

Metastable States

Common occurrence: A thermodynamic system can be taken beyond the point of equilibrium into the metastable region. For example,

- Liquids can be heated above the normal boiling point in an open container (→ need for 'nucleation stones' in organic chemistry labs)
- Bubble chambers for detection of high-energy particles contain superheated liquids
- Atmosphere often contains supersaturated  $H_2O$  vapor that precipitates abruptly if suitable nuclei are introduced

However, there is a limit of stability beyond which systems become unstable. There is potential for catastrophic failure if the limit is reached, e.g. in large containers of LNG.

Starting point:  $\underline{u}$  min at const  $\underline{S}, \underline{V}, \underline{N}_i$   
or  $\Delta \underline{u} > 0$  for any perturbation

$$\text{or } \delta \underline{u} + \frac{1}{2} \delta^2 \underline{u} + \frac{1}{3!} \delta^3 \underline{u} + \dots > 0$$

for equilibrium,  $\delta \underline{u} = 0$

for stability,  $\delta^2 \underline{u} > 0$

$$\delta^2 u = \delta^2 y^{(0)} = \sum_{i=1}^{n+2} \sum_{j=1}^{n+2} y_{ij}^{(0)} \delta x_i \delta x_j > 0 \quad (1)$$

→ number of components

The expression above does not carry any information on the sign of the derivatives  $y_{ij}^{(0)}$ , since  $\delta x_i \delta x_j$  can have any sign - except for  $y_{ii}^{(0)}$ , which have to be positive.

Transform to a quadratic form:

$$\delta z_k = \delta x_k + \sum_{j=k+1}^{n+2} y_{kj}^{(k)} \delta x_j \quad k = 1, 2, \dots, n+1 \quad (2)$$

$$= \delta x_{n+2} \quad k = n+2$$

Substitute (2) into (1):

$$\delta^2 u = \delta^2 y^{(0)} = \sum_{k=1}^{n+2} y_{kk}^{(k-1)} (\delta z_k)^2 > 0 \quad (3)$$

where

$$y_{kk}^{(k-1)} = \begin{vmatrix} y_{ii}^{(0)} & \dots & y_{ik}^{(0)} \\ \vdots & & \vdots \\ y_{ki}^{(0)} & \dots & y_{kk}^{(0)} \end{vmatrix}$$

$$\begin{vmatrix} y_{ii}^{(0)} & \dots & y_{i,k-1}^{(0)} \\ \vdots & & \vdots \\ y_{k-1,i}^{(0)} & \dots & y_{k-1,k-1}^{(0)} \end{vmatrix}$$

$y_{n+2,n+2}^{n+1} = 0$  always ←

as it's a derivative of an intensive property w.r.t. an extensive property

example for  $\delta(x_1, x_2) = y^{(0)}$  (corresponds to  $n=1$ , intensive form of  $u$ )

$$\delta^2 u = y_{11}^{(0)} \delta x_1^2 + 2y_{12}^{(0)} \delta x_1 \delta x_2 + y_{22}^{(0)} \delta x_2^2$$

$$\delta z_1 = \delta x_1 + y_{12}^{(1)} \delta x_2$$

$$\delta z_2 = \delta x_2$$

$$\sum_{k=1}^2 y_{kk}^{(k-1)} \delta z_k^2 = y_{11}^{(0)} \delta z_1^2 + y_{22}^{(1)} \delta z_2^2 =$$

$$= y_{11}^{(0)} \cdot \left[ \delta x_1 + \frac{y_{12}^{(0)}}{y_{11}^{(0)}} \delta x_2 \right]^2 + \left[ y_{22}^{(0)} - \frac{(y_{12}^{(0)})^2}{y_{11}^{(0)}} \right] \delta x_2^2$$

Correct  
10/5

←

←

$$\begin{aligned}
 &= y_{11}^{(0)} \delta x_1^2 + 2y_{12}^{(0)} \delta x_1 \delta x_2 + \frac{(y_{12}^{(0)})^2}{y_{11}^{(0)}} \delta x_2^2 + y_{22}^{(0)} \delta x_2^2 - \frac{(y_{12}^{(0)})^2}{y_{11}^{(0)}} \delta x_2^2 \\
 &= y_{11}^{(0)} \delta x_1^2 + 2y_{12}^{(0)} \delta x_1 \delta x_2 + y_{22}^{(0)} \delta x_2^2 \quad \text{Q.E.D}
 \end{aligned}$$

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Since equation (3) is a quadratic form, all the coefficients multiplying  $\delta x_k$  must be positive:

$$y_{kk}^{(k-1)} > 0 \quad k=1, 2, \dots, n+1 \quad (4)$$

Equation (4) is a set of  $n+1$  stability criteria for an  $n$ -component system, all of which must be satisfied at equilibrium.

