

3.D.3. Liquid-Vapor Coexistence Region

The liquid-gas coexistence region as described by the van der Waals equation is shown by the shaded area in Fig.3.7, where all quantities with an overhead bar are normalized with respect to their values at the critical point (marked as C in figure). Solid curves are thermodynamically stable isotherms, colored blue for $\bar{T} > 1$, green for $\bar{T} < 1$, and red for $\bar{T} = 1$.

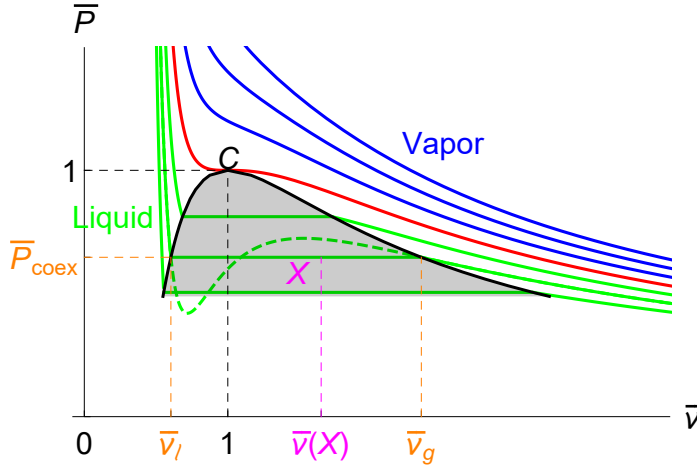


Fig.3.7. The liquid-gas coexistence region for a PVT system.

For a $\bar{T} < 1$ isotherm, whose construction will be discussed in §3.D.4, the pressure stays constant at $\bar{P}_{\text{coex}}(\bar{T})$ inside the coexistence region Γ_X . Let

$$v_\alpha(T, P) = \text{molar volume of phase } \alpha. \quad \alpha = l, g$$

$$v_\alpha^{\text{coex}}(T) \equiv v_\alpha[T, P^{\text{coex}}(T)] = \text{molar volume of phase } \alpha \text{ on the existence curve,}$$

$$x_\alpha = \frac{n_\alpha}{n} = \frac{n_\alpha}{n_l + n_g} = \text{fraction of system in phase } \alpha$$

where

$$x_l + x_g = 1 \quad (3.24a)$$

Note that the boundary of Γ_X is split by C into two coexistence curves, with one on the border of each phase. They are merged into the single coexistence curve $P^{\text{coex}}(T)$ when projected onto the T - P plane.

We shall use $f_\alpha^{\text{coex}}(T)$ to denote the value of $f(T)$ on the α phase side of the coexistence curve, and $f_{\text{coex}}(T)$ if $f(T)$ has the same value across Γ_X .

A system point X inside Γ_X has only 2 degrees of freedom, which can be chosen, e.g., as (x_g, T) . Since the properties of each phase at a fixed T remain the same throughout Γ_X , we have

$$V(X) = n_l v_l^{\text{coex}}(T) + n_g v_g^{\text{coex}}(T)$$

Dividing with the total number of moles $n = n_g + n_l$ gives the molar volume at X as

$$v(X) = x_l v_l^{\text{coex}}(T) + x_g v_g^{\text{coex}}(T) \quad (3.24)$$

$$\rightarrow \bar{v}(X) = x_l \bar{v}_l^{\text{coex}}(T) + x_g \bar{v}_g^{\text{coex}}(T) \quad (3.24b)$$

Multiplying (3.24b) with (3.24a) gives

$$(x_l + x_g) \bar{v}(X) = x_l \bar{v}_l^{\text{coex}} + x_g \bar{v}_g^{\text{coex}}$$

$$\begin{aligned} \rightarrow x_l [\bar{v}(X) - \bar{v}_l^{\text{coex}}] &= x_g [\bar{v}_g^{\text{coex}} - \bar{v}(X)] \\ \frac{x_l}{x_g} &= \frac{\bar{v}_g^{\text{coex}} - \bar{v}(X)}{\bar{v}(X) - \bar{v}_l^{\text{coex}}} = \frac{v_g^{\text{coex}} - v(X)}{v(X) - v_l^{\text{coex}}} \end{aligned} \quad (3.25)$$

which is known as the **lever rule**.

