Problem 1:

② a) first law: energy is conserved
second law: heat flows only from hot to cold reservoirs
third law: the entropy difference between reversibly connected states vanishes as $T \to 0$.

② b) The entropy is maximized in thermodynamic equilibrium.

c) A thermodynamic phase transition is a non-analyticity ① in the Gibbs free energy of a system. At a first order phase transition the first derivative of G is not continuous. At a continuous phase transition all ① first derivatives of G are continuous.

② d) If $N(E)$ is the number of microscopic states $S = k_B \ln N(E)$ is the entropy of the corresponding macroscopic state

e) If $N(E)$ is the number of states with energy E, the probability for state i with energy E_i in the microcanonical ensemble at energy E is

$$p_i = \begin{cases} \frac{1}{N(E)} & E_i = E \\ 0 & E_i \neq E \end{cases}$$ ①

It corresponds to a closed and adiabatically isolated system. ①

Problem 2

a) $$H(\vec{x}^{N}) \leq E \Leftrightarrow \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2mE} + \sum_{i=1}^{N} \frac{(\vec{r}_i - \vec{r}_{0,i})^2}{2E/m\omega^2} \leq 1$$

$\Rightarrow H(\vec{x}^{N}) \leq E$ describes a $6N$ dimensional ellipsoid with $3N$ axis $\sqrt{2mE}$ and $3N$ axis of length $\sqrt{2E/m\omega^2}$ ②

b) $$\Omega(E,N) = \Omega_{6N} (2mE)^{\frac{3N}{2}} \left(\frac{2E}{m\omega^2}\right)^{\frac{3N}{2}} = \frac{\pi^{3N}}{3N\Gamma(3N)} (2mE)^{\frac{3N}{2}} \left(\frac{2E}{m\omega^2}\right)^{\frac{3N}{2}}$$

$$= \left(\frac{2\pi E}{\omega}\right)^{3N} \frac{1}{(3N)!} \quad ①$$

$$S = k_B \ln \frac{\Omega(E,N)}{C_N} \underset{\substack{\uparrow \\ \text{oscillators} \\ \text{distinguishable}}}{=} k_B \ln \left[\left(\frac{2\pi E}{\omega}\right)^{3N} \frac{1}{h^{3N}} \frac{1}{(3N)!}\right]$$

$$\approx 3N k_B \ln \frac{2\pi E}{h\omega} - k_B 3N \ln(3N) + 3N k_B$$

$$= 3N k_B \left[1 + \ln \frac{E}{3N\hbar\omega}\right] \quad ②$$

c) QM result from lecture: $E = \hbar\omega M + \frac{3}{2}N\hbar\omega$

$$S = k_B (3N+M)\ln(3N+M) - k_B M \ln M - k_B 3N \ln(3N)$$

$$= k_B \left(3N + \frac{E\left(-\frac{3}{2}N\right.}{\left.\hbar\omega\right)}\right) \ln\left(3N + \frac{E\left(-\frac{3}{2}N\right.}{\left.\hbar\omega\right)}\right) - k_B \frac{E\left(-\frac{3}{2}N\right.}{\left.\hbar\omega\right)} \ln \frac{E\left(-\frac{3}{2}N\right.}{\left.\hbar\omega\right)}$$

$$- k_B 3N \ln(3N)$$

$$= 3N k_B \Big[\cancel{\left(1 + \frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln 3N} + \left(1 + \frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{1}{2} + \frac{E}{3N\hbar\omega}\right)$$
$$\cancel{- \left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln 3N} - \left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) - \cancel{\ln(3N)} \Big]$$

$$= 3N k_B \left[\left(\frac{E}{3N\hbar\omega} + \frac{1}{2}\right) \ln\left(\frac{1}{2} + \frac{E}{3N\hbar\omega}\right) - \left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right)\right]$$

If the number of quanta is large compared to the number of oscillators, i.e., $\frac{E}{3N\hbar\omega} >> \frac{1}{2}$

also accept $k_BT >> \hbar\omega$

$$S \simeq 3Nk_B\Big[\left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\ln\frac{E}{3N\hbar\omega} + \left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\ln\left(1+\frac{3N\hbar\omega}{2E}\right)$$

$$-\left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\ln\frac{E}{3N\hbar\omega} - \left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\ln\left(1-\frac{3N\hbar\omega}{2E}\right)\Big]$$

$$\approx 3Nk_B\left[\ln\frac{E}{3N\hbar\omega} + \left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\frac{3N\hbar\omega}{2E} + \left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\frac{3N\hbar\omega}{2E}\right]$$

$$= 3Nk_B\left[1+\ln\frac{E}{3N\hbar\omega}\right] \quad ③$$

d) If the oscillators were indistinguishable we have to use $C_N = N!\,h^{3N}$

Then $S \simeq 3Nk_B\left[1+\ln\frac{E}{3N\hbar\omega}\right] - Nk_B\ln N + k_BN$

$$= Nk_B\left[4 + \ln\left(\frac{E}{3N\hbar\omega}\right)^3\frac{1}{N}\right] \quad ①$$

This is <u>not</u> an extensive quantity. ①

Problem 3:

a) $E = m\varepsilon \Rightarrow$ m right angle turns and N-m straight

① There are $\binom{N}{m}$ ways to arrange the m turns.

Each right angle turn can go in two directions

$$\Rightarrow \quad N(E) = \binom{N}{E/\varepsilon} 2^{E/\varepsilon} \quad \textcircled{1}$$

b)
$$S \overset{\textcircled{1}}{=} k_B \ln N(E) = k_B \ln \binom{N}{E/\varepsilon} 2^{E/\varepsilon} \simeq k_B \frac{E}{\varepsilon} \ln 2$$
$$+ N k_B \ln N - \left(N - \frac{E}{\varepsilon}\right) k_B \ln \left(N - \frac{E}{\varepsilon}\right) - \frac{E}{\varepsilon} k_B \ln \frac{E}{\varepsilon}$$

$$= k_B N \left[\frac{E}{N\varepsilon} \ln 2 \cancel{+ \ln N} - \left(1 - \frac{E}{N\varepsilon}\right) \ln\left(1 - \frac{E}{N\varepsilon}\right) \cancel{- \left(1 - \frac{E}{N\varepsilon}\right) \ln N} \right.$$
$$\left. - \frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} \cancel{- \frac{E}{N\varepsilon} k_B \ln N} \right]$$

$$= k_B N \left[\frac{E}{N\varepsilon} \ln 2 - \frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} - \left(1 - \frac{E}{N\varepsilon}\right) \ln\left(1 - \frac{E}{N\varepsilon}\right) \right] \textcircled{1}$$

c)
$$\frac{1}{T} \overset{\textcircled{1}}{=} \left(\frac{\partial S}{\partial E}\right)_N = \frac{k_B}{\varepsilon} \left[\ln 2 - \ln \frac{E}{N\varepsilon} \cancel{- 1} + \ln\left(1 - \frac{E}{N\varepsilon}\right) \cancel{+ 1} \right] \quad \textcircled{1}$$

d)
$$\frac{\varepsilon}{k_B T} = \beta\varepsilon = \ln \frac{2 - 2\frac{E}{N\varepsilon}}{E/N\varepsilon}$$

$$\Rightarrow e^{\beta\varepsilon} = \frac{2 - 2\frac{E}{N\varepsilon}}{E/N\varepsilon} \Rightarrow \frac{E}{N\varepsilon}\left(e^{\beta\varepsilon} + 2\right) = 2 \Rightarrow E = \frac{2N\varepsilon}{2 + e^{\beta\varepsilon}} \quad \textcircled{2}$$

e)
$$C_N \underset{\textcircled{1}}{=} \left(\frac{\partial E}{\partial T}\right)_N = \left(\frac{\partial \frac{1}{k_B T}}{\partial T}\right)_N \left(\frac{\partial E}{\partial \beta}\right)_N = + \frac{1}{k_B T^2} \frac{2N\varepsilon}{(2 + e^{\beta\varepsilon})^2} \varepsilon e^{\beta\varepsilon}$$

$$= N k_B (\beta\varepsilon)^2 \frac{2e^{\beta\varepsilon}}{(2 + e^{\beta\varepsilon})^2} \quad \textcircled{1}$$

Problem 4:

a) The only two possible values are the energies $-\varepsilon_0$ and ε_0 themselves. ②

b) The probability for the two states in the canonical ensemble which is applicable to this situation are

$$p_1 = \frac{e^{\frac{\varepsilon_0}{k_BT}}}{e^{\frac{\varepsilon_0}{k_BT}} + e^{-\frac{\varepsilon_0}{k_BT}}} \qquad p_2 = \frac{e^{-\frac{\varepsilon_0}{k_BT}}}{e^{\frac{\varepsilon_0}{k_BT}} + e^{-\frac{\varepsilon_0}{k_BT}}}$$

②

c)

$$U \underset{\textcircled{1}}{=} p_1(-\varepsilon_0) + p_2(+\varepsilon_0) = -\varepsilon_0 \frac{e^{\frac{\varepsilon_0}{k_BT}} - e^{-\frac{\varepsilon_0}{k_BT}}}{e^{\frac{\varepsilon_0}{k_BT}} + e^{-\frac{\varepsilon_0}{k_BT}}}$$

$$= -\varepsilon_0 \tanh \frac{\varepsilon_0}{k_BT}$$

①

d) $T \to 0 \Rightarrow \frac{\varepsilon_0}{k_BT} \to +\infty \Rightarrow \tanh \frac{\varepsilon_0}{k_BT} \to 1 \Rightarrow U \to -\varepsilon_0$

$T \to \infty \Rightarrow \frac{\varepsilon_0}{k_BT} \to 0 \Rightarrow U \to 0$ ①

all values in between are possible, i.e., $]-\varepsilon_0, 0[$ ①

(if $T \to 0$ *from below* $U \to \varepsilon_0$, i.e., if negative temperatures are possible (depends on the heat bath), the range is $[-\varepsilon_0, \varepsilon_0]$)

Problem 5

a) $$Z(T) \underset{②}{=} \sum_{n_1\in\{L,R,S\}} \cdots \sum_{n_N\in\{L,R,S\}} e^{-\beta\sum_{i=1}^{N}\left\{\begin{matrix}\varepsilon & n_i\in\{L,R\}\\ 0 & n_i=S\end{matrix}\right\}}$$

$$\underset{①}{=} \left(\sum_{n\in\{L,R,S\}} e^{-\beta\left\{\begin{matrix}\varepsilon & n\in\{L,R\}\\ 0 & n=S\end{matrix}\right\}}\right)^N$$

$$= \left(1+2e^{-\beta\varepsilon}\right)^N \; ②$$

b) $$U \underset{①}{=} -\left(\frac{\partial \ln Z}{\partial \beta}\right)_N = -N\left(\frac{\partial \ln\left(1+2e^{-\beta\varepsilon}\right)}{\partial\beta}\right)_N = -N\,\frac{2e^{-\beta\varepsilon}(-\varepsilon)}{1+2e^{-\beta\varepsilon}}$$

$$= \frac{2N\varepsilon}{e^{\beta\varepsilon}+2} \; ②$$

c) They are identical. ②

If they are not identical because of some mistake in parts a) or b) accept <u>only</u> if it is acknowledged that something must be wrong.

