

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**
- XI. Experimental methods**

Course Summary

I. Introduction:

Define Terms;

Basic Definitions;

Gibbs Thompson;

Hess' Law (not path dependent);

Second law and reversibility;

Equilibrium;

Third law $T = 0$ 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)**

$$dq = C dT$$

$$C = dq/dT$$

-S U V
H A
-P G T

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

$$dU = dq + dw = dq - pdV \text{ (only e/c work, i.e. no shaft work)}$$

Invent Entropy $H = U + PV$ so $dH = dU + pdV + Vdp$

$$(dH)_p = dU + pdV \text{ for constant pressure}$$

With only pV work (expansion/contraction), $dw_{ec} = -pdV$

$$dq = dU + pdV = (dH)_p$$

$$C_p = (dH/dT)_p, \text{ or the enthalpy change with T: } (dH)_p = C_p dT$$

Constant Volume
Computer **Simulation**
Helmholtz Free Energy, A
 $A = U - TS = G - pV$

Constant Pressure
Atmospheric **Experiments**
Gibbs Free Energy, G
 $G = H - TS = A + pV$

**Size dependent enthalpy of melting
(Gibbs-Thompson Equation)**

-S U V
H A
-P G T

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_{∞} , Greater randomness
gain on melting leads to lower T_{∞} .

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_{∞} against $1/r$

Derive the expression for $C_p - C_v$

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

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

$$\kappa_T = (1/V) (dV/dP)_T$$

-S	U	V
H		A
-p	G	T

$$C_v = (dU/dT)_v$$

From the Thermodynamic Square

$$dU = TdS - pdV \text{ so } C_v = (dU/dT)_v = T (dS/dT)_v - p (dV/dT)_v$$

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

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

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

$$dS = (dS/dT)_v dT + (dS/dV)_T dV \text{ using expression for } C_v \text{ above and Maxwell for } (dS/dV)_T$$

$$dS = C_v / T dT + (dp/dT)_v dV \text{ use chain rule: } (dp/dT)_v = -(dV/dT)_p (dP/dV)_T = V\alpha / (V\kappa_T)$$

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

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

Gibbs-Duhem Equation

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \sum_i n_i \bar{G}_i = \sum_i n_i \mu_i$$

Consider a binary system A + B makes a solution

$$G = n_A \mu_A + n_B \mu_B$$

$$dG = n_A d\mu_A + dn_A \mu_A + n_B d\mu_B + dn_B \mu_B$$

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:

$$SdT - Vdp + \sum_i n_i d\mu_i = 0$$

Intensive properties are not independent, T, p, μ

For I components, only I – 1 have independent properties (Gibbs phase rule) if T and p are variable.

Determine partial molar quantities at equilibrium from number of moles

Partial vapor pressure from total vapor pressure

-S U V
H A
-p G T

Clausius-Clapeyron Equation

Consider two phases at equilibrium, α and β

$$d\mu_\alpha = d\mu_\beta$$

$$\begin{matrix} -S & U & V \\ H & A \\ -p & G & T \end{matrix}$$

$$dG = Vdp - SdT$$

so

$$V^\alpha dp - S^\alpha dT = V^\beta dp - S^\beta dT$$

so

$$dp_{\text{trans}}/dT = \Delta S/\Delta V$$

and

$$\Delta G = 0 = \Delta H - T_{\text{trans}}\Delta S \quad \text{so} \quad \Delta S = \Delta H/T_{\text{trans}}$$

and

$$dp_{\text{trans}}/dT = \Delta H/(T_{\text{trans}}\Delta V) \quad \text{Clapeyron Equation}$$

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

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

$$d(\ln p_{\text{vap}})/dT = \Delta H_{\text{vap}}/(RT_{\text{vap}}^2) \quad \text{Clausius-Clapeyron Equation}$$

This allows calculation of the vapor pressure as a function of T

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

$$d(\ln p^{\text{Sat}})/dT = \Delta H_{\text{vap}}/(RT_{\text{vap}}^2) \text{ Clausius-Clapeyron Equation}$$

$$d(\ln p^{\text{Sat}}) = (-\Delta H_{\text{vap}}/R) d(1/T) \text{ So, plot } \ln p^{\text{Sat}} \text{ vs } 1/T$$

$$\ln[p^{\text{Sat}}/p_c^{\text{Sat}}] = (-\Delta H_{\text{vap}}/R) [1/T - 1/T_c] \text{ Use the critical point as the reference state}$$

Shortcut Vapor Pressure Calculation:

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(1 + \omega)\left(1 - \frac{1}{T_r}\right)$$

**Like the Van't Hoff Equation for Reaction Equilibria
so escape of an ideal gas from liquid state is like a
chemical reaction equilibria**

Consider a chemical reaction with equilibrium constant K_{eq}

$$d\mu_{\alpha} = d\mu_{\beta}$$

$$\begin{array}{l} -S \quad U \quad V \\ H \quad A \\ -p \quad G \quad T \end{array}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K_{eq}$$

$$\text{So } \ln K_{eq} = -\Delta H/RT + \Delta S/R$$

Take derivative relative to T

$$d(\ln K_{eq}) = \Delta H/RT^2 dT \quad \text{Van't Hoff Equation}$$

So, plot $\ln K_{eq}$ vs $1/T$

Can determine ΔH from the mole fraction of reactants and products

Clausius Clapeyron Equation

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

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

$$\log_{10} P_r^{\text{sat}} = \frac{7}{3}(1 + \omega) \left(1 - \frac{1}{T_r}\right)$$

This is similar to the Arrhenius Plot

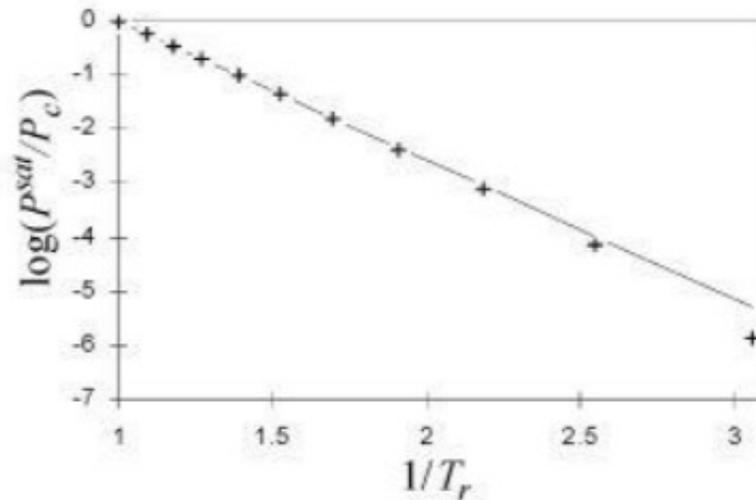
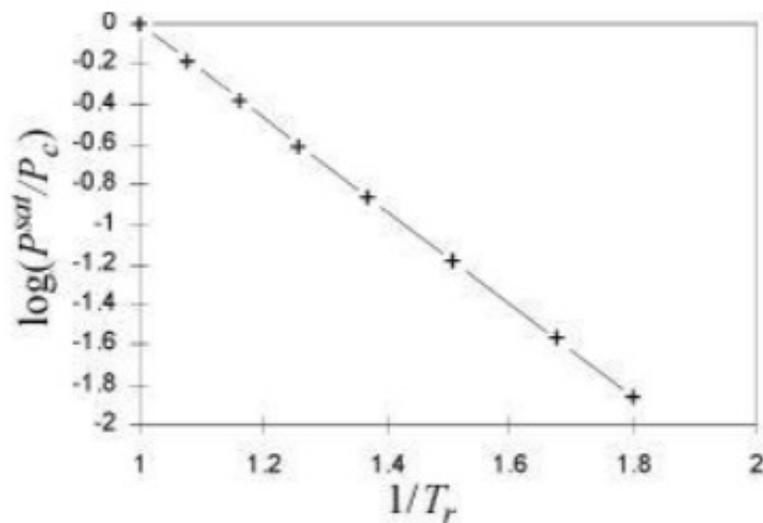


Figure 9.1. Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).

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

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)

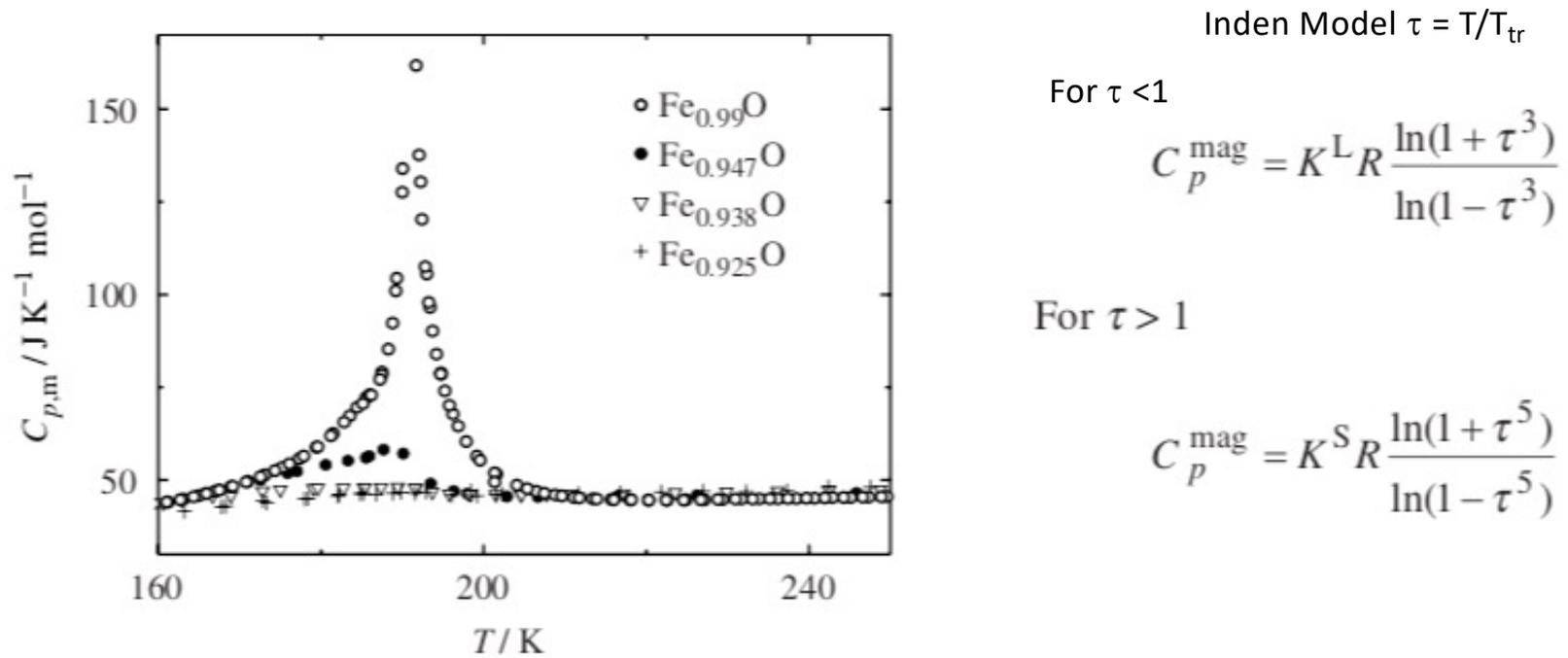


Figure 2.13 Heat capacity of wüstite around the Néel temperature [19]. ○: Fe_{0.99}O; ●: Fe_{0.947}O; ▽: Fe_{0.938}O; +: Fe_{0.925}O. Reproduced by permission of the Mineralogical Society of America.

Single Component Phase Diagrams

Isochoric phase diagram

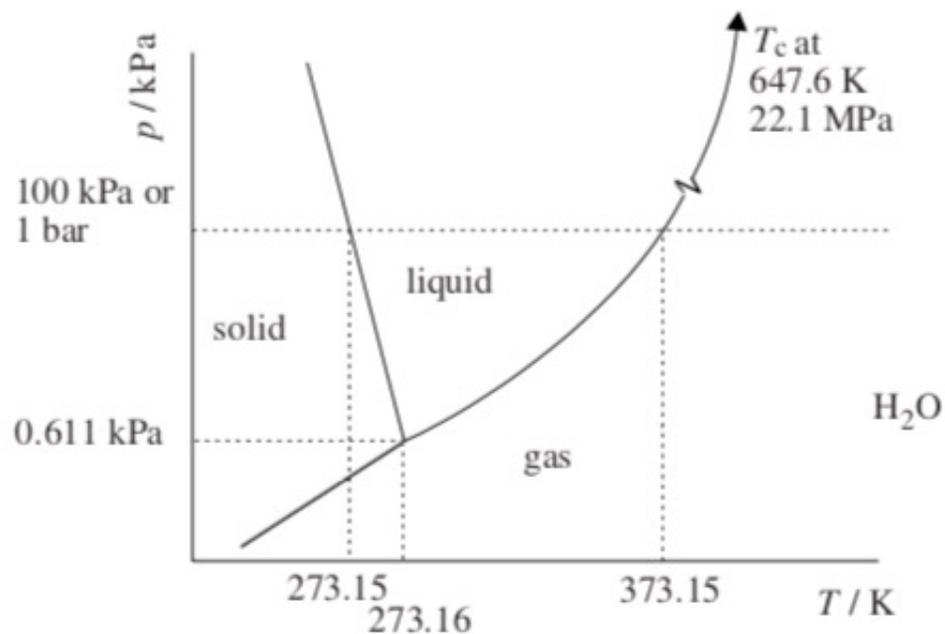


Figure 2.7 The p, T phase diagram of H_2O (the diagram is not drawn to scale).

For a single component, an equation of state relates the variables of the system, PVT

Gibbs Phase Rule

$$F = C - Ph + 2 \quad (2.15)$$

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 H₂O, $C = 1$ 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, $F = 0$.