For illustrative purposes, we also show a $\bar{T} < 1$ isotherm, as given by the equation of state (the vdW equation), by a dashed green curve that differs from the stable isotherm only inside the coexistence region. It represents a path that is mechanically stable but energetically unfavorable (see §3.D.4). Now, the correct T & P are only necessary conditions. The actual occurrence of a phase transition also depends on other factors such as the availability of impurities on which condensation can grow. Thus, by careful experimental arrangements, one can follow the dashed path and place the system in a metastable state. If one enters the coexistence region on the vapor (liquid) side, one gets a **super-cooled vapor** (**superheated liquid**).

Guggenheim found that the experimentally measured coexistence curves in the \bar{p} - \bar{T} plane are almost identical for many pure substances [see Fig.3.8 in Reichl's text]. This is supportive evidence for the **law of corresponding states**, which says that the normalized (or reduced) state variables of all classical fluids have approximately the same **compressibility factor** Z_C at the critical point, where

$$Z_C \equiv \left. \frac{PV}{nRT} \right|_c \quad (3.25a)$$

Guggenheim also found that the coexistence curve data can be described by

$$\bar{p}_l^{\text{coex}} = \frac{1}{4} [7 - 3\bar{T} + 7(1 - \bar{T})^{1/3}] \quad (3.26a)$$

$$\bar{p}_g^{\text{coex}} = \frac{1}{4} [7 - 3\bar{T} - 7(1 - \bar{T})^{1/3}] \quad (3.26b)$$

which can be combined to give

$$\frac{1}{2} (\bar{p}_l^{\text{coex}} + \bar{p}_g^{\text{coex}}) = 1 + \frac{3}{4} (1 - \bar{T}) \quad (3.26)$$

$$\bar{p}_l^{\text{coex}} - \bar{p}_g^{\text{coex}} = \frac{7}{2} (1 - \bar{T})^{1/3} \quad (3.27)$$

The plot of (3.26a-b) is given in Fig.3.8a. Experimental data can be found in Fig.3.8 in Reichl's text .

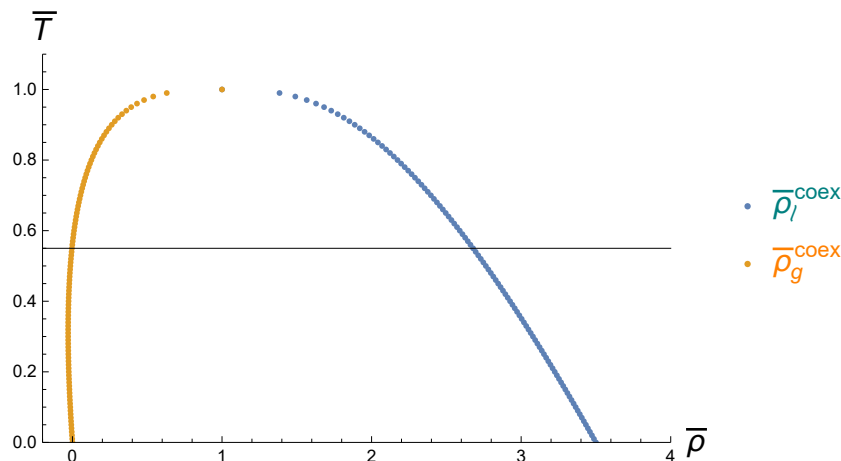


Fig.3.8a. Vapor-liquid coexistence curve as given by (3.27a-b). Measured data as shown in Fig.3.8 in Reichl's text are above the horizontal line at $\bar{T} = 0.55$.

We now turn to the response functions in the coexistence region.

