1/3/06

Liquid-gas phase transition

p: pressure, $\rho = N/V$ = density,
T = temperature.

Equation of state:– $p = g(\rho, T)$

$\downarrow$ some function

Relation betn. ρ & T

$$p/kT = \frac{\partial}{\partial V} \ln Q = \frac{1}{V} \ln Q$$

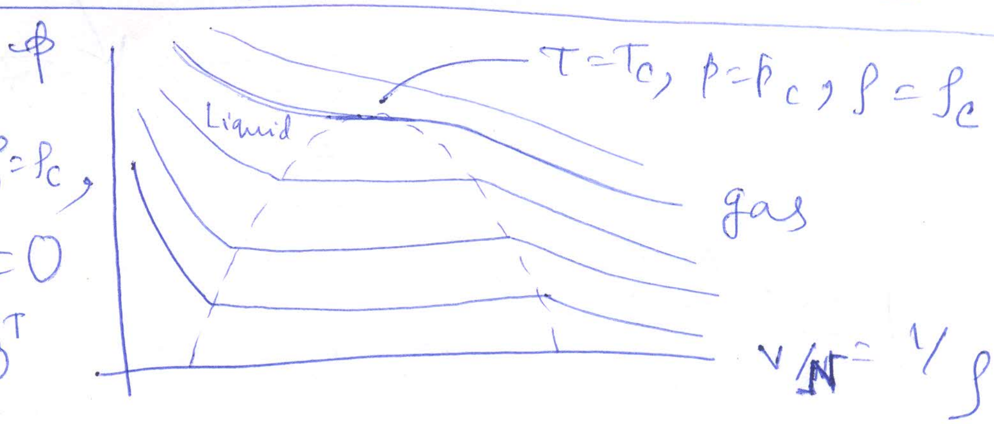
Since $\ln Q \propto V f(z, \beta)$

Phase diagram for Liquid-gas system

At $T=T_c$, $p=p_c$, $\rho=\rho_c$,

$$\left(\frac{\partial p}{\partial V}\right)_{N,T} = 0, \left(\frac{\partial^2 p}{\partial V^2}\right)_{N,T} = 0$$

$\Rightarrow \partial p/\partial \rho = 0, \frac{\partial^2 p}{\partial \rho^2} = 0$



Q) Can we understand this from Statistical mechanics?

$$p = p_c + a(\rho - \rho_c)^3 \quad \text{at } T = T_c.$$

$$\rho - \rho_c = \left(\frac{p - p_c}{a}\right)^{1/3}$$

$$\partial\rho/\partial p \propto (p - p_c)^{-2/3} \longrightarrow \infty \text{ as } p \to p_c.$$

There is some kind of non analyticity in the fn. det. $\rho - \rho_c$ in terms of $p - p_c$

In order to understand phase transition from statistical mechanics, we need to understand the origin of non-analyticity.

[we haven't gotten this diag. from stat. mech. Till now we have used only thermodyn. relations.]

$\Rightarrow$ p is discontinuous as a fn. of ρ.

Model of imperfect gas (classical)

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_1, \ldots, \vec{r}_N)$$

$$V = \sum_{i<j} v(\vec{r}_i - \vec{r}_j)$$

Assumptions

1. $v(\vec{r}) = \infty$ for $|\vec{r}| \le a$.
2. $v(\vec{r}) \ge -\epsilon_0$ for $a < |\vec{r}| < r_0$
3. $v(\vec{r}) = 0$ for $r \ge r_0$

known as Hard sphere interaction

Hard core int.

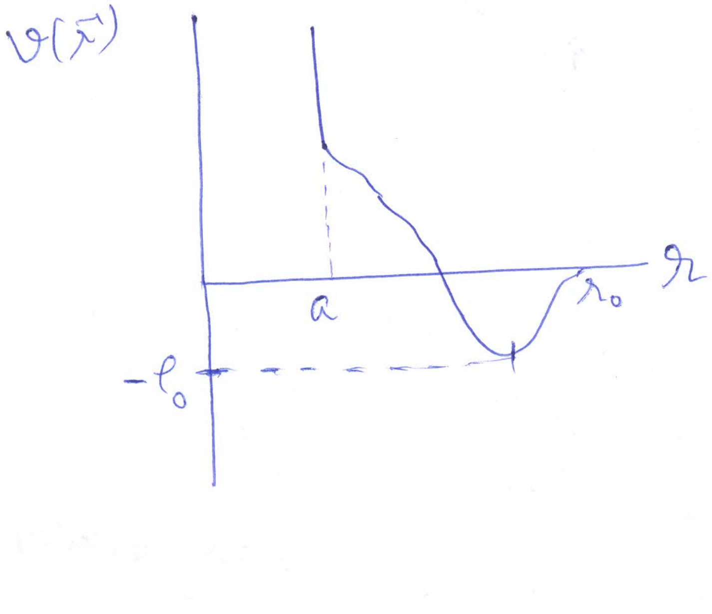
Molecules are rep. for very near approach

