Lecture Ch. 5a

- Surface tension (Kelvin effect)
  - Hygroscopic growth (sub saturated humidity)
  - Saturation
- Chemical potential (Raoult effect)
- Nucleation
  - Competition between surface and chemical effects
  - Köhler curves
- Aerosol-cloud interactions

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1
Optional: Pruppacher and Klett, Ch. 6
Homework Problem 3 and 7 (Ch. 5) {7d misprint given in Errata!}

Surface Thermodynamics

- Surfaces require energy (work) to form
- Smaller particles have
  - higher surface-to-volume ratios
  - higher curvature
- Higher curvature requires more energy per mass

\[
dW_\sigma = \sigma \, dA
\]
Extrinsic for fixed mass.

Kelvin Effect

- Work to form surface:
  \[
dW_\sigma = \sigma \, dA \tag{5.1}
\]
- Expansion against pressure difference
  \[
  \sigma \, dA = \Delta p \, dV \tag{5.4}
  \]
  \[
  \Delta p = \frac{2\sigma}{R}
  \tag{5.6}
  \]

<table>
<thead>
<tr>
<th>Surface tension</th>
<th>200</th>
<th>100</th>
<th>10</th>
<th>1</th>
</tr>
</thead>
<tbody>
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<td>( \frac{\sigma}{\rho} )</td>
<td>1.001</td>
<td>1.010</td>
<td>1.114</td>
<td>2.00</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Kelvin Effect</th>
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</table>
| Force Balance: \( F_p = F_\sigma \)
  - Area of spherical cap:
    - \( 2\pi R \sin(\theta/2) \)
    - Approximate for small \( \theta \):
      - \( \sin(\theta/2) \approx R/r \)
    - So area of surface force:
      - \( 2\pi R \sin(\theta/2) \approx 2\pi R^2 / r \)
  - Result: \( p_\sigma = 2\sigma / r \)
  - Or: \( \Delta p = 2\sigma / r \)

Chemical Effects

- Gibbs for an open system (this allows number of moles to change), from Ch. 4:
  \[
  dG = -\Pi dT + V \, dp + \sum \frac{\partial G}{\partial n_j} \, dn_j
  \tag{4.5}
  \]
  \[
  dG = -\Pi dT + V \, dp + \sum \mu_j \, dn_j
  \tag{4.7}
  \]
Lecture Ch. 5b

- Chemical Potential (from last time)
- Combining Surface and Solute Effects
- Köhler Curves
- Chapter 5, Problem 3 homework
  - Kelvin effect
  - Raoult effect

Chapter 5
p. 158, problem 7b

\[ \eta = \frac{3}{4} \frac{\partial\left\{ \right\} }{\partial \eta} \]

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1

Macro-Thermodynamics

- Hot air rises
- Rising air cools
- Cooled moist air saturates
- (Sub & Super)-saturated water vapor condenses
- Condensation liberates heat

Micro-Thermodynamics

- Saturation has the most possible dissolved species
- Equilibrium means two phases are balanced
- Supersaturated states are not stable
- Nucleation initiates a change of “phase” (from particle to droplet)

Bohren, 1987

Nucleation (Pure Water)

- Using Gibbs for open system and surface:
  \[ dG = -N\Delta F + Vdp + \sigma_a d\alpha - \mu_a d\alpha_a + \mu_v d\alpha_v \]  
  (5.8)
- At constant T and p, and \( d\eta = -d\eta_v \):
  \[ dG = \sigma_a \delta x d\alpha + (\mu_v - \mu_v) d\alpha_v \]  
  (5.9)
- For phase equilibrium (flat surface):
  \[ \mu_v - \mu_v = R T \ln\left( \frac{\sigma}{\eta} \right) \]  
  (5.10)
- For spherical droplet:
  \[ \eta = \frac{1}{M_v} d\eta_v = \frac{3}{4} \eta_v, 4\pi r^2 d\eta_v \]  
  (5.11)

Nucleation (Pure Water) Part 2

- Differential:
  \[ dG = \left[ -R T \ln \left( \frac{\sigma}{\eta} \frac{\delta x}{x^2} \sigma_a + \sigma_v \right) \right] d\alpha \]  
  (5.12)
- Integrated:
  \[ \Delta G = 4\pi \sigma_a \delta x - \frac{4\pi^2}{3} \rho R T \ln(S) \]  
  (5.13)
- Find minima:
  \[ \left. \frac{dG}{dr} \right| _{r_0} = \sigma_a \delta x - 4\pi^2 \rho R T \ln(S) = 0 \]
- Solve for S:
  \[ \epsilon_S(r) = \epsilon_S(\eta_0) \exp \left( \frac{2a_0}{\rho R T} \right) = \epsilon_S(\eta_0) \]  
  (5.14c)
  \[ \eta = \frac{3}{4} \frac{\partial\left\{ \right\} }{\partial \eta} \]
Chemical Potential

