19) Entropy of Identical Particles:

consider entropy when $N \gg 1$

a) Consider gas to be identical non-interacting fermions. Show:

$$S = -k_B \sum_j \left[\langle n_j \rangle \ln \langle n_j \rangle + (1 - \langle n_j \rangle) \ln (1 - \langle n_j \rangle) \right]$$

where $\langle n_j \rangle = \left(e^{\beta(\varepsilon_j - \mu)} + 1 \right)^{-1}$ for fermion

$$\ln \Xi = \sum_j \ln \left(1 + e^{-\beta(\varepsilon_j - \mu)} \right) \text{ for fermion}$$

grand canonical potential

$$\Phi = -k_B T \ln \Xi$$

$$\stackrel{!}{=} -k_B T \left(\sum_j \ln \left(1 + e^{-\beta(\varepsilon_j - \mu)} \right) \right)$$

since $\langle n_j \rangle = \left(e^{\beta(\varepsilon_j - \mu)} + 1 \right)^{-1}$

$$e^{-\beta(\varepsilon_j - \mu)} = \left(\frac{1}{\langle n_j \rangle} - 1 \right)^{-1}$$

$$e^{-\beta(\varepsilon_j - \mu)} = \frac{\langle n_j \rangle}{1 - \langle n_j \rangle}$$

then $\Phi = -k_B T \left(\sum_j \ln \left(1 + \frac{\langle n_j \rangle}{1 - \langle n_j \rangle} \right) \right)$

$$\stackrel{!}{=} -k_B T \sum_j \ln \left(\frac{1}{1 - \langle n_j \rangle} \right)$$

$$\stackrel{!}{=} k_B T \sum_j \ln \left(1 - \langle n_j \rangle \right)$$

use relation: $S = \left(-\frac{\partial \Phi}{\partial T}\right)_{V,u}$

$$S = \left(-\frac{\partial \Phi}{\partial \beta}\right)_{V,u}\left(\frac{\partial \beta}{\partial T}\right)_{V,u} = \frac{1}{k_B T^2}\left(\frac{\partial \Phi}{\partial \beta}\right)_{V,u}$$

$$\hookrightarrow = \frac{1}{k_B T^2}\frac{\partial}{\partial \beta}\left(\frac{1}{\beta}\sum_j \ln\left(1 - \langle n_j\rangle\right)\right)_{u,V}$$

$$= \frac{1}{k_B T^2}\left(\frac{-1}{\beta^2}\ln(1-\langle n_j\rangle) + \frac{1}{\beta}\frac{1}{1-\langle n_j\rangle}\left(\frac{-\partial}{\partial \beta}\langle n_j\rangle\right)_{u,V}\right)$$

$$= \frac{1}{k_B T^2}\left(\frac{-1}{\beta^2}\ln(1-\langle n_j\rangle) + \frac{1}{\beta}\frac{1}{1-\langle n_j\rangle}\frac{-\partial}{\partial \beta}\left(\left[e^{\beta(\varepsilon_j - u)} - 1\right]^{-1}\right)\right)$$

$$= \frac{1}{k_B T^2}\left(\frac{-1}{\beta^2}\ln(1-\langle n_j\rangle) + \frac{1}{\beta}\frac{1}{1-\langle n_j\rangle}\langle n_j\rangle^2(\varepsilon_j - u)\, e^{\beta(\varepsilon_j - u)}\right)$$

Since $e^{\beta(\varepsilon_j - u)} = \frac{1}{\langle n_j\rangle} - 1 = \frac{1-\langle n_j\rangle}{\langle n_j\rangle}$

and $\varepsilon_j - u = \frac{1}{\beta}\ln\left(\frac{1-\langle n_j\rangle}{\langle n_j\rangle}\right)$

$$= \frac{1}{k_B T^2}\left(\frac{-1}{\beta^2}\ln(1-\langle n_j\rangle) + \frac{1}{\beta^2}\frac{1}{\cancel{1-\langle n_j\rangle}}\langle n_j\rangle^{\cancel{2}}\frac{\cancel{1-\langle n_j\rangle}}{\cancel{\langle n_j\rangle}}\ln\left(\frac{1-\langle n_j\rangle}{\langle n_j\rangle}\right)\right)$$

$$= -k_B\left(\ln(1-\langle n_j\rangle) - \langle n_j\rangle\ln\left(\frac{1-\langle n_j\rangle}{\langle n_j\rangle}\right)\right)$$

$$= -k_B\left(\ln(1-\langle n_j\rangle) - \langle n_j\rangle\left(\ln(1-\langle n_j\rangle) - \ln\langle n_j\rangle\right)\right)$$

$$\boxed{S = -k_B\sum_j\left[(1-\langle n_j\rangle)\ln(1-\langle n_j\rangle) + \langle n_j\rangle\ln\langle n_j\rangle\right]}$$

b) Show $S = -k_B \sum_j \left[\langle n_j \rangle \ln \langle n_j \rangle - (1 + \langle n_j \rangle) \ln (1 + \langle n_j \rangle) \right]$
for bosons

know $\Phi = -k_B T \ln \Xi$

$$\ln \Xi = -\sum_j \ln \left(1 - e^{-\beta(\varepsilon_j - \mu)} \right) \text{ for bosons}$$

$$\Phi = k_B T \sum_j \ln \left(1 - e^{-\beta(\varepsilon_j - \mu)} \right)$$

know $\langle n_j \rangle_{Boson} = \left[e^{\beta(\varepsilon_j - \mu)} - 1 \right]^{-1}$

$$e^{-\beta(\varepsilon_j - \mu)} = \left[\frac{1}{\langle n_j \rangle} + 1 \right]^{-1} = \frac{\langle n_j \rangle}{1 + \langle n_j \rangle}$$

$$\Phi = k_B T \sum_j \ln \left(1 - \frac{\langle n_j \rangle}{1 + \langle n_j \rangle} \right)$$

$$= k_B T \sum_j \ln \left(\frac{1}{1 + \langle n_j \rangle} \right)$$

$$= -k_B T \sum_j \ln \left(1 + \langle n_j \rangle \right)$$

$$S = -\left(\frac{\partial \Phi}{\partial T} \right)_{V,\mu} = \left(-\frac{\partial \Phi}{\partial \beta} \right)_{V,\mu} \left(\frac{\partial \beta}{\partial T} \right)_{V,\mu}$$

$$= \frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left(-\frac{1}{\beta} \ln (1 + \langle n_j \rangle) \right)_{V,\mu}$$

$$= \frac{1}{k_B T^2} \left(\frac{1}{\beta^2} \ln (1 + \langle n_j \rangle) - \frac{1}{\beta} \frac{1}{1 + \langle n_j \rangle} \left(\frac{\partial}{\partial \beta} \langle n_j \rangle \right)_{V,\mu} \right)$$