The molar internal energy u_α of phase α has two independent variables, which we shall choose as (T, v_α) . On the coexistence curve, we have

$$u_\alpha^{\text{coex}} \equiv u_\alpha[T, v_\alpha^{\text{coex}}(T)] = u_\alpha^{\text{coex}}(T) \quad (3.28a)$$

Similar to (3.24), the internal energy of point X inside Γ_X is

$$U(X) = n_g u_g^{\text{coex}}(T) + n_l u_l^{\text{coex}}(T) \quad (3.28)$$

$$\rightarrow u(X) = x_g u_g^{\text{coex}}(T) + x_l u_l^{\text{coex}}(T) \quad (3.29)$$

Now, changing T will cause transitions between the phases so that $x_\alpha = x_\alpha(T)$.

The molar heat capacity at constant volume of point X is

$$\begin{aligned} c_v(X) &= \left(\frac{dq}{dT} \right)_{v_X} = \left(\frac{\partial u(X)}{\partial T} \right)_{v(X)} \\ &= \left(\frac{\partial x_g}{\partial T} \right)_{v(X)} u_g^{\text{coex}} + x_g \left(\frac{\partial u_g^{\text{coex}}}{\partial T} \right)_{v(X)} + \left(\frac{\partial x_l}{\partial T} \right)_{v(X)} u_l^{\text{coex}} + x_l \left(\frac{\partial u_l^{\text{coex}}}{\partial T} \right)_{v(X)} \\ &= x_g \left(\frac{\partial u_g^{\text{coex}}}{\partial T} \right)_{v(X)} + x_l \left(\frac{\partial u_l^{\text{coex}}}{\partial T} \right)_{v(X)} + \left(\frac{\partial x_l}{\partial T} \right)_{v(X)} (u_l^{\text{coex}} - u_g^{\text{coex}}) \end{aligned} \quad (3.30)$$

where (3.24b) was used.

We shall rewrite (3.30) in terms of directly measurable quantities. To begin, (3.24) gives

$$dv(X) = x_l dv_l^{\text{coex}} + x_g dv_g^{\text{coex}} + (v_l^{\text{coex}} - v_g^{\text{coex}}) dx_l$$

so that keeping $v(X)$ constant means

$$\begin{aligned} dx_l &= \frac{1}{v_g^{\text{coex}} - v_l^{\text{coex}}} (x_l dv_l^{\text{coex}} + x_g dv_g^{\text{coex}}) \\ \rightarrow \left(\frac{\partial x_l}{\partial T} \right)_{v(X)} &= \frac{1}{v_g^{\text{coex}} - v_l^{\text{coex}}} \left[x_l \left(\frac{\partial v_l^{\text{coex}}}{\partial T} \right)_{v(X)} + x_g \left(\frac{\partial v_g^{\text{coex}}}{\partial T} \right)_{v(X)} \right] \\ &= \frac{1}{v_g^{\text{coex}} - v_l^{\text{coex}}} \left(x_l \frac{dv_l^{\text{coex}}}{dT} + x_g \frac{dv_g^{\text{coex}}}{dT} \right) \end{aligned} \quad (3.36)$$

where

$$\left(\frac{\partial v_l^{\text{coex}}}{\partial T} \right)_{v(X)} = \frac{dv_l^{\text{coex}}}{dT}$$

since v_α^{coex} is a function of T only. By the same token,

$$\begin{aligned} \left(\frac{\partial u_\alpha^{\text{coex}}}{\partial T} \right)_{v(X)} &= \frac{du_\alpha^{\text{coex}}}{dT} = \left(\frac{\partial u_\alpha^{\text{coex}}}{\partial T} \right)_{v_\alpha^{\text{coex}}} + \left(\frac{\partial u_\alpha^{\text{coex}}}{\partial v_\alpha^{\text{coex}}} \right)_T \frac{dv_\alpha^{\text{coex}}}{dT} \\ &= c_{v\alpha}^{\text{coex}} + \left(\frac{\partial u_\alpha}{\partial v_\alpha} \right)_{T}^{\text{coex}} \frac{dv_\alpha^{\text{coex}}}{dT} \end{aligned} \quad (3.31-2)$$

where

$$c_{v\alpha}^{\text{coex}} = \left(\frac{\partial u_\alpha^{\text{coex}}}{\partial T} \right)_{v_\alpha^{\text{coex}}}$$

= constant volume molar heat capacity of phase α on the coexistence curve.