It is possible that v never becomes -ve

But it can't be arbitrarily large negative

ϵ_0 can be +ve or -ve

In the realistic case ϵ_0 should be positive bcos there is some attractive component



$$\mathcal{Q} = \sum_N z^N Z_N(V, \beta)$$

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

Canonical partition fn. of N-particle system

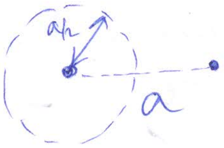
$$Z_N(V, T) = \frac{1}{N!}\left(\frac{2m\pi kT}{h^2}\right)^{\frac{3}{2}N} \int d^{3N}r\, e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)}$$

$$P/kT = \frac{1}{V}\ln \mathcal{Q}$$

$$\frac{N}{V} = z\frac{\partial}{\partial z}\left(\frac{1}{V}\ln\mathcal{Q}\right)_{\beta, V}$$

Write

For a given volume V, $Z_N = 0$ for $N > N_m(V)$



[As if a molecule is a hard sphere of radius $a/2$]

Bound changes a little bit if we take into account that there is always some other unoccupiable vol. when you pack N hard spheres

In fact this expansion stops at a little less than N_m - But of course it can't go beyond N_m

$$N_m(V) = \frac{V}{\frac{4}{3}\pi(a/2)^3}$$

$$\frac{P}{kT} = \frac{1}{V}\ln\left(1 + zZ_1 + z^2Z_2 + \dots + z^{N_m(V)}Z_{N_m(V)}\right)$$

$$\frac{N}{V} = \frac{1}{V}\,\frac{zZ_1 + 2z^2Z_2 + 3z^3Z_3 + \dots + N_m(V)\,z^{N_m(V)}Z_{N_m(V)}}{1 + zZ_1 + z^2Z_2 + \dots + z^{N_m(V)}Z_{N_m(V)}}$$

$$\frac{N}{V} = \frac{1}{V}\,\frac{\sum_{l=0}^{N_m} l\,z^l Z_l}{\sum_{l=0}^{N_m} z^l Z_l}$$

$$z \,\partial/\partial z \,\frac{N}{V} = \frac{1}{V}\left[\frac{\sum_{l=0}^{N_m} l^2 z^l Z_l}{\sum_{l=0}^{N_m} z^l Z_l} - \frac{\left(\sum_{l=0}^{N_m} l z^l Z_l\right)^2}{\left(\sum_{l=0}^{N_m} z^l Z_l\right)^2} \right]$$

$$\Rightarrow z \frac{\partial}{\partial z} N/V = \frac{1}{V} \frac{1}{\left(\sum_{l=0}^{N_m} z^l Z_l\right)^2} \left[\sum_{l=0}^{N_m} l^2 z^l Z_l \sum_{l'=0}^{N_m} z^{l'} Z_{l'} - \sum_{l=0}^{N_m} l z^l Z_l \sum_{l'=0}^{N_m} l' z^{l'} Z_{l'} \right]$$

$$= \frac{1}{V} \frac{1}{\left(\sum_{l=0}^{N_m} z^l Z_l\right)^2} \sum_{l=0}^{N_m} \sum_{l'=0}^{N_m} \left[l^2 z^l z^{l'} Z_l Z_{l'} - l l' z^l z^{l'} Z_l Z_{l'} \right]$$

$$\sum_{l=0}^{N_m} \sum_{l'=0}^{N_m} \underbrace{\left\{ \frac{1}{2}(l^2 + l'^2) - l l' \right\}}_{\frac{1}{2}(l-l')^2} z^l z^{l'} Z_l Z_{l'} > 0$$

1st sum is sym. w.r.t. the interchange betn l & l'

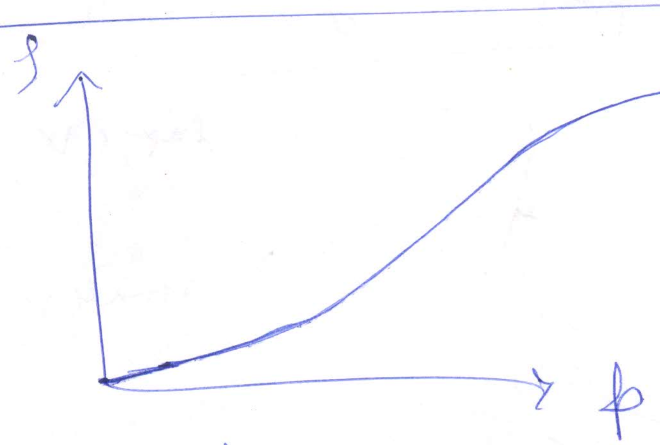
$Z_l \geq 0$ for each l

$\frac{P}{kT} > 0$ for $z > 0$, $\frac{P}{kT} \to 0$ as $z \to 0$, $\to \infty$ as $z \to \infty$

$\partial/\partial z \, P/kT = \partial/\partial z \frac{1}{V} \ln \mathcal{Q} = N/V > 0 \Rightarrow \frac{P}{kT}$ is monotonic increasing fn. of z.

