Course Summary

I. Introduction
II. Single component systems
III. Solutions
IV. Phase diagrams
V. Phase stability
VI. Surfaces
VII. Heat of formation
VIII. Heat capacity
IX. Solution models and equations of state
X. Thermodynamics and materials modeling
Course Summary

I. Introduction:
Define Terms;
Basic Definitions;
Gibbs Thompson;
Hess’ Law (not path dependent);
second law and reversibility;
equilibrium; third law $T = 0 \text{ K Boltzmann equation}$;
Legendre transform;
Maxwell equations;
Gibbs-Duhem equation (Gibbs phase rule)
What happens to the energy when I heat a material?
Or How much heat, \( dq \), is required to change the temperature \( dT \)? (Heat Capacity, \( C \))

\[
dq = C \, dT
\]
\[
C = \frac{dq}{dT}
\]

**Constant Volume, \( C_v \)**

\[
dU = dq + dw
\]
With only \( pV \) work (expansion/contraction), \( dw_{ec} = -pdV \)
\[
dU = dq - pdV
\]
For constant volume
\[
(dU)_V = dq, \text{ so }
\]
\[
C_v = (dU/dT)_V, \text{ or the energy change with } T: \ (dU)_V = C_v \ dT
\]

**Constant Pressure, \( C_p \)**

\[
dU = dq + dw = dq - pdV \text{ (only } e/c \text{ work, i.e. no shaft work)}
\]
Invent Entropy \( H = U + PV \) so \( dH = dU + pdV + Vdp \)
\[
(dH)_p = dU + pdV \text{ for constant pressure}
\]
With only \( pV \) work (expansion/contraction), \( dw_{ec} = -pdV \)
\[
dq = dU + pdV = (dH)_p
\]
\[
C_p = (dH/dT)_p, \text{ or the enthalpy change with } T: \ (dH)_p = C_p \ dT
\]

**Computer Simulation**

**Helmholtz Free Energy, \( A \)**

\[
A = U - TS = G - pV
\]

**Atmospheric Experiments**

**Gibbs Free Energy, \( G \)**

\[
G = H - TS = A + pV
\]
Size dependent enthalpy of melting  
(Gibbs-Thompson Equation)

For bulk materials, $r = \infty$, at the melting point $\Delta G = \Delta H - T_\infty \Delta S = 0$

So $T_\infty = \Delta H/\Delta S$ Larger bonding enthalpy leads to higher $T_\infty$,
Greater randomness gain on melting leads to lower $T_\infty$.

For nanoparticles there is also a surface term,
$(\Delta G) V = (\Delta H - T_r \Delta S)V + \sigma A = 0$, where $T_r$ is the melting point for
size $r$ nanoparticle
If $V = r^3$ and $A = r^2$ and using $\Delta S = \Delta H/T_\infty$ this becomes,
$r = \sigma/((\Delta H(1 - T_r/T_\infty))$ or $T_r = T_\infty (1 - \sigma/(r \Delta H))$
Smaller particles have a lower melting point and the dependence
suggests a plot of $T_r/T_\infty$ against $1/r$
Derive the expression for $C_p - C_v$

$$C_p - C_v = \alpha^2 VT / kT$$

$$\alpha = (1/V) (dV/dT)_p$$

$$k_T = (1/V) (dV/dP)_T$$

$C_v = (dU/dT)_v$

From the Thermodynamic Square

$$dU = TdS - pdV$$

so $C_v = (dU/dT)_v = T (dS/dT)_v - p (dV/dT)_v$

Second term is 0 $dV$ at constant $V$ is 0

$$(dS/dT)_v = C_v / T$$

Similarly

$$C_p = (dH/dT)_p$$

From the Thermodynamic Square

$$dH = TdS + Vdp$$

so $C_p = (dH/dT)_p = T (dS/dT)_p - V (dp/dT)_p$

Second term is 0 $dp$ at constant $p$ is 0

$$(dS/dT)_p = C_p / T$$

Write a differential expression for $dS$ as a function of $T$ and $V$

$$dS = (dS/dT)_v dT + (dS/dV)_T dV$$

using expression for $C_v$ above and Maxwell for $(dS/dV)_T$

$$dS = C_v / T dT + (dp/dT)_v dV$$

use chain rule: $(dp/dT)_v = -(dV/dT)_p (dP/dV)_T = V \alpha / (V k_T)$

Take the derivative for $C_p$: $C_p / T = (dS/dT)_p = C_v / T (dT/dT)_p + (\alpha / k_T)(dV/dT)_p = C_v / T + (V \alpha^2 / k_T)$

$$C_p - C_v = \alpha^2 VT / kT$$
Consider a binary system A + B makes a solution

\[ G = n_A \mu_A + n_B \mu_B \]

\[ dG = n_A d\mu_A + \mu_A n_A dA + n_B d\mu_B + \mu_B n_B dB \]

Fundamental equation with chemical potential:

\[ dG = -SdT + Vdp + \sum_i \mu_i dn_i \]

At constant T and p:

\[ dG = \mu_A dn_A + \mu_B dn_B \]

So, at constant T and p:

\[ n_A d\mu_A + n_B d\mu_B = 0 \quad \text{i.e.} \quad \sum_i n_i d\mu_i = 0 \]

Reintroducing the T and p dependences:

\[ SdT - Vdp + \sum_i n_i d\mu_i = 0 \]
Course Summary

II. Single Component Systems:
First order transition;
Clausius-Clapeyron equation (vapor pressure calculation);
Second order transition;
Virial equation of state for phase diagram;
Phase diagram P vs T (Gibbs phase rule)
Fugacity;
Van der Waals equation (Cubic equation of state);
CALPHAD and PREOS programs
Clausius-Clapeyron Equation

Consider two phases at equilibrium, \( \alpha \) and \( \beta \)

\[
d\mu_\alpha = d\mu_\beta
\]

\[
dG = V dp - S dT
\]

so

\[
V^\alpha dp - S^\alpha dT = V^\beta dp - S^\beta dT
\]

so

\[
dp/dT = \Delta S/\Delta V
\]

and

\[
\Delta G = 0 = \Delta H - T \Delta S \quad \text{so} \quad \Delta S = \Delta H/T
\]

and

\[
dp/dT = \Delta H/(T \Delta V) \quad \text{Clapeyron Equation}
\]

For transition to a gas phase, \( \Delta V \sim V^{\text{gas}} \)

and for low density gas (ideal) \( V = RT/p \)

\[
d(ln p)/dT = \Delta H/(RT^2) \quad \text{Clausius-Clapeyron Equation}
\]
**Clausius Clapeyron Equation**

\[
d(ln \ p)/dT = \frac{\Delta H}{RT^2} \quad \text{Clausius-Clapeyron Equation}
\]

\[
d(ln \ p^{Sat}) = (-\Delta H_{vap}/R) \ d(1/T)
\]

\[
\ln[p^{Sat}/ p_{R^{Sat}}] = (-\Delta H_{vap}/R) \ [1/T - 1/T_R]
\]

**Shortcut Vapor Pressure Calculation:**

\[
\log_{10} p_{R}^{Sat} = \frac{7}{3} (1 + \omega) \left(1 - \frac{1}{T_R} \right)
\]
Clausius Clapeyron Equation

\[ d(\ln p^{\text{Sat}}) = (-\Delta H_{\text{vap}}/R) \ d(1/T) \]

\[ \ln[p^{\text{Sat}}/p_R^{\text{Sat}}] = (-\Delta H_{\text{vap}}/R) [1/T - 1/T_R] \]

This is a kind of Arrhenius Plot

Figure 9.1. Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).
What About a Second Order Transition?
For Example: Glass Transition $T_g$ versus $P$?

There is only one “phase” present. A flowing phase and a “locked-in” phase for $T_g$.
There is no discontinuity in $H, S, V$

\[
dV = 0 = (dV/dT)_p \ dT + (dV/dP)_T \ dP = V\alpha dT - V\kappa_T dp
\]

\[
dp/dT_g = \Delta\alpha/\Delta\kappa_T
\]

$T_g$ should be linear in pressure.
Second order transition Neel Temperature (like Curie Temp for antiferromagnetic)

\[ \text{Inden Model } \tau = \frac{T}{T_{tr}} \]

For \( \tau < 1 \)

\[ C_{p,\text{mag}}^\text{mag} = K^L R \frac{\ln(1 + \tau^3)}{\ln(1 - \tau^3)} \]

For \( \tau > 1 \)

\[ C_{p,\text{mag}}^\text{mag} = K^S R \frac{\ln(1 + \tau^5)}{\ln(1 - \tau^5)} \]

**Figure 2.13** Heat capacity of wüstite around the Néel temperature [19]. ○: Fe_{0.99}O; ●: Fe_{0.947}O; ▽: Fe_{0.938}O; +: Fe_{0.925}O. Reproduced by permission of the Mineralogical Society of America.
Single Component Phase Diagrams

Figure 2.7 The $p,T$ phase diagram of H$_2$O (the diagram is not drawn to scale).

