

## 5.1 The cumulant expansion

Interaction is responsible for materials and phase.

General Hamiltonian:  $\mathcal{H}_N = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \mathcal{U}(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$

Partition func.:  $Z(N, V, T) = \frac{1}{N!} \int \prod_{i=1}^N \left( \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{h^3} \right) \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \exp \left[ -\beta \mathcal{U}(\vec{q}_1, \dots, \vec{q}_N) \right]$   
 $= \frac{1}{N!} \int \prod_{i=1}^N \left( \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{h^3} \right) \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \cdot \frac{\int \prod_{i=1}^N (d^3 \vec{q}_i) \exp \left[ -\beta \mathcal{U}(\vec{q}_1, \dots, \vec{q}_N) \right]}{\int \prod_{i=1}^N (d^3 \vec{q}_i)}$   
 $= Z_0(N, V, T) \langle \exp \left[ -\beta \mathcal{U}(\vec{q}_1, \dots, \vec{q}_N) \right] \rangle^0$  (  $\mathcal{U}$  only depends on  $\{\vec{q}_i\}$  ) uniformly and independently distri. in  $V$   
 $= Z_0(N, V, T) \sum_{l=0}^{\infty} \frac{(-\beta)^l}{l!} \langle \mathcal{U}^l \rangle^0$

where  $Z_0(N, V, T) = \left( \frac{V}{\lambda^3} \right)^N \cdot \frac{1}{N!}$  and  $\langle \langle \rangle \rangle^0$  denotes the expectation value of

$\langle \rangle$  computed with the prob. distribution of non-interacting system

similar to cumulant generating func in section 2.2  $\Rightarrow \ln Z = \ln Z_0 + \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \langle \mathcal{U}^l \rangle_c^0$

\*  $\langle \mathcal{U}^l \rangle^0 = \int \left( \prod_{i=1}^N \frac{d^3 \vec{q}_i}{V} \right) \mathcal{U}(\vec{q}_1, \dots, \vec{q}_N)^l$  (  $\mathcal{U}$  only depends on  $\{\vec{q}_i\}$  ) uniformly and independently distri. in  $V$

$$\begin{aligned} \langle \langle \rangle \rangle &= \frac{1}{Z} \frac{1}{N!} \int \prod_{i=1}^N \left( \frac{d^3 \vec{q}_i d^3 \vec{p}_i}{h^3} \right) \exp \left[ -\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \right] \exp \left[ -\beta \mathcal{U}(\vec{q}_1, \dots, \vec{q}_N) \right] \times \langle \rangle \\ &= \frac{\langle \langle \exp[-\beta \mathcal{U}] \rangle \rangle^0}{\langle \exp[-\beta \mathcal{U}] \rangle^0} = i \frac{\partial}{\partial k} \ln \langle \exp[-ik\langle \rangle - \beta \mathcal{U}] \rangle^0 \Big|_{k=0} \end{aligned}$$

\* Average and derivative are linear operator.

:  $\ln \langle \exp[-ik\langle \rangle - \beta \mathcal{U}] \rangle^0 = \sum_{l, l'=1}^{\infty} \frac{(-ik)^{l'}}{l'!} \frac{(-\beta)^l}{l!} \langle \langle \rangle^{l'} * \mathcal{U}^l \rangle \rangle_c^0$

As  $k=0$ , all higher order terms of  $(-ik)^{l'}/l'! \rightarrow 0$  and  
 $\langle x^n \rangle_c = d^n / \ln \langle \exp(-ikx) \rangle / d(-ik)^n \Big|_{k=0}$

$$\langle \langle \rangle \rangle = \frac{\partial}{\partial (-ik)} \ln \langle \exp[-ik\langle \rangle - \beta \mathcal{U}] \rangle^0 \Big|_{k=0} = \sum_{l=0}^{\infty} \frac{(-\beta)^l}{l!} \langle \langle \rangle * \mathcal{U}^l \rangle \rangle_c^0$$

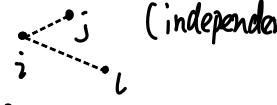
Dilute gas (weakly interacting gas)

$$U(\vec{q}_1, \dots, \vec{q}_N) = \sum_{i < j} V(\vec{q}_i - \vec{q}_j) \quad \text{pairwise interaction between particles}$$

First correction:  $\langle U \rangle_c^0 = \sum_{i < j} \int \frac{d^3 \vec{q}_i}{V} \frac{d^3 \vec{q}_j}{V} V(\vec{q}_i - \vec{q}_j) \quad \text{and} \quad \begin{cases} \vec{Q} = \frac{1}{2} (\vec{q}_i + \vec{q}_j) \\ \vec{q} = (\vec{q}_i - \vec{q}_j) \end{cases} \quad J = \left| \frac{\partial \vec{q}_i}{\partial \vec{Q}} \frac{\partial \vec{q}_j}{\partial \vec{q}} \right| = 1 \\ = \binom{N}{2} \int \frac{d^3 \vec{Q}}{V} \frac{d^3 \vec{q}}{V} V(\vec{q}) = \frac{N(N-1)}{2V} \int d^3 \vec{q} V(\vec{q}) \quad \nwarrow \text{each pair makes identical distribution} \quad \uparrow \text{each pair makes identical distribution} \end{math>$

Second correction  $\langle U^2 \rangle_c^0 = \sum_{i < j, k < l} [\langle V(\vec{q}_i - \vec{q}_j) V(\vec{q}_k - \vec{q}_l) \rangle^0 - \langle V(\vec{q}_i - \vec{q}_j) \rangle^0 \langle V(\vec{q}_k - \vec{q}_l) \rangle^0]$

Translational symmetry  
(absence of an external potential) {

- (i)  $\{i, j, k, l\}$  are different  $\Rightarrow$  independently distributed  
 $\langle V(\vec{q}_i - \vec{q}_j) V(\vec{q}_k - \vec{q}_l) \rangle^0 = \langle V(\vec{q}_i - \vec{q}_j) \rangle^0 \langle V(\vec{q}_k - \vec{q}_l) \rangle^0$
- (ii) One common index between two pairs; for example  $\{(i, j), (i, l)\}$   
 $\Rightarrow$  let  $\vec{q}_{ij} = \vec{q}_i - \vec{q}_j$  and  $\vec{q}_{il} = \vec{q}_i - \vec{q}_l$        (independently distri.)  
 $\langle V(\vec{q}_i - \vec{q}_j) V(\vec{q}_i - \vec{q}_l) \rangle^0 = \langle V(\vec{q}_i - \vec{q}_j) \rangle^0 \langle V(\vec{q}_i - \vec{q}_l) \rangle^0$
- (iii) Remain  $N(N-2)/2$  terms are identical

$$\langle U^2 \rangle_c^0 = \frac{N(N-1)}{2} \left[ \int \frac{d^3 \vec{q}}{V} V(\vec{q})^2 - \underbrace{\left( \int \frac{d^3 \vec{q}}{V} V(\vec{q}) \right)^2}_{\text{underbrace}}$$

\* smaller by a factor of  $\ell^3/V$ ,  $\ell$  is a characteristic range for  $V$   
 $V$  decreases with distances, and this term vanishes in thermo limit ( $N \rightarrow \infty$ ).

High-order correction  
in cumulant expansion

(a) order  $p$ , draw  $p$  pairs connected by bonds ( $V_{ij}$ )  
overall factor  $1/p!$  accompanies graphs

$$\frac{1}{3!} \sum_{i < j, k < l, m < n} \quad \begin{matrix} \bullet & \cdots & \bullet & \cdots & \bullet & \cdots & \bullet \\ i & j & k & l & m & n \end{matrix}$$

(b) multiple selections of the same index  $i$   
 $\Rightarrow$  more bonds joined together to form interconnected points

$S_p$ : permutation number assigning labels 1 through  $N$  to different points of the graph.