Problem 6:

a) $$Z(T) = \frac{1}{C_N}\int d\vec{x}^{N}\, e^{-\beta H(\vec{x}^N)}$$

$$= \frac{1}{h^{3N}N!} A^N \int_0^\infty dz_1 \cdots \int_0^\infty dz_N \int d^3\vec{p}_1 \cdots \int d^3\vec{p}_N\, e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}}\, e^{-\beta mg\sum_{i=1}^{N} z_i} \quad ②$$

$$= \frac{1}{h^{3N}N!} A^N \left(\int_0^\infty dz\, e^{-\beta mgz}\right)^N \left(\int d^3\vec{p}\, e^{-\frac{\beta}{2m}\vec{p}^{\,2}}\right)^N$$

$$= \frac{1}{N!}\left[\frac{A}{h^3}\,\frac{k_BT}{mg}\,(2\pi m k_BT)^{3/2}\right]^N \quad ②$$

b) $$\rho(\vec{r}) = \int d\vec{x}^{N}\, \frac{e^{-\beta H(\vec{x}^N)}}{C_N Z(T)}\, \delta(\vec{r}_1-\vec{r}) \quad ②$$

$$= \left(\frac{mg}{Ak_BT}\right)^N (2\pi m k_BT)^{-\frac{3N}{2}} \int d^3\vec{r}_1 \cdots \int d^3\vec{r}_N \int d^3\vec{p}_1 \cdots \int d^3\vec{p}_N\, e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} - \beta mg\sum_{i=1}^{N} z_i}\, \delta(\vec{r}_1-\vec{r})$$

$$= \left(\frac{mg}{Ak_BT}\right)^N (2\pi m k_BT)^{-\frac{3N}{2}} \left(\int d^3\vec{p}\, e^{-\frac{\beta}{2m}\vec{p}^{\,2}}\right)^N A^{N-1}\left(\int_0^\infty dz\, e^{-\beta mgz}\right)^{N-1} \int d^3\vec{r}_1\, e^{-\beta mg z_1}\, \delta(\vec{r}_1-\vec{r})$$

$$= \left(\frac{mg}{Ak_BT}\right)^N (2\pi m k_BT)^{-\frac{3N}{2}} (2\pi m k_BT)^{\frac{3N}{2}} A^{N-1}\left(\frac{k_BT}{mg}\right)^{N-1} e^{-\beta mgz}$$

$$= \frac{mg}{Ak_BT}\, e^{-\beta mgz} \quad ②$$

c) law of large numbers →
there are $N\rho(\vec{r})A\Delta z$ particles within the volume $A\Delta z$ ①

$$\Rightarrow P(z)\,\overbrace{A\Delta z}^{V} = \overbrace{N\rho(\vec{r})A\Delta z}^{\text{"}N\text{"}}\, k_BT$$

$$\Rightarrow P(z) = \rho(\vec{r})Nk_BT = \frac{Nmg}{A}\, e^{-\frac{mgz}{k_BT}} = P(0)\, e^{-\frac{mgz}{k_BT}} \quad ①$$

Problem 7:

a) $$Z(T) \underset{\textcircled{1}}{=} \frac{1}{C_N}\int dx^N e^{-\beta H(x^N)} = \frac{V^N}{h^{3N}N!}\int d^3\vec{p}_1 \dots d^3\vec{p}_N \, e^{-c\beta \sum_{i=1}^{N}|\vec{p}_i|}$$

$$= \frac{V^N}{h^{3N}N!}\left(\int d^3\vec{p}\, e^{-c\beta|\vec{p}|}\right)^N \textcircled{2}$$

$$\underset{\text{polar coordinates}}{=} \frac{V^N}{h^{3N}N!}\left(4\pi\int_0^\infty dp\, p^2 e^{-c\beta p}\right)^N = \frac{V^N}{h^{3N}N!}\left(\frac{4\pi k_B^3 T^3}{c^3}\underbrace{\int_0^\infty dp\, p^2 e^{-p}}_{=2}\right)^N$$

$$= \frac{1}{N!}\left(\frac{V 8\pi k_B^3 T^3}{c^3 h^3}\right)^N \textcircled{2}$$

b) $$F \underset{\textcircled{1}}{=} -k_B T \ln Z(T) = -Nk_B T \ln\left[8\pi V\left(\frac{k_B T}{hc}\right)^3\right] + k_B T \overbrace{\ln N!}^{\approx N\ln N - N}$$

$$= -Nk_B T\left\{1 + \ln\left[8\pi \frac{V}{N}\left(\frac{k_B T}{hc}\right)^3\right]\right\} \textcircled{2}$$

c) $$P \underset{\textcircled{1}}{=} -\left(\frac{\partial F}{\partial V}\right)_{N,T} = -(-Nk_B T)\left(\frac{\partial \ln V}{\partial V}\right)_{N,T} = \frac{Nk_B T}{V}$$

$$\Rightarrow PV = Nk_B T \ \textcircled{1}$$

d) $$U \underset{\textcircled{1}}{=} -\left(\frac{\partial}{\partial\beta}\ln Z(T)\right)_{N,V} = -\left(\frac{\partial}{\partial\beta} N \ln \beta^{-3}\right)_{N,V} = \frac{3N}{\beta} = 3Nk_B T \ \textcircled{1}$$

Problem 8.

a) $$Z(T) = \sum_{\{n_i\}} e^{-\beta(E_0 - Lf)} = \sum_{n_1\in\{a,b\}} \cdots \sum_{n_N\in\{a,b\}} e^{-\beta\sum_{i=1}^{N}\varepsilon_{n_i}}\, e^{+\beta f\sum_{i=1}^{N} l_{n_i}}$$

$$\underset{\textcircled{2}}{=} \left(\sum_{n\in\{a,b\}} e^{-\beta\varepsilon_n+\beta f l_n}\right)^N = \left(e^{-\beta\varepsilon_a+\beta f l_a} + e^{-\beta\varepsilon_b+\beta f l_b}\right)^N$$ ①

b) $$U = -\left(\frac{\partial \ln Z(T)}{\partial\beta}\right) = +N\,\frac{(\varepsilon_a - f l_a)\,e^{-\beta\varepsilon_a+\beta f l_a} + (\varepsilon_b - f l_b)\,e^{-\beta\varepsilon_b+\beta f l_b}}{e^{-\beta\varepsilon_a+\beta f l_a} + e^{-\beta\varepsilon_b+\beta f l_b}}$$ ②

c) $$\langle L\rangle = \langle \sum_{i=1}^{N} l_{n_i}\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Z(T)}{\partial f}\right)_{\beta,N}$$ ②

$$= N\,\frac{l_a e^{-\beta\varepsilon_a+\beta f l_a} + l_b\, e^{-\beta\varepsilon_b+\beta f l_b}}{e^{-\beta\varepsilon_a+\beta f l_a} + e^{-\beta\varepsilon_b+\beta f l_b}}$$ ②

at $\varepsilon_a = \varepsilon_b$ and $f = 0$:

$$\langle L\rangle = N\,\frac{l_a e^{-\beta\varepsilon_a} + l_b\, e^{-\beta\varepsilon_a}}{e^{-\beta\varepsilon_a} + e^{-\beta\varepsilon_a}} = N\,\frac{l_a + l_b}{2}$$ ①

If (roughly) half of the building blocks are in state a and half of the building blocks are in state b the entropy is maximized. In the absence of energetic reasons ($\varepsilon_a = \varepsilon_b$, $f = 0$) this is therefore the preferred state. ②

Problem 9:

$$P_{p_r}(p) = \int d\vec{x}^N \rho(\vec{x}^N)\ \delta(|\vec{p}_1-\vec{p}_2|-p)$$ ③

$$= \frac{V^N \int d\vec{p}_1 - \int d\vec{p}_N\, e^{-\sum_{i=1}^{N}\frac{\beta}{2m}\vec{p}_i^{\,2}}\ \delta(|\vec{p}_1-\vec{p}_2|-p)}{V^N \int d\vec{p}_1 -- \int d\vec{p}_N\, e^{-\sum_{i=1}^{N}\frac{\beta}{2m}\vec{p}_i^{\,2}}}$$

$$= \frac{\int d\vec{p}_1 \int d\vec{p}_2\, e^{-\frac{\beta}{2m}\vec{p}_1^{\,2}-\frac{\beta}{2m}\vec{p}_2^{\,2}}\ \delta(|\vec{p}_1-\vec{p}_2|-p)}{\left(\int d\vec{p}\, e^{-\frac{\beta}{2m}p^2}\right)^2}$$ ②

$$= \frac{\int d\vec{P}\int d\vec{p}\, e^{-\frac{\beta}{m}\vec{P}^2}\, e^{-\frac{\beta}{4m}\vec{p}^{\,2}}\ \delta(|\vec{p}|-p)}{\sqrt{2\pi m k_B T}^{\,6/2}}$$ ③

$$= \frac{\sqrt{m\pi k_B T}^{\,3}}{(2\pi m k_B T)^3}\int d\vec{p}\, e^{-\frac{\beta}{4m}\vec{p}^{\,2}}\,\delta(|\vec{p}|-p)$$

$$= \frac{1}{8(m\pi k_B T)^{3/2}}\, 4\pi\, e^{-\frac{\beta}{4m}p^2}\, p^2 = \frac{1}{2\sqrt{\pi}}\,\frac{1}{(m k_B T)^{3/2}}\, p^2 e^{-\frac{\beta}{4m}p^2}$$ ②

Problem 10:

a) In a two-dimensional solid the frequency of a mode is

$$\omega^2_{(l_x, l_y, i)} = c_i^2\left[\left(\frac{\pi l_x}{L_x}\right)^2 + \left(\frac{\pi l_y}{L_y}\right)^2\right]$$

The number of modes of type i with frequency less or equal to ω is

$$\Omega_i(\omega) = \frac{1}{4}\pi\frac{\omega^2}{c_i^2}\frac{L_x}{\pi}\frac{L_y}{\pi} = \frac{L_x L_y}{4\pi}\frac{1}{c_i^2}\omega^2 \qquad ②$$

If we add all three types of modes we get

$$\Omega(\omega) = \frac{L_x L_y}{4\pi}\left(\frac{1}{c_{t,1}^2} + \frac{1}{c_{t,2}^2} + \frac{1}{c_e^2}\right)\omega^2$$

$$\Rightarrow n(\omega) = \frac{d}{d\omega}\Omega(\omega) = \frac{L_x L_y}{2\pi}\left(\frac{1}{c_{t,1}^2} + \frac{1}{c_{t,2}^2} + \frac{1}{c_e^2}\right)\omega$$

