

Real fluid

Model above assumes fluid particles don't interact

Real fluid molecules do interact

- they occupy volume and keep other molecules away
- they attract at long distance

CH_3CN → dipole-dipole type interactions
Average over orientations

$$U(r) \sim - \frac{|\mu_1|^2 |\mu_2|^2}{r^6}$$

Dipoles set up an ϵ -field that can induce dipoles in neighbor molecules

$$U(r) \sim - \frac{|\mu_1|^2 \alpha_2}{r^6} - \frac{|\mu_2|^2 \alpha_1}{r^6}$$

$\frac{\alpha}{4\pi\epsilon_0}$ polarizability "volume" —
susceptibility to being polarized scales with size

dipoles can arise instantaneously due to fluctuations in charge. Called London "dispersion" interaction

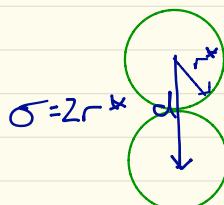
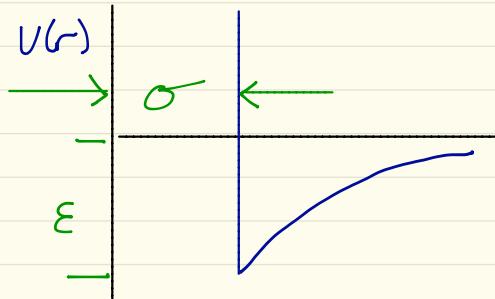
$$U(r) \sim - \frac{\alpha_1 \alpha_2}{r^6}$$

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Assume instead molecules have some radius r^* and have an attractive (dispersion) interaction

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon \left(\frac{\sigma}{r}\right)^6 & \end{cases}$$

Hill, J Chem Ed
derivation



Assume particles are uniformly distributed

Net attraction of a particle for all others is

$$\begin{aligned} \phi &= \int_{\sigma}^{\infty} u(r) \frac{N}{V} 4\pi r^2 dr \\ &= -4\pi \sigma^6 \epsilon \left(\frac{N}{V}\right) \int_{\sigma}^{\infty} \frac{1}{r^2} \cdot r^2 dr \\ &= \frac{4}{3} \pi \sigma^3 \epsilon \left(\frac{N}{V}\right) \frac{1}{r^3} \Big|_{\sigma}^{\infty} \\ &= -\frac{4}{3} \pi \sigma^3 \epsilon \left(\frac{N}{V}\right) \\ &= -2b \epsilon \left(\frac{N}{V}\right) \end{aligned}$$

$b = \text{excluded volume / molecule}$

$$b = \frac{1}{2} \left(\frac{4}{3} \pi \sigma^3 \right)$$

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$$\phi = -2a \frac{N}{V} \quad a = \epsilon \cdot b \quad \text{energy} \cdot \text{volume}$$

Molecules have both translational kinetic energy and potential energy.

$$Q = Q_{\text{trans}}^N \cdot Q_{\text{config}} / N! \quad Q_{\text{trans}} = (V - Nb) / N^3$$

$$Q_{\text{config}} = \left(\cdots \int e^{-U(r)/\beta} dr_1 \cdots dr_N \right)^N \approx (V - Nb)^N \exp \left[- \left(\frac{d}{2} \right) \beta \right]^N$$

pairwise interactions factor

reduce volume available Boltzmann factor of interactions / Z ASSUME uniform interaction
assumes non-overlapping Avoid double counting

$$\begin{aligned} \ln Q &= N \ln Q_{\text{trans}} + \ln Q_{\text{config}} - \ln N! \\ &= N \ln(V - Nb) - N \ln(N^3) + N \left(\frac{Na}{V} \cdot \beta \right) - \ln N! \end{aligned}$$

