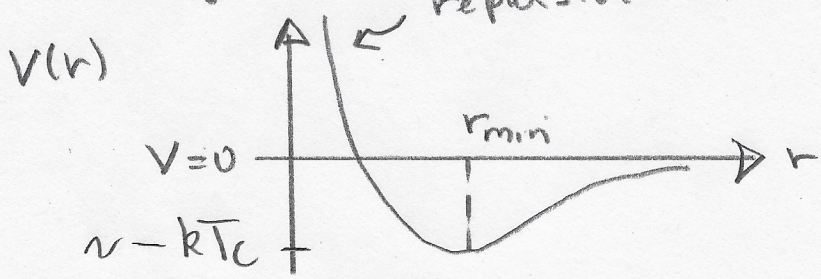
Phys 301 Fall 2020

Lecture #7 - Van der Waals

Van der Waals force is attractive force between electrically neutral molecules, Q.M. in origin.

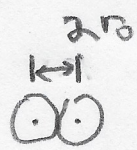
Qualitatively:



T_c critical temperature

Equation of state 1873, Nobel prize 1910

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$



<u>parameter b</u> hard core repulsion

exclusive volume $b = \frac{4\pi}{3}(2r_0)^3 = \frac{32\pi}{3} r_0^3 = (3.2 r_0)^3$

for N_2, $b \sim (.4\text{Å})^3 = (0.4\,\text{nm})^3$

<u>parameter a</u> $\frac{\text{Potential energy}}{\text{molecule}} \propto \frac{N}{V}$ number density

Total VdW P.E. $= -a\left(\frac{N}{V}\right)N$

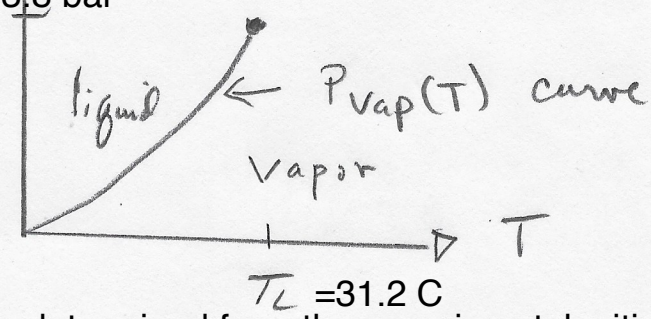
contribution to pressure is

$$-\frac{d}{dV}(\text{P.E. VdW}) = -\frac{aN^2}{V^2}$$

Van der Waals vaporization curve:

$\boxed{P-T}$

for CO_2 P_c =73.8 bar



→ a,b can be determined from the experimental critical P_c,T_c

prob 5.48 you will determine

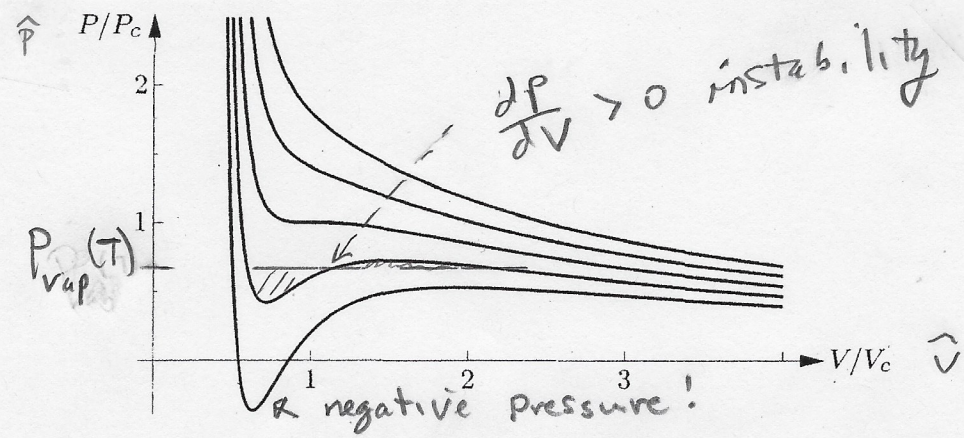
$$P_c = \frac{1}{27}\frac{a}{b^2}, \quad kT_c = \frac{8}{27}\frac{a}{b}, \quad V_c = 3Nb$$

then $\hat{t} \equiv \frac{T}{T_c}$, $\hat{p} \equiv \frac{P}{P_c}$, $\hat{v} \equiv \frac{V}{V_c}$

$$\left(\hat{p} + \frac{3}{\hat{v}^2}\right)\left(\hat{v} - \frac{1}{3}\right) = \frac{8}{3}\hat{t}$$

Note: $P \to \infty$ for $\hat{v} = \frac{1}{3} \Rightarrow V = \frac{1}{3}(3Nb) = Nb$

Isotherms: Maxwell equal area construction defines $P_{vap}(T)$



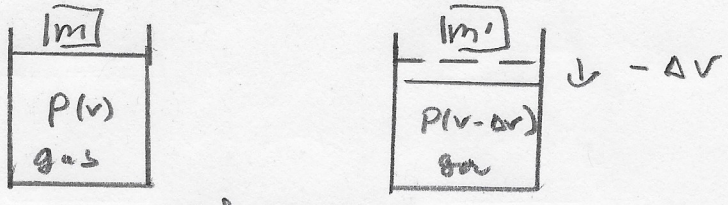
$\boxed{P-V}$

Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c, the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum volume (Nb) is 1/3.

