Final Exam Solution

1. (a) $\boxed{\rho(\varepsilon)\,d\varepsilon} = 2\,\rho(p)\,dp = 2\cdot 4\pi \frac{V}{h^3}\left(\frac{\varepsilon}{c}\right)^2 d\left(\frac{\varepsilon}{c}\right) = \boxed{8\pi \frac{V}{(hc)^3}\,\varepsilon^2\,d\varepsilon}$

(b) $E_{fermions} = 12\int_0^\infty d\varepsilon\,\rho(\varepsilon)\,\varepsilon\,\langle n(\varepsilon)\rangle = 12\cdot 8\pi \frac{V}{(hc)^3}\int_0^\infty d\varepsilon\,\varepsilon^2 \frac{\varepsilon}{e^{\varepsilon/kT}+1}$

$\mu=0$ since number not fixed

$= 12\cdot 8\pi \frac{V}{(hc)^3}(kT)^4\int_0^\infty du\,\frac{u^3}{e^u+1}$

From first page, $\int_0^\infty \frac{u^3}{e^u+1}\,du = \left(1-\frac{1}{2^3}\right)\cdot\frac{\pi^4}{15} = \frac{7}{8}\frac{\pi^4}{15}$

so $\boxed{\frac{E_{fermions}}{V}} = 12\cdot\frac{7}{8}\cdot 8\pi\cdot\frac{\pi^4}{15}\,\frac{(kT)^4}{(hc)^3} = \boxed{12\cdot\frac{7}{8}\cdot\frac{8}{15}\pi^5\frac{k^4}{(hc)^3}T^4}$

(c) For bosons, $\langle n(\varepsilon)\rangle = \frac{1}{e^{\varepsilon/kT}-1}$ and $12\to 8$, so

$E_{bosons} = 8\cdot 8\pi\frac{V}{(hc)^3}(kT)^4\underbrace{\int_0^\infty du\,\frac{u^3}{e^u-1}}_{=\pi^4/15 \text{ from front page}}$

$\Rightarrow \boxed{\frac{E_{bosons}}{V} = 8\cdot\frac{8}{15}\pi^5\frac{k^4}{(hc)^3}T^4}$

(d) $P = \frac{1}{3}\frac{N}{V}\langle pc\rangle = \frac{1}{3}\frac{N\langle\varepsilon\rangle}{V} = \frac{1}{3}\frac{E}{V}$ <u>for each species</u>

Then, with P = total pressure,

$P = \frac{1}{3}\left(\frac{E_{fermions}}{V} + \frac{E_{bosons}}{V}\right)$

$\Rightarrow \boxed{PV} = \frac{1}{3}\left(12\cdot\frac{7}{8}+8\right)\cdot\frac{8}{15}\pi^5\frac{k^4}{(hc)^3}T^4$

$= \boxed{\frac{4.37}{45}\pi^5\frac{k^4}{(hc)^3}T^4}$

(e) "Divide by dT with V constant": $-S + V\frac{dP}{dT} - N\frac{d\mu}{dT} = 0$

but $\mu=0$ because number is not fixed, so

$\boxed{\frac{S}{V}} = \left(\frac{\partial P}{\partial T}\right)_V = \frac{4.37}{45}\cdot\pi^5\frac{k^4}{(hc)^3}\cdot 4T^3 = \boxed{\frac{592}{45}\pi^5\frac{k^4}{(hc)^3}T^3}$

2. (a) $\boxed{Z = z^N}$, $z = \int \frac{d^3q\, d^3p}{h^3} e^{-H/kT}$, $H = \frac{p^2}{2m} + U(r)$

(This is the same as 3 harmonic oscillators.)

