Question 1 (Kevin Brown)

1.) Minimize $H = \int d^3p\, f(p) \ln(f(p))$ given $N = \int d^3p\, f(p)$; $E = \int d^3p \frac{p^2}{2m} f(p)$

- Lagrange multipliers:

$$\nabla_{f,\alpha,\beta}\left[H - \alpha\left(\int d^3p\, f(p)\right) - \beta\left(\frac{1}{N}\int d^3p \frac{p^2}{2m} f(p)\right)\right] = 0$$

$$\nabla_{f,\alpha,\beta} \int d^3p \left[f(p)\ln f(p) - \alpha f(p) - \frac{\beta}{N}\frac{p^2}{2m} f(p)\right] = 0$$

$$\nabla_{\alpha,\beta} \int d^3p \left[\ln f(p) + 1 - \alpha - \frac{\beta}{N}\frac{p^2}{2m}\right] = 0$$

- Can be satisfied by letting integrand be $= 0$:

$$\ln f(p) + 1 - \alpha - \frac{\beta}{N}\frac{p^2}{2m} = 0 \rightarrow f(p) = e^{\alpha + \frac{\beta}{N}\frac{p^2}{2m} - 1}$$

Let $C = e^{\alpha - 1} \rightarrow f(p) = C e^{\frac{\beta}{N}\frac{p^2}{2m}}$

- Now use $N = C \int d^3p\, e^{\frac{\beta}{N}\frac{p^2}{2m}} = 2\sqrt{2}\left(\frac{-\pi m N}{\beta}\right)^{3/2} C \rightarrow$

$$C = \frac{N}{2\sqrt{2}}\left(\frac{-\beta}{\pi m N}\right)^{3/2} = \left(\frac{-\beta N^{2/3}}{2\pi m N}\right)^{3/2} = \left(\frac{-\beta}{2\pi m N^{1/3}}\right)^{3/2}$$

- Now use $E = \frac{1}{N}\int d^3p \frac{p^2}{2m}\left[C e^{\frac{\beta}{N}\frac{p^2}{2m}}\right] = \frac{C}{N}\int d^3p \frac{p^2}{2m} e^{\frac{\beta}{N}\frac{p^2}{2m}} \rightarrow \frac{C}{2mN}\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \left(p_x^2 + p_y^2 + p_z^2\right) e^{\frac{\beta}{2Nm}\left(p_x^2 + p_y^2 + p_z^2\right)} = \frac{3\sqrt{2}\, C\, \pi^{3/2}\left(\frac{-mN}{\beta}\right)^{5/2}}{mN}$

$$E = \frac{3\cancel{\sqrt{2}}\,\cancel{\pi^{3/2}}}{mN}\left(\frac{-mN}{\beta}\right)^{5/2} \cdot \frac{N}{2\cancel{\sqrt{2}}}\left(\frac{-\beta}{\cancel{\pi} mN}\right)^{3/2} = \frac{3\cancel{m}N}{2\cancel{m}\beta}\cancel{\left(\frac{-mN}{\beta}\right)^{3/2}}\cancel{\left(\frac{-\beta}{mN}\right)^{3/2}} \rightarrow E = \frac{3N}{2\beta} \rightarrow \beta = \frac{3N}{2E} \rightarrow C = \frac{N}{2\sqrt{2}}\left(\frac{-1}{\pi m \cancel{N}} \cdot \frac{3N}{2E}\right)^{3/2} \rightarrow C = N\left(\frac{3}{4\pi m E}\right)^{3/2}$$

- By equipartition, $E = \frac{3}{2}k_B T \rightarrow \boxed{f(p) = \frac{N}{(2\pi m k_B T)^{3/2}} e^{-p^2/2mk_BT}}$

- This shows that the $f(p)$ that minimizes the H-factor is the Maxwell-Boltzmann distribution. For a classical gas in equilibrium, the distribution function will then almost always be Maxwell-Boltzmann.

Question 2 (Ankit Kundu)

PROBLEM - 2

Probability of being of devoid $= e^{-N(\vartheta/V)}$

where $N \equiv$ no. of particles,

$\vartheta \equiv$ volume devoid

$V \equiv$ Total volume.

Considering ideal gas, $PV = nRT$

at $P = 10^5\,Pa$, $T = 300\,K$, $V = 10\,m^3$

$$n = \frac{10^5 \times 10}{R \times 300} = \frac{10^6}{8.314459 \times 300} \text{ moles}$$

$$= 4 \times 10^3 \text{ moles}$$

$N = n \times 6.022 \times 10^{23}$ molecules/mole

$= 24.088 \times 10^{26}$ molecules.