Phase diagram shows unphysical features

$\frac{dp}{dV} > 0$ instability

Consider mass m compressing gas



add mass Δm

$m' = m + \Delta m$

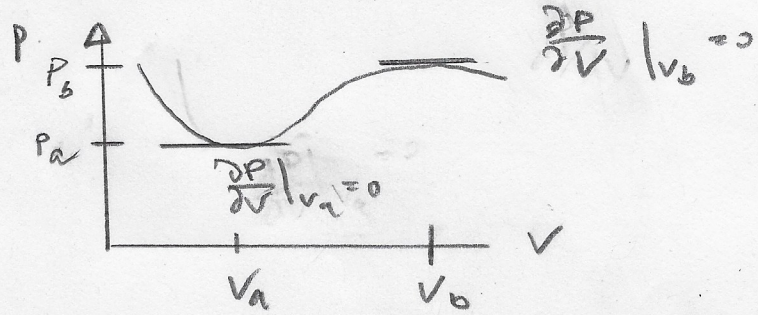
$$P(v-\Delta V) = P(v) - \underbrace{\frac{\partial P}{\partial V}}_{>0} \Delta V < P(v)$$

Collapses catastrophically – unstable

if we removed mass, catastrophic expansion.

Nevertheless, model can be salvaged

Critical Temperature T_c is minimum isotherm in P, V plane where instability disappears. Critical isotherm

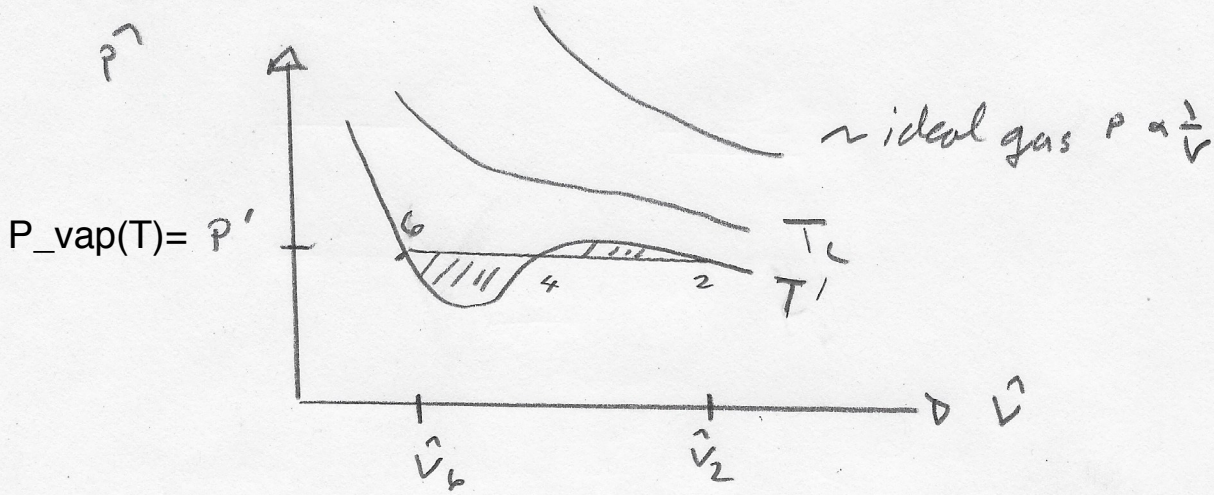


as T increases $V_a \to V_b$. Then T_c is where

$$\frac{\partial^2 P}{\partial V^2}\Big|_{T_c} = \frac{\frac{\partial P}{\partial V}\Big|_{V_b} - \frac{\partial P}{\partial V}\Big|_{V_a}}{V_b - V_a} = 0$$

and $\frac{\partial P}{\partial V}\Big|_{T_c} = 0$

Fixing P-V diagram and Latent heat for VdW



P' defined by equal hatched areas (Maxwell Construction) between V_6, V_2 liquid vapor co-exist

Fix P,V by <u>replacing</u> curve with solid horizontal line between $\hat{V}_6, \hat{V}_2$.

Maxwell Construction from Gibbs free energy

$$\Delta G = -S\Delta T + V\Delta P + \mu \Delta N \underset{\text{along isotherm}}{=} V\Delta P$$

Then $\int_2^6 dG = \int_2^6 V\,dP = 0$

G_6=G_2

horizontal line is single point on vaporization curve

define points 2,6 by

$$\int_2^4 dG + \int_4^6 dG = 0$$

$$\int_2^4 V\,dP = -\int_4^6 V\,dP$$

"At a given temperature and pressure,
the true equilibrium state of a system is determined by its Gibbs free energy."