Debye frequency given by

$$3N = \int_0^{\omega_0} d\omega\, n(\omega) = \frac{L_x L_y}{2\pi}\left(\frac{1}{c_{t,1}^2} + \frac{1}{c_{t,2}^2} + \frac{1}{c_e^2}\right)\int_0^{\omega_0} d\omega\, \omega$$

$$= \frac{L_x L_y}{4\pi}\left(\frac{1}{c_{t,1}^2} + \frac{1}{c_{t,2}^2} + \frac{1}{c_e^2}\right)\omega_D^2$$

$$\Rightarrow \omega_0 = \sqrt{\frac{12\pi N}{L_x L_y\left(\frac{1}{c_{t,1}^2} + \frac{1}{c_{t,2}^2} + \frac{1}{c_e^2}\right)}} \qquad ②$$

$$\Rightarrow n(\omega) = \begin{cases} 6N\frac{\omega}{\omega_D^2} & \omega \leq \omega_0 \\ 0 & \omega > \omega_D \end{cases}$$

b) lecture → $C_N = \frac{1}{k_B T^2}\int_0^\infty d\omega\, n(\omega)\,(\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$

$$= \frac{6N\hbar^2}{k_B T^2\omega_0^2}\int_0^{\omega_0} d\omega\, \omega^3\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

$$= \frac{6N\hbar^2}{k_B T^2 \omega_0^2} \frac{1}{(\beta\hbar)^4} \int_0^{T_D/T} dx\, x^3 \frac{e^{+x}}{(e^x-1)^2} = 6Nk_B \left(\frac{T}{T_D}\right)^2 \int_0^{T_D/T} dx\, x^3 \frac{e^x}{(e^x-1)}$$ ②

c) $T \to \infty \Rightarrow T_D/T \to 0 \Rightarrow$ we can expand the integrand

$$C_V \simeq 6Nk_B \left(\frac{T}{T_D}\right)^2 \int_0^{T_D/T} dx\, x^3 \frac{1}{x^2} = 6Nk_B \left(\frac{T}{T_D}\right)^2 \frac{1}{2} \left(\frac{T_D}{T}\right)^2 = 3Nk_B$$ ②

d) $T \to 0 \Rightarrow T_D/T \to \infty \Rightarrow$ can integrate to infinity

$$C_V \simeq 6Nk_B \left(\frac{T}{T_D}\right)^2 \int_0^{\infty} dx\, x^3 \frac{e^x}{(e^x-1)^2} = \frac{36Nk_B \zeta(3)}{T_D^2} \cdot T^2$$ ②

Problem 11:

a) $Z_p = \sum_{L=0,2,4,-} (2L+1) e^{-\frac{\beta\hbar^2}{2I}L(L+1)} = \sum_{n=0}^{\infty} (4n+1) e^{-\frac{\beta\hbar^2}{2I}2n(2n+1)}$ ①

b) $Z_o = \sum_{L=1,3,5,-} 3(2L+1) e^{-\frac{\beta\hbar^2}{2I}L(L+1)} = \sum_{n=0}^{\infty} (4n+3) e^{-\frac{\beta\hbar^2}{2I}(2n+1)(2n+2)}$ ①

c) $Z(T) = \overset{①}{\frac{1}{N!}} \sum_{N_p=0}^{N} \binom{N}{N_p} Z_p^{N_p} \overset{①}{Z_o}^{N-N_p} = \frac{1}{N!}\left(Z_p + Z_o\right)^N$

particles indistinguishable

$$= \frac{1}{N!}\left(\sum_{n=0}^{\infty}(4n+1) e^{-\frac{\beta\hbar^2}{2I}2n(2n+1)} + 3\sum_{n=0}^{\infty}(4n+3) e^{-\frac{\beta\hbar^2}{2I}(2n+1)(2n+2)}\right)^N$$ ①

d) $\langle E_{rot}\rangle = -\frac{\partial \ln Z(T)}{\partial \beta} =$

$$= \frac{N\hbar^2}{2I}\,\frac{\sum_{n=0}^{\infty} 2n(2n+1)(4n+1) e^{-\frac{\beta\hbar^2}{2I}2n(2n+1)} + 3\sum_{n=0}^{\infty}(4n+3)(2n+1)(2n+2) e^{-\frac{\beta\hbar^2}{2I}(2n+1)(2n+2)}}{\sum_{n=0}^{\infty}(4n+1) e^{-\frac{\beta\hbar^2}{2I}2n(2n+1)} + 3\sum_{n=0}^{\infty}(4n+3) e^{-\frac{\beta\hbar^2}{2I}(2n+1)(2n+2)}}$$ ①

low T: $e^{-\frac{\beta\hbar^2}{2I}L(L+1)}$ vanishes very fast as L becomes larger → keep only dominant term ①

numerator: $L=0$ term is exactly 0 → $L=1$ term dominant

denominator: $L=0$ term dominant

$$\langle E_{rot}\rangle \approx \frac{N\hbar^2}{2I}\,\frac{3\cdot 6\, e^{-\frac{\beta\hbar^2}{2I}\cdot 2}}{1\, e^0} = \frac{9N\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}}$$ ①

T large ⇒ β small ⇒ difference between $e^{-\frac{\beta\hbar^2}{2I}L(L+1)}$ and $e^{-\frac{\beta\hbar^2}{2I}(L+2)(L+3)}$ small

⇒ can replace sums by integrals ①

$$N!\,Z(T) \simeq \left(\int_0^\infty (4n+1)\, e^{-\frac{\beta\hbar^2}{2I}2n(2n+1)}\, dn + 3\int_0^\infty (4n+3)\, e^{-\frac{\beta\hbar^2}{2I}(2n+1)(2n+2)}\, dn \right)^N$$

$$= \left(\int_0^\infty e^{-\frac{\beta\hbar^2}{I}u}\, du \quad + 3 \int_1^\infty e^{-\frac{\beta\hbar^2}{I}u}\, du \right)^N$$

$u = 2n^2+n \quad du = (4n+1)\,dn \qquad\qquad u = 2n^2+3n+1 \quad du = (4n+3)\,dn$

$$= \left(\frac{I}{\beta\hbar^2} + \frac{3I}{\beta\hbar^2} e^{-\frac{\beta\hbar^2}{I}} \right)^N$$

$$\langle E_{rot} \rangle = -\left(\frac{\partial \ln Z(T)}{\partial \beta}\right) \simeq N \frac{\frac{I}{\beta^2\hbar^2} + \frac{3I}{\beta^2\hbar^2} e^{-\frac{\beta\hbar^2}{I}} + \frac{3I}{\beta\hbar^2}\frac{\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}}}{\frac{I}{\beta\hbar^2} + \frac{3I}{\beta\hbar^2} e^{-\frac{\beta\hbar^2}{I}}}$$

$$= Nk_BT + N\frac{3\frac{\hbar^2}{I} e^{-\beta\frac{\hbar^2}{I}}}{1 + 3\, e^{-\frac{\beta\hbar^2}{I}}} \simeq Nk_BT + 3N\frac{\hbar^2}{I} \underset{T\,\text{large}}{\simeq} Nk_BT$$ ①

Problem 12   total for problem 11 = 8 points + 4 extra points

a)

$$Z = \sum_{\{s_i\}} e^{\beta\varepsilon_s \sum_{i=1}^{N} s_i s_{i+1} + \beta\varepsilon_0 \sum_{i=1}^{N} s_i}$$

$$= \sum_{s_1=\{0,1\}} \sum_{s_2=0}^{1} e^{\beta\varepsilon_0 s_1 + \beta\varepsilon_s s_1 s_2} \sum_{s_3=0}^{1} e^{\beta\varepsilon_0 s_2 + \beta\varepsilon_s s_2 s_3} \cdots \sum_{s_N=0}^{1} e^{\beta\varepsilon_0 s_{N-1} + \beta\varepsilon_s s_{N-1} s_N} \times e^{\beta\varepsilon_0 s_N + \beta\varepsilon_s s_N s_1}$$

$$= \operatorname{tr} \bar{T}^N \quad \text{with } \bar{T}_{ss'} = e^{\beta\varepsilon_0 s + \beta\varepsilon_s s s'}$$

②

$$\bar{T} = \begin{array}{c|cc|c} & 0 & s' \; 1 & \\ & 1 & 1 & 0 \\ & e^{\beta\varepsilon_0} & e^{\beta\varepsilon_0 + \beta\varepsilon_s} & s \; 1 \end{array}$$

$$\simeq \lambda_+^N \quad \text{where } (1-\lambda_+)(e^{\beta\varepsilon_0+\beta\varepsilon_s} - \lambda_+) - e^{\beta\varepsilon_0} = 0$$

$$\Leftrightarrow \lambda_+^2 - (1 + e^{\beta\varepsilon_0 + \beta\varepsilon_s})\lambda_+ + e^{\beta\varepsilon_0}(e^{\beta\varepsilon_s} - 1) = 0$$

$$\lambda_+ = \frac{1+e^{\beta\varepsilon_0+\beta\varepsilon_s}}{2} + \sqrt{\frac{(1+e^{\beta\varepsilon_0+\beta\varepsilon_s})^2}{4} - e^{\beta\varepsilon_0}(e^{\beta\varepsilon_s}-1)}$$ ②

b)

$$\langle s_1 \rangle = \frac{1}{N\beta}\left(\frac{\partial}{\partial\varepsilon_0}\ln Z(T)\right) = \frac{1}{\beta}\left(\frac{\partial}{\partial\varepsilon_0}\ln\lambda_+\right)$$

$$\underset{\varepsilon_0=0}{=} \frac{1}{\beta}\, \frac{\beta \frac{e^{\beta\varepsilon_s}}{2} + \dfrac{\frac{2(1+e^{\beta\varepsilon_s})\beta e^{\beta\varepsilon_s}}{4} - \beta(e^{\beta\varepsilon_s}-1)}{2\sqrt{\frac{(1-e^{\beta\varepsilon_s})^2}{4}+1}}}{\frac{1+e^{\beta\varepsilon_s}}{2} + \sqrt{\frac{(1+e^{\beta\varepsilon_s})^2}{4} - e^{\beta\varepsilon_s} + 1}}$$

$$= \frac{e^{\beta\varepsilon_s}\sqrt{\frac{(e^{\beta\varepsilon_s}-1)^2}{4}+1} + \frac{1}{2}e^{\beta\varepsilon_s}(1+e^{\beta\varepsilon_s}) - e^{\beta\varepsilon_s} + 1}{\left(1+e^{\beta\varepsilon_s} + \sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\sqrt{\frac{(e^{\beta\varepsilon_s}-1)^2}{4}+1}}$$

$$= \frac{e^{\beta\varepsilon_s}\sqrt{(e^{\beta\varepsilon_s}-1)^2+4} + e^{\beta\varepsilon_s}(e^{\beta\varepsilon_s}-1) + 2}{\left(1+e^{\beta\varepsilon_s} + \sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}$$ ②