Using

$$du = T ds - P dv$$

we have

$$\begin{aligned} \left(\frac{\partial u}{\partial v}\right)_T &= T \left(\frac{\partial s}{\partial v}\right)_T - P \\ &= T \left(\frac{\partial P}{\partial T}\right)_v - P \quad [\text{Maxwell relation (2.88) used.}] \end{aligned} \quad (3.38)$$

so that (3.31-2) becomes

$$\left(\frac{\partial u_\alpha^{\text{coex}}}{\partial T}\right)_{v(\chi)} = c_{v\alpha}^{\text{coex}} + \left[T \left(\frac{\partial P}{\partial T}\right)_{v_\alpha} - P \right]^{\text{coex}} \frac{dv_\alpha^{\text{coex}}}{dT} \quad (3.38a)$$

where we have made use of the fact that P_{coex} is a function of T only.

Using (2.8), we have

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_{P_{\text{coex}}} &= \left(\frac{\partial P}{\partial T}\right)_{v_\alpha} + \left(\frac{\partial P}{\partial v_\alpha}\right)_T \left(\frac{\partial v_\alpha}{\partial T}\right)_{P_{\text{coex}}} \\ \rightarrow \left(\frac{\partial P}{\partial T}\right)_{v_\alpha} &= \left(\frac{\partial P}{\partial T}\right)_{P_{\text{coex}}} - \left(\frac{\partial P}{\partial v_\alpha}\right)_T \left(\frac{\partial v_\alpha}{\partial T}\right)_{P_{\text{coex}}} \end{aligned} \quad (3.38b)$$

Since P & v_α are independent of P_{coex} , we have

$$\begin{aligned} \left[\left(\frac{\partial P}{\partial T}\right)_{P_{\text{coex}}}\right]^{\text{coex}} &= \left(\frac{\partial P}{\partial T}\right)^{\text{coex}} = \frac{dP_{\text{coex}}}{dT} \\ \left[\left(\frac{\partial v_\alpha}{\partial T}\right)_{P_{\text{coex}}}\right]^{\text{coex}} &= \left(\frac{\partial v_\alpha}{\partial T}\right)^{\text{coex}} = \frac{dv_\alpha^{\text{coex}}}{dT} \end{aligned}$$

so that (3.38b) gives

$$\left(\frac{\partial P}{\partial T}\right)_{v_\alpha}^{\text{coex}} = \frac{dP_{\text{coex}}}{dT} - \left(\frac{\partial P_{\text{coex}}}{\partial v_\alpha}\right)_T \frac{dv_\alpha^{\text{coex}}}{dT} \quad (3.39)$$

(3.38a) thus becomes

$$\left(\frac{\partial u_\alpha^{\text{coex}}}{\partial T}\right)_{v(\chi)} = c_{v\alpha}^{\text{coex}} + \left[T \frac{dP_{\text{coex}}}{dT} - T \left(\frac{\partial P_{\text{coex}}}{\partial v_\alpha}\right)_T \frac{dv_\alpha^{\text{coex}}}{dT} - P_{\text{coex}} \right] \frac{dv_\alpha^{\text{coex}}}{dT} \quad (3.39a)$$

Consider now the Clausius-Clapeyron equation (3.14) of §3.D.2 in the present notations

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{dP_{\text{coex}}}{dT} = \frac{\Delta h^{\text{coex}}}{T \Delta v^{\text{coex}}} \quad (3.39b)$$

where

$$\Delta f^{\text{coex}}(T) = f_g^{\text{coex}}(T) - f_l^{\text{coex}}(T) \quad \text{for any } f$$

Since

$$h = u + P v$$

we have

$$\Delta h = \Delta u + P \Delta v + v \Delta P$$

$$\rightarrow \Delta h^{\text{coex}} = \Delta u^{\text{coex}} + P_{\text{coex}} \Delta v^{\text{coex}}$$

since $P = P_{\text{coex}}$ throughout Γ_χ for a given T .