Because x, y, z and p_x, p_y, p_z make the same contributions,

$$\boxed{z =} \frac{1}{h^3}\left(\int_{-\infty}^{\infty} dp_x\, e^{-(p_x^2/2m)/kT}\right)^3 \left(\int_{-\infty}^{\infty} dx\, e^{-(x^2/2R^2)/kT}\right)$$

$$= \frac{1}{h^3}\left((2mkT)^{1/2}\underbrace{\int_{-\infty}^{\infty} du\, e^{-u^2}}_{=\sqrt{\pi}}\right)^3 \left((2R^2kT)^{1/2}\underbrace{\int_{-\infty}^{\infty} dv\, e^{-v^2}}_{=\sqrt{\pi}}\right)^3$$

$$= \frac{1}{h^3}\left((2\pi kT)\, m^{1/2}\, V^{1/3}\right)^3 \quad [V \equiv R^3]$$

$$= \boxed{\left(\frac{2\pi kT}{h}\right)^3 m^{3/2} V}$$

(b) $\boxed{F =} -kT \ln Z = \boxed{-NkT \ln z}$ with z above

$dF = -S\,dT - P\,dV + \mu\, dN$

$\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = +NkT\frac{\partial}{\partial V}\left(\ln V + \ln(\text{function of } T)\right)$

$= \frac{NkT}{V} \Rightarrow \boxed{PV = NkT}$

(c) $\boxed{S =} -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk \ln z + NkT\underbrace{\frac{\partial}{\partial T}\ln(T^3)}_{=3/T}$

$= \boxed{Nk \ln z + 3Nk}$ with z above

$\boxed{E =} kT^2 \frac{\partial}{\partial T}\ln Z = NkT^2\frac{\partial}{\partial T}\ln(T^3) = \boxed{3NkT}$

$\boxed{C_V =} \left(\frac{\partial E}{\partial T}\right)_V = \boxed{3Nk}$

(d) For $x, y,$ or z, $kT = \left\langle x \frac{\partial H}{\partial x}\right\rangle = \left\langle x\frac{2x}{2R^2}\right\rangle = 2\left\langle\frac{x^2}{2R}\right\rangle$

& for $p_x, p_y,$ or p_z, $kT = 2\left\langle \frac{p_x^2}{2m}\right\rangle$,

so each variable (of course) contributes $\frac{1}{2}kT$,

and $\boxed{E =} N\cdot 6\cdot(\frac{1}{2}kT) = \boxed{3NkT}$.

3. $\boxed{\sigma_X^2} \equiv \langle (X - \langle X\rangle)^2 \rangle = \langle X^2\rangle - 2\langle X\rangle^2 + \langle X\rangle^2$

$\boxed{= \langle X^2\rangle - \langle X\rangle^2}$

(a) $\boxed{\langle E\rangle =} \sum_r E_r \frac{e^{-\beta E_r}}{Z} = -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_r e^{-\beta E_r} = \boxed{-\frac{\partial}{\partial\beta}\ln Z}$ [of course]

$$\langle E^2\rangle = \sum_r E_r^2 \frac{e^{-\beta E_r}}{Z} = -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_r E_r e^{-\beta E_r}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\left(Z\langle E\rangle\right) = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\langle E\rangle + Z\frac{\partial\langle E\rangle}{\partial\beta}\right)$$

$$= \langle E\rangle^2 - \frac{\partial\langle E\rangle}{\partial\beta}$$

$$\Rightarrow \boxed{\sigma_E^2 =} \langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial\langle E\rangle}{\partial\beta} = kT^2\frac{\partial\langle E\rangle}{\partial T} = \boxed{kT^2 C_V}$$

since $\frac{\partial}{\partial T}(\ ) = \frac{\partial}{\partial\beta}(\ )\frac{\partial\beta}{\partial T} = -\frac{1}{kT^2}\frac{\partial}{\partial\beta}(\ )$ & $C_V = \frac{\partial\langle E\rangle}{\partial T}$

(b) $\boxed{\langle N\rangle =} \sum_{Nr} N \frac{e^{-\beta E_r}e^{\gamma N}}{\mathcal{Z}} = \frac{1}{\mathcal{Z}}\frac{\partial}{\partial\gamma}\sum_{Nr} e^{-\beta E_r}e^{\gamma N} = \boxed{\frac{\partial}{\partial\gamma}\ln\mathcal{Z}}$

$$\langle N^2\rangle = \sum_{Nr} N^2\frac{e^{-\beta E_r}e^{\gamma N}}{\mathcal{Z}} = \frac{1}{\mathcal{Z}}\frac{\partial}{\partial\gamma}\sum_{Nr} N e^{-\beta E_r}e^{\gamma N}$$

