C. Relating results to van der Waals equation

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

OR for 1 mole

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (18)$$

$\bar{n}$ = # moles ⇒ $N = \bar{n} N_A$

[v = molar volume]

$$\left(P + \frac{N^2}{V^2}\frac{a}{N_A^2}\right)\left(V - N\frac{b}{N_A}\right) = NkT \Rightarrow \frac{P}{kT} \approx \left(\frac{N}{V}\right) + \underbrace{\left(\frac{b}{N_A} - \frac{a}{N_A^2 kT}\right)}_{\text{this is the term } \left(b' - \frac{a'}{kT}\right) \text{ we got}} \left(\frac{N}{V}\right)^2 \quad (19)$$

we can redefine $b \equiv N_A b'$

$a \equiv N_A^2 a'$

and we obtain van der Waals equation to the same order.

∴ Considering particles' interaction gives van der Waals equation

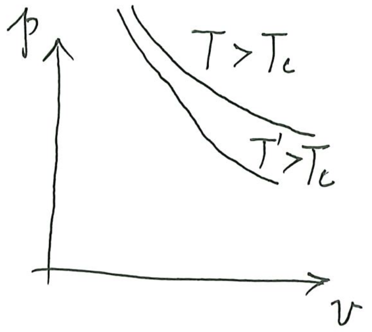
⇒ phase transitions and physics around the critical point

D. Much Physics behind Van der Waals Equation

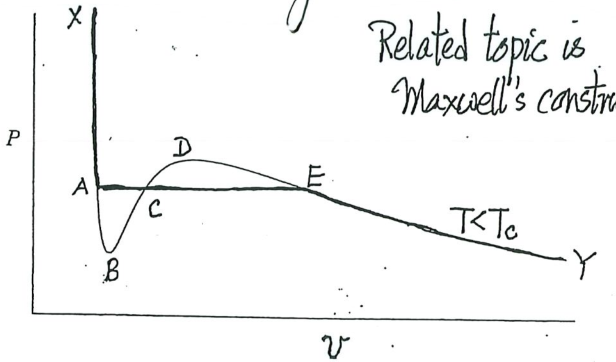
$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (18) \quad (1 \text{ mole})$$

gives p-V-T relation with phases (liquid-vapor transition)

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0 \quad (20) \quad (\underline{\text{cubic eq.}} \text{ for } v)$$

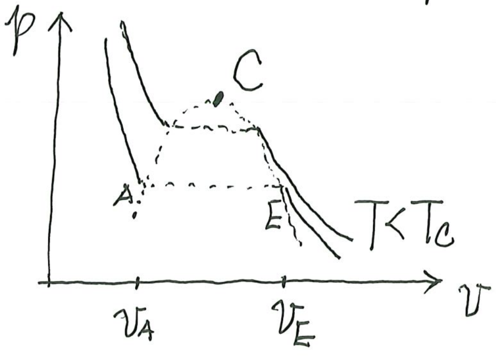


- $T > T_c$ (thus given T): one real v for a value of p
- $T < T_c$ (thus given T): three real v's for a value of p



Related topic is Maxwell's construction

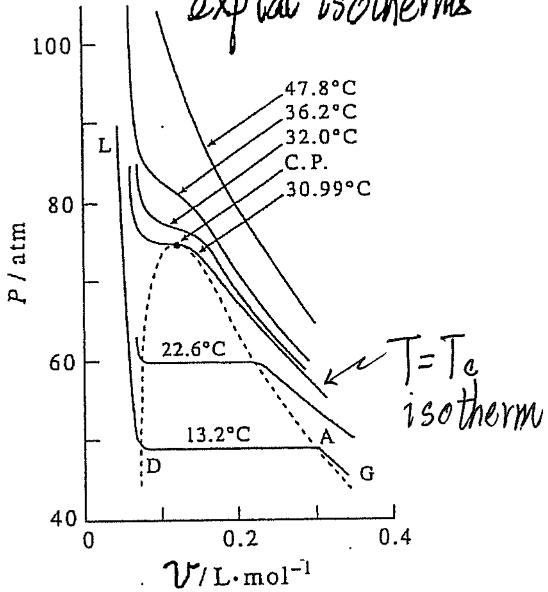
A typical van der Waals pressure-volume isotherm at a temperature less than the critical temperature. The horizontal line has been drawn so that areas of the loop above and below are equal.