$N/V > 0$ for $z > 0$, $N/V \to 0$ as $z \to 0$

N/V is monotone increasing fn. of z.



There is a one-to-one correspondence betn. P & z in the range 0 to ∞

∴ z is also a monotone ↑ fn. of P

① p is monotone increasing fn. of z, $p \to 0$ as $z \to 0$
$p \to \infty$ as $z \to \infty$

$\Longrightarrow$ z is a monotone increasing fn. of p for $0 < p < \infty$.

② f is a monotone increasing fn. of z. $\xrightarrow{\text{Hence}}$ f is a monotone increasing fn. of p.

log has singularity at 0 & ∞ – clearly, ∞ is excluded. Also, z is always +ve

$$\frac{p}{kT} = \ln\left(1 + z Z_1 + z^2 Z_2 + \cdots + z^{N_m} Z_m\right)$$

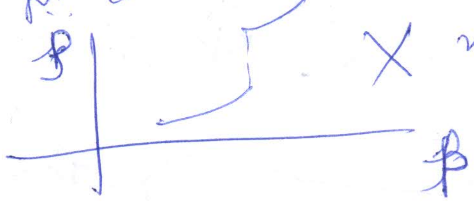
is an analytic fn. of z unless

[p is ∞, $(1 + \cdots)$ is zero]

The relation between p & z & betn. f & z is analytic.

$\Longrightarrow$ $f(p, T)$ is also an analytic fn. of p for fixed T.

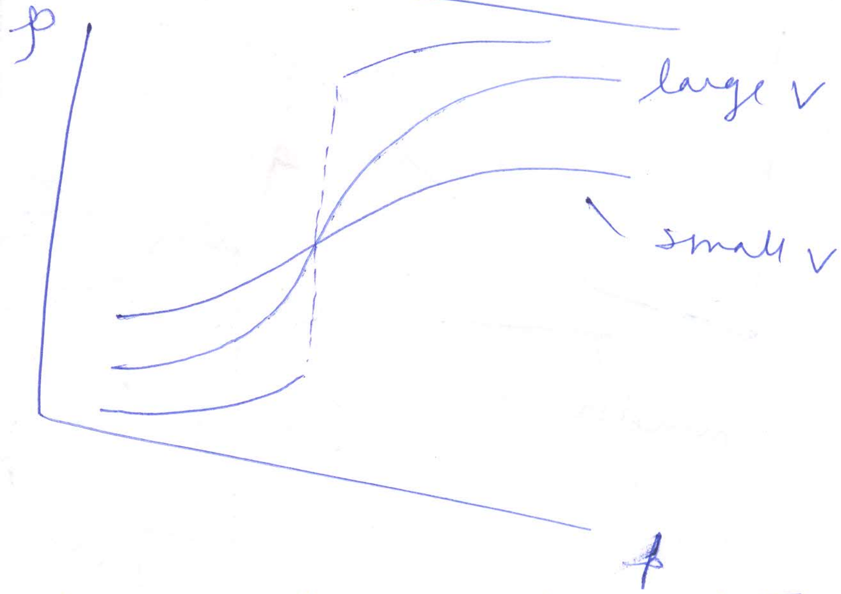
(Such a fn. can never show discontinuity as shown below.)



X not possible at finite V

(we must see phase transition even with the approx. of hard core int. — hard core int. isn't a unreasonable int.)

The only possibility



$\Rightarrow$ In order to see phase transition in this system we need to take $V \to \infty$ limit.

Quantum System

$$Q = \sum_{N=0}^{\infty} z^N Z_N , \quad [\text{where } Z_0 = 1]$$

$$Z_N = \sum_{\alpha} \langle \alpha | e^{-\beta \mathcal{H}} | \alpha \rangle$$

$\alpha \hookrightarrow$ Basis of N-particle states

(1) $Z_N \geq 0$ for every N

(2) $\psi_\alpha(\vec{r}_1, \dots, \vec{r}_N)$ is a basis state for N particle system

If $|\vec{r}_i - \vec{r}_j| < a$, $\psi(\vec{r}_1, \dots, \vec{r}_N) = 0$.

If $N > N_m = \dfrac{V}{\frac{4}{3}\pi (a/2)^3}$, then we cannot have

$$|\vec{r}_i - \vec{r}_j| > a \text{ for every pair } (i,j)$$

$$\langle \alpha | e^{-\beta \hat{H}} | \alpha \rangle = \int d^3 r_1 \cdots d^3 r_N \, \Psi^*_\alpha(\vec{r}_1, \ldots, \vec{r}_N) e^{-\beta \hat{H}}$$

$$\Psi_\alpha(\vec{r}_1, \ldots, \vec{r}_N) = 0$$

$$\Rightarrow Z_N = 0 \text{ for } N > N_m(V)$$

[So you can't get phase transition in interacting quantum system also unless in the $V \to \infty$ limit, as in classical system]

What can we say about the system for $V \to \infty$?

