$\boxed{\text{問題4}}$

(1) $dG = dF + VdP + PdV$

$= -SdT - \cancel{PdV} + \mu dN + VdP + \cancel{PdV}$

$= -SdT + VdP + \mu dN$

(2) 適当な a を用いて

$$aG(T, p, N) = G(T, p, aN)$$

が成り立ち、両辺を微分すると

$$G(T, p, N) = \frac{\partial(aN)}{\partial a} \cdot \frac{\partial G}{\partial(aN)}$$

$$= N\mu$$

$$\therefore \quad G = \mu N$$

また $dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)}_{=-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)}_{=V} dP + \underbrace{\left(\frac{\partial G}{\partial N}\right)}_{=\mu} dN$

$\mu = \frac{G}{N}$ より $d\mu = \frac{1}{N}\underbrace{\left(\frac{\partial G}{\partial T}\right)}_{=-S} dT + \frac{1}{N}\underbrace{\left(\frac{\partial G}{\partial P}\right)}_{=V} dP$

なので $d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$

$= -s\,dT + v\,dp$

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Ⅱ.

(3)

$$Z(T,V,N) = \frac{V^N}{h^{3N} N!} \int d^3p_1 \, d^3p_2 \cdots d^3p_N \, \exp\left(-\frac{1}{k_B T} \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

$$(積分部分) = \int d^3p_1 \cdots d^3p_N \, \exp\left(-\frac{1}{2mk_BT} \sum_{i=1}^{N} p_i^2\right)$$

$$= \left\{ \underbrace{\int d^3p_k \exp\left(-\frac{p_k^2}{2mk_BT}\right)}_{} \right\}^N$$

$$= (2mk_BT\pi)^{\frac{3}{2}}$$

$$= (2mk_BT\pi)^{\frac{3}{2}N}$$

$$Z(T,V,N) = \frac{V^N}{h^{3N} N!} (2mk_BT\pi)^{\frac{3}{2}N}$$

$$= \frac{V^N}{N!} \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^{3N}$$

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

ヘルムホルツの自由エネルギー F は.

$$F(T,V,N) = -k_BT \log Z$$

$$= -k_BT \underline{\log \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N} \; ⊛$$

$$⊛ = N \log\left(\frac{V}{\lambda^3}\right) - \log N!$$

$$= N \log\left(\frac{V}{\lambda^3}\right) - N\log N + N$$

$$\therefore \quad F = k_BTN \left(\log \frac{\lambda^3}{V} + \log N - 1 \right)$$

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(4)

$$G = F + PV$$

$$= k_BTN \left(\log \frac{\lambda^3}{V} + \log N - 1 \right) + PV$$

また. $\mu = \frac{G}{N}$

$$= k_BT \left(\log \frac{\lambda^3}{V} + \log N - 1 \right) + \frac{PV}{N}$$

理想気体なので

$PV = nRT$

$= \frac{N}{N_A} RT$

$= \frac{N}{\cancel{N_A}} \cancel{N_A} k_B T$

$v = \frac{k_B T}{P}$

$$= k_B T \left(\log \lambda^3 - \log V + \log N - 1 \right) + P \cdot \frac{V}{N}$$

$$= k_B T \left(3\log\lambda - \log \underbrace{\boxed{\frac{V}{N}}}_{v} - 1 \right) + P \cdot \underbrace{\boxed{\frac{V}{N}}}_{v}$$

練習.

ここで $d\mu(T,P) = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \underbrace{\left(\frac{\partial \mu}{\partial P}\right)_T}_{v} dP$ より $\frac{\partial \mu}{\partial P}$ を計算する。

$$\left(\frac{\partial \mu}{\partial P}\right)_T = k_B T \left(-\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T \right) + \cancel{v} + P\left(\frac{\partial v}{\partial P}\right)_T = \cancel{v}$$

$$\therefore \quad -\frac{k_B T}{v} + P = 0 \quad \text{より} \quad v = \frac{k_B T}{P}$$

ゆえに.
$$\mu = k_B T \left(3\log\lambda - \log\frac{k_B T}{P} - 1 \right) + k_B T$$

$$= 3 k_B T \log\left(\frac{\lambda P}{k_B T}\right)$$

(5) ボーズ粒子の $\overbrace{\text{状態密度}}^{\text{単位体積あたりの}}$ は.

$$D(\varepsilon) = \frac{1}{V} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}})$$

$$= \frac{1}{V} \int \frac{d\mathbf{k}^3}{\left(\frac{2\pi}{L}\right)^3} \delta(\varepsilon - \varepsilon_{\mathbf{k}})$$

$$= \frac{1}{\cancel{V}} \cdot 4\pi \int_0^\infty \frac{dk}{\left(\frac{2\pi}{\cancel{L}}\right)^3} k^2 \delta(\varepsilon - \varepsilon_k)$$

$$= \frac{1}{2\pi^2} \int_0^\infty dk\, k^2\, \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right)$$

$$= \frac{1}{2\pi^2} \int_0^\infty dk\, k^2 \cdot \frac{2m}{\hbar^2} \delta\left(k^2 - \frac{2m}{\hbar^2}\varepsilon\right)$$

$$= \frac{1}{2\pi^2} \int_0^\infty dk\, k^2 \frac{2m}{\hbar^2} \delta\left(\left(k + \frac{\sqrt{2m\varepsilon}}{\hbar}\right)\left(k - \frac{\sqrt{2m\varepsilon}}{\hbar}\right)\right)$$

$$= \frac{1}{2\pi^2} \cdot \frac{2m\boxed{\varepsilon}}{\hbar^2} \cdot \frac{2m}{\hbar^2} \cdot \frac{\cancel{\hbar}}{2\sqrt{2m\boxed{\varepsilon}}}$$

$$= \frac{1}{4\pi^2} \underline{\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}}\, \underline{\sqrt{\varepsilon}}$$