$$\ln 1 = \ln 1 - \frac{1}{2} \ln 2\pi m - \frac{1}{2} \ln k_B T$$

$$f = -\frac{k_B T}{N} \ln Q =$$

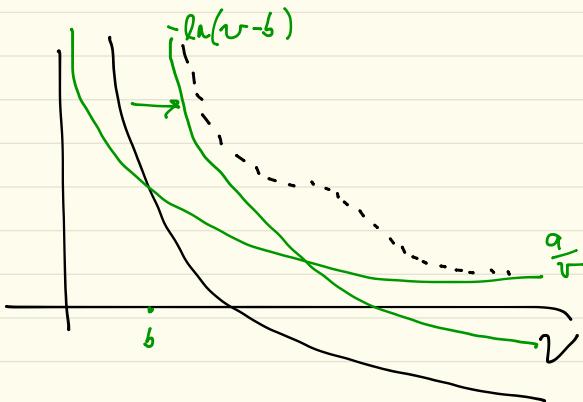
$$-k_B T \left[\ln(V - nb) - \frac{3}{2} \ln k_B T - \frac{a}{v k_B T} - \ln N + 1 + 3 \ln h - \frac{3}{2} \ln 2\pi m \right]$$

$$= -k_B T \left[\ln \left[(V - b) (k_B T)^{3/2} \right] + \frac{a}{v} - k_B T \right] \quad \text{seem to miss } + \frac{3}{2}$$

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ideal gas $f \sim -T \ln v$ @ const T

this gas $f \sim -T \ln(v-b) + \frac{a}{v}$ @ const T



f does not go up uniformly ideal
w/v?

$$P = \frac{1}{\beta} \frac{\partial \ln f}{\partial v} = \frac{N k_B T}{v - N b} - \frac{N^2 a}{v^2}$$

$$P = \frac{nRT}{v-nb} - \frac{a}{v^2}$$

The van der Waals equation!!

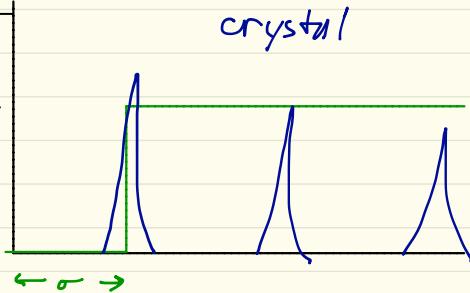
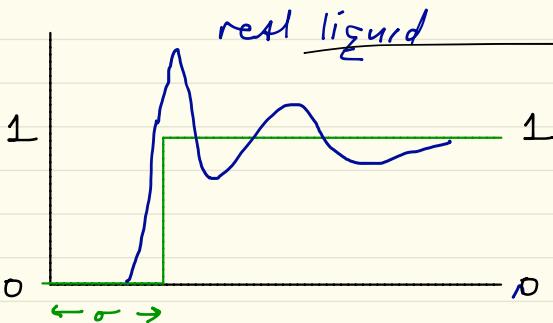
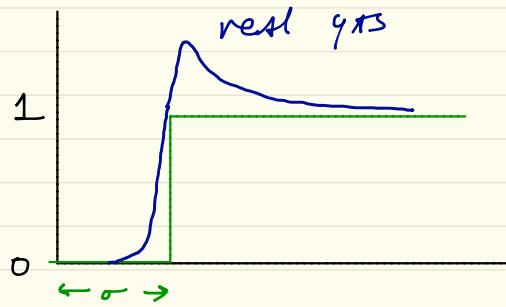
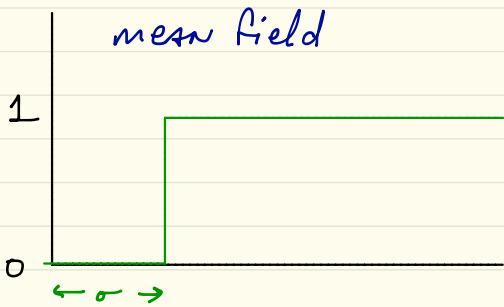
Simple consequence of simple interaction model

Made a mean field Approximation here, that molecules are uniformly distributed about each other.