For a single component an equation of state relates the variables of the system, PVT
\[ F = C - Ph + 2 \]  \hspace{1cm} (2.15)

In Chapter 4 the determination of the number of components in complex systems will be discussed in some detail. In this chapter we shall only consider single-component systems. For a single-component system, such as pure H$_2$O, \( C = 1 \) and \( F = 3 - Ph \). Thus, a single phase (\( Ph = 1 \)) is represented by an area in the \( p,T \) diagram and the number of degrees of freedom \( F \) is 2. A line in the phase diagram represents a heterogeneous equilibrium between two coexisting phases (\( Ph = 2 \)) and \( F = 1 \), while three phases (\( Ph = 3 \)) in equilibrium are located at a point, \( F = 0 \).
Ideal Gas Equation of State

\[ P = \frac{RT}{V} \]

Cubic Equation of State

\[ P = \frac{RT}{V-b} - \frac{a}{V^2} \]

Van der Waals Equation of State

\[ Z = \frac{PV}{RT} \]
\[ Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT} \]

Virial Equation of State

\[ B(T) = b - \frac{a}{RT} \]

Peng-Robinson Equation of State (PREOS)

\[ P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2} \] or
\[ Z = \frac{1}{1-b\rho} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2} \]
\[ Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2} \]
\[ Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \]

Cubic Equation of State

Solve cubic equations (3 roots)
Figure 1.3 Ideal gas behavior at five temperatures.

Figure 1.4 P-V-T behavior of water at the same temperatures used in Fig 1.3. The plot is prepared from the steam tables in Appendix E.

Figure 7.5 Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO$_2$ (T$_c$ = 304.2 K) at 275 K, 290 K, 306 K, 310 K, 320 K, and 359 K. Higher temperatures result in a high pressure for a given volume. The "humps" are explained in the text. The calculated vapor pressures are 36.42 bar at 275 K, 53.2 bar at 290 K, and 87.23 bar at 300 K.
III. Solutions:
Ideal mixing;
Real solutions;
Activity and activity coefficient;
Excess Gibbs free energy;
Raoult’s Law and Henry’s Law;
Hildebrand Model;
Hildebrand del parameter;
Asymmetric models (Redlich-Kister Expression);
Gibbs-Duhem for Solutions;
An “Ideal Solution” means:

The change on mixing:
\[ \Delta S = -nk_B \left( x_A \ln(x_A) + x_B \ln(x_B) \right) \]
Since \( \ln(x) \) is always negative or 0, \( \Delta S \) is always positive for ideal solutions
\[ \Delta G = -T \Delta S \]
Since \( \ln(x) \) is always negative or 0, \( \Delta G \) is always negative (or 0) and ideal solutions always mix
\( \Delta H \) is 0, there is no interaction in ideal mixtures, there is no excluded volume, particles are ghosts to each other
\[ \Delta V = (d\Delta G/dp)_T = 0 \], there is no loss or gain of volume compared to the summed volume
Real Solutions

\( x_A \) becomes \( a_A \) the activity so

\[ \Delta G_{\text{mixing}} = RT(x_A \ln a_A + x_B \ln a_B) \]

Excess \( \Delta G_{\text{mixing}} = \Delta G_{\text{mixing}} - RT(x_A \ln x_A + x_B \ln x_B) \)
\[ = RT(x_A \ln (a_A/x_A) + x_B \ln (a_B/x_B)) \]
\[ = RT(x_A \ln (\gamma_A) + x_B \ln (\gamma_B)) \]
\( \gamma \) is the activity coefficient

Excess \( \Delta S_{\text{mixing}} = -R(x_A \ln (\gamma_A) + x_B \ln (\gamma_B)) \)

Method to use departure functions for calculations (PREOS.xls)
1) Calculation of properties in the ideal state is simple
2) With an equation of state the departure function can be calculated
3) For any transition first calculate the departure function to the ideal state
4) Then carry out the desired change as an ideal mixture or gas
5) Then use the departure function to return to the real state
Hildebrand Regular Solution Model

The change on mixing:

\[ \Delta S = -nk_B (x_A \ln(x_A) + x_B \ln(x_B)) \] Ideal Solution

Since (\ln x) is always negative or 0, \( \Delta S \) is always positive for ideal solutions

\[ \Delta G = \Delta H - T \Delta S \]

Since (\ln x) is always negative or 0, \( \Delta G \) is positive or negative depending on \( \Delta H \) :: can mix or demix

Depending on the sign of \( \Delta H \)

\[ \Delta V = (d\Delta G/dp)_T = 0, \text{ there is no loss or gain of volume compared to the summed volume} \]

\[ \Delta H = n \Omega x_A x_B \]

\( \Omega \) is the interaction coefficient or regular solution constant

Molar Gibbs free energy of mixing

\[ \Delta G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega x_A x_B \]

\[ \Omega = zN_A[u_{AB} - (u_{AA} + u_{BB})/2] \]

The equation is symmetric

Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of \( \Omega/RT \).
Asymmetric equations for asymmetric phase diagram

Sub-regular solution model

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B (A_{21} x_A + A_{12} x_B) \]

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = \sum_{i=1}^{m} \sum_{j=1}^{n} x_A^i x_B^j A_{ij} \]

Redlich-Kister Expression

\[ \Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B [\Omega + A_1 (x_A - x_B) + A_2 (x_A - x_B)^2 + A_3 (x_A - x_B)^3 + \ldots ] \]
Use of the Gibbs-Duhem Equation to determine the activity of a component

\[ n_A \, d\mu_A + n_B \, d\mu_B = 0 \]
\[ x_A \, d\ln a_A + x_B \, d\ln a_B = 0 \]
\[ x_A \, d\ln x_A + x_A \, d\ln \gamma_A + x_B \, d\ln x_B + x_B \, d\ln \gamma_B = 0 \]
\[ x_A \, d\ln x_A + x_B \, d\ln x_B = x_A \, \frac{dx_A}{x_A} + x_B \, \frac{dx_B}{x_B} = dx_A + dx_B = 0 \]

Restatement of Gibbs-Duhem for Solutions

If you know \( \gamma_A \) you can obtain \( \gamma_B \) by integration

\[ \ln \gamma_B - \ln \gamma_B(x_B = 1) = - \int_{x_B=1}^{x_B} \frac{x_A}{x_B} \, d\ln \gamma_A \]
Course Summary

IV. Phase Diagrams:
Eutectic;
Solid Solution;
L/V vs S/L Ideal; Azeotrope/Congruent; Heteroazeotrope/Eutectic;
Regular solution model;
Lower critical solution behavior (LCST);
Freezing point depression;
Ternary phase diagram;
Gibbs Phase Rule

\[ F + Ph = C + 2 \]

Eutectic Phase Diagram Ag + Cu

Univariant Equilibrium
- Liquidus
- Solidus

Invariant Equilibrium
- Eutectic

Liquid \(\rightarrow\) Cu(ss) + Ag(ss)

Lever Rule

Tieline (conode)

\[ \mu_i^L = \mu_i^P = \mu_i = \ldots \quad \text{for } i = 1, 2, \ldots, C \]

\[ \mu_A(x_A) = \mu_A^P(x_A) = \mu_A^P(x_A) \]

and

Silver acts like a solvent to copper and copper acts like a solvent to silver with limited solubility that is a function of temperature with a solubility limit at the eutectic point (3 phases in equilibrium)