#7-5

Modified PV diagram for VdW

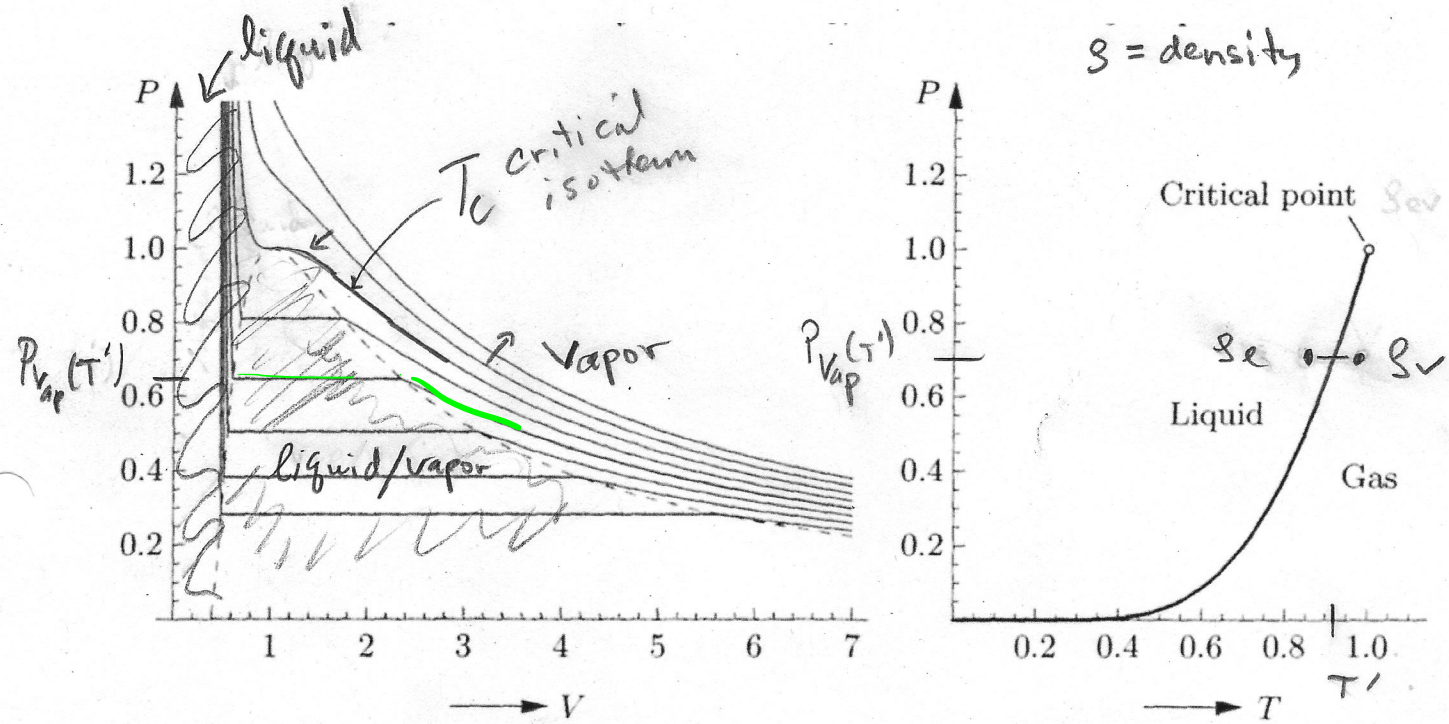


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.

below dashed line

liquid/vapor co-exist along vaporization curve P_vap(T) as well as beyond critical point

Physics 301: Andrews Experiments October 15, 2020

Liquefaction of gases was investigated by Thomas Andrews (1863). His experiment was capable of applying measured pressures up to 200 $\times$ atmospheric.

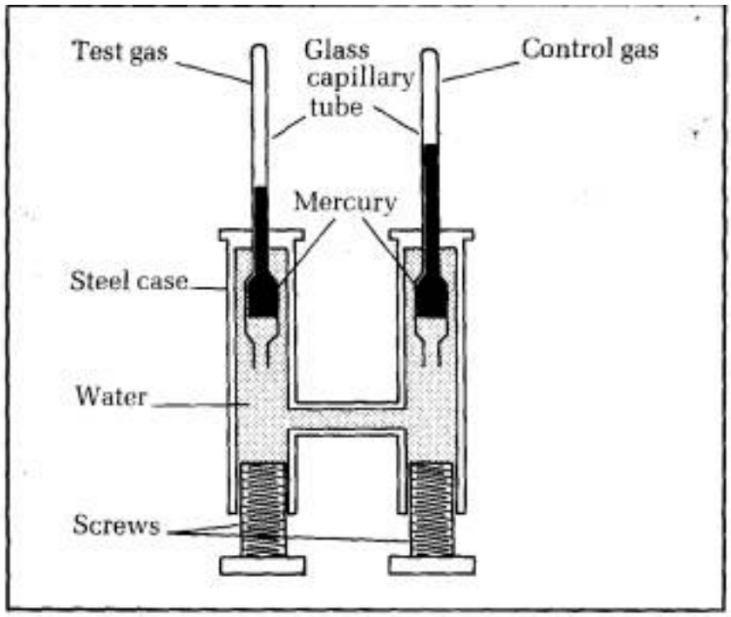


Figure 1: Andrew's xperimental apparatus. Gas compressed by murcury. Pressure increased by turning screws.

