1. Calculating the matrix elements $\langle \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N | e^{-\beta H} | \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N\rangle$, in class we formally obtained the partition function in the canonical ensemble for an N-particle non-interacting non-relativistic quantum system

$$Z_N = \mathrm{Tr}(e^{-\beta H}) = \int d^{3N}x \langle \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N | e^{-\beta H} | \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N\rangle,$$

where

$$\langle \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N | e^{-\beta H} | \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N\rangle = \frac{1}{N!\lambda^{3N}}\sum_P \delta_P f(P\mathbf{x}_1-\mathbf{x}_1)f(P\mathbf{x}_2-\mathbf{x}_2)\ldots f(P\mathbf{x}_N-\mathbf{x}_N)$$

$$f(u) = e^{-\frac{\pi u^2}{\lambda^2}}, \ \lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}, \ \delta_P \equiv 1 \text{ for Bosons and } \delta_P = (-1)^{[P]} \text{ for Fermions.}$$

In order to study lowest-order quantum corrections to classical non-interacting systems ($\lambda^3\left(\frac{N}{V}\right) << 1$), it is sufficient to consider only the trivial permutation ("no permutation") and two-particle permutations in the above expression, i.e.,

$$\langle \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N | e^{-\beta H} | \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N\rangle = \frac{1}{N!\lambda^{3N}}\left\{1 \pm \sum_{i<j} f^2(r_{ij}) + \ldots\right\}$$

where $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$, and the $\pm$ sign are for Bosons/Fermions).

(a) Find the equation of state in this first order approximation.
(b) Find $\langle E\rangle$ as a function of T, V, and N in the same approximation.

a. $Z_N = \int d_x^{3N} \frac{1}{N!\lambda^{3N}} \left\{1 \pm \sum_{i<j} f^2(r_{ij})\right\}$

$= \frac{1}{N!\lambda^{3N}} \int \left\{1 \pm \sum_{i<j} f^2(r_{ij})\right\} d_x^{3N}$

$= \frac{1}{N!\lambda^{3N}} V^N \left(1 \pm \frac{N(N-1)}{2} V^{-1}\right) \int f^2(r_{ij}) d_x^3$

$= \frac{1}{N!\lambda^{3N}} V^N \left(1 \pm \frac{N(N-1)}{2V}\right) \int 4\pi r^2 f^2(r) dr$

$= \frac{V^N}{N!\lambda^{3N}} \left(1 \pm \frac{N(N-1)}{2V} \frac{\lambda^3}{2^{3/2}}\right)$

$F = -kT \ln |Z_n|$

$$\ln|Z_n| = \ln\left|\frac{1}{N!}\right| + N\ln|V| - 3N|\lambda| + \ln\left|1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}\right|$$

$$= -\left(N\ln|N| - N - N\ln|V| + 3N\ln|\lambda| - \ln\left|1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}\right|\right)$$

$$F = KT\left(N\ln|N| - N - N\ln|V| + 3N\ln|\lambda| - \ln\left|1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}\right|\right)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N \text{ constant}}$$

* wolfram it

$$= \frac{NKT}{V} + KT\frac{1}{1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}}\left(\mp\frac{N(N-1)}{2^{5/2}}\frac{\lambda^3}{V^2}\right)$$

b.

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln|Z_n| \qquad \beta = \frac{1}{kT}$$

$$= -\frac{\partial}{\partial\beta}\left(\cancel{N\ln|N|} - \cancel{N} - \cancel{N\ln|V|} + 3N\ln|\lambda| - \ln\left|1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}\right|\right)$$

$$= -\frac{\partial}{\partial\beta}\left(3N\ln|\lambda| - \ln\left|1 \pm \frac{N(N-1)}{2V}\frac{\lambda^3}{2^{3/2}}\right|\right)$$

$$\lambda = \sqrt{\frac{h^2 \beta}{2\pi m}}$$

$$\underbrace{4\ \frac{\partial}{\partial\beta}\left(\frac{3}{2} N \ln|\beta| - \ln\left|1 \pm \frac{N(N-1)h^3}{2^{3/2} V (2\pi m)^{3/2}} \beta^{3/2}\right|\right)}$$

