Alternate derivation of van der Waals' equation of state

(derived by van der Waals long before Mayer expansion)

In ideal gas law \( pV = Nk_BT \)

\( p \) is the pressure of the kinetic energy of the molecules
\( V \) is the volume that the molecules can move around in.

For an interacting gas, the total energy is kinetic plus interaction. The average interaction energy one expects to be \( \alpha - \frac{(N/N)}{V}N \) since each of the \( N \) particles interacts with every other particle within a certain distance \( r_0 \) of it. The number of such particles is proportional to the particle density \( (N/V) \). The pressure is proportional to the energy per volume, hence the total pressure is

\[ P = P_{\text{kinetic}} - \alpha \left( \frac{N}{V} \right)^2 \]

or \( P_{\text{kinetic}} = P + \alpha \left( \frac{N}{V} \right)^2 \)

The volume the particles can move in is the "free volume" which equals the total volume minus the volume the particles themselves occupy

\[ V_{\text{free}} = V - Nb \]

\( b \) is volume occupied by one molecule

\( \uparrow \) excluded volume
Using Prandtl and V_{free} in ideal gas laws:

\[ P \text{ Pruche } V_{\text{free}} = N k_B T \]

\[ (P + a \left( \frac{N}{V} \right)^2)(V - N b) = N k_B T \]

\[ (P + a \left( \frac{N}{V} \right)^2) \left( \frac{V}{N} - b \right) = k_B T \]

van der Waals equation of state
van der Waals Theory of Liquid-Gas phase transition

Phase diagram

\[ p \begin{array}{c} \text{liquid} \rightarrow \text{gas} \\ \text{gas} \end{array} \]

\[ T \]

Liquid-Gas phase transition

if one crosses the liquid-gas phase boundary, there is a discontinuous change in particle density. This change in density vanishes continuously at the point C is approached. C is called the liquid-gas "critical point". The liquid-gas phase boundary ends at C. For T or P above C, there is no distinction between liquid and gas.

van der Waals equation of state

\[ (p + \frac{a}{v^2})(v-b) = k_B T \quad a, b > 0 \]

Isotherms (p-v curves at constant T) look like

There exists a critical isotherm \( T_c \) such that

For \( T > T_c \), \( \frac{dp}{dv} < 0 \) monotonic decreasing \( p(v) \)
At \( T = T_c \), the first appearance of a point on isotherm with \( \left( \frac{\partial^2 p}{\partial v^2} \right)_T = 0 \) will turn out to be the critical point.

For \( T < T_c \), isothers are not monotonic – there is a region where \( \left( \frac{\partial p}{\partial v} \right)_T > 0 \).

Recall: Isothermal compressibility

\[
K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \frac{1}{\left( \frac{\partial p}{\partial v} \right)_T}
\]

For \( T > T_c \), \( K_T > 0 \) everywhere.

For \( T = T_c \), \( K_T \to \infty \) at the point \( C \).

For \( T < T_c \), \( K_T < 0 \) when \( \frac{\partial p}{\partial v} > 0 \) this is unphysical region – leads to thermodynamically unstable system. We will see that this region of phase coexistence between liquid and gas.

For \( T < T_c \) the van der Waals isotherm, when viewed as a true \( N(p, T) \) becomes multi-valued – i.e. three values of \( V \) for fixed \( p \) and \( T \) within some region of \( p \).

We will see that the physical system follows an isotherm that is given by the dashed line. It zooms from \( v_e \) to \( v_g \) at a given pressure \( p^*(T) \). Thus \( p^*(T) \).
will be the location of the liquid gas phase boundary. \( \bar{v}_L - \bar{v}_g \) gives the discontinuity in density at \( p^*(T) \). The great line between \( v_L \) and \( v_g \) is coexistence region where system can be a mixture of both liquid and gas phases, with average specific volume \( \bar{v} \). Let \( \bar{v}_L < \bar{v} < \bar{v}_g \).

As \( T \to T_c^- \), \( \left( \frac{1}{v_L} - \frac{1}{v_g} \right) \to 0 \), \( v_L, v_g \to v_c \) and \( p^*(T) \to p_c \)

\[ \Rightarrow C \ is \ the \ critical \ end \ point \ of \ the \ liquid-gas \ phase \ boundary. \]

For \( T < T_c \) as \( T \to T_c^- \) we see that the local max and local min of \( p(v, T) \) both merge to the common \( \bar{v} = v_c \). \( \Rightarrow C \) is an inflection point. \( \frac{\partial^2 p}{\partial v^2} = 0 \) at \( C \).

Use \( \left( \frac{\partial^2 p}{\partial v^2} \right)_{T_c} = \left( \frac{\partial^2 p}{\partial v^2} \right)_{T} = 0 \) to determine the location of \( C \).

\[ p = \frac{bT}{(v-b)} - \frac{a}{v^2} \]

\[ \frac{dp}{dv} = -\frac{k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow k_B T = 2a \frac{(v-b)^2}{v_c^3} \]

\[ \frac{d^2p}{dv^2} = \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow k_B T = 3a \frac{(v-b)^3}{v_c^3} \]

\[ 2v_c = 3v_c - 3b \Rightarrow \bar{v}_c = \frac{3b}{2} \text{ critical specific volume} \]
\[ k_B T_c = \frac{8}{27} \frac{a}{b} \]

\[ P_c = \frac{k_B T_c}{v_c - b} - \frac{a}{v_c^2} = \frac{8}{27} \frac{a}{b} \left( \frac{1}{3b} - \frac{1}{b} \right) - \frac{a}{(3b)^2} \]

\[ = \frac{8}{27} \frac{a}{b} \left( \frac{1}{2b} - \frac{a}{9b} \right) = \left( \frac{4}{27} - \frac{1}{9} \right) \frac{a}{6^2} \]

\[ P_c = \frac{1}{27} \frac{a}{b^2} \]