$$= \frac{1}{k_B T^2} \left(\frac{1}{\beta^2} \ln (1 + \langle n_j \rangle) - \frac{1}{\beta} \frac{1}{1 + \langle n_j \rangle} \frac{\partial}{\partial \beta} \left(\left[e^{\beta(\varepsilon_j - \mu)} - 1 \right]^{-1} \right) \right)$$

$$= \frac{1}{k_B T^2} \left(\frac{1}{\beta^2} \ln (1 + \langle n_j \rangle) - \frac{1}{\beta} \frac{1}{1 + \langle n_j \rangle} \left(-\langle n_j \rangle^2 \right) (\varepsilon_j - \mu) e^{\beta(\varepsilon_j - \mu)} \right)$$

know $e^{\beta(\varepsilon_j - u)} = \frac{1}{\langle n_j \rangle} + 1 = \frac{1+\langle n_j \rangle}{\langle n_j \rangle}$

and $\varepsilon_j - u = \frac{1}{\beta} \ln \left(\frac{1+\langle n_j \rangle}{\langle n_j \rangle} \right)$

$$S \overset{!}{=} \frac{1}{k_B T^2} \left(\frac{1}{\beta^2} \ln\left(1+\langle n_j \rangle\right) + \frac{1}{\beta^2} \frac{1}{\cancel{1+\langle n_j \rangle}} \langle n_j \rangle^{\cancel{2}} \frac{\cancel{1+\langle n_j \rangle}}{\cancel{\langle n_j \rangle}} \ln\left(\frac{1+\langle n_j \rangle}{\langle n_j \rangle}\right) \right)$$

$$\overset{!}{=} -k_B \left(-\ln\left(1+\langle n_j \rangle\right) - \langle n_j \rangle \ln\left(\frac{1+\langle n_j \rangle}{\langle n_j \rangle} \right) \right)$$

$$\overset{!}{=} -k_B \left(-\ln\left(1+\langle n_j \rangle\right) - \langle n_j \rangle \left[\ln\left(1+\langle n_j \rangle\right) - \ln\left(\langle n_j \rangle\right) \right] \right)$$

$$\boxed{S \overset{!}{=} -k_B \left(\langle n_j \rangle \ln \langle n_j \rangle - \left(1+\langle n_j \rangle\right) \ln\left(1+\langle n_j \rangle\right) \right)}$$

c) $\langle n_j \rangle = \left(e^{\beta(\varepsilon_j - u)} \pm 1\right)^{-1}$ $+$ for fermion
$-$ for boson

As $T \to 0$:

if $\varepsilon_j > u$: $\quad \langle n_j \rangle = \left[e^{\infty} \pm 1\right]^{-1} = 0$

$$S = -k_B \left[\langle n_j \rangle \ln \langle n_j \rangle \pm (1 \mp \langle n_j \rangle) \ln (1 \mp \langle n_j \rangle)\right]$$

$$\overset{!}{=} -k_B \left[(0) \ln (0) \pm 1 \ln (1)\right]$$

since $\lim_{x \to 0} x \ln x = \lim_{x \to 0} \frac{\ln x}{\frac{1}{x}} = \lim_{x \to 0} \frac{\frac{1}{x}}{\frac{-1}{x^2}} = \lim_{x \to 0} x = 0$

$$\overset{!}{=} -k_B (0 \pm 1(0)) = 0$$

If $\varepsilon_j < u$: $\quad \langle n_j \rangle = \left[e^{-\infty} \pm 1\right]^{-1} = \pm 1$,

$$S = -k_B \left[\langle n_j \rangle \ln \langle n_j \rangle \pm (1 \mp \langle n_j \rangle) \ln (1 \mp \langle n_j \rangle)\right]$$

$$\overset{!}{=} -k_B \left[\pm 1 \ln (\pm 1) \pm (1 \mp (\pm 1)) \ln (1 \mp (\pm 1))\right]$$

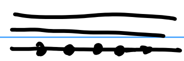
For Fermion: $\quad -k_B \left(\ln (1) + (1 - 1) \ln (0)\right) = 0$

For Boson: $\quad -k_B \left(\underbrace{-1 \ln (-1)} - (1 - 1) \ln (0)\right) = \text{undefined.}$

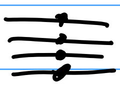
This makes sense since we assumed $\varepsilon_j > u$ when we do the Geometric sequence sum for Bosons.

$\Rightarrow$ $S = 0$ suggests that there is only one microstate at $T = 0$.

for bosons, all particles go to lowest energy state (Bose-Einstein Condensate).



For fermion, due to Pauli-exclusion, it can have a single configuration of



, each fermion occupying each state.

d) For $\langle n_j \rangle \ll 1$:

Taylor for $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots$

$$S = -k_B \sum \left[\langle n_j \rangle \ln \langle n_j \rangle \pm (1 \mp \langle n_j \rangle) \ln (1 \mp \langle n_j \rangle) \right]$$

$$\overset{!}{=} -k_B \sum \left[\langle n_j \rangle \ln \langle n_j \rangle \pm (1 \mp \langle n_j \rangle)(\mp \langle n_j \rangle + \mathcal{O}(\langle n_j \rangle^2)) \right]$$

$$\overset{!}{=} -k_B \sum \langle n_j \rangle \ln \langle n_j \rangle \pm \left(\mp \langle n_j \rangle + \mathcal{O}(\langle n_j \rangle^2) \right)$$

$$\overset{!}{=} -k_B \sum \langle n_j \rangle \left(\ln \langle n_j \rangle - 1 \right) \quad \text{for both case}$$

if $\langle n_j \rangle \ll 1$, $\ln \langle n_j \rangle$ = large negative

$$\boxed{S \overset{\sim}{=} -k_B \sum \langle n_j \rangle \ln \langle n_j \rangle}$$

e) Find entropy of single particle, S_1 then extend that to N particles

$$S = -k_B \sum_j \langle n_j \rangle \ln \langle n_j \rangle$$

For N-particle $\sum_j \langle n_j \rangle = N$

$$\sum_j \langle n_j \rangle = \sum_j \left[e^{\beta(\varepsilon_j - u)} \pm 1 \right]^{-1} = N$$

