

Chem. 1480
Feb. 21, 2007

A history of Non-ideal gas theory

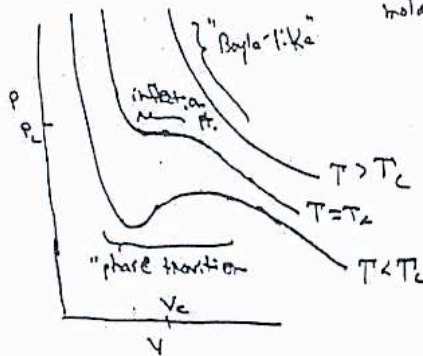
vdW Eqn. of state:
van der Waals

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 = \frac{RT}{v-b} - \frac{a}{v^2}$$

↑
molar Volume

PdD
[thesis: 1873]

For fixed a, b:



find T_c, v_c from:

$$\frac{\partial P}{\partial v} = 0$$

$$\Rightarrow P_c \quad \frac{\partial^2 P}{\partial v^2} = 0$$

Result: $T_c = \frac{8a}{27Rb}$
[Atkins]
 $v_c = 3b$
 $P_c = \frac{a}{27b^2}$

Can they re-express vdW eqn. in "universal" form [Law of Corresponding States]

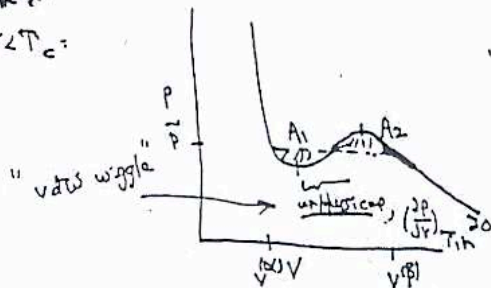
Let $P_r = P/P_c$
 $v_r = v/v_c = \frac{v}{3b}$
 $T_r = T/T_c$

Then in "reduced variables"

$$P_r = \frac{\frac{8}{3} T_r}{\left(v_r - \frac{1}{3}\right)} - \frac{3}{v_r^2}$$

For $T < T_c$ vdW predicts "phase transition", but w/ some unphysical features

Examine $T < T_c$:



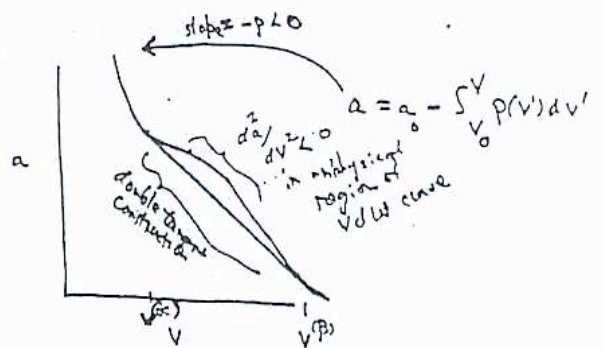
Motivation for Maxwell construction: Enforce "double tangent" condition

in 1874

equivalent

Double-tangent construction

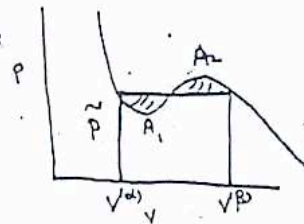
$a = A_m$ corresponding to $T < T_c$ isotherm looks like



But the pressure in transition region, \tilde{p} , then satisfies

$$\tilde{p} = \frac{a(v^{(a)}) - a(v^{(p)})}{v^{(p)} - v^{(a)}} = \frac{\int_{v^{(a)}}^{v^{(p)}} p(v) dv}{v^{(p)} - v^{(a)}}$$

This condition is equiv. geometrically to the "Maxwell construction":



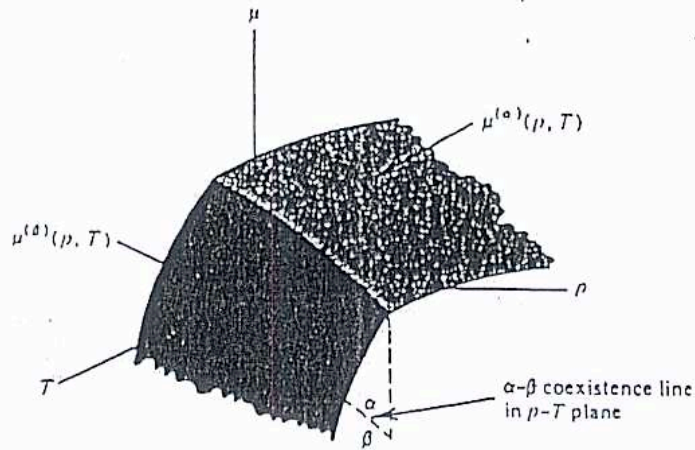


Fig. 2.5. Chemical potential surfaces for two phases.

