Maxwell construction [tln31]

Goal: Study the liquid-gas transition for a fluid system described by the van der Waals equation of state.

Consider an isotherm at $T < T_c$ with roadmarks A–I as shown in [tsl11]. Determine the variation of the Gibbs potential along the subcritical isotherm:

$$dG = -SdT + V dp = V dp \;\Rightarrow\; G(T,p) = G(T,p_A) + \int_{p_A}^{p} dp\, V(p).$$

Consider the self-intersecting curve in the plot G versus p.
$G(T,p_C) = G(T,p_G)$ implies that area 1 = area 2.

Discuss stability of thermodynamic state along all segments of the curve A–I:

- Segments ABC, GHI: $\left(\dfrac{\partial p}{\partial V}\right)_T < 0$, $\quad G(T,p)$ is either the only branch or the lowest branch of a multi-valued function. The state is *stable*.
- Segments CD, FG: $\left(\dfrac{\partial p}{\partial V}\right)_T < 0$, $\quad G(T,p)$ is not the lowest branch of a multi-valued function. The state is *metastable*.
- Segment DEF: $\left(\dfrac{\partial p}{\partial V}\right)_T > 0$. This implies that the state is *unstable*.

The physical isotherm includes only stable states. It is described by the curve ABCGHI in the plot G versus p.

Stability requires that the Gibbs potential $G(T,p)$ is a concave function p and that the Helmholtz potential $A(T,V)$ is a convex function of V:

$$\left(\frac{\partial p}{\partial V}\right)_T < 0 \;\Rightarrow\; \left(\frac{\partial^2 G}{\partial p^2}\right)_T < 0, \quad \left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0.$$

Variation of the Helmholtz potential along the subcritical isotherm:

$$dA = -SdT - pdV = -pdV \;\Rightarrow\; A(T,V) = A(T,V_A) - \int_{V_A}^{V} dv\, p(V).$$

In the unstable and metastable regions, $A(T,V)$ can be made smaller if we replace the homogeneous system by a system with two coexisting phases.

Note: the (shaded) metastable region is bounded by the *coexistence* curve (solid line) and the *spinodal* curve (dashed line).