

Review of Thermodynamics. 5: Phase Equilibrium and Phase Transitions

Phases of Single-Component Systems

- *Idea:* Many single-component systems can exist in different physical forms or phases. For a substance made of non-magnetic atoms, for example, the possible phases are solid, liquid, gas—but also plasma and Bose-Einstein condensate at very high or low T , respectively. How can we characterize each phase thermodynamically? In a fluid, a formal definition can be obtained from the convergence properties of virial expansions in ρ . Physically, we can consider each phase as a region of state space with a different type of equation of state. In particular, for a liquid the compressibility $\kappa_T = -(V \partial p / \partial V)^{-1}$ is much smaller than for a gas, since the isothermal lines in the p - V plane have a very large negative slope.

- *Goal:* For the time being we will focus on fluids, for which each phase is a different relationship among (p, V, T) , and determine which regions of the p - V state space each phase occurs in, and those in which phases can coexist. Our main example here will be the van der Waals gas; later we will consider the magnetization phases for a ferromagnet, in which each phase is a different relationship among (\vec{H}, \vec{M}, T) .

Conditions for Equilibrium

- *Second law reminder:* One consequence of the variational form of the second law is that, for a system partitioned into two parts, the equilibrium state the system adopts without any internal constraints minimizes the energy $E = E^{(1)} + E^{(2)}$ with respect to all virtual variations in which each part satisfies the first law.

- *Temperature:* Consider a system consisting of two subsystems 1 and 2 in thermal equilibrium, and impose an internal constraint by which $S_1 \mapsto S_1 + \delta S$ and $S_2 \mapsto S_2 - \delta S$, but no work is done on the two parts. Now the system is not in its unconstrained equilibrium state, so $\delta E \geq 0$, with $\delta E = \delta E_1 + \delta E_2 = (T_1 - T_2) \delta S$, so $(T_1 - T_2) \delta S \geq 0$. But we can repeat the argument switching 1 and 2, so consistency requires $T_1 = T_2$.

- *Pressure:* Divide a system in equilibrium at T into two parts and impose an internal constraint that changes their volumes, with $V_1 \mapsto V_1 + \delta V$ and $V_2 \mapsto V_2 - \delta V$. Using a similar argument to the one for T , for all δV we must have $\delta E = \delta E_1 + \delta E_2 = -(p_1 - p_2) \delta V + \dots \geq 0$, so consistency requires that $p_1 = p_2$.

- *Chemical potential:* Divide a system in equilibrium at T into two parts and impose an internal constraint that changes the number of particles in each part, with $N_1 \mapsto N_1 + \delta N$ and $N_2 \mapsto N_2 - \delta N$. Again, we must have $\delta E = \delta E_1 + \delta E_2 = (\mu_1 - \mu_2) \delta N + \dots \geq 0$ for all δN , so for consistency $\mu_1 = \mu_2$. Notice that, since $G = \mu N$, the equality of G at the values of (p, V) corresponding to the phase transition implies $\mu_1 = \mu_2$.

Types of Phase Transitions

- *Critical points:* The liquid-gas phase transition for a van der Waals gas has a critical point, above which no transition occurs. This is a common feature for liquid-gas transitions, where at high pressures/temperatures the fluid varies smoothly from one phase to the other, but does not occur usually in solid-liquid phase transitions, which involve the establishment of long-range correlations.

- *First-order phase transitions:* The ones that occur when there is a discontinuity in the first derivative of a thermodynamic potential. For example, in the van der Waals case and in other liquid-gas transitions the volume per particle is discontinuous, so the phase transition is first-order. These transitions involve the release or absorption of latent heat and may not happen all at once—the two phases can coexist.

- *Second-order phase transitions:* The ones that occur when the lowest derivative of a thermodynamic potential that has a discontinuity is the second one. For example, a discontinuity in the compressibility κ_T , but not in the volume V , would signal a second-order phase transition. An important example is that of ferromagnetic materials. The susceptibility for a paramagnetic or ferromagnetic material is defined as

$$\chi(T, B) = \frac{\partial \bar{M}}{\partial B} = N \mu \frac{\partial \langle s \rangle}{\partial B} .$$

In a ferromagnet, as one finds out from the mean-field approximation and Monte Carlo simulations (based on the Ising model, for example), there is a second-order transition at which χ is discontinuous (in the infinite-size or thermodynamic limit), between an unmagnetized phase and a magnetized one with long-range order.