c) At $\varepsilon_0 = 0$: $Z(T) = \left[\frac{1+e^{\beta\varepsilon_s}}{2} + \sqrt{\frac{(e^{\beta\varepsilon_s}-1)^2}{4}+1}\right]^N$

$$U = -\left(\frac{\partial \ln Z(T)}{\partial \beta}\right) = -N \frac{\varepsilon_s \frac{e^{\beta\varepsilon_s}}{2} + \frac{\frac{1}{2}(e^{\beta\varepsilon_s}-1)\varepsilon_s e^{\beta\varepsilon_s}}{2\sqrt{\frac{(e^{\beta\varepsilon_s}-1)^2}{4}+1}}}{\frac{1+e^{\beta\varepsilon_s}}{2} + \sqrt{\frac{(e^{\beta\varepsilon_s}-1)^2}{4}+1}}$$

$$= -N\varepsilon_s e^{\beta\varepsilon_s} \frac{e^{\beta\varepsilon_s}-1+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}{\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}} \quad ②$$

$$C = \frac{\partial U}{\partial T} = -k_B\beta^2\left(\frac{\partial U}{\partial \beta}\right)$$

$$= k_B\varepsilon_s^2\beta^2 N\Bigg[e^{\beta\varepsilon_s}\frac{e^{\beta\varepsilon_s}-1+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}{\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}$$

$$+e^{2\beta\varepsilon_s}\frac{\left(1+\frac{2(e^{\beta\varepsilon_s}-1)}{2\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}\right)\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}{\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)^2\left[(e^{\beta\varepsilon_s}-1)^2+4\right]}$$

$$-e^{2\beta\varepsilon_s}\frac{\left[(e^{\beta\varepsilon_s}-1)+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right]\left[\left(1+\frac{e^{\beta\varepsilon_s}-1}{\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}\right)\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}+\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)\frac{e^{\beta\varepsilon_s}-1}{\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}\right]}{\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)^2\left[(e^{\beta\varepsilon_s}-1)^2+4\right]}\Bigg]$$

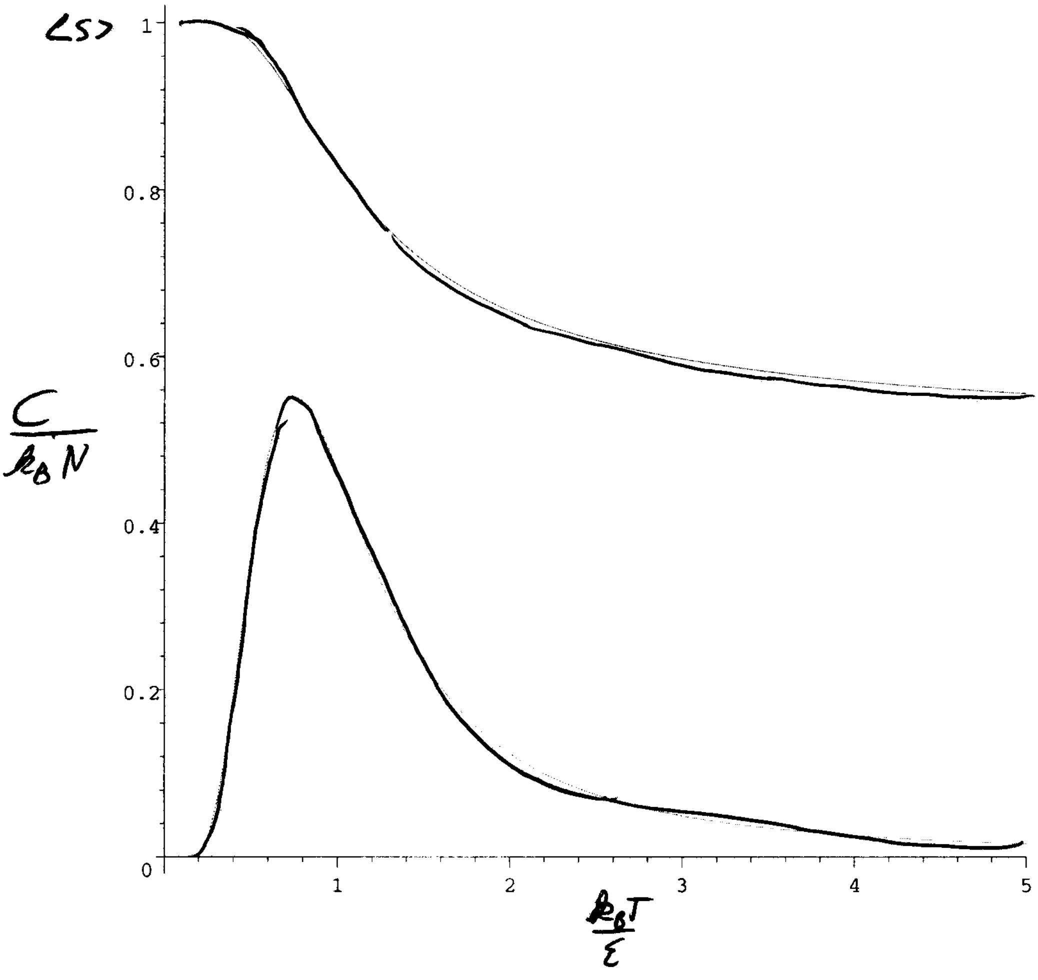
$$= 4\beta^2\varepsilon_s^2 e^{\beta\varepsilon_s} N \frac{2e^{2\beta\varepsilon_s}-e^{\beta\varepsilon_s}+5+2e^{\beta\varepsilon_s}\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}}{\left(1+e^{\beta\varepsilon_s}+\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}\right)^2\sqrt{(e^{\beta\varepsilon_s}-1)^2+4}^{\,3}} \quad ②$$

maple

↗ make these extra points

d)

② make those extra points



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Problem 13:

Lecture ⇒ $Z_N(T, B=0) = \left[e^{\beta\varepsilon}\left(1 \pm \sqrt{1-(1-e^{-4\beta\varepsilon})}\right)\right]^N$

$$= \left[e^{\beta\varepsilon}\left(1+e^{-2\beta\varepsilon}\right)\right]^N = \left[2\cosh\beta\varepsilon\right]^N$$

⇒ $Z_N(T, B=0) = \sum_{\{S_i\}} e^{\beta\varepsilon\sum_{i=1}^{N} S_i S_{i+1}}$

⇒ $\langle S_1 S_2\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle S_i S_{i+1}\rangle = \frac{1}{\beta N}\frac{\partial}{\partial\varepsilon}\ln Z_N(T, B=0)$

$= \beta k_B T\,\frac{\sinh\beta\varepsilon}{\cosh\beta\varepsilon} = \tanh\beta\varepsilon$ ④

$T \to 0$: $\beta \to \infty$: $\langle S_1 S_2\rangle \longrightarrow 1$ ②

$T \to \infty$: $\beta \to 0$: $\langle S_1 S_2\rangle \simeq \beta\varepsilon \to 0$ ②

By the way: $\varepsilon < 0$ → antiferromagnet

⇒ $T \to 0$ ⇒ $\langle S_1 S_2\rangle \longrightarrow -1$

Problem 14:

a) $$H = -\varepsilon \sum_{\{i,j\}} s_i s_j = -\frac{\varepsilon}{2}\sum_{i=1}^{N} s_i \sum_{j\ \text{neighbors of}\ i} s_j \simeq \overbrace{-\frac{\varepsilon}{2}\sum_{i=1}^{N}\sum_{j\ \text{ngbs}}(s_i-\langle s\rangle)(s_j-\langle s\rangle)}^{\text{neglect}}$$

$$\underbrace{-\frac{\varepsilon}{2}Nv\langle s\rangle^2}_{\text{irrelevant constant}} + \varepsilon v\langle s\rangle \sum_{i=1}^{N} s_i$$

$$Z = \sum_{\{s_i\}} e^{\beta\varepsilon v\langle s\rangle \sum_{i=1}^{N} s_i} = \left(\sum_{s=-1}^{1} e^{\beta\varepsilon v\langle s\rangle s}\right)^N = \left(1+2\cosh\beta\varepsilon v\langle s\rangle\right)^N$$ ①

$$\langle s\rangle = \frac{1}{N}\langle\sum_{i=1}^{N} s_i\rangle = \frac{1}{N\beta v\langle s\rangle}\left(\frac{\partial \ln Z}{\partial\varepsilon}\right)_{\beta,v,\langle s\rangle}$$

$$= \frac{1}{N\beta v\langle s\rangle}\cancel{N}\frac{2\sinh\beta\varepsilon v\langle s\rangle}{1+2\cosh\beta\varepsilon v\langle s\rangle}\cancel{\beta v\langle s\rangle} = \frac{2\sinh\beta\varepsilon v\langle s\rangle}{1+2\cosh\beta\varepsilon v\langle s\rangle}$$ ②

find solutions of

$$\frac{k_BT}{\varepsilon v}x = \frac{2\sinh x}{1+2\cosh x} \equiv g(x) \quad \left(x = \frac{\varepsilon v}{2k_BT}\langle s\rangle\right)$$

if $g'(0) > \frac{k_BT}{\varepsilon v}$: three solutions
if $g'(0) < \frac{k_BT}{\varepsilon v}$: one solution

$$\Rightarrow \frac{k_BT_c}{\varepsilon v} = g'(0) = \left.\frac{2\cosh x[1+2\cosh x]-2\sinh x\cdot 2\sinh x}{[1+2\cosh(x)]^2}\right|_{x=0} = \frac{2}{3}$$

$$\Rightarrow T_c = \frac{2\varepsilon v}{3k_B}$$ ①

b) $T > T_c$: $x = 0 \Rightarrow \langle s\rangle = 0$ ①

$T \to 0$: $\beta\to\infty \Rightarrow \frac{2\sinh\beta\varepsilon v\langle s\rangle}{1+2\cosh\beta\varepsilon v\langle s\rangle} \longrightarrow \pm 1$ ①

$$\Rightarrow \langle s\rangle = \pm 1$$

$T < T_c$ but $T \gtrsim T_c$: $\frac{T}{T_c} = 1-\delta$ $\quad \delta \ll 1$

$$\beta\varepsilon\upsilon = \frac{\varepsilon\upsilon}{k_BT} = \frac{3}{2}\frac{2\varepsilon\upsilon}{3k_BT} = \frac{3}{2}\frac{T_c}{T}$$

$$\langle s\rangle = \frac{2\sinh\frac{3}{2}\frac{T_c}{T}\langle s\rangle}{1+2\cosh\frac{3}{2}\frac{T_c}{T}\langle s\rangle} = \frac{2\sinh\frac{3}{2}\frac{\langle s\rangle}{1-\delta}}{1+2\cosh\frac{3}{2}\frac{\langle s\rangle}{1-\delta}}$$

