

3.D.4. The van der Waals Equation

Main features of the liquid-vapor phase transition can be illustrated by the van der Waals equation [see (2.12) of §2.C.3].

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (3.41a)$$

where $v = \frac{V}{n}$ is the molar volume. As can be seen in Fig.3.7 of §3.D.3, the critical point is an inflection point of the critical isotherm $P(v_c, T_c)$. Therefore, it satisfies the conditions

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + 2\frac{a}{v^3} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - 6\frac{a}{v^4} = 0 \quad (3.42)$$

The solution to (3.42) is

$$v_c = 3b \quad \text{and} \quad T_c = \frac{8a}{27bR} \quad (3.43)$$

so that (3.41a) gives

$$P_c = \frac{a}{27b^2} \quad (3.43a)$$

In terms of the normalized (or reduced) variables

$$\bar{X} = \frac{X}{X_c} \quad X = P, V, T, \dots$$

(3.41a) becomes

$$\bar{P} = \frac{8\bar{T}}{3\bar{v}-1} - \frac{3}{\bar{v}^2} \quad (3.44)$$

Note that (3.44) is independent of the material parameters a & b so that it is the same for all substances, in agreement with the law of corresponding states. The compressibility factor at the critical point is [see (3.25a) of §3.D.3]

$$Z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$$

while measurements on real gases give $Z_c \approx .30$.

Now, (3.41a) and (3.44) are cubic equations of the volume,

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0 \quad (3.41)$$

or

$$\bar{v}^3 - \frac{1}{3}\left(1 + \frac{8\bar{T}}{\bar{P}}\right)\bar{v}^2 + \frac{3}{\bar{P}}\bar{v} - \frac{1}{\bar{P}} = 0 \quad (3.41a)$$

Since all coefficients in (3.41a) are real, it has either 3 real, or 1 real and 2 complex, roots for \bar{v} . Since a physical quantity must be real, the isotherms $\bar{v}_T(\bar{P})$ are [see Figs.3.7 & 3.9]

completely single-valued for $\bar{T} \geq 1$ [All 3 real roots are equal for $\bar{T} = 1$.]