At classical limit: $\langle n_j \rangle \ll 1$

$$\left[e^{\beta\varepsilon_j} e^{-\beta u} \pm 1 \right]^{-1} \ll 1$$

This implies: $e^{\beta(\varepsilon_j - u)} \gg 1$ and $\varepsilon_j \gg u$

then $\langle n_j \rangle = \dfrac{1}{e^{\beta(\varepsilon_j - u)} \pm 1} \cong e^{-\beta(\varepsilon_j - u)}$

$$\langle N \rangle = \sum_j \langle n_j \rangle = \sum_j e^{-\beta(\varepsilon_j - u)}$$

$$\langle N \rangle = e^{\beta u} \sum_j e^{-\beta\varepsilon_j}$$

or $e^{\beta u} = \dfrac{\langle N \rangle}{\sum_j e^{-\beta\varepsilon_j}}$

then $\langle n_j \rangle = e^{-\beta\varepsilon_j} e^{\beta u} = \langle N \rangle \dfrac{e^{-\beta\varepsilon_j}}{\sum_j e^{-\beta\varepsilon_j}}$

$$\frac{\langle n_j \rangle}{\langle N \rangle} = \frac{e^{-\beta\varepsilon_j}}{\sum_j e^{-\beta\varepsilon_j}} =$$ probability of finding a particle in single particle state

$$S = -k_B \sum_j \langle n_j \rangle \ln \langle n_j \rangle$$

for $\langle n_j \rangle = \langle N \rangle \dfrac{e^{-\beta\varepsilon_j}}{\sum_j e^{-\beta\varepsilon_j}} = \dfrac{\langle N \rangle}{q_1} e^{-\beta\varepsilon_j}$

$$S = -k_B \sum_j \langle N \rangle \frac{e^{-\beta\varepsilon_j}}{q_1} \ln\left(\frac{\langle N \rangle}{q_1} e^{-\beta\varepsilon_j}\right)$$

we have $S(\langle N \rangle = 1) = S_1 = -k_B \sum_j \dfrac{e^{-\beta\varepsilon_j}}{q_1} \ln\left(\dfrac{e^{-\beta\varepsilon_j}}{q_1}\right)$

$$S = -k_B \sum_j \langle N \rangle \frac{e^{-\beta\varepsilon_j}}{q_1}\left(\ln(N) + \ln\left(\frac{e^{-\beta\varepsilon_j}}{q_1}\right)\right)$$

$$= \langle N \rangle S_1 - \sum_j k_B \langle N \rangle \ln(\langle N \rangle) \frac{e^{-\beta\varepsilon_j}}{q_1}$$

but $\sum_j \dfrac{e^{-\beta\varepsilon_j}}{q_1} = 1$

$\boxed{S = \langle N \rangle S_1 - k_B \langle N \rangle \ln(\langle N \rangle)}$ where $S_1 = -k_B \sum_j \dfrac{e^{-\beta\varepsilon_j}}{q_1} \ln\left(\dfrac{-e^{\beta\varepsilon_j}}{q_1}\right)$

We see that compared to N distinguishable particles $S = N S_1$ we have an extra factor of $-k_B N \ln N$ that we need to take account.

where $S_{dis} = \langle N \rangle S_1$
and $S_{ind} = \langle N \rangle (S_1 - k_B \ln N)$

which is equivalent to $Q_{dis} = Q_1^N$, vs $Q_{ind} = \frac{1}{N!} Q_1^N$

20) Consider a collection of non-interacting particles with mass m, 0 spin, confined to a region of dimension L,

with single-particle density of states:

$$g(k)dk \quad \text{and} \quad g(\varepsilon)d\varepsilon$$

Consider large containers, so $k \gg \frac{2\pi}{L}$

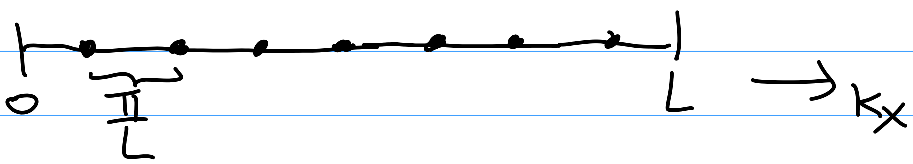
a) For non-relativistic ($\varepsilon \ll mc^2$) free particles find $g(k)$ and $g(\varepsilon)$ in 3D, 2D, 1D.

with QM, we know the solution for a 1D ∞ well with length: L: with hard wall BC:

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_x \pi}{L} x\right) = \sqrt{\frac{2}{L}} \sin(k_x x)$$

$$\text{with} \quad \varepsilon_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2} = \frac{k_x^2 \hbar^2}{2m} \quad \text{or} \quad k_x = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

$$\text{and} \quad k_x = \frac{n_x \pi}{L} \quad \text{for } n_x = 1, 2, 3 \cdots\cdots$$



for $k_x = \frac{n_x \pi}{L}$, we see that each point (single particle state) is spaced with distance $\frac{\pi}{L}$

$$g(k)dk = \# \text{ of S.P. states from } k + dk$$

since states are evenly distributed, with length dk_x, then # of states we find is

$$dN = \frac{dk_x}{\text{space between}} = \frac{dk_x}{\frac{\pi}{L}} = \frac{L}{\pi} dk_x$$

so $\underline{g(k) = \frac{L}{\pi} \quad \text{for 1D}}$

for: $\frac{L}{\pi} dk \Rightarrow g(\varepsilon) d\varepsilon$

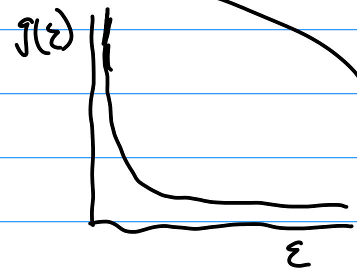
$$\hookrightarrow \frac{L}{\pi} \frac{dk}{d\varepsilon} d\varepsilon = \frac{L}{\pi} \frac{d}{d\varepsilon}\left(\sqrt{\frac{2m\varepsilon}{\hbar^2}}\right) d\varepsilon$$

$$= \frac{L}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2\sqrt{\varepsilon}} d\varepsilon$$

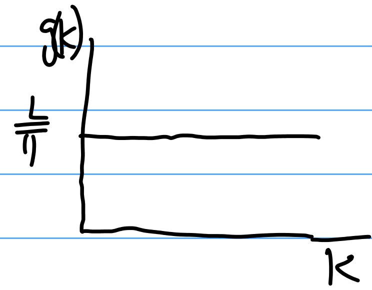
$$g(\varepsilon) d\varepsilon = \underbrace{\frac{L}{\pi} \sqrt{\frac{m}{2\hbar^2 \varepsilon}}}_{g(\varepsilon)} d\varepsilon \quad \text{for 1D}$$

1D:

