Interacting Classical Gases

Real gases differ from ideal gases in two important ways

① Interactions are present.

② there are (or may be) quantum mechanical effects.

Let us consider first the case of a gas sufficiently dilute so that the (mean) distance between the atoms (or molecules) is large compared to their ~~the~~ Broglie thermal wavelength, i.e.

$$\lambda_T = \frac{h}{p} = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2} \ll n^{-1/3} \qquad \left(n = \frac{N}{V}\right)$$

$$\Rightarrow \quad n^{2/3} \ll \frac{mkT}{2\pi^2\hbar^2}$$

In this regime quantum effects are ~~all~~ negligible. Also if n is low enough, interaction effects may also be weak. In this limit we should expect ~~the~~ to find that quantities of interest should be computable as a power series expansion of the density (in suitable units)

Thus consider a classical system of N particles of mass M (for the moment we will work in the canonical ensemble) with an energy (or Hamiltonian)

$$E_N(\vec{r}_1, \ldots, \vec{r}_N; \vec{p}_1, \ldots, \vec{p}_N) =$$
$$= \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2M} + \sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)$$

Here we are assuming that the particles are point-like and that as such we can work with central potentials. This assumption clearly breaks down at high densities and its failure is connected with the fact that, for instance, water has a complex phase diagram. However, at low densities the behavior of a real gas should differ from that of an ideal gas only by corrections which are analytic functions of a parameter controlled by the density.

For a system of N particles, the partition function is

$$Z_N = \frac{1}{N!} \int \frac{d^3p_1 \cdots d^3p_N \cdot d^3r_1 \cdots d^3r_N}{(2\pi\hbar)^{3N}} \; e^{-E_N([\vec{r}],[\vec{p}])/kT}$$

$$\equiv \frac{1}{N!} \left(\frac{V}{\lambda_T^3}\right)^N \frac{Q_N}{V^N} \qquad \left(\lambda_T = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2} \right)$$

$$Q_N = \int d^3r_1 \ldots d^3r_N \; e^{-\sum_{i<j} U(|\vec{r}_i - \vec{r}_j|)/kT}$$

which is known as the configurational Partition Function. For a classical ideal gas $\frac{Q_N}{V^N} = 1$.

Consider first a two-particle problem $(N=2)$

$$\Rightarrow Q_2 = \int d^3r_1 \, d^3r_2 \; e^{-\beta U(|\vec{r}_1 - \vec{r}_2|)}$$

In the coordinates

$$\vec{r}_1 = \vec{R} + \tfrac{1}{2}\vec{r} \qquad , \text{i.e.} \quad \vec{R} = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2) = \vec{R}_{CM}$$

$$\vec{r}_2 = \vec{R} - \tfrac{1}{2}\vec{r} \qquad \vec{r} = \vec{r}_1 - \vec{r}_2 = \text{rel. coord.}$$

(with Jacobian $= 1$) we can write Q_2 as

$$Q_2 = \int d^3R \, d^3r \; e^{-\beta U(r)} \equiv V \int d^3r \; e^{-\beta U(r)}$$

(since $\int d^3R \; 1 = V$)

Typical form of $U(r)$ for neutral systems

(for charged systems there is a Coulomb piece which goes like $\sim \frac{1}{r}$)

In many systems (e.g. He) there is a strong short-range repulsion and a weak longer range attraction (the latter due to van der Waals interactions ~~and~~ which have a quantum mechanical origin) of the form (Lennard-Jones)

$$U_{LJ} = \frac{A}{r^n} - \frac{B}{r^6} \qquad \text{(typically } n = 12\text{) ("6-12 potential")}$$

Let us define the quantity

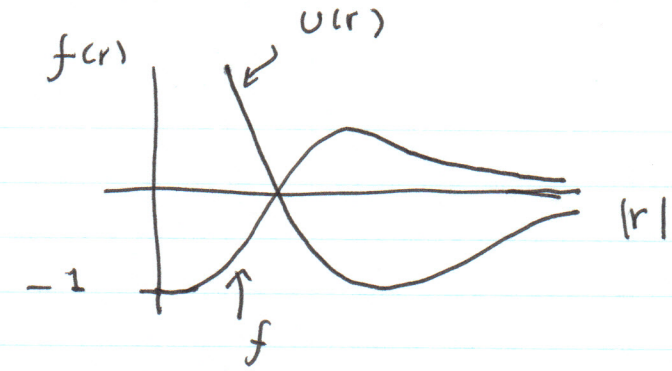
$$f_{0j}(r) = e^{-\beta U(|\vec{r}_0 - \vec{r}_j|)} - 1$$

Clearly $\lim_{r\to\infty} f(r) = 0 \quad (O(\beta U))$

and $\lim_{r\to 0} f(r) = -1 \quad (\text{if } U \underset{r\to 0}{\to} \infty)$

(otherwise $f(0) = e^{-\beta U(0)} - 1$)

$\Rightarrow$



$\Rightarrow$ $f(r)$ is bounded (everywhere) and becomes small at large distances.