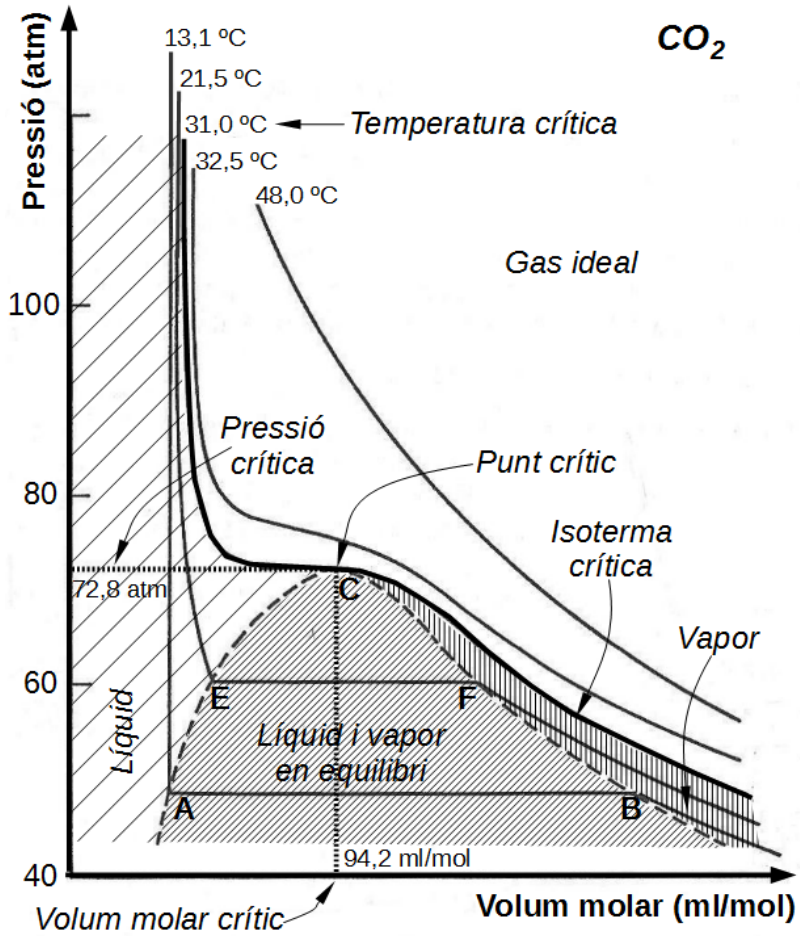


Figure 2: Isotherms in P versus V plane for carbon dioxide first measured by Andrews.

<u>Gibbs for VdW.</u>

along isotherm, $dG = VdP$ then

$$\frac{\partial G}{\partial V} = \frac{\partial G}{\partial P}\left(\frac{\partial P}{\partial V}\right) = V\frac{\partial P}{\partial V}$$

$$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

$$\frac{\partial P}{\partial V} = -\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3}$$

integrate $\frac{\partial G}{\partial V}$ to get:

$$G = -NkT\ln(V-Nb) + \frac{NkT}{(V-Nb)}(Nb) - \frac{2aN^2}{V} + C(T,N)$$

Then chemical potential should be

$$\frac{G}{N}.$$

Helmholtz Free energy for VdW

$$P_c = \frac{1}{27}\frac{a}{b^2} \; ; \; kT_c = \frac{8}{27}\frac{a}{b} \; ; \; V_c = 3Nb$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P \quad ; \quad \frac{1}{V_c}\frac{\partial F}{\partial \hat{V}} = -P_c \hat{P}$$

$$P_c V_c = \frac{1}{27}\left(\frac{a}{b^2}\right)3Nb = \frac{1}{9}N\frac{a}{b} = \frac{3}{8}NkT_c$$

$$\frac{\partial F}{\partial \hat{V}} = -\frac{3}{8}(NkT_c)\hat{P} = -\frac{3}{8}(NkT_c)\left[\frac{8}{3}\left(\frac{\hat{t}}{\hat{V}-\frac{1}{3}}\right) - \frac{3}{\hat{V}^2}\right]$$

$$= -NkT\left(\frac{1}{\hat{V}-\frac{1}{3}}\right) + \frac{9}{8}NkT_c\left(\frac{1}{\hat{V}^2}\right)$$

integrate,

$$F = -NkT\ln\left(\hat{V}-\frac{1}{3}\right) - \frac{9}{8}NkT_c\frac{1}{\hat{V}} + C(T,N)$$

$$kT_c V_c = \frac{8}{27}\left(\frac{a}{b}\right)3Nb = \frac{8}{9}Na$$

$$\hat{V} - \frac{1}{3} = \frac{V}{3Nb} - \frac{1}{3}$$

$$F = -NkT\ln\left(\frac{V}{Nb}-1\right) - \frac{N^2 a}{V} + C'$$

Baierlein tells us (ch 12)

$$F = -kT \ln Z_{vdW}$$

$$\ln Z_{vdW} = \ln\left[\frac{(V-Nb)^N}{V_Q^N\, N!}\right] + \frac{a N^2}{VkT}$$

$$\xrightarrow[a=b=0]{} \ln Z_{\text{ideal gas}}$$

$$V_Q = \left(\frac{h^2}{2\pi mkT}\right)^{3/2} = l_Q^3$$

l_Q is thermal de Broglie wavelength

by the way,

$$P = kT\frac{\partial}{\partial V}(\ln Z_{vdW}) = \frac{NkT}{V-Nb} - a\left(\frac{N}{V^2}\right)$$

vdW E.O.S.

then $F = -kT \ln Z_{vdW}$

$$= -kTN\ln(V-Nb) - \frac{kTaN^2}{VkT} + kT\ln(V_Q^N N!)$$

with $\ln N! = N\log N - N$

$$F = -kTN\ln(V-Nb) - \frac{N^2 a}{V} + NkT\ln V_Q + NkT(\log N - 1)$$

$$= -kTN\left[\ln\left(\frac{V-Nb}{N}\right) + 1\right] - \frac{N^2 a}{V} + NkT\ln V_Q$$