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



$$g(k) dk = \frac{L}{\pi} dk$$

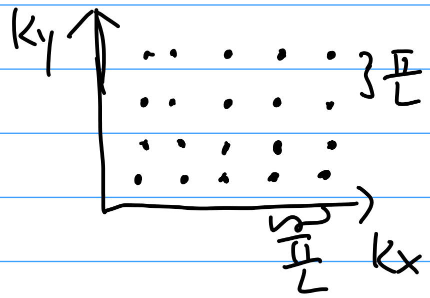


2D: Similarly: for 2D box:

$$\psi(x) = \sqrt{\frac{4}{L^2}} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right)$$

where $k_x = \frac{n_x \pi}{L}$, $k_y = \frac{n_y \pi}{L}$, $\varepsilon = \frac{\pi^2 \hbar^2 (n_x^2 + n_y^2)}{2mL^2} = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m}$

where $n_x = 1, 2, 3, \cdots$ $n_y = 1, 2, 3 \cdots$



where $\vec{k} = (k_x \hat{x} + k_y \hat{y})$
or $\vec{k} = k\hat{r}$
where $k = \sqrt{k_x^2 + k_y^2}$
and $\theta = \tan^{-1}\left(\frac{k_y}{k_x}\right)$

So # of s.p. states in $\vec{k}$ space over some area $dA = dk\, k d\theta$

$$dN = \frac{dA}{\text{area for each state}} = \frac{k\,dk\,d\theta}{\left(\frac{\pi}{L}\right)^2}$$

$$dN = \left(\frac{L}{\pi}\right)^2 k\,dk\,d\theta$$

$$\stackrel{!}{=} \left(\frac{L}{\pi}\right)^2 k\,dk \int_0^{\frac{\pi}{2}} d\theta$$

since only consider positive n_x and n_y, $\vec{k}$ can only span over one quarter.

$$\stackrel{!}{=} \left(\frac{L}{\pi}\right)^2 \frac{\pi}{2} k\,dk$$

$$dN \stackrel{!}{=} \underbrace{\frac{L^2}{2\pi}}_{g(k)} k\,dk \quad \text{for 2D}$$

$$g(k)\,dk = \frac{L^2}{2\pi} k\,dk \Rightarrow g(\varepsilon)\,d\varepsilon$$

$$\varepsilon = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m} = \frac{\hbar^2 k^2}{2m}$$

or $\sqrt{\frac{2m\varepsilon}{\hbar^2}} = k$

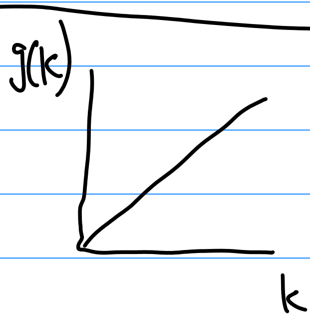
$$\frac{L^2}{2\pi} k \frac{dk}{d\varepsilon} d\varepsilon = \frac{L^2}{2\pi} \sqrt{\frac{2m\varepsilon}{\hbar^2}} \frac{d}{d\varepsilon}\left(\sqrt{\frac{2m\varepsilon}{\hbar^2}}\right) d\varepsilon$$

$$\hookrightarrow \quad = \frac{L^2}{2\pi} \frac{2m}{\hbar^2} \sqrt{\varepsilon} \frac{1}{2\sqrt{\varepsilon}} d\varepsilon$$

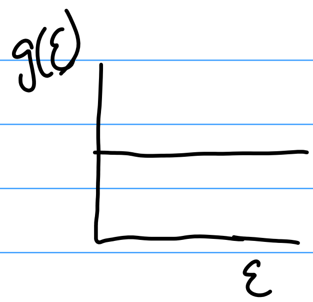
$$g(\varepsilon)\,d\varepsilon \overset{!}{=} \frac{mL^2}{2\hbar^2 \pi} d\varepsilon$$

2D summary:

$$g(k)\,dk = \frac{L^2}{2\pi} k\,dk$$



$$g(\varepsilon)\,d\varepsilon = \frac{mL^2}{2\pi\hbar^2} d\varepsilon$$



3D: Similarly:

$$\psi(x) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x\pi}{L}x\right) \sin\left(\frac{n_y\pi}{L}y\right) \sin\left(\frac{n_z\pi}{L}z\right)$$

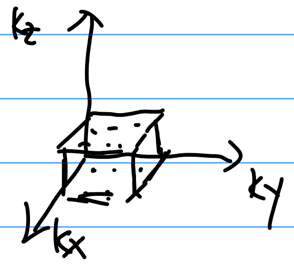
so $k_x = \frac{n_x\pi}{L}$, $k_y = \frac{n_y\pi}{L}$, $k_z = \frac{n_z\pi}{L}$

where $\varepsilon = \dfrac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}$

let $k = \sqrt{k_x^2+k_y^2+k_z^2}$

$\theta = \cos^{-1}\left(\frac{k_z}{k}\right)$

$\phi = \tan^{-1}\left(\frac{k_y}{k_x}\right)$



then $dV = dk\, k\,d\theta\, k\sin\theta\, d\phi = k^2 \sin\theta\, dk\, d\theta\, d\phi$

$$dN = \frac{dV}{\left(\frac{\pi}{L}\right)^3} = \left(\frac{L}{\pi}\right)^3 k^2 \sin\theta\, dk\, d\theta\, d\phi$$

$$= \left(\frac{L}{\pi}\right)^3 k^2 dk \int_0^{\pi/2} d\phi \underbrace{\int_0^{\pi/2} \sin\theta\, d\theta}_{1}$$

$$= \left(\frac{L}{\pi}\right)^3 \left(\frac{\pi}{2}\right) k^2 dk$$

$$g(k)\,dk = \underbrace{\frac{L^3}{2\pi^2}}_{g(k)} k^2 dk$$

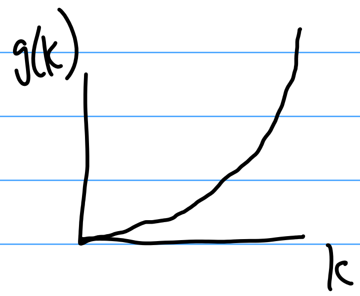
know $\quad \varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$

$$
\begin{aligned}
g(k)\,dk &= \frac{L^3}{2\pi^2} k^2\, dk \\
&= \frac{L^3}{2\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{dk}{d\varepsilon}\, d\varepsilon \\
&= \frac{L^3}{2\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{d}{d\varepsilon}\left(\sqrt{\frac{2m\varepsilon}{\hbar^2}}\right) d\varepsilon \\
&= \frac{L^3}{2\pi^2} \frac{2m\varepsilon}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2\sqrt{\varepsilon}}\, d\varepsilon \\
g(\varepsilon)\,d\varepsilon &= \underbrace{\frac{L^3}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}}_{g(\varepsilon)}\, d\varepsilon
\end{aligned}
$$