Let us write the Grand Partition Function $\mathcal{Z}$ (i.e. in the Grand Canonical Ensemble with fugacity $z = e^{\beta\mu}$; μ: chemical potential)

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \mathcal{Z}_N$$

$$\equiv \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{z}{\lambda_T^3}\right)^N Q_N(V,T)$$

$$\Rightarrow \quad e^{-\beta U(|\vec{r}_{ij}|)} = 1 + f_{ij}$$

$$f_{ij} = f(|r_{ij}|)$$

$$\Rightarrow \quad Q_N = \int d^3r_1 \cdots d^3r_N \prod_{i<j} (1 + f_{ij}[r])$$

Clearly

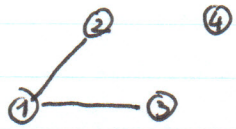
$$Q_N = \int d^3r_1 \cdots d^3r_N \left[1 + (f_{12} + f_{13} + \cdots) + (f_{12} f_{13} + f_{12} f_{14} + \cdots) + \cdots \right]$$

$\Rightarrow$ Q_N is a series (actually a polynomial) involving integrals of products of f's. What does it mean? The term "1" is the ideal gas term. Here each point particle does not interact with the others. The terms linear in f's involve two-particle "collisions", whereas terms with say $f_{12} f_{13}$ involve ~~an~~ 3-particle <u>cluster</u> of interacting particles. This leads to the notion of a <u>Cluster Expansion</u> (Meyer-Kirkwood)

We will use a graphical method to organize this series. We will construct a <u>graph</u> to represent an arbitrary term ~~in~~ contributing to Q_N as follows. Let represent each of the N particles by a circle ($\Rightarrow$ N circles).

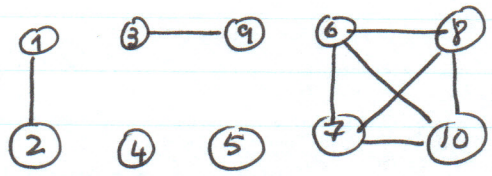
If a pair of particles interact (i.e. if there is an f for that pair in that contribution) we will link the two circles by a line

e.g.



$$\equiv f_{12}\, f_{13} \cdot \underset{\substack{\uparrow \\ (4)}}{1}$$

Or:



$$\Rightarrow f_{12}\, f_{39}\, f_{68}\, f_{8,10}\, f_{10,7}\, f_{76}\, f_{6,10}\, f_{78}$$

Note: only <u>one factor per pair</u>.

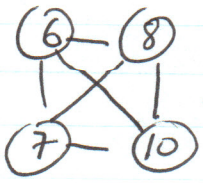
Some of these graphs involve separate integrals

e.g.  is disconnected from say 

$$\Rightarrow [(4)] \cdot [(5)] \cdot [(1)\text{—}(2)]\, [(3)\text{—}(9)]\, \Big[\text{(6–8, 7–10)} \Big]$$

connected connected connected

Let us define an <u>l-cluster integral</u> (i.e. an integral over a cluster with l connected particles)



$$\equiv \int d^3r_6\, d^3r_7\, d^3r_8\, d^3r_{10}\; f_{68}\, f_{8,10}\, f_{10,7}\, f_{7,6}\, f_{6,10}\, f_{78}$$

Let us define a cluster integral b_ℓ

$$b_\ell = \frac{1}{\ell!\ \lambda_T^{3\ell-3} V} \left[\text{sum of all possible } \ell\text{-clusters}\right]$$

note: b_ℓ is dimensionless and $\lim_{V\to\infty} b_\ell = \bar{b}_\ell(T) < \infty$

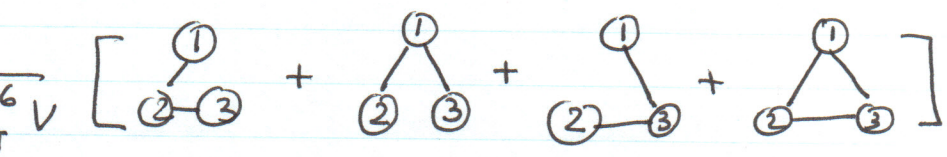
e.g.

$$b_1 = \frac{1}{V}\left[\textcircled{1}\right] = \frac{1}{V}\int d^3r_1 \cdot 1 = 1$$

$$b_2 = \frac{1}{2!\ \lambda_T^3 V}\left[\textcircled{1}\!-\!\textcircled{2}\right] =$$

$$= \frac{1}{2!\ \lambda_T^3 V}\int d^3r_1\, d^3r_2\ f_{12} =$$

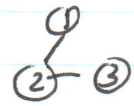
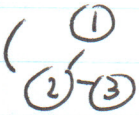
$$= \frac{1}{2!\ \lambda_T^3 \cancel{V}}\ \cancel{V}\int d^3r_{12}\ f_{12} < \infty$$

$b_3 =$ 

etc.

