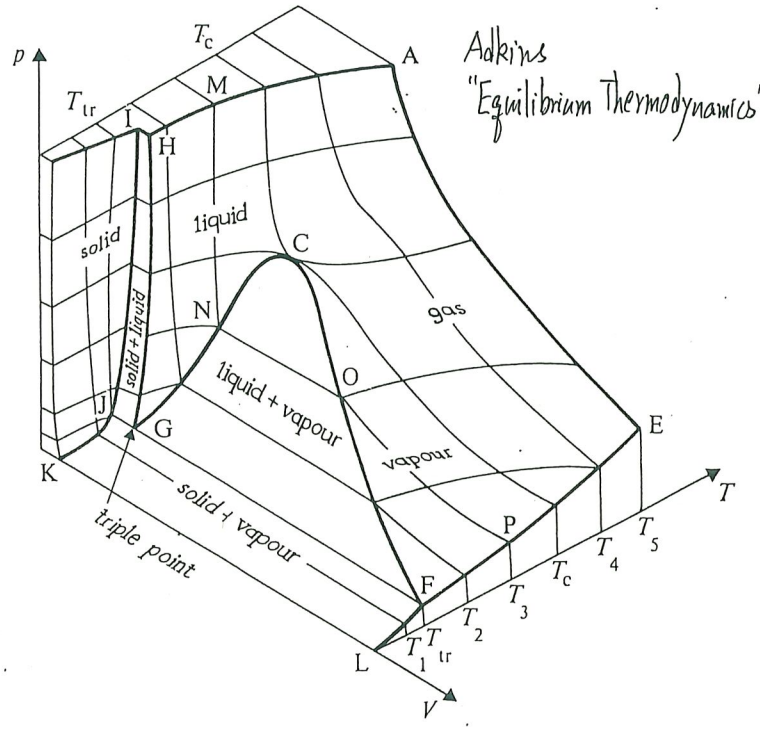
Ch. XIII. (Weakly) Interacting Classical Gas

Particles with interaction → Phase transitions (as illustrated by van der Waals gas law)

Discussed in Ch. VII

Typical PVT surface with Phase Transitions

The *p*–*V*–*T* relation of a pure substance.



Adkins "Equilibrium Thermodynamics"

- Follow constant temperature cut (isotherm) at T_3, for example, vapour → liquid → solid through compression

  [Points P → O → N → M →]

  O → N: vapour-liquid transition; M → : liquid-solid transition

- One point C [critical point] on diagram above which there is no distinction between vapour and liquid [usually use the word "gas" to describe this part]