$Z = 1$ $P = RT/V$ **Ideal Gas Equation of State**

Van der Waals Equation of State

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

Cubic Equation of State

$$a = \frac{27(RT_c)^2}{64 P_c}$$

$$b = \frac{RT_c}{8P_c}$$

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0$$

$$P = RT\rho/(1-b\rho) - a\rho^2$$

$$Z = \frac{PV}{RT}$$

Law of corresponding states

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

$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots$ **Virial Equation of State**

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

Peng-Robinson Equation of State (PREOS)

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2} \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2}$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2}$$

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \quad \text{Cubic Equation of State}$$

Solve cubic equations (3 roots)

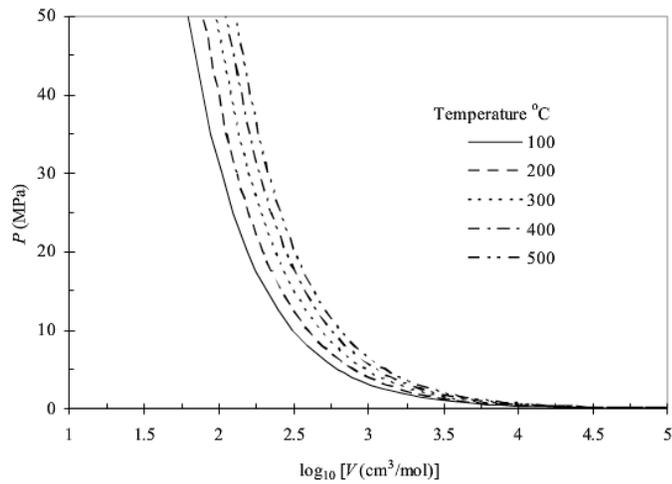


Figure 1.3 Ideal gas behavior at five temperatures.

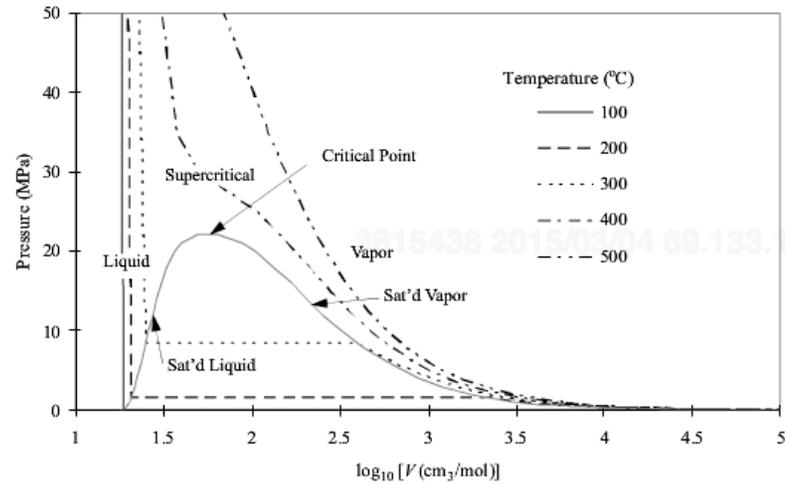


Figure 1.4 P - V - T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.

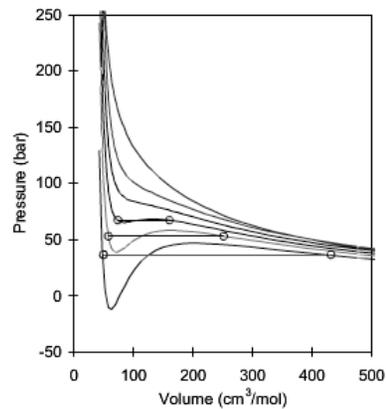


Figure 7.5 Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO_2 ($T_c = 304.2 \text{ K}$) at 275 K, 290 K, 300 K, 310 K, 320 K, and 350 K. Higher temperatures result in a high pressure for a given volume. The "humps" are explained in the text. The calculated vapor pressures are 36.42 bar at 275 K, 53.2 bar at 290 K, and 67.21 bar at 300 K.

Landau theory for 2'nd order transitions

The **order parameter** Γ could be concentration (normal phase separation), magnetization (magnets) , orientation (LCs)
 The point is to find a value for Γ above and below the critical point T_c (where phase separation become possible).
 Particularly above T_c , $\Gamma = 0$ and we have no "order" (think of no magnetization above the Curie temperature or no deviation from the average composition ($\rho - \langle \rho \rangle$) above the critical temperature).

- The free energy is analytic (there is a function in Γ and T)
- The free energy F is symmetric in Γ (only even powers of Γ)

For simplicity, take a two term Taylor series expansion $\Delta F = a(T) \Gamma^2 + b(T)/2 \Gamma^4$
 Near the critical temperature assume for simplicity

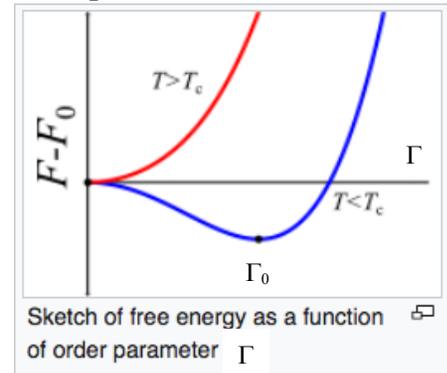
$$\Delta F = a_0 (T_c - T) \Gamma^2 + b_0/2 \Gamma^4$$

For a solution to Γ , you must have $b_0 > 0$ (this is obvious below); and $a(T)$ must change sign for phase separation to occur at T_c so $a(T) = a_0 (T_c - T)$

At the critical point $\partial F / \partial \Gamma = 0 = 2a_0 (T_c - T) \Gamma_0 + 2b_0 \Gamma_0^3$

To minimize free energy and make a stable phase either $\Gamma_0 = 0$ (above T_c) or $\Gamma_0^2 = -a_0 (T_c - T) / b_0$ (for $T \leq T_c$)

For $T \leq T_c$, $\Gamma_0 \sim (T_c - T)^{1/2}$ The critical exponent is $1/2$ for Landau theory.



Course Summary

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:

$$\Delta S = -nk_B (x_A \ln(x_A) + x_B \ln(x_B))$$

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

$$\Delta G = -T \Delta S$$

Since $(\ln x)$ is always negative or 0, ΔG is always negative (or 0) and ideal solutions **always mix**

ΔH 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

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

$$\begin{aligned} \text{Excess } \Delta G_{\text{mixing}} &= \Delta G_{\text{mixing}} - RT(x_A \ln x_A + x_B \ln x_B) \\ &= RT(x_A \ln(a_A/x_A) + x_B \ln(a_B/x_B)) \\ &= RT(x_A \ln(\gamma_A) + x_B \ln(\gamma_B)) \end{aligned}$$

γ is the activity coefficient

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

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:

$$\Delta S = -nk_B(x_A \ln(x_A) + x_B \ln(x_B)) \text{ Ideal Solution}$$

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

$$\Delta G = \Delta H - T \Delta S$$

Since $(\ln x)$ is always negative or 0, ΔG is positive or negative depending on ΔH :: can **mix or demix**

Depending on the sign of ΔH

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

$$\Delta H = n \Omega x_A x_B$$

Ω 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

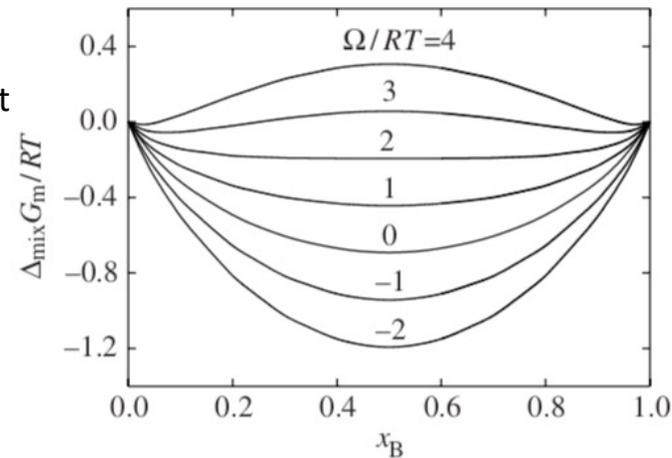


Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of Ω/RT .

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

$$\Delta_{\text{mix}}^{\text{exc}} G_m = x_A x_B [\Omega + A_1(x_A - x_B) + A_2(x_A - x_B)^2 + A_3(x_A - x_B)^3 + \dots]$$

Use of the Gibbs-Duhem Equation to determine the activity of a component

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{Constant } p, T$$

$$x_A d \ln a_A + x_B d \ln a_B = 0$$

$$x_A d \ln x_A + x_A d \ln \gamma_A + x_B d \ln x_B + x_B d \ln \gamma_B = 0$$

$$x_A d \ln x_A + x_B d \ln x_B = x_A \frac{dx_A}{x_A} + x_B \frac{dx_B}{x_B} = dx_A + dx_B = 0$$

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0 \quad \text{Restatement of Gibbs-Duhem for Solutions}$$

If you know γ_A you can obtain γ_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;

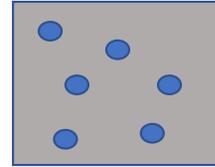
Lower critical solution behavior (LCST);

Freezing point depression;

Ternary phase diagram;

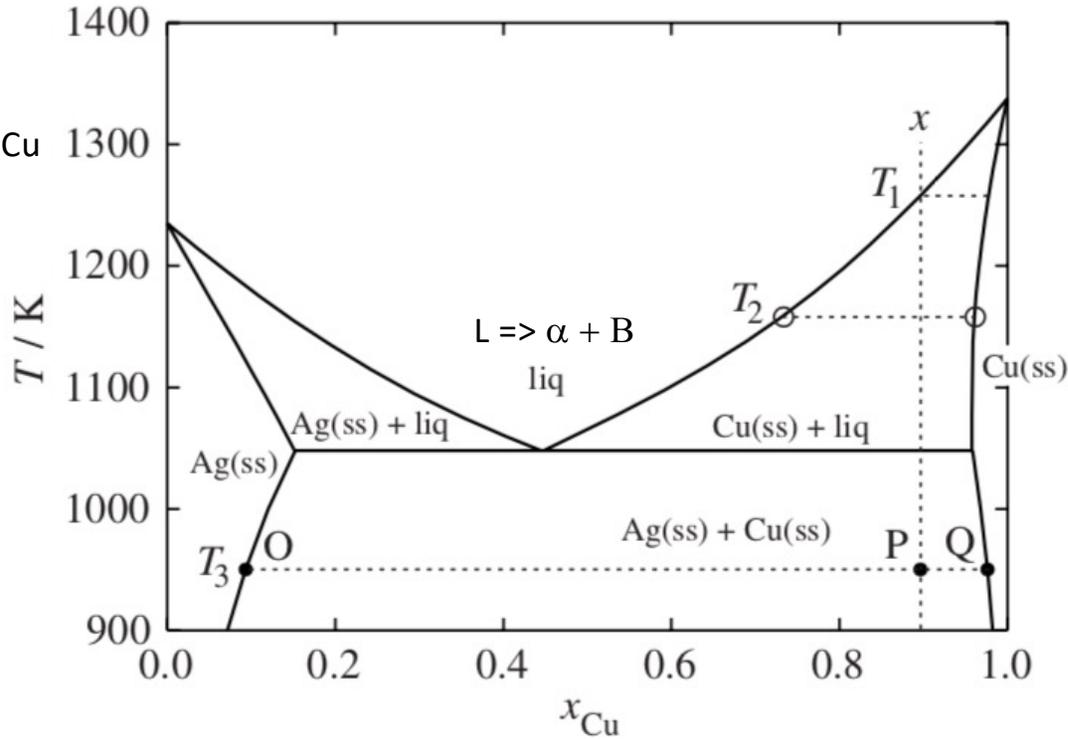
Gibbs Phase Rule
 $F + Ph = C + 2$

Phase Diagrams



Eutectic Phase Diagram Ag + Cu
 Univariant Equilibrium
 Liquidus
 Solidus
 Invariant Equilibrium
 Eutectic
 liquid \rightarrow Cu(ss) + Ag(ss)

Lever Rule
 Tieline (conode)
 $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$ for $i = 1, 2, \dots, C$
 $\mu_A^\alpha(x_A^\alpha) = \mu_A^\beta(x_A^\beta)$ and $\mu_B^\alpha(x_A^\alpha) = \mu_B^\beta(x_A^\beta)$



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].

$$\mu_A^{ss} = \mu_A^{s,o} + RT \ln a_A^{ss}$$

Calculate the Phase Diagram for a Solid Solution

$$\mu_A^{liq} = \mu_A^{l,o} + RT \ln a_A^{liq}$$

$$\begin{aligned} \mu_A^{ss} &= \mu_A^{liq} & \mu_A^{s,o} + RT \ln a_A^{ss} &= \mu_A^{l,o} + RT \ln a_A^{liq} \\ \mu_B^{ss} &= \mu_B^{liq} & \mu_B^{s,o} + RT \ln a_B^{ss} &= \mu_B^{l,o} + RT \ln a_B^{liq} \end{aligned}$$

$$\ln \left(\frac{a_A^{liq}}{a_A^{ss}} \right) = -\frac{\Delta\mu_A^{o(s \rightarrow l)}}{RT} \quad \ln \left(\frac{a_B^{liq}}{a_B^{ss}} \right) = -\frac{\Delta\mu_B^{o(s \rightarrow l)}}{RT}$$

$$\Delta\mu_i^{o(s \rightarrow l)} = \mu_i^{l,o} - \mu_i^{s,o} = \Delta_{fus} G_i^o = \Delta_{fus} H_i^o - T \Delta_{fus} S_i^o$$

$$\Delta_{fus} G_i^o = 0 \quad \Delta_{fus} S_i^o = \Delta_{fus} H_i^o / T_{fus,i}$$

$$\Delta\mu_i^{o(s \rightarrow l)} = \Delta_{fus} H_i^o - T \Delta_{fus} S_i^o = \Delta_{fus} H_i^o \left(1 - \frac{T}{T_{fus,i}} \right) \quad C_p(T) \text{ is constant}$$

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

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

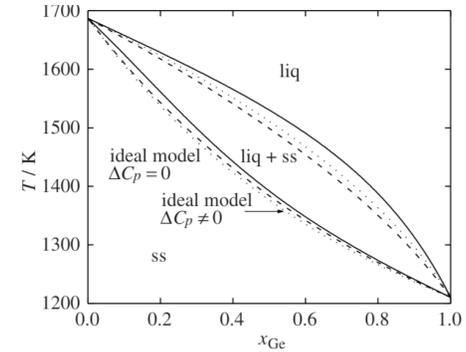


Figure 4.4 Phase diagram for the system Si-Ge at 1 bar. The solid lines represent experimental observations [2] while the dotted and dashed lines represent calculations assuming that the solid and liquid solutions are ideal with $\Delta C_p \neq 0$ and $\Delta C_p = 0$, respectively.