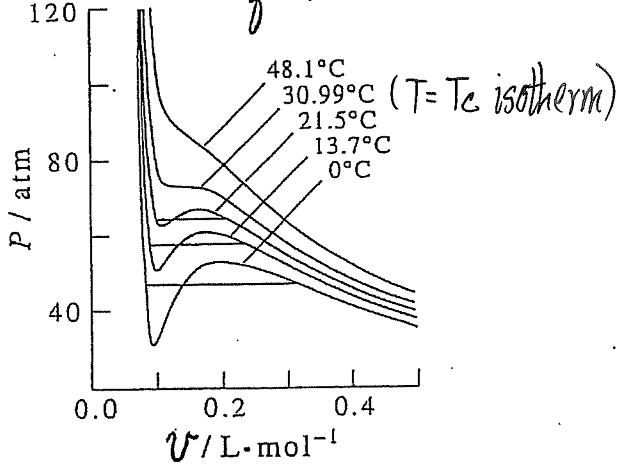
v_A = volume of liquid phase

v_E = volume of vapor phase

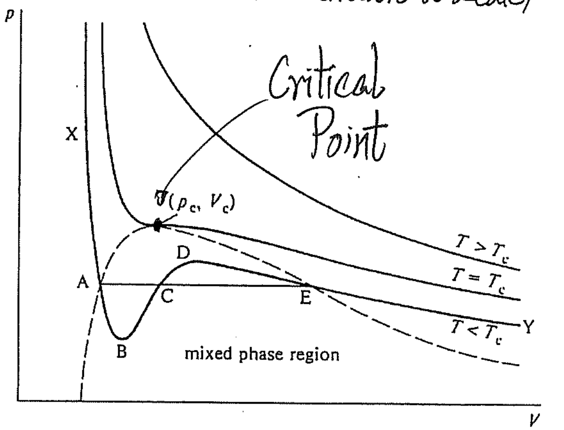
CO_2
exp'tal isotherms



CO_2
Isotherms by Van der Waals Equation



Van der Waals isotherms near the critical temperature
(not drawn to scale)



[Figures taken from D. McQuarrie, "Physical Chemistry : A molecular approach"]

$\underbrace{T = T_c \ : \ \text{there is a value}}_{\text{the critical point}}$ of p called p_c, v has three identical real roots

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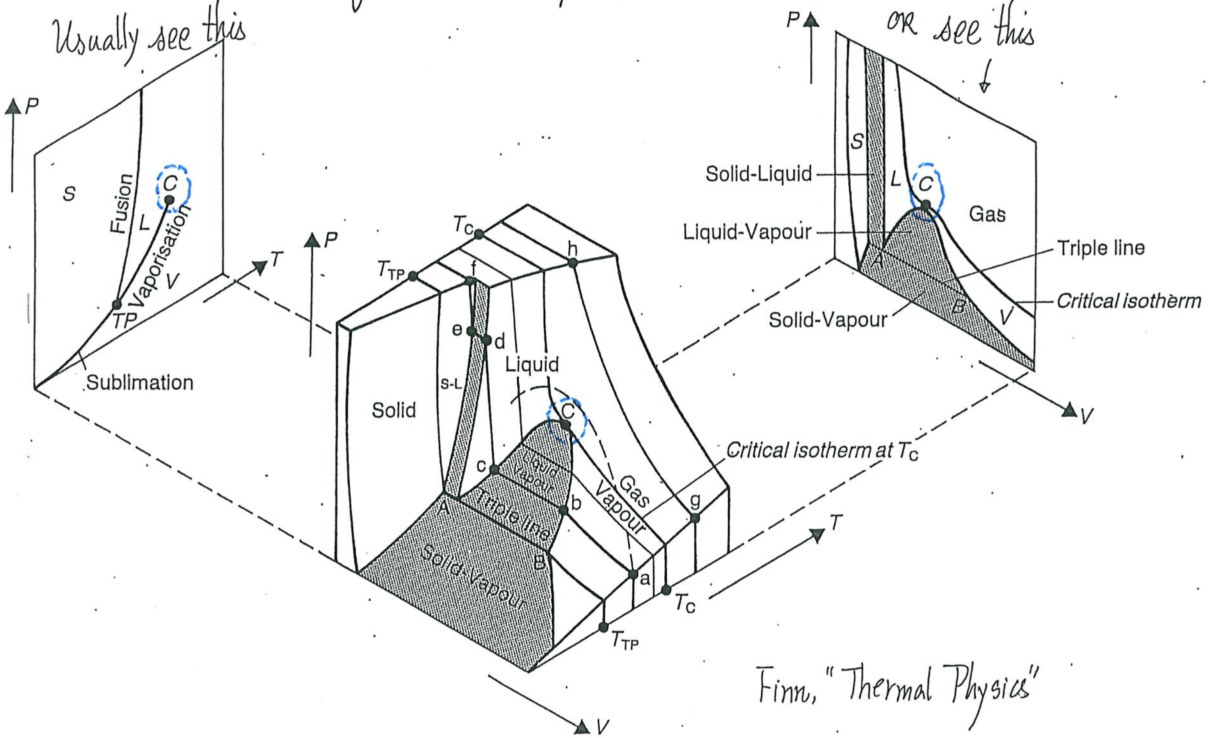
Projections onto P-T and P-V Planes