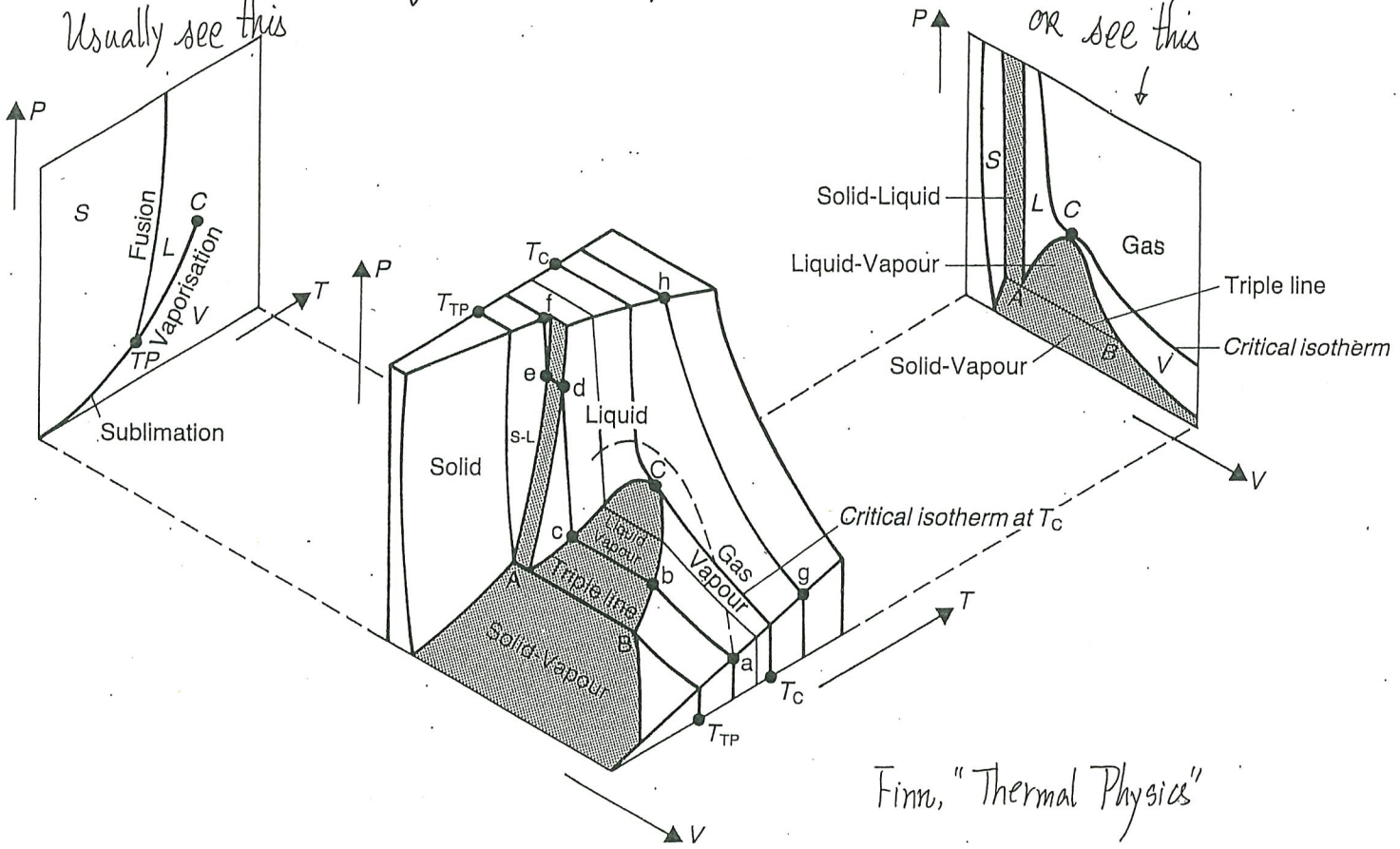
  Phenomena around point C are called Critical Phenomena.

- One Point Gr (triple Point) at which vapour-liquid-ice coexist

VII - (28)

Projections onto P-T and P-V Planes

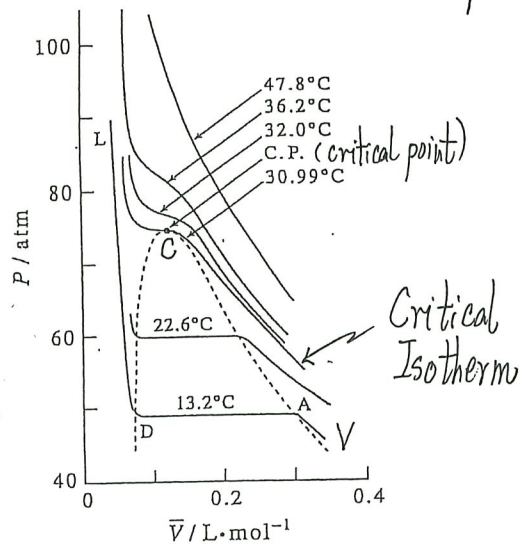
Usually see this



Finn, "Thermal Physics"

A typical *PVT* surface together with its *P–T* and *P–V* projections.