Chemical Potential and Gibbs

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$\frac{\partial F}{\partial N} = -kT\left[\ln\left(\frac{V-Nb}{N}\right)+1\right] - \frac{2Na}{V} + kT\ln V_Q$$

$$-\frac{kTN}{\frac{V-Nb}{N}}\left(\frac{-V}{N^2}\right)$$

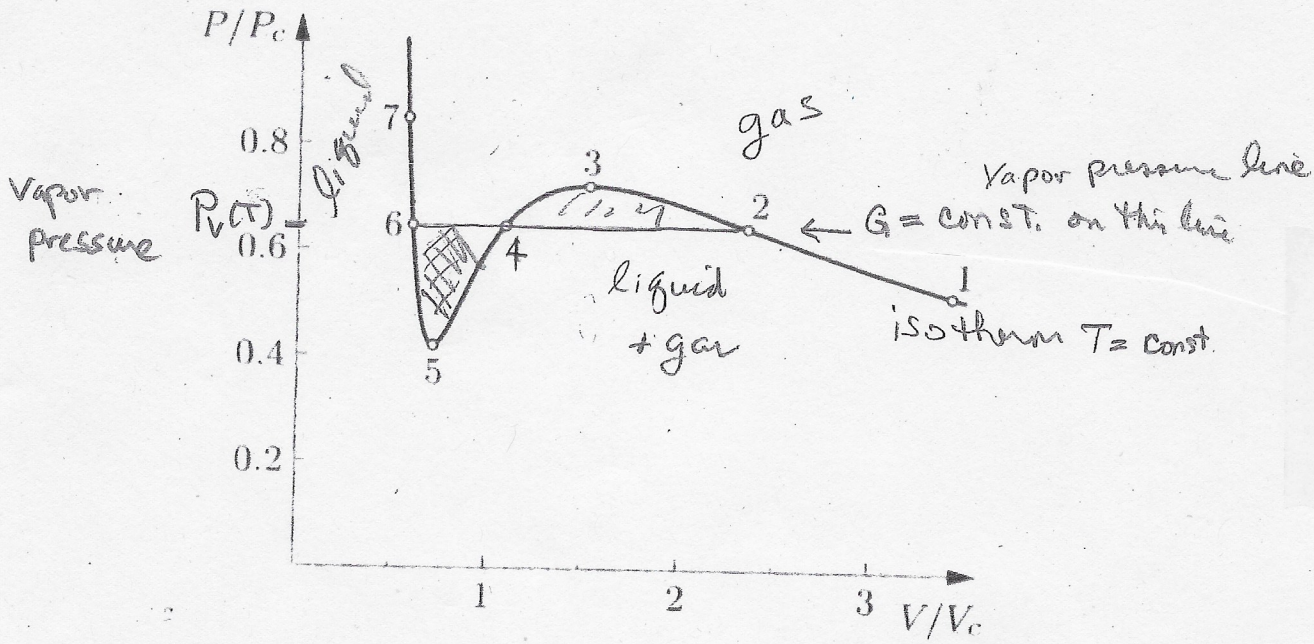
$$\mu = -kT\left[\ln\left(\frac{V-Nb}{b}\right)+1\right] - \frac{2Na}{V} + \frac{kTV}{V-Nb} + kT\ln V_Q$$

$$\frac{kTNb}{V-Nb}$$

$$\mu = -kT\ln\left(\frac{V-Nb}{N}\right) + \frac{kTNb}{V-Nb} - \frac{2Na}{V} + kT\ln V_Q$$

then $G = \mu N$ (eq. 5.6)