An arbitrary N-particle graph is decomposable into products of clusters. If we denote by m_ℓ the # of ℓ-particle clusters $\Rightarrow$

$$N = \sum_{\ell=1}^{N} \ell\, m_\ell$$

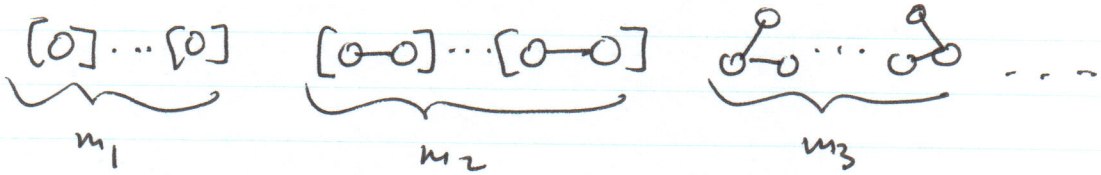
The integers $\{m_\ell\}$ do not specify a graph uniquely since there are many ways to form an ℓ-particle ~~graph~~ cluster (i.e.  or  etc) and there are many ways of assigning which particle belongs to which cluster ( or )

$\Rightarrow$ the set $\{m_\ell\}$ defines a <u>collection of graphs</u>.

$$\Rightarrow \mathcal{Q}_N = \sum_{\{m_\ell\}} S[\{m_\ell\}]$$

sum over sets

An arbitrary N-particle graph has m_1 1-clusters, m_2 2-clusters, etc.



$\Rightarrow$ the numbers $1, \ldots, N$ must be assigned to these circles in all possible ways. Given one assignment a <u>permutation</u> of the labels leads to another graph.

$$\Rightarrow S[\{m_\ell\}] = \sum_{P} \left\{ [\bigcirc]^{m_1} \cdot [\bigcirc\!-\!\bigcirc]^{m_2} \cdot \left[\text{diagram} + \text{diagram} + \text{diagram} + \text{diagram} \right]^{m_3} \cdots \right\}$$

permutations of N objects

Since each graph is an integral which does not depend on the way the variables (circles) are labelled

$\Rightarrow$ $S[m_\ell] = (\#$ of terms in $\sum_P$ $) \times$ value in ~~each~~ any term

How many terms do we have?

(1) we have m_ℓ ℓ-clusters and a permutation of those m_ℓ things does not lead to a new graph

(2) in the sum over ℓ-clusters a permutation of the ℓ particles does not lead to a new graph.

$\Rightarrow$ the # of terms in $\sum_P$ is : $\dfrac{N!}{[(1!)^{m_1}(2!)^{m_2}\cdots][m_1!\,m_2!\cdots]}$

The value of each term is

$$(1!\,V\,b_1)^{m_1}\,(2!\,\lambda_T^3\,V b_2)^{m_2}\,(3!\,\lambda_T^6\,V b_3)^{m_3}\cdots$$

$$\Rightarrow \quad S[\{m_\ell\}] = N! \prod_{\ell=1}^{N} \frac{(V\,\lambda_T^{3\ell-3}\,b_\ell)^{m_\ell}}{m_\ell!}$$

$$= N!\,\lambda_T^{3N} \prod_{\ell=1}^{N} \frac{1}{m_\ell!}\left(\frac{V}{\lambda_T^3}\,b_\ell\right)^{m_\ell}$$

$$\Rightarrow \quad Q_N = N!\, \lambda_T^{3N} \sum_{\{m_\ell\}}{}' \prod_{\ell=1}^{N} \frac{1}{m_\ell!} \left(\frac{V b_\ell}{\lambda_T^3}\right)^{m_\ell}$$

where $(')$ means that the sum is restricted to those m_ℓ's s.t. $\sum_{\ell=1}^{N} \ell m_\ell = N$

The Grand Partition Function has a simpler structure

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{z}{\lambda_T^3}\right)^N Q_N$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{\cancel{N!}\, \cancel{\lambda_T^{3N}}} \cancel{N!}\, \cancel{\lambda_T^{3N}} \sum_{\{m_\ell\}}{}' \prod_{\ell=1}^{N} \frac{1}{m_\ell!} \left(\frac{V b_\ell}{\lambda_T^3}\right)^{m_\ell}$$

$$= \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \cdots \frac{1}{m_1!} \left(\frac{V z b_1}{\lambda_T^3}\right)^{m_1} \frac{1}{m_2!} \left(\frac{V z^2 b_2}{\lambda_T^3}\right)^{m_2} \cdots$$

$$= \left(\sum_{m_1=0}^{\infty} \frac{1}{m_1!} \left(\frac{V z b_1}{\lambda_T^3}\right)^{m_1}\right) \left(\sum_{m_2=0}^{\infty} \frac{1}{m_2!} \left(\frac{V z^2 b_2}{\lambda_T^3}\right)^{m_2}\right) \cdots$$

$\Rightarrow$ each factor is an exponential!

$$\sum_{m_\ell=0}^{\infty} \frac{1}{m_\ell!} \left(\frac{V z^\ell b_\ell}{\lambda_T^3}\right)^{m_\ell} = e^{V z^\ell b_\ell / \lambda_T^3}$$

$$\Rightarrow \log \mathcal{Z} = \frac{V}{\lambda_T^3} \sum_{\ell=1}^{\infty} b_\ell z^\ell$$

and $\frac{1}{V}\log \mathcal{Z} = \frac{1}{\lambda_T^3}\sum_{l=1}^{\infty} b_l z^l$ [Linked Cluster Theorem]

Since $\log \mathcal{Z} = \frac{PV}{kT}$

$$\Rightarrow \boxed{\frac{P}{kT} = \frac{1}{\lambda_T^3}\sum_{l=1}^{\infty} b_l z^l} \qquad (1)$$

What is the density? Since $\frac{\partial \log \mathcal{Z}}{\partial \log z} = \langle N \rangle$

$$\Rightarrow n = \frac{1}{V}\frac{\partial \log \mathcal{Z}}{\partial \log z} = \frac{1}{v}$$ (v: ~~spa~~ volume per particle)

$$\Rightarrow \boxed{\frac{1}{v} = \frac{1}{\lambda_T^3}\sum_{l=1}^{\infty} l\, b_l z^l} \qquad (2)$$

The simultaneous solution of (1) + (2) leads to the <u>Equation of State</u>.