(Ignore difference among  $N, N-1, N-2, \dots$ )  $\propto N^S$

Symmetry factor: number of equivalent assignments. e.g., a pair of points, SF =  $\frac{1}{2}$

$$\Rightarrow \frac{1}{3!} \frac{N^S}{2 \times 2} \quad \begin{matrix} \bullet & \cdots & \bullet \\ 1 & 2 & 3 & 4 & 5 \end{matrix}$$

(c) Integral over all  $s$  coordinates  $\vec{q}_i$ , of products of corresponding  $-\beta V_{ij}$

$$\int d^3\vec{q}_1 d^3\vec{q}_2 d^3\vec{q}_3 d^3\vec{q}_4 d^3\vec{q}_5 V(\vec{q}_{12}) V(\vec{q}_{34}) V(\vec{q}_{45})$$

$n_c$  disconnected clusters  
integral over center of mass  
coordinates gives  $V^{n_c}$

$$\Rightarrow \underbrace{\left( \int d^3\vec{q}_1 d^3\vec{q}_2 V(\vec{q}_{12}) \right)}_{\downarrow d^3\vec{Q}_{12} d^3\vec{q}_{12}} \underbrace{\left( \int d^3\vec{q}_3 d^3\vec{q}_4 d^3\vec{q}_5 V(\vec{q}_{34}) V(\vec{q}_{45}) \right)}_{\downarrow d^3\vec{Q}_{345} d^3\vec{q}_{34} d^3\vec{q}_{45}}$$

$$\Rightarrow \frac{(-\beta)^3}{3!} \frac{N^5}{4V^5} V^2 \left( \int d^3\vec{q}_{12} V(\vec{q}_{12}) \right) \left( \int d^3\vec{q}_{34} d^3\vec{q}_{45} V(\vec{q}_{34}) V(\vec{q}_{45}) \right)$$

Cancellations in calculating  
cumulants

- $\langle UP \rangle^0$ , contribution of a disconnected diagram  $\equiv$  product of its disjoint clusters. The coordinates of these clusters are independent RV ;  
 $\Rightarrow$  no contributions to joint cumulant  $\langle UP \rangle_c^0$

$\Rightarrow$  extensivity of  $\ln Z$ . the survival connected diagrams only gives a factor of  $V$ . (Disconnected clusters have more factors of  $V$ , and are non-extensive )

- one-particle reducible clusters, which are fully connected  
 $\bullet \dots \bullet \dots \bullet \dots \bullet$  Remove one single coordinate point  
 $1 \quad 2 \quad 3 \quad 4 \quad 5$   $\Rightarrow$  disjoint fragments

The value of it is the product of its disjoint fragments in translational invariant system by measuring all other coordinates relative to special point.

$\Rightarrow$  no contributions to joint cumulant  $\langle UP \rangle_c^0$

e.g.,   $\star$  one-particle irreducible clusters with  $s$  sites and  $p$  bonds in order of  $V(N/V)^s (\beta V)^p$  to  $\ln Z$

$$\ln Z = \ln Z_0 + \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \langle U^l \rangle_c^0 = \ln Z_0 + V \sum_{p,s} \frac{(-\beta)^p}{p!} \frac{(N/V)^s}{s!} D(p,s)$$

$D(p,s)$ : sum over the contributions of all one-particle irreducible clusters of  $s$  sites and  $p$  bonds  $(p \geq 1; s \geq 2)$

$\frac{1}{s!}$  : the symmetry of permuting the vertices of clusters  
(comparison with the cluster expansion)

$$F = -k_B T \ln Z \Rightarrow F(T, V, N) = F_0(T, V, N) + \frac{N^2}{2V} \left( \int d^3 \vec{q} \mathcal{V}(\vec{q}) - \frac{\beta}{2} \int d^3 \vec{p} \mathcal{V}(\vec{p})^2 + \mathcal{O}(\beta^2 \mathcal{V}^3) \right) + \mathcal{O}\left(\frac{N^3 \beta^2 \mathcal{V}^3}{V^2}\right)$$

At second order in  $(\beta \mathcal{V})$

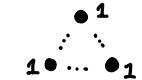
$P=1; S=2$

$P=2; S=2$

$P \geq 3; S=2$

$P \geq 3; S \geq 3$

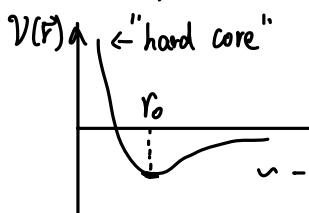
(self-to-self)



$$\text{At equilibrium, } dF(T, V, N) = -pdV - SdT + \mu dN \xrightarrow{\text{state func.}} P = -\frac{\partial F}{\partial V} \Big|_{T, N}$$

Drawbacks : the expansion in powers of  $\beta \mathcal{V}$

$\mathcal{V}(\vec{r})$  has an attractive tail due to van der Waals interaction decaying as  $-1/r^6$  at large separations  $\vec{r} \sim 10 \vec{r}_0$ . At short distance, electron clouds overlap triggers strong repulsion.



E.g. Correction at order of  $N^2/V \Rightarrow$  sum all two-point clusters

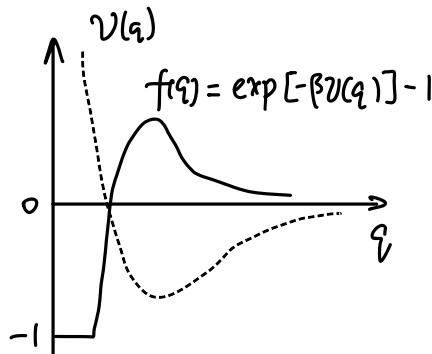
Solution  
alleriation A partial resummation of diagram.

$$\begin{aligned} \ln Z &= \ln Z_0 + \sum_{P=1}^{\infty} \frac{(-\beta)^P}{P!} \frac{N(N-1)}{2} \int d^3 \vec{q} \mathcal{V}(\vec{q})^P + \mathcal{O}\left(\frac{N^3}{V^2}\right) \\ &= \ln Z_0 + \frac{N(N-1)}{2V} \int d^3 \vec{q} [\exp(-\beta \mathcal{V}(\vec{q})) - 1] + \mathcal{O}\left(\frac{N^3}{V^2}\right) \end{aligned}$$

$$\bullet - \bullet \equiv \bullet \cdots \bullet + \frac{1}{2!} \bullet \cdots \bullet + \frac{1}{3!} \bullet \cdots \bullet + \cdots \cdots$$

Application:

- remove summation over  $P$
- recasting as a power series in density  $N/V \Leftarrow P = -\partial F/\partial V \Big|_{T, N}$
- perform for bonds connecting any pairs of vertices.



## 5.2 The cluster expansion

For short-range interactions with hard core, replace  $\mathcal{V}(\vec{q})$  by  $f(\vec{q}) = \exp(-\beta \mathcal{V}(\vec{q})) - 1$   
 (summing over all possible numbers of bonds between two points on a cumulant graph)  
 powers of the density  $N/V \Rightarrow$  virial expansion

From ideal gas eqn. :  $\frac{P}{k_B T} = \frac{N}{V} \left[ 1 + B_2(T) \frac{N}{V} + B_3(T) \left( \frac{N}{V} \right)^2 + \dots \right]$  Expansion

virial coefficients

temperature-dependent parameter  $B_i(T)$

(from the interparticle interactions)

Macrostate  $M \equiv (T, \mu, V)$

Grand partition function

$$Q(\mu, T, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{e^{\beta \mu}}{V} \right)^N S_N$$

(from section 4.7 and 4.9)

and  $S_N = \prod_{i=1}^N d^3 \vec{q}_i \prod_{i < j} (1 + f_{ij})$  ;  $f_{ij} = f(\vec{q}_i - \vec{q}_j)$

$$= \prod_{i=1}^N d^3 \vec{q}_i \left( 1 + \sum_{i < j} f_{ij} + \sum_{i < j, k < l} f_{ij} f_{kl} + \dots \right)$$

from binomial theorem

number of terms  $\Rightarrow 1 + \binom{N(N-1)/2}{1} + \binom{N(N-1)/2}{2} + \dots \dots$   
 $= (1+1)^{N(N-1)/2} = 2^{N(N-1)/2}$