CO_2 Data p-V projection



Experimental pressure-volume isotherms

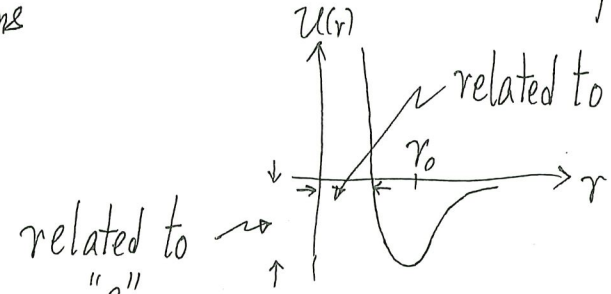
First theory that can give vapour-liquid transition

Van der Waals Equation (1910 Nobel Prize)

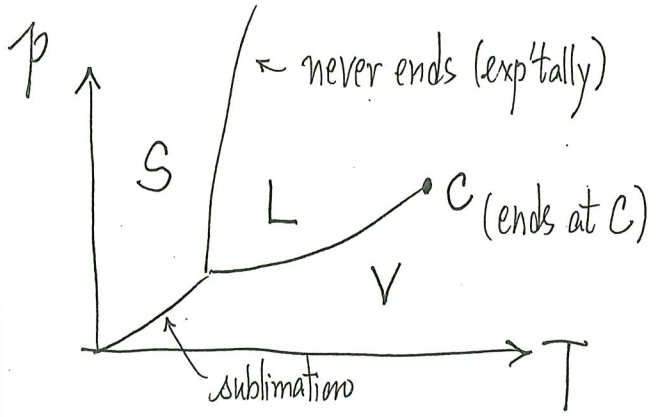
$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (19)$$

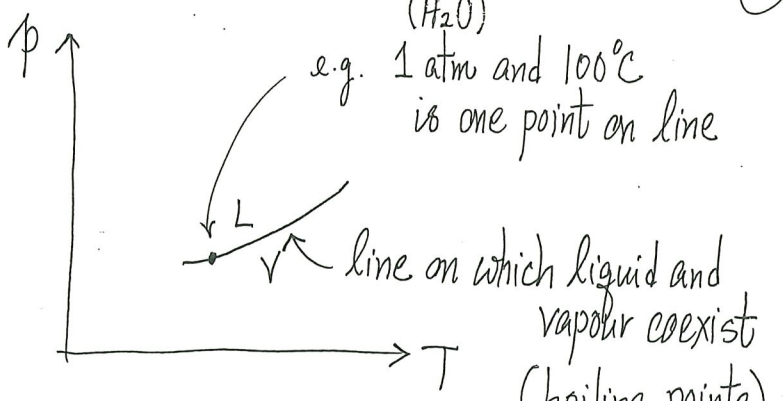
v: molar volume

Recall: Needs inter-particle interaction

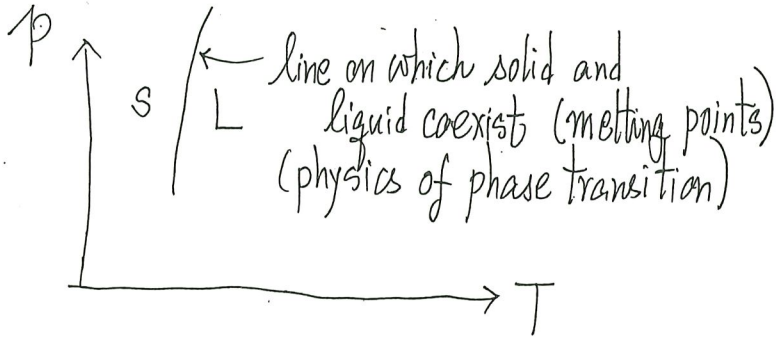


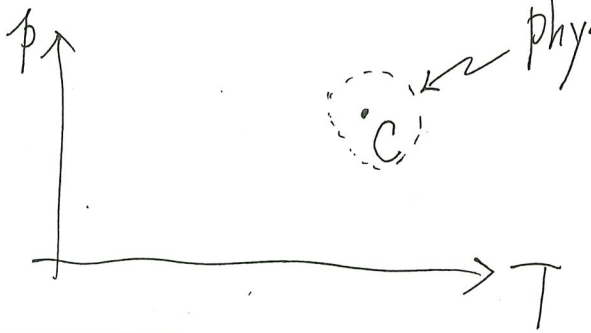
Would a Stat. Mech. calculation with interacting particles gives results related to van der Waals Eq.?





(physics of Phase transition)
相变 (相變)





physics around critical point C
Critical Phenomena (臨界現像)

Interaction → Van der Waals eg. → has critical point → anything special near critical point?