$$4\ \frac{3}{2}\frac{N}{\beta} - \frac{1}{1 \pm \frac{N(N-1)h^3}{2^{3/2} V (2\pi m)^{3/2}} \beta^{3/2}} \left(\frac{(N-1)h^3}{2^{3/2} V (2\pi m)^{3/2}}\right)$$

$$= \frac{3}{2}\frac{N}{\beta}\left(1 \mp \frac{1}{\frac{2^{3/2} V}{N-1} \underbrace{\frac{(2\pi m)^{3/2}}{h^3 \beta^{3/2}}}_{1/\lambda^3} \pm N}\right)$$

$$\boxed{= \frac{3}{2}\frac{N}{\beta}\left(1 \pm \frac{\lambda^3 (N-1)}{2^{5/2} V \mp \lambda^3 N(N-1}\right)}$$

2. We defined in class the Fermi-Dirac (+) and Bose-Einstein (-) integrals

$$f_\nu^\pm(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty \frac{dx\, x^{\nu-1}}{z^{-1}e^x \pm 1}.$$

Prove that for $z \ll 1$

$$f_\nu^\pm = \sum_{l=1}^\infty (\mp 1)^{l-1}\frac{z^l}{l^\nu} = z \mp \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} \mp \ldots$$

$$f_v^\pm(z) = \frac{1}{\Gamma(v)}\int \frac{dx\, x^{v-1}}{z^{-1}e^x \pm 1}$$

$$\frac{1}{z^{-1}e^x \pm 1} = \frac{1}{\frac{e^x}{z} \pm 1} = \frac{1}{\frac{e^x}{z}\left(1 \pm \frac{z}{e^x}\right)} = \frac{1}{e^x/z}\,\frac{1}{1 \pm z/e^x} = \frac{z}{e^x}\left(\frac{1}{1 \pm z/e^x}\right)$$

$z \ll 1$

$\Leftrightarrow \frac{z}{e^x} \lll 1$

$$= \sum_{n=1}^\infty \frac{z}{e^x}\left(\frac{z}{e^x}\right)^l (\pm 1)^l = \frac{z}{e^x}\sum_{n=1}^\infty \left(\frac{z}{e^x}\right)^l (\pm 1)^l$$

$$\frac{z^x}{e^x}\,\frac{1}{1 \pm z/e^x} = \sum_{n=0}^\infty \frac{z}{e^x}\left(\mp z/e^x\right)^{n-1} = \sum_{n=0}^\infty (\pm)\left(\frac{z}{e^x}\right)^n$$

Sub into integral

$$f_v^\pm = \frac{1}{\Gamma(v)}\int_0^\infty x^{v-1}\left[\sum_{n=0}^\infty (\pm)\left(\frac{z}{e^x}\right)^n\right] dx$$

$$\Leftrightarrow \quad \sum_{n=0}^\infty \frac{z^n}{\Gamma(v)}\int_0^\infty x^{v-1}(\pm)\left(\frac{z}{e^x}\right)^n dx$$

$$\int_0^\infty \frac{x^{v-1}}{e^{kx}}\,dx = \frac{\Gamma(v)}{k^v}$$

$$\frac{1}{\cancel{\Gamma(v)}}\sum_{n=0}^\infty (\pm)^{n-1} z^n \frac{\cancel{\Gamma(v)}}{n^v} \rightarrow \boxed{\sum_{n=0}^\infty (\pm)^{n-1}\frac{z^{n+1}}{(n+1)^v} = z \mp \frac{z^2}{2^v} + \frac{z^3}{3^v} \ldots}$$

3. Working in the grand-canonical ensemble, we obtained in class for the ideal non-relativistic Fermi (+) and Bose (-) systems with spin s:

$$N = (2s+1)\frac{V}{\lambda^3} f^{\pm}_{3/2}(z),$$

$$E = \frac{3}{2}kT\,(2s+1)\frac{V}{\lambda^3} f^{\pm}_{5/2}(z),$$

where $z = e^{\mu/kT}$ and $\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$.

