Some comments on the

Van der Waals equation of state

various equations of state (Raff Table 1.2)

Table 1.2 Some commonly used equations of state

Equation of State	Functional Form	Number of Parameters
Ideal gas	$PV_m = RT$	0
van der Waals	$(V_m - b)(P + a/V_m^2) = RT$	2
Dieterici	$P(V_m - b)\exp[a/RTV_m] = RT$	2
Berthelot	$(V_m - b)(P + a/TV_m^2) = RT$	2
Virial	$P = RT\left[V_m^{-1} + \sum_{n=2}^{\infty} C_n(T)V_m^{-n}\right]$	∞
Beattie–Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha$, with $\gamma = c_o/T^3V_m$, $\beta = b_o[1 - b/V_m]$, and $\alpha = a_o[1 + a/V_m]$	5
Redlich–Kwong	$P = \dfrac{RT}{(V_m - b)} - \dfrac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots$.	∞

van der Waals equation

$$P_{ideal} \qquad \bar{V}_{ideal} = RT$$

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

interpretation of parameters:

b is correction for actual volume of atoms/molecules

- volume available to molecules $\left(\bar{V} - b\right)$ smaller than $\bar{V}$
- b is associated with repulsive forces

van der Waals equation

$$\boldsymbol{P_{ideal} \qquad \bar{V}_{ideal} = RT}$$

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

interpretation of parameters:

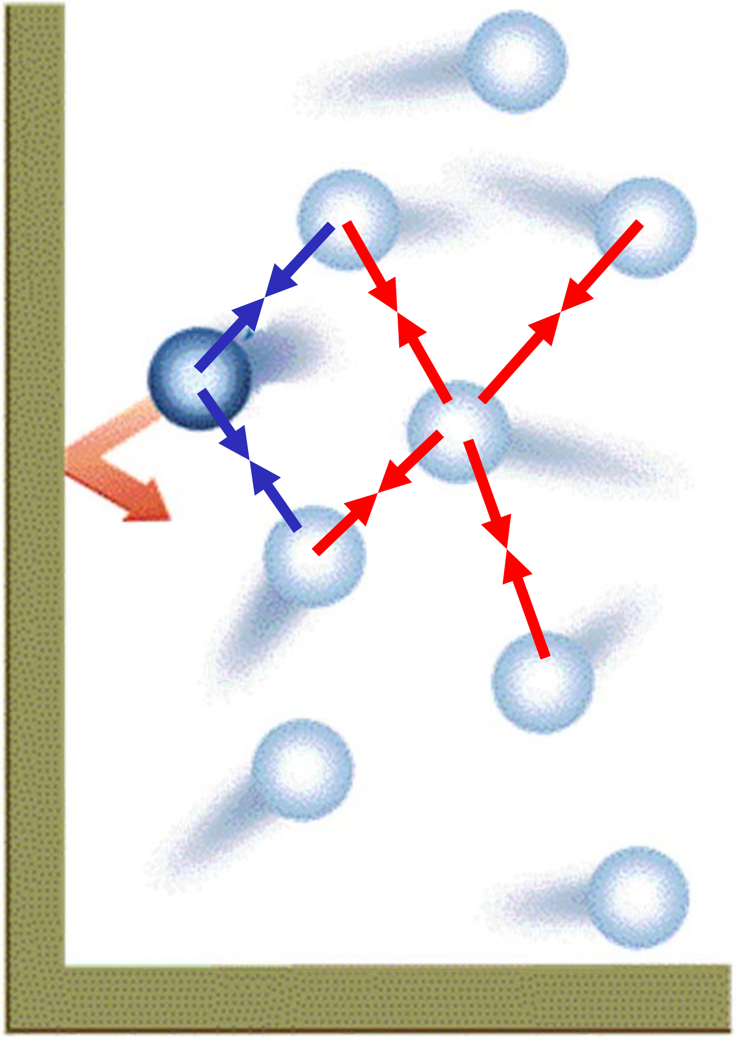
a is correction for attractive forces of atoms/molecules

- a is associated with attractive forces
- $P_{bulk} \equiv P_{ideal}$ is greater than $P \equiv P_{meas}$ measured at surface

$P_{bulk} = \left(P_{meas} + \frac{a}{\bar{V}^2}\right) \qquad P_{meas} \rightarrow P_{bulk} \quad \bar{V} \rightarrow \infty$

heuristic justification for attractive constant a

- asymmetric attractive forces for molecule at surface
- molecule at surface has less momentum less than molecule in bulk
- $P \equiv P_{meas} < P_{bulk}$
- $P_{bulk} = \left(P + \frac{a}{\overline{V}^2} \right)$



van der Waals equation

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

Table 1.1 van der Waals parameters

Gas	b (L mol^{-1})	a (L^2 bar mol^{-2})
He	0.0238	0.0346
Ne	0.01672	0.208
Ar	0.03201	1.355
Kr	0.0396	2.325
Acetylene	0.0522	4.516
N_2	0.0387	1.37
H_2O	0.03049	5.537
CO_2	0.04286	3.658

?

size

polarizability

polarity

Source: *Handbook of Chemistry and Physics*, 78th edition, CRC Press, Boca Raton, Fl, 1997–98

a little trash talk on VDW eqn, but instructive !!!

Validity

However, the Van der Waals model is not appropriate for rigorous quantitative calculations, remaining useful only for **teaching** and qualitative purposes.[1]

Nowadays, Eq. 2.9 belongs to **"pedagogical physics:"** it is the simplest equation that illustrates several important concepts, but its accuracy is not satisfactory.