Diagrammatic plot:

(a) dots  $i=1, \dots, N \Rightarrow$  coordinates  $\vec{q}_1$  through  $\vec{q}_N$

$$\begin{array}{ccccccc} \bullet & \bullet & \cdots & \bullet \\ 1 & 2 & \cdots & N \end{array}$$

(b) draw lines connecting  $i$  and  $j$  for each  $f_{ij}$

linked clusters  $\begin{array}{ccccccc} \bullet & \bullet-\bullet & \bullet-\bullet-\bullet & \cdots & \bullet \\ 1 & 2-3 & 4-5-6 & & N \end{array}$

$$(\int d^3 \vec{q}_1) (\int d^3 \vec{q}_2 d^3 \vec{q}_3 f_{23}) (\int d^3 \vec{q}_4 d^3 \vec{q}_5 d^3 \vec{q}_6 f_{45} f_{56}) \cdots (\int d^3 \vec{q}_N)$$

$b_l \equiv$  sum over all  $l$ -particle linked clusters (one-particle reducible or not)

$$b_1 = \bullet = \int d^3 \vec{q} = V$$

$$b_2 = \bullet - \bullet = \int d^3 \vec{q}_1 d^3 \vec{q}_2 f(\vec{q}_1 - \vec{q}_2)$$

$$b_3 = \begin{array}{c} \bullet \\ \backslash \end{array} - \begin{array}{c} \bullet \\ / \end{array} + \begin{array}{c} \bullet \\ \backslash \end{array} \begin{array}{c} \bullet \\ / \end{array} + \begin{array}{c} \bullet \\ / \end{array} \begin{array}{c} \bullet \\ \backslash \end{array}$$

$$= \int d^3 \vec{q}_1 d^3 \vec{q}_2 d^3 \vec{q}_3 [f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) + f(\vec{q}_2 - \vec{q}_1) f(\vec{q}_3 - \vec{q}_1) + f(\vec{q}_3 - \vec{q}_1) f(\vec{q}_1 - \vec{q}_2) + f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) f(\vec{q}_3 - \vec{q}_1)]$$

$N$ -particle graph  $\rightarrow n_1$  1-clusters ;  $n_2$  2-clusters ;  $n_3$  3-clusters ,  $\dots$  ,  $n_l$   $l$ -clusters

- Sum over all distinct divisions of  $N$  points into a set of clusters  $\{n_\ell\}$

$$\sum_\ell \ell n_\ell = N$$

- $W(\{n_\ell\}) \equiv$  number of ways of assigning  $N$  particles label to groups of  $n_\ell$   $l$ -clusters.

$$S_N = \sum_{\{n_\ell\}} \left( \prod_\ell b_\ell^{n_\ell} \right) W(\{n_\ell\})$$

sum of  $\bullet \dots \bullet$ ,  $\bullet \square \bullet$ ,  $\bullet \square \square \bullet$   
 $\dots \Rightarrow \bullet - \bullet$

e.g. 3 particles  $\Rightarrow \begin{cases} 1\text{-cluster} \\ 2\text{-cluster} \end{cases}$  ;  $\overset{\circ}{1} \overset{\circ}{2} \overset{\circ}{3}$ ,  $\overset{\circ}{2} \overset{\circ}{1} \overset{\circ}{3}$ ,  $\overset{\circ}{3} \overset{\circ}{1} \overset{\circ}{2}$   
 $\Rightarrow n_1=1; n_2=1$  and  $b_1 b_2$  to  $S_3$ ;  $W(1,1)=3$

$W(\{n_\ell\}) \equiv$  the number of  $S_3 = \overset{\circ}{\bullet} \bullet + 3 \overset{\circ}{\bullet} \bullet + (\overset{\circ}{\bullet} \overset{\circ}{\bullet} + \overset{\circ}{\bullet} \overset{\circ}{\bullet} + \overset{\circ}{\bullet} \overset{\circ}{\bullet} + \overset{\circ}{\bullet} \overset{\circ}{\bullet})$   
 distinct ways of grouping  
 $= b_1^3 + 3b_1 b_2 + b_3$

labels  $1, \dots, N$  into bins of  $n_\ell$   $\ell$ -cluster  
 Within each bin of  $\ell$ ne particles, equivalent assignments  
 $\Rightarrow$  (i) permuting  $\ell$  labels in each subgroup in  $\ell!$  ways, total of  $(\ell!)^{n_\ell}$   
 $(\ell \text{ size of cluster})$  ( $n_\ell$  number in each size)

(ii)  $n_\ell!$  of  $n_\ell$  subgroups

$$W(\{n_\ell\}) = \frac{N!}{\prod_\ell [n_\ell! (\ell!)^{n_\ell}]} \quad \text{e.g., } \ell=2, n_1=3$$

$$\bullet \bullet \bullet \bullet \bullet \bullet \equiv 3! 2! 2! 2!$$

Restriction:

$$\sum_{N=0}^{\infty} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} = \sum_{\{n_\ell\}}$$

$$\Rightarrow Q = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^N \sum_{\{n_\ell\}} \frac{N!}{\prod_\ell [n_\ell! (\ell!)^{n_\ell}]} \prod_\ell b_\ell^{n_\ell}$$

$$= \sum_{\{n_\ell\}} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^{\sum_\ell \ell n_\ell} \prod_\ell \frac{b_\ell^{n_\ell}}{n_\ell! (\ell!)^{n_\ell}} = \sum_{\{n_\ell\}} \prod_\ell \left[ \frac{1}{n_\ell!} \left( \frac{e^{\beta \mu} b_\ell}{\lambda^3 \ell!} \right)^{n_\ell} \right]$$

$$= \prod_\ell \sum_{n_\ell=0}^{\infty} \frac{1}{n_\ell!} \left[ \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]^{n_\ell} = \prod_\ell \exp \left[ \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]$$

$$= \exp \left\{ \sum_{\ell=1}^{\infty} \left[ \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right] \right\}$$

Sum over all graphs, connected or not  $\equiv$  the exponential of the sum over connected clusters.

$$\sum_{N=0}^{\infty} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} \equiv \exp \left( \sum_{\ell=1}^{\infty} \dots \right)$$

↳ Recheck Section 2.2 graphical connection between moments and cumulants

Grand potential  $\ln Q = -\beta \mathcal{G} = \frac{PV}{k_B T} = \sum_{\ell=1}^{\infty} \left[ \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]$  purpose of use: Grand canonical  
Grand potential:  $\mathcal{G} = PV$   
(the extensivity condition  $\uparrow$ )

proportional to  $V$ : Each  $b_\ell$  has an integral over the center of mass coordinates

$$\text{E.g., } b_2 = \int d^3 \vec{q}_1 d^3 \vec{q}_2 f(\vec{q}_1 - \vec{q}_2) = V \int d^3 \vec{q}_{12} f(\vec{q}_{12})$$

Let  $\lim_{V \rightarrow \infty} b_\ell = V b_\ell \Rightarrow \frac{P}{k_B T} = \sum_{\ell=1}^{\infty} \left[ \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]$  (no non-linked cluster  $\Rightarrow$  no higher power of  $V$ )

$f(\vec{q}) = \exp(-\beta \mathcal{V}(\vec{q})) - 1 \quad \left. \right\} \Rightarrow \frac{P}{k_B T} = \frac{N}{V} \left[ 1 + B_2(T) \frac{N}{V} + B_3(T) \left( \frac{N}{V} \right)^2 + \dots \right]$

density  $N/V$

$$N^* = \langle N \rangle = \frac{\partial \ln Q}{\partial (\beta \mu)} = \sum_{l=1}^{\infty} \left[ l \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^l \frac{V b_l}{l!} \right] \quad \text{and fugacity } \chi = \frac{e^{\beta \mu}}{\lambda^3} \quad \begin{cases} \text{fugacity coefficient } \phi = f/p \sim \lambda \\ \text{at CM: high T; low p} \end{cases}$$

$$n = \sum_{l=1}^{\infty} \frac{\chi^l}{(l-1)!} b_l \quad \text{and} \quad \frac{p}{k_B T} = \sum_{l=1}^{\infty} \frac{\chi^l}{l!} b_l$$