**Figure 4.1** Phase diagram of the system Ag–Cu at 1 bar [1].
Calculate the Phase Diagram for a Solid Solution

\[ \mu_A^{ss} = \mu_A^{s,0} + RT \ln a_A^{ss} \]
\[ \mu_A^{liq} = \mu_A^{l,0} + RT \ln a_A^{liq} \]
\[ \mu_B^{ss} = \mu_B^{s,0} + RT \ln a_B^{ss} = \mu_B^{l,0} + RT \ln a_B^{liq} \]

\[ \ln \left( \frac{a_A^{liq}}{a_A^{ss}} \right) = \frac{\Delta \mu_A^{(s \rightarrow l)}}{RT} \]
\[ \ln \left( \frac{a_B^{liq}}{a_B^{ss}} \right) = \frac{\Delta \mu_B^{(s \rightarrow l)}}{RT} \]

\[ \Delta \mu_i^{(s \rightarrow l)} = \mu_i^{l,0} - \mu_i^{s,0} = \Delta_{\text{fus}} G_i^0 = \Delta_{\text{fus}} H_i^0 - T \Delta_{\text{fus}} S_i^0 \]

\[ \Delta_{\text{fus}} G_i^0 = 0 \quad \Delta_{\text{fus}} S_i^0 = \Delta_{\text{fus}} H_i^0 / T_{\text{fus,i}} \]

\[ \Delta \mu_i^{(s \rightarrow l)} = \Delta_{\text{fus}} H_i^0 - T \Delta_{\text{fus}} S_i^0 = \Delta_{\text{fus}} H_i^0 \left( 1 - \frac{T}{T_{\text{fus,i}}} \right) \]

\[ \ln \left( \frac{a_A^{liq}}{a_A^{ss}} \right) = \frac{\Delta \mu_A^{(s \rightarrow l)}}{RT} - \frac{\Delta_{\text{fus}} H_A^0}{R} \left( 1 - \frac{T}{T_{\text{fus,A}}} \right) \]
\[ \ln \left( \frac{a_B^{liq}}{a_B^{ss}} \right) = \frac{\Delta \mu_B^{(s \rightarrow l)}}{RT} - \frac{\Delta_{\text{fus}} H_B^0}{R} \left( 1 - \frac{T}{T_{\text{fus,B}}} \right) \]

\[ x_A^{liq} = x_A^{ss} \exp \left[ \frac{\Delta_{\text{fus}} H_A^0}{R} \left( 1 - \frac{T}{T_{\text{fus,A}}} \right) \right] \]
\[ x_B^{liq} = x_B^{ss} \exp \left[ \frac{\Delta_{\text{fus}} H_B^0}{R} \left( 1 - \frac{T}{T_{\text{fus,B}}} \right) \right] \]

C\(_p\)(T) is constant

Solve for \( x_A^{ss} x_B^{liq} \) since \( x_A + x_B = 1 \)

Ideal
Figure 4.7 (a) Phase diagram of the system KCl–NaCl. (b) Gibbs energy curves for the solid and liquid solutions KCl–NaCl at 1002 K. Thermodynamic data are taken from reference [5].

Solid solution is flatter than ideal (Pos. deviation or destabilized)
Liquid is deeper than ideal (Neg. Deviation or stabilized)
Deviations are associated with minima in phase diagram
**Liquid/Vapor Equilibria**

- **Ideal**
- **Azeotrope**
- **Heteroazeotrope**

**Solid/Liquid Equilibria**

- **Ideal**
- **Non-Ideal**
  - Congruent melting solid solution
- **Eutectic**
  - Different crystallographic structures in solid solution phases

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**Phase diagram is split into two phase diagrams with a special composition that acts as a pure component**

- **L => α + L**
  - Same crystallographic structure in solid solution phase
- **L => α**
  - L => α + β

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**Phase diagram of a positive azeotrope. Vertical axis is temperature, horizontal axis is composition.**

**Phase diagram of a negative azeotrope. Vertical axis is temperature, horizontal axis is composition.**

**Phase diagram of a heteroazeotrope.**

**Phase diagram of a eutectic.**

**Phase diagram of a congruent melting solid solution.**
Two Different Crystallographic Phases at Equilibrium

\[ \gamma \rightarrow \alpha + \beta \]

**Figure 4.9** (a) Immiscibility gap of the binary solid solution \( V_2O_3-Cr_2O_3 \) as described by the regular solution model. (b) Gibbs energy of mixing curve of the solid solution at the temperatures marked in the phase diagram. Thermodynamic data are taken from reference [7].
Polyvinylmethyl Ether/Polystyrene (LCST Phase behavior)

\[ \Delta G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega_{xAxB} \]

\(\Omega\) must have a temperature dependence for UCST
\(\Omega = A + B/T\) so that it gets smaller with increasing temperature this is a non-combinatorial entropy i.e. ordering on mixing
Freezing Point Depression

Pure solid in equilibrium with a binary solution following Henry’s Law

$$d\mu_{B,\text{Solid}} = V_{m,\text{B,\text{Solid}}} dP - S_{m,\text{B,\text{Solid}}} dT + RT d(ln a_{B,\text{Solid}})$$

Isobaric, pure component B so $$ln a_{B,\text{Solid}} = 0$$

$$d\mu_{B,\text{Solid}} = - S_{m,\text{B,\text{Solid}}} dT_{fp}$$

Binary solution following Henry’s Law

$$d\mu_{B,\text{Solution}} = - S_{m,\text{B,\text{Solution}}} dT_{fp} + RT_{fp} d(ln y_{B,\text{Solution}})_{P,T}$$

For small x: $$e^{-x} = 1 - x + ...$$ or $$ln(1-x) = -x$$

So for small $$y_{B,\text{Solution}}$$: $$ln y_{B,\text{Solution}} \sim -y_{A,\text{Solution}}$$

So,

$$S_{m,\text{B,\text{Solid}}} dT_{fp} = S_{m,\text{B,\text{Solution}}} dT_{fp} + RT_{fp} dy_{A,\text{Solution}}$$

$$d y_{A,\text{Solution}} = (S_{m,\text{B,\text{Solid}}} - S_{m,\text{B,\text{Solution}}})/(RT_{fp}) dT_{fp} \sim -\Delta S_{m,\text{B}}/(RT_{fp}) dT_{fp} = -\Delta H_{m,\text{B}}/(RT_{fp}) (dT_{fp})/T_{fp}$$

$$y_{A,\text{Solution}} = -\Delta H_{m,\text{B}}/(RT_{f}) ln(T_{fp}/T_{f})$$ For small x: $$ln(x) = x - 1$$

$$y_{A,\text{Solution}} = -\Delta H_{m,\text{B}}/(RT_{f}) (T_{fp}/T_{f} - 1) = -\Delta H_{m,\text{B}}/(RT_{f}^2) \Delta T$$

$$T_{fp} = T_{f} - y_{A,\text{Solution}}RT_{f}^2/\Delta H_{m,\text{B}}$$
Course Summary

V. Phase Stability:
Metastable;
Supercool; superheat; supersaturate;
Kauzmann Paradox;
Thermal/density fluctuations;
Spinodal decomposition;
Binodal; spinodal; critical conditions;
Polymorphs; allotropes;
The book considers first a reversible chemical reaction A $\rightleftharpoons$ B
Cyclohexane from boat to chair conformation for instance

As temperature changes you can observe a different mix of states, $E = k_B T \sim 2.5 \text{ kJ/mole}$ at RT
But fluctuations allow for 0.1% boat conformation. At 1073K 30% boat. Probability is $\exp(-E/kT)$.
The percent in boat can be measured using NMR spectroscopy.
Superheating and Melting

Superheating can occur since melting occurs at surfaces and if the surfaces are stabilized then superheated solids can be produced.

Growth of a liquid phase relies on growth of a mechanical instability

A mechanical instability will not spontaneously grow if it occurs in a meta-stable region in $T$ and $P$:

$(dG/dx) = 0$ defines equilibrium or binodal; $(d^2G/dx^2) = 0$ defines the metastable limit or spinodal

$(d^3G/dx^3) = 0$ defines the critical point

$$G = -ST + Vp, \quad dG = -SdT + Vdp$$

$$(d^2G/dp^2)_T = (dV/dp)_T < 0 \quad \text{and} \quad (d^2G/dT^2)_p = -(dS/dT)_p < 0$$

First requires that the bulk modulus be positive,

Second requires positive heat capacity. $(dS/dT)_p = C_p/T > 0$

Shear modulus goes to 0 at highest possible supercritical solid
**Kauzmann Paradox,**
a thermodynamic basis for the

glass transition

The entropy of the liquid becomes smaller than the entropy of the solid at the Kauzmann temperature, $T_K$. This could be the infinite cooling glass transition temperature.
Since $\chi N$ depends on $1/T$ specifying $\chi N$ specifies the temperature. Large $\chi N$ is low temperature.

**Fig. 4.3.** Gibbs free energy of mixing of a symmetric binary polymer mixture ($N_A = N_B = N$), as described by the Flory–Huggins equation.

**Fig. 4.4.** Phase diagram of a symmetric polymer mixture ($N_A = N_B = N$). In addition to the binodal (continuous line) the spinodal is shown (broken line).
Allotroph: Carbon as diamond or graphite

Polymorph: Titania as anatase or rutile
     Silica as $\alpha$-quartz, $\beta$-quartz, tridymite, cristobalite, moganite, coesite, and stishovite
     Calcium carbonate as calcite or argonite

**Ostwald’s rule:** Most stable polymorph does not always crystallize, rather, meta-stable polymorphs form at a higher rate if the surface tension difference between the melt/liquid solution and the polymorph is small.

**Ostwald ripening:** Metastable polymorphs may form small crystals. Over time stable polymorphs grow from these small crystals into large crystals. This has been generalized to growth of large phases due to ripening such as in crushed ice or ice cream.