You have worked out that the van der Waals equation can be seen as a correction to the classical ideal gas eq. of state

$$\frac{p}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2$$

Problem Set 2

5. **Solution:** As $nN_A = N$, one could first rewrite the van der Waal equation into

$$\left(p + \frac{N^2 a}{N_A^2 V^2}\right)\left(V - \frac{Nb}{N_A}\right) = NkT \tag{32}$$

$$\left(p + \frac{\tilde{n}^2 a}{N_A^2}\right)\left(\tilde{n}^{-1} - \frac{b}{N_A}\right) = kT \tag{33}$$

After expanding the terms and some rearrangement, one could arrive at

$$\frac{p}{kT} = \left(\tilde{n}^{-1} - \frac{b}{N_A}\right)^{-1} - \frac{\tilde{n}^2 a}{N_A^2 kT} \tag{34}$$

$$= \tilde{n}\left(1 - \frac{\tilde{n}b}{N_A}\right)^{-1} - \frac{\tilde{n}^2 a}{N_A^2 kT} \tag{35}$$

As van der Waals gas is a 'correction' to ideal gas in describing real gas, it can be expected that it is applicable to 'relatively dilute' gas, so $\frac{\tilde{n}b}{N_A} << 1$. Therefore, to first order, $\left(1 - \frac{\tilde{n}b}{N_A}\right)^{-1} \approx 1 + \frac{\tilde{n}b}{N_A}$. Then,

$$\frac{p}{kT} \approx \tilde{n}\left(1 + \frac{\tilde{n}b}{N_A}\right) - \frac{\tilde{n}^2 a}{N_A^2 kT} \tag{36}$$

$$= \tilde{n} + \tilde{n}^2\left(\frac{b}{N_A} - \frac{a}{N_A^2 kT}\right). \tag{37}$$

One could then identify the second virial coefficient $B_2 = \frac{b}{N_A} - \frac{a}{N_A^2 kT}$. Here a arises due to the attraction between gas molecules, and b arises due to non-zero volume of the molecules. Whereas the contribution of a term to pressure is negative, since the molecules become 'stickier', the contribution of b term is positive as it is more likely for the molecules to collide. At low temperature, the effect due to a term is stronger, but as temperature increases, the effect of b term is stronger, since the molecules have more K.E at higher temperature to escape the attraction of other molecules.

← $B_2(T)$ has a positive term (from repulsive part of interaction) and a negative term (from attractive part of interaction)

We have also seen that

for Ideal Fermi Gas at high temperature

$$\frac{P}{kT} = \frac{N}{V} + \underbrace{\frac{1}{4\sqrt{2}} \frac{\lambda_{th}^3}{2}}_{B_2} \left(\frac{N}{V}\right)^2$$

for Ideal Bose Gas at high temperature

$$\frac{P}{kT} = \frac{N}{V} - \underbrace{\frac{1}{4\sqrt{2}} \frac{\lambda_{th}^3}{2}}_{B_2} \left(\frac{N}{V}\right)^2$$

even the Fermions / Bosons are non-interacting.

There seems to be an effective interaction due to the quantum nature of particles.

Goal: Interacting Gas Particles

$$H(\{p,x\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\sum_{(ij)\ \text{pairs}} U(\vec{x}_i - \vec{x}_j)}_{\text{2-body interaction}}$$

Calculate $Z(T,V,N)$

and obtain 1st correction term to $\frac{p}{kT} = \frac{N}{V} + \underbrace{B_2(T)\left(\frac{N}{V}\right)^2}_{\text{1st correction term}}$ ($B_2(T)$: ?)

and see how $B_2(T)$ is related to the interaction $U(\vec{x})$.

We have set this problem up in Ch. IX.

