Thermodynamics of Phase Transitions II

We begin this module with a closer look at the liquid-gas transition of a fluid by briefly focusing on three aspects:

- The law of corresponding states near the critical point, as manifest in model equations of state, which looks ahead to the general feature of universality in critical behavior.
- The Maxwell construction of coexisting macrostates along the vapor-pressure curve, based on free-energy minimization and mechanical stability criteria.
- The nucleation of droplets which initiate condensation or bubbles which initiate evaporation – processes whose rates greatly differ in the regimes of metastability and instability.

Law of corresponding states:

Use the critical-point values, p_c, V_c, T_c, ρ_c, for the thermodynamic variables and introduce rescaled quantities:

$$\bar{p} \doteq \frac{p}{p_c}, \quad \bar{V} \doteq \frac{V}{V_c}, \quad \bar{T} \doteq \frac{T}{T_c}, \quad \bar{\rho}_l \doteq \frac{\rho_l}{\rho_c}, \quad \bar{\rho}_g \doteq \frac{\rho_g}{\rho_c}.$$

Empirical fact: Near the critical point, the relations between (rescaled) thermodynamic quantities exhibit features of universality as evident in experimental data (see e.g. Guggenheim plot in [tsc5]).
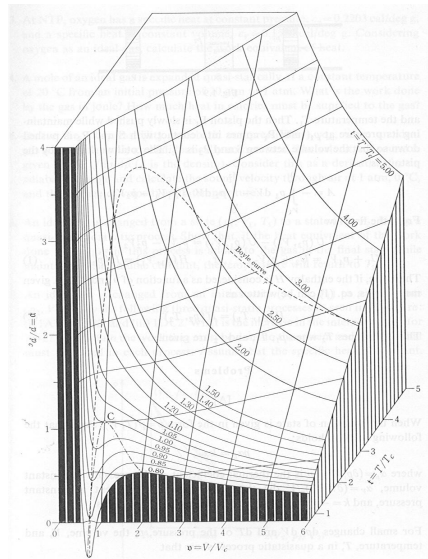
In the van der Waals equation of state,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT,$$

the critical point is identified by the two criteria of zero slope and zero curvature,

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial^2 V}\right)_T = 0.$$

The critical-point values are:

$$p_c = \frac{a}{27b^2}, \quad V_c = 3nb, \quad T_c = \frac{8a}{27bR}.$$

The two parameters a, b of van der Waals equation of state assume different values in applications to different fluids. The third parameter n is a measure for the amount of fluid.

In rescaled units, the van der Waals equation of state is parameter-free:

$$\left(\bar{p} + \frac{3}{\bar{V}^2}\right)(3\bar{V} - 1) = 8\bar{T}.$$

Each point on that universal curve corresponds to different values of p, V, T in different fluids, all close to the critical point.

Maxwell construction:

We study the (discontinuous) liquid-gas transition for a fluid system described by the van der Waals equation of state.

We begin by investigating how the Gibbs free energy varies as the fluid undergoes a quasi-static process (with road marks $A, B, \ldots, I$) along an isotherm at the subcritical temperature $T < T_c$:

$$dG = -SdT + Vdp = Vdp \implies G(T, p) = G(T, p_A) + \int_{p_A}^{p} dp\, V(p).$$
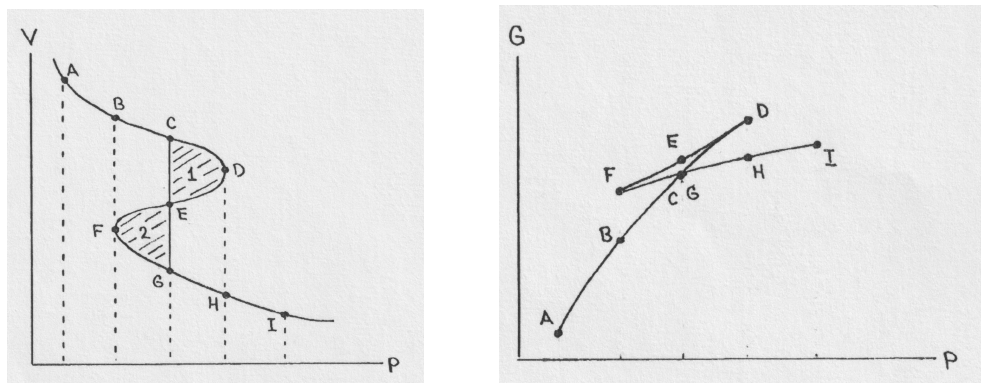
The path in the (p, V)-plane is sketched on the left and the integral is sketched on the right.