Example: pure component,  $n=1 \rightarrow k=1, 2$

Ordering (arbitrary)  $\underline{u} = \underline{u}(S, V, N)$

$$k=1 \quad y_{11}^{(0)} = u_{SS} = \left( \frac{\partial T}{\partial S} \right)_{V, N} = \frac{T}{C_V} > 0 \Rightarrow C_V > 0$$

$$k=2 \quad y_{22}^{(1)} = A_{VV} = - \left( \frac{\partial P}{\partial V} \right)_{T, N} = \frac{1}{V K_T} > 0 \Rightarrow K_T > 0$$

Now, let's take one additional step:

$$y_{kk}^{(k-1)} = y_{kk}^{(k-2)} - \frac{(y_{k, k-1}^{(k-2)})^2}{(y_{k-1, k-1}^{(k-2)})}$$

Since  $y_{kk}^{(k-2)} > 0$  (since it is also a stability criterion), if the system is originally in a stable equilibrium region, also we must have:

$$y_{k-1, k-1}^{(k-2)} > 0$$

If  $y_{k-1, k-1}^{(k-2)}$  approaches zero, assuming that  $y_{kk}^{(k-2)}$  does not become infinitely large,

$y_{kk}^{(k-1)}$  is going to go to zero before  $y_{k-1, k-1}^{(k-2)}$

Therefore, only one condition is sufficient to determine the limit of stability, if we start from a stable region; the one that is violated first:

$k \rightarrow n \Rightarrow$  

$$y_{n+1, n+1}^{(n)} > 0$$

$$= 0$$
 for stable systems at limit of stability

Applications

Pure components:

Ordering

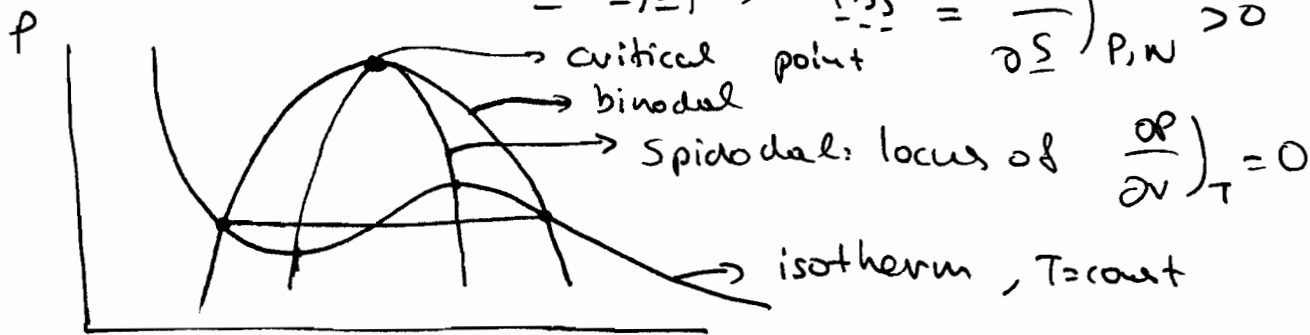
Stability criterion

$\underline{u} = \underline{u}(s, v, N)$

$\underline{A}_{vv} = - \left( \frac{\partial P}{\partial v} \right)_{T, N} > 0$

$\underline{u} = \underline{u}(v, s, N)$

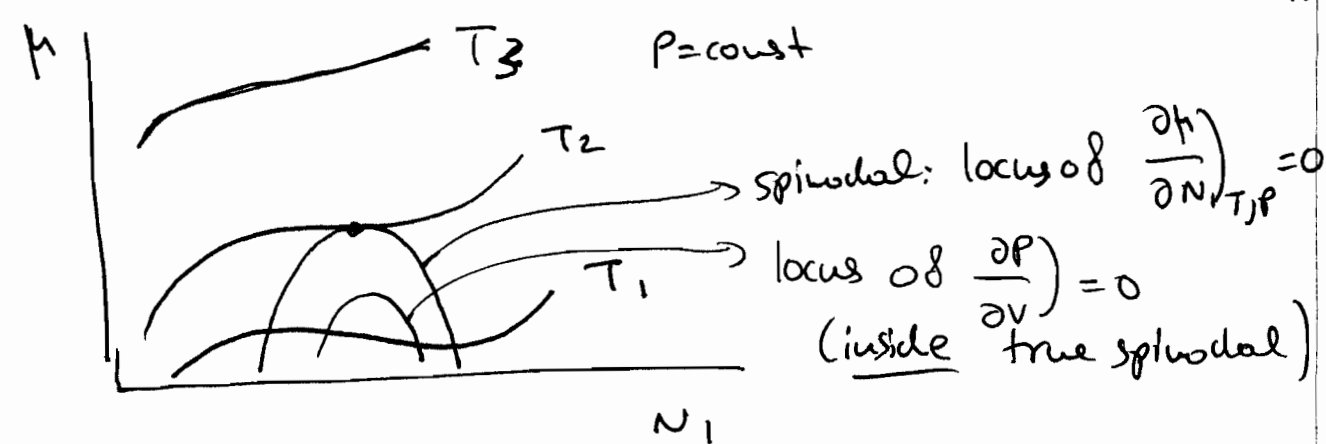
$\underline{H}_{ss} = \left( \frac{\partial T}{\partial s} \right)_{P, N} > 0$