- By definition $\mu_v = \mu^0_v + R^* T \ln \frac{\varepsilon}{\varepsilon_0}$
  - With respect to reference state “0”
  - Increase is proportional to concentration
- At saturation $\mu^s_v = \mu^0_v + R^* T \ln \frac{\varepsilon^s}{\varepsilon_0}$
- But saturation=liquid $\mu^s_l = \mu^0_l$
- So we get

$$\mu^s_l - \mu^s_v = R^* T \ln \left( \frac{\varepsilon^s}{\varepsilon_v} \right)$$

Raoult’s Law

- True for “ideal” solutions and $X_i=1$: $p_x = X_i p^*_x$
  
  $$\frac{p_{\text{total}}}{p^*_x} = X_{\text{H}_2\text{O}} + X_{\text{solute}} \frac{p_{\text{solute}}}{p^*_x}$$
  
- For dilute solution with $n_{\text{solute}} \ll n_{\text{H}_2\text{O}}$
  - Use expansion of $(1/(1+x)) \approx 1 - x + \text{H.O.T.}$ for small $x$

$$p_{\text{total}} = X_{\text{H}_2\text{O}} \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{solute}}} = 1 - \frac{n_{\text{solute}}}{n_{\text{H}_2\text{O}}}$$  \hspace{1cm} (4.45)

Van’t Hoff Factor

$$n^c_{\text{solute}} = n_{\text{H}_2\text{O}}$$  \hspace{1cm} (4.47)

$$p_{\text{solute}} = 1 - \frac{n^c_{\text{solute}}}{n_{\text{H}_2\text{O}}}$$  \hspace{1cm} (4.48)

$$e_s \left( \frac{n_{\text{solute}}}{n_{\text{H}_2\text{O}}} \right) = 1 - \frac{3n_{\text{solute}} M_v}{4 \pi n_{\text{solute}} \rho^2} = 1 - \frac{b^3}{r^3}$$ \hspace{1cm} (5.16a)

$$b = 3^3 M_{\text{solute}} \frac{\varepsilon_{\text{solute}}}{4 \pi \varepsilon_{\text{H}_2\text{O}} \rho_0^2}$$

Now, combining surface+solute

- Substitute $e_s(\text{solute})$ for $e_s$
  
  $$e_s = e^{0}(1 - \frac{a}{r})^n(\exp(b/r + \ldots))$$
  
- Expand for $\exp(x)$ for small $x=a/r$

$$e_s \approx (1 - b/r)^n(1 + a/r + \ldots)$$

- Could also go back to $dg_{r,solute}=dg_{solute}+dg_{\text{H}_2\text{O}}$
  - $dg_{\text{H}_2\text{O}}=\text{fcn}(a)$
  - $dg_{\text{solute}}=\text{fcn}(b)$ (i.e. dg for Raoult Effect)

Chemical and Surface Effects

$$e_s \left( \frac{n_{\text{solute}}}{n_{\text{H}_2\text{O}}} \right) = \frac{1 - \frac{a}{r}}{\exp(b/r)}$$ \hspace{1cm} (5.17)

- Both Raoult and Kelvin effects

$$a = 2 \rho_0 \varepsilon_{\text{H}_2\text{O}} \rho R T$$

$$b = 3 \varepsilon_{\text{solute}} \frac{M_{\text{solute}}}{4 \pi \varepsilon_{\text{H}_2\text{O}} \rho_0^2}$$

If $r$ is not too small, (5.17) can be written as

$$e_s \left( \frac{n_{\text{solute}}}{n_{\text{H}_2\text{O}}} \right) = 1 + \frac{a}{r} - \frac{b}{r^3}$$ \hspace{1cm} (5.18)

*What this means is that, for small $x$, use expansion $\exp(x) = 1 + x + \text{H.O.T.}$, then drop terms with $1/r^4$ and smaller.
Critical Radius and Supersaturation

- Integrate then find maximum

\[ \Delta S' = 4\pi r'^2 s_0 \exp \left( \frac{\alpha}{r'^2} \right) \ln \left( \frac{T}{T_s} \right) \]

(5.13)

where, \( S' \) is the supersaturation ratio and \( s_0 \) is the saturated vapor pressure over a plane surface. \( \alpha \) is the surface tension and \( \alpha \) is the equilibrium saturation ratio.

Solving for \( r' \) yields

\[ r' = \frac{2s_0}{\alpha \Delta H / T} \]

(5.14a)

We can write explicitly

\[ \ln S = \frac{2s_0}{\rho c_p T} \]

(5.14b)