The integral is the area under curve, counted positively (negatively) when the path moves to the right (left).

The vertical line CEG is positioned such that the two shades areas are equal. The consequence is that the points C and G coincide on the right.

The Gibbs free energy $G(T, p)$ as a function of p has two concave segments $A - D$, $F - I$, and one convex segment $D - F$.

- Concavity implies $\left(\dfrac{\partial V}{\partial p} \right)_T < 0$, which indicates mechanical stability.

- Convexity implies $\left(\dfrac{\partial V}{\partial p} \right)_T > 0$, which indicates mechanical instability.

The Gibbs free energy $G(T, p)$ as a function of p is multiple-valued between road marks B and H.

- The lowest branch is thermodynamically stable.

- Higher branches are either thermodynamically unstable if they are mechanically unstable or thermodynamically metastable if they are mechanically stable.

Consequence for the isotherm under scrutiny:

- Segments ABC and GHI are thermodynamically stable.
- Segments CD and FG are thermodynamically metastable.
- Segment DEF is thermodynamically unstable.

The isotherm of a quasi-static process includes only stable states. It is described by the curve $ABCGHI$ in the (p, V)-plane.

The straight (vertical) segment describes a two-phase macrostate. During that segment, the Gibbs free energy does not change.

As noted above, mechanical stability requires that the Gibbs potential $G(T, p)$ is a concave function p:

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

The same criterion requires that the Helmholtz potential $A(T, V)$ is a convex function of V:

$$-p = \left(\frac{\partial A}{\partial V} \right)_T, \quad -\left(\frac{\partial p}{\partial V} \right)_T = \left(\frac{\partial^2 A}{\partial V^2} \right)_T > 0.$$

It is instructive to also investigate how the Helmholtzs free energy varies as the fluid undergoes a quasi-static process (with road marks $A, B, \ldots, I$) along the same isotherm at the subcritical temperature $T < T_c$:

$$dA = -SdT - pdV = -pdV \ \Rightarrow \ A(T, V) = A(T, V_A) - \int_{V_A}^{V} dv \, p(V).$$
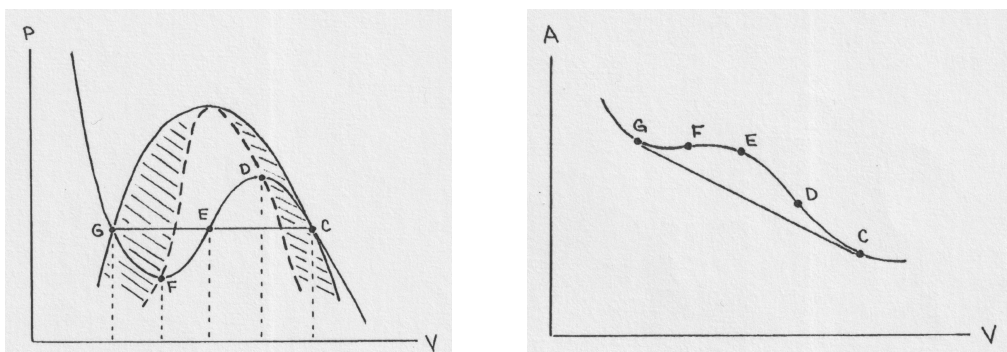
The path in the (V, p)-plane is sketched on the left and the integral is sketched on the right. In this case the function to be integrated is single-valued.

Fewer roadmarks are shown. The segments $G - F$ and $D - C$ of $A(T, V)$ versus V are convex (mechanically stable), whereas the segment FED is concave (mechanically unstable).

Mechanical stability does not guarantee thermodynamic stability. Between roadmarks G and C, $A(T, V)$ can be made smaller if we replace the homogeneous system by a system with two coexisting phases.

The straight line segment represents the coexistence with shifting volume fractions of the two phases with pressure fixed at roadmarks G and C.

This implies that the mechanically stable segments GF and DC are thermodynamically metastable.

The shaded region in the graph on the left outlines the extent of the region of metastability, not just for this particular isotherm, but for all subcritical isotherms. It is bounded by the *coexistence* curve (solid line) and the *spinodal* curve (dashed line).

