PHY 418 Solutions Final Exam

1) $2A \leftrightarrow A_2$ let's denote $A_2 \equiv B$

Chemical equilibrium is determined by the condition on the chemical potentials

$$\boxed{2\mu_A = \mu_B}$$ see Notes Eq. (2.19.4)

or in terms of the fugacity $z = e^{\beta\mu}$, $\boxed{z_A^2 = z_B}$

To find the relation between the number of particles N and fugacity z we can use the result for classical non-interacting particles

$$\boxed{z = N Q_1}$$ see Notes (2.18.6)

where Q_1 is the classical single-particle partition function

proof: First we show this using the grand canonical ensemble

$$\mathcal{L} = \sum_N z^N Q_N = \sum_N z^N \frac{Q_1^N}{N!} = e^{zQ_1}$$

grand potential:

$$\Phi = -k_BT \ln \mathcal{L} = -k_BT zQ_1 = -k_BT e^{\beta\mu} Q_1$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = +k_BT\beta e^{\beta\mu} Q_1 = \boxed{zQ_1 = N}$$

We could also have derived this from the canonical ensemble

$$Q_N = \frac{Q_1^N}{N!}$$ Helmholtz free energy $A = -k_BT \ln Q_N$

$$A = -k_BT\left[N \ln Q_1 - N \ln N + N\right]$$ using Sterling formula

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -k_BT\left[\ln Q_1 - \ln N - \frac{N}{N} + 1\right]$$

$$\mu = -k_BT \ln \frac{Q_1}{N} \Rightarrow e^{\beta\mu} = \frac{N}{Q_1}$$

$$\Rightarrow \boxed{zQ_1 = N}$$

So $N_A = z_A Q_{1A}$, $N_B = z_B Q_{1B} = z_A^2 Q_{1B}$

$N = N_A + 2N_B$ is fixed

$$\Rightarrow \quad N = z_A Q_{1A} + 2 z_A^2 Q_{1B}$$

or
$$z_A^2 + \frac{Q_{1A}}{2Q_{1B}} z_A - \frac{N}{2Q_{1B}} = 0$$

solve the quadratic equation – take the (+) solution since we need $z_A \geqslant 0$

$$z_A = -\frac{Q_{1A}}{4Q_{1B}} + \sqrt{\left(\frac{Q_{1A}}{4Q_{1B}}\right)^2 + \frac{N}{2Q_{1B}}}$$

So
$$\frac{N_A}{N_B} = \frac{z_A Q_{1A}}{z_A^2 Q_{1B}} = \frac{Q_{1A}}{z_A Q_{1B}}$$

$$\frac{N_A}{N_B} = \frac{Q_{1A}}{Q_{1B}} \frac{1}{-\frac{Q_{1A}}{4Q_{1B}} + \left(\frac{Q_{1A}}{4Q_{1B}}\right)\sqrt{1 + \frac{8NQ_{1B}}{Q_{1A}^2}}}$$

$$\frac{N_A}{N_B} = \frac{1}{-\frac{1}{4} + \frac{1}{4}\sqrt{1 + \frac{8NQ_{1B}}{Q_{1A}^2}}}$$

$$\boxed{\frac{N_A}{N_B} = \frac{4}{-1 + \sqrt{1 + \frac{8NQ_{1B}}{Q_{1A}^2}}}}$$

All we need now is to evaluate Q_{1A} and Q_{1B}

For point particles A $\quad \varepsilon(p) = p^2/2m_A$

So
$$Q_{1A} = \frac{1}{h^3}\int_V d^3r \int_{-\infty}^{\infty} d^3p \, e^{-p^2/2m_A k_B T} = \frac{V}{h^3}\left(2\pi m_A k_B T\right)^{3/2}$$

For point particles A_2 we need that the energy is now

$\varepsilon(p) = \frac{p^2}{2m_B} - \Delta$ since there is the binding energy Δ

So
$$Q_{1B} = \frac{1}{h^3}\int_V d^3r \int_{-\infty}^{\infty} d^3p \, e^{-p^2/2m_B k_B T + \Delta/k_B T} = \frac{V}{h^3}\left(2\pi m_B k_B T\right)^{3/2} e^{\Delta/k_B T}$$