partially triple-valued for $\bar{T} < 1$

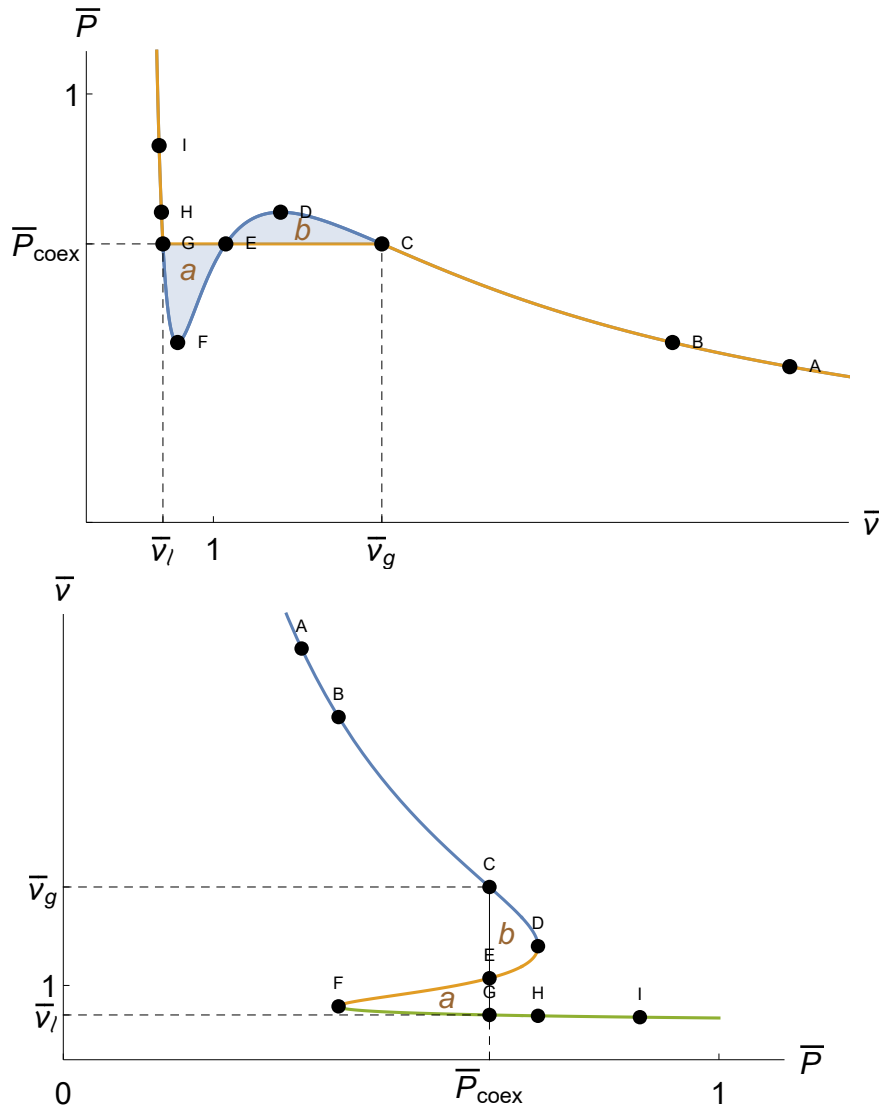


Fig.3.9. Isotherm at $\bar{T} = 0.9$. Shaded areas a & b are equal.

The 3 roots of (3.41a) are represented by curves of different colors in the $\bar{v}(\bar{P})$ plot.

For the $\bar{T} < 1$ isotherms, we shall take the smallest (largest) root of (3.41a) as a system point in the liquid (vapor) phase.

The presence of multiple roots means that the actual position of the system point depends, besides the values of \bar{T} & \bar{P} , also on the history of the system, as well as other extraneous factors such as the presence of impurities or defects on the surface of the container. Thus, for very pure samples, one can enter the multi-root region on either the liquid or vapor side following the vdW isotherm, thus creating a super-heated liquid or under-cooled vapor, as already discussed in §3.D.3.

Now, along an isotherm,

$$dg = v dP = v_c P_c \bar{v} d\bar{P} = \frac{a}{9b} \bar{v} d\bar{P}$$

$$\rightarrow g(\bar{P}, \bar{T}) = g(\bar{P}_0, \bar{T}) + \frac{a}{9b} \int_{\bar{P}_0}^{\bar{P}} \bar{v}(\bar{P}, \bar{T}) d\bar{P} \quad (3.46)$$

where \bar{P}_0 is some arbitrary reference pressure. A plot of $g(\bar{P}, \bar{T})$ with $\bar{T} = .9$ is shown in Fig.3.10.

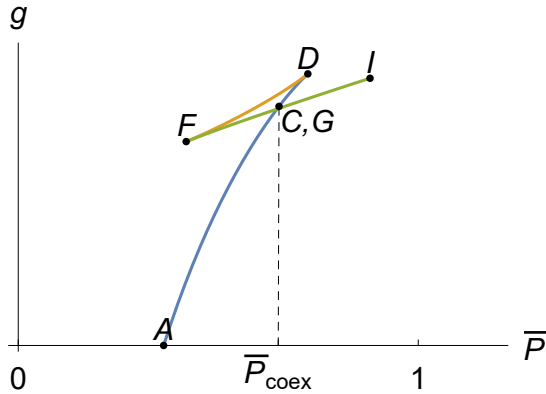


Fig.3.10. Molar Gibbs energy along the isotherm $\bar{T} = .9$ with $g = 0$ at point A [see Fig.3.9].

Since the stable phase has the lower g ,

liquid (green curve) is the stable phase for $P > \bar{P}_{\text{coex}}$

both liquid and vapor phases are stable at $P = \bar{P}_{\text{coex}}$

vapor (blue curve) is the stable phase for $P < \bar{P}_{\text{coex}}$

where the coexistence pressure \bar{P}_{coex} is given by the condition [see points C & G]

$$g_l[\bar{T}, \bar{P}_{\text{coex}}(\bar{T})] = g_g[\bar{T}, \bar{P}_{\text{coex}}(\bar{T})] \quad (3.46a)$$

$$\rightarrow \mu_l[\bar{T}, \bar{P}_{\text{coex}}(\bar{T})] = \mu_g[\bar{T}, \bar{P}_{\text{coex}}(\bar{T})]$$

where μ is the chemical potential. Thus, (3.46a) is also the condition for the two phases to be in chemical equilibrium with each other.