C. Classical Gas and Classical Ideal Gas

$$Z(T,V,N) = \sum_{\text{all } N\text{-particle states } i} e^{-\beta E_i}$$

① for the N-particle state i of energy E_i

② weight it by $e^{-\beta E_i}$

③

Classical Physics: N particles in 3D $\Rightarrow$ $6N$ Phase space

$$Z(T,V,N) = \frac{1}{h^{3N} N!} \int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; e^{-\beta H(\{p,x\})}$$

① $H(\{p,x\})$ of energy

① an N-particle state is specified by $\{p,x\}$ — $6N$ of them

② weight it by $e^{-\beta H(\{p,x\})}$

③ summing over all N-particle states ($6N$ integrals)

integrate over all phase space

correct overcounting

turn phase space into states

$$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; e^{-\beta H(\{p,x\})} \qquad (C1)$$

$$H(\{p,x\}) = H(p_{1x}, p_{1y}, p_{1z}, x_1, y_1, z_1; p_{2x}, p_{2y}, p_{2z}, x_2, y_2, z_2; \cdots, p_{Nx}, p_{Ny}, p_{Nz}, x_N, y_N, z_N)$$

= Hamiltonian of N particles (3D) in a volume V)

• Starting Point for interacting (non-ideal) gas/liquid and ideal gas

$$H(\{p,x\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{(ij)\ \text{pairs}} u(\vec{x}_i - \vec{x}_j) \qquad (C2)^{+}$$ general interacting case

$$H(\{p,x\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \qquad (C3)^{+}$$ Classical ideal (Non-interacting) case

$^{+}$Both cases have the same k.e. $\left(\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}\right)$ term.

Ch. IX CE-(C3)

$$Z(T,V,N) = \frac{1}{N!}\frac{1}{h^{3N}}\int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; e^{-\beta \vec{p}_1^{\,2}/2m} \cdots e^{-\beta \vec{p}_N^{\,2}/2m} \cdot e^{-\beta \sum_{(ij)\,pairs} u(\vec{x}_i - \vec{x}_j)} \quad \text{(general)}$$

$$= \frac{1}{N!}\frac{1}{h^{3N}} \underbrace{\underbrace{\left(\int d\vec{p}_1\, e^{-\beta \vec{p}_1^{\,2}/2m}\right)}_{3 \text{ integrals}} \cdots \underbrace{\left(\int d\vec{p}_N\, e^{-\beta \vec{p}_N^{\,2}/2m}\right)}_{3 \text{ integrals}}}_{3N \text{ integrals}} \cdot \underbrace{\int d\vec{x}_1 \cdots \int d\vec{x}_N}_{3N \text{ integrals}} e^{-\beta \sum_{(ij)\,pairs} u(\vec{x}_i - \vec{x}_j)} \quad \text{(general)} \qquad \text{(C4)}$$

- [starting point of liquid state physics and non-ideal gas physics, and other classical stat. mech. problems]
- Note integrals $\left(\int d\vec{p}_i\, e^{-\beta \vec{p}_i^{\,2}/2m}\right)$ are there

  $\Rightarrow$ results coming from these terms are general for interacting and ideal gases

We will start from Eq. (C4).

A. Non-ideal Classical Gas: Partition Function Z and 2nd Virial coefficient $B_2(T)$

From Eq. (C4), if $\mathcal{U}(\vec{x}_i - \vec{x}_j) = 0$, then $\int d\vec{x}_1 \cdots d\vec{x}_N = V^N$ and $Z = Z_{ideal}(T, V, N)$

which gives $pV = NkT$

$\therefore$

$$Z(T,V,N) = \underbrace{\frac{V^N}{N!\,h^{3N}} \left(\int d\vec{p}_1 e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}}\right) \cdots \left(\int d\vec{p}_N e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}}\right)}_{\text{interacting}} \cdot \underbrace{\frac{1}{V^N} \int d\vec{x}_1 \cdots \int d\vec{x}_N \, e^{-\beta \sum_{(ij\ pairs)} \mathcal{U}(\vec{x}_i - \vec{x}_j)}}_{Z_{configuration}(T,V,N)}$$

$$= Z_{ideal} \cdot Z_{configuration} \qquad (1)$$

With interacting particles, the task is to evaluate (approximately)

$$Z_{conf.} \equiv \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \; e^{-\beta \sum_{(ij\ pairs)} \mathcal{U}(\vec{x}_i - \vec{x}_j)} \qquad (2)$$

If $\mathcal{U}(\vec{x}) = 0$, $Z_{conf.} = 1$, $Z = Z_{ideal}$ as expected/required.