(a) Solve  $\chi(n)$  from ( $b_1 = \int d^3 \vec{q} / V = 1$ )

$$\chi = n - b_2 \chi^2 - \frac{b_3}{2!} \chi^3 - \dots$$

$$\left. \begin{aligned} e^{\beta \mu} (\mu < 0) &\sim 10^{-50} \\ \lambda (300K) &\sim 10^{-11} \end{aligned} \right\} \chi \ll 0$$

The perturbative solution at each order,

$$\chi_1 = n + \mathcal{O}(n^2)$$

$$\chi_2 = n - b_2 \chi_1^2 + \mathcal{O}(n^3) = n - b_2 n^2 + \mathcal{O}(n^3)$$

$$\chi_3 = n - b_2 (n - b_2 n^2)^2 - \frac{b_3}{2} (n - b_2 n^2)^3 + \mathcal{O}(n^4)$$

$$= n - b_2 n^2 + 2b_2^2 n^3 - \frac{b_3}{2} n^3 + \mathcal{O}(n^4) = n - b_2 n^2 + \left( 2b_2^2 - \frac{b_3}{2} \right) n^3 + \mathcal{O}(n^4)$$

$$(b) \quad \beta P = \chi + \frac{b_2}{2} \chi^2 + \frac{b_3}{6} \chi^3 + \dots \quad (\chi \ll \chi_3)$$

$$= \left\{ n - b_2 n^2 + \left( 2b_2^2 - \frac{b_3}{2} \right) n^3 \right\} + \left\{ \frac{b_2}{2} n^2 - b_2^2 n^3 \right\} + \left\{ \frac{b_3}{6} n^3 \right\} + \dots$$

$$= n - \frac{b_2}{2} n^2 + \left( b_2^2 - \frac{b_3}{3} \right) n^3 + \mathcal{O}(n^4)$$

$$\text{virial expansion} \Rightarrow \beta P = n + \sum_{l=2}^{\infty} B_l(T) n^l$$

1st term: ideal gas result

$$\text{2nd term: } B_2 = -\frac{b_2}{2} = -\frac{1}{2} \int d^3 \vec{q} (e^{-\beta V(\vec{q})} - 1)$$

$$\text{3rd term: } B_3 = b_2^2 - \frac{b_3}{3} = \left[ \int d^3 \vec{q} (e^{-\beta V(\vec{q})} - 1) \right]^2 - \frac{1}{3} \left[ 3 \int d^3 \vec{q}_{12} d^3 \vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) \right.$$

$$\left. + \int d^3 \vec{q}_{12} d^3 \vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) f(\vec{q}_{12} - \vec{q}_{13}) \right]$$

$$= -\frac{1}{3} \int d^3 \vec{q}_{12} d^3 \vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) f(\vec{q}_{12} - \vec{q}_{13})$$

Cancellation of the one-particle reducible clusters appearing in  $b_3$   
While all clusters (reducible or not) appear in the sum for  $b_l$ , only  
the **one-particle irreducible** ones can appear in an expansion in powers of  
density.

Final expression for  $l$ -th  
virial coefficient

$$B_l(T) = -\frac{(l-1)}{l!} \bar{d}_l \quad \left\{ \begin{array}{l} \bar{d}_l: \text{the sum over all one-particle irreducible clusters} \\ \text{of } l \text{ points} \end{array} \right\}$$

$$\ln Z = \ln Z_0 + V \sum_{p,s} \frac{(-\beta)^p}{p!} \frac{(N/V)^s}{s!} D(p,s) \xrightarrow[\text{clusters with pairs of sites connected by f}]{\text{(multiple connections but pairs of sites)}} \ln Z = \ln Z_0 + V \sum_{l=2}^{\infty} \frac{n^l}{l!} \bar{d}_l$$

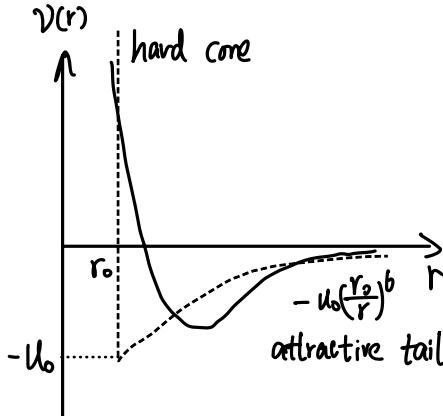
$$\text{sum of } \bullet \dots \bullet, \bullet \cdots \bullet, \bullet \cdots \bullet, \dots \Rightarrow \bullet \cdots \bullet \quad \sum_p \frac{(-\beta)^p}{p!} D(p, l) = \bar{d}_l \quad \text{Virial expansion: } \beta P = \frac{\partial \ln Z}{\partial V}$$

### 5.3 The second virial coefficient and van der Waals equation

Study the 2nd virial coefficient  $B_2 = -\frac{1}{2} b_2 = -\frac{1}{2} \int d^3 \vec{q} (e^{-\beta V(\vec{q})} - 1)$

two-body potential  $f(\vec{q}) = e^{-\beta V(\vec{q})} - 1$       hard core repulsion      ( $r \neq 0$ )  
 van der Waals attraction      ( $r \rightarrow \infty$ )

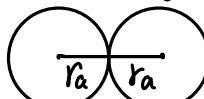
Set  $V(r) = \begin{cases} +\infty & r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^b & r > r_0 \end{cases}$        $b_2 = \int_0^\infty d^3 \vec{r} (e^{-\beta V(\vec{r})} - 1)$   
 $= \int_0^{r_0} 4\pi r^2 dr (-1) + \int_{r_0}^\infty 4\pi r^2 dr \left[ e^{\beta U_0 (r_0/r)^b} - 1 \right]$



In high temperature limit,  $\beta U_0 \ll 1$ ,  $e^{\beta U_0 (r_0/r)^b} - 1 \approx \beta U_0 (r_0/r)^b$

$$B_2 = -\frac{1}{2} \left[ -\frac{4}{3} \pi r_0^3 + 4\pi \beta U_0 r_0^b \left( -\frac{r_0^3}{3} \right) \Big|_{r_0}^\infty \right] = \frac{2}{3} \pi r_0^3 (1 - \beta U_0)$$

Excluded volume  $\Omega = \frac{4}{3} \pi r_0^3$  (8 times the atomic volume  $V_a$ )



$|r_0 - |$  distance of minimum approach  $r_0$

$$\Rightarrow B_2(T) = \frac{\Omega}{2} \left( 1 - \frac{U_0}{k_B T} \right)$$

Remarks and observations : (1) Tail of the attractive van der Waals interaction ( $\propto r^{-6}$ ) extends to very long separations. At high temperature limit, however, the van der Waals potential is short-ranged, and results in corrections to ideal gas law analytical in density  $n$ , leading to virial series.

(2) If potential that falls off with separation as  $1/r^3$  or slower are long-ranged, the integral in second virial coefficient is divergent, so non-analytic.

Problem 5.1 > An example is the Coulomb plasma. Non-analytic corrections can be obtained by summing all the ring diagrams in cumulant (cluster) expansions.

\* potential with typical strength  $U$ , and range  $\lambda$ . Each bond in the cumulant expansion contributes a factor of  $\beta U$ , while each node contributes  $N \int d^3 \vec{q} / V$ . A diagram with  $b$  bonds and  $s$  nodes is proportional to  $(\beta U)^b (N \lambda^3 / V)^s$ . At a given order in  $\beta U$ , the factor of  $n \lambda^3$  discriminates between weakly and strongly interacting systems.

$n \lambda^3 \ll 1$  (dilute gas, or short-range interactions) the diagrams with the fewest nodes should be included.

$n \lambda^3 \gg 1$  (dense gas, or long-range interactions) the ring diagrams, which have the most nodes, dominate.

