\langle \vec k_1, \vec k_2 | e^{-\beta \hat H} | \vec k_1, \vec k_2 \rangle_b$$

$$= \sum_{|\vec k_1| > |\vec k_2|} \frac{\langle \vec k_1 | \langle \vec k_2 | + \langle \vec k_2 | \langle \vec k_1 |}{\sqrt{2}} e^{-\beta \hat H} \frac{|\vec k_1\rangle |\vec k_2\rangle + |\vec k_1\rangle |\vec k_2\rangle}{\sqrt{2}}$$



$$+ \sum_{\vec k} \langle \vec k | \langle \vec k | e^{-\beta \hat H} | \vec k \rangle | \vec k \rangle$$

$$= \frac{1}{2} \sum_{\vec k_1, \vec k_2} e^{-\beta \frac{\hbar^2}{2m}(k_1^2 + k_2^2)} + \frac{1}{2} \sum_{\vec k} e^{-\beta \frac{\hbar^2}{\cancel{2}m} \cancel{2} k^2}$$

$$Z_b = \frac{1}{2} \frac{V^2}{(2\pi)^6} \int d^3k_1 d^3k_2\, e^{-\beta \frac{\hbar^2}{2m}(k_1^2 + k_2^2)}$$

$$+ \frac{1}{2} \frac{V}{(2\pi)^3} \int d^3k\, e^{-\beta \frac{\hbar^2}{2m} k^2}$$

$$= \frac{1}{2} \frac{V^2}{(2\pi)^6} \left(\frac{2m\pi}{\beta \hbar^2}\right)^3 + \frac{1}{2} \frac{V}{(2\pi)^3} \left(\frac{m\pi}{\beta \hbar^2}\right)^{3/2}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \Rightarrow Z_b = \frac{1}{2} \frac{V^2}{\lambda^6} \Big(1 + \underbrace{\frac{1}{2^{3/2}} \frac{\lambda^3}{V}}_{\text{small when } T \to \infty \text{ and/or } V \to \infty}\Big)$$

$$\ln Z_b = \ln Z_b^{CSM} + \ln\left(1+\frac{1}{2^{3/2}}\frac{\lambda^3}{V}\right) \approx \ln Z_b^{CSM} + \underbrace{\frac{1}{2^{3/2}}\frac{\lambda^3}{V}}_{Z_b^{QC}}$$

QC $\Leftrightarrow$ quantum correction

$\lambda^3/V \ll 1$ for nondegenerate systems

$$E_b^{QC} = -\frac{\partial}{\partial\beta}\ln Z_b^{QC} = -\frac{3}{2^{5/2}}k_B T\frac{\lambda^3}{V}$$

$$C_b^{QC} = \left.\frac{\partial E_b^{QC}}{\partial T}\right|_V = \frac{3}{2^{7/2}}k_B\frac{\lambda^3}{V}$$

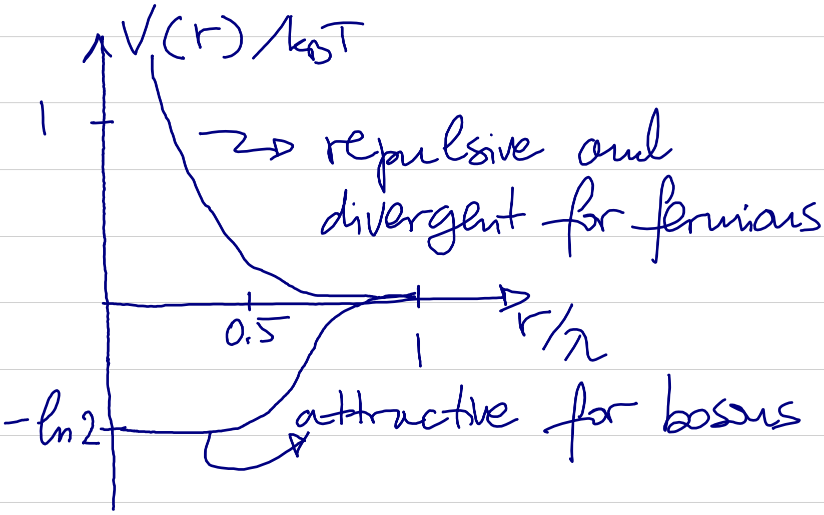
2° "Effective force" between two bosons or fermions