Summary 3D:

$$g(k)\,dk = \frac{L^3}{2\pi^2} k^2\, dk$$

$$g(\varepsilon)\,d\varepsilon = \frac{L^3}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}\, d\varepsilon$$



b) Find $\langle E\rangle / L^d$ and compare with P, σ, and λ

1D:

$$q_1 = \sum e^{-\beta\varepsilon(k)} = \int g(k)\, e^{-\beta\varepsilon(k)}\, dk$$

$$= \int_0^\infty \frac{L}{\pi} e^{-\beta\left(\frac{\hbar^2 k^2}{2m}\right)} dk$$

let $du = \sqrt{\frac{\beta\hbar^2}{2m}}\, dk$

$$= \int_0^\infty \sqrt{\frac{2m}{\beta\hbar^2}} \frac{L}{\pi} e^{-u^2} du$$

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

$$q_1 = \sqrt{\frac{m}{2\pi\beta\hbar^2}}\, L$$

$$Q = \frac{1}{N!} q_1^N = \frac{1}{N!} \left(\sqrt{\frac{m}{2\pi\beta\hbar^2}}\, L\right)^N$$

$$\langle E\rangle = \left(-\frac{\partial}{\partial\beta} \ln Q\right)_{N,V}$$

$$= -\frac{\partial}{\partial\beta}\left(-\ln N! + N\ln L + \frac{N}{2}\ln\left(\frac{m}{2\pi\hbar^2}\right) - \frac{N}{2}\ln\beta\right)$$

$$= \frac{N}{2}\frac{1}{\beta}$$

$$\langle E\rangle_{1D} = \frac{N}{2} k_B T$$

$$dA = -SdT + \lambda dL + \mu dN \quad \text{where } A = -k_B T \ln Q$$

$$\lambda = \left(\frac{\partial A}{\partial L}\right)_{T,N}$$

$$\lambda = -k_B T \left(\frac{\partial}{\partial L} \ln Q\right)_{T,N}$$

$$\stackrel{!}{=} -k_B T \left(\frac{\partial}{\partial L}\left[N \ln L + \text{terms not related to } L\right]\right)$$

$$\lambda \stackrel{!}{=} \frac{-N k_B T}{L}$$

1D: $\boxed{\text{then} \quad \frac{\frac{\langle E \rangle}{L}}{\lambda} = \frac{\frac{N k_B T}{2L}}{\frac{-N k_B T}{L}} = \frac{-1}{2}}$

2D:

$$q_1 = \int_0^\infty \frac{L^2}{2\pi} k \, e^{-\frac{\beta \hbar^2 k^2}{2m}} dk$$

$$\stackrel{!}{=} \frac{L^2}{2\pi} \int_0^\infty k e^{-\frac{\beta \hbar^2 k^2}{2m}} dk$$

$du = \sqrt{\frac{\beta\hbar^2}{2m}} dk$

$$\stackrel{!}{=} \frac{L^2}{2\pi}\left(\frac{2m}{\beta\hbar^2}\right) \underbrace{\int_0^\infty u e^{-u^2} du}_{1/2}$$

$$q_1 \stackrel{!}{=} \frac{m L^2}{2\pi \beta \hbar^2} = \frac{m \sigma}{2\pi \beta \hbar^2} \quad \text{let } \sigma = \text{area} = L^2$$

$$Q = \frac{1}{N!} q_1^N$$

$$\langle E \rangle = \left(-\frac{\partial}{\partial \beta} \ln Q\right)_{N,V}$$

$$\overset{!}{=} -\frac{\partial}{\partial \beta}\left(-N \ln \beta + \text{terms not related to } \beta\right)_{N,V}$$

$$\overset{!}{=} N \frac{1}{\beta}$$

$$\overset{!}{=} N k_B T$$

$$dA = -S\,dT + \gamma\, d\underset{\text{area}}{\sigma} + \mu\, dN \quad , \quad A = -k_B T \ln Q$$

surface tension $\rightarrow \gamma = \left(\frac{\partial A}{\partial \sigma}\right)_{T,N}$

$$\overset{!}{=} -k_B T \frac{\partial}{\partial \sigma}\left(N \ln \sigma + \text{terms not related to } \sigma\right)_{T,N}$$

$$\overset{!}{=} -N k_B T \frac{1}{\sigma} = \frac{-N k_B T}{L^2}$$

2D: $\dfrac{\frac{\langle E \rangle}{L^2}}{\gamma} = \dfrac{\frac{N k_B T}{L^2}}{\frac{-N k_B T}{L^2}} = -1$ ← same in magnitude.

$\underline{3D}$:

$$q_1 = \int_0^\infty \frac{L^3}{2\pi^2} k^2 e^{-\frac{\beta\hbar^2 k^2}{2m}}$$

$$= \frac{L^3}{2\pi^2} \int_0^\infty e^{-\frac{\beta\hbar^2 k^2}{2m}} k^2 dk$$

$du = \sqrt{\frac{\beta\hbar^2}{2m}}\, dk$

$$= \frac{L^3}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \underbrace{\int_0^\infty u^2 e^{-u^2} du}_{\frac{\sqrt{\pi}}{4}}$$

$$= \frac{L^3}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \frac{\sqrt{\pi}}{4}$$

$$= \frac{V}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \frac{\sqrt{\pi}}{4}$$

$$Q = \frac{1}{N!} q_1^N$$

$$= \frac{1}{N!} \left[\frac{V}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \frac{\sqrt{\pi}}{4}\right]^N$$

$$\langle E \rangle = \left(-\frac{\partial}{\partial\beta} \ln Q\right)_{N,V}$$

$$= -\frac{\partial}{\partial\beta}\left(-\frac{3}{2}N \ln(\beta) + \text{terms not related to } \beta\right)_{N,V}$$

$$= \frac{3}{2} N \frac{1}{\beta}$$

$$= \frac{3}{2} N k_B T$$

$$dA = -SdT - pdV + \mu dN \qquad A = -k_B T \ln Q$$

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

$$p = k_B T \left(\frac{\partial}{\partial V} \ln Q\right)_{T,N}$$

$$\stackrel{!}{=} k_B T \frac{\partial}{\partial V}\left[N \ln V + \text{terms not related to } V\right]$$

$$\stackrel{!}{=} \frac{N k_B T}{V}$$

$$\boxed{\text{Summary:} \quad \frac{\frac{\langle E \rangle}{L^3}}{p} = \frac{\frac{\frac{3}{2} N k_B T}{V}}{\frac{N k_B T}{V}} = \frac{3}{2}}$$

c) For relativistic, dispersion relation changes:

$$\varepsilon = \sqrt{(\hbar k c)^2 + (mc^2)^2}$$

$$\cong \hbar k c \quad \text{for} \quad \varepsilon \gg mc^2$$

but $g(k)\,dk$ remains the same:

1D: $g(k)\,dk \quad \frac{L}{\pi}\,dk$

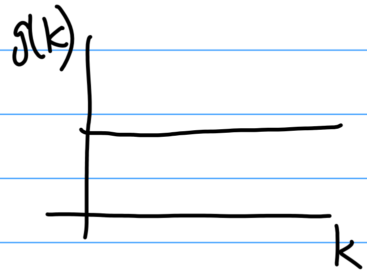
$$g(\varepsilon)\,d\varepsilon = g(k(\varepsilon))\frac{dk}{d\varepsilon}\,d\varepsilon$$

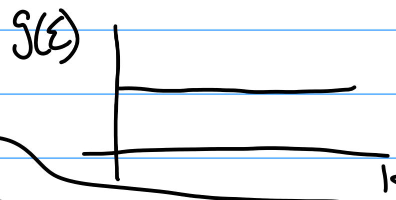
$$= \frac{L}{\pi}\frac{d}{d\varepsilon}\left(\frac{\varepsilon}{\hbar c}\right)d\varepsilon$$

$$g(\varepsilon)\,d\varepsilon = \frac{L}{\pi}\frac{1}{\hbar c}\,d\varepsilon$$

then 1D: $g(k)\,dk = \frac{L}{\pi}\,dk$

$$g(\varepsilon)\,d\varepsilon = \frac{L}{\pi}\frac{1}{\hbar c}\,d\varepsilon$$



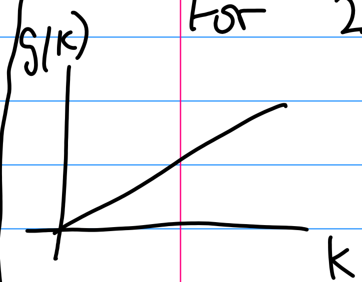


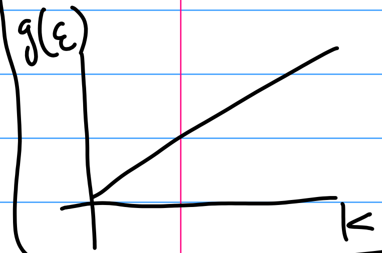
For 2D: $g(k)\,dk = \frac{L^2}{2\pi}k\,dk$ found previously.

$$g(\varepsilon)\,d\varepsilon = g(k(\varepsilon))\frac{dk}{d\varepsilon}\,d\varepsilon$$

$$= \frac{L^2}{2\pi}\left(\frac{\varepsilon}{\hbar c}\right)\frac{d}{d\varepsilon}\left(\frac{\varepsilon}{\hbar c}\right)d\varepsilon$$

$$g(\varepsilon)\,d\varepsilon = \frac{L^2}{2\pi}\frac{\varepsilon}{(\hbar c)^2}\,d\varepsilon$$





For 3D: $g(k)dk = \frac{L^3}{2\pi^2} k^2 dk$ from part a

$$g(\varepsilon)d\varepsilon = g(k(\varepsilon)) \frac{dk}{d\varepsilon} d\varepsilon$$

$$= \frac{L^3}{2\pi^2}\left(\frac{\varepsilon}{\hbar c}\right)^2 \frac{d}{d\varepsilon}\left(\frac{\varepsilon}{\hbar c}\right) d\varepsilon$$

$$= \frac{L^3}{2\pi^2}\left(\frac{\varepsilon}{\hbar c}\right)^2 \frac{1}{\hbar c} \; d\varepsilon$$

$$g(\varepsilon)d\varepsilon = \frac{L^3}{2\pi^2} \frac{\varepsilon^2}{(\hbar c)^3} d\varepsilon = \frac{V}{2\pi^2}\frac{\varepsilon^2}{(\hbar c)^3} d\varepsilon$$

d) 1D: $q_1 = \int_0^\infty \frac{L}{\pi} e^{-\beta(\hbar k c)} dk$

$$= -\frac{L}{\pi} \frac{1}{\beta\hbar c} \underbrace{e^{-\beta\hbar k c}\Big|_0^\infty}_{-1} dk$$

$$q_1 = \frac{L}{\pi}\frac{1}{\beta\hbar c}$$

$$Q = \frac{1}{N!} q_1^N = \frac{1}{N!}\left(\frac{L}{\pi}\frac{1}{\beta\hbar c}\right)^N$$

$$\langle E \rangle = -\left(\frac{\partial}{\partial\beta} \ln Q\right)_{N,V}$$

$$= -\frac{\partial}{\partial\beta}\left(-N\ln\beta + \text{non-related terms}\right)$$

$$= \frac{N}{\beta}$$

$$= N k_B T$$

$$dA = -S\,dT + \lambda\,dL + \mu\,dN \qquad A = -k_B T \ln Q$$

$$\lambda = \left(\frac{\partial A}{\partial L}\right)_{T,N}$$

$$\overset{!}{=} -k_B T \frac{\partial}{\partial L}\left(N \ln L\right)$$

$$\overset{!}{=} -\frac{N k_B T}{L}$$

$$\boxed{1D: \quad \frac{\frac{\langle E \rangle}{L}}{\lambda} = \frac{\frac{N k_B T}{L}}{-\frac{N k_B T}{L}} = -1}$$

2D: $$q_1 = \int_0^\infty \frac{L^2}{2\pi} k\, e^{-\beta\hbar k c}\, dk$$

use Mathematica

$$\overset{!}{=} \frac{L^2}{2\pi}\left(-\frac{(\beta\hbar c k + 1)e^{-\beta\hbar k c}}{(\beta\hbar c)^2}\right)\Bigg|_0^\infty$$

$$q_1 \overset{!}{=} \frac{L^2}{2\pi}\frac{1}{(\beta\hbar c)^2} = \frac{\sigma}{2\pi}\frac{1}{(\beta\hbar c)^2}$$

$$Q = \frac{1}{N!} q_1^N = \frac{1}{N!}\left(\frac{\sigma}{2\pi}\frac{1}{(\beta\hbar c)^2}\right)^N \quad \text{where } \sigma = L^2$$

$$\langle E \rangle = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_{N,V}$$

$$\overset{!}{=} -\frac{\partial}{\partial\beta}\left(-2N\ln\beta + \text{non-related terms}\right)$$

$$\overset{!}{=} \frac{2N}{\beta} = 2N k_B T$$

$$dA = -S\,dT + \gamma\, d\sigma + \mu\, dN \qquad A = -k_B T \ln Q$$

$$\gamma = \left(\frac{\partial A}{\partial \sigma}\right)_{T,N}$$

$$\overset{!}{=} -k_B T \frac{\partial}{\partial \sigma}\left(N \ln \sigma \right)$$

$$\gamma \overset{!}{=} -\frac{N k_B T}{\sigma}$$

$$\boxed{\text{2D:} \quad \frac{\frac{\langle E \rangle}{L^2}}{\gamma} = \frac{\frac{2 N k_B T}{L^2}}{\frac{-N k_B T}{L^2}} = -2}$$