Theorems (Lee-Yang)

① $\lim_{V \to \infty} [V^{-1} \ln \mathcal{Q}(z, V, T)]$ exists for all z on the positive real axis. The limit is independent of the shape of the box and is a continuous, non-decreasing fn of z.

Assumption :- as $V \to \infty$, $\frac{\text{surface area}}{\text{volume}}$ falls off as $V^{-1/3}$.

For all finite V, the zeros are in the complex plane for $\ln \mathcal{Q} = \ln(1 + \cdots)$

$$\ln \mathcal{Q} = \ln(1 + z Z_1 + z^2 Z_2 + \cdots + z^{N_m(V)} Z_{N_m})$$

(Can't have any zero for real z

Nevertheless, it has N_m zeros on the complex plane.

In the lim $V \to \infty$, some of the zeros may come down to the ~~complex plane~~ real axis)

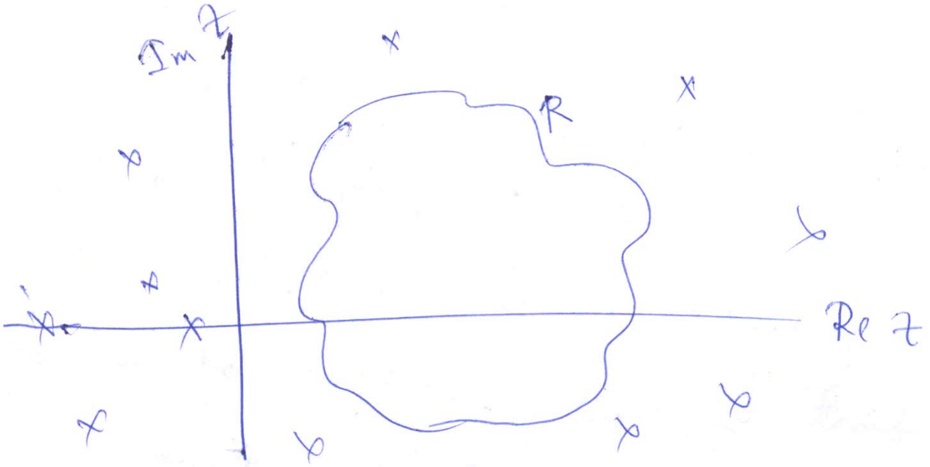
$\therefore \frac{\partial}{\partial z} \lim_{V \to \infty} [\quad - \quad]$ is finite

$Q = 1 + z z_1 + \cdots + z^{N_m(V)} Z_{N_m(V)}$ has $N_m(V) = 0$ roots in the complex plane.

As $V \to \infty$, some of these roots may come down to the real axis.

② Theorem 2 :-

Suppose R is a fixed (V-independent) region of the complex plane containing part of the real axis such that it contains no root of $Q(z, V) = 0$ for any V.



No zero ever enters this region as $V \to \infty$

Then for all $z \in R$, $V^{-1} \ln Q(z, V, T)$ converges uniformly to a limit as $V \to \infty$.

This limit is an analytic function of z for all $z \in R$.

Notion of pointwise convergence vs uniform convergence

Pointwise convergence :-

fix $z = z_0$ (some value)

The sequence $\{f_V(z_0)\}$ converges to

$f(z_0)$ if for every $\epsilon > 0$ we can find V_0 such that

$$\left| f_V(z_0) - f(z_0) \right| < \epsilon \quad \text{for} \quad V > V_0.$$

Uniform Convergence :- $\{f_V(z)\}$ converges to $f(z)$ if for every $\epsilon > 0$, there is a V_0 such that $\left| f_V(z) - f_{V_0}(z) \right| < \epsilon$ for $V > V_0$ and every $z \in R$.

In general, V_0 will be a fn. of z_0

2/3/06

System of interacting molecules with intermolecular interaction $v(\vec{r}_i - \vec{r}_j)$.

Assume:-

1. $v(\vec{r}) = \infty$ for $|\vec{r}| \leq a$
2. $v(\vec{r}) = 0$ for $|\vec{r}| \geq r_0$
3. $v(\vec{r}) \geq -e_0$ for $a < r < r_0$

$$\frac{1}{V} \ln Q(z, V, T) = F(z, V, T)$$

$F(z, V, T)$ is analytic, monotone increasing on the positive real axis of z for finite V.

