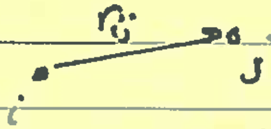
Yang and Lee I PR 87, 404 (1952). (1)

Consider a monatomic gas with interactions

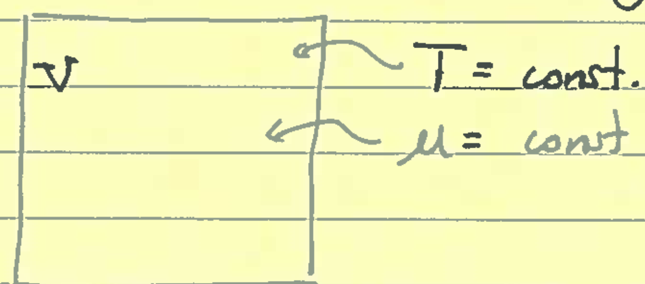
$$U = \sum u(r_{ij})$$



$u(r) = \infty \quad r \leq a \leftarrow$ hard core repulsion

$u(r) = 0$ for $r \geq b \leftarrow$ finite range.

$u > -\infty$ for all r. No infinitely deep traps.



Relative prob of there being N atoms in the box: $Q_N \, y^N \frac{1}{N!}$

where $Q_N = \int \prod_{i=1}^{N} d^3x_i \, e^{-U/k_BT}$ and

$$y = e^{\mu/k_BT} \frac{1}{\lambda_B^3} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{\mu/k_BT}$$

Note $y \to 0 \iff \mu \to -\infty$ "fugacity"

$y \to \infty \iff \mu \to +\infty$

Grand Partition Sum $\mathcal{Z}_V = \sum_{N=0}^{M} \frac{Q_N}{N!} y^N$

Note: (a) M = maximum # atoms due to hard core.

$M < \infty$.

(b) $\mathcal{Z}_V \to 1$ as $N \to 0$

We want to investigate the thermodynamic limit $V \to \infty$ (μ, T fixed)

$$\frac{P}{k_B T} = \lim_{V\to\infty} \frac{1}{V} \ln \mathcal{Z}_V \quad \leftarrow \text{"Grand Potential"}$$

$$\rho = \lim_{V\to\infty} \frac{\partial}{\partial \ln y}\left(\frac{1}{V} \ln \mathcal{Z}_V\right) \quad \leftarrow \text{Number density}$$

Do these limits exist for the system in both the gas and liquid phases?

Yang and Lee propose (and prove) two theorems:

☆ <u>Thm I.</u> For all y, $\mathrm{Im}(y) = 0$ and $\mathrm{Re}(y) > 0$

$\frac{1}{V} \ln \mathcal{Z}_V \xrightarrow[V\to\infty]{}$ has a limit that is independent of the shape of V and that limit $\frac{P}{k_B T}$ is a continuous, monotonically increasing function of y.

This ensures that pressure is well-defined and a monotonically increasing function of density.

Now what about the other limit?

$$\frac{\partial}{\partial \log y} \frac{1}{V} \ln \mathcal{Z}_V$$

$\mathcal{Z}_V$ is a polynomial in y of finite degree M.

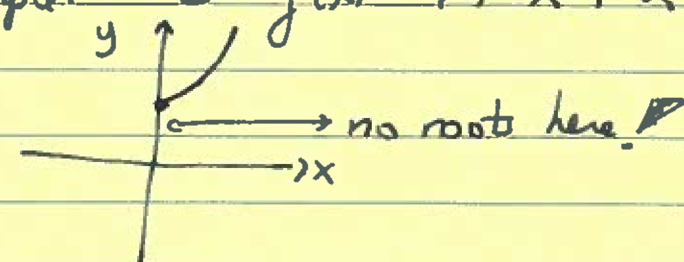
$$\mathcal{Z}_V = \prod_{i=1}^{M} \left(1 - \frac{y}{y_i}\right) \quad \longleftarrow \text{ensures that } \mathcal{Z}_V(0) = 1$$

y_i ← roots of $\mathcal{Z}_V$.