Phase Boundary / Coexistence

- *Setup*: Suppose that a one-component fluid has two phases that can coexist at some (T, p) . Then those values are on the boundary $p = p_0(T)$ between two regions in the T - p plane in which the system has two different equations of state of the form $\mu = \mu_1(T, p)$ and $\mu = \mu_2(T, p)$. On the boundary, however, because the two phases coexist in equilibrium there, we have $\mu_1(T, p_0(T)) = \mu_2(T, p_0(T))$. Using this condition, we want to find an equation that determines that line in terms of measurable quantities for the fluid.

- *Clausius-Clapeyron equation*: To obtain an equation for the separating line $p_0(T)$, consider the equilibrium condition $\mu_1(T, p_0(T)) = \mu_2(T, p_0(T))$, and take the T derivative of both sides. We get

$$\left. \frac{\partial \mu_1}{\partial T} \right|_p + \left. \frac{\partial \mu_1}{\partial p} \right|_T \frac{dp_0}{dT} = \left. \frac{\partial \mu_2}{\partial T} \right|_p + \left. \frac{\partial \mu_2}{\partial p} \right|_T \frac{dp_0}{dT},$$

which, using $dG = -S dT + V dp + \mu dN$ with $G = \mu(T, p)N$, so $s = -\partial\mu/\partial T|_p$ and $v = \partial\mu/\partial p|_T$, becomes

$$\frac{dp_0}{dT} = \frac{\Delta s}{\Delta v} = \frac{Q_{\text{latent}}}{T\Delta V}, \quad \text{the Clausius-Clapeyron equation .}$$

Notice that it allows us to find ΔS just from measurements of V , p and T .

- *Remark*: For a second-order phase transition with $\Delta V = 0$, one uses the Ehrenfest equations instead.

Phase Transitions

- *Setup*: We saw how to find the phase coexistence line in the p - T plane, by integrating the Clausius-Clapeyron equation $dp_0(T)/dT = \Delta s/\Delta v$. Now we look at phase transitions in more detail, and in particular see if using the equation of state in the form $p = p(V, T)$ we can predict under what conditions transitions will occur. (Notice that phase transitions are very far from the behavior of ideal gases, so we cannot assume that the fluid is close to an ideal gas and use, for example, a virial expansion of the equation of state.)

- *Liquid-gas phenomenology*: If we follow the behavior of a fluid along an isothermal line in the p - V plane, the discontinuity in V at the phase transition is more obvious, and we can also clearly see the difference with respect to an ideal gas. Consider the isothermal lines of the van der Waals gas in the p - V plane, considered here as representative of a real gas situation. If we imagine starting in the liquid phase at $T < T_c$, and lowering p by increasing V isothermally, when p reaches the value $p_0(T)$, some of the fluid starts becoming gas and increases its volume, without lowering p further until all of it is gas. How can we determine which of the phases allowed by the equation of state a fluid will actually be in, at given T and p ? How can we find the values of $p_0(T)$ and ΔV in terms of the $p(V, T)$ equation of state?

- *The Maxwell construction*: Start from the fact that

$$dG = -S dT + V dp + \sum_i \mu_i dN_i,$$

with G minimized in stable equilibrium, and phase coexistence occurs when the chemical potentials coincide, with $G = \mu N$. Then one can find the pressure $p_0(T)$ at which the transition happens and V_A , V_B from

$$\Delta G = \int_A^B V(p, T) dp = 0.$$

The volume change ΔV and pressure p_0 are then also related by $p_0(T) \Delta V = \int_A^B p(V, T) dV$.

Reading

- *Kennett*: There is no specific chapter on phase transitions in thermodynamics.
- *Other books*: Chandler, Sec 2.3 (37-44); Halley, first half of Ch 9 (pp 161-172); Mattis & Swendsen, Secs 3.6-3.8; Plischke & Bergersen, Secs 1.8 and 4.4 [for the Maxwell construction]; Pathria & Beale, Secs 12.1 and 12.2; Reichl, Ch 4; Reif, Secs 8.5-8.10; Schwabl, Secs 3.8-3.9.