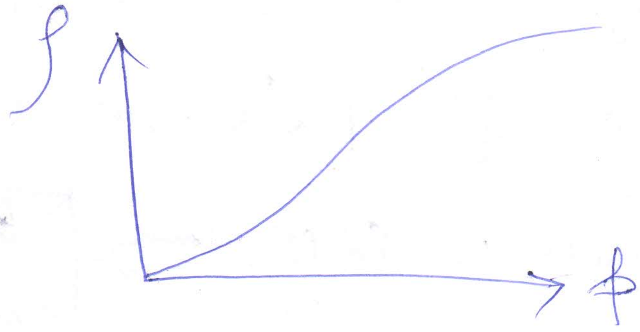
$\Rightarrow p/kT$ is monotone increasing fn. of z

$p \to 0$ as $z \to 0$

$p \to \infty$ as $z \to \infty$

$z \frac{\partial F(z, V, T)}{\partial z}$ is analytic & monotone increasing on positive real z-axis.

$\Rightarrow \rho(z, V, T) = z \frac{\partial}{\partial z}\left(\frac{1}{V} \ln Q\right)$ is analytic & monotone increasing.



for finite V

$\rho = \bar{N}/V$

ρ is smooth — continuous & can't have any singularity

What happens as $V \to \infty$?

Lee-Yang theorem

① $\lim_{V \to \infty} \left[V^{-1} \ln \mathcal{Q}(z, V, T) \right]$ exists for all z on the +ve real axis. The limit is independent of the shape of V & is a continuous non-decreasing function of z.

This result is valid for both classical & quantum systems

Assumption :- As $V \to \infty$, $\left(\text{Surface Area} / V^{2/3} \right) \to$ constant

Bcos $V \sim L^3$ while $A \sim L^2$

If the surface is highly fractal — surface goes up & down several times — then this result isn't true — for complex shapes this isn't true. In normal cases, it is true

② Let R be a region in the complex z - plane containing part of the real axis such that it contains no root of $\mathcal{Q}(z, V, T) = 0$ for any V. Then for all $z \in R$, $V^{-1} \ln \mathcal{Q}(z, V, T)$ converges uniformly to a limit as $V \to \infty$.

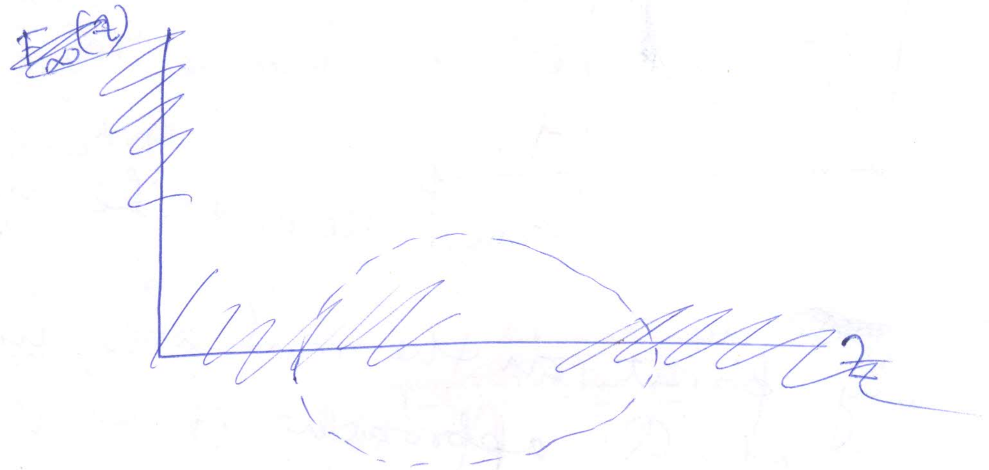
This limit is an analytic function of z for all $z \in R$.

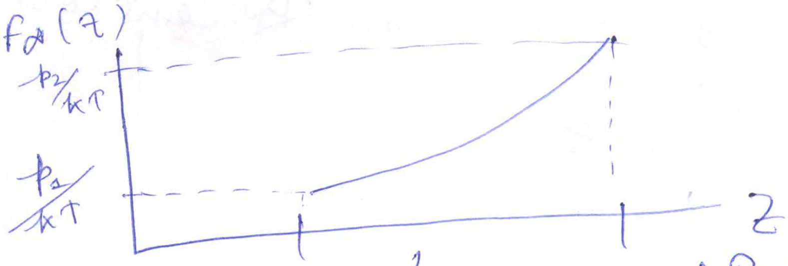
infinitely differentiable for all $z \in R$

Here, it means complex analytic fn — no poles, no branch pts. — inside R — all derivatives exist within R

$$F_\infty(z) = \lim_{V\to\infty} \frac{1}{V} \ln \mathcal{Q}(z, V, T)$$

Consider a segment of the real axis inside the region R.