**Ostwald Freundlich Equation:** Small crystals dissolve more easily than large crystals. This is the reason for Ostwald ripening. Also true for vapor pressure of a liquid droplet (replace $x$ with $p$)

**Ostwald step rule:** Least stable polymorph crystallizes first since it has a free energy that is closest to the liquid or solution state. This means that metastable phases form kinetically first if they exist. If many polymorphs exist they will form in order of free energy with the highest forming first.

During the course of his academic career, Ostwald published more than 500 original research papers for the scientific literature and approximately 45 books.
Course Summary

VI. Surfaces:
Surface excess properties;
Surface area and curvature;
Laplace equation (pressure versus curvature/size);
Contact angle;
Kelvin equation (vapor pressure for a droplet/bubble);
Solubility versus size;
Critical nucleus size;
Ostwald ripening;
Heterogeneous versus homogeneous nucleation;
Gibbs-Thompson and Ostwald-Freundlich equations;
Chemical (irreversible) or physical adsorption (reversible);
Adsorption isotherm (Langmuir, BET);
Block copolymers;
Laplace Equation

\[ dU = [(p^β - p^α) + \sigma(c_1 + c_2)]A_s dl \]

At equilibrium \((dU)_{S,V,n_i} = 0\),

\[ p^β - p^α = \sigma(c_1 + c_2) = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]

For a 100 nm \((1e^{-5} \text{ cm})\) droplet of water in air \((72 e^{-7} \text{ J/cm}^2\) or 7.2 Pa·cm\)
Pressure is 720 MPa \((7,200 \text{ Atmospheres})\)
Figure 6.9 Two-dimensional projection of equilibrium at a plane of contact between three phases $\alpha$, $\beta$ and $\chi$ where the angles between the three two-phase boundaries meeting in a line of contact are denoted $\theta^\alpha$, $\theta^\beta$ and $\theta^\chi$.

\[
\sigma^{\alpha\beta} + \sigma^{\beta\chi} + \sigma^{\alpha\chi} = 0
\]

\[
\frac{\sigma^{\alpha\beta}}{\sin \theta^\alpha} = \frac{\sigma^{\beta\chi}}{\sin \theta^\beta} = \frac{\sigma^{\alpha\chi}}{\sin \theta^\chi} = 0
\]
Figure 6.10  Contact angle $\theta$ of a liquid drop resting on a solid surface. The definition of the forces used in the figure eliminates the contribution from gravity.

$$\gamma^{sg} = \gamma^{sl} + \sigma^{lg} \cos \theta = 0$$  
Young Dupre Equation
Pressure for equilibrium of a liquid droplet of size "r"

\[ \ln \frac{p^g}{p^g_{r=\infty}} = \frac{V^1}{RT} \frac{2\sigma^{lg}}{r} \]

Reversible equilibrium
At constant temperature
Differential Laplace equation

Small drops evaporate, large drops grow
Solubility and Size, \( r \)

Consider a particle of size \( r_i \) in a solution of concentration \( x_i \) with activity \( a_i \)

\[
d(p^s - p^d) = d \left( \frac{2y^d}{r} \right)
\]

Derivative form of the Laplace equation

\[
d\mu^s_j = d\mu^s_j = V_i^s dp^s = V_i^s d \left( \frac{2y^d}{r} \right)
\]

Dynamic equilibrium

\[
(\mu^s_i)_{r} - (\mu^s_i)_{r=\infty} = V_i^s \frac{2y^d}{r}
\]

For an incompressible solid phase

\[
\mu_A = \mu_A^s + RT \ln a_A
\]

Definition of activity

\[
\ln \frac{(x_i^s)_r}{(x_i^s)_{r=\infty}} = \frac{V_i^s}{RT} \frac{2y^d}{r}
\]

Solubility increases exponentially with reduction in size, \( r \)

\[
(x_i^s)_r = (x_i^s)_{r=\infty} \exp \left( \frac{2y^d}{(\rho RT) r} \right)
\]

Small particles dissolve to build large particles with lower solubility

- To obtain nanoparticles you need to supersaturate to a high concentration (far from equilibrium).
- Low surface energy favors nanoparticles. (Such as at high temperatures)
- High temperature and high solid density favor nanoparticles.

Supersaturation is required for any nucleation
Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

**Bulk decreases free energy**

\[ \Delta_{1-s}G = -\frac{4}{3} \pi r^3 \left( \frac{\rho}{M} \right) \Delta_{fus}G_m + 4\pi r^2 \gamma^{sl} \]

**Surface increases free energy**

\( (M/r) \) is molar volume

\[ \frac{d\Delta_{1-s}G}{dr} = -4\pi r^2 \left( \frac{\rho}{M} \right) \Delta_{fus}G_m + 8\pi r \gamma^{sl} \]

**Barrier energy for nucleation at the critical nucleus size beyond which growth is spontaneous**

\[ r^* = \frac{[2(M/\rho)\gamma^{sl}]}{\Delta_{fus}G_m} \]

\[ \Delta_{1-s}G^* = \frac{16\pi (\gamma^{sl})^3 M^2}{3\rho^2 \Delta_{fus}G_m^2} \]
Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

\[ r^* = \frac{[2(M/\rho)\gamma_{sl}]}{\Delta_{fus}G_m} \]

\[ \Delta_{1-s}G^* = \frac{16\pi(\gamma_{sl})^3 M^2}{3\rho^2 \Delta_{fus}G_m^2} \]

\[ \Delta_{fus}G_m = \Delta_{fus}H_m - T\Delta_{fus}S_m \]

Lower T leads to larger \( \Delta_{fus}G_m \) (Driving force for crystallization)
smaller \( r^* \) and smaller \( \Delta_{1-s}G^* \)

Deep quench, far from equilibrium leads to nanoparticles

Figure 6.16 (a) The critical radius \( (r^*) \) and thermodynamic barrier for nucleation of Al \( (\Delta G^*) \) versus degree of supercooling \( \Delta T_{fus} \). (b) The Gibbs energy of a spherical Al crystal relative to the supercooled Al(1) as a function of its radius. \( \Delta_{fus}H_m = 10.794 \text{ kJ mol}^{-1}, \Delta_{fus}S_m = 933.47 \text{ K and } \rho = 2.55 \text{ g cm}^{-3} \) [8].
Ostwald Ripening

Dissolution/precipitation mechanism for grain growth
Consider small and large grains in contact with a solution

\[
(\mu^S_{i})_{r'} - (\mu^S_{i})_{r''} = 2V^S_{i} \gamma^{sl}\left(\frac{1}{r'} - \frac{1}{r''}\right)
\]

Grain Growth and Elimination of Pores

Figure 6.17: The difference in the chemical potential of Au(s) between a spherical particle with radius 10 μm and a smaller particle with radius \( r \), \( \rho = 18.4 \text{ g cm}^{-3} \) and \( \gamma^{sl} = 1.38 \text{ J m}^{-2} \) [21].
Formation of a surface nucleus versus a bulk nucleus from n monomers

Homogeneous

$$\Delta G_n = -n\phi + \psi_n$$
$$\phi = \mu - \mu_0 = kT \ln \left( \frac{x}{x_n} \right)$$

$$\psi_n = \mu^s_n - n\mu_0$$

Heterogeneous (Surface Patch)

$$\Delta G'_n = -\phi n' + \psi'_n$$

$$\psi'_n = 2\pi h \gamma = 2\gamma \sqrt{n_n \mu'} = \psi'_n^{1/2}$$

Bulk vs n-mer
So surface excess chemical potential

$$\Delta G_n = -\phi n + \psi n^3$$

$$n^* = \left( \frac{2\psi}{3\phi} \right)^3$$

Surface energy from the sides of the patch

$$\Delta G'_n = -\phi n' + \psi' n'^{1/2}$$

$$n'^* = \left( \frac{\psi'}{2\phi} \right)^2$$

$$\Delta G^*_n = \frac{4\psi^3}{27\phi^2} = \frac{\psi n^*^{2/3}}{3} = \frac{\phi n^*}{2}$$

$$\Delta G'^*_n = \frac{\psi'^2}{4\phi} = \frac{\psi' \sqrt{n'^*}}{2} = \phi n'^* = \frac{\pi h \gamma^2}{\phi}$$
Barrier is half the height for nucleation
Size is half

\[ \Delta G^* = \frac{4\psi^3}{27\phi^2} = \frac{\psi n^*^2}{3} = \frac{\phi n^*}{2} \]

\[ \Delta G'^* = \frac{\psi'^2}{4\phi} = \frac{\psi'\sqrt{n'^*}}{2} = \frac{\phi n'^*}{\phi} = \frac{\pi \hbar \nu_1 \gamma^2}{\phi} \]

\[ r^* = \frac{2\gamma \nu_1}{\phi} = 2r'^* \]

\[ r'^* = \sqrt{\frac{n'^* \nu_1}{\pi \hbar}} = \frac{\gamma \nu_1}{\phi} \]
Three forms of the Gibbs-Thompson Equation