$$\langle \vec r_1, \vec r_2 | \hat\rho | \vec r_1, \vec r_2\rangle_{b,f} = \frac{1}{Z_{b,f}\lambda^6}\left[1 \pm e^{-\frac{2\pi}{\lambda^2}(\vec r_1-\vec r_2)^2}\right]$$

analogy with phase space density allows us to extract $V(\vec r_1,\vec r_2)$

$$\underbrace{\rho(\vec r_1,\vec r_2) \propto e^{-\beta V(\vec r_1,\vec r_2)} = 1 \pm e^{-\frac{2\pi}{\lambda^2}(\vec r_1-\vec r_2)^2}}$$

$$\Downarrow\ V(\vec r_1,\vec r_2) = -k_B T\ln\left[1 \pm e^{-\frac{2\pi}{\lambda^2}\underbrace{(\vec r_1-\vec r_2)^2}_{r^2}}\right]$$



"strange" potential:

i) temperature-dependent

ii) cannot simulate transition probabilities described by off-diagonal elements of $\hat\rho$

■ consider 2 spinless bosons or fermions in 1D

$$\psi_b = 1/\sqrt{2}\,[\psi(x_1,E_p)\psi(x_2,E_q) + \psi(x_2,E_p)\psi(x_1,E_q)]$$

we cannot say which particle has energy E_p or E_q

$$\psi_f = 1/\sqrt{2}\,[\psi(x_1,E_p)\psi(x_2,E_q) - \psi(x_2,E_p)\psi(x_1,E_q)]$$

$$\psi_{dist}(x_1,x_2) = \psi(x_1,E_p)\,\psi(x_2,E_q)$$

$$\langle(\hat{x}_1-\hat{x}_2)^2\rangle_{dist} = \langle\hat{x}^2\rangle_p + \langle\hat{x}^2\rangle_q - 2\langle\hat{x}\rangle_p\langle\hat{x}\rangle_q$$

$$\langle\hat{x}^n\rangle_{p,q} = \int_{-\infty}^{\infty}\psi^*(x,E_{p,q})\,\hat{x}^n\,\psi(x,E_{p,q})\,dx$$

$$E_p \neq E_q \Rightarrow \underbrace{\int_{-\infty}^{\infty}\psi^*(x,E_p)\,\psi(x,E_q) \equiv 0}_{\text{eigenstates are orthogonal}}$$

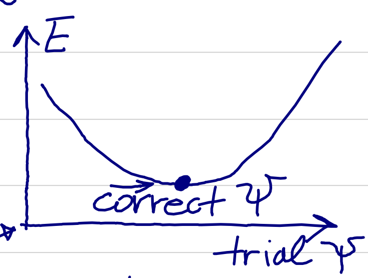
$$\boxed{\begin{gathered}\langle(\hat{x}_1-\hat{x}_2)^2\rangle_{b,f} = \langle(\hat{x}_1-\hat{x}_2)^2\rangle_{dist} \mp 2|\langle\hat{x}\rangle_{ab}|^2 \\ \langle\hat{x}\rangle_{pq} = \int_{-\infty}^{\infty}\psi^*(x,E_p)\,\hat{x}\,\psi(x,E_q)\,dx\end{gathered}}$$

→ if $\psi(x,E_a)$ and $\psi(x,E_b)$ do not overlap $\langle\hat{x}\rangle_{ab} \equiv 0$ so that fermions or bosons behave as distinguishable particles