$$= \frac{1}{\mathcal{Z}}\frac{\partial}{\partial\gamma}\left(\mathcal{Z}\langle N\rangle\right) = \frac{1}{\mathcal{Z}}\left(\frac{\partial\mathcal{Z}}{\partial\gamma}\langle N\rangle + \mathcal{Z}\frac{\partial\langle N\rangle}{\partial\gamma}\right)$$

$$= \langle N\rangle^2 + \frac{\partial\langle N\rangle}{\partial\gamma}$$

$$\Rightarrow \boxed{\sigma_N^2 =} \langle N^2\rangle - \langle N\rangle^2 = \boxed{kT\frac{\partial\langle N\rangle}{\partial\mu}}$$

since $\gamma = \beta\mu = \frac{\mu}{kT} \Rightarrow \frac{\partial}{\partial\gamma} = kT\frac{\partial}{\partial\mu}$

But $\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} = \frac{1}{(\partial\mu/\partial\langle N\rangle)_{V,T}} = -\frac{N^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{N,T}$

implicitly held constant was given, so

$$\boxed{\sigma_N^2 =} kT\frac{N^2}{V}\left(-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}\right) = \boxed{\frac{N^2}{V}kT\kappa_T}$$

4. We consider only the vibrations, and leave out the factor of $1/h$ which makes no difference in the heat capacity.

$$Z_{vib} = \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2} e^{+\beta (g x^3 + f x^4)}$$

$$\approx \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2} \left(1 + (\beta g x^3 + \beta f x^4) + \frac{1}{2}(\beta g x^3 + f x^4)^2\right)$$

The odd integrands give zero, and f^2 & gf are higher order

So

$$Z_{vib} \approx \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2} \left(1 + \beta f x^4 + \frac{1}{2}\beta^2 g^2 x^6\right)$$

$$= \left(\frac{\pi}{\beta c}\right)^{1/2} + \beta f \left(\frac{1}{\beta c}\right)^{5/2} \underbrace{\int_{-\infty}^{\infty} du\, u^4 e^{-u^2}}_{= \frac{3}{4}\sqrt{\pi}} + \frac{1}{2}\beta^2 g^2 \left(\frac{1}{\beta c}\right)^{7/2} \underbrace{\int_{-\infty}^{\infty} du\, u^6 e^{-u^2}}_{= \frac{15}{8}\sqrt{\pi}}$$

from integral table provided

$$= \left(\frac{\pi}{\beta c}\right)^{1/2} \left[1 + \frac{3}{4}\frac{\beta f}{(\beta c)^2} + \frac{15}{16}\frac{\beta^2 g^2}{(\beta c)^3}\right]$$

$$\Rightarrow \boxed{\ln Z_{vib} \approx \ln\left(\frac{\pi}{\beta c}\right)^{1/2} + \frac{3}{4}\frac{f}{\beta c^2} + \frac{15}{16}\frac{g^2}{\beta c^3}}$$

$[\ln(1+x) \approx x]$

$$\Rightarrow \boxed{E_{vib} =} kT^2 \frac{\partial}{\partial T} \ln Z_{vib} \qquad \text{with } \frac{1}{\beta} = kT$$

$$\approx kT^2 \frac{\partial}{\partial T}\left[\ln T^{1/2} + \frac{3}{4}\frac{f}{c^2} kT + \frac{15}{16}\frac{g^2}{c^3} kT\right]$$

$$= kT^2 \left[\frac{1}{2}\frac{1}{T} + \frac{3}{4}\frac{f}{c^2} k + \frac{15}{16}\frac{g^2}{c^3} k\right]$$

$$= \frac{1}{2} kT + \frac{3}{4}\frac{f}{c^2} k^2 T^2 + \frac{15}{16}\frac{g^2}{c^3} k^2 T^2$$

$$\Rightarrow C_{vib} = \frac{1}{2} k + \frac{3}{2}\frac{f}{c^2} k^2 T + \frac{15}{8}\frac{g^2}{c^3} k^2 T$$

so $\boxed{C_{anh} = \frac{3}{2} k^2 \left(\frac{f}{c^2} + \frac{5}{4}\frac{g^2}{c^3}\right) T}$