Solve for x_B^{ss} x_B^{liq} since $x_A + x_B = 1$

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

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

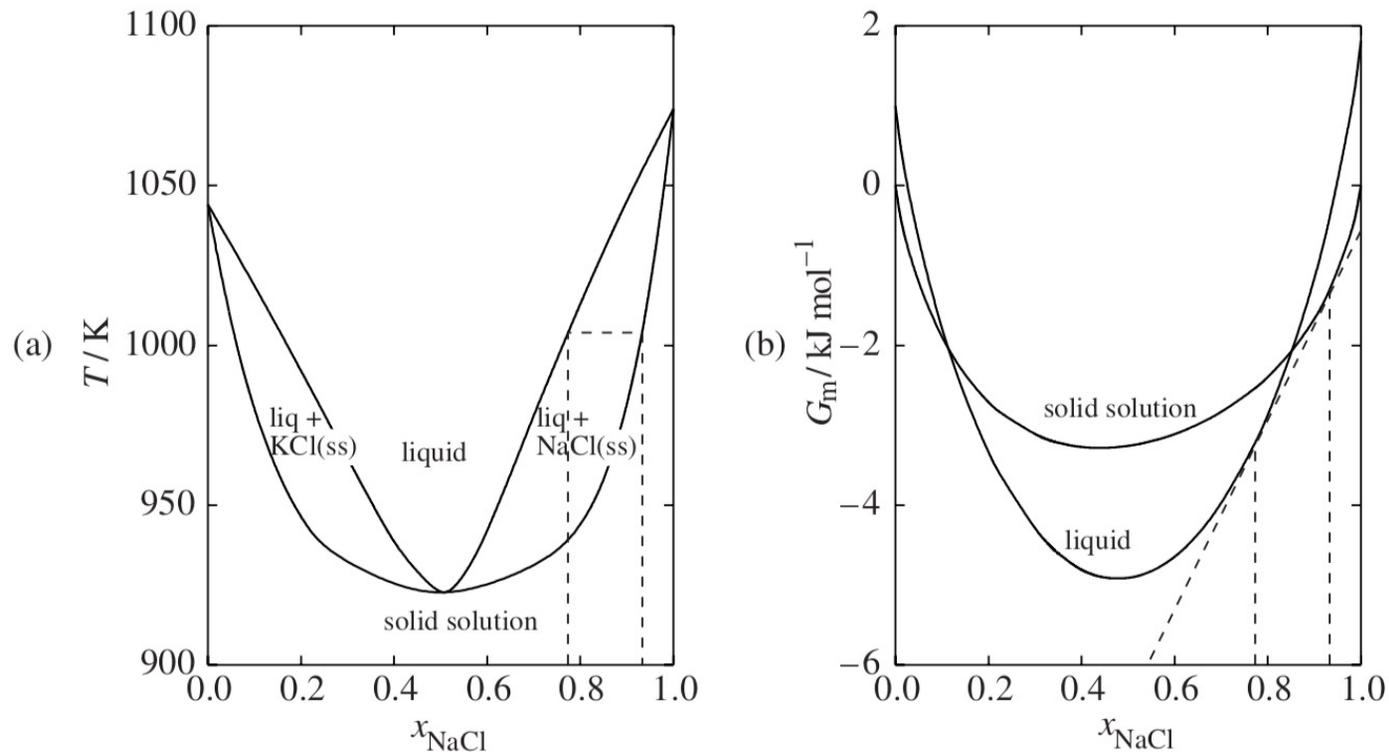
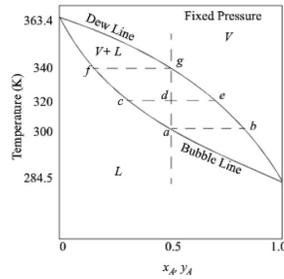


Figure 4.7 (a) Phase diagram of the system KCl–NaCl. (b) Gibbs energy curves for the solid and liquid solutions KCl–NaCl at 1002 K. Thermodynamic data are taken from reference [5].

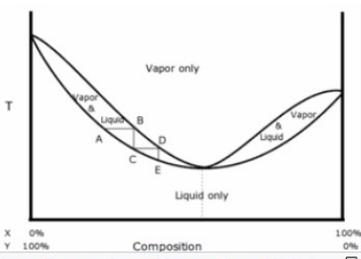
Solid solution is flatter than ideal (Pos. deviation or destabilized)
 Liquid is deeper than ideal (Neg. Deviation or stabilized)
 Deviations are associated with minima in phase diagram

Liquid/Vapor Equilibria

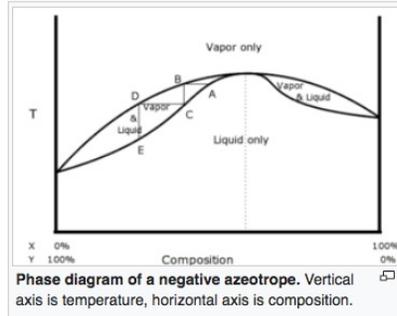
Ideal



Azeotrope

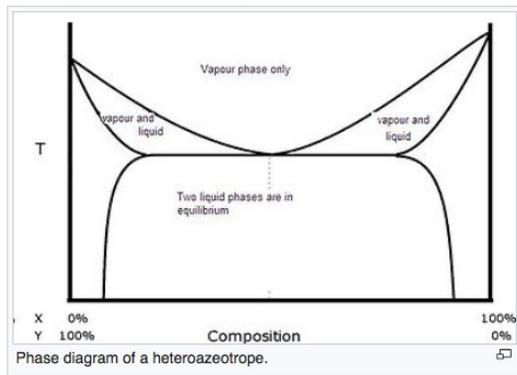


Phase diagram of a positive azeotrope. Vertical axis is temperature, horizontal axis is composition.



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

Heteroazeotrope

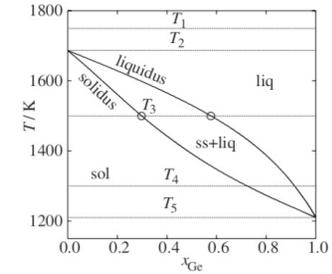


Phase diagram of a heteroazeotrope.

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

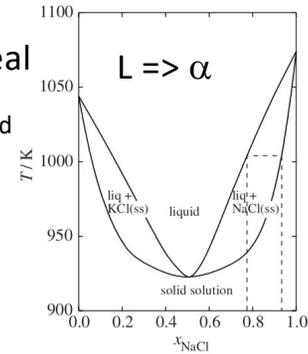
Solid/Liquid Equilibria

Ideal



$L \Rightarrow \alpha + L$

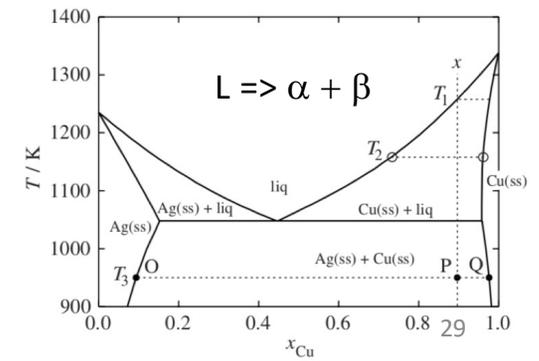
Non-Ideal
Congruent
melting solid
solution



$L \Rightarrow \alpha$

Same
crystallographic
structure in solid
solution phase

Eutectic



Different
crystallographic
structures in solid
solution phases

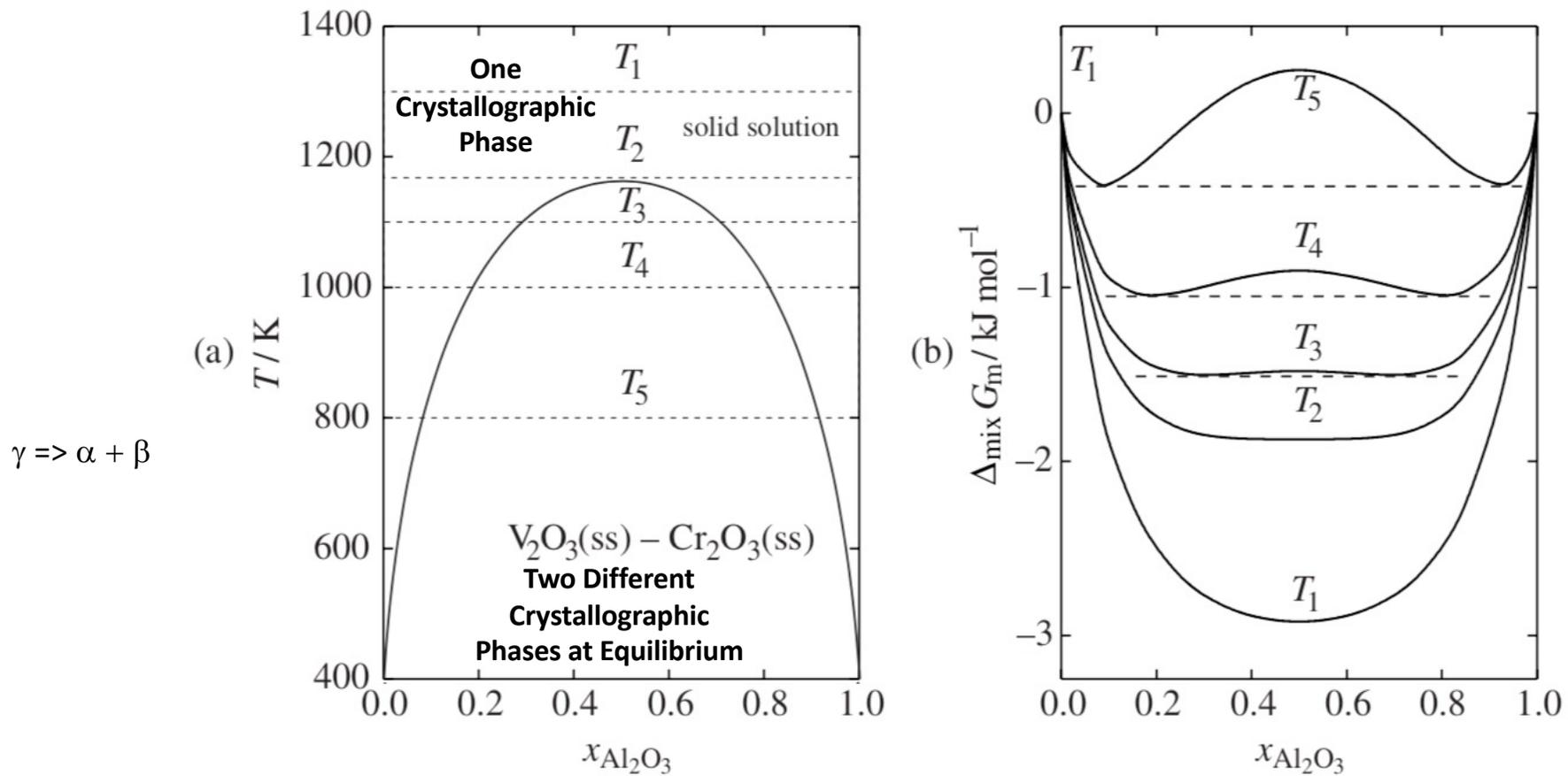
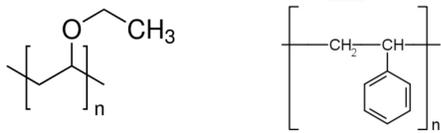


Figure 4.9 (a) Immiscibility gap of the binary solid solution $V_2O_3-Cr_2O_3$ as described by the regular solution model. (b) Gibbs energy of mixing curve of the solid solution at the temperatures marked in the phase diagram. Thermodynamic data are taken from reference [7].



Polyvinylmethyl Ether/Polystyrene (LCST Phase behavior)

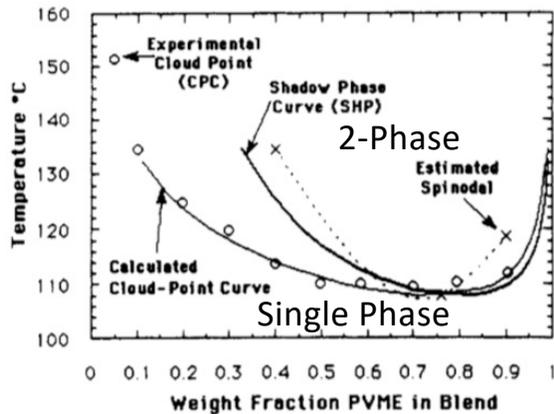


Figure 4. Flory-Huggins-Staverman fit to the CPC of the i89/120 blend.

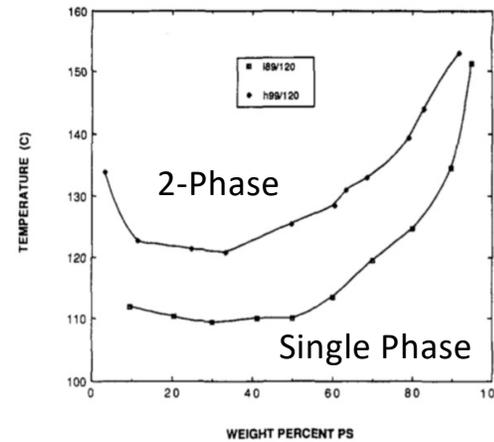


Figure 7. Cloud-point curves for i89/120 and h99/120 blends.

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

Ω 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

$$\frac{\Delta G}{NRT} = \frac{\phi_1}{m_1} \ln \phi_1 + \sum \left(\frac{\phi_{2i}}{m_{2i}} \ln \phi_{2i} \right) + g\phi_1\phi_2$$

$$g = a + \frac{(b_0 + b_1/T)}{(1 - c\phi_2)}$$

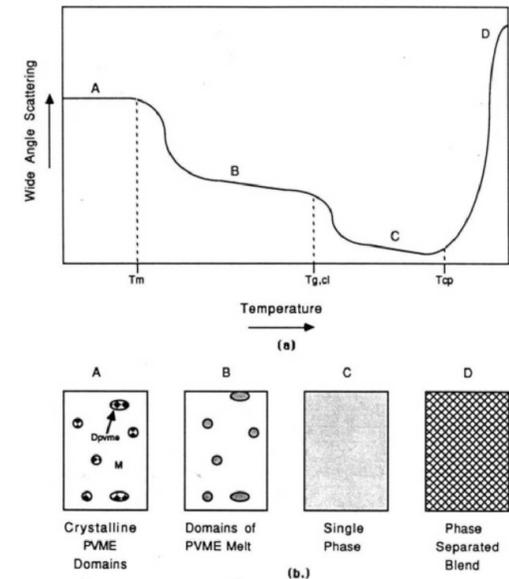


Figure 4. Clearing behavior of higher crystallinity blends. (a) Wide-angle scattering versus temperature. (b) Schematic of phase behavior.