Usually see this

or see this ↓



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

Finn, "Thermal Physics"

The Point "C" is the critical point.

Physics near the critical point is called critical phenomena.

The critical point from van der Waals equation

Aim: One point (p_c, v_c, T_c) on phase diagram

The van der Waals equation should become $(v - v_c)^3 = 0$ at critical point

$$v^3 - 3v^2 v_c + 3 v v_c^2 - v_c^3 = 0 \quad (21)$$ at critical point

compare with $$v^3 - \left(b + \frac{RT_c}{p_c}\right) v^2 + \frac{a}{p_c} v - \frac{ab}{p_c} = 0 \quad (20)$$ (van der Waals eq. with T_c, p_c to solve v)

$$\underbrace{3v_c = b + \frac{RT_c}{p_c}, \quad 3v_c^2 = \frac{a}{p_c}, \quad v_c^3 = \frac{ab}{p_c}}$$

$$\Rightarrow \left(v_c = 3b, \; p_c = \frac{a}{27b^2}, \; T_c = \frac{8a}{27bR}\right)^{+} \quad (22)$$

(recall: a, b are related to interaction between particles)

Remark: Measuring the critical point (macroscopic) gives information on a and b.

+ The p-v curve 

also suggests finding the critical point by calculus (point of inflection).

- Van der Waals Equation suggests

$$\frac{p_c V_c}{RT_c} = \frac{\frac{a}{27b^2}\cdot 3b}{R\cdot\frac{8a}{27bR}} = \underbrace{\frac{3}{8}}_{\text{for all substances! } (0.375)} \quad (23)$$

Is it really the case?

Species	T_c/K	P_c/bar	P_c/atm	V_c/L·mol^{-1}	P_cV_c/RT_c
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443
Water	647.126	220.55	217.66	0.05595	0.2295

(i) Not quite $\frac{3}{8}$

(ii) but numbers are close to each other

Noting that van der Waals eq. is just an approximate equation of state, it is doing a good job in predicting the behavior of real systems.

Taken from McQuarrie and Simon, "Physical Chemistry: A molecular approach"

Different substances behave the same way when expressed in reduced quantities

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT \qquad (18)$$

Found $\begin{cases} 3v_c^2 = \dfrac{a}{p_c} \Rightarrow a = 3v_c^2 p_c \\ v_c = 3b \Rightarrow b = \dfrac{v_c}{3} \end{cases}$

$$\left(p + \frac{3v_c^2}{v^2}p_c\right)\left(v - \frac{v_c}{3}\right) = RT$$

$$\left(\underbrace{\frac{p}{p_c}}_{\overset{|||}{p_R}} + 3\underbrace{\left(\frac{v_c}{v}\right)^2}_{\frac{1}{v_R^2}}\right)\left(\underbrace{\frac{v}{v_c}}_{\overset{|||}{v_R}} - \frac{1}{3}\right) = \frac{RT}{p_c v_c} = \underbrace{\frac{RT_c}{p_c v_c}}_{\frac{8}{3}}\underbrace{\left(\frac{T}{T_c}\right)}_{\overset{|||}{T_R}}$$

$$\boxed{\begin{aligned} p_R &\equiv \frac{p}{p_c} \\ v_R &\equiv \frac{v}{v_c} \\ T_R &\equiv \frac{T}{T_c} \end{aligned}}$$

$$\boxed{\left(p_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \frac{8}{3}T_R} \qquad (24)$$