binary systems:

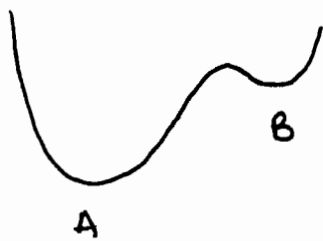
$\underline{u} = \underline{u}(s, v, N_1, N_2)$

$\underline{G}_{NN} = \left( \frac{\partial \mu}{\partial N_1} \right)_{T, P} > 0$

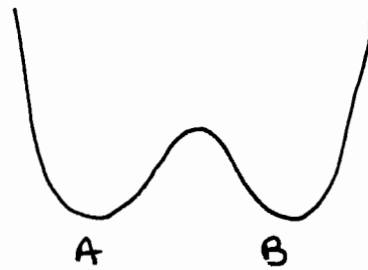


# Critical Points

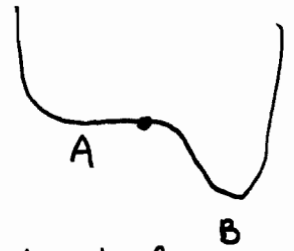
What happens if  $y_{n+1, n+1}^{(n)} = \emptyset$  for an  $n$ -component system? Normally, this is an unstable point (limit of stability):



A stable

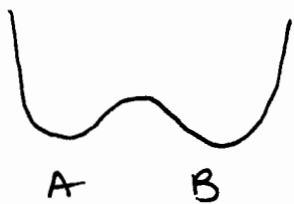


Equilibrium between A+B



Limit of Stability of A

There is, however, another possibility: If A and B start approaching each other, one gets a "critical" state



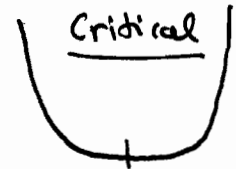
A B

→



A B

→



e.g.  $f(x) = x^4$

At the critical state, one has

$$\frac{df}{dx} = 0 \quad \frac{d^2f}{dx^2} = 0 \quad \frac{d^3f}{dx^3} = 0 \quad \frac{d^4f}{dx^4} \neq 0$$

Generalization for many-variable functions leads to the critical state condition:

$$y_{n+1, n+1}^{(n)} = 0 \quad \text{and} \quad y_{n+1, n+1, n+1}^{(n)} = 0$$

E.g. for  $n=1$ ,  $y_{22}^{(1)} = 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = 0$   $y_{222}^{(1)} = 0 \Rightarrow \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

**Example 7.2**

Determine the spinodal curves for both liquid and vapor phases of a van der Waals fluid.

*Solution*

We begin with the *PVT* van der Waals equation of state (vdW EOS) (see Section 8.3)

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

Using limiting stability criteria to define the spinodal condition, for a pure fluid ( $m = n + 2 = 3$ ), we need to evaluate both

$$y_{22}^{(1)} = A_{VV} = -\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad y_{222}^{(1)} = A_{VVV} = -\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

where  $A_{VV} = A_{VVV} = 0$  defines the liquid-vapor critical point. The spinodal curves themselves are given by  $A_{VV} = 0$ , and can be analytically determined by differentiating the vdW EOS directly:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

while at the critical point:

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

as well. We can use these two criteria to obtain values of the parameters  $a$  and  $b$  in terms of  $V_c$ ,  $T_c$ , and  $P_c$ . Doing this we get

$$b = \frac{V_c}{3} \quad \text{and} \quad a = \frac{27}{8} RT_c b = \frac{9}{8} RT_c V_c$$