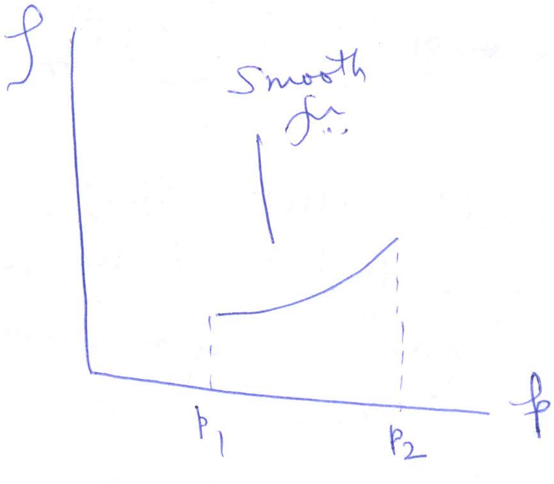




intersection of R with real Z axis

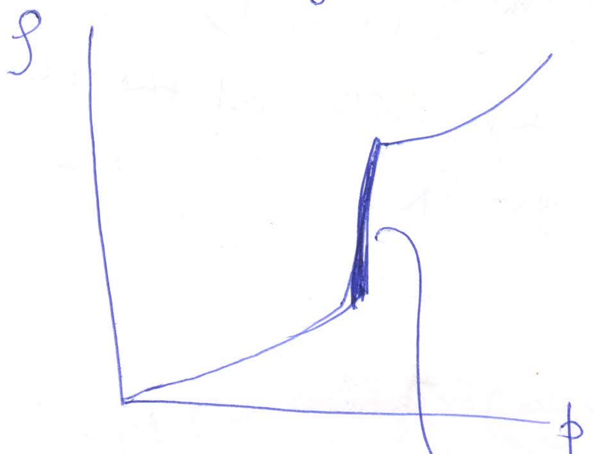
$\rho = z \, df_\infty/dz$

Eliminate z using this & plot ρ vs p



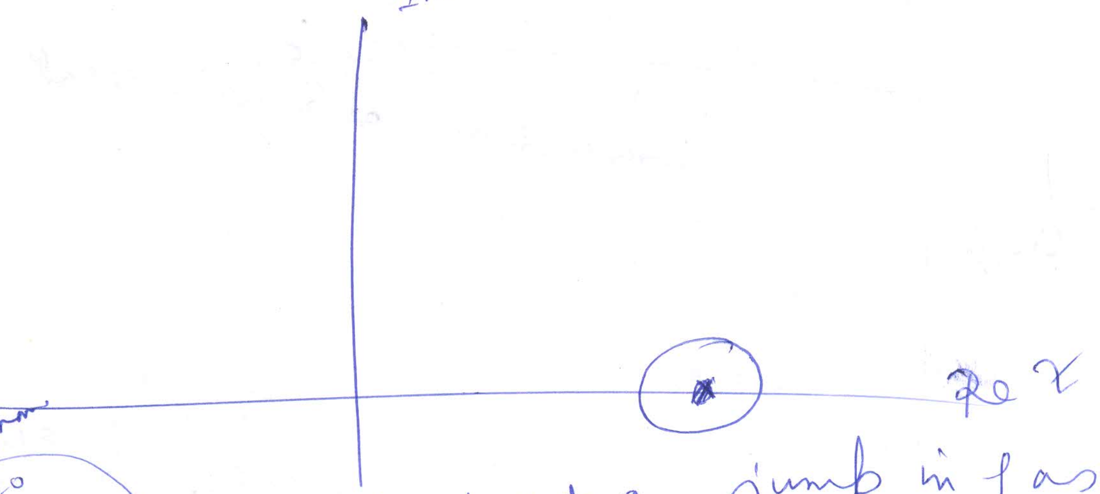
There is no way we can get a discontinuous jump by eliminating Z

We are looking for



must lie outside any R

Given any point on the real axis, unless some zero of $\mathcal{Q}$ approach it as $V \to \infty$, we can always choose an R enclosing that point.



In order to get a jump in ρ as a fn. of p at $z = z_0$, we need one or more zeroes of $\mathcal{Q}$ to approach the point z_0 in the real z-axis.

should have an ∞ order polynom. $1 + z + \cdots = 0$ can have only a finite no. of zeros & so it cannot be a limit pt. of the zeros as $V \to \infty$ unless some zero approach this pt.

α, γ can depend on temperature T

We shall illustrate this in the context of a hypothetical grand canonical partition function:

$$\mathcal{Q}(z, V) = (1+z)^{[\gamma V]} \left(1 + z^{[\alpha V]}\right)$$

α, γ: two constants

$[x]$ = integer part of x

$$F_\infty(z) = \lim_{V\to\infty} \frac{1}{V} \ln \mathcal{G}$$

$$= \lim_{V\to\infty} \frac{1}{V} \ln \left\{ (1+z)^{[\gamma V]} (1+z^{[\alpha V]}) \right\}$$

① $\mathcal{G}$ is clearly a polynomial of finite degree

② All the coeff. of Taylor series exp. are +ve

So the general inputs we have used in deriving the results are true for this choice of $\mathcal{G}$