→ "the force" is not really force, but a purely geometric consequence of the symmetrization postulate ⇒ such as, for two identical fermions wavefunction must vanish when they are at the same position which increases its curvature and enhances momentum distribution ⇔ it increases kinetic energy

→ to understand direct connection between wavefunction curvature and kinetic energy, consider 1D:

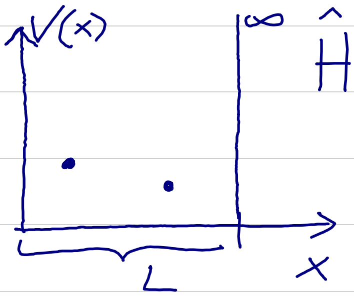
- $d^2\psi/dx^2$ is curvature of real wavefunction in 1D
  (assume time-reversal invariance)
- $d^2\psi/dx^2 \cdot \psi^{-1}$ is relative magnitude of curvature
  - ψ^2 is probability to find particle at x
- $\psi(x) \cdot \frac{d^2\psi}{dx^2}$ which is (up to a constant) kinetic energy density $\frac{-\hbar^2}{2m}\psi(x) \cdot \frac{d^2}{dx^2}\psi(x)$
- $V(x)\,\psi^2(x)$ is potential energy density
- $E = \int dx \left[\frac{-\hbar^2}{2m}\psi(x)\frac{d^2}{dx^2}\psi(x) + V\psi^2(x)\right]$



- $\psi \to \psi + \delta\psi$ must give $dE \equiv 0$ because →
  which leads to Schrödinger equation that can be viewed as relation between curvature and $V(x)$ at each point x
- $$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\,\psi(x) = E\,\psi(x)$$

→ so, even if forces are absent, $V(x) \equiv 0$, kinetic energy can be modified by changing $d^2/dx^2\,\psi(x)$

■ EXAMPLE: Two particles in 1D infinite potential well



$$\hat{H}\psi(x) = E\psi(x) \Rightarrow \begin{cases} E = \underbrace{\dfrac{\hbar^2\pi^2}{2mL^2}}_{C} \cdot n^2, \quad n = 1, 2, \dots \\ \psi(x) = \sqrt{\dfrac{2}{L}} \sin\dfrac{n\pi x}{L} \end{cases}$$

i) two distinguishable particles:

ground state: $\psi_{1,1}(x_1, x_2) = \dfrac{2}{L} \sin\dfrac{\pi x_1}{L} \sin\dfrac{\pi x_2}{L}$

ground state energy: $E_{11} = (1^2 + 1^2)\cdot C = 2C$

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In[26]:= Plot3D[2 * Sin[1 * Pi * x1] * Sin[1 * Pi * x2],
  {x1, -Pi / 2, Pi / 2}, {x2, -Pi / 2, Pi / 2}, AxesLabel → Automatic]
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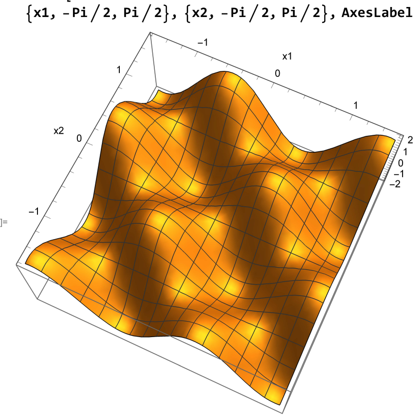
Out[26]=



ii) two indistinguishable fermions: $\psi^f_{1,1}(x_1, x_2) \equiv 0$

ground state: $\psi^f_{1,2}(x_1, x_2) = \dfrac{1}{\sqrt{2}}\left[\dfrac{2}{L}\sin\dfrac{\pi x_1}{L}\sin\dfrac{2\pi x_2}{L} - \dfrac{2}{L}\sin\dfrac{\pi x_2}{L}\sin\dfrac{2\pi x_1}{L}\right]$