Part 1 $\quad \vartheta =$ Volume devoid $= 1\,cm^3 = (0.01)^3\,m^3$

$= 10^{-6}\,m^3$

$\therefore$ Prob. of $1\,cm^3$ being devoid

$$= e^{-24.088 \times 10^{26} \times 10^{-6}/10}$$

$= 0$ no chance almost.

Part 2 $\quad V =$ Volume devoid $= 1\ \mathring{A}^3 = (10^{-10})^3\ m^3$

$= 10^{-30}\ m^3$

$\therefore$ Probability of $1\ \mathring{A}^3$ being devoid

$= e^{-24.088 \times 10^{26} \times 10^{-30}\ \cancel{m^3} / 10\ \cancel{m^3}}$

$= e^{-24.088 \times 10^{-3}}$

$= 0.976$ high chance of being void.

(Ans)

Question 3 (Kevin Brown)

3.) Density fluctuations: $\langle N^2\rangle - \langle N\rangle^2 = z\frac{\partial}{\partial z} z\frac{\partial}{\partial z}\ln\Xi = kTV\frac{\partial^2 P}{\partial\mu^2}$

where $z = e^{\beta\mu}$ = fugacity, $\Xi = \sum_{n=0}^{\infty} z^N \sum_n e^{-\beta E_n + \beta\mu N_n}$

- Helmholtz energy is extensive: $A(N,V,T) = Na(v)$, $v \equiv V/N$

$$\mu = \left[\frac{\partial A(N_2,V,T)}{\partial N_2}\right]_{N_2=N} \quad ; \quad P = -\left[\frac{\partial A(N,V_2,T)}{\partial V_2}\right]_{V_2=V}$$

$$\hookrightarrow \frac{\partial\mu}{\partial v} = -v\frac{\partial^2 a(v)}{\partial v^2} \qquad \frac{\partial P}{\partial\mu} = \frac{\partial P/\partial v}{\partial\mu/\partial v} = \frac{1}{v}$$

$$\frac{\partial^2 P}{\partial\mu^2} = -\frac{1}{v^2}\frac{\partial v}{\partial\mu} = \frac{1}{v^3\partial^2 a/\partial v^2} = -\frac{1}{v^3\partial P/\partial v} \rightarrow$$

$$\boxed{\langle N^2\rangle - \langle N\rangle^2 = \bar{N}kTk_T/v \quad ; \quad K_T = \frac{1}{v(-\partial P/\partial v)}}$$

- As $\bar{N}\to\infty$, almost all systems in the ensemble have density $\langle N\rangle$

Question 4 (Mingi Kim)

Problem 4. Grand partition fn of ideal gas

$z = e^{\beta\mu}$

$$\Xi(z,V,T) = \sum_{N=0}^{\infty} z^N \left(\int \frac{d^{3N}q\, d^{3N}p}{h^{3N} N!} e^{-\beta H} \right)^N$$

$$= \sum_{N=0}^{\infty} z^N \frac{V}{h^{3N} N!} \left(\int d^3p\, e^{-\frac{\beta p^2}{2m}} \right)^N$$

$$\hookrightarrow \left(\int dp\, e^{-\frac{\beta p^2}{2m}} \right)^3 = \sqrt{\frac{\pi}{\beta/2m}}^{\,3}$$

$$= \sum_{N=0}^{\infty} z^N \frac{V^N}{h^{3N} N!} \left(\frac{2m\pi}{\beta} \right)^{3N/2}$$

$$= \sum_{N=0}^{\infty} \frac{V^N}{N!} z^N \left(\frac{2m\pi}{\beta h^2} \right)^{3N/2}$$

$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$: Thermal wavelength

$$= \sum_{N=0}^{\infty} \frac{V^N}{N!} z^N \left(\frac{m k_B T}{2\pi\hbar^2} \right)^{3N/2}$$

$$= \sum_{N=0}^{\infty} \frac{V^N}{N!} z^N \left(\frac{1}{\lambda_T} \right)^{3N} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{Vz}{\lambda_T^3} \right)^N$$

$$= \exp\left(e^{\beta\mu} \frac{V}{\lambda_T^3} \right).$$

$$\Phi = U - TS - \mu N$$

$$= -k_B T \ln \Xi = -P(\mu,T) V$$

$$d\Phi = -SdT - PdV - Nd\mu$$

\# of ptcl

$$N = -\frac{\partial \Phi}{\partial \mu} = \frac{\partial}{\partial \mu}(k_B T \ln \Xi) = k_B T\, \partial_\mu \left(V \cdot e^{\beta\mu} \frac{1}{\lambda_T^3} \right)$$

$$= \frac{V e^{\beta\mu}}{\lambda_T^3}$$

chemical potential

$$\therefore\ \mu = \frac{1}{\beta} \ln\left(\frac{N\lambda_T^3}{V} \right)$$

$$= k_B T \ln\left(\frac{N\lambda_T^3}{V} \right)$$

entropy $S = -\frac{\partial \Phi}{\partial T} = \frac{\partial}{\partial T}(k_BT \ln \Xi)$