Van der Waals equation in reduced quantities

- A substance has its own critical point (p_c, v_c, T_c)
- Express (p, v, T) by (p_R, v_R, T_R) for different substances, same behavior for different substances
- It is an example of the "Law of Corresponding States"

Collapsing data of different substances

From $\left(p + \frac{3}{v_R^2} p_c\right)\left(v - \frac{v_c}{3}\right) = RT \Rightarrow \frac{pv}{RT} \cdot \overbrace{\left(1 + \frac{3}{p_R} \cdot \frac{1}{v_R^2}\right)\left(1 - \frac{1}{3v_R}\right)}^{\text{function of } (p_R, v_R), \text{ thus } (p_R, T_R)} = 1$

$$\therefore \underbrace{\frac{pv}{RT}}_{} = \frac{1}{\text{function of } (p_R, T_R)} = \mathcal{F}(p_R, T_R) \qquad (25)$$

measure $\frac{pv}{RT}$
for many substances
under different conditions
(many experimental measurements)

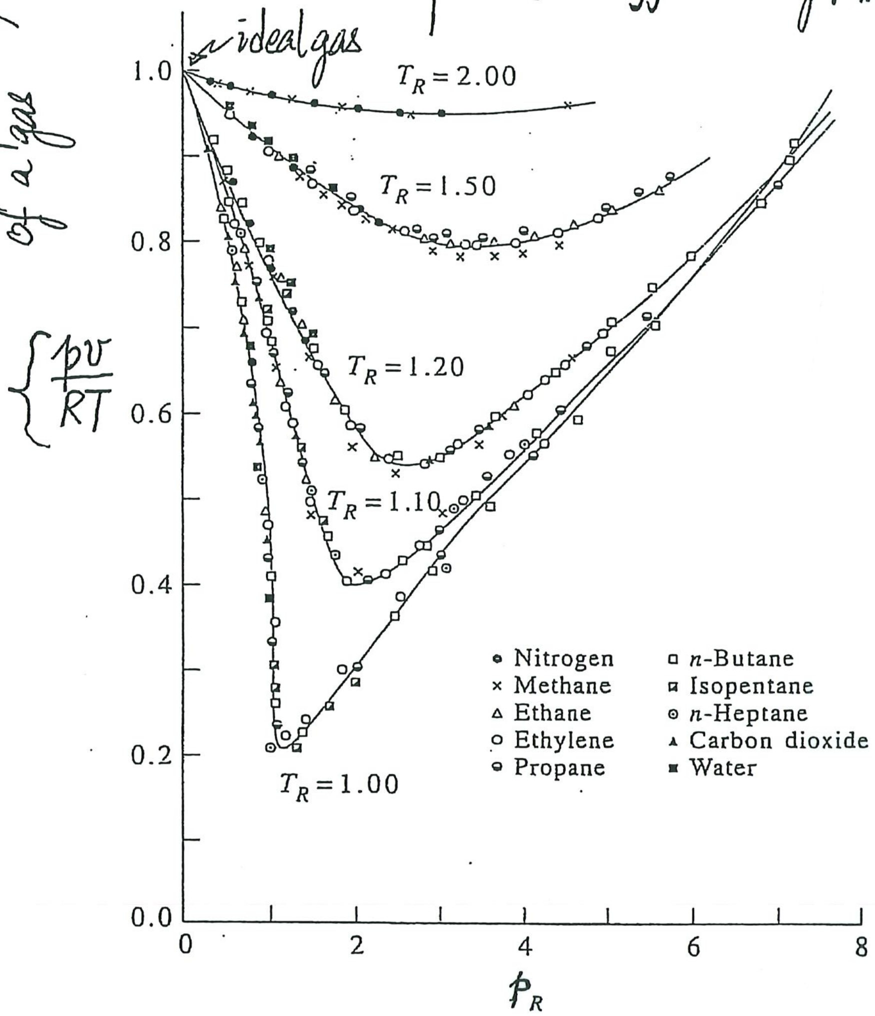
take data from different measurements,
express (p, T) in (p_R, T_R),
then say, choose data of same T_R value
for different substances, and plot pv/kT
vs p_R, data of different experiments
should fall on the same curve⁺
["universal curve"]

⁺An obvious "trivial" case is $\mathcal{F} = 1$, when measurements on different gases are made under conditions in which the ideal gas behavior is valid.