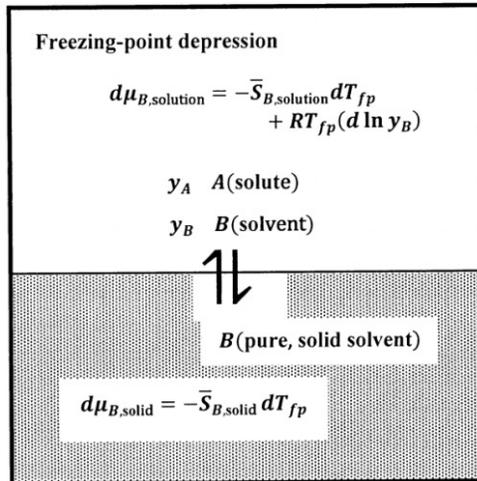


Figure 8. Schematic description of freezing-point depression.

Freezing Point Depression

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

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

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

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

Binary solution following Henry's Law

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

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

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

So,

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

$$dy_{A,\text{Solution}} = (S_{B,\text{Solid}}^m - S_{B,\text{Solution}}^m) / (RT_{fp}) dT_{fp} \sim -\Delta S_B^m / (RT_{fp}) dT_{fp} = -\Delta H_B^m / (RT_F) (dT_{fp}) / T_{fp}$$

$$y_{A,\text{Solution}} = -\Delta H_B^m / (RT_F) \ln(T_{fp} / T_F) \text{ For small } x: \ln(x) = x - 1$$

$$y_{A,\text{Solution}} = -\Delta H_B^m / (RT_F) (T_{fp} / T_F - 1) = -\Delta H_B^m / (RT_F^2) \Delta T$$

$$T_{fp} = T_F - y_{A,\text{Solution}} RT_F^2 / \Delta H_B^m$$

Course Summary

V. Phase Stability:

Metastable;

Supercool; superheat; supersaturate;

Kauzmann Paradox;

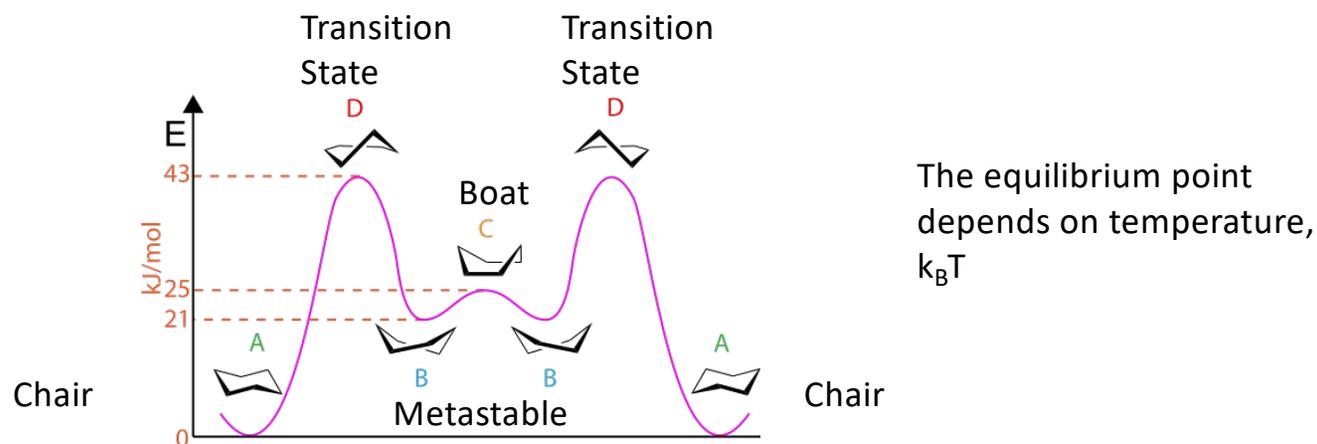
Thermal/density fluctuations;

Spinodal decomposition;

Binodal; spinodal; critical conditions;

Polymorphs; allotrophs;

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, $E = k_B T \sim 2.5$ 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

-S U V
H A
-p G T

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, $K_T = \frac{1}{\kappa_T} = -\frac{V}{(\partial V / \partial p)_T} > 0$

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

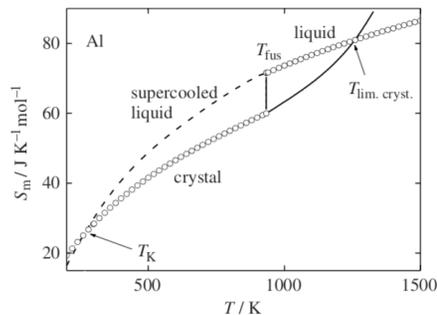
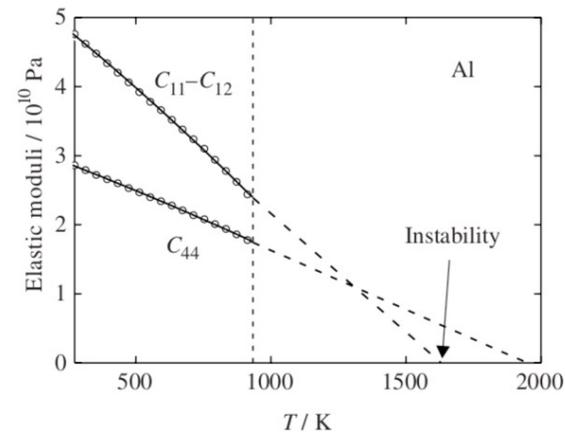


Figure 5.3 Entropy of liquid and crystalline aluminium in stable, metastable and unstable temperature regions [12]. The temperatures where the entropy of liquid and crystalline aluminium are equal are denoted T_K and $T_{lim,cryst}$, respectively.



Shear modulus goes to 0 at highest possible supercritical solid

Figure 5.2 Temperature dependence of the isothermal elastic stiffness constants of aluminium [10].

Kauzmann Paradox, a thermodynamic basis for the glass transition

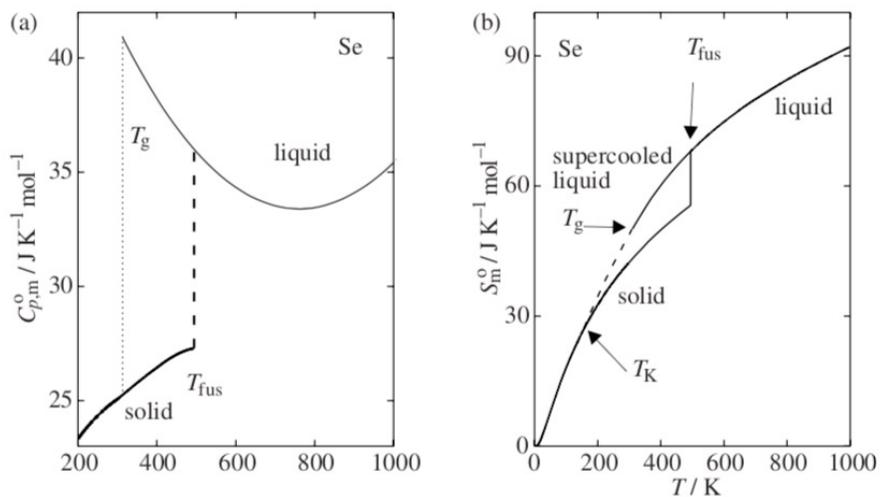
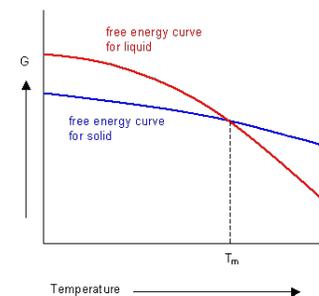


Figure 5.1 (a) Heat capacity of crystalline, liquid and supercooled liquid Se as a function of temperature [1–3]. (b) Entropy of crystalline, liquid and supercooled liquid Se as a function of temperature.



$$\Delta_{\text{fus}} S_m^{\circ}(T) = \Delta_{\text{fus}} S_m^{\circ}(T_{\text{fus}}) + \int_{T_{\text{fus}}}^T \frac{\Delta C_p^{\circ}}{T} dT$$

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 χN depends on $1/T$ specifying χN specifies the temperature. Large χN is low temperature.

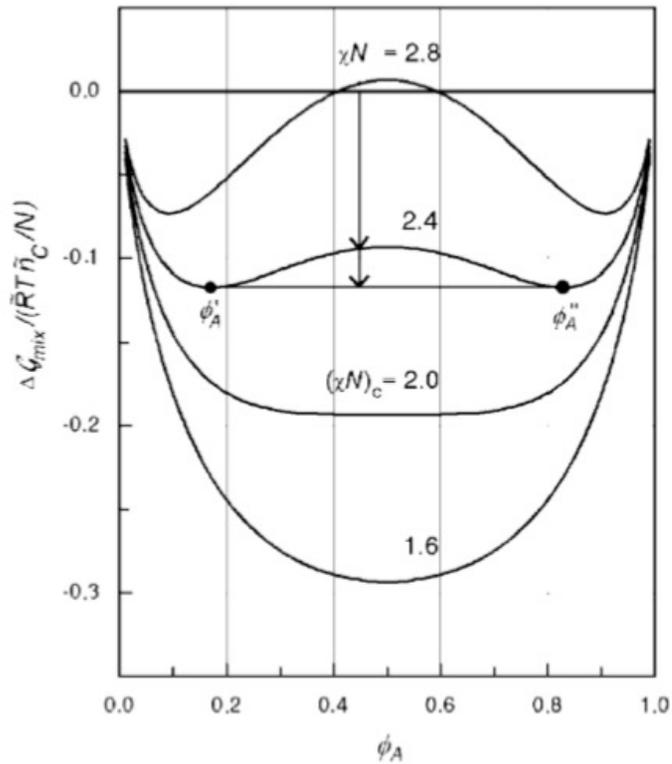


Fig. 4.3. Gibbs free energy of mixing of a symmetric binary polymer mixture ($N_A = N_B = N$), as described by the Flory–Huggins equation

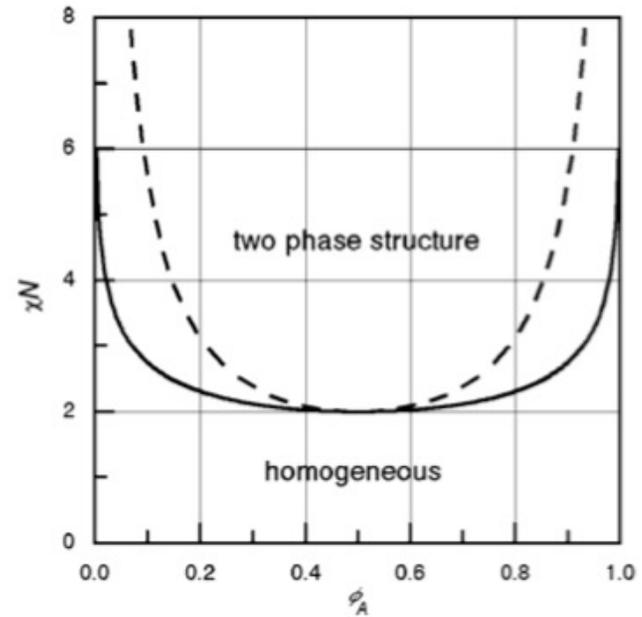


Fig. 4.4. Phase diagram of a symmetric polymer mixture ($N_A = N_B = N$). In addition to the binodal (*continuous line*) the spinodal is shown (*broken line*)

Polymorphs and Allotropes

Allotroph: Carbon as diamond or graphite

Polymorph: Titania as anatase or rutile

Silica as α -quartz, β -quartz, tridymite, cristobalite, moganite, coesite, and stishovite

Calcium carbonate as calcite or aragonite



Calcite (on left) and Aragonite (on right). Both crystals are made out of calcium carbonate, making these crystals dimorphic.