Maxwell Construction and Gibbs



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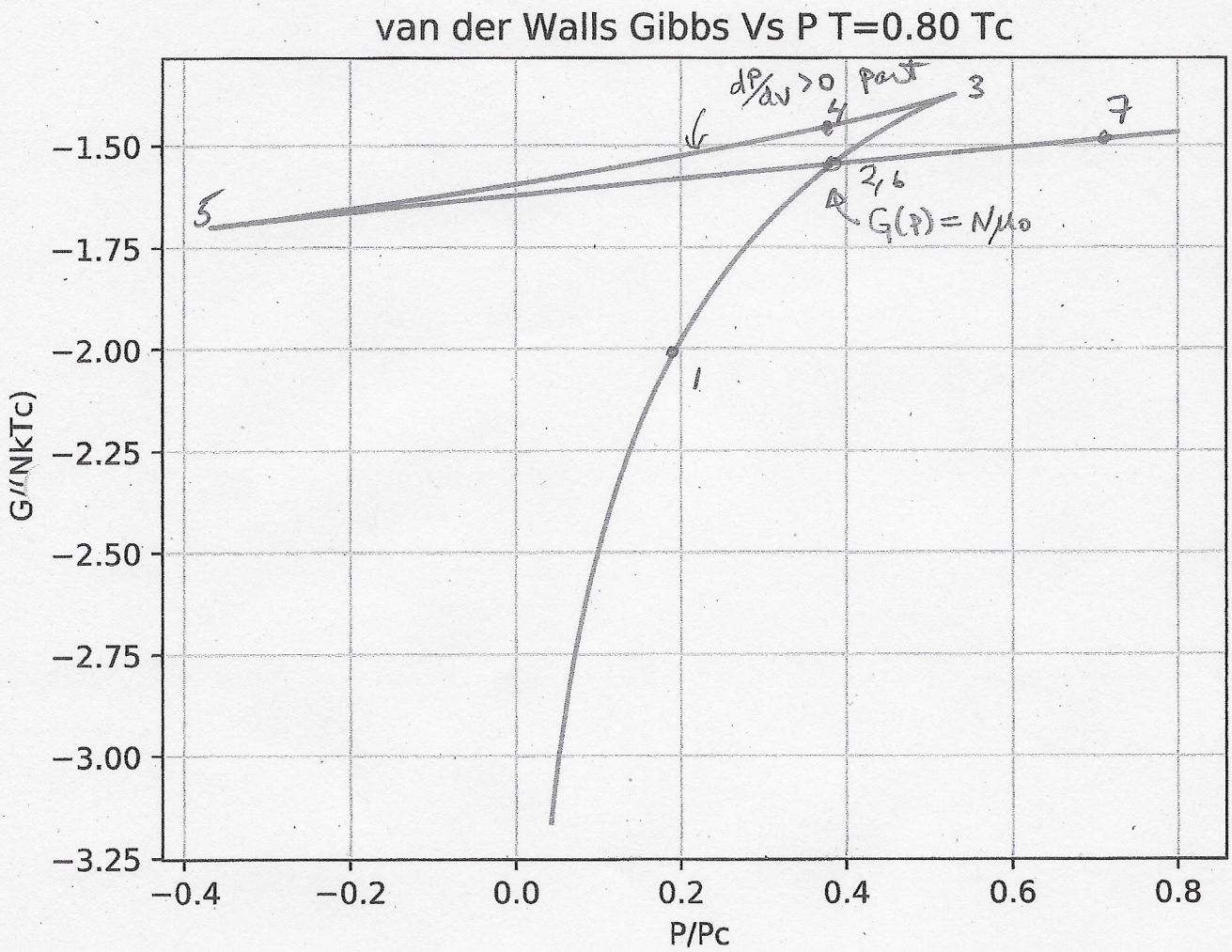


Maxwell construction “erases” 2-3-4-5-2 portion

Physics 301: Problem 5.54 October 14, 2020

$$\hat{p} = \frac{8\hat{t}}{3\hat{v} - 1} - \frac{3}{\hat{v}^2}$$

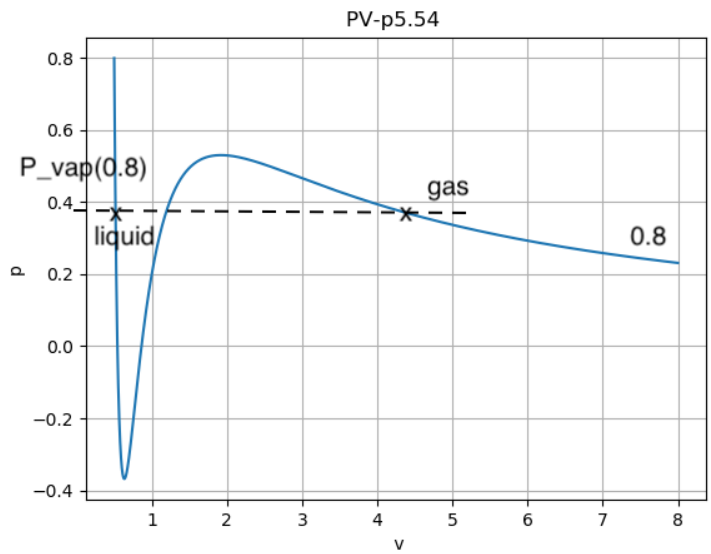


Figure 1: $\hat{p}$ versus $\hat{v}$ for $\hat{t} = 0.8$. Horizontal line is approximate Maxwell construction giving vapor pressure p_{vap} at $\hat{t} = 0.8$. Labeled are points where liquid and gas phase begins.

$$\frac{\mathrm{F}}{\mathrm{NkT_c}} = -\hat{\mathrm{t}}\log\left(3\hat{\mathrm{v}} - 1\right) - \frac{9}{8\hat{\mathrm{v}}} + \mathrm{const}$$

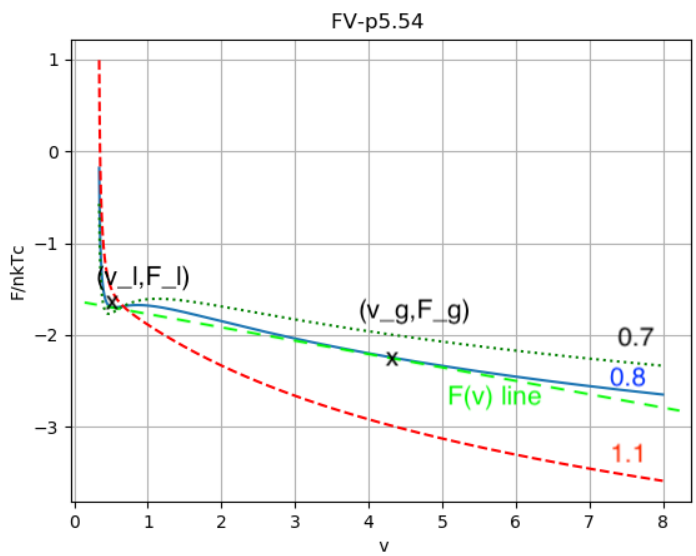


Figure 2: $\hat{F}$ versus $\hat{v}$ for $\hat{t} = 0.7, 0.8, 1, 1$. Dashed green line $F(\hat{v})$ is tangent to $\hat{t} = 0.8$ at points $(F_l, \hat{v}_l)$ and $(F_g, \hat{v}_g)$.