Data on Different Gases ($T \geq T_c$)

This combination is called the "compressibility factor" of a gas

Data Collapse (10 different systems)



For same T_R (different isotherms for different substances), $\frac{pv}{RT} = \mathcal{F}(p_R, T_R)$

same curve!

(athough the curve is not what the van der Waals equation suggested)

This is what made physics a fascinating subject!

Look for general principles for universal behavior.

[Taken from McQuarrie and Simon]

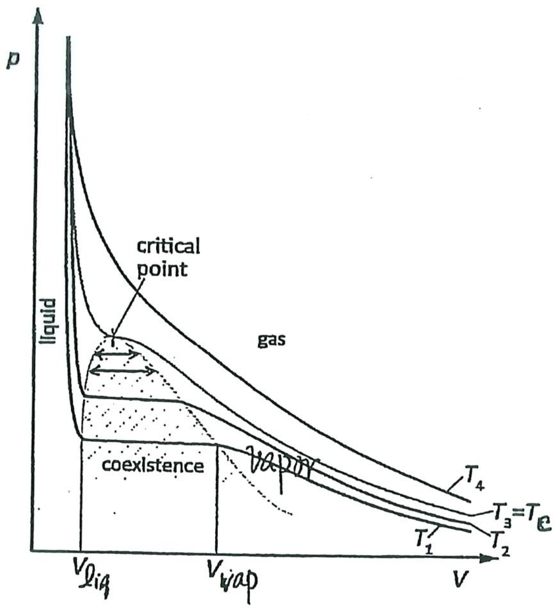
E. Description of Behavior near the Critical Point

Look at $\Delta v = v_{vapor} - v_{liquid}$

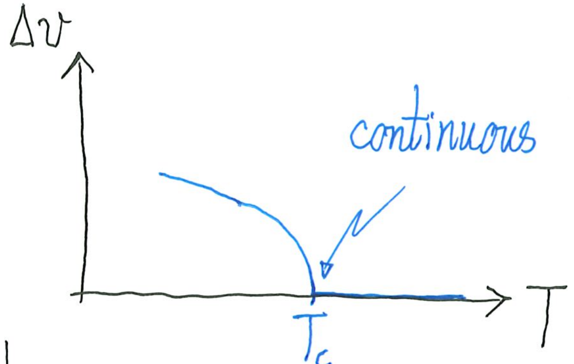
$T < T_c$ (vapor and liquid phases): $\Delta v > 0$ $(\neq 0)$

$T \to T_c^-$: $\Delta v \to 0$ continuously

$T > T_c$ (no distinction of "liquid" and "vapor", only gas phase)
if still talk about Δv, $\Delta v = 0$



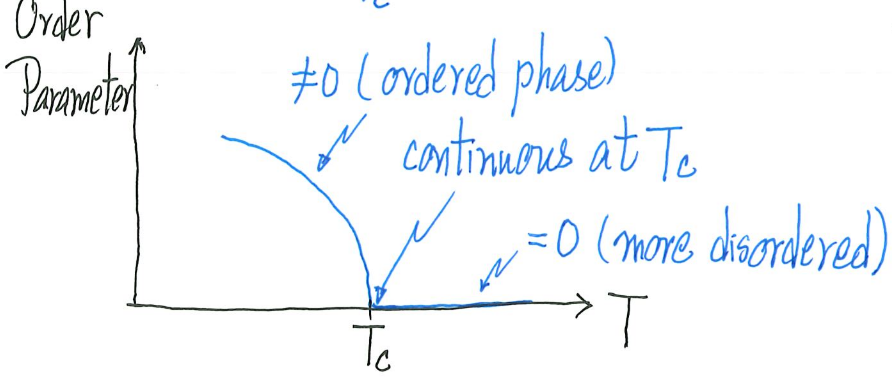
Δv decreases as $T \to T_c^-$



$T > T_c$: Gas (less ordered phase)