<u>Thermodynamic Limit</u>: Consider the limit $V \to \infty$ while keeping the density $n = \frac{\langle N \rangle}{V}$ <u>finite</u>

We will discuss below when is this limit legitimate and why. We will assume for now that it exists.

$\Rightarrow$ we can replace $b_\ell \equiv b_\ell(V,T) \xrightarrow[V\to\infty]{} \bar{b}_\ell(T) < \infty$

and write

$$\frac{P}{kT} = \frac{1}{\lambda_T^3} \sum_{\ell=1}^{\infty} \bar{b}_\ell z^\ell \qquad (\bar{1})$$

$$\frac{1}{v} = \frac{1}{\lambda_T^3} \sum_{\ell=1}^{\infty} \ell \bar{b}_\ell z^\ell \qquad (\bar{2})$$

If these series are convergent (which is what we are assuming) $\Rightarrow$ within their radii of convergence we can invert $(\bar{2})$ and find z in terms of v and T (through the $\bar{b}_\ell$'s)

$\Rightarrow$ at least formally we can write $\frac{Pv}{kT}$ as an expansion in powers of $\frac{1}{v}$ of the form

$$\frac{Pv}{kT} = \sum_{\ell=1}^{\infty} a_\ell(T) \left(\frac{\lambda_T^3}{v}\right)^{\ell-1} \qquad \underline{\text{Virial Expansion}}$$

The virial coefficients $a_\ell(T)$ are related to the cluster integrals $\bar{b}_\ell(T)$ in a complicated manner.

$$\frac{\sum_{\ell=1}^{\infty} \bar{b}_\ell z^\ell}{\sum_{\ell=1}^{\infty} \ell \bar{b}_\ell z^\ell} = \sum_{\ell=1}^{\infty} a_\ell \left(\sum_{n=1}^{\infty} n \bar{b}_n z^n\right)^{\ell-1}$$

By expanding the series out we get

$$a_1 = \bar{b}_1 = 1$$

$$a_2 = -\bar{b}_2$$

$$a_3 = 4\bar{b}_2^{\,2} - 2\bar{b}_3$$

$$a_4 = -20\bar{b}_2^{\,3} + 18\,\bar{b}_2\bar{b}_3 - 3\bar{b}_4$$

etc.

where each $\bar{b}_n$ is an integral (or integrals)

For example

$$\bar{b}_2 = \lim_{V\to\infty} \frac{1}{2!\,\lambda_T^3 V} \int d^3r_1\, d^3r_2 \left(e^{-\beta U(r_{12})} - 1\right)$$

$$= \lim_{V\to\infty} \frac{1}{2!\,\lambda_T^3 \cancel{V}} \cancel{V} \int d^3r\; f_{12}(r) \quad < \infty$$

$$\bar{b}_2 = \frac{4\pi}{2!\,\lambda_T^3} \int_0^\infty dr\, r^2 f_{12}(r)$$

$$= \frac{2\pi}{\lambda_T^3} \int_0^\infty dr\, r^2 f_{12}(r)$$

$$f_{12}(r) = e^{-\beta U(r)} - 1$$

$$\Rightarrow \frac{pv}{kT} = 1 + a_2(T)\frac{\lambda_T^3}{v} + a_3(T)\left(\frac{\lambda_T^3}{v}\right)^2 + \cdots$$

second virial coefficient

This expansion is accurate if $\frac{\lambda_T^3}{v} \ll 1$

where $a_2(T) = -\frac{2\pi}{\lambda_T^3}\int_0^\infty dr\, r^2 f_{12}(r)$

Since $f_{12}(r) = e^{-\beta U(r)} - 1 = 0$ if $U=0$ for some r_0

$$\Rightarrow \int_0^\infty dr\, r^2 f(r) = -\left|\int_0^{r_0} dr\, r^2 f(r)\right| + \int_{r_0}^\infty dr\, r^2 f(r)$$

provided $U<0$ for $r>r_0$ and $U>0$ for $r<r_0$

$$\Rightarrow a_2(T) = +\frac{2\pi}{\lambda_T^3}\left|\int_0^{r_0} dr\, r^2 f(r)\right| - \frac{2\pi}{\lambda_T^3}\int_{r_0}^\infty dr\, r^2 f(r)$$

If $U(r) \to +\infty$ for $|r| \leq r_0$ ("hard core")

$$\Rightarrow f(r) = -1 \quad \forall\ |r|<r_0$$

$$a_2(T) = \frac{2\pi}{3}\frac{1}{\lambda_T^3} - \frac{2\pi}{\lambda_T^3}\int_{r_0}^\infty dr\, r^2 f(r)$$