$\alpha, \gamma \Rightarrow$ +ve constants

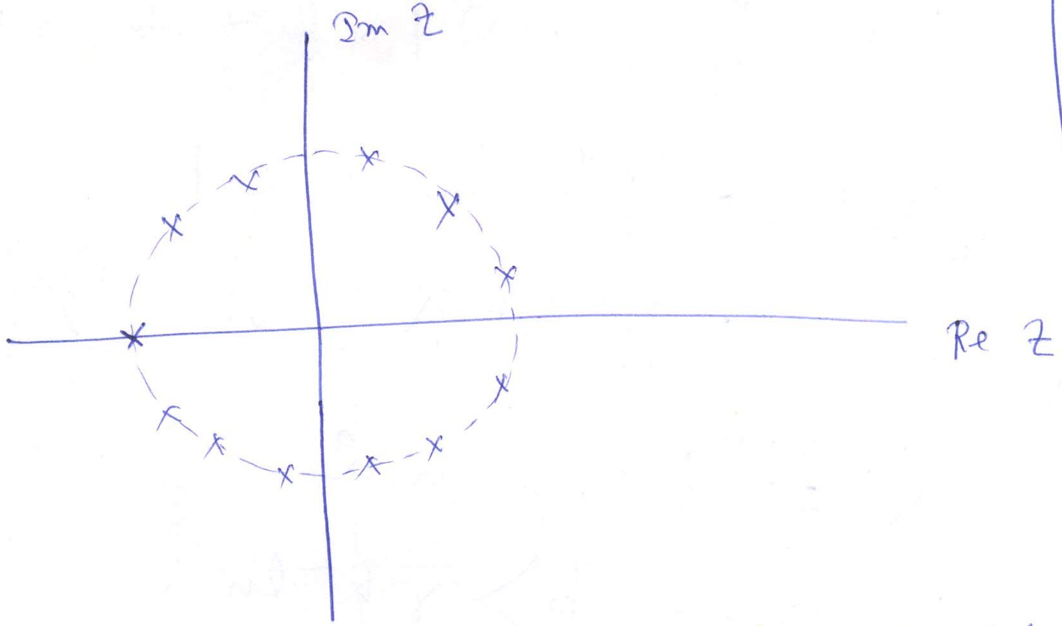
So this $\mathcal{G}$ will illustrate whatever results we have stated

① $F_\infty(z)$ should be continuous & monotone increasing for $0 < z < \infty$.

② Zeroes of $\mathcal{G}$:-

$$z = -1, \quad (-1)^{\frac{1}{[\alpha V]}} = e^{2\pi i (k+1/2)/[\alpha V]}$$

$$k = 0, 1, 2, \ldots, [\alpha V] - 1$$



Roots become denser & denser as you increase V, as the unit circle is fixed. However no root is on +ve real axis

Nevertheless Roots approach $z = 1$ as $V \to \infty$

But $z = 1$ may be the limit pt. of a set of zeroes

Then you can't find R around $z = 1$ where the fn. ~~is analytic~~ -

$R_1 : 0 \le |z| < 1$

$R_2 : |z| > 1$

$F_\infty(z)$ should be analytic inside R_1 & also inside R_2

$0 < \mathrm{Re}\, z < 1$

$\mathrm{Re}\, z > 1$

$$F_\infty(z) = \lim_{V\to\infty} \frac{1}{V} \left[[\gamma V] \ln(1+z) + \ln\left(1+z^{[\alpha V]}\right) \right]$$

$= \gamma \ln(1+z)$ if $|z| < 1$

$\because \ln(1+z^{[\alpha V]}) \to 0$ as $V \to \infty$ for $|z| < 1$

$= \gamma \ln(1+z) + \alpha \ln z$ if $|z| > 1$

(On the real z-axis, it is analytic inside & outside $z=1$)

~~It is ca~~

$\cancel{\ln(1+z^{(\alpha v)})}$
$\cancel{= 0}$

As $v \to \infty$,
$\ln(1+z^{(\alpha v)}) \to (\alpha v) z$

① $F_\infty(z)$ is monotone increasing & continuous on the real z-axis.

② $F_\infty(z)$ is analytic for $|z|<1$ & $|z|>1$.

At $z=1$, the ~~derivative~~ F_∞ isn't differentiable

$$p/kT = \lim_{v\to\infty} \frac{1}{v} \ln \mathcal{Q} = F_\infty(z)$$

$$p/kT = \gamma \ln(1+z) \text{ for } |z|<1$$
$$= \gamma \ln(1+z) + \alpha \ln z \text{ for } |z|>1$$

$$\rho = z\frac{\partial}{\partial z} F_\infty(z) = \frac{\gamma z}{1+z} \text{ for } |z|<1$$
$$= \frac{\gamma z}{1+z} + \alpha \quad \text{for } |z|>1$$