Because  $V_c$  is frequently not known accurately, it is eliminated by using a third relationship, the vdW EOS itself. Now we obtain the conventional defining equation forms for  $a$  and  $b$  in terms of just  $T_c$  and  $P_c$  with  $R =$  gas constant:

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \text{and} \quad b = \frac{R T_c}{8 P_c}$$

To actually estimate the spinodal curves for a particular fluid, we would need to know  $T_c$  and  $P_c$  to calculate  $a$  and  $b$  which we would then use in the two equations  $A_{VV} = 0$  and  $A_{VVV} = 0$  along with the EOS. However, there is a much more straightforward and general approach. We can recast the vdW EOS in dimensionless form by scaling  $T$ ,  $P$ , and  $V$  with values of these parameters at the critical point. Thus, in reduced coordinates:

$$T_r \equiv T/T_c \quad P_r \equiv P/P_c \quad \text{and} \quad V_r \equiv V/V_c$$

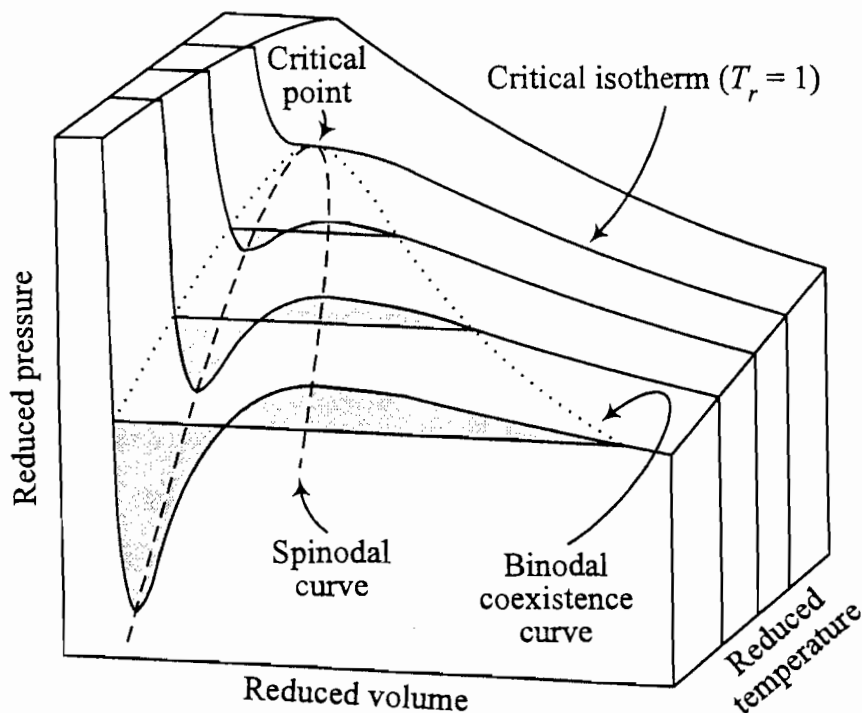
By making these substitutions, we rewrite the vdW EOS as,

$$P_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2} \quad \text{with} \quad Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

We can now develop completely general spinodal and critical point criteria following the same procedures that we used before. The results are plotted in Figure 7.6. Note that we have a cubic equation in  $V_r$ , so there are three roots. Below the critical temperature and pressure, three real roots are obtained; the largest volume root is taken as the vapor, the smallest volume root as the liquid, and the intermediate one is rejected because it is inside the unstable region. To see the three roots pick the  $T_r = 0.9$  isotherm and draw a line at a particular pressure in the vicinity of  $P_r = 0.6$ . For  $T_r > 1.0$ , there is only one real root, the two imaginary roots are discarded.

Also shown in Figure 7.6 is the equilibrium liquid-vapor binodal curve which corresponds to the condition of phase equilibrium developed in Section 6.5 where the chemical potential of the liquid and vapor phases are equal at  $T_r < 1.0$  and particular values of  $P_r$  corresponding to the reduced vapor pressure  $P_{vp,r} \equiv P_{vp}/P_c$ . Thus along the binodal or liquid-vapor coexistence curve:

$$\mu(T_r, P_{vp,r}, V_r^{liquid}) = \mu^{liquid} = \mu^{vapor} = \mu(T_r, P_{vp,r}, V_r^{vapor})$$



**Figure 7.6** PVT phase diagram for the reduced form of the van der Waals equation of state. Vapor and liquid equilibrium coexistence (binodal) lines and limits of stability (spinodal) lines shown (see Example 7.2) [produced with EOS program from Jolls (1990)].