High density breaks down (3)  $B_2(T)$  has dimensions of volume and (for short-range potentials) is proportional to the atomic volume  $\Omega$ .

In the high-temperature limit, compare first two terms in virial expansion.

$$\frac{B_2 n^2}{n} = \frac{B_2}{N!} \sim \frac{\text{atomic volume}}{\text{volume per particle in gas}} \times \frac{\text{gas density}}{\text{liquid density}} \sim 10^{-3} \text{ (ambient T)}$$

$\frac{B_{l-1} n^l}{B_{l-1} n^{l-1}}$  (for higher-order terms) wary of the convergence of series at high density. (gas may liquify)

Low temperature breaks down the virial expansion (4) divergence of  $B_2(T)$  when  $T \rightarrow 0$ . \* The presence of attractive interactions lowers the energy at low  $T$  by condensing into a liquid state.

(5) Truncated virial expansion

$$\frac{P}{k_B T} = n + \frac{\Omega}{2} \left(1 - \frac{u_0}{k_B T}\right) n^2 + \dots$$

$$\frac{1}{k_B T} (P + \frac{u_0 \Omega}{2} n^2) = n \left(1 + n \frac{\Omega}{2} + \dots\right) \approx \frac{n}{1 - n \frac{\Omega}{2}} = \frac{N}{V - N \frac{\Omega}{2}}$$

van der Waals eqn:  $\Rightarrow \left[ P + \frac{u_0 \Omega}{2} \left(\frac{N}{V}\right)^2 \right] \left[ V - N \frac{\Omega}{2} \right] = N k_B T$

Physical Interpretation of VDW eqn:

(a) excluded volume  $b$  is half of the volume that is excluded around each particle. Because it measures a joint excluded volume involving all particles in phase space. The contribution of coordinates to the partition func. of hard-core gas at low densities, by adding particles one at a time.

$$S_N = \int' \frac{\prod_i d^3 \vec{q}_i}{N!} = \frac{1}{N!} V(V-\Omega) \dots (V-(N-1)\Omega) \approx \frac{1}{N!} \left(V - \frac{N}{2}\Omega\right)^N$$

It is only exact for spatial dimensions  $d=1$ , and at infinity (not correctly considering the effect of excluded volume involving  $\geq 2$  particles)

(b) Decrease in  $P$  due to attractive interactions.

Gas pressure is related to the impacts of particles on a wall (Section 3.6)

$$P = \underbrace{(nV_x)}_{\textcircled{1}} \underbrace{(2mV_x)}_{\textcircled{2}} \Big|_{V_x < 0} = n m \bar{V}_x^2 \quad (\text{equipartition theorem: } \frac{1}{2} m \bar{V}_x^2 = \frac{1}{2} k_B T)$$

① the number of collisions per unit time and area

② momentum impacted by each particle.

Attractive interactions lead to a reduction in pressure.

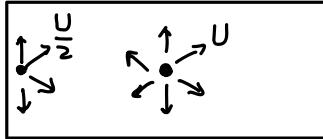
$$\delta P = \delta n (m \bar{V}_x^2) + n \delta (m \bar{V}_x^2)$$

(1) Relaxation of particles at the surface

If the range of decreased density is smaller than the mean free path of collision, surface particles can not be described by an equilibrium ensemble



In canonical ensemble, the gas density is reduced at the walls.



$$\delta n \approx n(e^{-\beta U/2} - e^{-\beta U}) \approx \beta n U / 2 \quad (\text{High } T)$$

\*  $U = \int d^3 \vec{r} V_{\text{attr}}(r) n = -n \Omega U_0$  (calculated from the pot. set at the start)

$$\delta P = \delta n (m \bar{V}_x^2) + n \delta (m \bar{V}_x^2) \rightarrow \text{uniformly distributed in } \vec{p}_x \text{ space}$$

$\Rightarrow$  Pressure correction:  $\delta P = -n^2 \Omega U_0 / 2$  (deviate from equilibrium)

The impinging particles lose kinetic energy in approaching walls to overcome the attractions of the bulk particles. (half of it due to the wall on one side)

$$\delta \frac{m \bar{V}_x^2}{2} = \frac{1}{2} U = \frac{1}{2} \int d^3 \vec{r} V_{\text{attr}}(\vec{r}) n = -\frac{1}{2} n \Omega U_0$$

The slower particles spend a long time  $\tau$  in vicinity of wall  
 $\rightarrow$  Reduced velocities  $\Rightarrow$  an increase in the surface density

$$\frac{\delta n}{n} = \frac{\delta \tau}{\tau} = -\frac{\delta V_x}{V_x} = -\frac{1}{2} \frac{\delta \bar{V}_x^2}{\bar{V}_x^2}, \Rightarrow \delta n = -\frac{1}{2} \beta n U = +\frac{1}{2} n^2 \Omega U_0 \beta$$

$\Rightarrow$  Pressure correction:  $\delta P = \delta n (m \bar{V}_x^2) + n \delta (m \bar{V}_x^2)$

$$= \frac{1}{2} n^2 \Omega U_0 - n^2 \Omega U_0$$

$$= -\frac{1}{2} n^2 \Omega U_0$$

$$\begin{aligned} * \int d^3 \vec{r} V_{\text{attr}}(r) &= \int_{r_0}^{+\infty} -U_0 \left(\frac{r_0}{r}\right)^b 4\pi r^2 dr \\ &= -U_0 \int_{r_0}^{+\infty} 4\pi r^b r^{-4} dr = \frac{4\pi}{3} U_0 r_0^b r^{-3} \Big|_{r_0}^{+\infty} \\ &= -\frac{4}{3} \pi r_0^3 U_0 = -\Omega U_0 \end{aligned}$$

## 5.4 Breakdown of the van der Waals equation.

Mechanical stability of a gas requires positivity of the isothermal compressibility  $\kappa_T = -V^{-1} \partial V / \partial P|_T$  (Section 1.9) and by examining density fluctuations in grand canonical ensemble (Section 4.9)

Prob. of finding  $N$  particles in a volume  $V$

for fixed  $T$ ,  $V = f(N, P)$

$$dV = \frac{\partial V}{\partial N}|_{P,T} dN + \frac{\partial V}{\partial P}|_{V,N} dP$$

$V \equiv \text{constant}$ ;  $dV = 0$

$$\frac{\partial P}{\partial N}|_{V,T} = -\frac{\partial V / \partial N}{\partial V / \partial P}|_{N,T}$$

$$\text{and } \frac{\partial V}{\partial N}|_{P,T} = \frac{1}{\partial N / \partial V|_{P,T}}$$

Positivity of  $\mu_T$  is tied to that of the variance of  $N$

Eqn of state satisfy the stable requirements

$$p(N,V) = \frac{e^{\beta \mu N} Z(N,V,T)}{Q} \text{ and } \ln Q = -\beta \mathcal{G} = \frac{PV}{k_B T}$$

★  $\Rightarrow \begin{cases} \langle N \rangle_c = N = \frac{\partial(\ln Q)}{\partial(\beta \mu)} = \frac{\partial}{\partial(\beta \mu)} (\beta PV) = V \frac{\partial P}{\partial \mu}|_{T,V} \quad \text{①} \\ \langle N^2 \rangle_c = \frac{\partial^2(\ln Q)}{\partial(\beta \mu)^2} = \frac{\partial \langle N \rangle_c}{\partial(\beta \mu)} = k_B T \frac{\partial N}{\partial \mu}|_{T,V} \quad \text{②} \end{cases}$

$$\frac{\text{②}}{\text{①}} : \frac{\langle N^2 \rangle_c}{\langle N \rangle} = \frac{k_B T}{V} \frac{\partial N}{\partial \mu}|_{T,V} = -\frac{k_B T}{V} \frac{\partial N}{\partial V}|_{P,T} \frac{\partial V}{\partial P}|_{N,T} = n k_B T \mu_T$$

⇒ ★ (Section 1:  $\frac{\partial N}{\partial V}|_{P,T} \frac{\partial V}{\partial P}|_{N,T} \frac{\partial P}{\partial N}|_{T,V} = -1$  chain rule of differentiation)

- stable value of  $N$  corresponds to a maximum of  $p(N,V)$ .
- Negative  $\mu_T$  corresponds to a minimum of  $p(N,V)$ , and system is least likely to be found at such densities. Fluctuations in density will occur spontaneously and change the density to a stable value.