$$= g(0) + g'(0)\left(\frac{3}{2}\frac{\langle s\rangle}{1-\delta}\right) + \frac{1}{2}g''(0)\left(\frac{3}{2}\frac{\langle s\rangle}{1-\delta}\right)^2 + \frac{1}{6}g'''(0)\left(\frac{3}{2}\frac{\langle s\rangle}{1-\delta}\right)^3 + \cdots$$

$$= 0 + \frac{2}{3}\frac{3}{2}\frac{\langle s\rangle}{1-\delta} + 0 - \frac{1}{9}\frac{27}{8}\frac{\langle s\rangle^3}{(1-\delta)^3} + \cdots$$

$$\frac{3}{8}\frac{\langle s\rangle^3}{(1-\delta)^3} = \langle s\rangle\left(\frac{1}{1-\delta}-1\right) = \langle s\rangle\frac{\delta}{1-\delta}$$

$$\frac{3}{8}\frac{\langle s\rangle^2}{(1-\delta)^2} = \delta \qquad \langle s\rangle^2 = \frac{8}{3}\delta + O(\delta^2)$$

$$\langle s\rangle \approx \pm\sqrt{\frac{8\delta}{3}}$$

②

c) $U = \langle H\rangle = -N\frac{\varepsilon}{2}\upsilon\langle s\rangle^2$

$$C = \left(\frac{\partial U}{\partial T}\right)_N = -N\varepsilon\upsilon\langle s\rangle\left(\frac{\partial\langle s\rangle}{\partial T}\right)_N$$

$$\left(\frac{\partial\langle s\rangle}{\partial T}\right)_N = g'(\beta\varepsilon\upsilon\langle s\rangle)\left[-\frac{\varepsilon\upsilon\langle s\rangle}{k_BT^2} + \frac{\varepsilon\upsilon}{k_BT}\frac{\partial\langle s\rangle}{\partial T}\right]$$

$$\left(\frac{\partial\langle s\rangle}{\partial T}\right)_N\left[\frac{3}{2}\frac{T_c}{T}g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)-1\right] = \frac{3}{2}\frac{T_c}{T^2}\langle s\rangle g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)$$

$$\left(\frac{\partial\langle s\rangle}{\partial T}\right)_N = \frac{\frac{3}{2}\frac{T_c}{T^2}\langle s\rangle g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)}{\frac{3}{2}\frac{T_c}{T}g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)-1} = \frac{3\frac{1}{T_c}\langle s\rangle g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)}{3\frac{T}{T_c}g'\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)-2\left(\frac{T}{T_c}\right)^2}$$

$$g'(x) = \frac{4+2\cosh x}{(1+2\cosh x]^2}$$

$$C = -\frac{N\varepsilon\upsilon\langle s\rangle^2}{T_c}\frac{12+6\cosh\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)}{3\frac{T}{T_c}\left[4+2\cosh\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)\right]-2\left(\frac{T}{T_c}\right)^2\left[1+2\cosh\left(\frac{3}{2}\frac{T_c}{T}\langle s\rangle\right)\right]}$$

②

$T > T_c \rightarrow \langle s \rangle = 0 \Rightarrow C = 0$

$T \rightarrow 0 \rightarrow \langle s \rangle^2 = 1$, cosh² term dominant

$$C \simeq \frac{N\varepsilon\nu T_c^2}{T_c T^2} \frac{6 \cosh \frac{3}{2}\frac{T_c}{T}}{8 \cosh^2 \frac{3}{2}\frac{T_c}{T}} \simeq \frac{3N\varepsilon\nu T_c}{2T^2} \frac{e^{\frac{3}{2}\frac{T_c}{T}} 4}{4 e^{2\frac{3}{2}\frac{T_c}{T}}}$$

$$\simeq \frac{3N\varepsilon\nu T_c}{2T^2} e^{-\frac{3}{2}\frac{T_c}{T}} = \frac{9}{4} N k_B \left(\frac{T_c}{T}\right)^2 e^{-\frac{3}{2}\frac{T_c}{T}} \quad ①$$

$T < T_c$ but $T \simeq T_c$ $\qquad \frac{T}{T_c} = 1 - \delta \quad 0 < \delta \ll 1 \quad \langle s \rangle = \pm\sqrt{\frac{8\delta}{3}}$

$$C \simeq -\frac{N\varepsilon\nu\, 8\delta}{3T_c} \frac{18}{3(1-\delta)\left[4 + 2\cosh\left(\frac{3}{2}\sqrt{\frac{8\delta}{3}}\frac{1}{1-\delta}\right)\right] - 2(1-\delta)^2\left[1 + 2\cosh\left(\frac{3}{2}\sqrt{\frac{8\delta}{3}}\frac{1}{1-\delta}\right)\right]^2}$$

$$\simeq -4Nk_B\delta \frac{18}{3(1-\delta)\left[6 + \frac{9}{4}\frac{8\delta}{3(1-\delta)^2}\right] - 2(1-\delta)^2\left[3 + \frac{9}{4}\frac{8\delta}{3(1-\delta)^2}\right]^2}$$

$$\simeq -4Nk_B\delta \frac{18}{3(1-\delta)6(1+\delta) - 2(1-2\delta)(3+6\delta)^2 + O(\delta^2)}$$

$$\simeq -4Nk_B\delta \frac{18}{18 - 36\delta - 18 + O(\delta^2)} = 2Nk_B + O(\delta)$$

①

Problem 15:

a) $$\mathcal{Z}(\mu',T) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu' N}}{C_N}\int d\vec{x}^N\, e^{-\beta H(N,\vec{x}^N)}$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu' N}}{h^{3N} N!} V^N \left(\int d\vec{p}\, e^{-\frac{\beta\vec{p}^2}{2m}}\right)^N$$ ①

② $$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu' N}}{h^{3N} N!} V^N \sqrt{2\pi m k_B T}^{\,3N} = \exp\left[V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'}\right]$$

b) $$\Omega = -k_B T \ln \mathcal{Z}(\mu',T) = -k_B T V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'}$$ ②

c) $$P = -\left(\frac{\partial\Omega}{\partial V}\right)_{\mu',T} = +k_B T\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'}$$ ①

$$N = -\left(\frac{\partial\Omega}{\partial\mu'}\right)_{V,T} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'}$$ ①

$$\Rightarrow PV = k_B T\, V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'} = N k_B T$$ ①

d) $$\Omega = -k_B T \ln \sum e^{-\beta E_i + \beta\mu' N_i}$$

$$\left(\frac{\partial\Omega}{\partial\mu'}\right)_T = -\frac{\sum N_i e^{-\beta E_i + \beta\mu' N_i}}{\sum e^{-\beta E_i + \beta\mu' N_i}} = -\langle N\rangle$$

$$\left(\frac{\partial^2\Omega}{\partial\mu'^2}\right)_T = -\frac{\beta\left(\sum N_i^2 e^{-\beta E_i + \beta\mu' N_i}\right)\left(\sum e^{-\beta E_i + \beta\mu' N_i}\right) - \beta\left(\sum N_i e^{-\beta E_i + \beta\mu' N_i}\right)^2}{\left(\sum e^{-\beta E_i + \beta\mu' N_i}\right)^2}$$

$$= -\beta\langle N^2\rangle + \beta\langle N\rangle^2 = -\beta\left[\langle N^2\rangle - \langle N\rangle^2\right]$$

$$\Rightarrow \langle N^2\rangle - \langle N\rangle^2 \overset{②}{=} -k_B T\left(\frac{\partial^2\Omega}{\partial\mu'^2}\right)_T = +k_B T\left(\frac{\partial}{\partial\mu'} V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'}\right)_T$$

$$= V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\beta\mu'} = N$$ ①

$$\frac{\sqrt{\langle N^2\rangle - \langle N\rangle^2}}{N} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \qquad \frac{1}{\sqrt{N}} = 1.3\cdot 10^{-12} \text{ for } N = 6\cdot 10^{23}$$ ①

Problem 16:

a) $Z(\mu',T) \overset{①}{=} \sum_{\{n_i\}} e^{\beta\varepsilon n_i + \beta\mu' n_i} = \left(\sum_{n=0}^{1} e^{(\beta\varepsilon+\beta\mu')n}\right)^{M}$

$= (1+e^{\beta\varepsilon+\beta\mu'})^{M}$ ②

b) $\Omega = -k_BT\ln Z(\mu',T) = -k_BTM\ln(1+e^{\beta\varepsilon+\beta\mu'})$ ①

c) $N = -\left(\frac{\partial\Omega}{\partial\mu'}\right) = k_BTM\,\frac{\beta e^{\beta\varepsilon+\beta\mu'}}{1+e^{\beta\varepsilon+\beta\mu'}} = \frac{M}{1+e^{-(\beta\varepsilon+\beta\mu')}}$ ②

d) $\frac{N}{M} = \frac{1}{e^{-\beta(\varepsilon+\mu')}+1}$ ①

ideal gas:

$$F = -Nk_BT - Nk_BT\ln\left[\frac{V}{N}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\right]$$

$$\mu' = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_BT - k_BT\ln\left(\frac{V}{N}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\right) + Nk_BT\frac{1}{N}$$

$$\underset{pV=Nk_BT}{\overset{}{=}} -k_BT\ln\left[\frac{(k_BT)^{5/2}}{p}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right]$$ ①

↑ OK to put one for last quantity

in equilibrium the chemical potential of the gas and the chemical potential of the atoms on the surface have to be identical

$$\Rightarrow \frac{N}{M} = \frac{1}{e^{-\beta\varepsilon\frac{(k_BT)^{5/2}}{p}\left(\frac{2\pi m}{h^2}\right)^{3/2}}+1}$$ ②

Problem 17

a) $\hat\rho$ hermitian

$$\Rightarrow \frac{1}{2}\begin{pmatrix} 1+a_1^* & a_3^* \\ a_2^* & 1-a_1^* \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1+a_1 & a_2 \\ a_3 & 1-a_1 \end{pmatrix}$$

$\Rightarrow$ a_1 real, $a_3 = a_2^*$ ②

$\mathrm{Tr}\,\hat\rho = 1 \Rightarrow \frac{1}{2}(1+a_1) + \frac{1}{2}(1-a_1) = 1 \Rightarrow 1 = 1$ always fulfilled ①