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.

$$\frac{p}{p_{\text{eq}}} = \exp\left(\frac{R_{\text{critical}}}{R}\right)$$
$$R_{\text{critical}} = \frac{2 \cdot \gamma \cdot V_{\text{atom}}}{k_{\text{B}} \cdot T}$$

V_{atom} = atomic volume

k_{B} = Boltzmann constant

γ = surface tension ($\text{J} \cdot \text{m}^{-2}$)

p_{eq} = equilibrium partial pressure (or chemical potential or concentration)

p = partial pressure (or chemical potential or concentration)

T = absolute temperature

During the course of his academic career, Ostwald published more than 500 original research papers for the scientific literature and approximately 45 books.^[9]

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;

-S U V
 H A
 -p G T

c is curvature 1/r

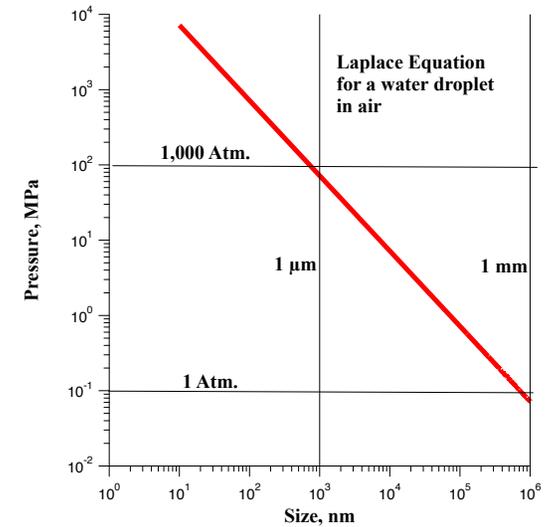
$$dU = [(p^\beta - p^\alpha) + \sigma(c_1 + c_2)]A_s dl$$

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

$$p^\beta - p^\alpha = \sigma(c_1 + c_2) = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

Laplace Equation

For a 100 nm ($1e^{-5}$ cm) droplet of water in air ($72 e^{-7}$ J/cm² or 7.2 Pa-cm)
 Pressure is 720 MPa (7,200 Atmospheres)



Dihedral angles

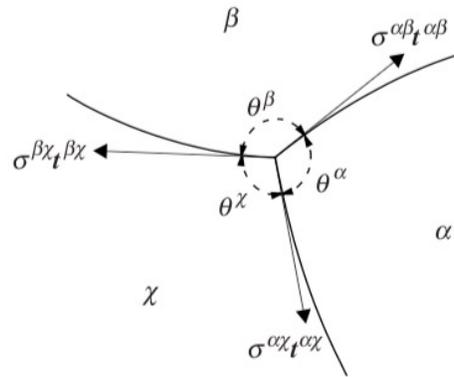


Figure 6.9 Two-dimensional projection of equilibrium at a plane of contact between three phases α , β and γ where the angles between the three two-phase boundaries meeting in a line of contact are denoted θ^α , θ^β and θ^γ .

$$\sigma^{\alpha\beta} \mathbf{t}^{\alpha\beta} + \sigma^{\beta\gamma} \mathbf{t}^{\beta\gamma} + \sigma^{\alpha\gamma} \mathbf{t}^{\alpha\gamma} = 0$$

$$\frac{\sigma^{\alpha\beta}}{\sin \theta^\gamma} = \frac{\sigma^{\beta\gamma}}{\sin \theta^\alpha} = \frac{\sigma^{\alpha\gamma}}{\sin \theta^\beta} = 0$$

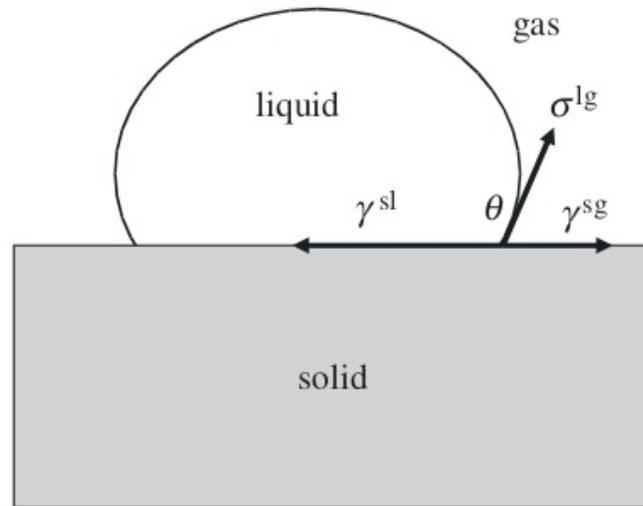


Figure 6.10 Contact angle θ of a liquid drop resting on a solid surface. The definition of the forces used in the figure eliminates the contribution from gravity.

$$\gamma^{sg} = \gamma^{sl} + \sigma^{lg} \cos \theta = 0 \quad \text{Young Dupre Equation}$$

-S U V
H A
-p G T

$$\ln \frac{p^g}{p_{r=\infty}^g} = \frac{V^l}{RT} \frac{2\sigma^{lg}}{r}$$

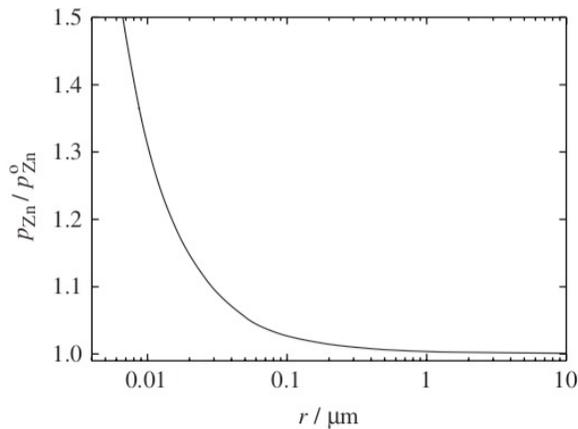


Figure 6.14 The vapour pressure of Zn over a spherical droplet of molten Zn at the melting temperature as a function of the droplet radius. $p_{Zn}^0 = 2 \cdot 10^{-4}$ bar, $\sigma^{lg} = 0.78$ J m⁻² and $\rho = 6.58$ g cm⁻³ [8].

Thomson's (or Kelvin's) equation

Pressure for equilibrium of a liquid droplet of size "r"

$$d\mu^l = d\mu^g \quad \text{Reversible equilibrium}$$

$$V^g dp^g = V^l dp^l \quad \text{At constant temperature}$$

$$d(p^g - p^l) = d\left(\frac{2\sigma^{lg}}{r}\right) \quad \text{Differential Laplace equation}$$

$$\frac{V^g - V^l}{V^l} dp^g = d\left(\frac{2\sigma^{lg}}{r}\right)$$

$$V^g = RT/p^g \quad V^g - V^l \approx V^g$$

$$\frac{RT}{V^l} \frac{dp^g}{p^g} = d\left(\frac{2\sigma^{lg}}{r}\right)$$

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

$$d(p^s - p^l) = d\left(\frac{2\gamma^{sl}}{r}\right) \quad \text{Derivative form of the Laplace equation}$$

$$d\mu_i^l = d\mu_i^s = V_i^s dp^s = V_i^s d\left(\frac{2\gamma^{sl}}{r}\right) \quad \text{Dynamic equilibrium}$$

$$(\mu_i^l)_r - (\mu_i^l)_{r=\infty} = V_i^s \frac{2\gamma^{sl}}{r} \quad \text{For an incompressible solid phase}$$

$$\mu_A = \mu_A^* + RT \ln a_A \quad \text{Definition of activity}$$

$$\ln \frac{(x_i^l)_r}{(x_i^l)_{r=\infty}} = \frac{V_i^s}{RT} \frac{2\gamma^{sl}}{r} \quad \text{Solubility increases exponentially with reduction in size, r}$$

$$(x_i^l)_r = (x_i^l)_{r=\infty} \exp(2\gamma^{sl}/(\rho RT r)) \quad \text{Small particles dissolve to build large particles with lower solubility}$$

- 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

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

Surface increases free energy

(M/ρ) is molar volume

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

maximum $d\Delta_{1-s}G/dr = 0$

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

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

$$\Delta_{1-s}G^* = \frac{16\pi(\gamma^{\text{sl}})^3 M^2}{3\rho^2 \Delta_{\text{fus}}G_m^2}$$

Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

$$r^* = [2(M/\rho)\gamma^{sl}] / \Delta_{\text{fus}}G_m \quad \Delta_{1-s}G^* = \frac{16\pi(\gamma^{sl})^3 M^2}{3\rho^2 \Delta_{\text{fus}}G_m^2}$$

$$\Delta_{\text{fus}}G_m = \Delta_{\text{fus}}H_m - T\Delta_{\text{fus}}S_m$$

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

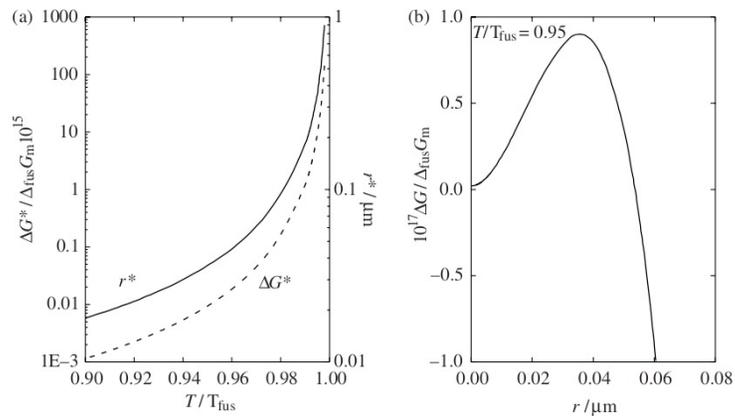


Figure 6.16 (a) The critical radius (r^*) and thermodynamic barrier for nucleation of Al (ΔG^*) versus degree of supercooling T/T_{fus} . (b) The Gibbs energy of a spherical Al crystal relative to the supercooled Al(l) as a function of its radius. $\Delta_{\text{fus}}H_m = 10.794 \text{ kJ mol}^{-1}$,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

Deep quench, far from
equilibrium leads to
nanoparticles

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

Ostwald Ripening

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

$$(\mu_i^s)_{r'} - (\mu_i^s)_{r''} = 2V_i^s \gamma^{sl} \left(\frac{1}{r'} - \frac{1}{r''} \right)$$

Grain Growth and Elimination of Pores

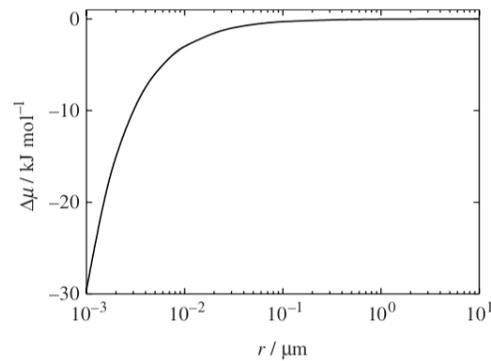


Figure 6.17 The difference in the chemical potential of Au(s) between a spherical particle with radius $10 \mu\text{m}$ and a smaller particle with radius r . $\rho = 18.4 \text{ g cm}^{-3}$ and $\gamma^{sl} = 1.38 \text{ J m}^{-2}$ [21].

Formation of a surface nucleus versus a bulk nucleus from n monomers

Homogeneous

$$\Delta G_n = -n\phi + \psi_n \quad \phi = \mu - \mu_\infty = kT \ln\left(\frac{x}{x_\infty}\right)$$

$$\psi_n = \mu_n^\sigma - n\mu_0 \quad \psi_n = a_n \gamma = \gamma \left(\frac{27\beta v_1^2}{4}\right)^{\frac{1}{3}} n^{\frac{2}{3}} = \psi n^{\frac{2}{3}}$$

Bulk vs n-mer

So surface excess chemical potential

$$\Delta G_n = -\phi n + \psi n^{\frac{2}{3}}$$

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

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

Heterogeneous (Surface Patch)

$$\Delta G'_{n'} = -\phi n' + \psi'_{n'}$$

$$\psi'_{n'} = 2\pi r h \gamma = 2\gamma \sqrt{\pi h v_1 n'} = \psi' n'^{\frac{1}{2}}$$

Surface energy from the sides of the patch

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

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

$$\Delta G'^* = \frac{\psi'^2}{4\phi} = \frac{\psi' \sqrt{n'^*}}{2} = \phi n'^* = \frac{\pi h v_1 \gamma^2}{\phi}$$

**Barrier is half the height for nucleation
Size is half**

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

$$\Delta G'^* = \frac{\psi'^2}{4\phi} = \frac{\psi' \sqrt{n'^*}}{2} = \phi n'^* = \frac{\pi h v_1 \gamma^2}{\phi}$$

$$r^* = \frac{2\gamma v_1}{\phi} = 2r'^*$$

$$r'^* = \sqrt{\frac{n'^* v_1}{\pi h}} = \frac{\gamma v_1}{\phi}$$

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_{∞} = 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

For a sphere

$$A = 4\pi r^2 = (4\pi)^{\frac{1}{3}} 3^{\frac{2}{3}} V^{\frac{2}{3}} \quad \frac{dA}{dV} \sim \frac{2}{r}$$

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

$$r = \frac{B\gamma T_{\infty}}{\Delta H_f (T_{\infty} - T)}$$

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

$$\Delta S = \frac{\Delta H}{T_{\infty}}$$

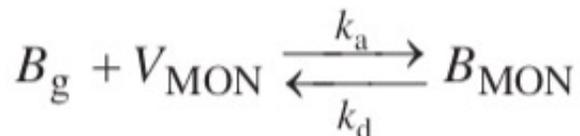
Crystallize from a melt, so supersaturate by a deep quench

$$\Delta f = 0 \sim r^3 \left(\Delta H_f - \frac{T}{T_{\infty}} \Delta H_f \right) - Br^2 \gamma = r^3 \frac{\Delta H_f}{T_{\infty}} (T_{\infty} - T) - Br^2 \gamma$$

Free energy of a crystal formed at supercooled temperature T

$$\frac{T}{T_{\infty}} = 1 - \frac{B\gamma}{r\Delta H_f} \sim \exp\left(\frac{-B\gamma}{r\Delta H_f}\right) \quad x = x_{\infty} \exp\left(\frac{2(\kappa_1 + \kappa_2)v_1\gamma}{kT}\right) \quad x = x_{\infty} \exp\left(\frac{2v_1\gamma}{rkT}\right)$$

Adsorption Isotherms



B_g - Gas species (N_2)

B_{mon} - Adsorbed (N_2) in an occupied surface site

V_{mon} - Available surface site

Equilibrium Constant:
$$K_L = \frac{k_a}{k_d} = \frac{\Gamma_B}{a_B^g (\Gamma_B^{\text{sat}} - \Gamma_B)}$$

a_B^g is activity of B in the gas phase

$$\frac{\Gamma_B / \Gamma_B^{\text{max}}}{1 - \Gamma_B / \Gamma_B^{\text{max}}} = \frac{\theta}{1 - \theta} = K_L a_B$$

Langmuir Adsorption Isotherm

$\theta = \Gamma_B / \Gamma_B^{\text{Max}}$ Fractional Coverage

Γ_B^{Max} Is the coverage for a monolayer.

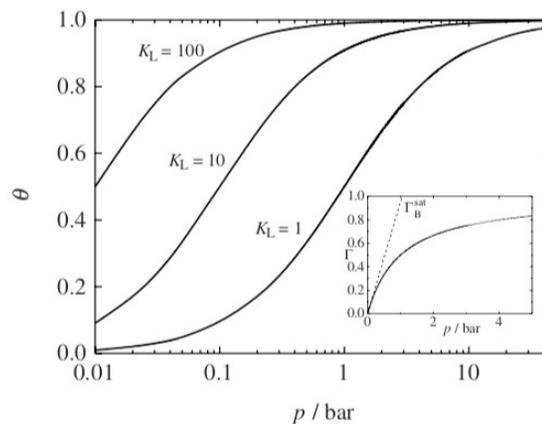


Figure 6.24 Adsorption isotherms following Langmuir adsorption isotherm.