From
Chandler

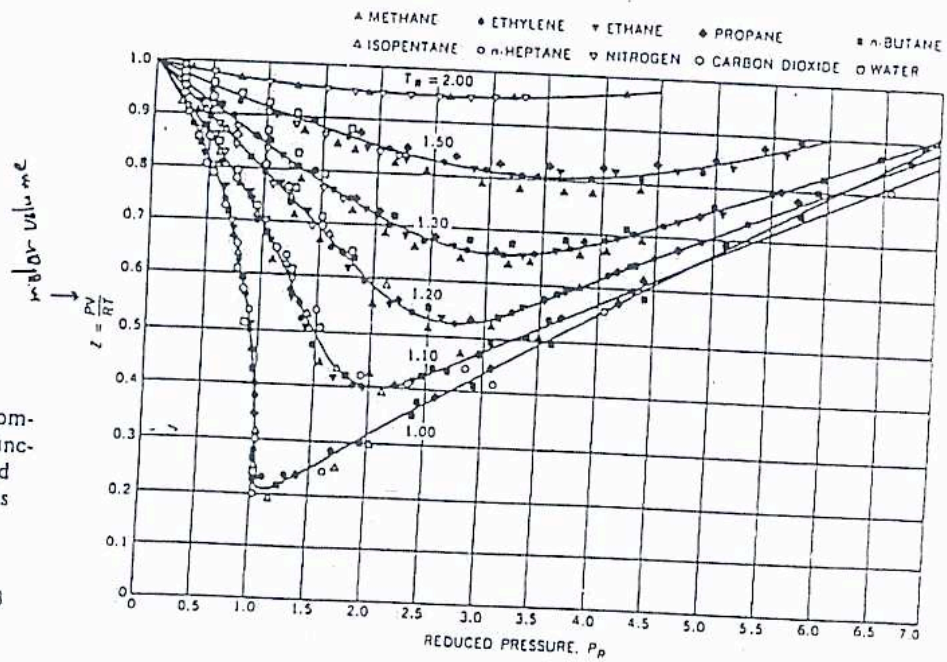


Figure 1-8. The compressibility as a function of the reduced pressure at various reduced temperatures. [From Gouq-Jen Su, *Ind. Eng. Chem.*, 38:803 (1946).]

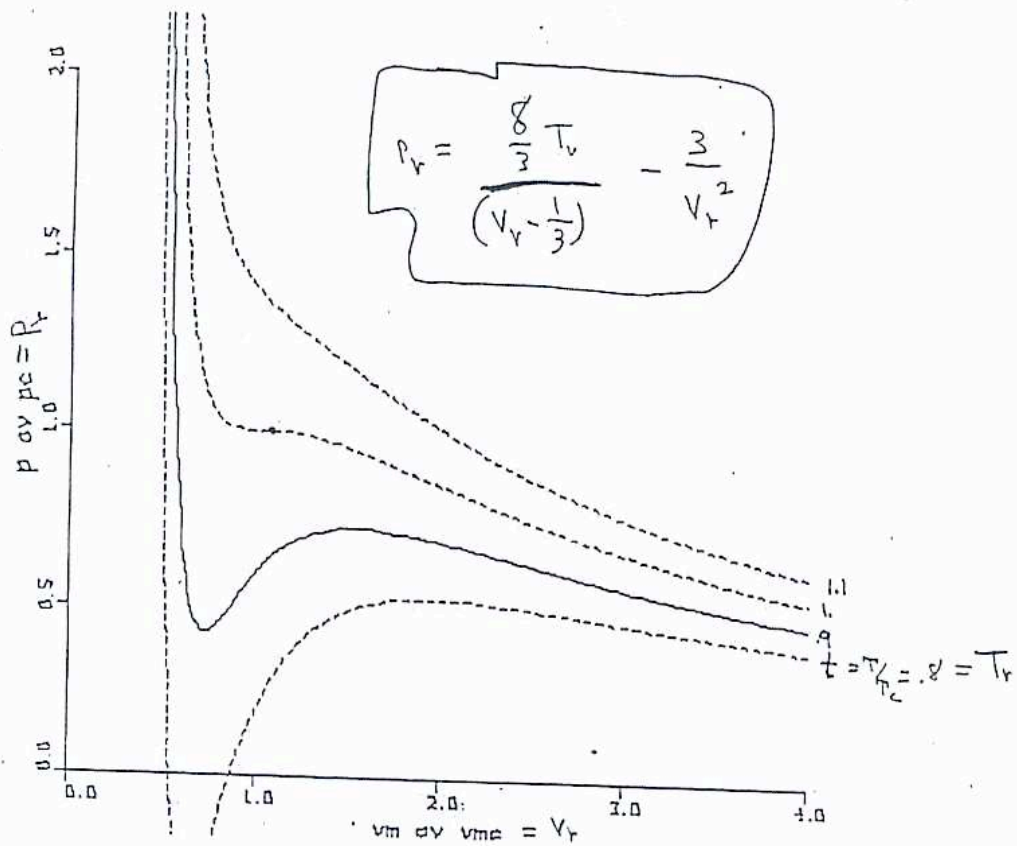
from: G.M. Barrow
Physical Chemistry, 5th Ed.
(McGraw Hill, 1988)

