General Considerations

• *Systems:* We will consider single-component systems, which can exist in different physical forms or phases. In terms of their thermodynamic description, each phase corresponds to a different equation of state, a relationship among the extensive and intensive variables $(\vec{f}, \vec{X})$, each one being valid in a different region of state space. Two of the most common examples are the solid-liquid-gas phases of a substance, in which each phase is a different relationship among (p, V, T), and the magnetization phases for a ferromagnet, in which each phase is a different relationship among $(\vec{H}, \vec{M}, T)$. [* plot *]

• *Goal:* We will focus on the former example, the solid-liquid-gas phases, and determine which regions of state space each phase occurs in, and those in which phases can coexist. The space of states can be represented as the p-T plane.

Conditions for Equilibrium

• *Reminder of second law:* One consequence of the variational form of the second law of thermodynamics can be stated as saying that, for a system partitioned into two parts 1 and 2, 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 of the two parts satisfies the first law.
• *Temperature:* Divide a system in equilibrium at T into two parts and impose an internal constraint that transfers some entropy from one to the other, with $S_1 \mapsto S_1 + \delta S$ and $S_2 \mapsto S_2 - \delta S$. Because now the system is not in its unconstrained equilibrium state, $\delta E \geq 0$ for all δS. But $\delta E = \delta E_1 + \delta E_2 = (T_1 - T_2)\, \delta S + ...$, 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 $\delta E = \delta E_1 + \delta E_2 = -(p_1 - p_2)\, \delta V + ... \geq 0$, 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 $\delta E = \delta E_1 + \delta E_2 = (\mu_1 - \mu_2)\, \delta N + ... \geq 0$ for all δN, so consistency requires that $p_1 = p_2$.

Phase Coexistence

• *Setup:* Suppose that a one-component fluid can be in two different phases coexisting at some (T, p). Then those values form 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:* Consider the chemical potential equilibrium condition, $\mu_1(T, P_0(T)) = \mu_2(T, P_0(T))$, and take the T derivative of both sides. We get

$$\frac{\partial \mu_1}{\partial T}\Big|_p + \frac{\partial \mu_1}{\partial p}\Big|_T \frac{\partial P_0}{\partial T} = \frac{\partial \mu_2}{\partial T}\Big|_p + \frac{\partial \mu_2}{\partial p}\Big|_T \frac{\partial P_0}{\partial T}\ ,$$

which, using $\mathrm{d}G = -S\, \mathrm{d}T + V\, \mathrm{d}p + \mu\, \mathrm{d}N$ with $G = \mu(T, p)N$, so $s = -\partial\mu/\partial T|_p$ and $v = \partial\mu/\partial p|_T$, becomes

$$\frac{\mathrm{d}P_0}{\mathrm{d}T} = \frac{\Delta s}{\Delta v} = \frac{Q_{\text{latent}}}{T\Delta V}\ , \qquad \text{the Clausius-Clapeyron equation}\ .$$

Notice that it allows us to find ΔS just from measurements of volume, pressure and temperature.

Relevant Sections: [Phys 731]; Chandler, Ch 2; Halley, pp 161-172; Reif; Schwabl, Sec 3.8-3.9.