Liquids.
Phase equilibria.

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SBU:CHE/PHY558, Physical & Quantitative Biology
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Monet: Houses of Parliament at Sunset
Basics of vapor and liquid phases

Vapor = Gas phase of material that is mostly liquid or solid at room temperature.

The conditions of equilibrium at constant $T$ and $p$ are defined by minimizing $G(T,p,N_v)$. 
Equilibrium between vapor and liquid phases

The conditions of equilibrium at constant $T$ and $p$ are defined by minimizing $G(T,p,N_v)$.

$$dG = -SdT + Vdp + \sum_{j=1}^{M} \mu_j dN_j = \mu_v dN_v + \mu_c dN_c = 0$$

$$N_v + N_c = N = \text{const} \implies dN_v = -dN_c$$

$$dG = (\mu_v - \mu_c) dN_v = 0 \quad \implies \quad \mu_v = \mu_c$$

The goal will be to determine $\mu_c$.

$$\mu_v = kT \ln \left( \frac{p}{p_{\text{int}}} \right)$$

$p = \text{vapor pressure}$

tendency of molecules to escape from bulk

$$p_{\text{int}} = q_0^\circ kT$$

describes molecular properties, and does not depend on vapor pressure.
The lattice model for the condensed phase

We consider liquid and condensed phases similar. We will try to calculate $F_c = U_c - T S_c$.

The translational entropy of the solid is: $S = k \ln(W) = 0$.

Assume that particles A attract each other, described by bond energies: $w_{AA} < 0$

Total energy = sum of all bond energies: $U = \frac{N z w_{AA}}{2}$

$z =$ connectivity, division by 2: to avoid counting twice

$F = U - T S = \frac{N z w_{AA}}{2}$

$\mu_c = \frac{\partial F}{\partial N} = \frac{z w_{AA}}{2}$
The vapor pressure

From the equality of chemical potentials, \( \mu_v = \mu_c \)

\[
kT \ln \left( \frac{p}{p_{\text{int}}} \right) = \frac{Z w_{AA}}{2} \quad \Rightarrow \quad p = p_{\text{int}} e^{\frac{Z w_{AA}}{2kT}} = \frac{N}{V} kT
\]

Stronger bonding promotes liquid phase. Vapor pressure increases with temperature. Vapor pressure decreases.
The vapor pressure

From the equality of chemical potentials, \( \mu_v = \mu_c \)

\[
kT \ln \left( \frac{p}{p_{\text{int}}} \right) = \frac{ZW_{AA}}{2} \Rightarrow p = p_{\text{int}} e^{\frac{ZW_{AA}}{2kT}} = \frac{N}{V}kT
\]

Applied pressure = vapor pressure: boiling

2 ways to boil water:

\( p \) (atm)

\( T \) (°C)
Inferring molecular attraction forces

The vapor pressure of water is 1 atm at 373 K (=100 C) and 0.03 atm at 298 K (=25 C). What is the bonding energy?

\[
\ln \left( \frac{p_1}{p_{\text{int}}} \right) = \frac{z w_{AA}}{2RT_1}
\]

\[
\ln \left( \frac{p_2}{p_\circ} \right) = \frac{z w_{AA}}{2RT_2}
\]

\[
\ln \left( \frac{p_2}{p_1} \right) = \frac{z w_{AA}}{2R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\ln(0.03) = \frac{z w_{AA}}{2 \times 8.314} \left( \frac{1}{298} - \frac{1}{373} \right)
\]

\[
w_{AA} = -21.604 \text{ kJ/mol} \quad \text{for } z=4.
\]
Phase equilibria and phase transitions

Conditions \((p, T)\) define various phases. Phase diagrams map phases versus \((p, T)\).

Phase boundaries indicate where phases are in equilibrium.