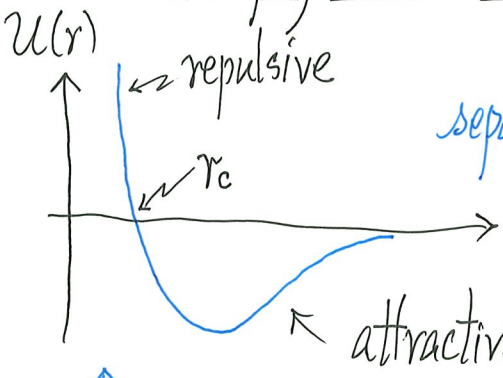
$U(\vec{x}_i - \vec{x}_j)$ typically is $U(|\vec{x}_i - \vec{x}_j|) = U(r_{ij})$

separation (but not in direction)

$\sum_{(ij)\,\text{pairs}} U(r_{ij})$ has $\left[\frac{N(N-1)}{2}\ \text{pairs}\right]$ altogether in the sum

$$Z_{\text{conf.}} = \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N\ e^{-\beta \sum_{\text{all pairs}} U(r_{ij})} = \frac{1}{V^N}\int d^3x_1 \cdots d^3x_N \prod_{\substack{\text{all pairs} \\ \left(\frac{N(N-1)}{2}\ \text{of them}\right)}} e^{-\beta U(r_{ij})} \qquad (3)\ \text{(exact)}$$

Think physics & make approximations



separation between 2 particles

depth reflects incentive to come close to

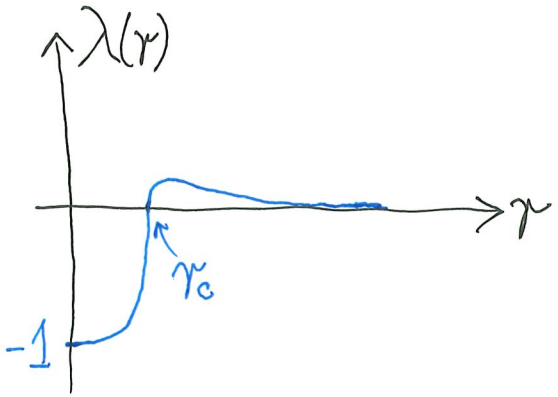
steep $U(r)$ for $r<r_c$ ⇒ particles don't like to get too close

This is the typical form of $U(r)$

Let's consider how

$$\left(e^{-\beta U(r_{ij})} - 1\right) \equiv \lambda(r_{ij}) = \lambda_{ij} \qquad (4)$$

behaves



$\lambda(r)$ is a nice function to handle (by computer)

$\lambda(r)$ differs from zero appreciably (≈ -1) only for $r \leq r_c$

$\lambda_{ij} \equiv \lambda(r_{ij}) \approx 0$ unless particles i and j come very close to each other (e.g. when they collide)

$$Z_{conf.} = \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \prod_{(pairs)} e^{-\beta U(r_{ij})} = \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \prod_{(pairs)} (1+\lambda_{ij}) \quad (5) \text{ (exact)}$$

$$= \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \underbrace{(1+\lambda_{12})(1+\lambda_{13}) \cdots (1+\lambda_{1N})(1+\lambda_{23}) \cdots (1+\lambda_{2N})(1+\lambda_{34}) \cdots (1+\lambda_{3N}) \cdots (1+\lambda_{N-1,N})}_{N(N-1)/2 \text{ factors}}$$

(Exact)

$$= \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \left(1 + \sum_{(pairs)} \lambda_{ij} + \sum \lambda_{ij}\lambda_{kl} + \cdots \right) \quad (6) \text{ (Exact)}$$

$\sim \lambda\lambda\lambda + O(\lambda^4) + \cdots$

- No λ term → zeroth order in λ → ideal gas
- one λ terms ($\frac{N(N-1)}{2}$ λ_{ij}'s) → 1st order approximation → 1st correction to ideal gas behavior
- 2nd order in λ

We will only keep the 1st order term

Consider $\lambda_{ij}\lambda_{ke}$ terms

- $\lambda_{12}\lambda_{23} \neq 0$ requires particles 1,2,3 are simultaneously close to each other (3-particle collision)

(rare occasion than λ_{12}, which only requires particles 1, 2 are close to each other)

$\lambda_{12}\ \lambda_{34} \neq 0$

both not zero [requires 1,2 AND 3,4 particles (two pairs) are simultaneous close to each other]

both are unlikely when $\frac{N}{V}$ is not too high!