Define \( \Phi = \frac{P}{P_c} \), \( \bar{T} = \frac{T}{T_c} \), \( \bar{v} = \frac{v}{v_c} \)

Then

\[ (\Phi + \frac{a}{v^2}) (v - b) = k_B \bar{T} \]

\[ \Rightarrow (p_c \bar{p} + \frac{a}{v_c^2 \bar{v}^2}) (v_c \bar{v} - b) = k_B T_c \bar{T} \]

\[ \left( \frac{1}{27} \frac{a}{b^2} \frac{a}{\bar{v}^2} + \frac{a}{9b^2 \bar{v}^2} \right) (3b \bar{v} - b) = \left( \frac{8}{27} \frac{a}{b} \right) \bar{T} \]

\[ \frac{1}{27} \frac{a}{b^2} \left( \bar{p} + \frac{3}{v^2} \right) (3b) (\bar{v} - \frac{1}{3}) = \frac{8}{27} \frac{a}{b} \bar{T} \]

\[ \Rightarrow \left( \bar{p} + \frac{3}{v^2} \right) (\bar{v} - \frac{1}{3}) = \frac{8}{3} \bar{T} \]
Also: \[ \frac{p_c v_c}{k_B T_c} = \frac{1}{2\pi} \frac{a}{b^2} \frac{3b}{(8\pi)^{1/2}} = \frac{3}{8} = 0.375 \]

universal for all gases 0.375

<table>
<thead>
<tr>
<th>Gas</th>
<th>( T_c ) (K)</th>
<th>( \frac{p_c v_c}{k_B T_c} )</th>
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<tr>
<td>Ne</td>
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<tr>
<td>Ar</td>
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<td>Kr</td>
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<tr>
<td>Xe</td>
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<td>( N_2 )</td>
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<td>( O_2 )</td>
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<tr>
<td>CO</td>
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</tr>
<tr>
<td>( CH_4 )</td>
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<td>0.289</td>
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</table>
**Law of corresponding states:** If scale $p$, $v$, $T$ by values at critical point to get $\bar{p}$, $\bar{v}$, $\bar{T}$, then isotherms in terms of $\bar{p}$, $\bar{v}$, $\bar{T}$ are independent of $a$ and $b$ — will be the same for any gas.

Now consider $T < T_c$ we want to determine the coexistence values of $v_e$ ad $v_g$ that the physical system will have.

Two ways to do this

1. **Maxwell Construction**

\[ P \]

\[ v_1 \quad v_2 \quad v \]

Gibbs free energy \( G(T,p,N) = \mu N \)

\[ dG = -SdT + Vdp + \mu dN \]

\[ = \mu dN + N d\mu \]

\[ \Rightarrow d\mu = -\left(\frac{S}{N}\right) dT + Vdp \]

Gibbs-Duhem relation along isotherm $dT = 0$

\[ \Rightarrow d\mu = Vdp \]

Now at liquid-gas coexistence, the condition for chemical equilibrium \( \Rightarrow M_e = M_g \)

\[ \Rightarrow \int_1^2 d\mu = M_2 - M_1 = \int_1^2 Vdp = 0 \] if

\[ v_1 \leftrightarrow v_2 \quad \text{and} \quad v_2 \leftrightarrow v_g \] for coexistence $v_e$ ad $v_g$.
\[ \text{graph of } \int v dp \rightarrow \mu = \frac{G}{N} \]

So \( \int_1^2 v dp = 0 \) determines \( v_0 = v_1 \), \( v_0 = v_2 \)

to see the geometric meaning of \( H \)

\[ \int_1^2 v dp = \int_A^B v dp + \int_B^C v dp \]

\[ + \int_C^D v dp + \int_D^E v dp \]

\[ = \text{area}_I - \text{area}_II \]

So we get condition of "equal areas".

\[ v_e \text{ and } v_g \text{ determined by the } \]

cord at constant \( p^* \) such that

\[ \text{area above cord} = \text{area below cord} \]

2. Consider Helmholtz free energy

\[ A(T, V) \text{ fixed } N \]

\[ dA = -SdT -p dV \]

\[ A = -\int pdV \text{ along isotherm } \]

\[ \frac{A}{N} = -\int pdV \]

\[ p = -\frac{\partial A}{\partial V} = -\frac{\partial A}{N \partial V} \]

\( p \) must be const from \( v_e \) to \( v_g \)

\text{and } A \text{ should be convex}

\( \Rightarrow \text{coexistence is given by dashed line} \)
\[ p^* = \frac{\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_e}{v_g - v_e} \]

coeexistence pressure is slope of dashed line

\[ p^* (v_g - v_e) = -\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_e = \int p \, dv \]

The shaded area is \( \int p \, dv \)

Shaded area is \( p^* (v_g - v_e) \)

The two areas are equal only if

The shaded area above \( p^* \) equals shaded area below \( p^* \)

The locus of points \( v_e(T), v_g(T) \) in \( p - v \) plane as \( T \) varies is called the coexistence curve.