ground state energy: $E^f_{1,2} = (1^2 + 2^2)C = 5C$

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In[27]:= Plot3D[2 * Sin[1 * Pi * x1] * Sin[2 * Pi * x2] - 2 * Sin[1 * Pi * x2] * Sin[2 * Pi * x1],
  {x1, -Pi / 2, Pi / 2}, {x2, -Pi / 2, Pi / 2}, AxesLabel → Automatic]
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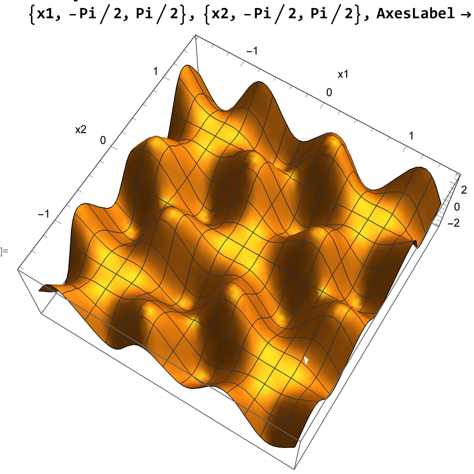


3° Grand canonical partition function

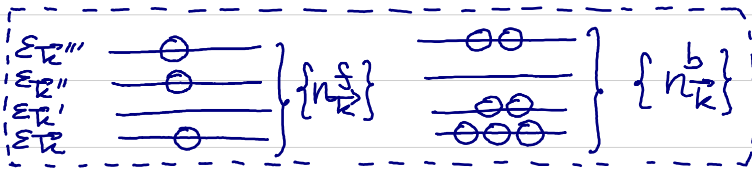
⇒ particles do not interact, so they occupy single-particle energy levels (single-particle Hamiltonian)

$\varepsilon_{\vec k}$ is energy − momentum dispersion $\Leftrightarrow \hat H_1 |\varepsilon_{\vec k}\rangle = \varepsilon_{\vec k} |\varepsilon_{\vec k}\rangle$

$n_{\vec k}$ is number of particles in state $|\varepsilon_{\vec k}\rangle$, so

$n_{\vec k} = 0, 1, 2, \ldots$ for bosons $n_{\vec k} = 0, 1$ for fermion

$E_n = \sum_{\vec k} \varepsilon_{\vec k} n_{\vec k}$ is many − body energy level $\hat H_N |E_n\rangle = E_n |E_n\rangle$ s



⇒ illustration of microstate $\{n_{\vec k}\}$ for fermions (f) or bosons (b)

■ canonical ensemble:

$$Z = \mathrm{Tr}\, e^{-\beta \hat H} = \sum_n e^{-\beta E_n} = \sum_{\{n_{\vec k}\}}{}' e^{-\beta \sum_{\vec k} \varepsilon_{\vec k} n_{\vec k}}$$

$$\sum_{\vec k} n_{\vec k} = N$$

■ grand canonical ensemble removes constraint:

$$Z_G = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{\{n_{\vec k}\}}{}' e^{-\beta \sum_{\vec k}' \varepsilon_{\vec k} n_{\vec k}}$$

$$= \prod_{\vec k} \sum_{\{n_{\vec k}\}} e^{-\beta(\varepsilon_{\vec k} - \mu) n_{\vec k}} = \prod_{\vec k} Z_{G,\vec k}$$

this product of "partition functions for each single particle energy level" can be interpreted as if each level is populated independently of others by exchanging particles with macroscopic reservoir

$\rightarrow$ FERMIONS: $$Z_{G,\vec{k}} = \sum_{n_{\vec{k}}=0}^{1} e^{-\beta(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}}} = 1 + e^{-\beta(\varepsilon_{\vec{k}}-\mu)}$$