To treat $\lambda\cdot\lambda$, $\lambda\cdot\lambda\cdot\lambda$, ... terms, use "cluster expansion"

[a method ~ perturbation and Feynman diagrams]

We ignore these higher order terms here!

$$Z_{conf.} \approx \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \left(1 + \sum_{(pairs)} \lambda_{ij}\right) \qquad (7)$$

lowest-order approximation

$$Z_{conf.} = \underbrace{1}_{\text{ideal gas term}} + \frac{1}{V^N} \int d^3x_1 \cdots d^3x_N \sum_{(pairs)} \lambda_{ij}$$

$$= 1 + \frac{1}{V^N} \frac{N(N-1)}{2} \int d^3x \cdots d^3x_N \, \lambda_{12}$$

[can be any λ_{ij}, but $\frac{N(N-1)}{2}$ identical integrals]

$$= 1 + \frac{1}{V^N} \frac{N(N-1)}{2} \cdot V^{N-2} \underbrace{\int d^3x_1 d^3x_2 \, \lambda(r_{12})}_{\text{transform to CM and relative coordinates}}$$

↖ only separation matters (relative separation)

∵ integrand relates only to 2 particle's separation

(CM freely moves in V)

$$= 1 + \frac{N(N-1)}{2V} \int d^3r \, \underbrace{\lambda(r)}_{\text{retains } \lambda \text{ terms only}} \cong 1 + \frac{N^2}{2V} \int d^3r \left(e^{-\beta u(r)} - 1\right) = 1 + N \cdot \frac{n}{2} \overbrace{I_2(\beta)}$$

$$\approx \left(1 + \frac{n}{2} I_2(\beta)\right)^N \qquad (8)$$

- All information on interaction $U(r)$ is put into an integral

$$I_2(\beta) \equiv \int d^3r \left[e^{-\beta U(r)} - 1 \right] = 4\pi \int_0^\infty dr\, r^2 \left[e^{-\beta U(r)} - 1 \right] \qquad (9)$$

(β: $1/kT$; one single integration (radial distance))

- We expect $Z_{conf.} = \left(1 + \frac{n}{2} I_2(\beta) + \underbrace{\cdots}_{n^2 I_3 + \cdots} \right)^N$

($n^2 I_3 + \cdots$ when $O(\lambda^3)$, $O(\lambda^4)\cdots$ are kept)

We will handle $I_2(\beta)$ later. Let's say we evaluated $I_2(\beta)$.

$$Z_{non\text{-}ideal}(T,V,N) = Z_{ideal} \cdot Z_{conf.} \; ; \quad F_{non\text{-}ideal} = -kT \ln Z_{non\text{-}ideal} = -kT \ln Z_{ideal} - kT \ln Z_{conf.}$$

($Z_{non\text{-}ideal}$: interacting gas)

$$\therefore F_{non\text{-}ideal} = F_{ideal} - kT \ln \left(1 + \frac{n}{2} I_2(\beta) \right)^N = F_{ideal} - \underbrace{N}_{\text{extensive}} kT \ln \left(1 + \frac{n}{2} I_2(\beta) \right)$$

($\frac{n}{2} I_2(\beta)$: correction to "1")

$\therefore$ $F_{non\text{-}ideal} = F_{ideal} - NkT \cdot \frac{n}{2} I_2(\beta) = F_{ideal} - \frac{kT}{2}\frac{N^2}{V} I_2(\beta)$ (10)