$\hat\rho$ positive semidefinite $\Leftrightarrow$ both eigenvalues of $\hat\rho$ non-negative

$$\det\frac{1}{2}\begin{pmatrix} 1+a_1-2\lambda & a_2 \\ a_2^* & 1-a_1-2\lambda \end{pmatrix} = (1+a_1-2\lambda)(1-a_1-2\lambda) - a_2 a_2^* = 0$$

$$4\lambda^2 - 4\lambda + 1 - a_1^2 - |a_2|^2 = 0$$

$$\lambda_{1,2} = +1 \pm \sqrt{1 + \frac{a_1^2 + |a_2|^2 - 1}{4}}$$

both ~~positive~~ non-negative $\Leftrightarrow \frac{a_1^2 + |a_2|^2 - 1}{4} \le 0 \Leftrightarrow a_1^2 + |a_2|^2 \le 1$ ②

pure state $\Leftrightarrow \lambda_2 = 0 \Leftrightarrow a_1^2 + |a_2|^2 = 1$ ①

b) $\hat\rho^H = \left(\frac{e^{-\beta\hat H}}{\mathrm{Tr}\,e^{-\beta\hat H}}\right)^H = \frac{e^{-\beta\hat H^H}}{(\mathrm{Tr}\,e^{-\beta\hat H})^*} = \frac{e^{-\beta\hat H}}{\mathrm{Tr}\,e^{-\beta\hat H}} = \hat\rho \Rightarrow \hat\rho$ hermitian ①

$|\psi\rangle$ any vector $\quad |\varphi\rangle \equiv e^{-\frac{\beta}{2}\hat H}|\psi\rangle$

$$0 \le \langle\varphi|\varphi\rangle = \langle\psi| e^{-\frac{\beta}{2}\hat H} e^{-\frac{\beta}{2}\hat H} |\psi\rangle = \langle\psi| e^{-\beta\hat H} |\psi\rangle$$

$$= \underbrace{\mathrm{Tr}\,e^{-\beta\hat H}}_{>0} \langle\psi|\hat\rho|\psi\rangle$$

$\Rightarrow \langle\psi|\hat\rho|\psi\rangle \ge 0$ ②

$\mathrm{Tr}\,\frac{e^{-\beta\hat H}}{\mathrm{Tr}\,e^{-\beta\hat H}} = \frac{1}{\mathrm{Tr}\,e^{-\beta\hat H}}\mathrm{Tr}\,e^{-\beta\hat H} = 1$ ①

Problem 18:

a) $\hat{\rho}(0) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ ②

b) $\hat{S}_z^2 = \hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $\hat{S}_x^2 = \frac{\hbar^2}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix}$ $\hat{S}_y^2 = -\frac{\hbar^2}{2} \begin{pmatrix} -1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & -1 \end{pmatrix}$

$$\Rightarrow \hat{H} = \hbar^2 \begin{pmatrix} A & 0 & B \\ 0 & 0 & 0 \\ B & 0 & A \end{pmatrix}$$ ②

eigenvalues : $\hbar^2(A+B), 0, +\hbar^2(A-B)$ ①

eigenvectors : $\hbar^2(A+B) : \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$ $0 : \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ $+\hbar^2(A-B) : \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \Rightarrow U^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} = U$$ ①

$$e^{\cancel{\frac{i}{\hbar}\hat{H}t}} = \quad \hat{H} = \hbar^2 U \begin{pmatrix} A+B & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & A-B \end{pmatrix} U^{-1}$$

$$\Rightarrow e^{\frac{i}{\hbar}\hat{H}t} = U \begin{pmatrix} e^{i\hbar(A+B)t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\hbar(A-B)t} \end{pmatrix} U^{-1}$$

$$\begin{pmatrix} e^{i\hbar(A+B)t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\hbar(A-B)t} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} e^{i\hbar(A+B)t} & 0 & \frac{1}{\sqrt{2}} e^{i\hbar(A+B)t} \\ 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} e^{i\hbar(A+B)t} & 0 & -\frac{1}{\sqrt{2}} e^{i\hbar(A-B)t} \end{pmatrix} \begin{pmatrix} e^{i\hbar At} \cos\hbar Bt & 0 & i e^{i\hbar At} \sin\hbar Bt \\ 0 & 1 & 0 \\ i e^{i\hbar At} \sin\hbar Bt & 0 & e^{i\hbar At} \cos\hbar Bt \end{pmatrix}$$ ②

$$\rho(t) = e^{-\frac{i}{\hbar}\hat{H}t}\,\rho(0)\,e^{\frac{i}{\hbar}\hat{H}t}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} e^{i\hbar At}\cos\hbar Bt & 0 & ie^{i\hbar At}\sin\hbar Bt \\ 0 & 1 & 0 \\ ie^{i\hbar At}\sin\hbar Bt & 0 & e^{i\hbar At}\cos\hbar Bt \end{pmatrix}$$

$$= \begin{pmatrix} e^{-i\hbar At}\cos\hbar Bt & 0 & -ie^{-i\hbar At}\sin\hbar Bt \\ 0 & 1 & 0 \\ -ie^{-i\hbar At}\sin\hbar Bt & 0 & e^{-i\hbar At}\cos\hbar Bt \end{pmatrix}\cancel{\begin{pmatrix} 0 & 0 & e^{i\hbar At}\,i\sin\hbar Bt \\ 0 & 0 & B \\ 0 & 0 & e^{i\hbar At}\cos\hbar Bt \end{pmatrix}}\begin{pmatrix} e^{-i\hbar At}\cos\hbar Bt & 0 & 0 \\ 0 & 0 & 0 \\ -ie^{-i\hbar At}\sin\hbar Bt & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} \cos^2\hbar Bt & 0 & i\cos\hbar Bt\sin\hbar Bt \\ 0 & 0 & 0 \\ -i\cos\hbar Bt\sin\hbar Bt & 0 & \sin^2\hbar Bt \end{pmatrix} \quad ②$$

c) $\langle\hat{S}_z(t)\rangle = \mathrm{Tr}\,\hat{S}_z\,\rho(t) = \hbar\,\mathrm{Tr}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \cos^2\hbar Bt & 0 & i\cos\hbar Bt\sin\hbar Bt \\ 0 & 0 & 0 \\ -i\cos\hbar Bt\sin\hbar Bt & 0 & \sin^2 \end{pmatrix}$

$$= \hbar\left[\cos^2\hbar Bt - \sin^2\hbar Bt\right] = \hbar\cos 2\hbar Bt \quad ②$$

Problem 19:

Since $\mathrm{Tr}\, AB^+ = \langle A, B\rangle$ is a scalar product, it fulfils the Cauchy-Schwarz inequality

$$|\langle A,B\rangle| \le \|A\|\,\|B\| = \sqrt{\langle A,A\rangle}\sqrt{\langle B,B\rangle}$$

$$\Rightarrow |\mathrm{Tr}\, AB^+| \le \sqrt{\mathrm{Tr}\, AA^+}\sqrt{\mathrm{Tr}\, BB^+}$$

a) $A = \hat\rho_1^{1/2}$ $\quad B = \hat\rho_2^{1/2}$ $\quad B^+ = B$ (ρ_2 hermitian)

$$\Rightarrow \left|\mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_2^{1/2}\right| \overset{\textcircled{2}}{\le} \sqrt{\mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_1^{1/2}}\sqrt{\mathrm{Tr}\, \hat\rho_2^{1/2}\hat\rho_2^{1/2}}$$

$$= \sqrt{\mathrm{Tr}\, \hat\rho_1}\sqrt{\mathrm{Tr}\, \hat\rho_2} = 1\cdot 1 \underset{\textcircled{2}}{=} 1$$

$$\langle \hat\rho_1^{1/2}, \hat\rho_2^{1/2}\rangle = \mathrm{Tr}\, \hat\rho_1^{1/2}(\hat\rho_2^{1/2})^+ = \mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_2^{1/2} = \mathrm{Tr}\, (\hat\rho_1^{1/2})^+\hat\rho_2^{1/2} = \mathrm{Tr}\, \hat\rho_2^{1/2}(\hat\rho_1^{1/2})^+$$

$$= \langle \hat\rho_2^{1/2}, \hat\rho_1^{1/2}\rangle$$

$$\Rightarrow \langle \hat\rho_1^{1/2}, \hat\rho_2^{1/2}\rangle = \mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_2^{1/2} \text{ real}$$

$$\Rightarrow \mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_2^{1/2} \le 1$$

b) $\mathrm{Tr}\, \hat\rho_1^{1-2^{-n}}\hat\rho_2^{2^{-n}}$ real for the same reason

$n=1$: see part a)

$n-1 \to n$: $\mathrm{Tr}\, \hat\rho_1^{1-2^{-n}}\hat\rho_2^{2^{-n}} = \mathrm{Tr}\, \hat\rho_1^{1/2}\hat\rho_1^{\frac12-2^{-n}}\hat\rho_2^{2^{-n}} = \mathrm{Tr}\, \hat\rho_1^{1/2}\left(\underset{\textcircled{1}}{\hat\rho_2^{2^{-n}}\hat\rho_1^{\frac12-2^{-n}}}\right)^+$

$$= \langle \hat\rho_1^{1/2}, \hat\rho_2^{2^{-n}}\hat\rho_1^{\frac12-2^{-n}}\rangle \le \left|\langle \hat\rho_1^{1/2}, \hat\rho_2^{2^{-n}}\hat\rho_1^{\frac12-2^{-n}}\rangle\right|$$

$$\le \sqrt{\mathrm{Tr}\, \hat\rho_1^{1/2}(\hat\rho_1^{1/2})^+}\sqrt{\mathrm{Tr}\, \underset{\textcircled{1}}{\hat\rho_2^{2^{-n}}\hat\rho_1^{\frac12-2^{-n}}}\left(\hat\rho_2^{2^{-n}}\hat\rho_1^{\frac12-2^{-n}}\right)^+}$$

$$= \sqrt{\mathrm{Tr}\, \hat\rho_1}\sqrt{\mathrm{Tr}\, \hat\rho_2^{2^{-n}}\underset{\textcircled{1}}{\hat\rho_1^{\frac12-2^{-n}}\hat\rho_1^{\frac12-2^{-n}}}\hat\rho_2^{2^{-n}}} = 1\cdot\sqrt{\mathrm{Tr}\, \hat\rho_1^{1-2^{-(n-1)}}\hat\rho_2^{2^{-(n-1)}}}$$

$$\underset{\substack{\uparrow\\ \text{by induction for } n-1}}{\le} \underset{\textcircled{1}}{1}$$

c) $\mathrm{Tr}\, \hat{\rho}_1^{\,1-2^{-n}} \hat{\rho}_2^{\,2^{-n}} \leq 1$

$$\mathrm{Tr}\, \hat{\rho}_1 \exp(-2^{-n} \log \hat{\rho}_1) \exp(2^{-n} \log \hat{\rho}_2) \leq 1$$ ①

