10. Phase Transformations

Homework  Chapter 9, Prob. 2, 5
          Chapter 10, Prob. 1, 2, 3, 5

Phase transitions: Most active subject of research in modern statistical physics

Basic phenomenon — small change in a variable (e.g. \( T \)) causes large qualitative change in equilibrium configuration

Examples:
- Water (at \( p = 1 \) atm)
  - ice-liquid at 0 \( ^\circ \) C
  - liquid-steam at 100 \( ^\circ \) C
- Conductor-insulator transition
- \( \text{O}_2 \) \text{g} \text{ase} \rightleftharpoons \text{O}_2 \text{molecule}
  - Ferromagnetism (iron won't magnetize above critical temp)
  - Superfluidity (7.17 K in \text{He}^4)
  - Superconductivity ("High - Tc")

Mathematics:
- Hallmark of phase transition is discontinuous behavior (compare \( \frac{\partial \rho}{\partial T} \))
- \[ \mathcal{Z} = \sum_{\text{states}} e^{-E_{\text{stat}}/T} \]
  - must have discontinuous derivatives
This means that sum must be infinite
strictly speaking phase transitions can only occur
in volume $V \to \infty$.
In practice rounding off discontinuity due to
finite volume may be unobservable.

Two things to investigate:

1) How much can we understand about
phase transitions using thermodynamics,
without worrying about details of a microscopic
picture.

2) How do we understand phase transitions from
a fundamental, microscopic point of view,
fig. calculate $T_c$, $\mu$, etc. from first
principles.

Coexistence of Phases

Example: 3 phases of water
At given pressure, 2
phases can be in stable
contact (in equilibrium)
only at particular transition
temperature.

Or -- fix $T$ and vary
available volume --

\[ \text{ice} \quad \text{water} \quad \text{steam} \]

Critical point $647^\circ K$

Kip LEVEL $T = 273.16^\circ K$
At sufficiently high T (or p), there is no coexistence of liquid and gas.

At a given T, liquid coexists with vapor at a particular pressure.

Gas and liquid are in thermal equilibrium (same T) or in mechanical equilibrium (same p) in a container with movable walls.

Coexistence Curve:

How does p at coexistence vary with T?

\[ \mu_L(p, T) = \mu_G(p, T) \]

One condition determines a curve in p-T plane. Find slope of the curve.
\[ p \Rightarrow m_e (p + dp, \tau + d\tau) = m_e (p + dp, \tau + d\tau) \]

\[ \Rightarrow \left[ \left( \frac{\partial m_e}{\partial \tau} \right)_p - \left( \frac{\partial m_e}{\partial p} \right)_\tau \right] dp = \left[ \left( \frac{\partial m_e}{\partial p} \right)_\tau - \left( \frac{\partial m_e}{\partial \tau} \right)_p \right] d\tau \]

\[ \Rightarrow \frac{dp}{d\tau} = \frac{\left( \frac{\partial m_e}{\partial \tau} \right)_p - \left( \frac{\partial m_e}{\partial p} \right)_\tau}{\left( \frac{\partial m_e}{\partial p} \right)_\tau - \left( \frac{\partial m_e}{\partial \tau} \right)_p} \]

Recall Gibbs free energy (Chapter 9)

\[ G(\tau, p, N) = N \mu(\tau, p) \]

and \( \left( \frac{\partial G}{\partial p} \right)_\tau, N = \nabla, \left( \frac{\partial G}{\partial \tau} \right)_p, N = -\beta \)

If we denote \( v = V/N \quad s = S/N \)

then \( \left( \frac{dp}{d\tau} \right)_{H, \tau} = \frac{s - s_e}{s_e - s_H} \)

can relate as to latent heat

\[ Q = \tau \Delta H \quad \text{or} \quad L = \tau \Delta s \quad \text{is amount of heat (per particle) required to boil ke/kmol} \]
So \[ \left( \frac{dP}{dT} \right)_\text{cpx} = \frac{7}{2} \Delta \sigma \] is the Clapeyron Eqn (which is well verified)

This applies to water-ice transition as well. Note: \( \Delta S < 0 \) (ice floats)
\( \Delta S > 0 \) (need heat to melt ice)

Here \( \left( \frac{dP}{dT} \right)_\text{cpx} < 0 \).

Pressure lowers the coexistence temperature (unusual) which is why we can skate on ice.