Van der Waal isotherms contain a portion with  $-\frac{\partial P}{\partial V}|_T < 0$  ( $T < T_c$ )

$\Rightarrow$  Negative compressibility implies an instability towards forming domain of low and high density (phase separation)

i.e., Attractive interactions in real gases  $\Rightarrow$  liquid-gas phase separation at low  $T$

i.e.,  $\frac{\partial P}{\partial V}|_T = 0$  at the coexistence of two phase

Maxwell construction:

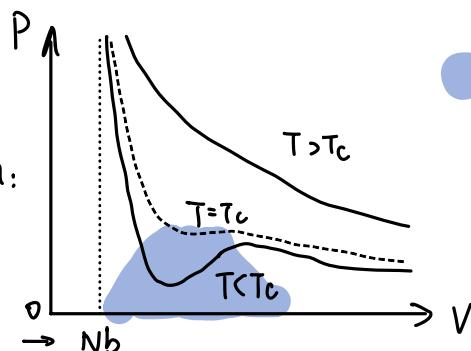
use van der Waal eqn to construct the phase diagram of real gas

Variations of  $\mu(T,P)$  along an isotherm

$$d\mu = \frac{V}{N} dP \quad (\text{from } N = V \frac{\partial P}{\partial \mu}|_{T,V}) \Rightarrow \mu(T,P) = \mu(T,p_A) + \int_{p_A}^P \frac{V(T,p')}{N} dp'$$

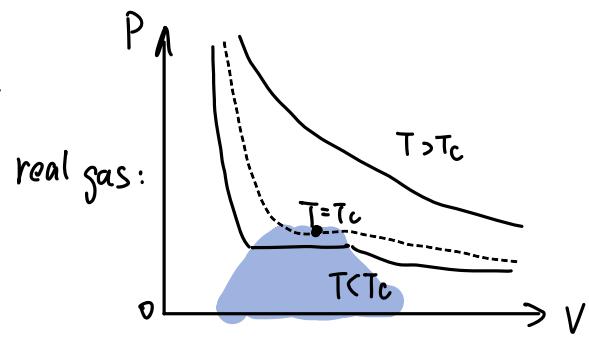
van der Waals isotherms for  $T < T_c$  are non-monotonic

$\Rightarrow$  range of pressures correspond to 3 values of  $\{V\}$ ,  $\{\mu\}$



van der Waals eqn:

phase coexistence



real gas:

In equilibrium, number of particles in each phase  $N_\alpha$

$$\Rightarrow \text{minimize } G = \sum_\alpha M_\alpha N_\alpha$$

$\Rightarrow$  phase with lowest  $M_\alpha$  will acquire all particles ( $N_\alpha$ )

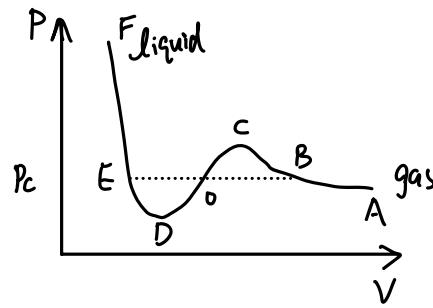
A phase transition occurs when two branches of allowed  $M$  intersect.

$\Rightarrow$  the critical pressure for intersection

$$M(T, P) = M(T, P_c) \Rightarrow \oint_{P_c}^{P_c} dp' V(T, p') = 0$$

Geometrical interpretation:

$P_c$  corresponds to a pressure that encloses equal areas of the non-monotonic isotherm on each side.



$$C \rightarrow D \Rightarrow B \rightarrow E$$

Area of  $CDB$  = Area of  $OED$

$BC$  and  $DE$  are metastable

intersection of



Drawbacks: Integrating a clearly unphysical portion of van der Waals isotherm.

## 5.5 Mean-field theory of condensation

Thermodynamic potential  $[Z(T,N) \text{ or } \Omega(T,\mu)] \Rightarrow$  all properties of interacting system, including phase separation

Discontinuities in state funcs.; singularities in partition funcs.  $\Rightarrow$  Phase transition.

Most partition funcs are well-behaved integrals  
(for short-ranged interactions)

$$Z(T,N,V) = \int \frac{\prod_{i=1}^N d^3 \vec{p}_i d^3 \vec{q}_i}{N! h^{3N}} \exp \left[ -\beta \sum_{i=1}^N \frac{p_i^2}{2m} - \beta \sum_{i < j} V(\vec{q}_i - \vec{q}_j) \right]$$

$\Rightarrow$  approximation scheme: separately treat contributions of hard core and attractive portions (not perturbatively)

$$Z(T,N,V) \approx \frac{1}{N!} \underbrace{\frac{1}{\lambda^{3N}} V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)}_{\text{Excluded volume effects}} \exp(-\beta \bar{U})$$

\*  $\bar{U}$  represents an average attraction energy

Assume a uniform density  $n = N/V$ ,

$$\begin{aligned} \bar{U} &= \frac{1}{2} \sum_{i,j} V_{\text{attr}}(\vec{q}_i - \vec{q}_j) \xrightarrow[N \rightarrow \infty]{\substack{\text{integral all space}}} \frac{1}{2} \int d^3 \vec{r}_1 d^3 \vec{r}_2 n(\vec{r}_1) n(\vec{r}_2) V_{\text{attr}}(\vec{r}_1 - \vec{r}_2) \\ &\approx \frac{n^2}{2} V \int d^3 \vec{r} V_{\text{attr}}(\vec{r}) \equiv -\frac{N^2}{2V} u \end{aligned}$$

\* Parameter  $u$ : the net effect of the attractive interactions

$$u = u_0 \Omega \text{ in Section 5.3}$$

$$\text{Approximate partition func.} \Rightarrow Z(N,T,V) \approx \frac{(V - N\Omega/2)^N}{N! \lambda^{3N}} \exp \left[ \frac{\beta u N^2}{2V} \right]$$

$$\text{approximate free energy.} \Rightarrow F = -k_B T \ln Z = -N k_B T \ln(V - \frac{N\Omega}{2}) + N k_B T \ln(\frac{N}{e}) + 3N k_B T \ln \lambda - \frac{uN^2}{2V}$$

approximate pressure in canonical ensemble

$$\Rightarrow P_{\text{can}} = -\frac{\partial F}{\partial V} \Big|_{T,N} = \frac{N k_B T}{V - \frac{N\Omega}{2}} - \frac{uN^2}{2V^2} \quad \sim \text{Van der Waals eqn.}$$

uniform density approximation  $\Rightarrow$  van der Waals eqn.

Check the self-consistency of the approximation  
(Criterion:  $\mu_T > 0$ )



~~uniform density assumption~~



Grand canonical ensemble

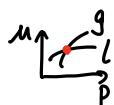
When  $\mu_T > 0$ , variances of density vanishes ( $V \rightarrow +\infty$ ) as  $\langle n^2 \rangle_c = k_B T n^2 \kappa_T / V$

$$* \langle n^2 \rangle_c = \frac{\langle (\frac{N}{V})^2 \rangle_c}{N} N = \frac{N}{V^2} n k_B T \kappa_T = \frac{n^2 k_B T \kappa_T}{V}$$

At  $T_c$ ,  $\kappa_T$  diverges;

At lower  $T$ , instability toward density fluctuation ( $\exists \mu_T < 0$ )

condensation occurs, phase separation into high (liquid) and low (gas) density

fixed chemical potential  , number of particles (density)  $\rightarrow$  distinct phases

As the assumption of a uniform density is correct for both liquid and gas phases respectively.