We can assume $m_B = 2m_A \equiv 2m$

Then $$\frac{Q_{1B}}{Q_{1A}^2} = \frac{\frac{V}{h^3}(4\pi m k_BT)^{3/2} e^{\Delta/k_BT}}{\frac{V^2}{h^6}(2\pi m k_BT)^3} = \frac{h^3}{V} 2^{3/2} \frac{e^{\Delta/k_BT}}{(2\pi m k_BT)^{3/2}}$$

$$= \frac{2^{3/2}}{V}\lambda^3 e^{\Delta/k_BT}$$ with $\lambda = \left(\frac{h^2}{2\pi m k_BT}\right)^{3/2}$ the thermal wavelength

So

$$\boxed{\frac{N_A}{N_B} = \frac{4}{\sqrt{1+\frac{8N\lambda^3 2^{3/2} e^{\Delta/k_BT}}{V}} - 1}}$$

Now for the system to be classical, we must have $z \ll 1$ (Notes 3-8)

$$zQ_1 = N \Rightarrow z = \frac{N}{Q_1} = \frac{N}{V}\lambda^3 \ll 1$$

If we also have $k_BT \gg \Delta$, so that $e^{\Delta/k_BT} \approx O(1)$, we can expand the square root to get $\sqrt{1+\delta} = 1 + \frac{\delta}{2}$

$$\frac{N_A}{N_B} \approx \frac{4}{\frac{8N\lambda^3 2^{3/2}}{2V} e^{\Delta/k_BT}} = \frac{e^{-\Delta/k_BT}}{2^{3/2}\left(\frac{N\lambda^3}{V}\right)} \gg 1 \quad \text{for } \Delta \ll k_BT$$

In this case $N_A \gg N_B$

But if $k_BT \ll \Delta$, so that $\frac{N\lambda^3}{V}e^{\Delta/k_BT} \gg 1$, then we have

$$\frac{N_A}{N_B} \approx \frac{4}{\sqrt{\frac{8N\lambda^3 2^{3/2}}{V} e^{\Delta/k_BT}}} = \frac{e^{-\Delta/2k_BT}}{2^{1/4}\sqrt{\frac{N\lambda^3}{V}}} \ll 1$$

In this case $N_A \ll N_B$

So when $k_BT \gg \Delta$, the thermal energy tends to break apart the molecules A_2 and so $N_A \gg N_B$

But when $k_BT \ll \Delta$, the thermal energy is too small the break apart the A_2 and so $N_B \gg N_A$

2) 1D fermi gas, non-relativistic $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$
spin degeneracy $g_s = 2$

a) The number of single-particle states, per unit volume, is given by

$$G(\varepsilon) = \frac{1}{L}\, g_s\, \frac{2k}{\Delta k} \qquad \text{with } k = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

The factor of 2 is because for each ε there is $+k$ and $-k$. $\qquad \Delta k = \frac{2\pi}{L}$

$$G(\varepsilon) = \frac{1}{L}\, \frac{2\cdot 2\cdot}{(2\pi/L)} \sqrt{\frac{2m\varepsilon}{\hbar^2}} = \frac{2}{\pi}\sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

Then the density of states is

$$g(\varepsilon) = \frac{dG}{d\varepsilon} = \frac{2}{\pi}\,\frac{1}{2}\sqrt{\frac{2m}{\hbar^2}}\,\frac{1}{\sqrt{\varepsilon}}$$

$$\boxed{g(\varepsilon) = \frac{1}{\pi}\sqrt{\frac{2m}{\hbar^2 \varepsilon}}}$$

b) $n = \frac{N}{L} = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon) = G(\varepsilon_F)$ at $T=0$

$$n = \frac{2}{\pi}\sqrt{\frac{2m\varepsilon_F}{\hbar^2}} \Rightarrow \boxed{\varepsilon_F = \left(\frac{\pi n}{2}\right)^2 \frac{\hbar^2}{2m}}$$

c) At finite T, $p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$

But since $A = E - TS$, then at $T=0$ we have

$$p = -\left(\frac{\partial E}{\partial L}\right)_{T,N} \qquad \text{where } V \to L \text{ in 1D}$$