Law of Corresponding States

③

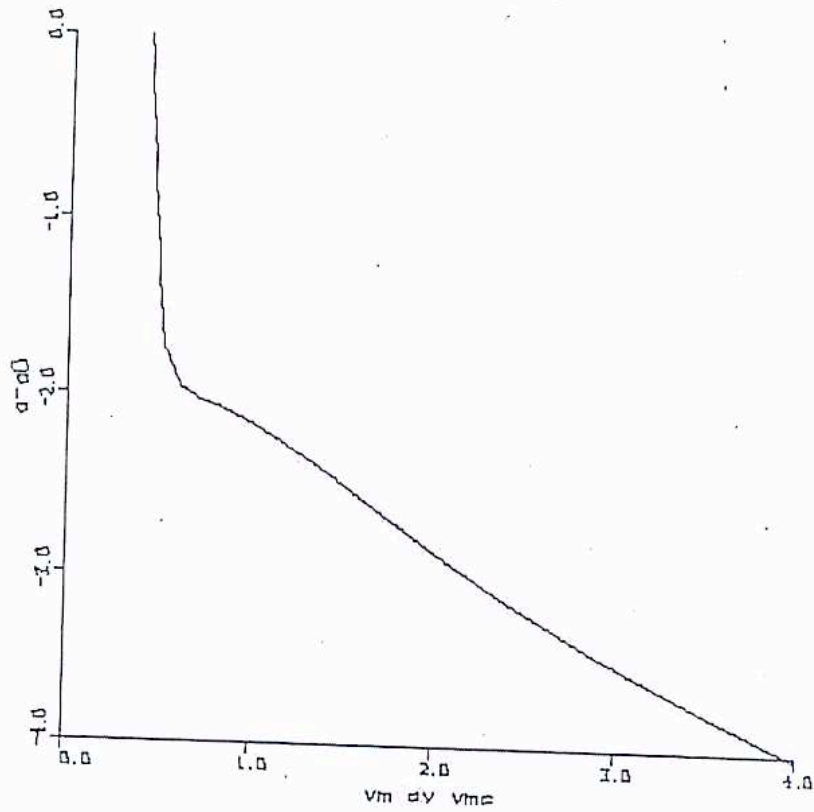
wlw.f

vdw Isotherms at $t/t_c = .8, .9, 1., 1.1$



vdw.F

vdw a at $t/t_0=0.9$



```
$  
$ ty for005.dat  
  .9  
  0.4  4.0  0.1  
$
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Lattice Gas Models: From adsorption on solid surfaces to phase separation in polymer

(i) Noninteracting Lattice Gas

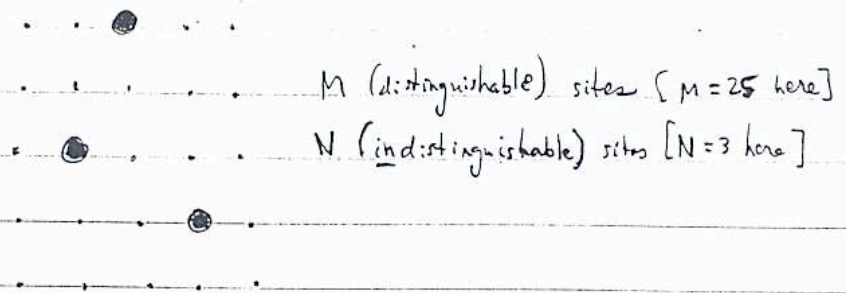


Fig. 1

Let $g = \sum_i e^{-\epsilon_i/kT}$ = site partition funct. $\left[= g_x g_y g_z e^{-U_{00}/kT} \right]$

single particle states \rightarrow energy levels relevant to particle trapped at a site

g_x, g_y, g_z \rightarrow 1-d harmonic osc. partition funct. based on vibrational

U_{00}/kT \rightarrow Energy at bottom of vib. well ("binding energy")

for surface adsorption problem

Then: $\Phi(N, M) = \sum_{\text{accessible states}} e^{-E_i/kT} = \frac{M!}{N!(M-N)!} g^N$ (exact)

$\Phi(N, M)$ \rightarrow canonical partition funct.

Compute the chemical pot.: $\mu = \frac{\partial A}{\partial N} \Big|_{V, T} = -kT \frac{\partial \ln \Phi(N, M)}{\partial N} \Big|_{M, T}$

or: $\frac{\mu}{kT} = \frac{\partial}{\partial N} \ln \Phi(N, M) \Big|_{M, T} = \ln g - \ln N + \ln(M-N)$

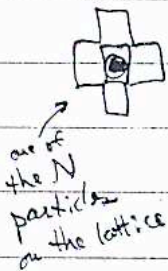
i.e. $\frac{\mu}{kT} = -\ln g + \ln \frac{N}{(M-N)} = -\ln g + \ln \frac{\theta}{1-\theta}$; $\theta = \frac{N}{M} = \left\{ \begin{array}{l} \text{volume fraction of gas particles} \\ \text{or} \\ \text{fractional adsorption} \end{array} \right.$