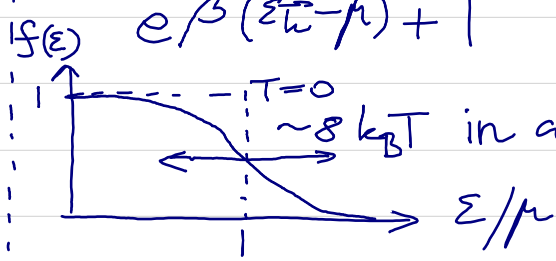
$$\Phi_{\vec{k}} = -k_BT \ln Z_{G,\vec{k}} = -k_BT \ln\left[1 + e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right]$$

$$Z_G = \prod_{\vec{k}} Z_{G,\vec{k}} = \prod_{\vec{k}}\left[1 + e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right]$$

$$\langle \hat{n}_{\vec{k}}\rangle_f = \sum_{n_{\vec{k}}=0}^{1} n_{\vec{k}}\, e^{-\beta(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}}} \Big/ \sum_{n_{\vec{k}}=0}^{1} e^{-\beta(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}}} = -\frac{\partial \Phi_{\vec{k}}}{\partial \mu}$$

$$= e^{-\beta(\varepsilon_{\vec{k}}-\mu)} \Big/ \left[e^{-\beta(\varepsilon_{\vec{k}}-\mu)} + 1\right]$$

$$= \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)}+1} \equiv f(\varepsilon_{\vec{k}})$$ standard label in condensed matter physics for Fermi-Dirac distribution function



$\rightarrow$ BOSONS: $$Z_{G,\vec{k}} = \sum_{n_{\vec{k}}=0}^{\infty} e^{-\beta(\varepsilon_{\vec{k}}-\mu)n_{\vec{k}}} = \underbrace{\sum_{n_{\vec{k}}=0}^{\infty}\left[e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right]^{n_{\vec{k}}}}_{\mu<0 \text{ to converge}}$$

$$= \frac{1}{1-e^{-\beta(\varepsilon_{\vec{k}}-\mu)}} \Rightarrow \Phi_{\vec{k}} = -k_BT \ln Z_{G,\vec{k}} = k_BT \ln\left[1-e^{-\beta(\varepsilon_{\vec{k}}-\mu)}\right]$$

$$Z_G = \prod_{\vec{k}} Z_{G,\vec{k}} = \prod_{\vec{k}} \frac{1}{1-e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}$$

$$\langle \hat{n}_{\vec{k}}\rangle_b = -\frac{\partial \Phi_{\vec{k}}}{\partial \mu} = -k_BT \frac{-\beta e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}{1-e^{-\beta(\varepsilon_{\vec{k}}-\mu)}} = \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)}-1} \equiv n(\varepsilon_{\vec{k}})$$ Bose-Einstein distribution function

$\langle n_{\vec{k}}\rangle_{b,f} \approx e^{-\beta(\varepsilon_{\vec{k}}-\mu)}$ Maxwell-Boltzmann when $T\to\infty$, $\langle n_{\vec{k}}\rangle \ll 1$

→ Grand potential or Landau free energy

$$\Phi = F - \mu N = E - TS - \mu N = -pV$$

$$= -k_B T \ln Z_G = \overset{-f}{+b} \sum_{\vec{k}} \ln\left[1 \pm e^{-\beta(\varepsilon_{\vec{k}} - \mu)}\right]$$

$$N = -\frac{\partial \Phi}{\partial \mu} = \sum_{\vec{k}} \langle \hat{n}_{\vec{k}} \rangle = \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta \varepsilon_{\vec{k}}} - \eta}$$

$$E = \sum_{\vec{k}} \varepsilon_{\vec{k}} \langle n_{\vec{k}} \rangle = \sum_{\vec{k}} \frac{\varepsilon_{\vec{k}}}{z^{-1} e^{\beta \varepsilon_{\vec{k}}} - \eta}$$

$z = e^{\beta\mu}$ is fugacity
$\eta = -1$ fermions
$\eta = +1$ bosons

4° Nondegenerate ⇔ high temperature and low density limit for noninteracting fermions or bosons