To compute $\frac{E}{L}$ at $T=0$ we have

$$\frac{E}{L} = \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\,\varepsilon = \frac{1}{\pi}\sqrt{\frac{2m}{\hbar^2}} \int_0^{\varepsilon_F} d\varepsilon\, \frac{\varepsilon}{\sqrt{\varepsilon}}$$

$$\frac{E}{L} = \frac{1}{\pi}\sqrt{\frac{2m}{\hbar^2}}\,\frac{2}{3}\,\varepsilon_F^{3/2} = \frac{1}{\pi}\sqrt{\frac{2m}{\hbar^2}}\,\frac{2}{3}\left[\left(\frac{\pi n}{2}\right)^2 \frac{\hbar^2}{2m}\right]^{3/2}$$

$$= \frac{1}{\pi}\sqrt{\frac{2m}{\hbar^2}}\,\frac{2}{3}\left(\frac{\pi n}{2}\right)^3 \frac{\hbar^3}{(2m)^{3/2}}$$

$$= \frac{1}{\pi}\,\frac{\hbar^2}{2m}\,\frac{2}{3}\left(\frac{\pi}{2}\frac{N}{L}\right)^3 = \frac{\pi^2\hbar^2}{24m}\,\frac{N^3}{L^3}$$

$$\Rightarrow \quad E = \frac{\pi^2\hbar^2}{24\,m}\,\frac{N^3}{L^2}$$

so $$P = -\left(\frac{\partial E}{\partial L}\right)_{T,N} = \frac{\pi^2\hbar^2 N^3}{12\,m\,L^3}$$

$$\boxed{P = \frac{\pi^2\hbar^2 n^3}{12\,m}} = 2\frac{E}{L}$$

d) The argument is the same as in 3D. The number of electrons/volume that are excited at small finite T are those within $k_B T$ of ε_F, ie $g(\varepsilon_F)k_B T$

They each gain an energy $\sim k_B T$, so the total change in energy/volume is $g(\varepsilon_F)(k_B T)^2$

$$c_V = \frac{C_V}{V} = \frac{\partial}{\partial T}\left(g(\varepsilon_F)(k_B T)^2\right) \simeq \boxed{2g(\varepsilon_F)k_B^2\,T = c_V}$$

now $g(\varepsilon_F) = \frac{1}{\sqrt{\pi}} \sqrt{\frac{2m}{\hbar^2 \varepsilon_F}}$ and $\varepsilon_F = \left(\frac{\pi M}{2}\right)^2 \frac{\hbar^2}{2m}$

so $g(\varepsilon_F) = \frac{1}{\sqrt{\pi}} \frac{\sqrt{2m}}{\hbar} \frac{2}{\pi M} \frac{\sqrt{2m}}{\hbar} = \frac{2m}{\hbar^2} \frac{2}{\pi M}$

So $C_V \approx 2 g(\varepsilon_F) k_B^2 T$

$$\boxed{C_V \simeq \frac{8m}{\hbar^2 M} k_B^2 T}$$

e) At $T=0$, if $m_x = m_y = 0$ for all occupied states, then the particles will fill up to the energy ε_F of part (b).

So that we don't fill up the states with $m_x = \pm 1$ or $m_y = \pm 1$ we need that

$$\varepsilon_F < \frac{\hbar^2}{2m}\left(\frac{2\pi}{L_\perp}\right)^2$$

← lowest energy of a state with m_x or $m_y \neq 0$

So $\varepsilon_F = \left(\frac{\pi n}{2}\right)^2 \frac{\hbar^2}{2m} < \frac{\hbar^2}{2m}\left(\frac{2\pi}{L_\perp}\right)^2$

$$\Rightarrow \quad \frac{\pi n}{2} < \frac{2\pi}{L_\perp} \Rightarrow L_\perp < \frac{4}{n}$$

$$\boxed{L_\perp < 4\frac{L}{N}} \quad \text{or} \quad \frac{L_\perp}{L} < \frac{4}{N}$$

If $l = \frac{L}{N}$ is the average spacing between the particles, then

$$\boxed{L_\perp < 4l}$$

3)a) We expect that T_c will be <u>smaller</u> than T_{c0} since, compared to the case of point particles, there are more excited states in which to put the particles, hence the "normal" component of the gas can accomodate a larger particle density and we will only have to start macroscopically populating the ground state at a lower temperature.

b) the density of particles in the Bose gas is given by

$$n = n_0 + \frac{1}{V}\sum_{\vec{k},i} \frac{1}{z^{-1}e^{\beta(\varepsilon_k+\varepsilon_i)}-1}$$

where $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ and $\varepsilon_i = 0$ or ε_1

the ground state is $\varepsilon_k = \varepsilon_i = 0$

, n_0 is the density of particles in the ground state.