と表せるから. $A = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}$, $a = \frac{1}{2}$

(b) $\Omega = F - \mu N$

$$= \underline{k_BTN}(3\log\lambda - \log\frac{k_BT}{P} - 1) - 3\underline{k_BTN(\log\lambda} - \log\frac{k_BT}{P})$$

$$= 2k_BTN\log\frac{k_BT}{P} - k_BTN$$

$$= (2k_BT\log\frac{k_BT}{P} - k_BT)N$$

$\varepsilon - \mu > 0$

ここで N の表式

$\varepsilon > \mu$.

$$N = V\int_0^\infty \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-\mu)/k_BT} - 1}\, d\varepsilon$$

$$\frac{\partial N}{\partial V} = \int_0^\infty \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-\mu)/k_BT} - 1}\, d\varepsilon$$

Maxwell の関係式の両辺を μ で積分する：

$$(\text{左辺}) = \int_{-\infty}^{\mu} \frac{\partial P}{\partial \mu} d\mu = P(T, V, \mu) - P(T, V, \mu \to \infty)$$

$$= P(T, V, \mu)$$

$$(\text{右辺}) = \int_{-\infty}^{\mu} \frac{\partial N}{\partial V} d\mu$$

$$= \int_{-\infty}^{\mu} d\mu \left\{ \int_0^\infty \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-\mu)/k_BT} - 1}\, d\varepsilon \right\}$$

$$= \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \underline{\int_{-\infty}^{\mu} \frac{d\mu}{e^{(\varepsilon-\mu)/k_BT} - 1}}$$

$$\underline{\quad\quad} = \int_{-\infty}^{\mu} \frac{e^{-(\varepsilon-\mu)/k_BT}}{1 - e^{-(\varepsilon-\mu)/k_BT}} d\mu$$

$$= \left[-k_BT\log(1 - e^{-(\varepsilon-\mu)/k_BT})\right]_{-\infty}^{\mu}$$

$$= -k_BT\log(1 - e^{-\beta(\varepsilon-\mu)})$$

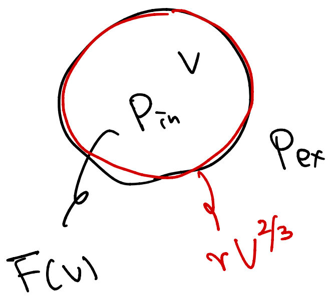
$$\therefore\ P(T, V, \mu) = -k_BT\int_0^\infty \frac{\sqrt{\varepsilon}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \log(1 - e^{-\beta(\varepsilon-\mu)})\, d\varepsilon$$

III.

(7) ヘルムホルツの自由エネルギー $F(T,V,N)$ は,

$$dF = \underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,N}}_{=-S} dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_{T,N}}_{=-P} dV + \underbrace{\left(\frac{\partial F}{\partial N}\right)_{T,V}}_{=\mu} dN$$

以上より $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ がいえる.



$$P_{in} = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

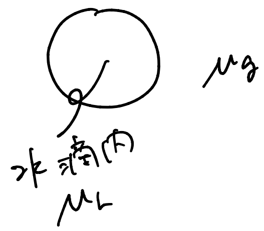
$$P_{ex} = -\left(\frac{\partial F_{tot}}{\partial V}\right)_{T,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} - \frac{2}{3} r V^{-\frac{1}{3}}$$

以上より

$$\Delta P = P_{in} - P_{ex} = +\frac{2}{3} r V^{-\frac{1}{3}}$$

よって. $B = +\frac{2}{3} r$, $b = -\frac{1}{3}$

IV



(8) $$P_L - P_G = \frac{2}{3} r V^{-\frac{1}{3}}$$

$$\frac{\partial P_L}{\partial V} - \frac{\partial P_G}{\partial V} = \frac{2}{3}\cdot\left(-\frac{1}{3}\right) r V^{-\frac{4}{3}}$$

$\mu_L = \mu_G$ より $v_L dP_L = v_G dP_G$

$$dP_L = \frac{v_G}{v_L} dP_G$$

$$\frac{v_G}{v_L}\frac{\partial P_G}{\partial V} - \frac{\partial P_G}{\partial V} = -\frac{2}{9} r V^{-\frac{4}{3}}$$

$$\left(\frac{v_G}{v_L} - 1\right)\frac{\partial P_G}{\partial V} = -\frac{2}{9} r V^{-\frac{4}{3}}$$

$\frac{v_G}{v_L} \gg 1$ より $$\frac{v_G}{v_L}\frac{\partial P_G}{\partial V} = -\frac{2}{9} r V^{-\frac{4}{3}}$$ //

(9)

$$\frac{k_B T}{v_L} \frac{1}{P_G} dP_G = -\frac{2}{9} \gamma V^{-\frac{4}{3}} dV$$

$$\frac{k_B T}{v_L} \log P_G = \frac{2}{3} \gamma V^{-\frac{1}{3}} + \text{Const}$$

$$\log P_G = \frac{2 \gamma v_L}{3 k_B T} V^{-\frac{1}{3}} + \text{Const}$$

$$P_G = A e^{\frac{2 \gamma v_L}{3 k_B T} V^{-\frac{1}{3}}}$$

よって. $$P_G = P_\infty e^{\frac{2 \gamma v_L}{3 k_B T} V^{-\frac{1}{3}}}$$ //