$n \to \infty$: $\mathrm{Tr}\, \hat{\rho}_1 (1 - 2^{-n} \log \hat{\rho}_1)(1 + 2^{-n} \log \hat{\rho}_2) + O(2^{-2n}) \leq 1$ ①

$$\underbrace{\mathrm{Tr}\, \hat{\rho}_1}_{=1} - 2^{-n}\, \mathrm{Tr}\, \hat{\rho}_1 \log \hat{\rho}_1 + 2^{-n}\, \mathrm{Tr}\, \hat{\rho}_1 \log \hat{\rho}_2 + O(2^{-2n}) \leq 1$$

$$2^{-n}\, \mathrm{Tr}\, \hat{\rho}_1 (\ln \hat{\rho}_2 - \ln \hat{\rho}_1) + O(2^{-2n}) \leq 0$$

$$\mathrm{Tr}\, \hat{\rho}_1 (\ln \hat{\rho}_2 - \ln \hat{\rho}_1) + O(2^{-n}) \leq 0$$ ①

$$\xrightarrow[n \to \infty]{} \quad \mathrm{Tr}\, \hat{\rho}_1 (\ln \hat{\rho}_2 - \ln \hat{\rho}_1) \leq 0$$ ①

Problem 20:

a) $\mathrm{Tr}\, \rho_1 (\ln \hat{\rho}_2 - \ln \hat{\rho}_1) \leq 0$

$$\mathrm{Tr}\, \hat{\rho}_1 \ln \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}} \leq \mathrm{Tr}\, \hat{\rho}_1 \ln \hat{\rho}_1$$

$$\underset{S'}{\underset{\uparrow}{-k_B}} \mathrm{Tr}\, \hat{\rho}_1 \ln \hat{\rho}_1 \leq -k_B \mathrm{Tr}\, \hat{\rho}_1 \ln \underset{①}{e^{-\beta \hat{H}}} + k_B \ln \mathrm{Tr}\, e^{-\beta \hat{H}} \underbrace{\mathrm{Tr}\, \hat{\rho}_1}_{=1}$$

$$= \frac{1}{T} \mathrm{Tr}\, \hat{\rho}_1 \hat{H} - \frac{E}{T} + \frac{1}{T} \mathrm{Tr}\, \hat{\rho}_2 \hat{H} + k_B \ln \mathrm{Tr}\, e^{-\beta \hat{H}} \overbrace{\mathrm{Tr}\, \hat{\rho}_2}^{=1}$$

$$= \frac{E' - E}{T} + \cancel{\frac{1}{k_B}} \mathrm{Tr}\, \hat{\rho}_2 \ln \underset{①}{e^{-\beta \hat{H}}} + k_B \ln \mathrm{Tr}\, e^{-\beta \hat{H}} \mathrm{Tr}\, \hat{\rho}_2$$

$$= \frac{E' - E}{T} - k_B \mathrm{Tr}\, \hat{\rho}_2 \ln \hat{\rho}_2 = \frac{E' - E}{T} + S$$

$$\Rightarrow \quad S \geq S + \frac{1}{T}(E - E') \quad ②$$

(or $E - TS \geq E' - TS'$ $\Rightarrow$ the free energy is maximized)

b) $$\mathrm{Tr}\, \hat{\rho}_1 \ln \frac{e^{-\beta \hat{H} + \beta \mu' \hat{N}}}{\mathrm{Tr}\, e^{-\beta \hat{H} + \beta \mu' \hat{N}}} \leq \mathrm{Tr}\, \hat{\rho}_1 \ln \hat{\rho}_1$$

$$\Rightarrow S' = -k_B \mathrm{Tr}\, \hat{\rho}_1 \ln \hat{\rho}_1 \leq \mathrm{Tr}\, \hat{\rho}_1 \ln \frac{e^{-\beta \hat{H} + \beta \mu' \hat{N}}}{\mathrm{Tr}\, e^{-\beta \hat{H} + \beta \mu' \hat{N}}}$$

$$= \frac{1}{T} \underset{①}{\mathrm{Tr}(\hat{\rho}_1 \hat{H} - \mu \hat{\rho}_1 \hat{N})} + k_B \ln \mathrm{Tr}\, e^{-\beta \hat{H} + \beta \mu' \hat{N}} \underbrace{\mathrm{Tr}\, \hat{\rho}_1}_{=1}$$

$$= \frac{1}{T}(E' - \mu' N') - \frac{1}{T}(E - \mu' N) + \frac{1}{T} \mathrm{Tr}(\hat{\rho}_2 \hat{H} - \mu' \hat{\rho}_2 \hat{N})$$

$$+ k_B \ln \mathrm{Tr}\, \underset{①}{e^{-\beta \hat{H} + \beta \mu' \hat{N}}} \underbrace{\mathrm{Tr}\, \hat{\rho}_2}_{=1}$$

$$= -\frac{1}{T}\left[(E - E') - \mu'(N - N')\right] - k_B \mathrm{Tr}\, \hat{\rho}_2 \ln \hat{\rho}_2$$

$$= -\frac{1}{T}\left[(E - E') - \mu'(N - N')\right] + S \quad ②$$

Problem 21: Also accept periodic boundary condition

a) $$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\mathrm{Tr}\, e^{-\beta\hat{H}}}$$

$$\mathrm{Tr}\, e^{-\beta\hat{H}} = \sum_{\vec{k}} e^{-\beta\frac{\hbar^2 k^2}{2m}} = \sum_{n_x,n_y,n_z\geq 1} e^{-\beta\frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2+n_z^2)}$$

$$\approx \int_{n_x,n_y,n_z\geq 0} d^3\vec{n}\, e^{-\beta\frac{\hbar^2\pi^2}{2mL^2}\vec{n}^2} = \frac{1}{8}\left(\frac{2\pi m L^2 k_B T}{\hbar^2\pi^2}\right)^{3/2} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$= \frac{V}{\lambda_T^3} \quad ②$$

$$\langle\vec{k}'|\hat{\rho}|\vec{k}\rangle = \frac{\lambda_T^3}{V}\langle\vec{k}'|\vec{k}\rangle e^{-\beta\frac{\hbar^2 k^2}{2m}}$$

$$= \frac{\lambda_T^3}{V} e^{-\beta\frac{\hbar^2 k^2}{2m}}\delta_{\vec{k},\vec{k}'} \quad ②$$

b) $$\langle\vec{r}'|\hat{\rho}|\vec{r}\rangle = \sum_{\vec{k},\vec{k}'}\langle\vec{r}'|\vec{k}'\rangle\langle\vec{k}'|\hat{\rho}|\vec{k}\rangle\langle\vec{k}|\vec{r}\rangle$$

$$= \frac{\lambda_T^3}{V}\sum_{\vec{k}}\langle\vec{r}'|\vec{k}\rangle e^{-\beta\frac{\hbar^2 k^2}{2m}}\langle\vec{k}|\vec{r}\rangle$$

$$= \frac{\lambda_T^3}{V^2}\sum_{\vec{k}} e^{-\beta\frac{\hbar^2 k^2}{2m}} e^{i\vec{k}(\vec{r}'-\vec{r})} \quad ②$$

$$= \frac{\lambda_T^3}{V^2}\sum_{n_x,n_y,n_z\geq 1} e^{-\beta\frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2+n_z^2)} e^{i\frac{\pi}{L}(\vec{r}'-\vec{r})\begin{pmatrix}n_x\\n_y\\n_z\end{pmatrix}}$$

$$\approx \frac{\lambda_T^3}{8V^2}\int d^3\vec{n}\, e^{-\frac{\beta\hbar^2\pi^2}{2mL^2}\vec{n}^2} e^{i\frac{\pi}{L}(\vec{r}'-\vec{r})\vec{n}} \quad ②$$

$$= \frac{\lambda_T^3}{8V^2}\frac{V}{\pi^3}\int d^3\vec{n}\, e^{-\frac{\beta\hbar^2}{2m}\vec{n}^2 + i\vec{n}(\vec{r}'-\vec{r})}$$

$$= \frac{\lambda_T^3}{\;} e^{-\frac{m(\vec{r}'-\vec{r})^2}{2\beta\hbar^2}}\int d^3\vec{n}\, e^{-\frac{\beta\hbar^2}{2m}\left(\vec{n}-\frac{mi}{\beta\hbar^2}(\vec{r}'-\vec{r})\right)^2}$$

$$= \frac{\lambda_T^3}{8V\pi^3}\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} e^{-\frac{m}{2\beta\hbar^2}(\vec{r}-\vec{r}')^2}$$

$$= \frac{1}{V}\, e^{-\frac{m k_B T 4\pi^2}{2\hbar^2}(\vec{r}-\vec{r}')^2} = \frac{1}{V}\, e^{-\frac{\pi}{\lambda_T^2}(\vec{r}-\vec{r}')^2}$$ ②

Problem 22:

a) $p_n = \langle n|\hat{\rho}|n\rangle = \langle n|\dfrac{e^{-\beta\hat{H}+\beta\mu'\hat{N}}}{Tr\, e^{-\beta\hat{H}+\beta\mu'\hat{N}}}|n\rangle$

$$= \frac{e^{-\beta(\varepsilon-\mu')n}}{\sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu')n}} = \left(1-e^{-\beta(\varepsilon-\mu')}\right)e^{-\beta(\varepsilon-\mu')n}$$

$$= \left(1-ze^{-\beta\varepsilon}\right)\left(ze^{-\beta\varepsilon}\right)^n \quad 2$$

b) $$Tr\,\hat{\rho}\hat{N} = \sum_{n=0}^{\infty}\langle n|\hat{\rho}\hat{N}|n\rangle = \sum_{n=0}^{\infty} n\left(1-ze^{-\beta\varepsilon}\right)\left(ze^{-\beta\varepsilon}\right)^n \quad ①$$

$$= \left(1-ze^{-\beta\varepsilon}\right) z\frac{d}{dz}\sum_{n=0}^{\infty}\left(ze^{-\beta\varepsilon}\right)^n$$

$$= \left(1-ze^{-\beta\varepsilon}\right) z\frac{d}{dz}\frac{1}{1-ze^{-\beta\varepsilon}}$$

$$= \left(1-ze^{-\beta\varepsilon}\right) z \frac{+e^{-\beta\varepsilon}}{\left(1-ze^{-\beta\varepsilon}\right)^2} = \frac{z}{e^{\beta\varepsilon}-z} \quad ②$$

c) $\langle n|\hat{\rho}|n\rangle = \langle n|\dfrac{e^{-\beta\hat{H}+\beta\mu'\hat{N}}}{Tr\, e^{-\beta\hat{H}+\beta\mu'\hat{N}}}|n\rangle$

$$= \frac{e^{-\beta(\varepsilon-\mu')n}}{\sum_{n=0}^{1} e^{-\beta(\varepsilon-\mu')n}} = \frac{\left(ze^{-\beta\varepsilon}\right)^n}{1+ze^{-\beta\varepsilon}} \quad ②$$

d) $$Tr\,\hat{\rho}\hat{N} = \sum_{n=0}^{1}\langle n|\hat{\rho}\hat{N}|n\rangle = \frac{0\cdot\left(ze^{-\beta\varepsilon}\right)^0 + 1\cdot\left(ze^{-\beta\varepsilon}\right)^1}{\left(1+ze^{-\beta\varepsilon}\right)} \; ① = \frac{z}{e^{\beta\varepsilon}+z} \; ②$$