(II) Interacting lattice Gas: Given N particles occupying M sites in some configuration G what is the energy of this configuration G ?

(i) Assume only nearest neighbor particles interact w/ interaction energy w [$w < 0 \Rightarrow$ attraction between adjacent particles]

(ii) Different configurations w/ same (N, M) have different energies!!

Because of (ii) invoke "random mixing" [Bragg-Williams] approximation [$E_G \rightarrow E(N, M)$]



; for this particle, average interaction E is

$$w \left(\frac{N}{M} \right) c \cdot \frac{1}{2} \left\{ \leftarrow \text{don't double count} \right.$$

↑
nearest neighbor sites

↑
fraction of occupied (nearest neighbor) sites

Thus $E_G(N, M) \cong N \cdot w \left(\frac{N}{M} \right) c \cdot \frac{1}{2} = \frac{1}{2} w c \frac{N^2}{M}$

Hence $Q(N, M) \cong \frac{M!}{N!(M-N)!} e^{-\frac{\beta w c N^2}{2M}}$ ($\beta = \frac{1}{kT}$)

Now, extract thermodynamics \rightarrow [let $K \equiv \frac{-\beta w c}{2} =$ "mixing parameter"] (7)

as (Helmholtz) free energy, $\frac{A}{kT} = -\ln Q = N \ln N + (m-N) \ln (m-N) - m \ln m$

$$-N \ln \theta - \chi \frac{N^2}{m}$$

[13]

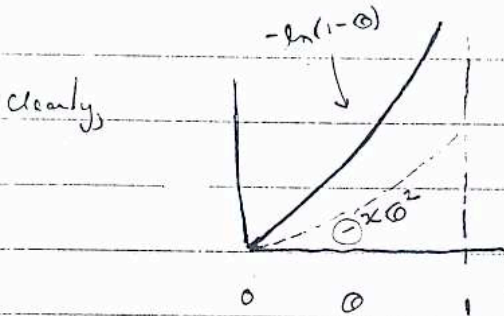
Calculate the pressure of the gas (think, for simplicity, in 3-d):

$$P = - \left. \frac{\partial A}{\partial V} \right|_{N, T} \Rightarrow \frac{P}{kT} = \frac{\partial}{\partial V} \ln Q \Rightarrow \boxed{\frac{PV_0}{kT}} = \ln \frac{M}{M-N} - \chi \frac{N^2}{M^2}$$

$$= \boxed{-\ln(1-\theta) - \chi \theta^2} \equiv f(\theta)$$

↑
volume/site

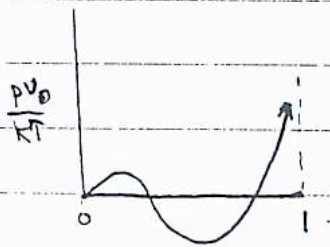