(a) Obtain the energy E as a function of T, V, N, and the equation of state up to *first order* in $\frac{\lambda^3 N}{V}$. Note that after using the small z approximation for $f^{\pm}_{\nu}(z)$, z must be eliminated from the equations in favor of $\frac{\lambda^3 N}{V}$. To this end you should use the first equation above for N. How do your final results compare with those of Problem 1.(a) and (b)?

(b) Using $E(T,V,N)$, obtain the specific heat of the quantum gas up to the same order in $\frac{\lambda^3 N}{V}$.

a $f^{\pm}_{3/2}(z) = z \mp \frac{z^2}{2^{3/2}}$ * Small z

$$\frac{E}{N} = \frac{3}{2}kT\frac{f^{+/-}_{5/2}(z)}{f^{+/-}_{3/2}(z)}$$

$$= \frac{3}{2}kT\frac{z \mp \frac{z^2}{2^{5/2}}}{z \mp \frac{z^2}{2^{3/2}}}$$

$$= \frac{3}{2}kT\left(1 \mp \frac{z}{2^{5/2}}\right)\left(1 \pm \frac{z}{2^{3/2}}\right)$$

$$= \frac{3}{2}kT\left(1 \pm \frac{1}{2^{5/2}} z\right)$$

$$f^{\pm}_{3/2}(z) = \frac{\lambda^3 N}{V(2S+1)} = z \mp \frac{z^2}{2^{3/2}}$$

$$\frac{E}{N} = \frac{3}{2}kT\left(1 \pm \frac{1}{2^{5/2}}\frac{\lambda^3 N}{V(2S+1)}\right)$$

$$E = \frac{3}{2}NkT\left(1 \pm \frac{1}{2^{5/2}}\frac{\lambda^3 N}{V(2S+1)}\right)$$

Similar to 1B!

b. $C_V = \left(\frac{\partial E}{\partial T}\right)_{VN}$

$$\lambda^3 = \frac{h^3}{(2\pi mkT)^{3/2}}$$

$$\to E = \frac{3}{2}Nk\left(T \pm \frac{1}{\sqrt{T}}\frac{h^3}{(2\pi mk)^{3/2}} \cdots\right.$$

$$\frac{1}{2^{5/2}}\frac{N}{V(2S+1)}$$

$$C_V = \frac{3}{2}Nk\left(1 \mp -\frac{1}{2}T^{-3/2}\frac{h^3}{(2\pi mk)^{3/2}}\frac{1}{2^{5/2}}\frac{N}{V(2S+1)}\right)$$

$$= \frac{3}{2}Nk\left(1 \mp \frac{1}{2^{7/2}}\frac{\lambda^3 N}{V(2S+1)}\right)$$

4. Consider He gas at room temperature and atmospheric pressure, and determine whether the classical approximation for the equation of state ($PV = NkT$) is justified or not. Repeat the above considerations for the electron "gas" at room temperature.

$PV = NkT$

Prove $\frac{\lambda^3 N}{V} << 1$

$\frac{P}{KT} = \frac{N}{V}$

$\lambda = \frac{h}{\sqrt{2\pi m K T}} = \frac{6.626E-34}{\sqrt{2\pi(6.64E-27)(1.38E-23)(293.15)}} = 5.10E-11$

He mass =

Room Temp = 293.15 k

Atm = 101325

$\frac{101325}{(293.15)(1.38E-23)} = \frac{N}{V}$

$\Leftrightarrow 2.50465E25$

$\cdot \lambda^3$

$\Leftrightarrow \underline{3.323E-6 << 1}$

Applies!!

Electron gas

$\lambda = \frac{h}{\sqrt{2\pi m K T}} = 1.37667e-7$

$m = 9.109383e-34$

$\frac{N}{V} = \frac{P}{KT}$

Room Temp = 293.15 k

Atm = 101325

$\frac{101325}{(293.15)(1.38E-23)} = \frac{N}{V}$

$\Leftrightarrow 2.50465E25 \cdot \lambda^3 = \underline{65348 \not<< 1}$

Therefore ideal / classical model does not apply at room temp for electron gas