$$\text{More generally, } \phi = \int_0^{\infty} u(r) g(r) 4\pi r^2 dr$$

$$g(r) \equiv \text{radial distribution function}$$

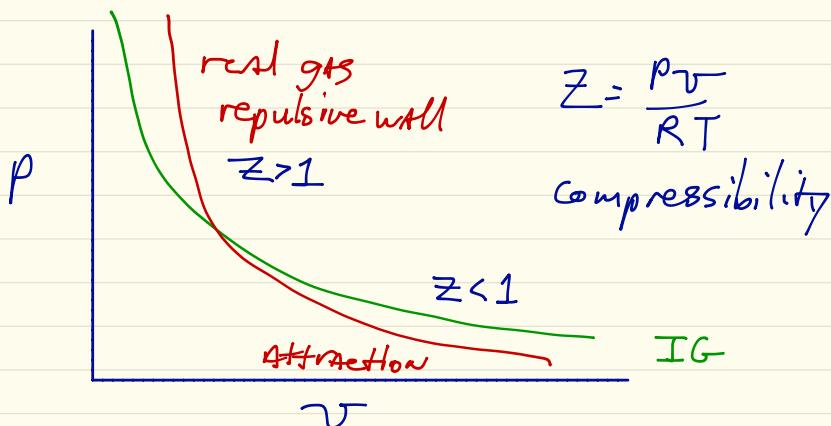
$$\equiv \rho(r)/\rho$$



coordination shells

sharp peaks corresponds to lattice positions

For fluids PVT can be measured. Encodes information about intermolecular interactions



Fluids are non-ideal because

- molecules have volume, repel at short distances

$$P > P_{ig} \quad Z > 1$$

- molecules attract one another

$$P < P_{ig} \quad Z < 1$$

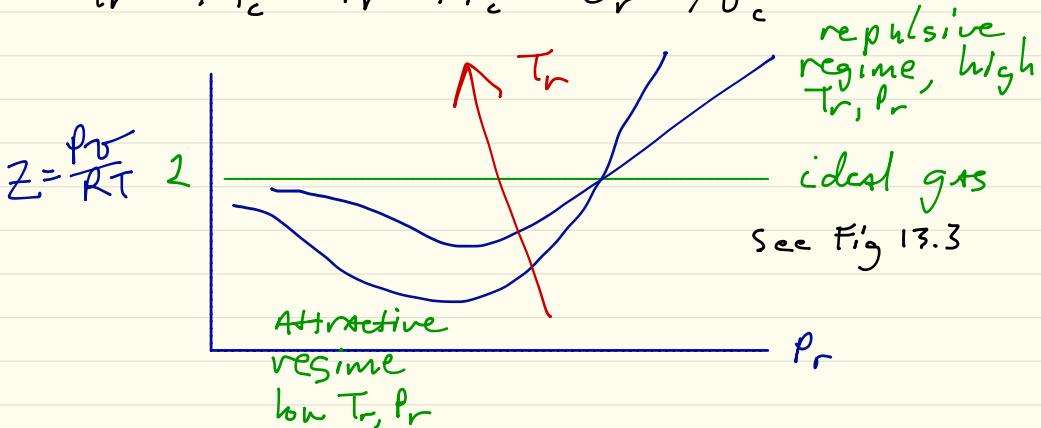
Empirically observed that the compressibility of all fluids are the same when scaled to their critical T_c, P_c, V_c . (Table 13.1)

All "normal" fluids have $Z_c = \frac{P_c V_c}{R T_c} \sim 0.27$

Reflects fact that the three are not independent, can be traced back to two underlying physical origins of non-ideality

Origin of "Law of Corresponding States"
All fluids are the same when presented in reduced coordinates

$$T_r = T/T_c \quad P_r = P/P_c \quad \nu_r = \nu/\nu_c$$



see Fig 13.3

From this can prepare generalized compressibility charts. Old school - hard to compute with.

Does vdW equation obey law of corresponding states?