Check: this result is equivalent to a low density

expansion of the Van der Waals Equation of State

$$\left(P + \frac{a}{V^2}\right)(V-b) = NkT$$

to lowest order in the density $\frac{N}{V} = n = \frac{1}{v} \ll 1$

$$P = \frac{NkT}{V-b} - \frac{a}{V^2}$$

$$\frac{Pv}{kT} = \frac{1}{1-\left(\frac{b}{N}\right)\frac{1}{v}} - \left(\frac{a}{N^2}\frac{1}{kT}\right)\frac{1}{v} \approx 1 + \frac{1}{v}\left[\frac{b}{N} - \frac{a}{N^2 kT}\right] + \cdots$$

$$\frac{b}{N} = \frac{2\pi}{3} r_0^3 \qquad \text{(i.e. excluded volume effect)}$$

$$\frac{a}{N^2 kT} = 2\pi \int_{r_0}^{\infty} dr\, r^2 f(r)$$

Note: $a \equiv a(T)$ ~~exactly~~ except at very high temperatures

where $f(r) \approx -\frac{U(r)}{kT} = \frac{|U(r)|}{kT}$ (for $r > r_0$)

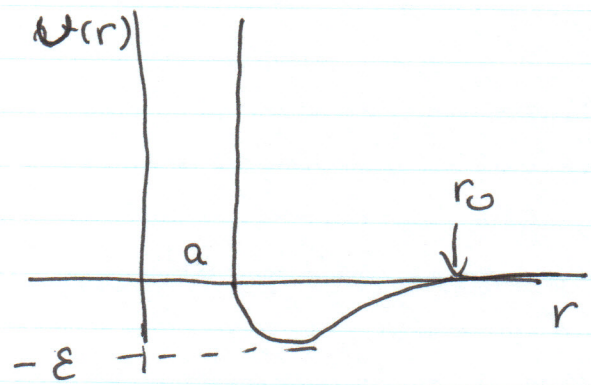
$\Rightarrow$ we can "fit Van der Waals" only for high T.

Otherwise, even at low densities, $a = a(T)$

Analytic Properties of the (Grand) Partition Function and Phase Transitions

We saw before that, at low densities, it is possible to determine the Equation of State of a gas as a ~~power~~ series expansion in powers of the fugacity z. To find the actual equation of state $P = P(\frac{V}{N}, T)$ it is also necessary to determine the density in terms of z and to further invert this relation. The basic assumptions that we made were that (a) these series converge (uniformly) in the thermodynamic limit ($V \to \infty$, n fixed) and (b) that the relation between n and μ (or z) is a bijection (i.e. one-to-one). This picture breaks down if there are <u>singularities</u> which put bounds on the radii of convergence of these expansions. These singularities represent <u>phase transitions</u>.

To see how this can happen we have to be more careful with the thermodynamic limit. Imagine that we have a gas of particles in a large but finite volume V and that the pair-interaction has a hard core radius a and a finite range (attractive) interaction tail



Under these assumptions there is a maximum # of molecules $M(V)$ that one can fit in V.

$\Rightarrow$ the grand partition function

$$\mathcal{Z}(z,V) = 1 + \frac{1}{1!} z Q_1 + \cdots + \frac{z^N}{N!} Q_N + \cdots + \frac{z^M}{M!} Q_M$$

with $Q_N = 0$ for $N > M(V)$ (I have absorbed the factor of λ_T^{3N} in Q_N)

$Q_N = Q_N(V,T)$

$\Rightarrow$ in this case $\mathcal{Z}$ is a polynomial with real positive coefficients $\Rightarrow$ $\mathcal{Z}$ has <u>no</u> <u>real</u> <u>positive</u> <u>roots</u>.

We determine the equation of state by solving

$$\begin{cases} \dfrac{P}{kT} = \dfrac{1}{V} \log \mathcal{Z}(z,V) \\[2ex] \dfrac{1}{v} = \dfrac{1}{V}\, z \dfrac{\partial}{\partial z} \log \mathcal{Z}(z,V) \end{cases} \qquad v = \frac{1}{n}$$

$\Rightarrow$ for V finite P <u>and</u> v are analytic functions of z in a region of the complex plane that includes the (entire) real axis. $\Rightarrow$ P is an analytic function of v for all physical values of v (i.e. the >0 real axis)

$\Rightarrow$ all thermodynamic functions are free of singularities. $\Rightarrow$

$$P > 0 \quad \text{and} \quad \frac{\partial P}{\partial v} = \frac{\partial P}{\partial z}\frac{\partial z}{\partial v} = \frac{-kT}{z v^2 [\langle n^2\rangle - \langle n\rangle^2]} \leq 0$$

$\Rightarrow$ the <u>isotherms</u> are monotonically <u>decreasing</u> functions of v.

To get singularities we must take the thermodynamic limit $V \to \infty$ with $v = \frac{1}{n}$ fixed.

$$\frac{P}{kT} = \lim_{V\to\infty} \frac{1}{V} \log \mathcal{Z}(z,V)$$

$$\frac{1}{v} = \lim_{V\to\infty} \frac{1}{V}\, z \frac{\partial}{\partial z} \log \mathcal{Z}(z,V)$$

The differentiation $z\frac{\partial}{\partial z}$ and the thermodynamic limit only commute if the convergence is uniform (i.e. inside the radius of convergence).

