

1.11 Maxwell construction and subcritical isotherms

As shown in Fig. (1.5) the mathematical solution of the van der Waals gas equation shows two extrema while experimentally a straight line is found for slow volume changes, i.e. for changes representing thermodynamic equilibrium. For fast changes, i.e. non-equilibrium condition the features of subcritical isotherms represent

- Metastable states, i.e. $(\partial p/\partial V)_T < 0$: a-d and e-c represent states of super-heated liquid and super-cooled vapor, respectively.
- Unstable states, i.e. $(\partial p/\partial V)_T > 0$: d-e, defining the spinodal. This regime with positive slope is physically impossible, thus leading to spontaneous spinodal demixing.

For the two-phase regime the Maxwell construction replaces the isothermal loops by one isobaric straight line parallel to the V -axis for each isotherm so that equal areas are found for $adb = bec$.

The reversible expansion work performed by evaporating a liquid isothermally is represented by a STATE FUNCTION, the so-called Helmholtz free energy (F):

$$w_{rev,p,T} = \Delta F = \int_{V_a}^{V_c} p dV \quad (1.15)$$

State functions are independent from the path of change. Thus isothermal and isobaric change must give the same w_{rev} . The isobaric change is represented by a rectangle $\Delta F(a \rightarrow c)$. The height of the rectangle is adjusted so that negative (a-d-b) and positive (b-e-c) contributions of the isothermal loops cancel out. Thus F remains independent from the path as demanded for state functions.

The van der Waals equation assumes a homogeneous single phase, thus implying the inconsistencies and instabilities discussed above. The Maxwell construction implies two stable phases with the composition of points a and c simultaneously existing in the system with varying volume fractions along the line $a \rightarrow c$.

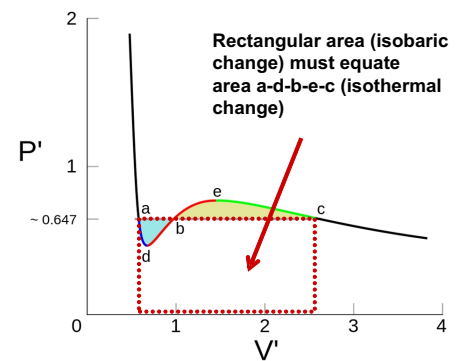


Figure 1.5: Maxwell construction for van der Waals isotherm for $T' = 0.9$