Application of 2nd law of thermodynamics to liquid-gas phase transition.

Preliminaries: * systems with variable particle numbers; * chemical potentials; * Gibbs-Duhem equation

\[ U = U(S, V, \sum N_i) \]

\[ dU = TdS - pdV + \sum_i \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_i} dN_i \]

\( \mu_i \) - chemical potential of species \( \text{i} \)

(-generalized force corresponding to \( N_i \); \( \mu_i \) - intensive quantity)

- Helmholtz free energy

\[ F(T, V, \sum N_i) = U - TS \]

\[ dF = -SdT - pdV + \sum_i \mu_i dN_i \]

\( \Rightarrow \) \( \mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T, V, N_i} \)

- general property when taking derivatives over "untouched" variables under Legendre transform

- Gibbs free energy

\[ \Theta(T, p, \sum N_i) = U - TS + pV \]

\[ d\Theta = -SdT + Vdp + \sum_i \mu_i dN_i \]

\( \mu_i = \left( \frac{\partial \Theta}{\partial N_i} \right)_{T, p, N_i} \)
Gibbs-Duhem relation

\[ U(S, V, \sum N_i) \] extensive function of extensive variables \( S, V, \sum N_i \)

\[ U(\lambda S, \lambda V, \sum \lambda N_i) = \lambda U(S, V, \sum N_i) \]

Differentiate \( u \) wrt \( \lambda \) and set \( \lambda = 1 \) \( \Rightarrow \) Euler's theorem on homogeneous functions:

\[
\left( \frac{\partial U}{\partial S} \right)_{V, N_i} + \left( \frac{\partial U}{\partial V} \right)_{S, N_i} V + \sum_i \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_{i \neq i}} N_i = U
\]

\[
\frac{T}{\mu_i} - p
\]

\[ TS - pV + \sum \mu_i N_i = U \]

\( \Rightarrow \)

\[ G = U - TS + pV = \sum \mu_i N_i \]

In differential form:

\[
dG = -SdT + Vdp + \sum \mu_i dN_i = \sum (\mu_i dN_i + d\mu_i N_i)
\]

\[
SdT - Vdp + \sum N_i d\mu_i = 0 \]

- shows that intensive variables \( T, p, \sum \mu_i \) are not all independent.

\( c \)-component system has \( c + 2 - 1 = c + 1 \) independent variables.

For one-component system

\[ G = \mu N, \quad \mu = \frac{G}{N} \] - chemical potential is
Gibbs free energy per particle
Liquid-gas transition

Experimental facts: along the coexistence segment, the liquid remains in the same state as @1 and the gas remains in the same state as @2, only the proportions change.

\[ N_{\text{total}} = N_1 + N_2 = N = \text{const} \]

\[ G = \mu_1 N_1 + \mu_2 N_2 = \mu_1 N_1 + \mu_2 (N-N_1) \] - must be minimum

\[ \left. \left( \frac{\partial G}{\partial N_1} \right) \right|_{T, P, N} = \mu_1 - \mu_2 = 0 \]

\[ \mu_1 = \mu_2 \]
Using the second law of thermodynamics, one can relate the $T$-dependence of $P_{\text{coexist}}(T)$ to measurable quantities like latent heat and change in volume per particle between gas and liquid.

**Phase 1 (liquid @ 1):**

\[ S_1 \, dT - V_1 \, dp + N_1 \, d\mu_1 = 0 \]

\[ d\mu_1 = \frac{1}{N_1} \left( -S_1 \, dT + V_1 \, dp \right) = \]

\[ = -S_1 \, dT + \frac{V_1}{N_1} \, dp \]

- Entropy per particle
- Volume per particle

**Phase 2 (gas @ 2):**

\[ \mu_2 = -S_2 \, dT + V_2 \, dp \]

**Coexistence condition:**

\[ d\mu_1 = d\mu_2 \]

\[ -S_1 \, dT + V_1 \, dp = -S_2 \, dT + V_2 \, dp \]

\[ \frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\ell}{T(V_2 - V_1)} - \text{Clapeyron equation} \]

**Coexistence ($T$)**

\[ \ell = T'(S_2 - S_1) - \text{latent heat per particle} \]

**Approximation:**

\[ V_{\text{gas}} = V_2 = \frac{V}{N} = \frac{k_B T}{P} \]

- Nearly ideal

\[ V_1 = V_{\text{liquid}} \approx 0 \]

\[ \frac{dp}{dT} = \frac{\ell P}{k_B T^2} \]

\[ \frac{dp}{P} = \frac{\ell}{k_B} \frac{dT}{T^2} \]

\[ \ln \frac{P}{P_0} = \frac{\ell}{k_B} \left( \frac{1}{T^2} + \frac{1}{T_0^2} \right) - \text{Clapeyron equation} \]
\[ p = p_0 \exp \left[ -\frac{E}{k_B \left( \frac{1}{T} - \frac{1}{T_0} \right)} \right] \]

Remark: we used thermodynamic potentials (Gibbs potential) to obtain the Clapeyron equation. The ability to use such potentials is provided by the existence of entropy as state function and ultimately by the 2nd law of thermodynamics.

If the Clapeyron equation were not true, one could trace back our "construction" of thermodynamics and conclude that \( E \) engine violating second law—operating here near liquid-gas interface.

— this is often how one "derives" the Clapeyron equation by building a Carnot engine out of liquid-gas system.

\[ \delta Q = L \cdot dN \]
\[ \delta W = dp \cdot dV = dp \cdot dN \cdot (v_2 - v_1) \]
\[ \frac{\delta W}{\delta Q} = \frac{(v_2 - v_1) dp}{L} = \frac{dT}{T} \]
\[ \text{Carnot!} \]