It is possible to show that phase transitions (i.e. singularities) are controlled by the distribution of roots of $\mathcal{Z}$ in the complex z-plane (z: fugacity). These conditions are summarized in two theorems due to T.D. Lee and C.N. Yang (we will not prove them)

(1) Existence of the Thermodynamic Limit

$$\lim_{V\to\infty} \frac{1}{V} \log \mathcal{Z}(z, V) \quad \text{exists for}$$

all $z>0$ and it is a continuous non-decreasing function of z. The limit is independent of the shape of V if the surface area of V increases no faster than $V^{2/3}$ (i.e. not a fractal)

(2) Distribution of Zeros:

Let R be a region of the complex plane z that includes a segment of the positive real axis,

and contains no roots of $\mathcal{Z}$. Then, in $\mathcal{R}$, $\frac{1}{V}\log \mathcal{Z}$ converges uniformly to its limit as $V \to \infty$. The limiting function is analytic for all $z \in \mathcal{R}$

~~A~~ A consequence of these theorems is that a thermodynamic phase is the set of values of z contained in any single region of $\mathcal{R}$. Since inside this region we have uniform convergence we set

$$F_\infty(z) = \lim_{V\to\infty} \frac{1}{V} \log \mathcal{Z}(V, z)$$

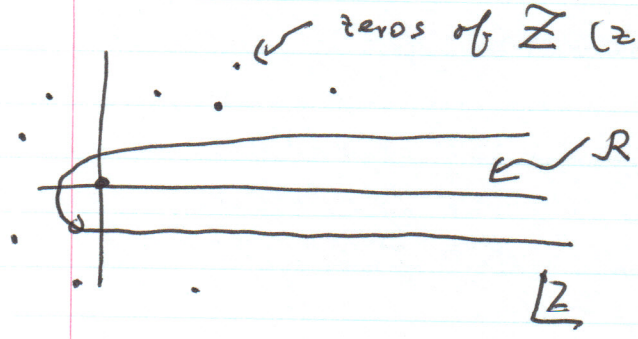
and $$\frac{P(z)}{kT} = F_\infty(z) \quad \text{and} \quad \frac{1}{v(z)} = z\frac{\partial}{\partial z} F_\infty(z)$$

(Note the exchange of the order of operations)

$\Rightarrow$ inside a particular region $P > 0$ and $\frac{\partial P}{\partial v} < 0$

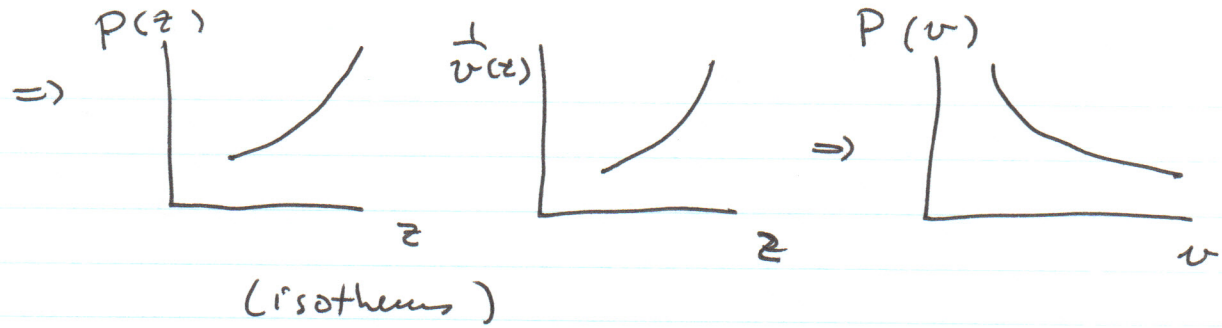
Let us consider several possible situations:

(a) $\mathcal{R} = \mathbb{R}^+$ (i.e. $\mathcal{R}$ is the entire positive real axis)



$\Rightarrow$ the system is always in a single phase

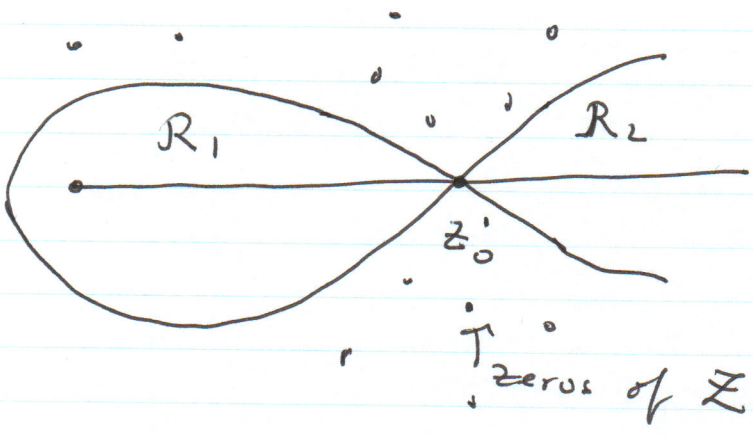
Inside this region continuous and $P>0$, ~~and~~ monotonic and so is $\frac{1}{v}$



(isotherms)