Ostwald-Freundlich Equation

\[ x = x_\infty \exp \left( \frac{2v_1 \gamma}{rkT} \right) \]

- \( x = \) supersaturated mole fraction
- \( x_\infty = \) equilibrium mole fraction
- \( v_1 = \) the molar volume

\[ \Delta G = -n\phi + \gamma A \]

Free energy of formation for an \( n \)-mer nanoparticle from a supersaturated solution at \( T \)

\[ \phi = \mu - \mu_\infty = kT \ln \left( \frac{x}{x_\infty} \right) \]

Difference in chemical potential between a monomer in supersaturated conditions and equilibrium with the particle of size \( r \)

\[ \frac{d(\Delta G)}{dn} = 0 = -\phi + \gamma v_1 \frac{dA}{dV} \]

At equilibrium

\[ A = 4\pi r^2 = (4\pi)^{\frac{1}{3}} 3^3 V^\frac{2}{3} \]

For a sphere

\[ \frac{dA}{dV} \sim \frac{2}{r} \]
Three forms of the Gibbs-Thompson Equation

**Ostwald-Freundlich Equation**

\[ x = x_\infty \exp\left(\frac{2v_1\gamma}{rkT}\right) \]

Areas of sharp curvature nucleate and grow to fill in. Curvature \( \kappa = 1/r \)

\[ x = x_\infty \exp\left(\frac{2(\kappa_1 + \kappa_2)v_1\gamma}{kT}\right) \]

Second Form of GT Equation
Three forms of the Gibbs-Thompson Equation

Third form of GT Equation/ Hoffman-Lauritzen Equation
B is a geometric factor from 2 to 6

Crystallize from a melt, so supersaturate by a deep quench

Free energy of a crystal formed at supercooled temperature T
Adsorption Isotherms

\[ B_g + V_{MON} \xrightleftharpoons[k_d]{k_a} B_{MON} \]

- \( B_g \) - Gas species (N\(_2\))
- \( B_{mon} \) - Adsorbed (N\(_2\)) in an occupied surface site
- \( V_{mon} \) - Available surface site

Equilibrium Constant:

\[ K_L = \frac{k_a}{k_d} = \frac{\Gamma_B}{a_B^g(\Gamma_{sat} - \Gamma_B)} \]

\[ \frac{\Gamma_B / \Gamma_B^{max}}{1 - \Gamma_B / \Gamma_B^{max}} = \frac{\theta}{1 - \theta} = K_L a_B \]

**Langmuir Adsorption Isotherm**

\( \theta = \Gamma_B / \Gamma_B^{max} \) Fractional Coverage

\( \Gamma_B^{max} \) is the coverage for a monolayer.

\( a_B^g \) is activity of B in the gas phase

**Figure 6.24** Adsorption isotherms following Langmuir adsorption isotherm.
Derivation of Langmuir Equation (as derived by Hill)

Langmuir Equation is for equilibrium of a monolayer with a solution of concentration $x_2$

A surface has adsorption sites that can hold solvent (1) or solute (2)

Some fraction of the surface bound to solute, $x_2^b$, and some fraction to solvent, $x_1^b$.

The concentration of solute in the solution ((partial pressure or pressure)/saturated pressure) is $x_2^s = \theta$

The equilibrium involves $x_1^b + x_2^s \Leftrightarrow x_1^s + x_2^b$

The equilibrium constant is given by, $K = (x_1^b x_2^s)/(x_1^s x_2^b) = \frac{1 - x_2^b}{(1 - \theta) x_2^b}$

Rearranging yields $\theta = Kx_2^b/(1 - x_2^b + Kx_2^b) \sim Kx_2^b/(1 + Kx_2^b) = \frac{p}{p_0}$
Derivation of BET Theory

Langmuir Equation is for monolayers
BET is for multilayers where the first layer has an energy of adsorption, $E_1$, and second and higher layers use the energy of liquification, $E_L$
Langmuir Equation is applied for each layer (gas and adsorbed layer are at dynamic equilibrium)
At $P_{sat}$ the surface is in the liquid (For Langmuir this was a monolayer)

Fractional coverage of layer $i$, $\theta_i$
Rate of adsorption on layer $i$ to fill layer $i$, $R_{i-1,ads} = k_{i,ad} P \theta_{i-1}$
Rate if desorption from layer $i$, $R_{i,des} = k_{i,des} \theta_i$
$k_{i,ads} = k_{i,des} = \exp(-E_i/kT)$

\[
\frac{1}{v [(p_0/p) - 1]} = \frac{c - 1}{v m c} \left( \frac{p}{p_0} \right) + \frac{1}{v m c},
\]

\[
c = \exp \left( \frac{E_1 - E_L}{RT} \right)
\]

$v_m = \text{monolayer amount of gas}$
$v = \text{experimental amount of gas adsorbed}$
How can you predict the phase size? (Meier and Helfand Theory)
Consider lamellar micro-phase separation.

\[ d_{AB}^3 = \frac{N_{AB}^3 v_c^3}{\sigma_p^3} \propto \chi \delta t v_c^{2/3} N_{AB}^2 \]

**Fig. 4.30.** Set of samples of Fig. 4.28. Molecular weight dependence of the layer spacing \( d_{AB} \)
Course Summary

VII. Heat of Formation:
- Dependencies in periodic table;
- Electronegativity;
- Energetics of formation (electrostatic, repulsion, dispersion, polarization, crystal field);
- Atomic size (perovskites, spinels, zeolites);
- Substitutional solids;
- Conformational entropy of polymers
Electronegativity, the ability of an atom to attract electrons in a bond
Linus Pauling
<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>d-orbitals</th>
<th>Acidic (at high oxidation state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
<td>10 valence electrons</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td></td>
<td></td>
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<tr>
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<td>4</td>
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<td>5</td>
<td>5</td>
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<td>6</td>
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<td></td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Basic (at low oxidation state)
- Transition Metals
- Acidic (at high oxidation state)

**Blocks in the periodic table**

- Basic
- Acidic
- s-orbitals
- p-orbitals
- d-orbitals
- f-orbitals

2 valence electrons (more basic to right)
14 valence electrons (more acidic to right)
Energetics of compound formation

\[ M^+(g) + X^-(g) = MX(s) \quad -\Delta_{\text{latt}}H_m \]

\[ \Delta_{\text{latt}}H_m = \Phi_{\text{electrostatic}} + \Phi_{\text{repulsion}} + \Phi_{\text{dispersion}} + \Phi_{\text{polarization}} + \Phi_{\text{crystal field}} \]

Electrostatic attraction +-  
Electron electron repulsion  
Van der Waals or dispersion (\(\delta^+\) makes \(\delta^\-) leads to net attraction)  
Polarization (shifting within compound of electrons)  
Crystal field effects
Conformational Enthalpy of Polymers

The Rotational Isomeric State Model of Volkenstein and Paul Flory (Nobel Prize)

Carbon has a tetrahedral bonding arrangement
For a chain of carbon the two side groups interact with the side groups of neighboring carbons

For Butene

“Trans” is sterically the most favorable arrangement
“Gauche +” and “Gauche -” are less favorable

The Boltzmann equation gives the probability of a particular conformation, \( Z \) is the partition function or the sum of all of the different Boltzmann expressions in an ensemble

\[
P(\varphi_i) = \frac{\exp(-E(\varphi_i)/kT)}{Z}
\]

\[
Z = \sum_i e^{-\beta E_i}
\]
Conformational Enthalpy of Polymers

The Rotational Isomeric State Model of Volkenstein and Paul Flory (Nobel Prize)

For a polymer with N carbons there are N-2 covalent bonds.