We need to eliminate z from these 2 relations to express p as a fn. of ρ & T

$$z<1 \xrightarrow[\text{to}]{\text{corresponds}} p < \gamma kT \ln 2$$

$$z> \xrightarrow[\text{to}]{\text{corresponds}} p > \gamma kT \ln 2$$

$$\frac{\gamma}{\rho} = \frac{1+z}{z} = \frac{1}{z}+1 \text{ for } |z|<1$$

$$\frac{1}{z} = (\gamma/\rho - 1) \Rightarrow z = \frac{1}{\gamma/\rho - 1} \text{ for } |z|<1,$$

$$z = \frac{1}{\frac{\gamma}{\rho-\alpha} - 1} \text{ for } |z|>1$$

$$\frac{p}{kT} = \gamma \ln\left(1 + \frac{1}{\gamma/\rho - 1}\right) = \gamma \ln\left(\frac{\gamma/\rho}{\gamma/\rho - 1}\right)$$
$$= \gamma \ln\left(\frac{1}{1-\rho/\gamma}\right)$$

$z=1 \Rightarrow p = \gamma kT \ln 2,\ \rho = \gamma/2$

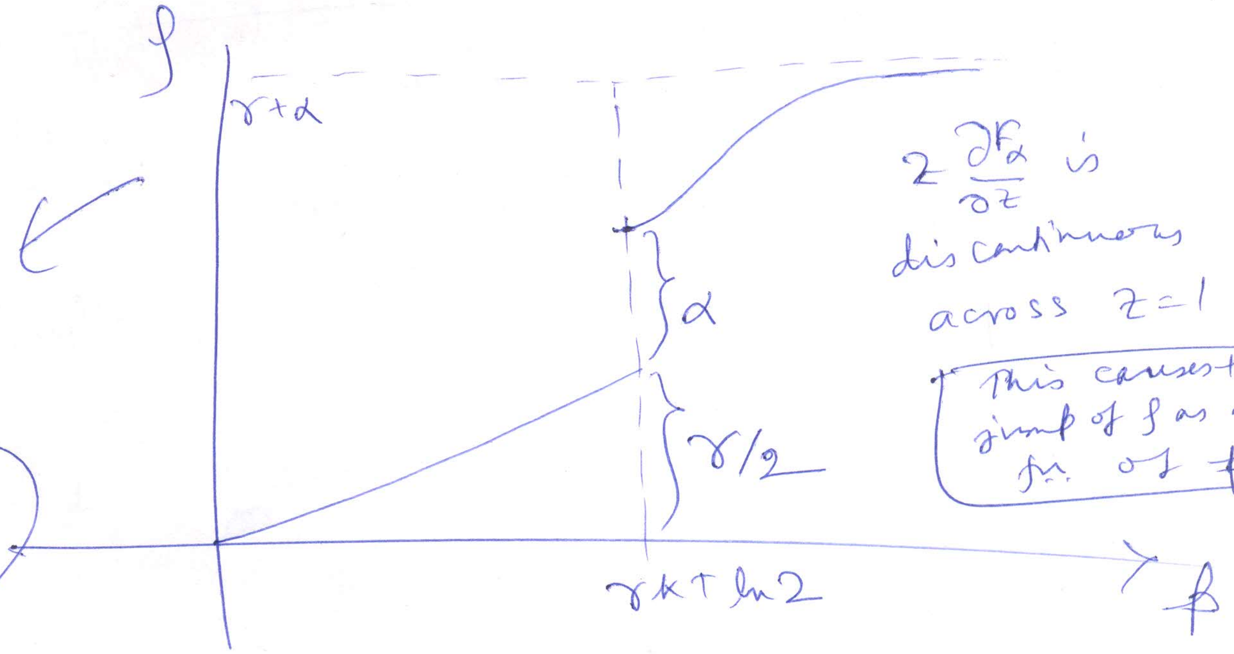
$z \to 0 \Rightarrow p \to 0$ (relation for) $p < \gamma kT \ln 2$

$z > 1,\ p > \gamma kT \ln 2$

$$\frac{p}{kT} = \gamma \ln\left(\frac{1}{1 - \frac{\rho - \alpha}{\gamma}}\right) + \alpha \ln\left(\frac{1}{\frac{\gamma}{\rho - \alpha} - 1}\right)$$

For $p = \gamma kT \ln 2 \Rightarrow z = 1 \Rightarrow \rho = \gamma/2 + \alpha$

$z \to \infty \Rightarrow p \to \infty,\ \rho \to \gamma + \alpha$



first order phase transition

Bcos the 1st derivative is discontinuous

$z \frac{\partial F_\alpha}{\partial z}$ is discontinuous across $z=1$

This causes the jump of ρ as a fn. of p

As $z \to 0$, $p \to 0$ & $\rho \to 0$.

As $z \to \infty$, $p \to \infty$ & $\rho \to \gamma + \alpha$

$\#$ If $\frac{d^m F_\infty}{dz^m}$ is continuous for $m < n$ & discontinuous for $m = n$, then we have an n^{th} order phase transition.

[As you change temp., the jump 'α' will change. As you $\uparrow$ T, $\alpha \downarrow$ & at ~~the~~ the critical temp. T_c, α vanishes & there is no phase transition.

This is just a model we have used & hence the displaced + dependence of α]

In a real situation, we always get a behaviour like :-