Find tangent line $F(\hat{v}$

$$v = xv_l + (1-x)v_g$$
$$F = xF_l + (1-x)F_g$$

Eliminate x to get

$$F(v) = F_g - \frac{v_g - v}{v_g - v_l}\left(F_g - F_l\right)$$

Line $F(v)$ is lowest possible straight line corresponding to stable state. Stable states have minimum free energy.

Order parameter for liquid-gas critical exponent

density fluctuations near critical point

Problem 5.55 critical exponent

$$\hat{p}(\hat{v}) = \frac{8\hat{t}}{3\hat{v}-1} - \frac{3}{\hat{v}^2}$$

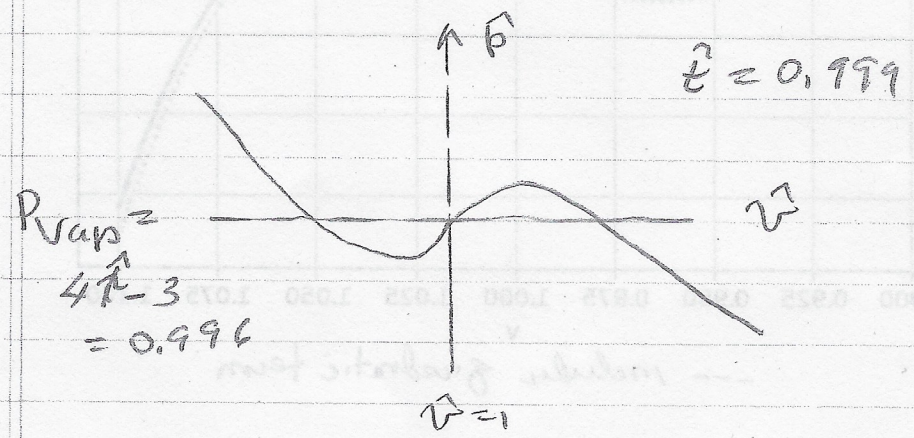
$$= \hat{p}(1) + \left.\frac{d\hat{p}}{d\hat{v}}\right|_1 (\hat{v}-1) + \frac{1}{2}\left.\frac{d^2\hat{p}}{d\hat{v}^2}\right|_1 (\hat{v}-1)^2$$

$$+ \frac{1}{6}\left.\frac{d^3\hat{p}}{d\hat{v}^3}\right|_1 (\hat{v}-1)^3$$

$$= 4\hat{t} - 3 + 6(1-\hat{t})(\hat{v}-1) + \underbrace{9(1-\hat{t})(\hat{v}-1)^2}_{\text{neglect near } \hat{t}=1,\ \hat{v}=1}$$

$$+ \frac{3}{2}(8-9\hat{t})(\hat{v}-1)^3$$

$$\cong 4\hat{t} - 3 + 6(1-\hat{t})(\hat{v}-1) - \frac{3}{2}(\hat{v}-1)^3$$



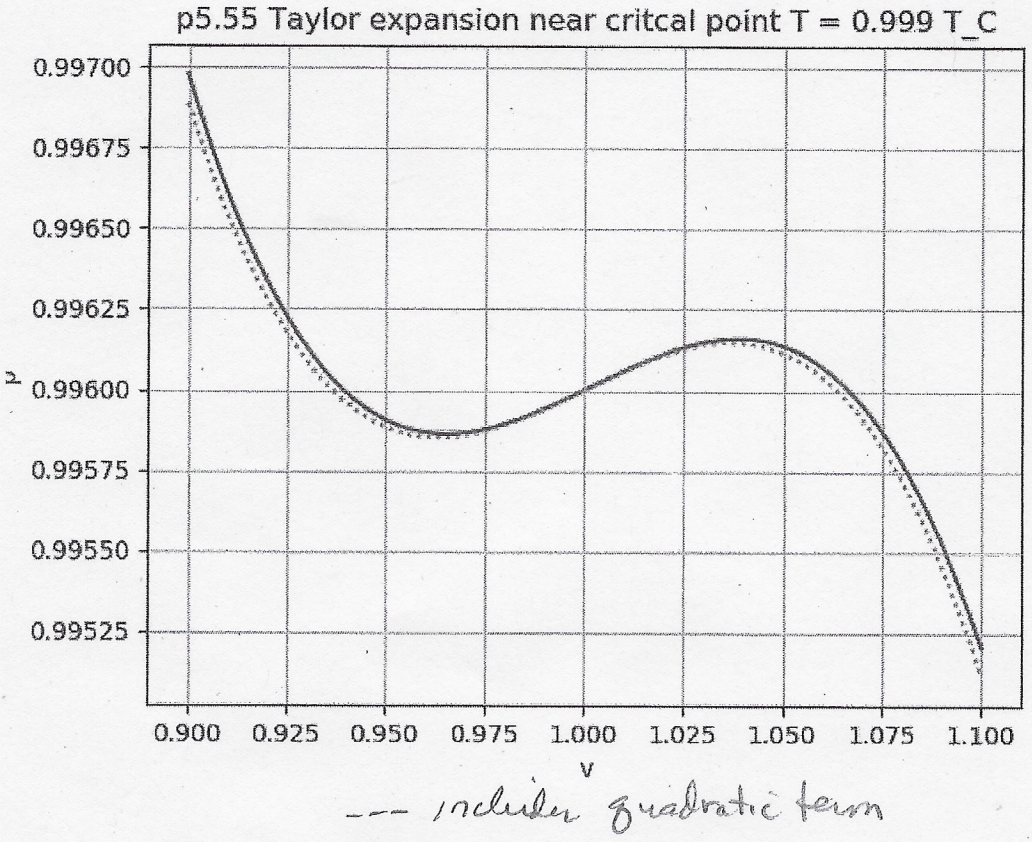
perfectly asymmetric about $\hat{v}=1$ so