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Nucleation of droplets or bubbles:

Supersaturated gases and *superheated* liquids owe their metastable existence to the surface tension σ, impeding the growth of *droplets* or *bubbles*.

Consider a liquid droplet of radius R in equilibrium with the surrounding vapor in a box of volume V_{tot} at constant temperature T:

- Thermal equilibrium: $T_l = T_g = T$.
- Chemical equilibrium: $\mu_l = \mu_g$.
- Mechanical equilibrium: $p_l > p_g$ due to surface tension.

Find the gas pressure $p_g(R)$ at equilibrium with a liquid droplet of radius R.

Work done on droplet of volume $V_l = (4\pi/3)R^3$ and surface area $A = 4\pi R^2$:

$$dW = -p_l dV_l - p_g dV_g + \sigma dA = -(p_l - p_g)dV_l + \sigma dA.$$

Condition of mechanical equilibrium: $dW = 0$

$$\Rightarrow \ (p_l - p_g)(4\pi R^2 dR) = \sigma(8\pi R dR).$$

Excess pressure in droplet: $p_l - p_g = \dfrac{2\sigma}{R}.$ \hfill (1)

Gibbs-Duhem equations (with $dT = 0$), $N_l d\mu_l = V_l dp_l, \quad N_g d\mu_g = V_g dp_g.$

Condition of chemical equilibrium: $d\mu_l = d\mu_g$

$$\Rightarrow \ \frac{V_l}{N_l} dp_l = \frac{V_g}{N_g} dp_g \ \ \Rightarrow \ d(p_l - p_g) = \frac{V_g/N_g - V_l/N_l}{V_l/N_l} dp_g.$$

Use ideal gas attributes: $\dfrac{V_g}{N_g} \gg \dfrac{N_l}{V_l}, \quad \dfrac{V_g}{N_g} \simeq \dfrac{k_B T}{p_g}.$

Excess pressure in droplet: $d(p_l - p_g) = \dfrac{k_B T/p_g}{V_l/N_l} dp_g.$ \hfill (2)

Assemble (1) and (2), then integrate:

$$\int_{p_g(\infty)}^{p_g(R)} \frac{dp_g}{p_g} = \frac{V_l}{N_l k_B T} \int_{\infty}^{R} d\left(\frac{2\sigma}{R}\right) \ \ \Rightarrow \ \ln \frac{p_g(R)}{p_g(\infty)} = \frac{2\sigma V_l}{R N_l k_B T} = \frac{2\sigma m}{R \rho_l k_B T}.$$

$$\Rightarrow \ p_g(R) = p_g(\infty) \exp\left(\frac{2\sigma m}{R \rho_l k_B T}\right).$$

In a supersaturated gas, the ambient pressure is p_{amb}. It is at equilibrium with droplets of threshold radius R_c:

$$p_{\mathrm{amb}} = p_g(R_c) > p_g(\infty).$$

Droplets of various sizes are spontaneously nucleated by thermal fluctuations. The probability of spontaneous nucleation decreases with size.

Droplets with $R < R_c$ will shrink and disappear. Droplets with $R > R_c$ will grow and initiate condensation.

Metastability depends on the absence of droplets with radius $R > R_c$. The boundary of the metastable region (spinodal line) corresponds to a value of R_c comparable to the molecular radius. Supersaturation cannot be pushed beyond that point.
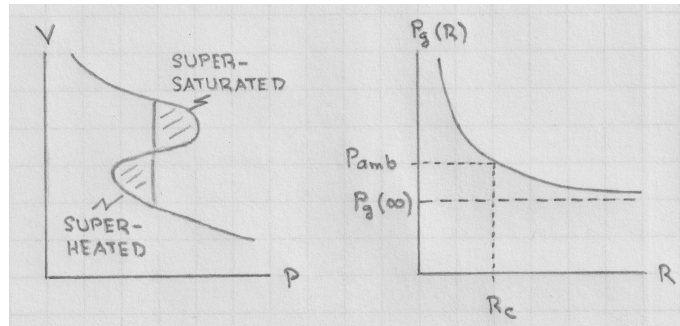
For a vapor bubble surrounded by superheated liquid, the argument proceeds along analogous lines. Bubbles are nucleated spontaneously, small bubbles at a higher rate than larger bubbles.

Bubbles above a certain threshold size must be present for evaporation to be initiated. The threshold size shrinks with increased superheating.