Phase Coexistence & First-Order Phase Transitions

Ice Water: $T_c = 0°C$ at $P_{atm}$

Boiling Water: $T_c = 100°C$ at $P_{atm}$

Review of Thermodynamics

Microcanonical Ensemble
- Closed, Constant $V, E, N$
- $S = \frac{\rho}{\Omega}$ Phase Space Volume
- $S = k_B \log \Omega$ maximum

$\frac{\delta S_1}{\delta E_1} = \frac{\delta S_2}{\delta E_2}$

$\Rightarrow \frac{1}{4} = \frac{\delta S_1}{\delta E_1} = \frac{1}{4} = \frac{\delta S_2}{\delta E_2}$

Equation of State: Surface in $3D$ VSM Space

$E(S, V, N)$

$dE = T dS - pdV + \mu dN$
Canonical Ensemble

- Heat Bath, Temperature $T$
  - $Z = \sum e^{-\beta H}$ (AKA $F$)
  - $A(T,V,N) = -kT \log Z = E - TS$
  - (Total System: Liquid, Gas separately)

- $\frac{A}{T} = \frac{E}{T} - S \Rightarrow S_{\text{maximum}} \Leftrightarrow A_{\text{minimum}}$

- Entropy Flow from Environment "Cost"

- $dA = dE - TdS - SdT = -SdT - pdV + \mu dN$
  - $\Rightarrow \frac{\partial A}{\partial V}_{T,N} = -P$

- Boundary moves to minimize $A$
  - $P_1 = P_2 \Rightarrow \left. \frac{\partial A}{\partial V_1} \right|_{T,N} = - \left. \frac{\partial A}{\partial V_2} \right|_{T,N}$
Gibbs Ensemble

- Heat Bath & Piston $P$
- $G(T, p, N) = A + PV = E - TS + PV$
- $G$ minimized at equilibrium
  \[ G = -kT \log \sum S dV \frac{Tr e^{-\beta (H(V) + PV)}}{\beta} \]
- Euler equation $E = TS - pV + \mu N$
  \[ \rightarrow G = \mu N \]

Good thing! Boundary between liquid & gas moves to equalize $T, P \Rightarrow$ automatically equalizes chemical potential. Particle transfer across boundary agrees...

- At constant pressure, $T, N$, no two-phase region

\[ \rightarrow \text{Whichever phase has lower } G \text{ wins.} \]
\[ dG = -SdT + Vdp + \mu dN \]

\[ \Rightarrow \frac{\partial G}{\partial T} |_{V,N} = -S \]

- Talk about resonances in QM

\[ S_{\text{liquid}} < S_{\text{gas}} \]

**"Coarse Grained" Gibbs Free Energy Density**

\[ G_{\text{gr}}(p(x), T, p) = -kT \log \left\{ \text{Tr} e^{-\beta(H(U)-pV)} \right\} \]

\[ G(N, T, p) = F(N, T, V) + PV \]

\[ \mu(p, T, p) = \beta\left(F(p(x), T, V(T, P)) + P\right) \]
What about spatially dependent densities $p(x)$? Can we write the probability of having a state $p(x)$

$$P[p(x)] \propto e^{-\beta \int p(x) \, dV}$$

- Fluctuations in density
- Correlation Functions $C(r,t)$
- Susceptibilities $\chi(r,t)$

**Interfaces:**

\[ P_e \quad \text{Liquid} \quad \leftarrow \quad \text{Surface} \quad \rightarrow \quad \text{Gas} \]

Surface Tension

\[ \frac{G(\frac{LSC}{v_i v_j}) - G(\frac{G_1}{v_i}) - G(\frac{G_2}{v_2})}{\text{Area}} \]

Writable as calculus of variations?
Problem: At constant pressure, volume isn't fixed, so Gibbs energy per unit volume not the right variable.

Instead, we can use Gibbs energy per particle

\[ \mu = \frac{G}{N}. \]

How do we define \( \mu(p(x), T, p) \)?

At a given pressure, \( p \) is fixed in equilibrium.

- Know \( G(T, p, N) = -kT \log \left[ S \Delta V \text{ Tr} e^{-\frac{B(H_v + PV)}{kT}} \right] \)

- Partial Trace: Hold volume at fixed (non-equilibrium) value.

\[ G_{PT}(T, p, N', V) = -kT \log \text{ Tr} (e^{-\beta(H_v + PV)}) \]

\[ (e^{-\beta G} = \int e^{-\beta \mathcal{E}(\mathcal{G})} dV) \]

- Chemical Potential \( G = \mu N \)

\[ G_{PT}(T, p, N', V) = \mu(T, p, N', V) N \]

Depends only on \( N/V = p \)

\[ = \mu(p, T, p) N. \]
Probability of having a uniform density
\[ p(x) \equiv p = N/V \] away from equilibrium \[ N/V(p) \]

\[ P(p) \propto e^{-\beta G_{PT}} = e^{-\beta N\mu(p, T, p)} \]

\[ = e^{-\beta V(N/V)\mu(p, T, p)} = e^{-\beta V p\mu(p, T, p)} \]

\[ = e^{-\beta \int d^3x \rho \mu(p, T, p)} . \]

Obvious generalization to general \( p(x) \)

\[ P(p) \propto e^{-\beta \int d^3x \rho(x) \mu(p(x), T, P)} \]

Problem 6.2:

Convexity!

Barrier only for local, uniform density

Phase separates for large systems.

First order phase transition

⇒ "Double-well potential" for coarse-grained free energy (μ)

⇒ Jump from one well to another

• Surface tension between phases
  Energy to cross barrier (as in 5.3: Bloch wall)