Vander Waals Equation of State (1873)

We'll consider how interactions among gas molecules modify the ideal gas relation \( pV = nRT \). This will lead us to a crude model of the gas-liquid phase transition.

\[ \text{potential energy} \]

\[ \text{long-range attraction} \]

\[ \text{short-range repulsion} \]

Effect of KS hard core: \( V \rightarrow V-N \delta \)
Exclude some volume (\( \delta = \text{vol. per particle} \))
Effect of re-attraction:
\[ U = \sum_{\text{pairs}} V_{\text{pair}} = \frac{1}{2} \int d^3x d^3y n(x) n(y) V(x-y) \]

Foot density as uniform, \( n = \) constant
"Mean field theory" ignores density fluctuations
\[ = n^2 V_0 \int d^3x \overline{N} = -a \frac{N^2}{V} \]
Correction to the pressure: \( p = \frac{\partial U}{\partial V} = -a \frac{N^2}{V} \)

So:
\[ \rho V = N \overline{N} \]
\[ \Rightarrow P = \frac{N \overline{N}}{V-Nb} - a \frac{N^2}{V} \]

Vande Waals equation

This is reasonable approximation when gas is close to ideal (\( \overline{N}/N \) sufficiently small)
but we will use it (without justification)
even when corrections to ideal behavior are big (e.g., when gas liquefies)
Van der Waals Equation of State

Idealize: not hard core

\[ \text{Excluded Volume} \rightarrow \text{separation} \]

\[ V \rightarrow V - N b \quad b = \text{well per particle} \]

Effect of attraction

\[ \Delta U = \sum_{\text{pairings}} V_{ij} \]

\[ = \frac{1}{2} \int d^3x d^3y \quad \eta(x) \eta(y) \quad V(\mid x - y \mid) \]

Many fold theory - treat density as uniform, ignoring fluctuations

\[ = \frac{1}{2} n^2 V \int d^3x \quad V(x) = -a \frac{n^2}{V} \]

(a > 0, because potential energy is negative)

Some write

\[ F_{\text{vdw}} = F_{\text{ideal}} (V-Nb) - a \frac{n^2}{V} \]

\[ = - NT \ln \left[ \frac{V-Nb}{N} \right] - a \frac{n^2}{V} \]

Pressure

\[ p = -\left( \frac{\partial F}{\partial V} \right)_T N = \frac{NT}{V-Nb} - a \frac{n^2}{V} \]

(over)
We have
\[
(p + \frac{N^2}{v^2} a)(V-N6) = NT
\]

It is not to be taken too seriously. At best an approximation that applies to sufficiently dilute gas. Without justification, we will apply it to dense gas.
For given $p$ and $r$, what is $V$? Solve a cubic equation
\[(V^2 + \frac{N^2 a}{p})(V - N b) = N \frac{c}{p} V^2\]

(we multiplied both eqns by $V^2/p$)

\[V^3 - (N b + \frac{N c}{p}) V^2 + \frac{N a}{p} V - N^3 b = 0\]

Has either one or 3 real solutions.

In terms of $p$.

As we'll soon see, can regard $p, \theta, \phi$ as an $F$-plane of first-order phase transitions in $p, r$ plane.

Lots done for $p, \theta, \phi, V, N$ terms of $N, a, b$.

At critical point: $(V - V_c)^2 = 0$.

equation shows 3 different solutions.
\[
\text{Expand: } V^3 - 3VcV^2 + 3Vc^2V - Vc^3 = 0
\]

\text{Equate:}

1. \[3Vc = N_6 + N_{6c}/\rho_c\]
2. \[3Vc^2 = \frac{N_{6c}^2}{\rho_c}\]
3. \[Vc^3 = \frac{N_{6c}^3}{\rho_c}\]

\text{Divide (3) by (2): } \frac{Vc}{\sqrt{3}} = N_6 \text{ or } \frac{\sqrt{Vc}}{\sqrt{3}} = 3N_6

\text{(Three times excluded volume)}

\[27N_{6c}^2 - N_{6c}/\rho_c \]
\[\Rightarrow \rho_c = \frac{a}{276^2}\]

\[\Rightarrow \tau_c = \frac{\rho_c}{N} \left(3Vc - N_6\right) = \frac{a}{276^2} \times 86 = \frac{8a}{276} = \tau_c\]