Solid-gas: sublimation/deposition
Liquid-gas: boiling/condensation
Solid-liquid: melting/freezing

Boiling temperature goes up with pressure. What is the slope \(dp/dT\)?
Deriving the Clapeyron Equation

Take two nearby points \((T_1, p_1)\) and \((T_2, p_2)\) on the liquid-gas phase boundary.

\[
\mu_L(T_1, p_1) = \mu_G(T_1, p_1) \\
\mu_L(T_2, p_2) = \mu_G(T_2, p_2) \\
\mu_L(T_2, p_2) = \mu_L(T_1, p_1) + d\mu_L(T, p) \\
\mu_G(T_2, p_2) = \mu_G(T_1, p_1) + d\mu_G(T, p)
\]

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

\[
d\mu(T, p) = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} dT + \left(\frac{\partial \mu}{\partial p}\right)_{T,N} dp = -\left(\frac{\partial S}{\partial N}\right)_{T,p} dT + \left(\frac{\partial V}{\partial N}\right)_{T,p} dp
\]

\[
d\mu(T, p) = -sdT + vdp
\]
The Clapeyron and Clausius-Clapeyron Equations

Take two nearby points \((T_1, p_1)\) and \((T_2, p_2)\) on the liquid-gas phase boundary.

\[
d\mu_G = -s_GdT + v_Gdp = d\mu_L = -s_LdT + v_Ldp \quad \Rightarrow \quad \frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} = \frac{\Delta s}{\Delta v}
\]

At the phase transition,
\[
\Delta \mu = \Delta h - T \Delta s = 0 \implies \Delta h = T \Delta s
\]

From here we obtain the Clapeyron equation:
\[
\frac{dp}{dT} = \frac{\Delta h}{T \Delta v}
\]

\[
\Delta v = v_G - v_L \approx v_G = \frac{RT}{p}
\]

This is the Clausius-Clapeyron equation.
Clausius-Clapeyron equation: Applications

Starting with the Clausius-Clapeyron equation:

\[
\frac{d \ln(p)}{dT} = \frac{\Delta h}{RT^2} \quad \Rightarrow \quad \int_{p_1}^{p_2} d \ln(p) = \int_{p_1}^{p_2} \frac{\Delta h}{RT^2} dT \quad \Rightarrow \quad \ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta h}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

The boiling point of water is 373 K at 1 atm. What is the boiling point of water at 0.5 atm?

\[
\Delta h = 40.66 \frac{kJ}{mol}
\]

\[
\ln\left(\frac{1}{2}\right) = \frac{40.66}{8314} \left(\frac{1}{T_2} - \frac{1}{373}\right)
\]

\[
T_2 = 354K = 81^\circ C
\]

Linearity of the following graph indicates that \( \Delta h \) does not depend on temperature \( T \):
Cavities in liquids and solids

Some processes remove a particle from the bulk. The energy for creating such a cavity is:

\[ \Delta U_{\text{remove}} = -zW_{AA} \]

In other cases a cavity is created and then closed. The energy for that process is:

\[ \Delta U_{\text{remove+close}} = U(N-1) - U(N) = \frac{(N-1)zW_{AA}}{2} - \frac{NZW_{AA}}{2} = -\frac{ZW_{AA}}{2} \]

\[ \Delta U_{\text{close}} = \frac{ZW_{AA}}{2} \quad \Delta U_{\text{open}} = -\frac{ZW_{AA}}{2} \]
Surface tension

Surface = boundary between condensed phase and vapor.

Surface tension arises from the energy cost of increasing the surface area. \[ \gamma = \left( \frac{\partial U}{\partial A} \right)_{T,V,N} \]

Consider the lattice shown below.
Bulk particles have \( z \) neighbors. Surface particles have \( z-1 \) neighbors.

The total energy is:

\[ U = \left( \frac{ZW_{AA}}{2} \right)(N - n) + \left[ \frac{(z-1)W_{AA}}{2} \right] n = \frac{W_{AA}}{2} (NZ - n) \]
Relating surface tension to binding energies

\[ U = \frac{w_{AA}}{2} (Nz - n) \quad \Rightarrow \quad \gamma = \left( \frac{\partial U}{\partial A} \right)_{T,V,N} = \left( \frac{\partial U}{\partial n} \right)_{T,V,N} \left( \frac{\partial n}{\partial A} \right) = -\frac{w_{AA}}{2a} \]

Here, \( a \) is the area associated with a surface particle.

This plot indicates that \(~6\)-fold more bonds are broken in vaporization than in creating a surface.