At critical point, $\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$

Apply to vdW EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \rightarrow \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_{T=T_c} = 0 \rightarrow \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

eliminate $a \rightarrow$

$$b = V_c/3$$

back-substitute $\rightarrow a = \frac{9}{8} RT_c V_c$

"universal" vdW EOS

$$P_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^3} \rightarrow Z_c^{vdW} = \frac{3}{8} = 0.375$$

only qualitatively useful

More reliable EOS's - mostly phenomenological

Redlich-Kwong

$$P = \frac{RT}{v-B} - \frac{A}{T'^L v(v+B)}$$

$B \rightarrow$ molecular size } fitted, different
 $A \rightarrow$ molecular interaction } from vdW parameters.

Still cubic, still corresponding states

$$V_c = 3.8473B \quad P_c = 0.029894 \left(\frac{A^2 R}{B^5} \right)^{1/3}$$

$$T_c = 0.34504 \left(\frac{A}{BR} \right)^{2/3}$$

$$\text{Peng-Robinson} \quad P = \frac{RT}{v-b} - \frac{a(\omega, T_r)}{v(v+b) + b(v-b)}$$

$a(\omega, T_r)$ complicated empirical fn

$$\omega = -\log \left(\frac{P_{sat}/P_c}{|T_r=0.7}} - 1 \right)$$

"centrifugal factor"

Also cubic, also corresponding states

<u>EoS</u>	<u>Zc</u>	
vdW	0.375	better treatment
Redlich-Kwong	0.333	near critical pt.
P-R	0.307	

Virial EOS physically based EOS

Recall we started with the general expression

$$Q = \sum_{\text{trans}}^N \cdot Q_{\text{config.}} / N!$$

$$Q_{\text{config.}} = \int \dots \int e^{-U(\vec{r})\beta} d\vec{r}_1 \dots d\vec{r}_N$$

Configuration integral involves integrations over all positions of all species. Can show that this can be expanded in $\frac{1}{r}$ into 2-body, 3-body, ..., contributions in a so-called cluster expansion.

$$Z_1 = \int d\vec{r}_1 = V$$

$$Z_2 = \iint e^{-U(\vec{r}_1, \vec{r}_2)\beta} d\vec{r}_1 d\vec{r}_2 \quad \dots$$

$$Z_3 = \iiint e^{-U(\vec{r}_1, \vec{r}_2, \vec{r}_3)\beta} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \quad \Delta$$

...

$$\text{Get } f(T, \rho) = -k_B T \ln Q$$

$$= f_{\text{rig}}(T, \rho) - RT \left[\frac{B_2(T)}{V} + \frac{B_3(T)}{V^2} + \dots \right]$$

Called a virial expansion, And B_2, \dots called 2nd ... virial coefficients.

where B_i depend on terms up to Z_i

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Because $\rho = -\left(\frac{\partial f}{\partial v}\right)_T$ Helmholtz

$$\Rightarrow \rho = \frac{RT}{v} \left(1 + \frac{B_2(T)}{v} + \dots \right)$$

or

$$Z = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \quad \text{guaranteed to converge ... eventually}$$

2nd virial
coeff

↙ shows this is Taylor exp of Z

$$\frac{\rho v}{RT} = Z = Z \Big|_{\rho \rightarrow 0} + \rho \left(\frac{\partial Z}{\partial \rho} \right)_T \Big|_{\substack{\rho \rightarrow 0 \\ v \rightarrow \infty}} + \frac{\rho^2}{2!} \left(\frac{\partial^2 Z}{\partial \rho^2} \right)_T \Big|_{\substack{\rho \rightarrow 0 \\ v \rightarrow \infty}} + \dots$$

Other thermo functions follow

How well does expansion work?