Note that the orange curve between D & F in Fig.3.10 is concave and hence mechanically unstable. The same conclusion can also be drawn from Fig.3.9, which shows $\left(\frac{\partial \bar{v}}{\partial \bar{P}}\right)_{\bar{T}} > 0$, & hence $\kappa_T < 0$, for the orange curve.

According to (3.46a), if we keep the system at temperature $\bar{T} < 1$ and pressure $\bar{P}_{\text{coex}}(\bar{T})$, both phases of the system can coexist in thermodynamic equilibrium with each other. Treating the system as two-component, we gain an extra independent variable, which can be chosen as the molar fraction of the gas phase $x_g = \frac{n_g}{n}$. The corresponding isotherm within the coexistence region is then the straight line $\bar{P} = \bar{P}_{\text{coex}}(\bar{T})$, with the volume \bar{v} given by the lever rule (3.25) of §3.D.3, instead of the vdW equation.

Consider now the case where energy is supplied at a constant rate to the system starting at point A in the gas phase [see Fig.3.10]. Since g is increasing steadily, the system point will move along the blue curve towards C. Upon reaching C, the system can move either towards D or G. Now, transition from the liquid to the gas phase requires an extra supply of energy equal to the enthalpy of vaporization. Therefore, moving towards G means using the external energy supply to convert portions of the liquid phase into vapor. Moving towards D means keeping the system in the liquid phase that is meta-stable. With the enthalpy of vaporization available, it will convert spontaneously into the gas phase and hence back to C. Therefore, the natural system path follows the coexistence path C to G.

The same conclusion is obtained if one withdraws energy at a steady rate starting at point I in the gas phase.

We now turn to the determination of \bar{P}_{coex} for a given \bar{T} .

Let $\{\bar{v}_1(\bar{P}), \bar{v}_2(\bar{P}), \bar{v}_3(\bar{P})\}$ be the 3 roots, in ascending magnitude, of (3.41a) at a fixed $\bar{T} < 1$. They are shown as curves in green, orange, and blue in Fig3.9, respectively.

Let point $C = (\bar{v}_3(\bar{P}_{\text{coex}}), \bar{P}_{\text{coex}})$ be the reference point. Putting (3.46) into (3.46a) gives

$$\int_C^G \bar{v} d\bar{P} = 0 \quad (3.47a)$$

where \bar{v} is evaluated along the vdW isotherm. In terms of the roots $\bar{v}_j(\bar{P})$, (3.47a) becomes

$$\int_C^D \bar{v}_3(\bar{P}) d\bar{P} + \int_D^F \bar{v}_2(\bar{P}) d\bar{P} + \int_F^G \bar{v}_1(\bar{P}) d\bar{P} = 0 \quad (3.47b)$$

Using the point $E = (\bar{v}_2(\bar{P}_{\text{coex}}), \bar{P}_{\text{coex}})$ to break up the 2nd integral, we have

$$\int_C^D \bar{v}_3(\bar{P}) d\bar{P} + \int_D^E \bar{v}_2(\bar{P}) d\bar{P} + \int_E^F \bar{v}_2(\bar{P}) d\bar{P} + \int_F^G \bar{v}_1(\bar{P}) d\bar{P} = 0 \quad (3.47)$$

$$\rightarrow \int_C^D \bar{v}_3(\bar{P}) d\bar{P} + \int_D^E \bar{v}_2(\bar{P}) d\bar{P} = - \int_E^F \bar{v}_2(\bar{P}) d\bar{P} - \int_F^G \bar{v}_1(\bar{P}) d\bar{P}$$

$$\int_C^D \bar{v}_3(\bar{P}) d\bar{P} - \int_E^D \bar{v}_2(\bar{P}) d\bar{P} = \int_E^F \bar{v}_2(\bar{P}) d\bar{P} - \int_F^G \bar{v}_1(\bar{P}) d\bar{P} \quad (3.48)$$

Since the integral $\int \bar{v}_j(\bar{P}) d\bar{P}$ is equal to the signed area between the single-valued curve $\bar{v}_j(\bar{P})$ and the \bar{P} -axis, (3.48) implies

$$\text{Area}(b) = \text{Area}(a) \quad [\text{ see Fig.3.9. }] \quad (3.49)$$

which is called the **Maxwell condition** for finding \bar{P}_{coex} .

Relevant *Mathematica* code can be found in the files “vdW.nb” & “construct.nb”.