→ $pV = N k_B T$ is equation of state for Boltzmannons

$g = 2s + 1$ is spin degeneracy factor

$\varepsilon_{\vec{k}} = \hbar^2 k^2 / 2m$ is parabolic energy-momentum dispersion

$$\beta p_\eta = \frac{\ln Z_G}{V} = -\eta g \int \frac{d^3k}{(2\pi)^3} \ln\left[1 - \eta z e^{-\beta \hbar^2 k^2 / 2m}\right]$$

$$n_\eta = \frac{N_\eta}{V} = g \int \frac{d^3k}{(2\pi)^3} \frac{1}{z^{-1} e^{\beta \hbar^2 k^2 / 2m} - \eta}$$

$$E_\eta / V = g \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \frac{1}{z^{-1} e^{\beta \hbar^2 k^2 / 2m} - \eta}$$

$\Rightarrow$ change variables:

$$x = \beta \hbar^2 k^2/2m \,, \quad k = \frac{\sqrt{2mk_BT}}{\hbar} x^{1/2} = \frac{2\pi^{1/2}}{\lambda} x^{1/2}$$

$$dk = \frac{\pi^{1/2}}{\lambda} x^{-1/2} dx$$

$$\beta p_\eta = -\eta \frac{g}{2\pi^2} \frac{4\pi^{3/2}}{\lambda^3} \int_0^\infty \underbrace{dx\, x^{1/2}}_{dv} \underbrace{\ln\left[1 - \eta z e^{-x}\right]}_{u}$$

$$= \frac{g}{\lambda^3} \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{dx\, x^{3/2}}{z^{-1} e^x - \eta}$$

$$n_\eta = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx\, x^{1/2}}{z^{-1} e^x - \eta}$$

$$\beta E_\eta / V = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx\, x^{3/2}}{z^{-1} e^x - \eta} \Rightarrow E_\eta / V = \frac{3}{2} P_\eta$$

$\Rightarrow$ define: $$f_m^\eta(z) = \frac{1}{(m-1)!} \int_0^\infty \frac{dx\, x^{m-1}}{z^{-1} e^x - \eta}$$

need factorial of non-integer numbers $\Rightarrow$ $m! = \Gamma(m+1) = \int_0^\infty dx\, x^m e^{-x}$

$(1/2)! = \sqrt{\pi}/2 \,, \quad (3/2)! = \frac{3}{2}\sqrt{\pi}/2$

$$\boxed{\begin{aligned} \beta P_\eta &= \frac{g}{\lambda^3} f_{5/2}^\eta(z) \\ n_\eta &= \frac{g}{\lambda^3} f_{3/2}^\eta(z) \\ E_\eta/V &= \frac{3}{2} P_\eta \end{aligned}}$$

$\Rightarrow$ solve for z (or μ) in terms of n_η and then replace in the other two equations

$\rightarrow$ in the high temperature and low density limit $z = e^{\beta\mu} \ll 1$ because $\beta = \frac{1}{k_B T} > 0$, $\mu < 0$

$$f_m^\eta(z) = \frac{1}{(m-1)!}\int_0^\infty \frac{dx\, x^{m-1}}{z^{-1}e^x - \eta} = \frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1}\, \underbrace{\frac{\eta\, \eta z e^{-x}}{1-\eta z e^{-x}}}_{\updownarrow}$$

$$\frac{r}{1-r} = \sum_{\alpha=1}^\infty r^\alpha$$

$$= \frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1}\sum_{\alpha=1}^\infty (z e^{-x})\,\eta^{\alpha+1}$$

$$= \sum_{\alpha=1}^\infty \eta^{\alpha+1} z^\alpha \underbrace{\frac{1}{(m-1)!}\int_0^\infty dx\, x^{m-1} e^{-\alpha x}}_{\frac{1}{\alpha^m}\int_0^\infty d(\alpha x)(\alpha x)^{m-1}e^{-\alpha x} = \frac{\Gamma(m-1)!}{\alpha^m}}$$

$$= \sum_{\alpha=1}^\infty \eta^{\alpha+1}\frac{z^\alpha}{\alpha^m} = z + \eta z^2/2^m + z^3/3^m + \ldots$$

$$n_\eta \lambda^3/g = f_{3/2}^\eta(z) = z + \eta z^2/2^{3/2} + z^3/3^{3/2} + \eta z^4/4^{3/2} + \ldots$$