The number of discrete conformation states per chain is \( \nu^{N-2} \) where \( \nu \) is the number of discrete rotational states for the chain, tttt, g\( \cdot \)g\( \cdot \)g\( \cdot \)g, g\( \cdot \)g\( \cdot \)g\( \cdot \)g\( \cdot \), g\( \cdot \)+g\( \cdot \)+g\( \cdot \)+g\( \cdot \), etc. for N = 4; N\( \approx \)1, N4=4, etc. assuming no end effects.

\[
Z = \sum_{\{N_1, \ldots, N_\nu\}} \frac{(N-2)!}{N_1! \cdots N_\nu!} \exp\left(-N_1 E(\varphi_1)/kT\right) \cdots \exp\left(-N_\nu E(\varphi_\nu)/kT\right)
\]

Average rotational angle

\[
\langle \cos \varphi \rangle = \frac{\sum_{i=1}^{\nu} \exp\left(-E(\varphi_i)/kT\right) \cos \varphi_i}{\sum_{i=1}^{\nu} \exp\left(-E(\varphi_i)/kT\right)} = \frac{1 - \sigma}{1 + 2\sigma}
\]

Q is the bond angle
180° - 109° = 71°

\( E_{g^+} = 2100 \) J/mole

\( C_\infty = 3.6 \)

Exp. 6.7
Course Summary

VIII. Heat Capacity:
Cp-Cv;
Internal energy of a gas;
Dulong-Petit Law for solids;
Phonons; longitudinal; transverse; optical; acoustic
Brillouin Zones;
Acoustic phonons; Optical Phonons
Density of states;
Bose-Einstein statistics;
Einstein model;
Debye model;
Dispersion relations;
Debye temperature; Debye frequency;
Modulus and heat capacity;
Grüneisen parameter Cp-Cv
Spectroscopy; density of states; heat capacity;
Entropy from heat capacity;
Heat capacity from group contribution;
Electronic heat capacity;
Heat capacity at second order transitions;
Heat capacity of polymers
Derive the expression for $C_p - C_v$

$$C_p - C_v = \alpha^2 VT/kT$$
$$\alpha = (1/V) (dV/dT)_p$$
$$k_T = (1/V) (dV/dP)_T$$

$C_v = (dU/dT)_V$

From the Thermodynamic Square

$$dU = TdS - pdV$$ so $C_v = (dU/dT)_V = T (dS/dT)_V - p (dV/dT)_V$

Second term is 0 $dV$ at constant $V$ is 0

$$(dS/dT)_V = C_v / T$$

Similarly

$C_p = (dH/dT)_p$

From the Thermodynamic Square

$$dH = TdS + Vdp$$ so $C_p = (dH/dT)_p = T (dS/dT)_p - V (dp/dT)_p$

Second term is 0 $dp$ at constant $p$ is 0

$$(dS/dT)_p = C_p / T$$

From Chapter 1

Write a differential expression for $dS$ as a function of $T$ and $V$

$$dS = (dS/dT)_V dT + (dS/dV)_T dV$$ using expression for $C_v$ above and Maxwell for $(dS/dV)_T$

$$dS = C_v / T dT + (dp/dT)_V dV$$ use chain rule: $(dp/dT)_V = -(dV/dT)_p (dP/dV)_T = V\alpha / (V\kappa T)$

Take the derivative for $C_p$: $C_p/T = (dS/dT)_p = C_v / T (dT/dT)_p + (\alpha/\kappa_T)(dV/dT)_p = C_v / T + (V\alpha^2/k_T)$

$C_p - C_v = \alpha^2 VT/kT$
Table 8.1 Number of modes and heat capacity of gases in the classical limit.

<table>
<thead>
<tr>
<th></th>
<th>Number of modes</th>
<th>Classical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Translational</td>
<td>Rotational</td>
</tr>
<tr>
<td>A(g)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>AB(g)</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>AB$_2$(g)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>non-linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_2$(g)</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_{n-1}$(g)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>non-linear</td>
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<td></td>
</tr>
<tr>
<td>AB$_{n-1}$(g)</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
Monoatomic H(g) with only translational degrees of freedom is already fully excited at low temperatures. The vibrational frequencies \( n \) of H2(g) and H2O(g) are much higher, in the range of 100 THz, and the associated energy levels are significantly excited only at temperatures above 1000 K. At room temperature only a few molecules will have enough energy to excite the vibrational modes, and the heat capacity is much lower than the classical value. The rotational frequencies are of the order 100 times smaller, so they are fully excited above \( \sim 10 \) K.
Atoms in a crystal (Dulong and Petit Model)

Works at high temperature

Three Harmonic oscillators, x, y, z
Spring (Potential Energy)
\[ \frac{dU}{dx} = F = -kx \] where x is 0 at the rest position
\[ U = -\frac{1}{2} kx^2 \]
Kinetic Energy
\[ U = \frac{1}{2} mc^2 \]

Each atom in a solid has 6 springs
Each spring with \( \frac{1}{2} kT \) energy
So \( 6/2R = 3R = C_v \)

\[ U = \frac{1}{2} mc^2 + \frac{1}{2} Kx^2 = \frac{1}{2} mA^2 \omega^2 \cos^2 \omega t + \frac{1}{2} KA^2 \sin^2 \omega t \]

\[ x = A \sin \omega t \]
\[ \omega = 2\pi v = \sqrt{\frac{K}{m}} \]

Three oscillator per atom so \( U_m = 3RT \)

\[ CV,m = 3R = 24.94 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ dU = -pdV + TdS \]
\[ d(U/dT)_V = T(dS/dT)_V = C_v \]
Phonons

Two size scales, a and λ.

If λ ≥ a you are within a Brillouin Zone

Wavevector $k = 2\pi/\lambda$

k-vector is like the inverse-space vectors for the lattice
It is seen to repeat in inverse space making an inverse lattice

A phonon with wavenumber $k$ is thus equivalent to an
infinite family of phonons with
wavenumbers $k \pm 2\pi/\lambda$, $k \pm 4\pi/\lambda$, and so forth.

Brillouin zones, (a) in a square lattice, and (b) in a
hexagonal lattice

those whose bands become zero at the center of
the Brillouin zone are called acoustic phonons, since they
correspond to classical sound in the limit of long
wavelengths. The others are optical phonons, since they
can be excited by electromagnetic radiation.
Phonons

Two size scales, a and λ

If $\lambda \geq a$ you are within a Brillouin Zone

Wavevector $k = \frac{2\pi}{\lambda}$

The density of states is defined by

$$D(E) = \frac{1}{V} \cdot \frac{dZ_m(E)}{dE}$$

The partition function can be defined in terms of $E$ or in terms of $k$

$E$ and $k$ are related by the dispersion relationship which differs for different systems

For a longitudinal Phonon in a string of atoms the dispersion relation is:

$$E = 2\hbar\omega_0 \left| \sin \left( \frac{ka}{2} \right) \right|$$

where $\omega_0 = \sqrt{k_F/m}$ is the oscillator frequency, $m$ the mass of the atoms, $k_F$ the inter-atomic force constant and $a$ inter-atomic spacing.
Phonons

Bose-Einstein statistics gives the probability of finding a phonon in a given state:

\[ n(\omega_{k,s}) = \frac{1}{\exp\left(\frac{\hbar \omega_{k,s}}{k_B T}\right) - 1} \]
Phonons

Dispersion relation for phonons

\[ \omega^2_{\pm} = K \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \pm K \sqrt{\left( \frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2 \frac{ka}{2}}{m_1 m_2}} \]

Plus optical
Minus Acoustic
Einstein Model

*Works at low and high temperature*

*Lower at low temperature*

Quantized energy levels

\[ \varepsilon_n = (n + \frac{1}{2}) \hbar \omega \]

Bose-Einstein statistics determines the distribution of energies

The mean “n” at T is given by

\[ \bar{n} = \frac{1}{\exp(\hbar \omega / k_B T) - 1} \]

Average energy for a crystal with three identical oscillators

\[ \bar{U} = 3N(\frac{1}{2} + \bar{n}) \hbar \omega_E = 3N\left(\frac{\hbar \omega_E}{2} + \frac{\hbar \omega_E}{\exp(\hbar \omega_E / k_B T) - 1}\right) \]
Einstein Model

*Works at low and high temperature*

*Lower at low temperature*

Average energy for a crystal with three identical oscillators

\[ \bar{U} = 3N \left( \frac{1}{2} + \bar{n} \right) \hbar \omega_E = 3N \left( \frac{\hbar \omega_E}{2} + \frac{\hbar \omega_E}{\exp(\hbar \omega_E / k_B T) - 1} \right) \]

\[ C_{V,m} = \left( \frac{d\bar{U}}{dT} \right)_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E / T)}{[\exp(\Theta_E / T) - 1]^2} \]

**Einstein temperature:**

\[ \Theta_E = \frac{\hbar \omega_E}{k_B} \]
Dispersion Curve

\[ \omega(q) = \sqrt{\frac{4K}{m}} \sin\left(\frac{qa}{2}\right) \]

Angular frequency of vibrations as a function of wavevector, q

First Brillouin Zone of the one-dimensional lattice

- \( -\frac{\pi}{a} < q < \frac{\pi}{a} \)

Longer wavevectors are smaller than the lattice

Figure 8.5 The dispersion curve for a one-dimensional monoatomic chain of atoms.
Longitudinal and Transverse dispersion relationships for [100], [110], and [111] for lead.

Transverse degenerate for [100] and [111] (4 and 3 fold rotation axis).
Not for [110] (two fold rotation axis).