3D:

$$q_1 = \int_0^\infty \frac{L^3}{2\pi^2} e^{-\beta\hbar k c} k^2 dk$$

$$\overset{!}{=} \frac{L^3}{2\pi^2}\left(-\frac{\left[(\beta\hbar k c)^2 + 2\beta\hbar k c + 2\right] e^{-\beta\hbar k c}}{(\beta\hbar c)^3} \right)\Bigg|_0^\infty$$

$$\overset{!}{=} \frac{L^3}{2\pi^2} \frac{2}{(\beta\hbar c)^3} = \frac{V}{\pi^2} \frac{1}{(\beta\hbar c)^3}$$

$$Q = \frac{1}{N!} q_1^N = \frac{1}{N!}\left[\frac{V}{\pi^2}\frac{1}{(\beta\hbar c)^3}\right]^N$$

$$\langle E \rangle = \left(-\frac{\partial}{\partial \beta} \ln Q\right)_{N,V}$$

$$\overset{!}{=} -\frac{\partial}{\partial \beta}\left(-3N \ln \beta + \text{non-related terms}\right)$$

$$\overset{!}{=} \frac{3N}{\beta} = 3 N k_B T$$

$$dA = -S\,dT - p\,dV + \mu\,dN \qquad A = -k_B T \ln Q$$

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

$$p = k_B T \left(\frac{\partial}{\partial V} \ln Q\right)_{T,N}$$

$$= k_B T \left(\frac{\partial}{\partial V} N \ln V\right)$$

$$= \frac{N k_B T}{V}$$

$$\boxed{3D: \quad \frac{\frac{\langle E \rangle}{L^3}}{p} = \frac{\frac{3 N k_B T}{L^3}}{\frac{N k_B T}{L^3}} = 3}$$

e) Consider non-relativistic particles in 2D, periodic potential

so that $\varepsilon(\vec{k}) = \alpha[1-\cos(k_x a)\cos(k_y a)]$

with $-\frac{\pi}{a} < k_{x,y} < \frac{\pi}{a}$

With periodic condition: $\vec{k} = \left(n_x \frac{2\pi}{L}, n_y \frac{2\pi}{L}\right)$

then $g(k)\,d^2k = \left(\frac{L}{2\pi}\right)^2 d^2k$

$d\varepsilon = \vec{\nabla}_k \varepsilon \cdot d\vec{k}$

$\vec{\nabla}_k \varepsilon = \frac{\partial \varepsilon}{\partial k_x}\hat{k_x} + \frac{\partial \varepsilon}{\partial k_y}\hat{k_y}$

$\stackrel{!}{=} \frac{\partial}{\partial k_x}\left(\alpha[1-\cos(k_x a)\cos(k_y a)]\right)\hat{k_x}$

$+ \frac{\partial}{\partial k_y}\left(\alpha[1-\cos(k_x a)\cos(k_y a)]\right)\hat{k_y}$

$g(\varepsilon)\,d\varepsilon = \int_{\partial\varepsilon} g(k)\,dk_x\,dk_y$ ⇒ line integral where the boundary is over const energy, ε

lets choose a new set of coordinate such that

$dk_x\,dk_y = dk_x'\,dk_y'$

where $\hat{k_y}$ is $\perp$ to the contour line of constant ε.

then $\quad d\varepsilon = |\nabla_k \varepsilon|\, dk_y'$

$$\overset{|}{=} 2a\left[\sin^2(k_x'a)\cos^2(k_y'a) + \cos^2(k_x'a)\sin^2(k_y'a)\right]^{1/2} dk_y'$$

then

$$g(\varepsilon)\, d\varepsilon = g(\vec{k})\, dk_x'\, dk_y'$$

$$g(\varepsilon)\, |\nabla_k \varepsilon|\, \cancel{dk_y'} = g(\vec{k})\, dk_x'\, \cancel{dk_y'}$$

$$g(\varepsilon) = \int_{\partial\varepsilon} g(\vec{k})\, \frac{dk_x'}{|\nabla_k \varepsilon|}$$

with $g(k) = \dfrac{L^2}{(2\pi)^2}$

$$\boxed{g(\varepsilon) = \frac{L^2}{(2\pi)^2} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{dk_x}{2a\left[\sin^2(k_x a)\cos^2(k_y a) + \cos^2(k_x a)\sin^2(k_y a)\right]}}$$

$g(\varepsilon)$ is not well defined when $|\nabla_k \varepsilon|$ goes 0, e.g. when $\varepsilon(\vec{k})$ is at its local max, min, or saddle points.

Examples of local max when $(k_x = 0, k_y = \pm\frac{\pi}{a})$ or $(k_x = \pm\frac{\pi}{a}, k_y = 0)$

Local Min when $(k_x = 0, k_y = 0)$, or $(k_x = \pm\frac{\pi}{a}, k_y = \pm\frac{\pi}{a})$

Saddle points when $(k_x = \pm\frac{\pi}{2a}, k_y = \pm\frac{\pi}{2a})$

21) $\mu = \frac{G}{N} = \left(\frac{\partial A}{\partial N}\right)_{T,V}$ $\quad A = -SdT - pdV + \mu dN$

or $\quad \mu = dA)_{T,V} = dE)_{T,V} - TdS)_{T,V}$

at high T, low ρ: classical limit:

entropy term dominates over single-particle energy level, setting ground energy level to zero, then μ is large and negative.

at low T and high density, $\mu(T=0) = \varepsilon_F$ for fermion and $\mu(T=0) = 0$ for bosons.

a) Show for non-interacting system at const V,

$$\mu = dE)_{T,V} - TdS)_{T,V} = \langle \varepsilon \rangle - Ts$$

where $\langle \varepsilon \rangle = \frac{1}{N} \sum \varepsilon_i \langle n(\varepsilon_i) \rangle$ and $s = S/N$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial E}{\partial N}\right)_{T,V} - T\left(\frac{\partial S}{\partial N}\right)_{T,V}$$

$$\int \mu dN = \int dE)_{T,V} - \int TdS)_{T,V}$$

$$\hookrightarrow \mu N = \underbrace{\langle E \rangle}_{\sum \varepsilon_j \langle n_j \rangle} - TS$$

$$\boxed{\hookrightarrow \mu = \frac{1}{N} \sum_j \varepsilon_j \langle n_j \rangle - T\frac{S}{N}}$$

b) show $\left(\frac{\partial u}{\partial T}\right)_p = -s$ using Gibbs Duhem relation:

Gibbs - Duhem:

$$0 = SdT - Vdp + Nd\mu$$

$$-d\mu N = SdT - Vdp$$

$$d\mu = \frac{-S}{N} dT + \frac{V}{N} dp$$

$$\boxed{\frac{-S}{N} = \left(\frac{\partial \mu}{\partial T}\right)_p} \qquad \frac{V}{N} = \left(\frac{\partial \mu}{\partial p}\right)_T$$

c) Show $\left(\frac{\partial u}{\partial T}\right)_v = -\frac{V}{N}\left(\frac{S}{N} - \left(\frac{\partial S}{\partial V}\right)_T\right)$

use relation:

$$\left(\frac{\partial x}{\partial y}\right)_w = \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_w$$

then: $$\left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_p + \left(\frac{\partial u}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v$$

from part b: we see $\left(\frac{\partial u}{\partial T}\right)_p = \frac{-S}{N}$

$$\left(\frac{\partial u}{\partial p}\right)_T = \frac{V}{N}$$

use Maxwell for $dA = -SdT - pdV + \mu dN$

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial^2 A}{\partial T \partial V}$$

then $$\boxed{\left(\frac{\partial u}{\partial T}\right)_v = \frac{-S}{N} + \frac{V}{N}\left(\frac{\partial S}{\partial V}\right)_T \overset{!}{=} -v\left[\frac{S}{V} + \left(\frac{\partial S}{\partial V}\right)_T\right] \quad \text{where } v = \frac{V}{N}}$$

d) Describe a scenario where $\left(\frac{\partial u}{\partial T}\right)_V > 0$

$$\left(\frac{\partial u}{\partial T}\right)_V = -v\underbrace{\left[\frac{S}{V} - \left(\frac{\partial S}{\partial V}\right)_T\right]}_{<0} > 0$$

need $\left(\frac{\partial S}{\partial V}\right)_T > \frac{S}{V}$, need S grow faster than V
e.g. grow nonlinearly with V

My Hypothesis:

Suppose we have a supersaturated solution. If we decrease volume, then pressure increases, then the solubility decreases. Then the solution could crystallize, so the entropy decreases dramatically during this phase caused by the change in volume,

This could potentially suggest a nonlinear relationship between S and V, that happens near phase transition phase transition.

22) Consider surface having M sites to absorb molecules each site can adsorb one molecule.

It is in contact with non-degenerate ideal gas, with $\mu(\rho, T) = k_B T \ln(\rho \lambda_{th}^3)$, ρ is # density

$$\lambda_{th} = \left[\frac{h^2}{2\pi m k_B T}\right]^{1/2}$$

a) Find $\theta = \dfrac{\text{\# molecules adsorbed}}{\text{\# of sites to adsorb} = M} = \dfrac{\text{\# adsorbed}}{M}$

need to find # adsorbed:

assume process happen at a given T, and since we have an exchange of particle and energy, use grand canonical ensemble

we know: $$N = \left(-\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

Find $\Phi = -k_B T \ln \Xi$

$$\Xi = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)}$$

$$\overset{!}{=} \sum_\nu \exp\left\{\sum_j -\beta(\varepsilon_j - \mu) n_j\right\}$$

$\{n_j\} = 0, 1$

at most, a single molecule can occupy (fermion-like)

$$\overset{!}{=} \prod_j \sum_{\{n_j\}} \exp\{-\beta(\varepsilon_j - \mu) n_j\}$$

$$\ln \Xi = \sum_j \ln\left(\sum_0^1 \exp\{-\beta(\varepsilon_j - \mu) n_j\}\right)$$

$$\ln \Xi = \sum_j \ln\left(1 + \exp\{-\beta(\varepsilon_j - \mu)\}\right)$$

$$\Rightarrow \Phi = -k_B T \ln \Xi$$

$$= -k_B T \sum_j \ln\left(1 + \exp\{-\beta(\varepsilon_j - \mu)\}\right)$$ ← grand canonical potential for fermion.

Suppose all adsorption has same energy: $-\varepsilon$ and sum over M sites.

$$\Rightarrow = -k_B T M \ln\left(1 + \exp\{-\beta(-\varepsilon - \mu)\}\right)$$

$$\Phi = -k_B T M \ln\left(1 + \exp\{\beta(\varepsilon + \mu)\}\right)$$

$$\Rightarrow N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

$$= \cancel{k_B} T M \left(1 + \exp\{\beta(\varepsilon + \mu)\}\right)^{-1} \cancel{\beta} \exp\{\beta(\varepsilon + \mu)\}$$

$$= \frac{M \exp\{\beta(\varepsilon + \mu)\}}{1 + \exp\{\beta(\varepsilon + \mu)\}}$$

$$N = \frac{M}{1 + \exp\{-\beta(\varepsilon + \mu)\}}$$

$$\boxed{\theta = \frac{\#\text{ adsorbed}}{\text{total sites}} = \frac{N}{M} = \frac{1}{1 + \exp\{-\beta(\varepsilon + \mu)\}}}$$

b) Find pressure p_0 for $\theta = \frac{1}{2}$

assume ideal gas then $pV = N k_B T$

$$\mu = k_B T \ln\left(\rho \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right)$$

density $= \frac{N}{V} = \rho = \frac{p}{k_B T}$

$$\mu = k_B T \ln\left(\frac{p}{k_B T} \lambda^3\right)$$

with $\theta = \frac{1}{2} = \left[1 + \exp\left\{-\beta\left(\varepsilon + k_B T \ln\left(\frac{p}{k_B T} \lambda^3\right)\right)\right\}\right]^{-1}$

$$2 - 1 = \exp\left\{-\beta\varepsilon - \ln\left(\frac{p}{k_B T} \lambda^3\right)\right\}$$

$$\cancel{\ln(1)} + \beta\varepsilon = -\ln\left(\frac{p}{k_B T} \lambda^3\right)$$

$$e^{-\beta\varepsilon} = \frac{p}{k_B T} \lambda^3$$

$$\boxed{p = \frac{e^{-\beta\varepsilon} k_B T}{\lambda^3} = \frac{e^{-\beta\varepsilon}}{\beta \lambda^3}}$$

see code for plot.

We're likely neglecting the vibrational and other movement of the molecule, and only accounted for the binding energy.