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, $K = (x_1^b x_2^s)/(x_1^s x_2^b) = (1 - x_2^b) \theta / ((1 - \theta) x_2^b)$

Rearranging yields $\theta = Kx_2^b/(1 - x_2^b + K x_2^b) \sim Kx_2^b/(1 + K x_2^b) = p/p_0$

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 , θ_i

Rate of adsorption on layer $i-1$ to fill layer i , $R_{i-1,\text{ads}} = k_{i,\text{ad}} P \theta_{i-1}$

Rate of desorption from layer i , $R_{i,\text{des}} = k_{i,\text{des}} \theta_i$

$k_{i,\text{ads}} = k_{i,\text{des}} = \exp(-E_i/kT)$

$$\frac{1}{v [(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c}, \quad \begin{array}{l} v_m = \text{monolayer amount of gas} \\ v = \text{experimental amount of gas adsorbed} \end{array}$$

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

How can you predict the phase size? (Meier and Helfand Theory)
 Consider lamellar micro-phase separation.

$$d_{AB}^3 = \frac{N_{AB}^3 v_c^3}{o_p^3} \propto \chi d_t v_c^{2/3} N_{AB}^2$$

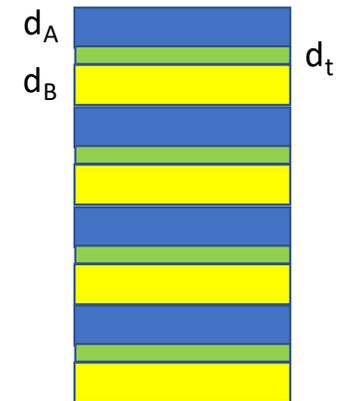
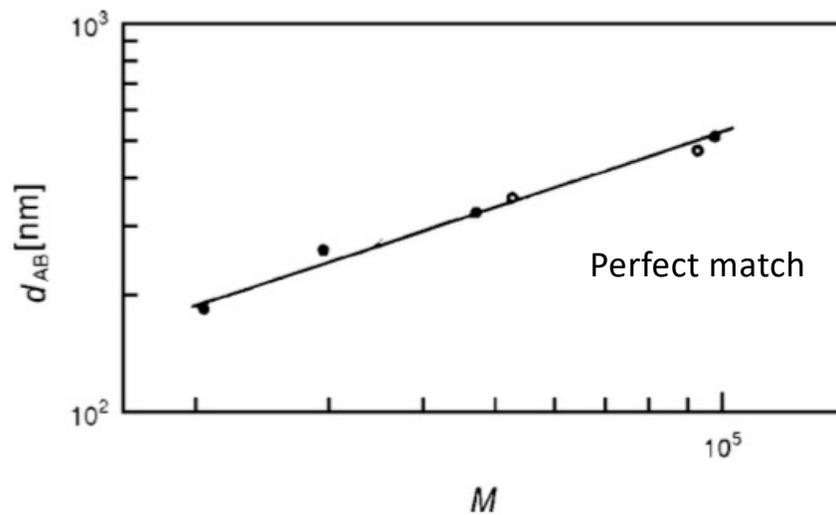


Fig. 4.30. Set of samples of Fig. 4.28. Molecular weight dependence of the layer spacing d_{AB}

Course Summary

VII. Heat of Formation:

Dependencies in periodic table;

Electronegativity;

Energetics of formation (electrostatic, repulsion, dispersion, polarization, crystal field);

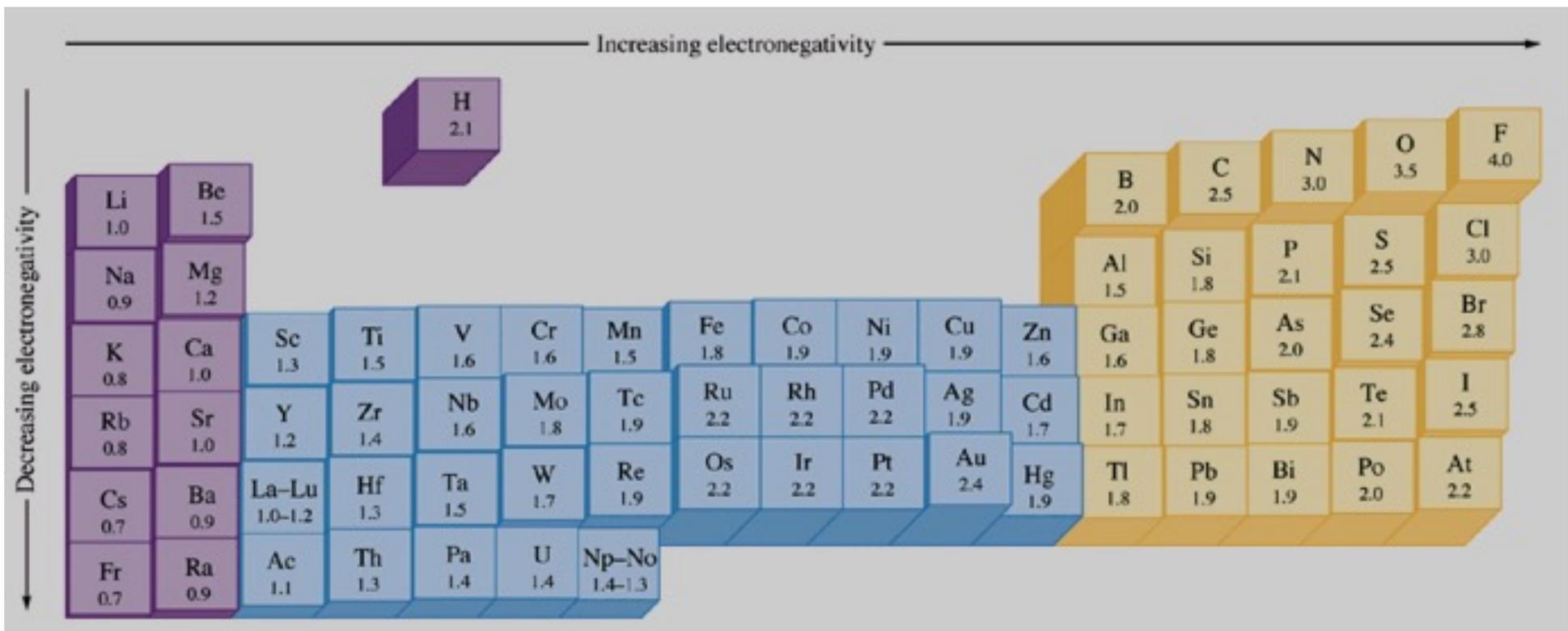
Atomic size (perovskites, spinels, zeolites);

Substitutional solids;

Conformational entropy of polymers

Electronegativity, the ability of an atom to attract electrons in a bond

Linus Pauling



Energetics of compound formation



$$\Delta_{\text{latt}}H_{\text{m}} = \Phi_{\text{electrostatic}} + \Phi_{\text{repulsion}} + \Phi_{\text{dispersion}} + \Phi_{\text{polarization}} + \Phi_{\text{crystal field}}$$

Electrostatic attraction +-

Electron electron repulsion

Van der Waals or dispersion (δ^+ makes δ^- leads to net attraction)

Polarization (shifting within compound of electrons)

Crystal field effects

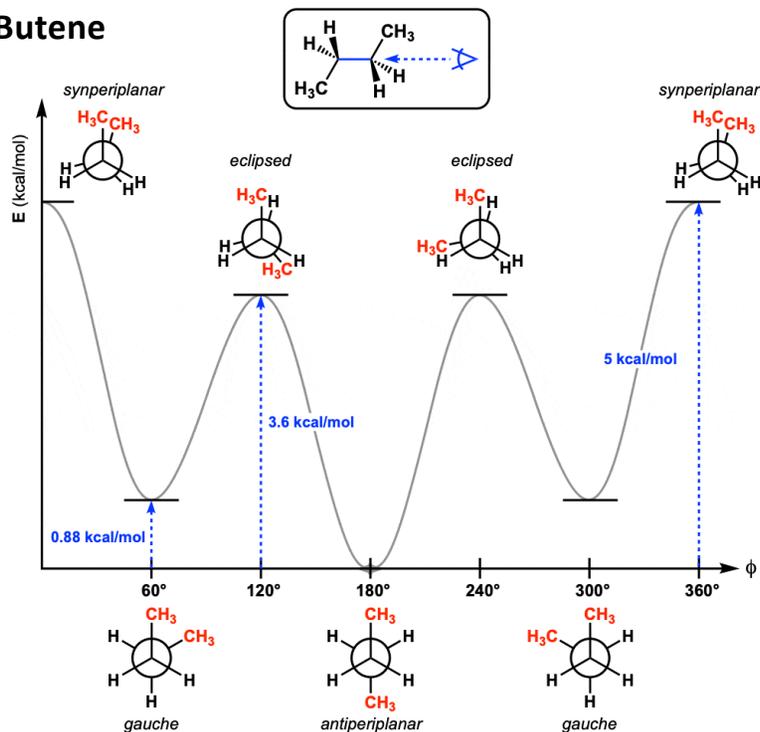
Conformational Enthalpy of Polymers

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 v^{N-2} where v is the number of discrete rotational states for the chain, tttt, g-g-g-g, g+g+g+g+, g+ttt, etc. for N = 4; $N_1=1$, $N_4=4$, etc. assuming no end effects

$$Z = \sum_{\{N_\eta\}} \frac{(N-2)!}{N_1! \dots N_v!} \exp(-N_1 E(\varphi_1)/kT) \dots \exp(-N_v E(\varphi_v)/kT)$$

Average rotational angle

$$\langle \cos \varphi \rangle = \frac{\sum_{i=1}^v \exp(-E(\varphi_i)/kT) \cos \varphi_i}{\sum_{i=1}^v \exp(-E(\varphi_i)/kT)} = \frac{1 - \sigma}{1 + 2\sigma}$$

Characteristic Ratio

$$C_\infty = \lim_{N \rightarrow \infty} \frac{\langle r^2 \rangle_0}{Nl^2} = \frac{(1 + \cos \theta) (1 + \langle \cos \varphi \rangle)}{(1 - \cos \theta) (1 - \langle \cos \varphi \rangle)}$$

Q is the bond angle
 $180^\circ - 109^\circ = 71^\circ$
 $E_{g+} = 2100 \text{ J/mole}$
 $C_\infty = 3.6$
 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

Heat Capacity

DSC

Heat is not a state function, so we define a state function related to heat, $dS = dQ/T$

$$dH = VdP + TdS$$

$$\text{At constant P } (dH = TdS = dQ)_P$$

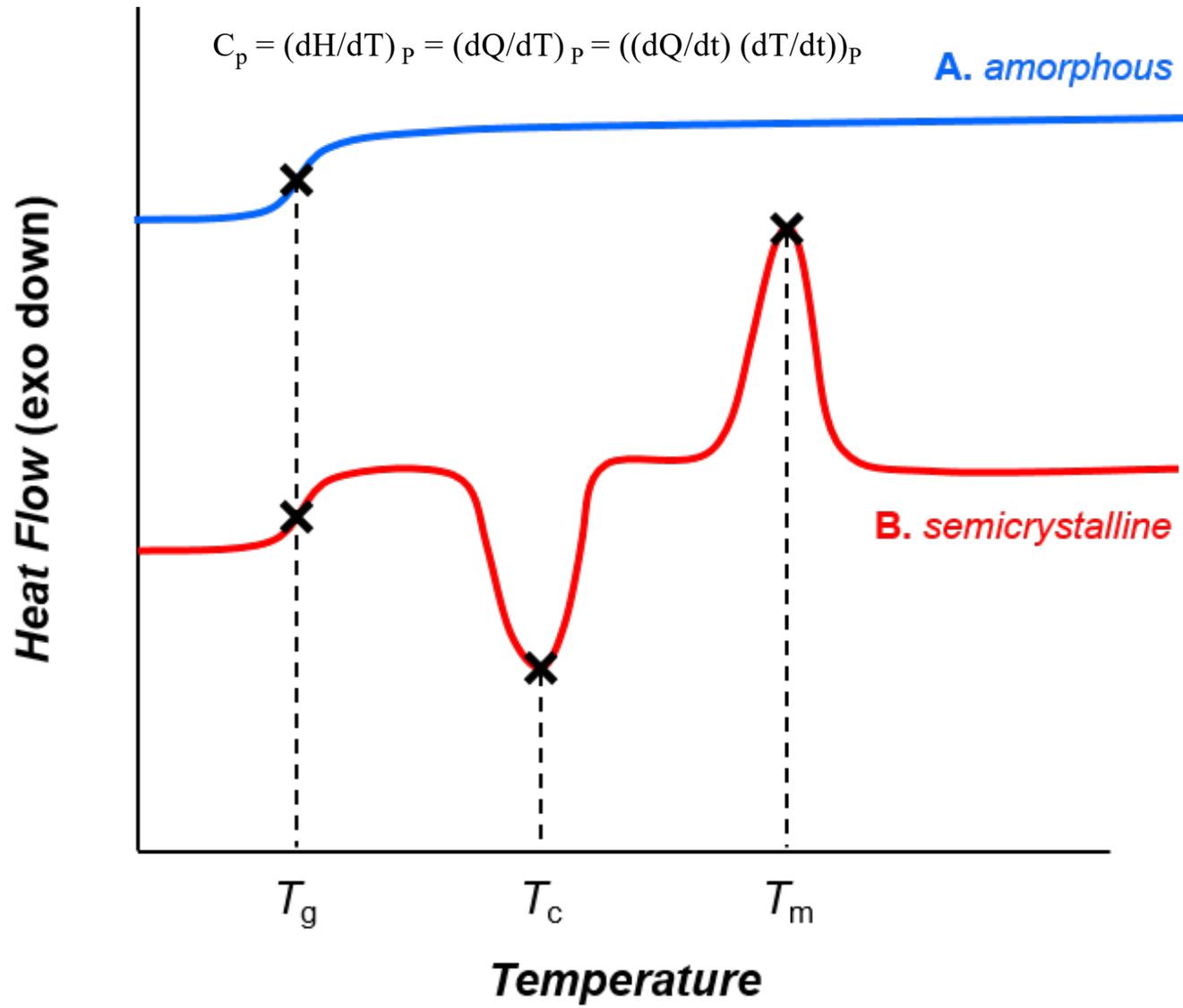
$$\text{We have } C_p = (dH/dT)_P = (dQ/dT)_P$$

$$\begin{array}{lll} -S & U(E) & V \\ H & & A(F) \\ -p & G & T \end{array}$$

In the DSC we measure the heat flow dQ/dt (Watts) at a constant heating rate dT/dt at constant pressure,

$$(dQ/dT)_P = C_p$$

So, the y-axis is C_p times dT/dt the latter of which is constant



Derive the expression for $C_p - C_v$

From Chapter 1

-S	U	V
H		A
-p	G	T

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

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

$$\kappa_T = (1/V) (dV/dP)_T$$

$$C_v = (dU/dT)_v$$

From the Thermodynamic Square

$$dU = TdS - pdV \text{ so } C_v = (dU/dT)_v = T (dS/dT)_v - p (dV/dT)_v$$

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

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

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

$$dS = (dS/dT)_v dT + (dS/dV)_T dV \text{ using expression for } C_v \text{ above and Maxwell for } (dS/dV)_T$$

$$dS = C_v / T dT + (dp/dT)_v dV \text{ use chain rule: } (dp/dT)_v = -(dV/dT)_p (dP/dV)_T = V\alpha / (V\kappa_T)$$

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

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

Table 8.1 Number of modes and heat capacity of gases in the classical limit.