Problem 23

a)
$$Z_{cl}(T) = ①\frac{1}{2}\sum_{n_1,n_2=0}^{\infty} e^{-\beta\hbar\omega[n_1+n_2+1]}$$
$$= \frac{1}{2}\left[\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)}\right]^2 = \frac{e^{-\beta\hbar\omega}}{2(1-e^{-\beta\hbar\omega})^2} \quad ①$$

b) Use basis
$$|n_1 n_2\rangle^{(+)} = \frac{1}{\sqrt{2}}(|n_1 n_2\rangle + |n_2 n_1\rangle) \quad \text{for } n_1 \neq n_2$$
$$|n\, n\rangle^{(+)} = |n\, n\rangle \quad \text{for all } n$$

$$Z_B(T) = \frac{1}{2}\sum_{n_1\neq n_2} {}^{(+)}\langle n_1 n_2| e^{-\beta \hat{H}} |n_1 n_2\rangle + \sum_{n=0}^{\infty} {}^{(+)}\langle n\, n| e^{-\beta\hat{H}} |n\, n$$
②

avoid double counting

$$= \frac{1}{2}\sum_{n_1\neq n_2} e^{-\beta\hbar\omega(n_1+n_2+1)} + \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(2n+1)}$$

$$= \frac{1}{2}\left(\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty} e^{-\beta\hbar\omega(n_1+n_2+1)} - \sum_{n} e^{-\beta\hbar\omega(2n+1)}\right) + \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(2}$$

$$= \frac{e^{-\beta\hbar\omega}}{2(1-e^{-\beta\hbar\omega})^2} + \frac{e^{-\beta\hbar\omega}}{2(1-e^{-2\beta\hbar\omega})} \quad ②$$

c) Use basis
$$|n_1 n_2\rangle^{(-)} = \frac{1}{\sqrt{2}}(|n_1 n_2\rangle - |n_2 n_1\rangle) \quad \text{for } n_1 \neq n_2$$

$$Z_F(T) = ②\frac{1}{2}\sum_{n_1\neq n_2} {}^{(-)}\langle n_1 n_2| e^{-\beta\hat{H}} |n_1 n_2\rangle^{(-)} = \frac{1}{2}\sum_{n_1\neq n_2} e^{-\beta\hbar\omega(n_1+n_2+1)}$$

$$= \frac{1}{2}\left(\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty} e^{-\beta\hbar\omega(n_1+n_2+1)} - \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(2n+1)}\right)$$

$$= \frac{e^{-\beta\hbar\omega}}{2(1-e^{-\beta\hbar\omega})^2} - \frac{e^{-\beta\hbar\omega}}{2(1-e^{-2\beta\hbar\omega})} \quad ②$$

Problem 24:

1) $Z(\mu',T) = \mathrm{Tr}\, e^{-\beta\hat{H} + \beta\mu'\hat{N}}$

$$= \sum_{\substack{\{n_{\vec{k},i}\} \\ i=0 \text{ or } 1}} \prod_{\vec{k}} e^{-\beta\epsilon_{\vec{k}} n_{\vec{k},0} + \beta\mu' n_{\vec{k},0}} \, e^{-\beta(\epsilon_{\vec{k}}+\Delta) n_{\vec{k},1} + \beta\mu' n_{\vec{k},1}}$$

$$= \prod_{\vec{k}} \underbrace{\left(\sum_{n=0}^{\infty} e^{-\beta\epsilon_{\vec{k}} n + \beta\mu' n} \right)}_{\frac{1}{1-e^{-\beta(\epsilon_{\vec{k}}-\mu')}}} \underbrace{\left(\sum_{n=0}^{\infty} e^{-\beta(\epsilon_{\vec{k}}+\Delta)n + \beta\mu' n} \right)}_{\frac{1}{1-e^{-\beta(\epsilon_{\vec{k}}+\Delta-\mu')}}}$$

$$\Rightarrow \Omega = -k_B T \sum_{\vec{k}} \ln(1 - e^{-\beta(\epsilon_{\vec{k}}-\mu')}) - k_B T \sum_{\vec{k}} (1 - e^{-\beta(\epsilon_{\vec{k}}+\Delta-\mu')})$$

$$= \Omega_0(\mu',T) + \Omega_0(\mu'-\Delta,T) \quad ②$$

if $\Omega_0(\mu',T)$ is grand potential of "conventional" ideal Bose-Einstein gas

for Ω_0 $\quad \langle n \rangle = \frac{1}{V}\frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) \qquad z = e^{\beta\mu}$

$z' = e^{\beta(\mu'-\Delta)}$

here $\quad \langle n \rangle = \frac{1}{V}\frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) + \frac{1}{V}\frac{z'}{1-z'} + \frac{1}{\lambda_T^3} g_{3/2}(z')$

$$= \frac{1}{V}\frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) + \underbrace{\frac{1}{V}\frac{z e^{-\beta\Delta}}{1-z e^{-\beta\Delta}}}_{\xrightarrow[V\to\infty]{} 0 \text{ even for } z=1} + \frac{1}{\lambda_T^3} g_{3/2}(z e^{-\beta\Delta}) \quad ②$$

maximal density in excited states at $z = z_{max} = 1$

$$\langle n \rangle_{max} = \frac{1}{\lambda_T^3} g_{3/2}(1) + \frac{1}{\lambda_T^3} g_{3/2}(e^{-\beta\Delta})$$

$\Rightarrow$ transition at $\quad n = \frac{1}{\lambda_{T_c}^3} g_{3/2}(1) + \frac{1}{\lambda_{T_c}^3} g_{3/2}(e^{-\beta\Delta})$

①

if $\beta\Delta \gg 1 \Rightarrow e^{-\beta\Delta} \ll 1 \Rightarrow g_{3/2}(e^{-\beta\Delta}) \approx e^{-\beta\Delta}$

$$\lambda_{T_c}^3 n = g_{3/2}(1) + e^{-\frac{\Delta}{k_B T_c}}$$ ① (*)

$$\shortparallel$$

$$n\left(\frac{h^2}{2\pi m k_B T_c}\right)^{3/2}$$ ← equation for T_c

b) ~~At see~~ Without the second state, we would have

$$\lambda_{T_c}^3 n = g_{3/2}(1)$$

With the second state the right hand side of (*) is larger than without the second state

⇒ T_c is lower ②

Problem 25:

a) one energy per $\vec{l}$, $\varepsilon = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \vec{l}^{\,2}$

→ number of $\vec{l}$'s below ε_F is

$$\frac{4}{3}\pi\left(\frac{2mL^2\varepsilon_F}{h^2}\right)^{3/2}$$

with spin = $\frac{1}{2}$ this has to equal $\frac{N}{2}$

$$\frac{N}{2} = \frac{4}{3}\pi\left(\frac{2m\,\varepsilon_F}{h^2}\right)^{3/2} V$$

$$\frac{\hbar^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{2/3} = \varepsilon_F \quad ②$$

$$\frac{N}{V} = 9\,\frac{g}{cm^3}\,\frac{1}{63{,}5\,\frac{g}{mol}}\cdot 6\cdot10^{23}\,\frac{1}{mol} = 8.5\cdot10^{28}\,\frac{1}{m^3} \quad ②$$

$$\varepsilon_F = 1{,}13\cdot10^{-18}\,J = 7\,eV \quad ①$$

b) ~~$T_F = \frac{k_B}{1{,}13\cdot10^{-18}\,J} = 1.2\cdot10^{25}\,K$~~

$$T_F = \frac{1{,}13\cdot10^{-18}\,J}{k_B} = 8.2\cdot10^{4}\,K \quad ①$$

Problem 26:

a) $\Omega(\varepsilon)$ = # states with energy less or equal ε

$$= \# \ \vec{l}\text{'s with } \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \vec{l}^{\,2} \le \varepsilon$$

$$= \pi\left(\frac{2m\varepsilon}{\hbar^2}\frac{L^2}{(2\pi)^2}\right) = \frac{2\pi m}{h^2} A\,\varepsilon$$

$$\Rightarrow n(\varepsilon) = \frac{2\pi m}{h^2} A \quad ②$$

b)

$$N = 2\int_0^{\varepsilon_F} n(\varepsilon)\,d\varepsilon = \frac{4\pi m}{h^2} A\,\varepsilon_F \ ① \quad \Rightarrow \quad \varepsilon_F = \frac{2h^2}{4\pi m}\frac{N}{A} = \frac{h^2}{4\pi m} n \ ①$$

$$n(\varepsilon) = \frac{N}{2\varepsilon_F} \quad ①$$

c)

$$N = \int_{-\infty}^{\infty} n(\varepsilon)\,\frac{2}{e^{\beta(\varepsilon-\mu')}+1}\,d\varepsilon \quad ①$$

$$= \int_{-\infty}^{\infty} \Omega(\varepsilon)\,\frac{2\beta e^{\beta(\varepsilon-\mu')}}{(e^{\beta(\varepsilon-\mu')}+1)^2}\,d\varepsilon$$

$$\underset{t=\beta(\varepsilon-\mu')}{=} \int_{-\infty}^{\infty} \Omega(\mu'+k_BTt)\,\frac{2e^t}{(e^t+1)^2}\,dt \quad ①$$

$$= \int_{-\infty}^{\infty} \frac{N}{2}\frac{\mu'+k_BTt}{\varepsilon_F}\,\frac{2e^t}{(e^t+1)^2}\,dt$$

$$= \frac{N}{2}\cdot 2\,\frac{\mu'}{\varepsilon_F} \quad \Rightarrow \quad \mu' = \varepsilon_F \quad ①$$

d) $U = \int_{-\infty}^{\infty} n(\varepsilon)\, \varepsilon \, \frac{2}{e^{\beta(\varepsilon-\mu')}+1}\, d\varepsilon$ ①

$$= \frac{N}{2\varepsilon_F} \cdot 2 \int_{-\infty}^{\infty} \varepsilon \, \frac{1}{e^{\beta(\varepsilon-\mu')}+1}\, d\varepsilon$$

$$= \frac{N}{\varepsilon_F} \int_{-\infty}^{\infty} \frac{\varepsilon^2}{2} \, \frac{e^{\beta(\varepsilon-\mu')}}{\left(e^{\beta(\varepsilon-\mu')}+1\right)^2}\, d\beta\varepsilon$$

$$= \frac{N}{2\varepsilon_F} \int_{-\infty}^{\infty} (\mu' + k_B T t)^2 \, \frac{e^{t}}{(e^{t}+1)^2}\, dt$$

$$= \frac{N}{2\varepsilon_F} \varepsilon_F^{\,2} + \frac{N}{2\varepsilon_F} (k_B T)^2 \frac{\pi^2}{3}$$

$$= \frac{N}{2} \varepsilon_F + \frac{N\pi^2}{6} \varepsilon_F \left(\frac{k_B T}{\varepsilon_F}\right)^2$$ ①