Very well above critical conditions, more poorly (more terms needed) as $\rho \uparrow v \downarrow$

Table 2.6

What does $B(T)$ mean?

$$\bar{Z} = 1 + B(T)\rho + C(T)\rho^2, \dots$$

$$B(T) = \lim_{\substack{\rho \rightarrow 0 \\ V \rightarrow \infty}} \frac{\bar{Z}-1}{\rho}$$

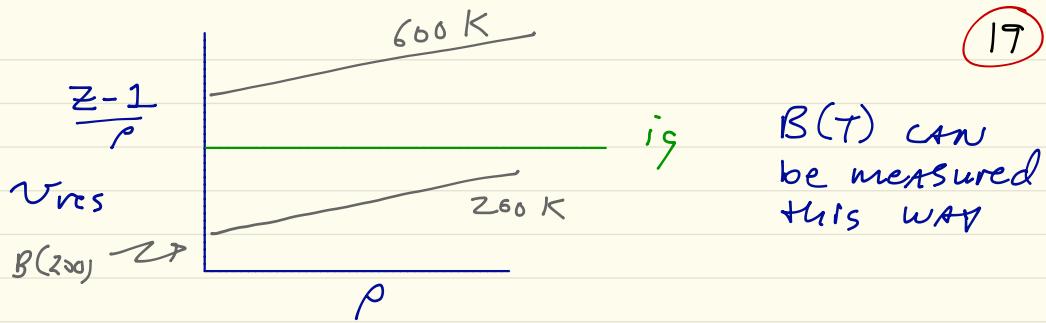
A departure fn!
Define residual volume

$$V_{res} = V - V_{is} = V - \frac{RT}{\rho} = \frac{RT}{\rho} \left[\frac{\rho V}{RT} - 1 \right]$$

$$V_{res} = \frac{RT}{\rho} [Z-1]$$

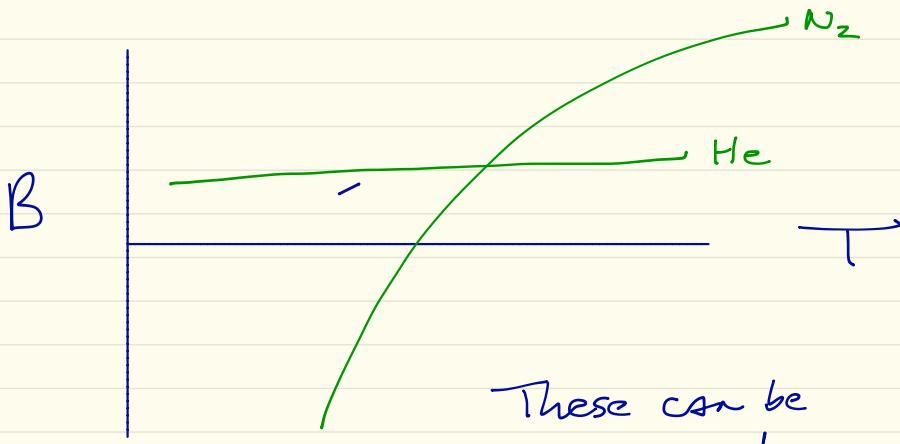
$$\lim_{\substack{\rho \rightarrow 0 \\ V \rightarrow \infty}} V_{res} = \lim_{\substack{\rho \rightarrow 0 \\ V \rightarrow \infty}} \frac{Z-1}{(\rho/RT)} = \lim_{\rho \rightarrow 0} \frac{Z-1}{\rho} = B(T) !$$

$B(T)$ is the low density limit of the residual volume.



Low T, where intermolecular attractions dominate, $B < 0$ $\frac{a}{RT} > b$

High T, repulsions dominate, $B(T) > 0$
 $b > \frac{a}{RT}$



Observing these quantities is useful in parameterizing EOS's.