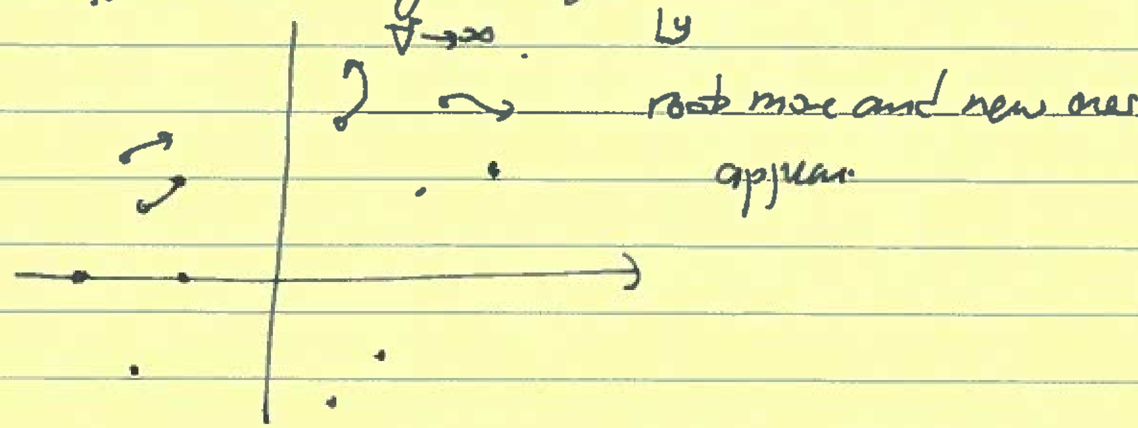
$\mathcal{Z}_V(y_i) = 0$ for $y_1, \ldots, y_M$.

None of the roots can lie on the positive real axis since each coefficient is > 0

example: $y(x) = 1 + x + x^2 + \cdots$



As V increases the roots may move around and new ones appear as M gets bigger



☆ Thm II. If in the complex y plane a region R containing part of the real axis (positive) is free of roots then all quantities

$$\frac{1}{V}\log \mathcal{Q}_V,\ \frac{\partial}{\partial \ln y}\frac{1}{V}\ln \mathcal{Q}_V,\ \ldots \left(\frac{\partial}{\partial \ln y}\right)^n \frac{1}{V}\ln \mathcal{Q}_V$$

approach limits that are analytic in y.

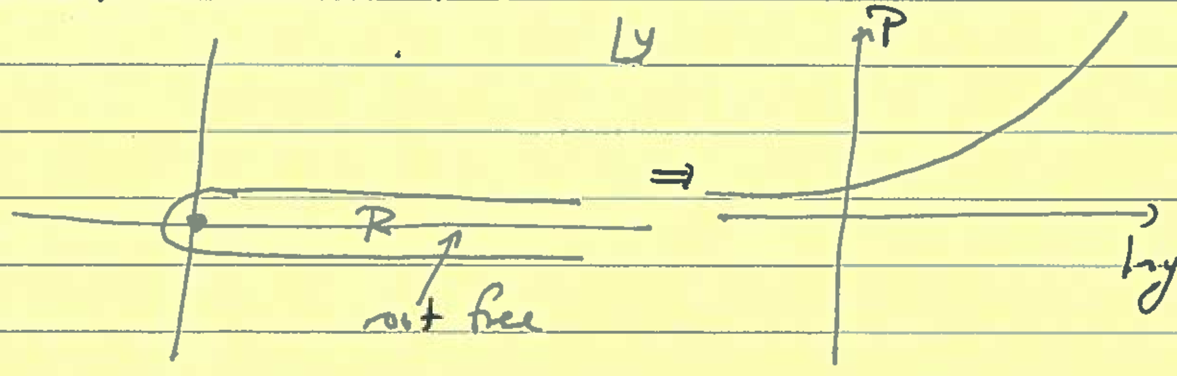
Furthermore, $\lim_{V\to\infty}$ and $\frac{\partial}{\partial \ln y}$ commute in R.

$$\Longrightarrow \underbrace{\lim_{V\to\infty}\frac{\partial}{\partial \ln y}\frac{1}{V}\ln \mathcal{Q}_V}_{\rho} = \frac{\partial}{\partial \ln y}\lim_{V\to\infty}\frac{1}{V}\ln \mathcal{Q}_V \text{ so}$$

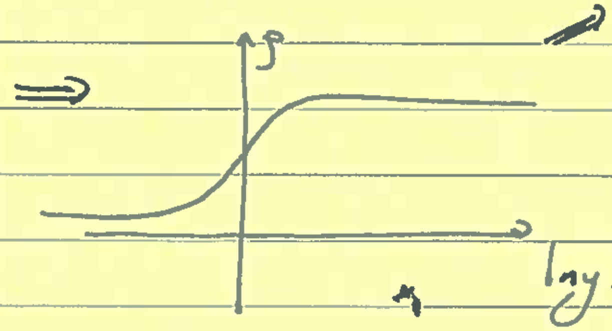
$$\rho = \frac{\partial}{\partial \ln y}\frac{P}{k_B T}$$

We have a single-valued equation of state. No phase transitions. So where are they?

Consider the following cases:
(1) The roots of $\mathcal{Q}_V(y) = 0$ do not close into the positive real axis as $V\to\infty$

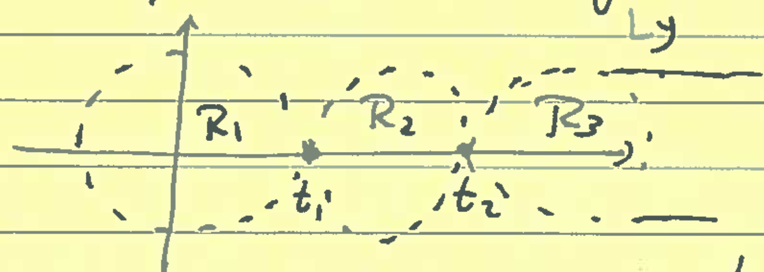


$\Longrightarrow$



There is a single ρ as a function of $\ln y$ $\Longleftrightarrow$ One phase.