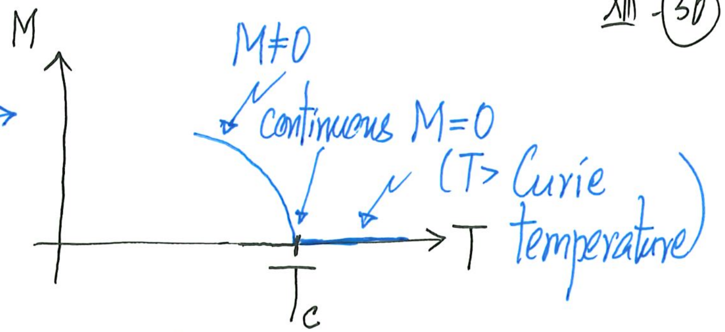
$T < T_c$: liquid phase enters
more ordered phase (some short-range order)

Δv (or $\Delta \rho$ (difference in densities)) is an example of an Order Parameter (序參數)

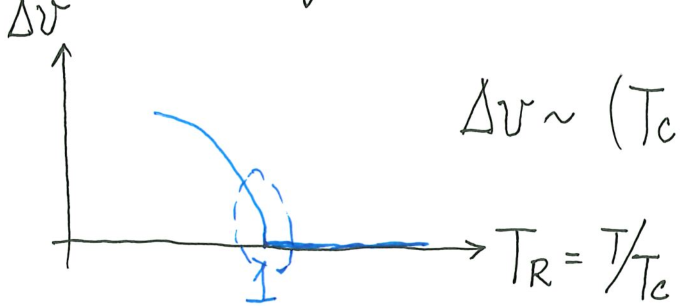


← General behavior near critical point

Why bother? Ferromagnetic - Paramagnetic Systems →



Different Systems exhibit same critical phenomena!



$\Delta v \sim (T_c - T)^{\beta} \underset{\text{"goes like"}}{\sim} (T_R - 1)^{\beta}$ ← critical exponent [NOT to be confused with $1/kT$] (臨界指數) (can be measured experimentally)

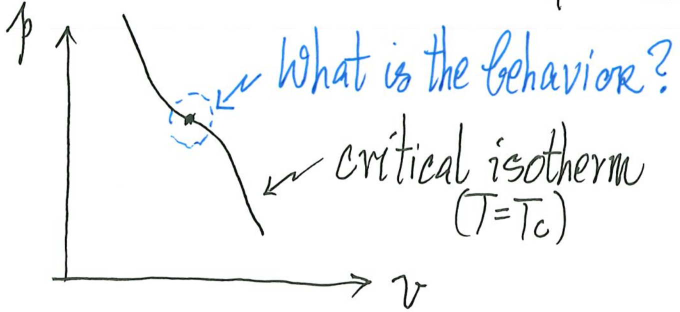
[Seemingly unrelated systems could have same value of β]

Theoretical side: Does van der Waals equation say anything about β?

$$\left(p_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \frac{8}{3} T_R \quad (24)$$

[Plug $p_R = 1 + \delta p_R$, $T_R = 1 + \delta T_R$, $v_R = 1 + \delta v_R$ with $\begin{matrix}\delta p_R \\ \delta T_R \\ \delta v_R\end{matrix} \ll 1$, and work out how δp_R, δv_R, δT_R are related] (Ex.)

$\delta v_R \sim \delta T_R^{1/2}$ $\quad \therefore \beta = 1/2$ (van der Waals)



← By eye (and by van der Waals eq.), δp_R is a cubic function of δv_R

$(p - p_c) \sim -(v - v_c)^{③}$ ← This is another critical exponent

References

- For a more systematic treatment (higher order terms) of interacting gas, see Pathria, "Statical Mechanics", Ch. 9 (cluster expansion and its extension to quantum systems)
  - ↓ related to this is the Lee and Yang method of binary collision
- For more on the Van der Waals equation and its applications, see McQuarrie's "Statistical Mechanics", and McQuarrie and Simon, "Physical Chemistry: A molecular Approach".