Doing the sum over the internal states i gives

$$n = n_0 + \underbrace{\frac{1}{V}\sum_{\vec{k}} \frac{1}{z^{-1}e^{\beta\varepsilon_k}-1}}_{i=0 \text{ term}} + \underbrace{\frac{1}{V}\sum_{\vec{k}} \frac{1}{z^{-1}e^{\beta(\varepsilon_k+\varepsilon_1)}-1}}_{i=1 \text{ term}}$$

$$= n_0 + \frac{1}{V}\sum_{\vec{k}} \frac{1}{z^{-1}e^{\beta\varepsilon_k}-1} + \frac{1}{V}\sum_{\vec{k}} \frac{1}{z^{-1}e^{\beta\varepsilon_1}e^{\beta\varepsilon_k}-1}$$

The density of states per unit volume with kinetic energy ε_k for particles with internal energy $\varepsilon_i = 0$ or $\varepsilon_i = \varepsilon_1$ is just the same $g(\varepsilon)$ as for point particles, so we get

$$n = n_0 + \int_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\beta\varepsilon} - 1} + \int_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\beta\varepsilon_1} e^{\beta\varepsilon} - 1}$$

The second term has exactly the same form as the first term, except with an effective fugacity

$\bar{z} = z e^{-\beta\varepsilon_1}$. Using $g(\varepsilon) = \frac{1}{\sqrt{\pi}\,\lambda^3} \frac{1}{k_B T} \sqrt{\frac{\varepsilon}{k_B T}}$

we get

$$\int_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\beta\varepsilon} - 1} = \frac{1}{\sqrt{\pi}\,\lambda^3} \int_0^\infty \frac{d\varepsilon}{k_B T} \frac{\sqrt{\frac{\varepsilon}{k_B T}}}{z^{-1} e^{\varepsilon/k_B T} - 1}$$

let $y = \varepsilon / k_B T$ and we get

$$\int_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\beta\varepsilon} - 1} = \frac{1}{\sqrt{\pi}\,\lambda^3} \int_0^\infty dy \, \frac{y^{1/2}}{z^{-1} e^{y} - 1} = \frac{g_{3/2}(z)}{\lambda^3}$$

And so,

$$n = n_0 + \frac{g_{3/2}(z)}{\lambda^3} + \frac{g_{3/2}(z e^{-\beta\varepsilon_1})}{\lambda^3}$$

Recall, the value of z is restricted to the range $0 \leq z \leq 1$ (since $\varepsilon_{min} = 0$), and that the largest values of the two right most terms in the above equation will occur when $z = 1$, and this value is finite.

Because $\frac{1}{\lambda^3} \sim T^{3/2}$, these two terms will decrease and eventually become smaller than n as T decreases, and it will then be necessary to populate the ground state with a finite n_0

The B-E transition temperature T_c therefore occurs when $z = 1$, $n_0 = 0$, and so is determined by

$$\boxed{\begin{gathered} n = \frac{g_{3/2}(1)}{\lambda_c^3} + \frac{g_{3/2}\left(e^{-\varepsilon_1/k_B T_c}\right)}{\lambda_c^3} \\ \text{where} \quad \lambda_c = \sqrt{\frac{h^2}{2\pi m k_B T_c}} \end{gathered}}$$

c) For $\frac{\varepsilon_1}{k_B T} \gg 1$ we have $e^{-\varepsilon_1/k_B T} \ll 1$ and so we can expand to lowest order

$$g_{3/2}\left(e^{-\varepsilon_1/k_B T_c}\right) \simeq e^{-\varepsilon_1/k_B T_c}$$