(2) The roots of $\mathcal{Q}_V(y) = 0$ close onto the real positive y axis at pts. $y = t_1, t_2$



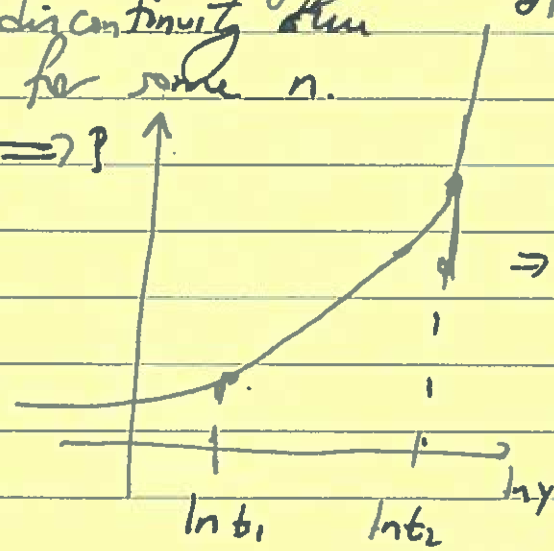
Note t_1, t_2 will dependent on T.
t_1 vanishes at T_c
$t_1 \to t_2$ at triple pt.

There is a single phase P ρ are analytic (and increasing) functions of $\ln y$ in each region R_1, R_2, R_3

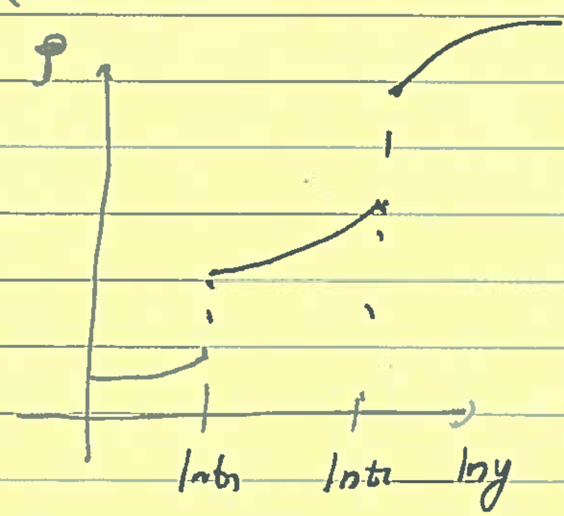
at $y = t_1, t_2$ P is continuous by Thm I.

But in general $\dfrac{\partial^n}{\partial \ln y^n}\left(\dfrac{1}{V}\ln \mathcal{Q}_V(y)\right)$ has a ~~disc~~ discontinuity there for some n.

$\Longrightarrow \rho$



$\Rightarrow$



Comparison with Meyer's Theory.

$$\frac{1}{V}\ln \mathcal{Z}_V = \sum_{l=1}^{\infty} b_l(V) y^l$$ Mayer cluster expansion.

Compare to $\mathcal{Z}_V = \prod_{i=1}^{M}(1 - y/y_i)$ and we see that.

$$\frac{1}{V}\ln \mathcal{Z}_V = \frac{1}{V}\sum_{i=1}^{M} \ln(1 - y/y_i) \leftarrow \text{expand the log.}$$

$$= -\sum_{i=1}^{M}\frac{1}{V}\frac{1}{l}\left(\frac{y}{y_i}\right)^l = \sum_{l=1}^{\infty} b_l(V) y^l$$

$$\Rightarrow \boxed{b_l(V) = -\frac{1}{lV}\sum_{i=1}^{M}\left(\frac{1}{y_i}\right)^l}$$

b_l = "reducible cluster integrals of Mayer"

And we see that

$$\frac{Q_N y^N}{N!} = \text{coefficient of } y^N \text{ in the expansion of:}$$

$$\exp\left[V\sum_{l=1}^{\infty} b_l y^l\right] = \mathcal{Z}_V.$$

Mayer theory $\Rightarrow$ replace $b_l(V)$ by $b_l(\infty)$.

mayer theory is really: $\chi(y) = \sum_{\ell=1}^{\infty} b_\ell(\infty)\, y^\ell$

Now say $y = t_1$ is the first singularity along the positive y axis.

$$\rho_1 = \lim_{y \to t_1^-} y\chi'(y)$$

For densities $\rho_\Phi < \rho_1$ we have a convergent cluster expansion.