$\int v\,dp = 0$ across $\hat{v}=1$ so

$P_{vab}(0.999) = 0.996$

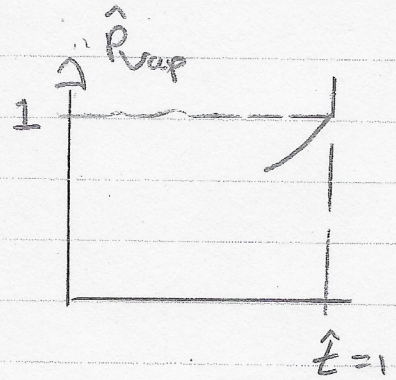
$$\boxed{\left.\frac{d\hat{p}}{d\hat{t}}\right|_{\hat{v}=1} = 4}$$

#7-14



graph showing Maxwell construction curve giving P_vap =0.996

Approach to critical point



phase boundary
near critical point

near $\hat{v}=1$, $\hat{t}=1$

$$P_{vap} = 4\hat{t}-3 = 4\hat{t}-3 + (\hat{v}-1)\Big[\underbrace{6(1-\hat{t}) - \tfrac{3}{2}(\hat{v}-1)^2}_{\text{2 roots}}\Big]$$

$$\hat{v}_{\pm} = 1 \pm 2\sqrt{1-\hat{t}}$$

two solutions correspond to volume of liquid (-) and gas (+) at transition pressure

difference $V_+ - V_- = V_g - V_\ell = 4\sqrt{1-\hat{t}}$

$$(V_g - V_\ell) \propto (T_c - T)^{\beta} \qquad \boxed{\beta = \tfrac{1}{2}}$$

This defines the critical exponent "density difference order parameter".

experimentally, $\beta \cong \frac{1}{3}$ "universally"

= 0.34 for carbon dioxide

discovered by T. Andrews, Phil. Trans. R. Soc. 159 (1869) 575.

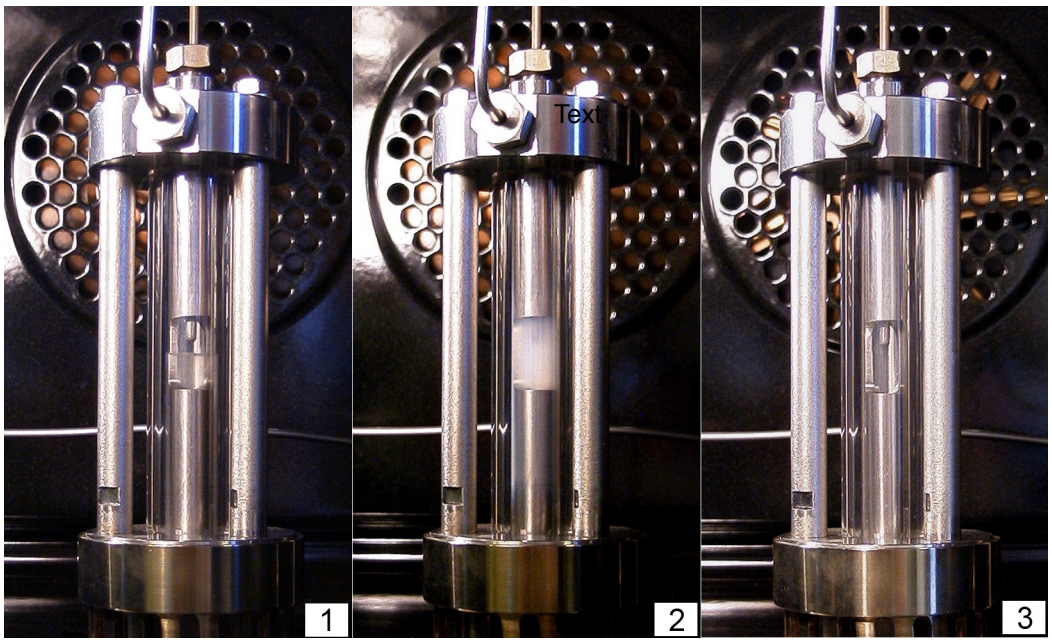
volume fluctuations correspond to density fluctuations.

See Bairelein Chapter 16 "Critical Phenomena"

critical opalescence

critical opalescence in ethane

1) two phases liquid and vapor
2) critical opalescence
3) single phase past critical point



By Dr. Sven Horstmann - Persönlich übergeben von Sven Horstmann. In ähnlicher Form verwendet in:Horstmann S., "Theoretische und experimentelle Untersuchungen zum Hochdruckphasengleichgewichtsverhalten fluider Stoffgemische für die Erweiterung der PSRK-Gruppenbeitragszustandsgleichung", Doktorabeit, C.-v.-O. Universität Oldenburg, 2000, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=17691627