We also know that, when $\varepsilon_1 \to \infty$, this term vanishes and so we have

$$n = \frac{g_{3/2}(1)}{\lambda_{c0}^3} \quad \text{where } \lambda_{c0} = \sqrt{\frac{h^2}{2\pi m k_B T_{c0}}}$$

so the result in part (b) becomes

$$n = \frac{g_{3/2}(1)}{\lambda_{c0}^3} = \frac{g_{3/2}(1)}{\lambda_c^3} + \frac{e^{-\varepsilon_1/k_B T_c}}{\lambda_c^3}$$

$$\Rightarrow \quad \frac{1}{\lambda_{c0}^3} = \frac{1}{\lambda_c^3}\left[1 + \frac{e^{-\varepsilon_1/k_B T_c}}{g_{3/2}(1)}\right]$$

$$\Rightarrow \quad \left(\frac{\lambda_{c0}}{\lambda_c}\right)^3 = \left(\frac{T_c}{T_{c0}}\right)^{3/2} = \left[1 + \frac{e^{-\varepsilon_1/k_B T_c}}{g_{3/2}(1)}\right]^{-1}$$

$$\frac{T_c}{T_{c0}} = \left[1 + \frac{e^{-\varepsilon_1/k_B T_c}}{g_{3/2}(1)}\right]^{-2/3}$$

$$\simeq 1 - \frac{2}{3}\frac{e^{-\varepsilon_1/k_B T_c}}{g_{3/2}(1)} \quad \text{for small } e^{-\varepsilon_1/k_B T_c}$$

So

$$\boxed{\frac{T_c - T_{c0}}{T_c} = -\frac{2}{3}\frac{e^{-\varepsilon_1/k_B T_{c0}}}{g_{3/2}(1)}}$$

so $T_c < T_{c0}$ as in part (a)

Note in the last step we took $e^{-\varepsilon_1/k_B T_c} \longrightarrow e^{-\varepsilon_1/k_B T_{c0}}$ since the difference will only give higher order terms in $e^{-\varepsilon_1/k_B T_{c0}}$

To see more explicitly the last step, ie that we can replace $\beta_c \to \beta_{c0}$ in the exponential term, we can do as follows

$$\frac{T_c}{T_{c0}} = 1 - \frac{2\, e^{-\beta_c \varepsilon_1}}{3\zeta(3/2)} = 1 - \frac{2}{3\zeta(3/2)}\, e^{-\beta_{c0}\varepsilon_1\left(\frac{T_{c0}}{T_c}\right)}$$

$$= 1 - \frac{2}{3\zeta(3/2)}\, e^{-\beta_{c0}\varepsilon_1\left(1 - \frac{2}{3\zeta(3/2)} e^{-\beta_c\varepsilon_1}\right)}$$

$$= 1 - \frac{2}{3\zeta(3/2)}\, e^{-\beta_{c0}\varepsilon_1}\, \underbrace{e^{\frac{2}{3\zeta(3/2)}\beta_{c0}\varepsilon_1 e^{-\beta_c\varepsilon_1}}}_{\substack{\text{expand. To lowest} \\ \text{order we get } e^{\delta} \simeq 1+\delta \\ 1 + \frac{2}{3\zeta(3/2)}\beta_{c0}\varepsilon_1 e^{-\beta_c\varepsilon_1}}}$$

where $e^{-\beta_c\varepsilon_1} \ll 1$ since $\beta_c\varepsilon_1 \gg 1$

$$\frac{T_c}{T_{c0}} \simeq 1 - \frac{2}{3\zeta(3/2)}\, e^{-\beta_{c0}\varepsilon_1} \underbrace{- \left[\frac{2}{3\zeta(3/2)}\right]^2 e^{-\beta_{c0}\varepsilon_1}\, e^{-\beta_c\varepsilon_1}\, \beta_{c0}\varepsilon_1}_{\uparrow}$$

this term is 2nd order in the small quantity $e^{-\beta_{c0}\varepsilon_1} \approx e^{-\beta_c\varepsilon_1}$ since we previously dropped such 2nd order terms, we should drop this one too, so the leading order we get

$$\frac{T_c}{T_{c0}} \simeq 1 - \frac{2}{3\zeta(3/2)}\, e^{-\beta_{c0}\varepsilon_1}$$