$\rightarrow$ solve perturbatively for z by substituting the solution up to a lower order

$z = n_\eta \lambda^3/g \ll 1$ is nondegenerate limit criterion

$$z = n_\eta \lambda^3/g - \eta\frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \ldots$$

$$\approx n_\eta\lambda^3/g - \frac{\eta}{2^{3/2}}\left(\frac{n_\eta\lambda^3}{g}\right)^2 + \left(1/4 - 1/3^{3/2}\right)\left(\frac{n_\eta\lambda^3}{g}\right)^3 - \ldots$$

$$\beta P_\eta \lambda^3/g = f_{5/2}^\eta(z) = z + \eta\frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \eta\frac{z^4}{4^{5/2}} + \ldots$$

$$\beta p_\eta \lambda^3/g = \frac{n_\eta \lambda^3}{g} - \frac{\eta}{2^{3/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^3$$

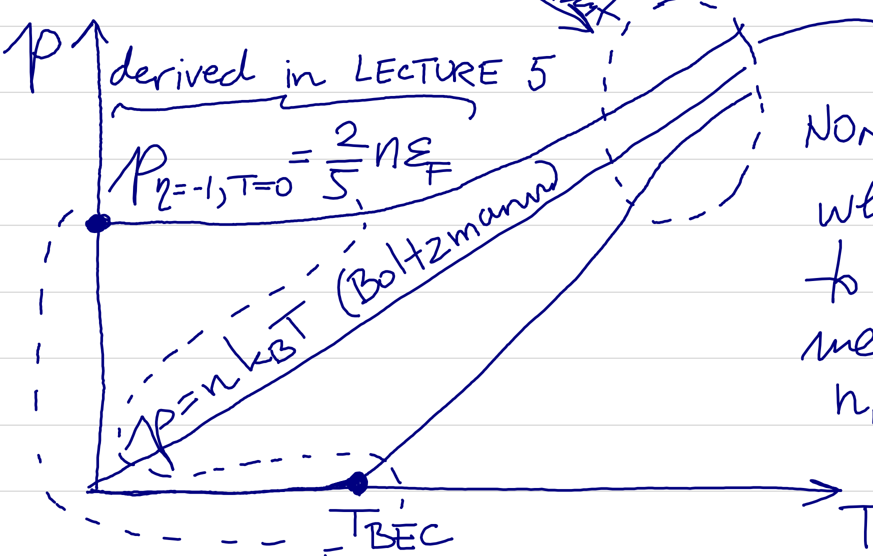
$$+ \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 - \frac{1}{8}\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \frac{1}{3^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \dots$$

$$p_\eta = n_\eta k_B T \left[1 - \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right) + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \dots\right]$$

valid in nondegenerate limit

$$B_2 = -\eta \lambda^3/(2^{5/2} g)$$

could be reproduced by $V(\vec{r}_1, \vec{r}_2)$ from p. 2 and virial expansion in classical SM



NONDEGENERATE limit where quantum corrections to classical statistical mechanics are small $n_\eta \lambda^3 \ll g$

$n_\eta \lambda^3/g \ll 1$ is natural dimensionless small parameter

$n_\eta \lambda^3 \gg g$ rigorously defines DEGENERATE (fully quantum) limit due to high densities AND/OR low temperatures; its physical meaning is $\lambda \gg$ interparticle distance, so wavepackets of de Broglie wavelength size start to overlap and physics is dominated by SYMMETRIZATION postulate