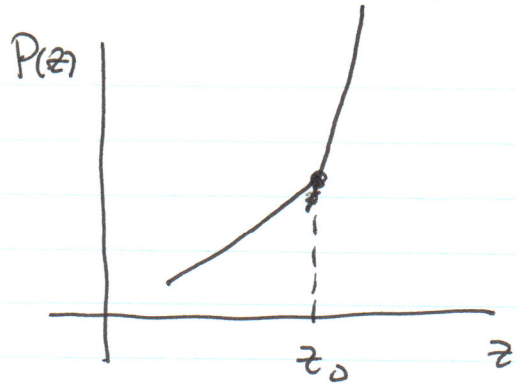
(b) Suppose that $\exists$ a zero z_0 of $Z(z,v)$ which <u>approaches the real axis as $v \to \infty$</u>

$\Rightarrow$ the real axis is split into two regions $\mathbb{R} = R_1 \cup R_2$, separated by z_0

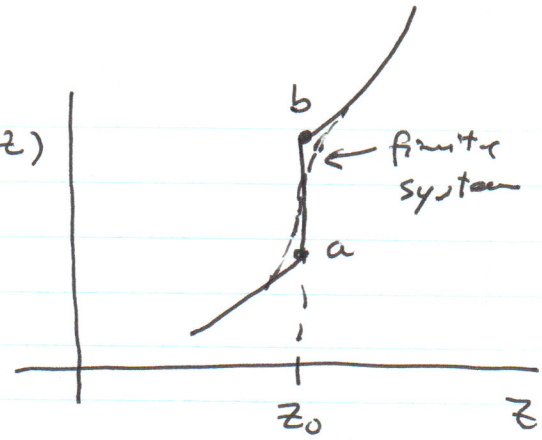


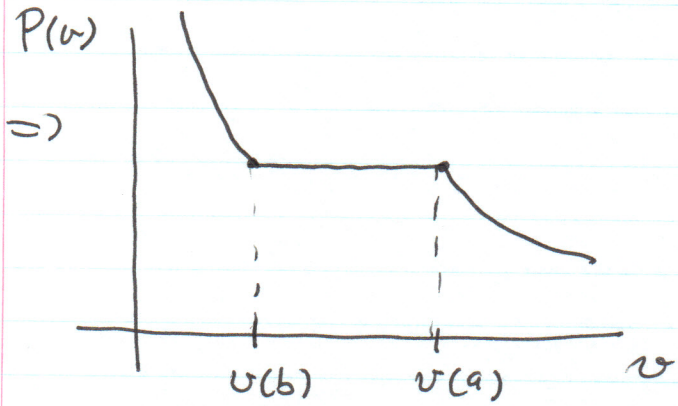
$\Rightarrow$ the conditions of the theorem are valid separately on R_1 and R_2. However Thm 1 requires that even at z_0 $P(z)$ be continuous. However it may not be differentiable.

Suppose that $P(z)$ is continuous at z_0 but that its derivative $\frac{\partial P}{\partial z}$ is discontinuous at z_0



$n = \frac{1}{v(z)}$





This happens since $\frac{1}{v(z)}$ is a non-decreasing function of z

$$z\frac{\partial}{\partial z}\frac{1}{v(z)} = \left(z\frac{\partial}{\partial z}\right)^2 \frac{1}{V}\log Z$$

$$= \langle n^2\rangle - \langle n\rangle^2 \geq 0$$

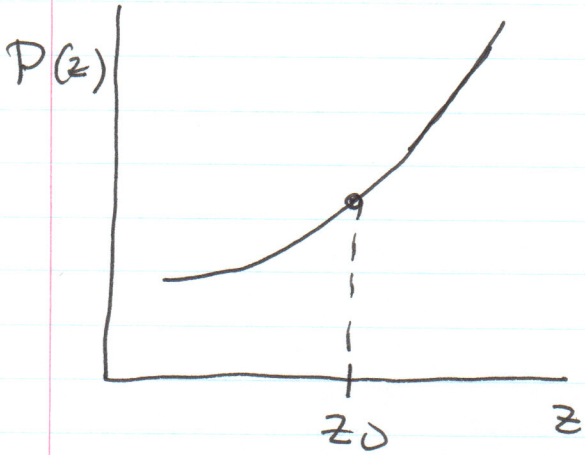
$\Rightarrow \frac{1}{v}$ must jump upwards as $z\uparrow$

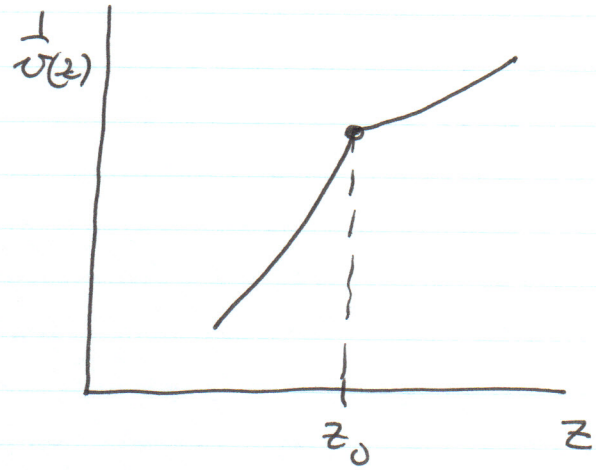
This is a <u>discontinuous</u> or <u>first order phase transition</u>

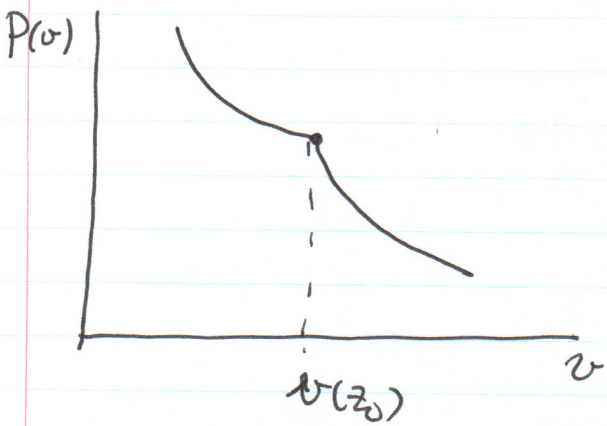
This happens because the grand potentials match up at z_0 with a discontinuity in their derivatives.