Figure 8.7 Experimental dispersion relations for acoustic modes for lead at 100 K [2].
Reproduced by permission of B. N. Brockhouse and the American Physical Society.
Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{v,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

Higher Characteristic $T$ represents stronger bonds.
Table 8.2. Debye temperature ($\Theta_D$ in K) and electronic heat capacity coefficient (see Section 8.4) ($\gamma$ in mJ K$^{-1}$ mol$^{-1}$) of the elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Theta_D$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>344</td>
<td>1440</td>
</tr>
<tr>
<td>Be</td>
<td>2</td>
<td>77</td>
</tr>
<tr>
<td>Na</td>
<td>158</td>
<td>400</td>
</tr>
<tr>
<td>K</td>
<td>91</td>
<td>230</td>
</tr>
<tr>
<td>Ca</td>
<td>360</td>
<td>147</td>
</tr>
<tr>
<td>Sc</td>
<td>420</td>
<td>280</td>
</tr>
<tr>
<td>Ti</td>
<td>380</td>
<td>291</td>
</tr>
<tr>
<td>V</td>
<td>630</td>
<td>450</td>
</tr>
<tr>
<td>Cr</td>
<td>410</td>
<td>600</td>
</tr>
<tr>
<td>Mn</td>
<td>470</td>
<td>480</td>
</tr>
<tr>
<td>Fe</td>
<td>445</td>
<td>274</td>
</tr>
<tr>
<td>Co</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>73</td>
<td>6</td>
</tr>
<tr>
<td>Cu</td>
<td>315</td>
<td>209</td>
</tr>
<tr>
<td>Zn</td>
<td>327</td>
<td>6</td>
</tr>
<tr>
<td>Ga</td>
<td>320</td>
<td>108</td>
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<tr>
<td>Ge</td>
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<td>230</td>
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<td>As</td>
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<td>Se</td>
<td>90</td>
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<td>Br</td>
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<td>18</td>
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<td>Nb</td>
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<td>Mo</td>
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<td>240</td>
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<td>Tc</td>
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<td>Rh</td>
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<td>Ag</td>
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<td>240</td>
</tr>
<tr>
<td>Cd</td>
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</tr>
<tr>
<td>In</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Sn</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>Sb</td>
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<tr>
<td>Te</td>
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<tr>
<td>I</td>
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</tr>
<tr>
<td>Re</td>
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<tr>
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</tr>
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</tr>
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<td>34</td>
</tr>
<tr>
<td>Bi</td>
<td>119</td>
<td>34</td>
</tr>
<tr>
<td>Po</td>
<td>At</td>
<td>Rn</td>
</tr>
</tbody>
</table>

Higher Characteristic $T$ represents stronger bonds.
Modulus and Heat Capacity

\[ \sigma = E \varepsilon \]
\[ \frac{F}{A} = E \frac{\Delta d}{d} \]

\[ F = K \Delta d \]
\[ K = \frac{F}{\Delta d} = \frac{E A}{d} \]

At large \( q \), \( \omega = \sqrt{4K/m} \)
This yields \( \omega_0 \) from \( E \)

For Cu, \( \theta_D = 344K \)

\[ \Theta_D = \frac{h \omega_D}{k_B} = 2\pi \frac{hv_D}{k_B} \]
\[ \omega_D = 32 \text{ THz} \]

\( K = 13.4 \text{ N/m} \)
\( \omega_D = 18 \text{ THz} \)
Spectroscopy measures vibrations, this can be used to calculate the density of states, this can be integrated to obtain the heat capacity

$$3N_A g(v) dv \quad \text{where} \quad \int_0^\infty g(v) dv = 1$$

Number of vibrational modes

IR: High Polarity
Motion of charged atoms under electromagnetic field

NaCl

Raman: High Polarizability
Motion of electrons in polarizable bonds under electromagnetic field

Benzene, Graphene, Nanotubes,
From the Thermodynamic Square

\[ dU = TdS - pdV \] so

\[ C_v = \left( \frac{dU}{dT} \right)_V = T \left( \frac{dS}{dT} \right)_V - p \left( \frac{dV}{dT} \right)_V \]

Second term is 0 \( dV \) at constant \( V \) is 0

\[ \left( \frac{dS}{dT} \right)_V = C_v / T \]

Similarly

\[ C_p = \left( \frac{dH}{dT} \right)_p \]

From the Thermodynamic Square

\[ dH = TdS + Vdp \] so

\[ C_p = \left( \frac{dH}{dT} \right)_p = T \left( \frac{dS}{dT} \right)_p - V \left( \frac{dp}{dT} \right)_p \]

Second term is 0 \( dp \) at constant \( p \) is 0

\[ \left( \frac{dS}{dT} \right)_p = C_p / T \]

Integrate \( C_p / T \) \( dT \) or Integrate \( C_v / T \) \( dT \) to obtain \( S \)

**Low Temperatures Solve Numerically**

**High Temperatures Series Expansion**
A striking example is the electronic heat capacity coefficients observed for Rh–Pd–Ag alloys given in Figure 8.22 [17]. In the rigid band approach the addition of Ag to Pd gives an extra electron per atom of silver and these electrons fill the band to a higher energy level. Correspondingly, alloying with Rh gives an electron hole per Rh atom and the Fermi level is moved to a lower energy. The variation of the electronic heat capacity coefficient with composition of the alloy maps approximately the shape of such an electron band.
For a system with quantized energy and two states $\varepsilon_1$ and $\varepsilon_2$, the ratio of the probabilities of the two states is given by the Boltzmann potentials, ($\tau$ is the temperature $k_B T$)

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}.$$  

If state $\varepsilon_2$ is the ground state, $\varepsilon_2 = 0$, and the sum of exponentials is called the partition function $Z$, and the sum of probabilities equals 1 then,

$$Z = \exp(-\varepsilon_2/\tau) + 1$$

$Z$ normalizes the probability for a state “$s$”

$$P(\varepsilon_s) = \exp(-\varepsilon_s/\tau)/Z$$

The average energy for the system is $U = \frac{\langle \Sigma \varepsilon_i e^{-\varepsilon_i/\tau} \rangle}{Z} = \tau^2 \left( \frac{d \ln Z}{d \tau} \right)$
Heat Capacity of Polymers

Amorphous structure but with regular order along the chain
1-d vibrational structure

Einstein method works well above 100K

\[ E(\theta/T) = \frac{[(\theta/T)^2 \exp(\theta/T)]}{[\exp(\theta/T) - 1]^2} \]

\[ C_E = N k \sum_{N_E} E(\theta/T) \]

\[ N_E = 3N_{\text{Atoms}} - N \]

\[ C_{V,m} = \left( \frac{dU}{dT} \right)_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2} \]

Einstein temperature:
\[ \Theta_E = \frac{h\omega_E}{k_B} \]

\[ N_{\text{Atoms}} = \text{number of atoms in a mer unit} \]
3 for CH₂

\[ N = \text{number of skeletal modes of vibration} \]
N = 2 for -(CH₂)ₙ-
**Course Summary**

IX. Solution Models and Equations of State:
- Regular solution;
- Quasi-regular solution with lattice vibrations;
- Accounting for correlations (mean field or specific interactions);
- Virial approach for mean field;
- Correlation function for specific interactions;
- Van der Waals model;
- Margulis model; Margulis acid-base;
- Redlich-Kister model (asymmetric phase diagrams);
- Scatchard-Hildebrand theory (volume versus mole fraction);
- Flory-Huggins model (polymers based on volume fraction);

Group Contribution Models:
- Hydrogen bonding MOSCED (Modified separation of cohesive energy density); SSCED (Simplified separation of cohesive energy density);
- Local Clustering Models: Wilson’s equation; NRTL (Non-random two liquid model);
- Surface area rather than volume fraction for interactions: UNIQUAC (Universal quasi-chemical model);
- UNIFAC (Universal functional activity coefficient model);
- Solutions with multiple sublattices (NaCl);
- Order-disorder systems
- Order parameter
- Non-stoichiometric compounds (perovskite oxides)
Regular Solution Solution Model

\[ G \approx A = -k_B T \ln \left[ \frac{N!}{N_A! N_B!} \right] + U_A + U_B + \frac{z N_A N_B}{N} \omega_{AB} \]

\[ \Delta_{\text{mix}} G_m = R T [x_A \ln x_A + x_B \ln x_B] + \Omega_{AB} x_A x_B \]

\[ \Omega_{AB} = z L \omega_{AB} \]

\[ \Delta_{\text{mix}} H_m \approx \Delta_{\text{mix}} U_m = \Omega_{AB} x_A x_B \]

\[ \mu_A \sim \frac{dG}{dx_A} \]

\[ \mu_A - \mu_A^o = R T \ln a_A = R T \ln x_A + \Omega_{AB} x_B^2 \]

\[ R T \ln \gamma_A = \Omega_{AB} x_B^2 \]
Excess molar Gibbs energy of mixing for quasi-regular solution

$$\Delta_{\text{mix}}^{\text{exc}} G_m = zL x_A x_B (\omega_{AB} - T \eta_{AB})$$

G = H –TS so first term is enthalpic, second is entropic

$$\Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B \Omega_{AB} \left(1 - \frac{T}{\tau}\right)$$

\(\tau\) is a characteristic temperature, when \(T = \tau\) ideal solution behavior is seen
Correlations

Dilute: Ideal behavior, there are no interactions.