← Helmholtz Free energy

pressure → $P = -\left(\frac{\partial F_{non\text{-}ideal}}{\partial V}\right)_{T,N} = \frac{NkT}{V} - \frac{kT}{2}\left(\frac{N}{V}\right)^2 I_2(\beta)$ (11)

[started to see $\left(\frac{N}{V}\right)$, $\left(\frac{N}{V}\right)^2$ structure]

did this in Ch. IX

$\therefore$ $\boxed{\frac{P}{kT} = \frac{N}{V} - \frac{1}{2} I_2(\beta)\left(\frac{N}{V}\right)^2 \equiv n + \overbrace{B_2(T)}^{\text{called 2nd virial coefficient}} n^2}$ (12) ← Key results

1st correction term

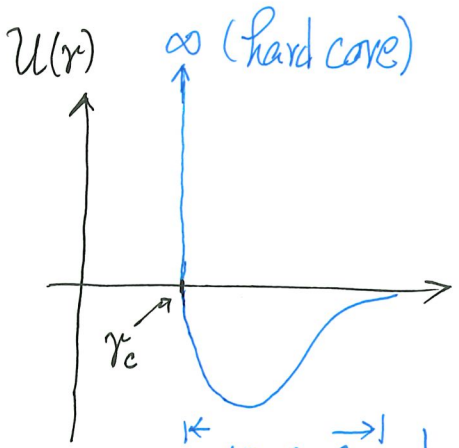
with

$$B_2(T) = \frac{-1}{2} I_2(\beta) = -2\pi \int_0^\infty dr\, r^2 \left(e^{-u(r)/kT} - 1\right) \quad (13)$$ +

No longer need the derivation again! (i) Evaluate $B_2(T)$, (ii) know correction to ideal gas behavior

+ We considered N particles in volume V. $B_2(T)$ has units $(\text{length})^3$, e.g. cm^3.
Chemists usually consider N_A particles in molar volume v. The prefer $P/kT = \frac{1}{v} + \frac{B_2(T)}{v^2}$ (1 mole).
In data books, $B_2(T)$ in $(cm^3 \cdot mol^{-1})$ is usually cited.

B. $B_2(T)$ for typical $u(r)$



- A simple model $u(r)$ is

$$u(r) = \begin{cases} \infty & r < r_c \\ -u_0 f\left(\frac{r}{r_c}\right), & r \geq r_c \end{cases} \qquad (14)$$

[r_c, $-u_0$, $f\left(\frac{r}{r_c}\right)$ characterize the interaction]

- $$\lambda(r) = e^{-\beta u(r)} - 1 = \begin{cases} -1, & r < r_c \\ e^{\beta u_0 f\left(\frac{r}{r_c}\right)} - 1, & r \geq r_c \end{cases} \qquad (15)$$

$$B_2(T) = +2\pi \int_0^{r_c} r^2 dr - 2\pi \int_{r_c}^{\infty} dr\, r^2 \left(e^{\frac{u_0}{kT} f\left(\frac{r}{r_c}\right)} - 1 \right)$$

$$\cong \frac{2\pi r_c^3}{3} - 2\pi \int_{r_c}^{\infty} dr\, r^2 \frac{u_0}{kT} f\left(\frac{r}{r_c}\right)$$

still close to ideal gas, so $\frac{u_0}{kT} f\left(\frac{r}{r_c}\right) \ll 1$

(repulsive) some hard sphere's volume emerging (+ve sign)

attractive part (-ve sign)

$$\therefore \quad B_2(T) = 4 \cdot \left[\frac{4\pi}{3}\left(\frac{r_c}{2}\right)^3\right] - \frac{2\pi}{kT} u_0 \int_{r_c}^{\infty} dr\, r^2 f\left(\frac{r}{r_c}\right) \qquad (16)$$

related to the volume of hard spheres

just an integral (gives unit) (assume exists)

Positive Contribution (from repulsive part of $u(r)$)†

Negative Contribution (from attractive part of $u(r)$)‡

$$= b' - \frac{a'}{kT} \qquad (17)$$

(c.f. result from van der Waals eq.)

† This supplements the discussion on Ideal Fermi Gas at high temperature

‡ This supplements the disaussion on Ideal Bose Gas at high temperature