However it may also be possible to have a singularity in which $\frac{\partial P}{\partial z}$ exists and it's a continuous function of z at z_0 $\Rightarrow$ we get instead

a <u>continuous</u> or <u>second order</u> phase transition





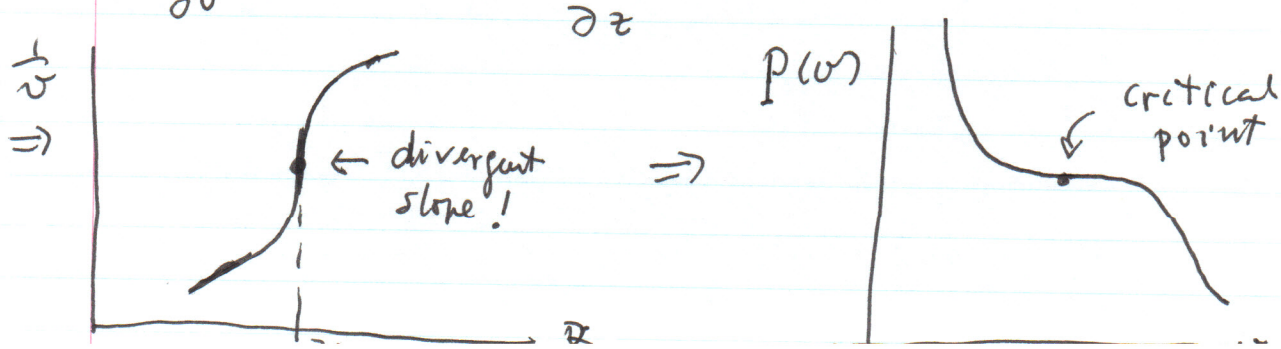


There is a special and very important type of second order transition called a <u>critical point</u>.

At a critical point $\frac{\partial P}{\partial v} \to 0$

Since $\frac{\partial P}{\partial v} = \frac{\partial P}{\partial z}\frac{\partial z}{\partial v} = -\frac{kT}{zv^3}\frac{1}{\frac{\partial \frac{1}{v}}{\partial z}}$

$$\frac{\partial P}{\partial v} \to 0 \iff \frac{\partial \frac{1}{v}}{\partial z} \to \infty \iff \langle n^2\rangle - \langle n\rangle^2 \to \infty$$



The Lee-Yang Circle Theorem

There is an explicit and simple model in which a phase transition can be demonstrated to occur. Consider a lattice and atoms to be regarded as point particles that can singly occupy the sites of this lattice, i.e. a "lattice gas". The interatomic potential is

$$u(\vec{r}) = \begin{cases} \infty & \vec{r} = 0 \quad \text{(i.e. only 1 atom/site} \\ u < 0 & \text{between } \neq \text{ sites} \end{cases}$$

(write it as an Ising Model)

Lee-Yang Thm: The roots of $\mathcal{Z}(z, V) = 0$ lie on the unit circle of the complex z plane.

Since $\mathcal{Z}$ is a real positive polynomial (finite system)

$\Rightarrow$ roots are complex conjugate pairs none of which can be on the >0 real axis, but can approach $\mathbb{R}^+$ if $V \to \infty$ $\Rightarrow$ In this case they must approach $z = 1$ $\Rightarrow$ there is a unique transition.

$$\Rightarrow \mathcal{Z}(z, V) = \text{const} \prod_{\text{roots}} (z - e^{i\theta_k})$$

As $V \to \infty \Rightarrow$ the roots become continuously distributed over the unit circle. Let $g(\theta)$ be the distribution function (i.e. the density of roots in $[\theta, \theta+d\theta]$) defined by

$$\frac{1}{V} \sum_k \to \int_0^{2\pi} \frac{d\theta}{2\pi} \, g(\theta)$$

Paired roots $\Rightarrow g(\theta) = g(-\theta)$

$$\Rightarrow \frac{P}{kT} = \int_0^{\pi} \frac{d\theta}{2\pi} \, g(\theta) \log\left(1 - 2z\cos\theta + z^2\right)$$

$$\frac{1}{v} = \int_0^{\pi} \frac{d\theta}{2\pi} \, g(\theta) \, \frac{z - \cos\theta}{1 - 2z\cos\theta + z^2}$$

$\Rightarrow$ the only singularity is at $z = 1$

$\Rightarrow$ there is a critical point only if $g(0) \neq 0$ and there are two solutions ξ, one for $|z| > 1$ and another one for $|z| < 1$ which cannot be continued into each other.