Grand canonical func.  $Q(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, N, V)$

$$\approx \sum_{N=0}^{\infty} \exp \left[ \beta \mu N + N \ln(V - N \frac{\Omega}{2}) - N \ln N + N - 3N \ln \lambda + \frac{\beta \mu N^2}{2V} \right]$$

$$= \sum_{N=0}^{\infty} \exp \left[ N \ln \left( \frac{V}{N} - \frac{\Omega}{2} \right) + \frac{\beta \mu N^2}{2V} + N \Delta \right]$$

\*  $\Delta = 1 + \beta \mu - \ln \lambda^3$

sum over exponentials in  $N$   
 $\sim$  saddle point approx. (section 2.b)

$$Q(T, \mu, V) \approx \exp \left\{ \max \left[ N \ln \left( \frac{V}{N} - \frac{\Omega}{2} \right) + \frac{\beta \mu N^2}{2V} + N \Delta \right] \right\}_N$$

For grand canonical expression of gas pressure

$$\beta P_{g.c.} = \frac{\ln Q}{V} = \max [\Psi(n)]_n$$

where  $\Psi(n) = n \Delta + n \ln(n^{-1} - \frac{\Omega}{2}) + \frac{\beta \mu}{2} n^2$

Maximum value at  $\frac{d\Psi}{dn} \Big|_{n_\alpha} = 0 \Rightarrow \Delta = -\ln(n_\alpha^{-1} - \frac{\Omega}{2}) + \frac{1}{1 - n_\alpha \Omega / 2} - \beta \mu n_\alpha$

\* multiple solutions  $n_\alpha$  for the density

$$P_{g.c.} = \max \left[ \frac{n \alpha k_B T}{1 - n \alpha \Omega / 2} - \frac{\mu}{2} n_\alpha^2 \right]_\alpha = \max [P_{can}(n_\alpha)]_\alpha$$

At particular density, grand canonical and canonical values of pressure are identical.  $\Delta = \Delta(\mu, T)$  admit multiple solutions for density at certain  $\mu$  and  $T$ , and the correct one is uniquely determined as the one maximizes the canonical expression for pressure (or  $\Psi(n)$ )

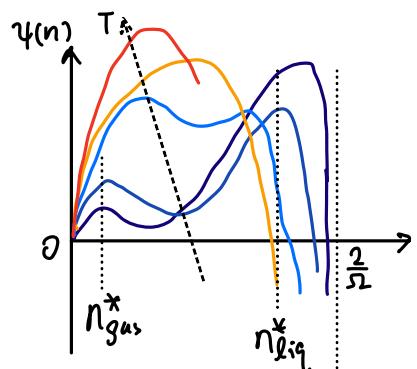
$Q(T, \mu, V) = \sum_{N=0}^{\infty} \exp \left[ N \ln \left( \frac{V}{N} - \frac{\Omega}{2} \right) + \frac{\beta \mu N^2}{2V} + N \Delta \right]$  is dominated by two

large terms at gas and liquid densities. At particular  $\mu$ , the stable phase is determined by the larger terms.

The phase transition occurs when the dominant term changes upon varying  $T$ .

$$\ln Q = \lim_{V \rightarrow \infty} \ln [e^{\beta V P_{\text{lia}}} + e^{\beta V P_{\text{gas}}}] = \begin{cases} e^{\beta V P_{\text{lia}}} & T < T^* \\ e^{\beta V P_{\text{gas}}} & T > T^* \end{cases}$$

Thermodynamic limit  $V \rightarrow \infty \Rightarrow$  singularity in density (noncontinuous)  
 (No phase transitions in finite systems!)

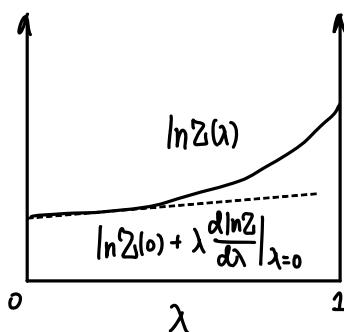


## 5.6 Variational methods (alternative approximation)

Perturbative methods incorporates the effect of interaction but are impractical for strongly interacting systems.  
First few terms in varial series  $\Rightarrow$  behaviour of gas ; infinite number of terms  $\Rightarrow$  condensation transition

"tr": the integral over the phase space of  $N$  particles

(sum over all allowed quantum microstates)



Gibbs inequality

↓  
grand canonical partition func Q

$H_0 \equiv$  a gas of hard-core particles of density  $n$

[ replace the sum by the dominate term (Section 2.b) ]

In canonical ensemble,  $Z = \text{tr}(e^{-\beta H})$

$H_0$  is easier to calculate, acting on the same set of degree of freedom.

$$H(\lambda) = H_0 + \lambda(H - H_0)$$

$Z(\lambda) = \text{tr}\{\exp[-\beta H_0 - \beta\lambda(H - H_0)]\}$  interpolate among  $\lambda$  from 0 through 1.

$$\frac{d^2 \ln Z(\lambda)}{d\lambda^2} = \beta^2 \langle (H - H_0)^2 \rangle_c > 0 \quad \text{convexity condition}$$

$$\ln Z(\lambda) \geq \ln Z(0) + \lambda \frac{d \ln Z}{d \lambda} \Big|_{\lambda=0} \quad \text{and} \quad \frac{d \ln Z}{d \lambda} \Big|_{\lambda=0} = -\beta \langle H - H_0 \rangle^o$$

\* superscript indicates expectation values w.r.t.  $H_0$

$$\Rightarrow \ln Z(\lambda) \geq \ln Z(0) - \beta \lambda \langle H - H_0 \rangle^o$$

Setting  $\lambda = 1$

$$\Rightarrow \ln Z \geq \ln Z(0) - \beta \langle H \rangle^o + \beta \langle H_0 \rangle^o \quad (\text{basis of variation estimation})$$

$H_0$  has several parameters { $n_{\alpha\beta}$ } and to find  $\max [\ln Z(0) - \beta \langle H \rangle^o + \beta \langle H_0 \rangle^o]$  for the best estimation of  $\ln Z$

$$\ln Q_0 = \beta \mu N + \ln Z = \sqrt{n \Delta + n \ln(n^{-1} \frac{\Omega}{2})} \quad (\text{from section 5.5})$$

$$\Delta = 1 + \beta \mu - \ln \lambda^3$$

\*  $H - H_0$  contains the attractive portion of the 2-body interactions

\* In the regions of phase space not excluded by the hard-core interactions, the gas in  $H_0$  is uniformly distributed (with density  $n$ )

$$\beta \langle H_0 - H \rangle^o = \beta \left\langle \sum_{i,j} V(\vec{q}_i - \vec{q}_j) \right\rangle^o \xlongequal{\text{in section 5.5}} \beta \sqrt{\frac{n^2}{2}} u$$

$$\Rightarrow \beta P = \frac{\ln Q}{\sqrt{...}} \geq \left[ n (1 + \beta \mu - \ln(\lambda^3)) + n \ln(n^{-1} \frac{\Omega}{2}) \right] + \frac{1}{2} \beta \mu n^2 \xrightarrow{\text{section 5.5}} \Psi(n)$$

Best variational estimate by maximizing w.r.t.  $n$  is equivalent to the result in section 5.5

## 5.7 Corresponding states

Perturbation method  
Mean-field approx. → dilute interacting gas at high temperature  
Variational approx. at low temperature: condensation

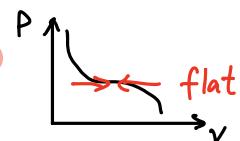
Qualitative behaviour of the phase diagram is the same for most simple gases

line of transitions in  $(P, T)$  > terminates at critical point  
coexistence of liquid and gas in  $(V, T)$   
⇒ transform liquid to gas without encountering any singularities.  
ideal gas law (universal) → Law of corresponding state [interacting gases / gas/liquid condensation]

E.g., critical point  $(P_c, T_c, V_c)$   
& van der Waals eqn.