Semi-dilute: weak or strong interactions are possible.

With weak interactions the system can be treated with a "mean field". No correlation is observed, we can use the second virial coefficient and Hildebrand Model.

With strong interactions we need to use detailed information about interactions, correlation function or other models.
\[ S(k) = 1 + \rho \int \text{d}r \left(g(r) - 1\right) \exp(ik \cdot r). \]

**Fig. 3.2.** Structure factor of liquid sodium near the normal melting temperature. The points are experimental x-ray scattering results\(^8\) and the curve is obtained from a Monte Carlo calculation\(^9\) for the \(r^{-4}\) potential under the same thermodynamic conditions.
Chapter 11 Elliot and Lira

Margulis one-parameter Model

$$\frac{G^E}{RT} = A_{12}x_1x_2$$

$$\ln \gamma_i = A_{12}(1-x_i)^2$$

Margulis acid-base Model

\textit{acidity parameter, }\alpha, \textit{ and basicity parameter, }\beta, \textit{ and} 

Hildebrand Model

$$\Delta_{mix}^{exc} G_m = x_A x_B \Omega_{AB}$$

Margulis acid-base Model

$$A_{12} = (\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)(4RT)$$

Table 11.1. Acidity (\(\alpha\)) and Basicity (\(\beta\)) Parameters in (J/cm\(^3\))\(^{1/2}\) and Molar Volumes (cm\(^3\)/mol) for Various Substances as Liquids at 298 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\nu^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0</td>
<td>11.14</td>
<td>73.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.63</td>
<td>2.24</td>
<td>89.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>5.80</td>
<td>0.12</td>
<td>80.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.58</td>
<td>13.29</td>
<td>58.2</td>
</tr>
<tr>
<td>(\alpha)-Hexane</td>
<td>0</td>
<td>0</td>
<td>130.3</td>
</tr>
<tr>
<td>Isoctane</td>
<td>0</td>
<td>0</td>
<td>162.9</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>9.23</td>
<td>11.86</td>
<td>76.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>17.43</td>
<td>14.49</td>
<td>40.5</td>
</tr>
<tr>
<td>MEK</td>
<td>0</td>
<td>9.70</td>
<td>90.1</td>
</tr>
<tr>
<td>Water</td>
<td>50.13</td>
<td>15.06</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Figure 11.7. Observations about complexation. (a) A mixture of acid with base suggests favorable interactions, as in acetone + chloroform. (b) Hydrogen bonding leads to unfavorable interactions when one component associates strongly and the other is inert, as in isoctane + water. (c) Hydrogen bonding solutions can also be ideal solutions if both components have similar acidity and basicity, as in methanol + ethanol.
Course Summary

X. Thermodynamics and materials modeling:
Quantum mechanics (ab initio method, electronic wave functions, nuclei don’t move);
Density functional theory (Minimize $E(\rho)$ as a function of $\rho(r)$);
Molecular dynamics modeling (potential fields between atoms);
Density functional theory
Mesoscale models (coarse graining; short range interaction potentials);
Dissipative particle dynamics (DPD);
Monte Carlo Metropolis method;
Ising model;
Packages to do materials simulations of different types: LAMMPS; HOOMD-blue; ESPResSo; etc.
Free servers for simulations from Google: Colaboratory
Thermodynamics and Materials Modeling

- Coarse Grain Simulations
- DPD Simulations
- Machine Learning
- Data Mining Techniques
Quantum mechanical/ab initio methods

1) Electronic wavefunction is independent of the nuclei since electrons are much smaller and move much faster: Born Oppenheimer Approximation

2) Solve the Schrödinger equation

\[ \hat{H} \Psi = E \Psi \]

Hamiltonian in atomic units:

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{|r_i - d_{\alpha}|} + \sum_i \sum_{j \neq i} \frac{1}{|r_i - r_j|} + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha}Z_{\beta}}{|d_{\beta} - d_{\alpha}|} \]

\[ r_i \text{ electron positions; } d_{\alpha} \text{ nuclear positions, } Z_{\alpha} \text{ nuclear charge} \]

Kinetic Energy – e⁻ nuc. attraction + e⁻ e⁻ repulsion + Nuc. Nuc. repulsion

3) Solve approximately since true wave function can’t be found directly. Compare proposed function results with data. Variational Principle: lowest energy wins.

\[ E = \frac{\int \Psi^* \hat{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \]

4) Obey Pauli exclusion principle.
Density functional theory

1) Ground state can be obtained through minimization of $E(\rho)$ of $\rho(r)$
2) Parallel non-interacting system (NIS)

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$

3) Write the energy functional as

$$E[\rho] = T_S[\rho] + V_{\text{nuc}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \int \psi_i^*(r) \nabla^2 \psi_i(r) \, dr - \sum_{\alpha} \int \rho(r) \frac{Z_\alpha}{|r - d_\alpha|} \, dr$$

$$+ \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r - r'|} \, dr \, dr' + E_{\text{xc}}[\rho]$$

KE of NIS + e- nuc. int. + Coulomb + exchange correlation energy

4) Minimize $E[\rho]$ to obtain wave functions then iterate to obtain the ground state density and energy
Molecular Dynamics

1) Generate initial condition with particles identified by position and velocity
2) Calculate the force on each particle using potentials
3) Forces (accelerations) remain constant for a time step, position and velocity change
   \[ v_i(t + \Delta t/2) = v_i(t - \Delta t/2) + \frac{f_i}{m_i} \Delta t \]
   \[ r_i(t + \Delta t) = r_i(t) + v_i(t + \Delta t/2) \Delta t \]
4) Repeat 3) until temperature is constant
   \[ \frac{3}{2} N k_B T = \frac{1}{2} \sum_i m_i v_i^2 \]
5) After steady state record velocities and positions so that \(<r^2> = 6Dt\) is found

Time calculation is on the order of nanoseconds.

Neither Monte Carlo nor Molecular Dynamics can calculate the free energy since they ignore large energy regions of phase space

They can calculate differences in free energy for phase diagram construction
Mesoscale Phenomena and Models

Due to the wide range of characteristic lengths - times, several simulation methods that describe length and time scales have been developed:
Dissipative Particle Dynamics (DPD)

**MD**
- MICROscopic level approach
- atomistic approach is often problematic because larger time/length scales are involved

**DPD**
- set of point particles that move off-lattice through prescribed forces
  - each particle is a collection of molecules
  - MESOscopic scales
  - momentum-conserving Brownian dynamics

**Navier-Stokes**
- continuum fluid mechanics
  - MACROscopic modeling

Ref on Theory: Lei, Caswell & Karniadakis, Phys. Rev. E, 2010
Monte Carlo Method

Periodic Boundary Conditions

Fix T, V, N

\[
\langle Q \rangle = \int Q(Z)P(Z) \, dZ \\
P(Z) = \frac{\exp(-U(Z)/k_BT)}{\int \exp(-U(Z)/k_BT) \, dZ}
\]

“Z” is a state of the system

1) Calculate \( \phi(Z) \) by molecular mechanics with potentials
2) Accept a configuration “Z” if it has a low energy relative to \( kT \) with some randomness
3) Calculate the average

\[
\langle Q \rangle = \frac{1}{M} \sum_{i=1}^{M} Q(Z)
\]

1) Start with a random configuration calculate \( \phi(Z) \)
2) Move one atom or molecule or group of molecules
3) Calculate \( \phi(Z') \) if lower than \( \phi(Z) \) accept
4) If higher than \( \phi(Z) \) calculate \( \exp(-\Delta\phi/kT) \) and a random number from 0 to 1
5) If higher than random number accept
6) Repeat
Dissipative Particle Dynamics (DPD)

FIG. 1. Dissipative particles interact pair-wise with a conservative linear repulsive force, and a Brownian dashpot made of a friction force that reduces the relative velocity between the particles and a stochastic force that gives kicks of equal size and opposite directions to the particles. These forces vanish beyond a cutoff radius $r_c$. 
Course Summary

I. Introduction
II. Single component systems
III. Solutions
IV. Phase diagrams
V. Phase stability
VI. Surfaces
VII. Heat of formation
VIII. Heat capacity
IX. Solution models and equations of state
X. Thermodynamics and materials modeling