$= \frac{\partial}{\partial T}\left(k_BT \; e^{\beta\mu}\frac{V}{\lambda_T^3}\right)$

$= k_B e^{\beta\mu}\frac{V}{\lambda_T^3} + k_BT e^{\beta\mu}\frac{V}{\lambda_T^3}\mu\frac{\partial\beta}{\partial T} + k_BT e^{\beta\mu}\frac{3V}{-\lambda_T^4}\frac{\partial\lambda_T}{\partial T}$

$\beta = \frac{1}{k_BT}$

$\frac{\partial\beta}{\partial T} = -\frac{1}{k_BT^2}$

$\frac{\partial\lambda_T}{\partial T} = \sqrt{\frac{2\pi\hbar^2}{mk_B}}\left(-\frac{1}{2}\frac{1}{\sqrt{T^3}}\right)$

$= \lambda_T \times \frac{1}{-2T} = -\frac{\lambda_T}{2T}$

$= k_B e^{\beta\mu}\frac{V}{\lambda_T^3} + k_BT e^{\beta\mu}\frac{V}{\lambda_T^3}\mu\left(-\frac{1}{k_BT^2}\right) + k_BT e^{\beta\mu}\frac{3V}{-\lambda_T^4}\cdot\left(-\frac{\lambda_T}{2T}\right)$

$= e^{\beta\mu}\left(\frac{k_BV}{\lambda_T^3} - \frac{k_BTV}{\lambda_T^3}\frac{\mu}{\cancel{k_BT^2}} + \frac{3V}{\lambda_T^3}k_B\cancel{T}\frac{\lambda_T}{2\cancel{T}}\right)$

$= e^{\beta\mu}\left(\frac{5}{2}\frac{k_BV}{\lambda_T^3} - \frac{\mu V}{T\lambda_T^3}\right)$

$= \frac{e^{\beta\mu}}{\lambda_T^3}V\left(\frac{5}{2}k_B - \frac{\mu}{T}\right)$

$= \boxed{\frac{e^{\beta\mu}}{\lambda_T^3}\frac{V}{T}\left(\frac{5}{2}k_BT - \mu\right)} = N\left(\frac{5}{2}k_B - \frac{\mu}{T}\right)$

equation of state $\Phi = -P(\mu,T)\cdot V = -k_BT\ln\Xi = -k_BT\; e^{\beta\mu}\frac{V}{\lambda_T^3} = -Nk_BT$

$\boxed{\therefore\; PV = Nk_BT}$

energy $\langle E\rangle = -\frac{\partial}{\partial\beta}\ln\Xi = -\frac{\partial}{\partial\beta}\left(e^{\beta\mu}\frac{V}{\lambda_T^3}\right)$

$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m}\beta}$

$\frac{\partial\lambda_T}{\partial\beta} = \sqrt{\frac{2\pi\hbar^2}{m}}\frac{1}{2}\frac{1}{\sqrt{\beta}}$

$= \lambda_T \frac{1}{}$

$= -\left(\mu e^{\beta\mu}\frac{V}{\lambda_T^3} - e^{\beta\mu}\frac{3V}{\lambda_T^4}\frac{\partial\lambda_T}{\partial\beta}\right)$

$= -e^{\beta\mu}\left(\mu\frac{V}{\lambda_T^3} - \frac{3V}{\cancel{\lambda_T^4}\,\lambda_T^3}\frac{\cancel{\lambda_T}}{2\beta}\right) = \boxed{\frac{e^{\beta\mu}}{\lambda_T^3}V\left(\frac{3}{2}k_BT - \mu\right)}$

$N\left(\frac{3}{2}k_BT - \mu\right)$

specific heat $c_V = \frac{\partial E}{\partial T}\Big|_{V,N}$

$= \frac{\partial}{\partial T}\left(N\left(\frac{3}{2}k_BT - \mu\right)\right)_{V,N} = \frac{3}{2}k_B.$