\text{Now we can eliminate } a, b, N \text{ and reexpress vdW eqn in terms of } Vc, \rho_c, \tau_c:

\[
\left(\frac{Vc - N_6}{Vc}\right)\left(\frac{\rho_c + \frac{Vc^2}{Vc^2} + \frac{N_{6c}^2}{\rho_c}}{Vc}\right) = \frac{\tau_c}{Vc} \frac{N_{6c}}{Vc^2\rho_c}
\]

\[\frac{N_6}{Vc} = \frac{1}{3} \text{; } \frac{N_{6c}^2}{Vc^2\rho_c} = \frac{a}{96^2} = \frac{276^2}{a} = \frac{3}{3}
\]

\[\frac{N_{6c}}{Vc^2\rho_c} = \frac{8a}{276} \times 86 \times \frac{a}{276^2} = \frac{8}{3}\]
We have
\[
\frac{V}{V_c} \left( \frac{P_c}{P} + 3 \left( \frac{V_c}{V} \right)^2 \right) = \frac{\Delta S}{\Delta V_c}
\]

- The Law of Corresponding States

Correction to ideal gas law takes "universal" form (same for all gases) can be expressed in terms of "critical" values.

 Doesn't work all that well, nor should it.

**The Maxwell Construction**

Consider xi-form
for \( T < T_c \)

there is a region with

\[ \frac{dp}{dV} > 0 \]

\[ \text{Note } \xi = -\frac{1}{V} (\frac{dV}{dp}) \]

and is significance of fluid.

Instability

Mathematically: system + reservoir change volume \( V \)

to minimize Helmholtz free energy \( F \)

\[ dF = \left[ (\frac{dE_{sys}}{dV}) |_{\xi} - (\frac{dE_{res}}{dV}) |_{\xi} \right] dV_{sys} = 0 \]

\[ \text{so } P_{sys} = P_{res} \quad \left( p = -\frac{\partial F}{\partial (\Delta V)} \right) \]

But for this to be minimum, need \( \frac{d^2F}{dV^2} > 0 \)

\[ \text{(over)} \]
\[-\frac{\partial}{\partial V_{\text{sys}}}(P_{\text{sys}} - P_{\text{env}}) > 0\]

\[\frac{\partial P_{\text{env}}}{\partial V} < 0\]

So

\[-\frac{\partial P}{\partial V} > 0\]

physically

If we push a little harder, the system pushes back less. More \(\Rightarrow\) it will collapse.
incidentally, a similar stability criterion applies to heat transfer

\[ dS = \left( \frac{\partial S_{sys}}{\partial U} \right)_{sys} \ dU_{sys} \]

\[ = \left( \frac{1}{T_{sys}} - \frac{1}{T_{res}} \right) \ dU_{sys} \Rightarrow T_{sys} \ >> \ T_{res} \]

must \( dS \geq 0 \) needed, if entropy is maximized

\[ \frac{\partial S_{sys}}{\partial U} = 0 \]

\[ \Rightarrow \frac{\partial}{\partial U} \left( \frac{1}{T_{sys}} - \frac{1}{T_{res}} \right) = -\frac{1}{T_{sys}^2} \leq 0 \]

this requires \( C < 0 \); heat capacity is positive

physically -- if system has negative heat capacity, heat flows into the system cools it down, so more heat flows in.

unstable with respect to what? what state does the system prefer to be in?

To see this, consider \( F \) as a function of \( V, U, T \) fixed.

\[ F = -\int_{res}^{} pdV \ ( + \ constant) \]
Here $F$ is the free energy of homogeneous phase, but we should consider an alternative of inhomogeneous phase — i.e., divide available volume into two different phases (at same p and T).

- Equaling pressure means same slope for $F$ vs $V$ at both points.
- Further $F$ vs $V$ in the mixed phase is a straight line $F = f_1 V_1 + f_2 V_2 = (f_1 - f_2) CV + \text{const.}$

Where $F$ is concave down, we can get lower $F$ in a mixed phase — and lowest possible $F$ along a line that is tangent to $F(V)$ at two points as shown.

$$V = (1 - \alpha)V_1 + \alpha V_2$$

$$F = (1 - \alpha)F_1 + \alpha F_2$$
So to find value of \( p(T) \) at which coexistence occurs, we find slopes of common tangent line.

Since \((\Delta F)_{\text{vol}} = (\Delta F)_{\text{mixed}}\), we have

\[
\int (p)_{\text{vol}} \, dV = p \int dV
\]

This means that regions above and below the horizontal line have equal areas ("Maxwell construction").

Another way to think about this:

Since the two phases are in diffusive equilibrium, they must have same chemical potential.

So all gas and all liquid phases have same free energy

\[
dG = V dp \Rightarrow \int V dp = 0
\]

- again, equal areas.

So the gas and liquid phases have same free energy but derivatives of \( G \) are not the same -- defining property of "first-order phase transition",