vdW fluid — virial expansion of vdW
eq gives

$$\rho = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow z = \frac{\rho v}{RT} = \frac{v}{v-b} - \frac{av}{v}$$

$$= \frac{1}{1-b/v} - \frac{av}{v}$$

b/v small $\frac{1}{1-x} \approx 1+x+x^2+\dots$ geometric series

$$z \approx 1 + \frac{b}{v} - \frac{a}{RTv} + \left(\frac{b}{v}\right)^2 + \dots$$

$$= 1 + \frac{1}{v} \left(b - \frac{a}{RT} \right) + \frac{b^2}{v^2} + \dots$$

$$B_2(T) = b - \frac{a}{RT} \quad B_3(T) = b^2 \quad B_4(T) = b^3 \dots$$

linear in $\frac{1}{T}$ constant, not so good
~ convex

Plot $B_2(T)$ vs $\frac{1}{T}$ and fit to line

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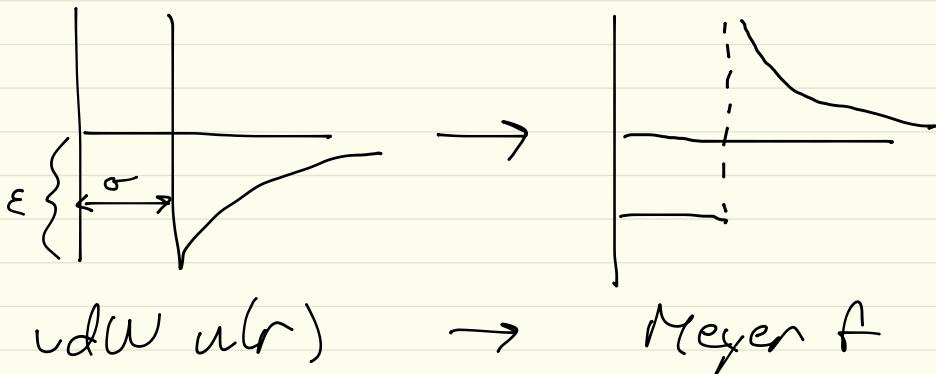
B₂ related to cluster integrals

$$\begin{aligned} \text{Eg } B_2(T) &= -\frac{1}{2V} (Z_2 - Z_1^2) \\ &= -\frac{1}{2V} \iint [e^{-u(r_1, r_2)\beta} - 1] d\vec{r}_1 d\vec{r}_2 \\ &= -\frac{1}{2V} \int d\vec{r}_1 \int [e^{-u(\vec{r}_2 - \vec{r}_1)\beta} - 1] d\vec{r}_2 \\ &= -\frac{1}{2V} V \cdot 4\pi \int [e^{-u(r_1)}\beta - 1] r^2 dr \end{aligned}$$

(Assume interaction only depends on separation
and is short ranged.)

$$B_2(T) = -2\pi \underbrace{\int_0^\infty [e^{-\beta u} - 1] r^2 dr}_{\text{Meyer f-function}}$$

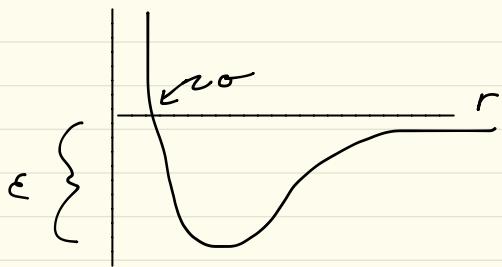
Meyer f-function



$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\frac{\epsilon}{r^6} & r > \sigma \end{cases} \Rightarrow B_2(T) = b - \frac{a}{RT}$$

Common more realistic potential is "Lennard-Jones"

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad 0 < r < \infty$$



Again, $B_2(T)$ can be evaluated by integration and depends on $\sigma + \epsilon$. Or, measure $B_2(T)$ and fit $\sigma + \epsilon$.

Result again follows corresponding states
Calculation shows

$$\frac{B_2(T)}{\frac{2}{3}\pi\sigma^3} = f\left(\frac{k_B T}{\epsilon}\right)$$

Normalized to $\sigma + \epsilon$, all gases are the same.

L-J model pretty realistic, VERY commonly used in atomistic models. $\sigma + \epsilon$ available for many molecules & atoms, fitted to exp't.

MD / MC