Hence,

$$\frac{dP_{\text{coex}}}{dT} = \frac{\Delta u^{\text{coex}}}{T \Delta v^{\text{coex}}} + \frac{P_{\text{coex}}}{T} \quad (3.33)$$

$$\rightarrow \Delta u^{\text{coex}} = \left(T \frac{dP_{\text{coex}}}{dT} - P_{\text{coex}} \right) \Delta v^{\text{coex}} \quad (3.34)$$

Putting (3.36), (3.39a) and (3.34) into (3.30) gives

$$\begin{aligned} c_v(\lambda) &= x_g \left\{ c_{v_g}^{\text{coex}} + \left[T \frac{dP_{\text{coex}}}{dT} - T \left(\frac{\partial P_{\text{coex}}}{\partial v_g} \right)_T \frac{dv_g^{\text{coex}}}{dT} - P_{\text{coex}} \right] \frac{dv_g^{\text{coex}}}{dT} \right\} \\ &\quad + x_l \left\{ c_{v_l}^{\text{coex}} + \left[T \frac{dP_{\text{coex}}}{dT} - T \left(\frac{\partial P_{\text{coex}}}{\partial v_l} \right)_T \frac{dv_l^{\text{coex}}}{dT} - P_{\text{coex}} \right] \frac{dv_l^{\text{coex}}}{dT} \right\} \\ &\quad - \left(x_l \frac{dv_l^{\text{coex}}}{dT} + x_g \frac{dv_g^{\text{coex}}}{dT} \right) \left(T \frac{dP_{\text{coex}}}{dT} - P_{\text{coex}} \right) \\ &= x_g \left[c_{v_g}^{\text{coex}} - T \left(\frac{\partial P_{\text{coex}}}{\partial v_g} \right)_T \left(\frac{dv_g^{\text{coex}}}{dT} \right)^2 \right] + x_l \left[c_{v_l}^{\text{coex}} - T \left(\frac{\partial P_{\text{coex}}}{\partial v_l} \right)_T \left(\frac{dv_l^{\text{coex}}}{dT} \right)^2 \right] \quad (3.40) \\ &= x_g \left[c_{v_g}^{\text{coex}} - \frac{T}{v_g^{\text{coex}} \kappa_T^{\text{coex}}} (\alpha_g^{\text{coex}})^2 \right] + x_l \left[c_{v_l}^{\text{coex}} - \frac{T}{v_l^{\text{coex}} \kappa_T^{\text{coex}}} (\alpha_l^{\text{coex}})^2 \right] \end{aligned}$$

where, as promised, every quantity is readily measured.

Code

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guEqs = { 1/2 (rho1 + rhoG) == 1 + 3/4 (1 - T), rho1 - rhoG == 7/2 (1 - T)^(1/3) };
sol = Solve[guEqs, {rho1, rhoG}] // Flatten
{rho1 -> 1/4 (7 + 7 (1 - T)^(1/3) - 3 T), rhoG -> 1/4 (7 - 7 (1 - T)^(1/3) - 3 T)}

rho1s[T_] = rho1 /. sol[[1]]
rhoGs[T_] = rhoG /. sol[[2]]
1/4 (7 + 7 (1 - T)^(1/3) - 3 T)
1/4 (7 - 7 (1 - T)^(1/3) - 3 T)

datf = Table[{rho1s[T], T}, {T, 0, 1, .01}];
datg = Table[{rhoGs[T], T}, {T, 0, 1, .01}];

Ta = .55;
ListPlot[{datf, datg}, Joined -> False,
  PlotRange -> {{-0.2, 4}, {0, 1.1}}, AxesOrigin -> {-0.2, 0},
  AxesLabel -> {"rho", "T"},
  PlotLegends -> {"rho_l^coex", "rho_g^coex"},
  Epilog -> Line[{-0.2, Ta}, {4, Ta}]
]

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