	Number of modes			Classical	
	Translational	Rotational	Vibrational	$C_{V,m}/R$	$C_{p,m}/R$
A(g)	3			3/2	5/2
AB(g)	3	2	1	7/2	9/2
AB ₂ (g) non-linear	3	3	3	6	7
AB ₂ (g) linear	3	2	4	13/2	15/2
AB _{n-1} (g) non-linear	3	3	$(3n - 6)$	$3 + (3n - 6)$	$4 + (3n - 6)$
AB _{n-1} (g) linear	3	2	$(3n - 5)$	$7/2 + (3n - 6)$	$9/2 + (3n - 6)$

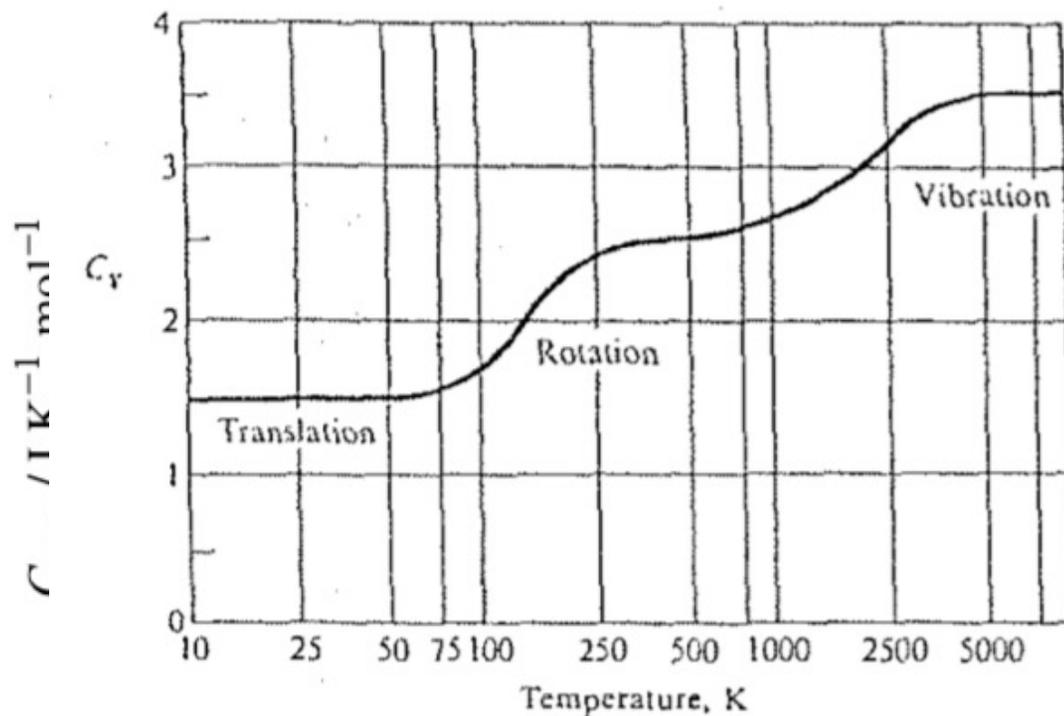


Figure 3.9 Heat capacity at constant volume of one molecule of H_2 in the gas phase. The vertical scale is in fundamental units; to obtain a value in conventional units, multiply by k_B . The contribution from the three translational degrees of freedom is $\frac{3}{2}$; the contribution at high temperatures from the two rotational degrees of freedom is 1; and the contribution from the potential and kinetic energy of the vibrational motion in the high temperature limit is 1. The classical limits are attained when $\tau \gg$ relevant energy level separations.

Monoatomic $H(g)$ with only translational degrees of freedom is already fully excited at low temperatures. The vibrational frequencies (ν) of $H_2(g)$ and $H_2O(g)$ 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 ~ 10 K.

Figure 8.2 Molar h symbols at 5000 K 1

and $H_2O(g)$. The open

Atoms in a crystal (Dulong and Petit Model)

Works at high temperature

Three Harmonic oscillators, x, y, z
 Spring (Potential Energy)
 $dU/dx = F = -kx$ where x is 0 at the rest position
 $U = -1/2 kx^2$
 Kinetic Energy
 $U = 1/2 mc^2$

Each atom in a solid has 6 springs
Each spring with $1/2 kT$ energy
So, $6/2R = 3R = C_v$

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

$$x = A \sin \omega t \qquad \omega = 2\pi\nu = \sqrt{\frac{K}{m}}$$

Three oscillator per atom so $U_m = 3RT$

$$C_{V,m} = 3R = 24.94 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$dU = -pdV + TdS$$

$$d(U/dT)_V = T(dS/dT)_V = C_V$$

-SUV
 H A
 -pGT

Phonons

Two size scales, a and λ

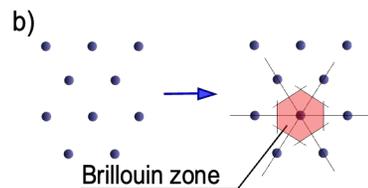
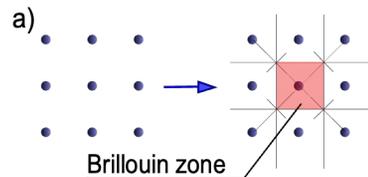
If $\lambda \geq a$ you are within a Brillouin Zone

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 $k \pm 2\pi/a$, $k \pm 4\pi/a$, 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 $k = 2\pi/\lambda$

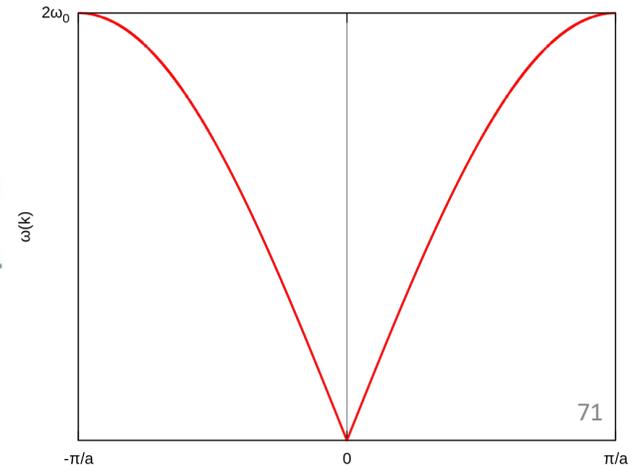
The density of states is defined by
$$D(E) = \frac{1}{V} \cdot \frac{dZ_m(E)}{dE}$$

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

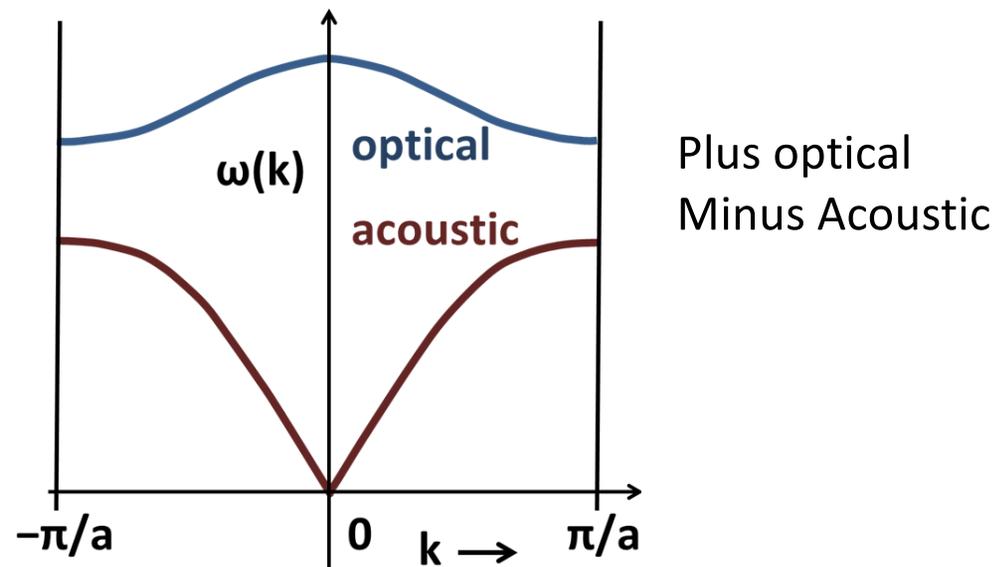
Bose-Einstein statistics gives the probability of finding a phonon in a given state:

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

Phonons

Dispersion relation for phonons

$$\omega_{\pm}^2 = K \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm K \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2 \frac{ka}{2}}{m_1 m_2}}$$



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

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

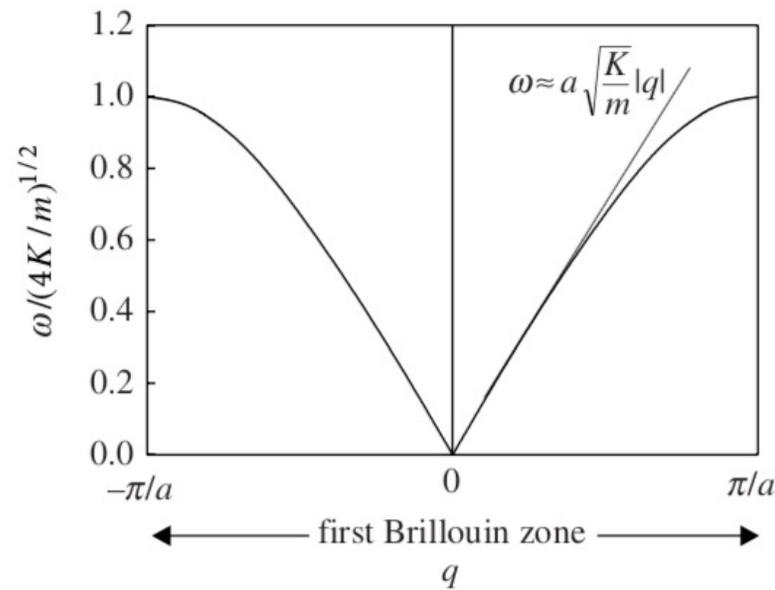
$$C_{V,m} = \left(\frac{d\bar{U}}{dT}\right)_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E / T)}{[\exp(\Theta_E / T) - 1]^2}$$

Einstein temperature: $\Theta_E = \frac{\hbar\omega_E}{k_B}$

Dispersion Curve

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

Angular frequency of vibrations as a function of wavevector, q

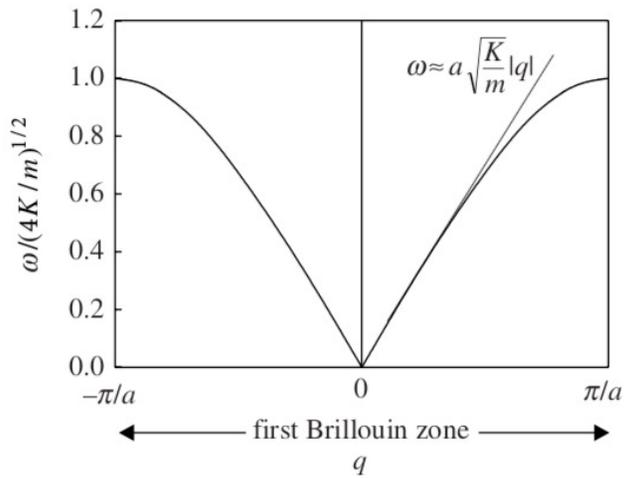


$$-\pi/a < q < \pi/a$$

**First Brillouin Zone of
the one-dimensional
lattice**

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)

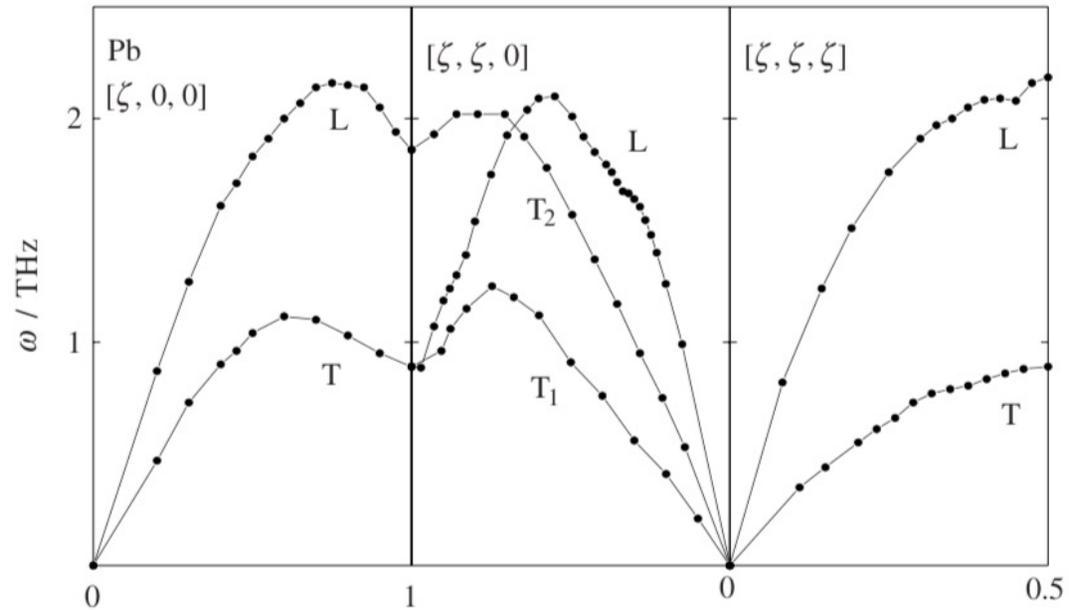
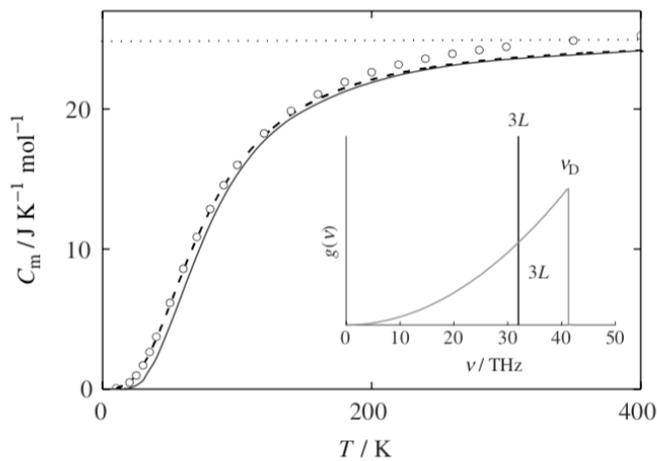


Figure 8.7 Experimental dispersion relations for acoustic modes for lead at 100 K [2].
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$$\Theta_D = 315 \text{ K}$$

$$\Theta_E = 244 \text{ K}$$

Higher Characteristic T
represents stronger
bonds

Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244 \text{ K}$ and $\Theta_D = 314 \text{ K}$. The vibrational density of states according to the two models is shown in the insert.