Eq. of state



← Nothing funny happens for $\chi < 2$
(p increases monotonically w/ θ)

But for

$\chi \gg 0$:



← A van der Waals wiggle !!

The critical pt is defined by

$$0 = \frac{df}{d\theta} = \frac{1}{1-\theta} - 2\chi\theta$$

$$0 = \frac{d^2f}{d\theta^2} = \frac{1}{(1-\theta)^2} - 2\chi$$

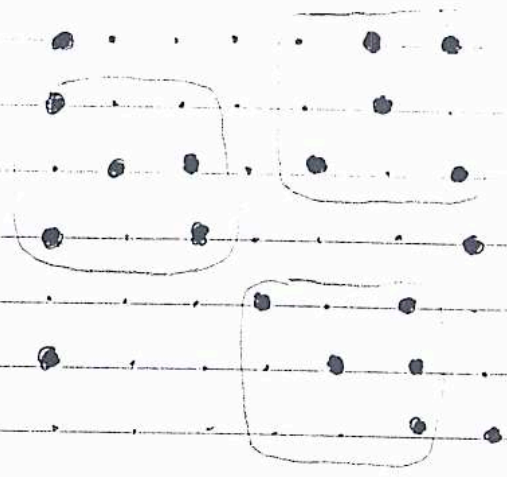
$$\boxed{\theta_c = 0.5; \chi_c = 2}$$

↓

i.e. $\frac{w_c}{kT_c} = -4$

⑧

in $X > X_c$, there is a coexistence region where 2 phases are in equilibrium (w/ one phase much denser than the other)



Conditions for physical equilibrium of 2 phases (ρ_1 and ρ_2 ; $\rho_1 \ll \rho_2$)

characterized by

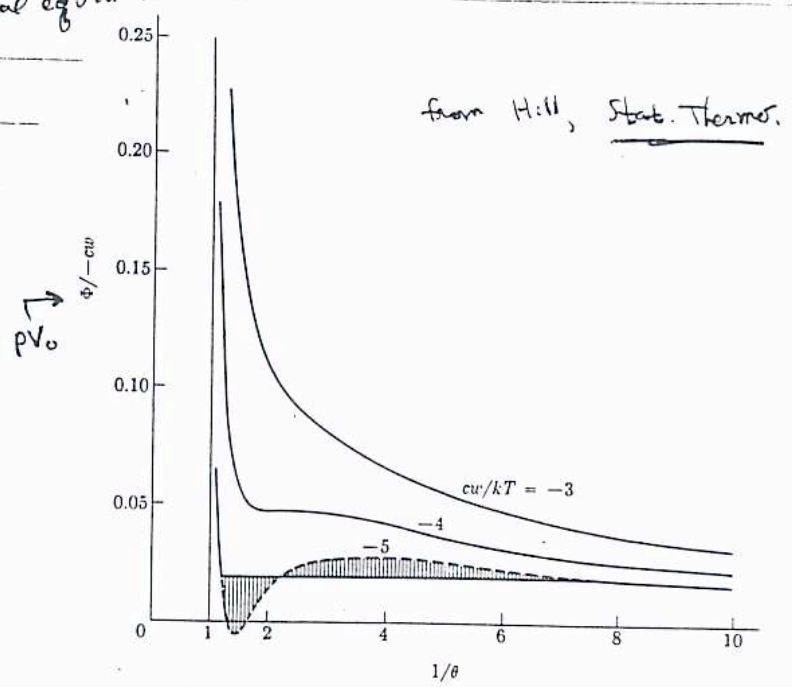
are

(i) $P(\rho_1) = P(\rho_2)$; (ii) $\mu(\rho_1) = \mu(\rho_2)$

mechanical equilibrium ; chemical equilibrium

Fig. 2

NB: Conditions (i), (ii) are equivalent to an "Equal Areas" construction:



from Hill, Stat. Therm.

FIG. 14-4. Pressure-volume isotherms for a Bragg-Williams lattice gas. The curve labeled $cw/kT = -4$ is the critical curve.

• finish the discussion, return to problem of adsorption on solid surface [2-D lattice gas]

From Eq. [1] for A $\mu = \frac{\partial A}{\partial N} \Big|_{M,T} = kT \left\{ \ln N - \ln(M-N) - \ln g - z\chi \frac{N}{M} \right\}$

or

$$\frac{\mu}{kT} = \ln \frac{N}{M-N} - \ln g - z\chi \theta \quad [2]$$

$\underbrace{\ln \left[\frac{\theta}{1-\theta} \right]}$

↑ effect of interaction between adsorbed particles

↑ shows same van der Waals loop as Eqn. of state (same critical pt)