Criteria of critical point :  $\left. \frac{\partial P}{\partial V} \right|_T = 0$  ①  
 $\left. \frac{\partial^2 P}{\partial V^2} \right|_T = 0$  ②

- ①: limit of flat coexistence portion of liquid/gas isotherms
- ②: Stability requirement  $K_T > 0$  (see in section 1.9)



\*  $V = V/N$   
volume per particle

$$\begin{cases} P = \frac{k_B T}{v-b} - \frac{a}{v^2} \\ \left. \frac{\partial P}{\partial v} \right|_T = -\frac{k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \\ \left. \frac{\partial^2 P}{\partial v^2} \right|_T = \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \end{cases} \implies \begin{cases} P_c = \frac{a}{27b^2} \\ V_c = 3b \\ k_B T_c = \frac{8a}{27b} \end{cases}$$

Critical point depends on the microscopic  $\mathcal{H}$  (e.g. 2-body interaction) via  $a$  and  $b$ .

Scaling out such dependence by  
⇒ measuring  $P, T, v$  in units of  $P_c, T_c$  and  $v_c$

$$\begin{cases} P_r = P/P_c \\ T_r = T/T_c \\ V_r = V/V_c \end{cases}$$

Reduced van der Waals eqn.:  $P_r = \frac{3}{3} \frac{T_r}{V_r - 1/3} - \frac{3}{V_r^2}$  (universal, material-independent eqn of state)

Universality ratio:  $\frac{P_c V_c}{k_B T_c} = \frac{3}{8} = 0.375$  (Experiments: 0.28 ~ 0.33)

\* Van der Waals eqn is not a putative universal equation of state.

Empirically generalized eqn:

- ① Using 3 independent critical coordinates
  - ② Finding  $P_r \equiv P_r(V_r, T_r)$  from the collapse of experimental data.  
→ bad performance on noble gas, e.g., Ne, Xe, Kr, etc
- Reason: Microscopic internal potential → difference in  $\mathcal{H}$  (perturbation approx.)

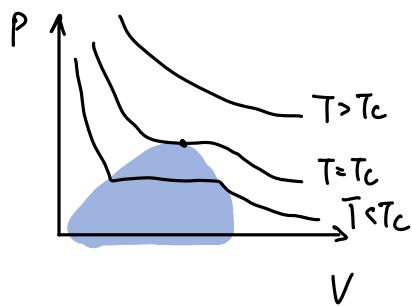
Vale is  
(always / 1st)  
right!

No theoretical or experimental justification → universal eqn of state for all gas and liq  
↳ study starting from microscopic  $\mathcal{H}$ .

## 5.8 Critical point behavior

Examine the isotherms in vicinity of  $(P_c, T_c, v_c)$  → universal behavior of gases near critical point.

Taylor Expansion of  $P(T, v)$   
in the vicinity of  $v_c$ , for  
any  $T > T_c$



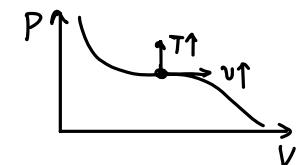
$$P(T, v) = P(T, v_c) + \frac{\partial P}{\partial v} \Big|_{T, v_c} (v - v_c) + \frac{1}{2!} \frac{\partial^2 P}{\partial v^2} \Big|_{T, v_c} (v - v_c)^2 + \frac{1}{3!} \frac{\partial^3 P}{\partial v^3} \Big|_{T, v_c} (v - v_c)^3 + \dots$$

$$P(T, v_c) = P_c + \alpha(T - T_c) + \mathcal{O}[(T - T_c)^2] \quad (\alpha > 0)$$

$$\frac{\partial P}{\partial v} \Big|_{T, v_c} = 0 - a(T - T_c) + \mathcal{O}[(T - T_c)^2] \quad (a > 0)$$

$$\frac{\partial^2 P}{\partial v^2} \Big|_{T, v_c} = 0 + b(T - T_c) + \mathcal{O}[(T - T_c)^2] \quad (b \text{ unknown})$$

$$\frac{\partial^3 P}{\partial v^3} \Big|_{T, v_c} = -c + \mathcal{O}[(T - T_c)] \quad (c > 0)$$



\*  $a, b$  and  $c$  are material-independent constants

\* stability properties ( $\delta P \delta v \leq 0$ ) in section 1.9  $\Rightarrow a > 0$  ( $T > T_c$ );  $c > 0$  ( $T = T_c$ )

no specific sign for  $b$

Isothermal of any gas in the vicinity of its critical point  $\Rightarrow P(T, v) = P_c + \alpha(T - T_c) - a(T - T_c)(v - v_c) + \frac{b}{2}(T - T_c)(v - v_c)^2 - \frac{c}{6}(v - v_c)^3 + \dots$

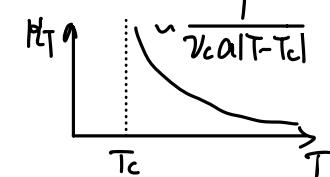
$v$  order 0 2 3 4 3

\*  $(T - T_c) \propto \text{velocity}^2 \propto (v - v_c)^2 \Rightarrow$  simplify the expression (ignore 4th term)

Prediction of behaviour close to critical point

(a) Gas compressibility diverges on approaching the critical point from high  $T$  side along the critical isochore ( $v = v_c$ )

$$\lim_{T \rightarrow T_c^+} K(T, v_c) = -\frac{1}{v_c} \frac{\partial P}{\partial v} \Big|_{T, v_c}^{-1} = \frac{1}{v_c a(T - T_c)}$$



(b) The critical isotherm ( $T = T_c$ ) behaves as

$$P = P_c - \frac{c}{b}(v - v_c)^3 + \dots$$

(c) Expansion on  $P(T, v)$  is inapplicable to  $T < T_c$   
problem > apply Maxwell construction to the unstable isotherms at low  $T$ .

Dimensional considerations :  $\lim_{T \rightarrow T_c^-} (v_{\text{gas}} - v_{\text{liquid}}) \propto (T_c - T)^{1/2}$

\*  $(T - T_c) \propto \text{velocity}^2 \propto (v - v_c)^2$

(Discontinuous)  
First-order transition: liquid-gas transition for  $T < T_c$  (discontinuity in density; release of latent heat  $L$ )

↓ At critical point, the difference between the two phases disappears

(Continuous)

Second-order transition: the singular behaviour at the critical point.

$$(1) P(T, V) = P_c + \alpha(T-T_c) - \alpha(T-T_c)(V-V_c) + \frac{b}{2}(T-T_c)(V-V_c)^2 - \frac{c}{6}(V-V_c)^3 + \dots$$

follows only the constraints of mechanical stability  
and assumption of analytical isotherms.

$$(2) a. \lim_{T \rightarrow T_c^+} K(T, V_c) = -\frac{1}{V_c} \left. \frac{\partial P}{\partial V} \right|_{T, V_c}^{-1} = \frac{1}{V_c \alpha(T-T_c)} \propto (T-T_c)^{-1} \quad (T > T_c)$$

$$b. P = P_c - \frac{c}{b}(V-V_c)^3 + \dots \propto (V-V_c)^3 \quad (T > T_c)$$

$$c. \lim_{T \rightarrow T_c^-} (V_{\text{gas}} - V_{\text{liquid}}) \propto (T_c - T)^{1/2}$$

Confirm the singular behaviour but the universality for different gases:

$$a. \lim_{T \rightarrow T_c^+} K(T, V_c) \propto (T-T_c)^{-\gamma}, \quad \gamma \approx 1.3$$

$$b. (P - P_c) \propto (V - V_c)^\delta, \quad \delta \approx 5.0$$

$$c. \lim_{T \rightarrow T_c^-} (\rho_{\text{liq}} - \rho_{\text{gas}}) \propto \lim_{T \rightarrow T_c^-} (V_{\text{gas}} - V_{\text{liq}}) \propto (T_c - T)^\beta, \quad \beta \approx 0.3$$

$\Rightarrow$  ~~analyticity of isotherms~~

$\Rightarrow \delta, \gamma, \beta$  are critical exponents.

Origin, universality, and numerical values of critical exponents

(modern theory of critical phenomena)

$\Rightarrow$  companion volume of SM in fields.