Table 8.2. Debye temperature (Θ_D in K) and electronic heat capacity coefficient (see Section 8.4) (γ in $\text{mJ K}^{-1} \text{mol}^{-1}$) of the elements.

Li 344 18	Be 1440 2	<div style="border: 1px dashed black; padding: 5px; display: inline-block;"> Θ_D γ </div> Higher Characteristic T represents stronger bonds										B	C 2050 0	N	O	F	Ne 75
Na 158 14	Mg 400 14											Al 428 14	Si 645	P	S	Cl	Ar 92
K 91 21	Ca 230 77	Sc 360	Ti 420 36	V 380 92	Cr 630 16	Mn 410 180	Fe 470 50	Co 445 48	Ni 450 73	Cu 315 7	Zn 327 6	Ga 320 6	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56 24	Sr 147 37	Y 280	Zr 291 30	Nb 275 88	Mo 450 21	Tc	Ru 600 34	Rh 480 49	Pd 274 100	Ag 225 6	Cd 209 7	In 108 18	Sn 200 18	Sb 211	Te 153	I	Xe 64
Cs 33 32	Ba 110 27	La 142	Hf 252 26	Ta 240 59	W 400 12	Re 430 25	Os 500 24	Ir 420 31	Pt 240 66	Au 165 7	Hg 72 19	Tl 79 15	Pb 105 34	Bi 119	Po	At	Rn

Modulus and Heat Capacity

$$\sigma = E \varepsilon$$

$$F/A = E \Delta d/d$$

$$F = K \Delta d$$

$$K = F/\Delta d = E A/d$$

At large q , $\omega = v(4K/m)$
This yields ω_D from E

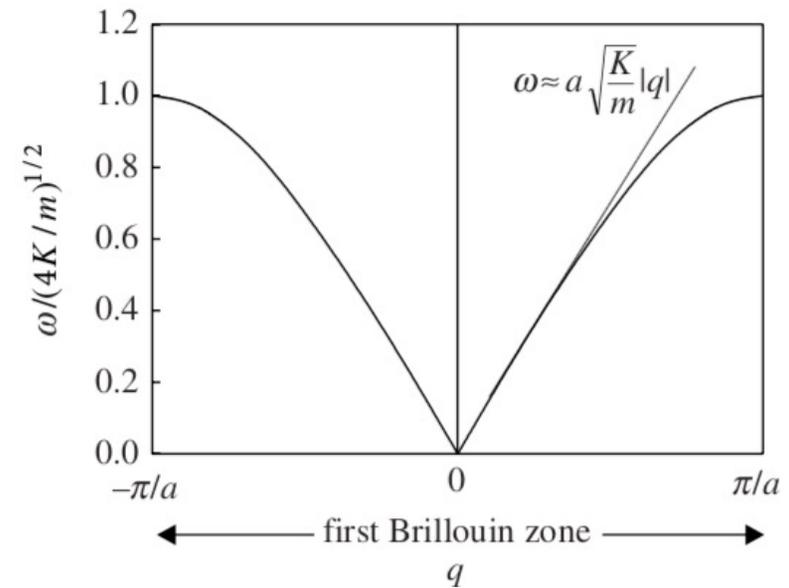
For Cu, $\theta_D = 344\text{K}$

$$\Theta_D = \frac{\hbar \omega_D}{k_B} = 2\pi \frac{h \nu_D}{k_B}$$

$$\omega_D = 32 \text{ THz}$$

$$K = 13.4 \text{ N/m}$$

$$\omega_D = 18 \text{ THz}$$



Spectroscopy measures vibrations, this can be used to calculate the density of states, this can be integrated to obtain the heat capacity

Number of vibrational modes $3N_A g(\nu) d\nu$ where $\int_0^{\infty} g(\nu) d\nu = 1$

IR: High Polarity
Motion of charged atoms under electromagnetic field

NaCl

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

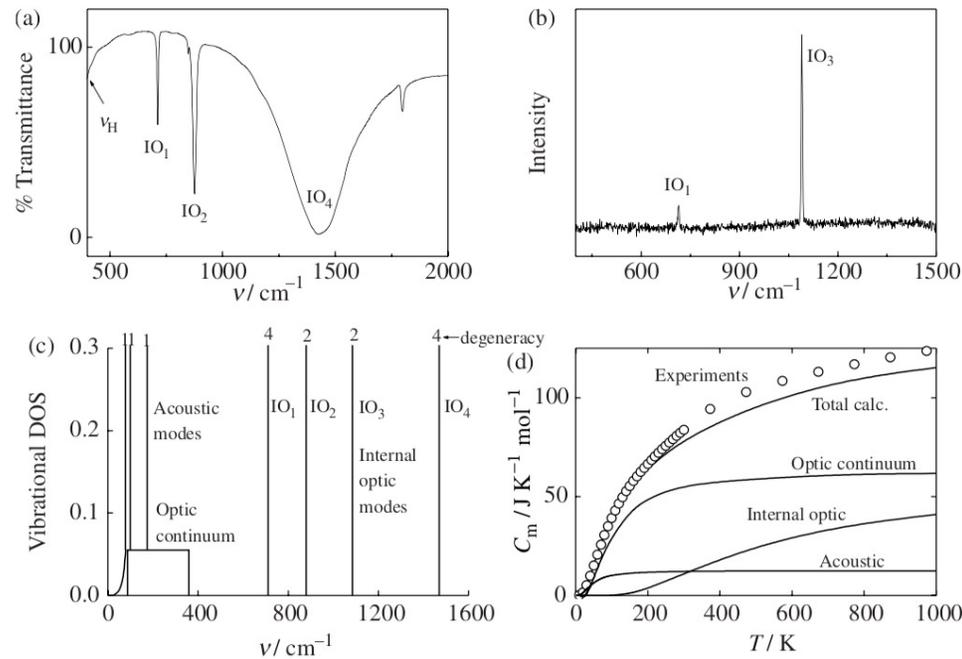


Figure 8.16 (a) IR and (b) Raman spectra for the mineral calcite, CaCO_3 . The estimated density of vibrational states is given in (c) while the deconvolution of the total heat capacity into contributions from the acoustic and internal optic modes as well as from the optic continuum is given in (d).

Benzene, Graphene,
Nanotubes,

Entropy from Heat Capacity

-SUV
H A
-pGT

$$C_V = (dU/dT)_V$$

From the Thermodynamic Square

$$dU = TdS - pdV \text{ so } C_V = (dU/dT)_V = T (dS/dT)_V - p (dV/dT)_V$$

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

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

Second term is 0 dp at constant p is 0

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

Integrate C_p/T dT or Integrate C_V/T dT to obtain S

Low Temperatures Solve Numerically
High Temperatures Series Expansion

$$S = 3R \left[\frac{4}{3} + \ln \left(\frac{T}{\theta_i} \right) + \frac{1}{40} \left(\frac{\theta_i}{T} \right)^2 - \frac{1}{2240} \left(\frac{\theta_i}{T} \right)^4 + \dots \right]$$

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

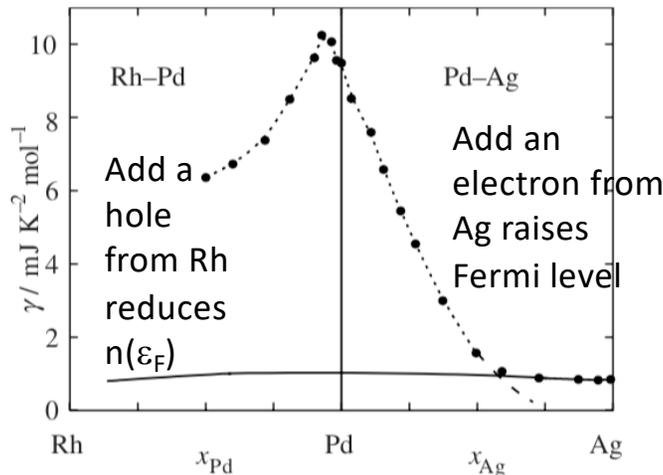
$$S_E = 3R \left[\frac{\Theta_E/T}{[\exp(\Theta_E/T) - 1]} - \ln[1 - \exp(-\Theta_E/T)] \right]$$

$$\theta_E = \hbar\omega_E/k_B$$

$$C_{V,m} = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^x}{(e^x - 1)^2} x^4 dx$$

$$S_D = 3R \left[\frac{4T^3}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{x^3 dx}{[\exp(x) - 1]} - \ln[1 - \exp(-\Theta_D/T)] \right]$$

$$\theta_D = \hbar\omega_D/k_B$$

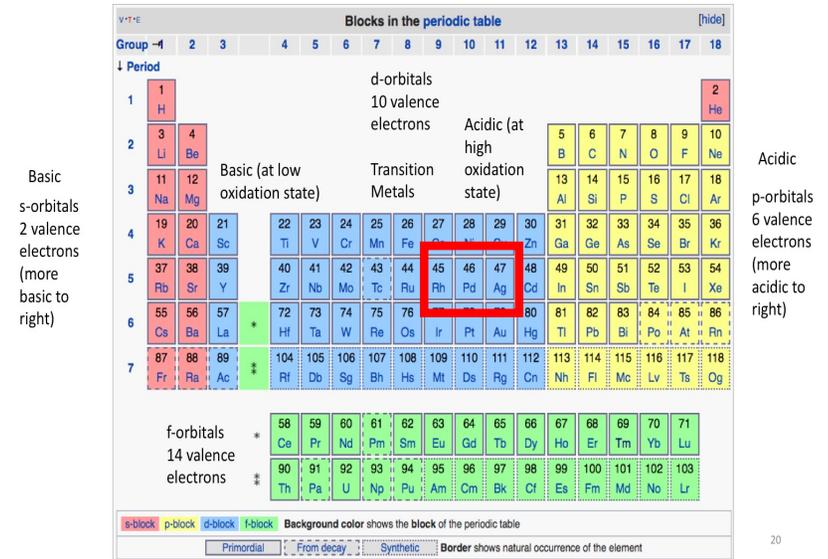


$$C_E = \frac{\partial \Delta U}{\partial T} = 2n(\epsilon_F)k_B^2 T$$

$$C_E = \gamma T$$

Figure 8.22 Variation of the electronic heat capacity coefficient with composition for the alloys Rh–Pd and Pd–Ag [17]. Solid and dotted lines represent the electronic DoS for the 5s and 4d bands, respectively.

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.



From Kittel and Kroemer Thermal Physics Chapter 2

For a system with quantized energy and two states ε_1 and ε_2 , the ratio of the probabilities of the two states is given by the Boltzmann potentials, (τ is the temperature $k_B T$)

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

If state ε_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,

$$Z = \exp(-\varepsilon_2/\tau) + 1 \quad U \equiv \langle \varepsilon \rangle = \frac{\varepsilon \exp(-\varepsilon/\tau)}{Z} = \varepsilon \frac{\exp(-\varepsilon/\tau)}{1 + \exp(-\varepsilon/\tau)}, \quad C_V \equiv (\partial U / \partial \tau)_V$$

Z normalizes the probability for a state "s"

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

$$C_V = k_B \left(\frac{\varepsilon}{k_B T} \right)^2 \frac{\exp(\varepsilon/k_B T)}{[\exp(\varepsilon/k_B T) + 1]^2}$$

The average energy for the system is $U = (\sum \varepsilon_i e^{-\varepsilon_i/\tau}) / Z = \tau^2 \left(\frac{d \ln Z}{d \tau} \right)$

Heat Capacity of Polymers

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

Einstein method works well above 100K

$$E(\theta/T) = [(\theta/T)^2 \exp(\theta/T)] / [\exp(\theta/T) - 1]^2$$

$$C_E = Nk \sum_{N_E} E(\theta/T)$$

$$N_E = 3N_{\text{Atoms}} - N$$

N_{atoms} = number of atoms in a mer unit
3 for CH_2

N = number of skeletal modes of vibration
 $N = 2$ for $-(\text{CH}_2)_n-$

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

Einstein temperature: $\Theta_E = \frac{\hbar\omega_E}{k_B}$

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 Model

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

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

$$\Omega_{AB} = zL\omega_{AB}$$

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

$$\mu_A \sim dG/dx_A$$

$$\mu_A - \mu_A^0 = RT \ln a_A = RT \ln x_A + \Omega_{AB} x_B^2$$

$$RT \ln \gamma_A = \Omega_{AB} x_B^2$$

Excess molar Gibbs energy of mixing for quasi-regular solution

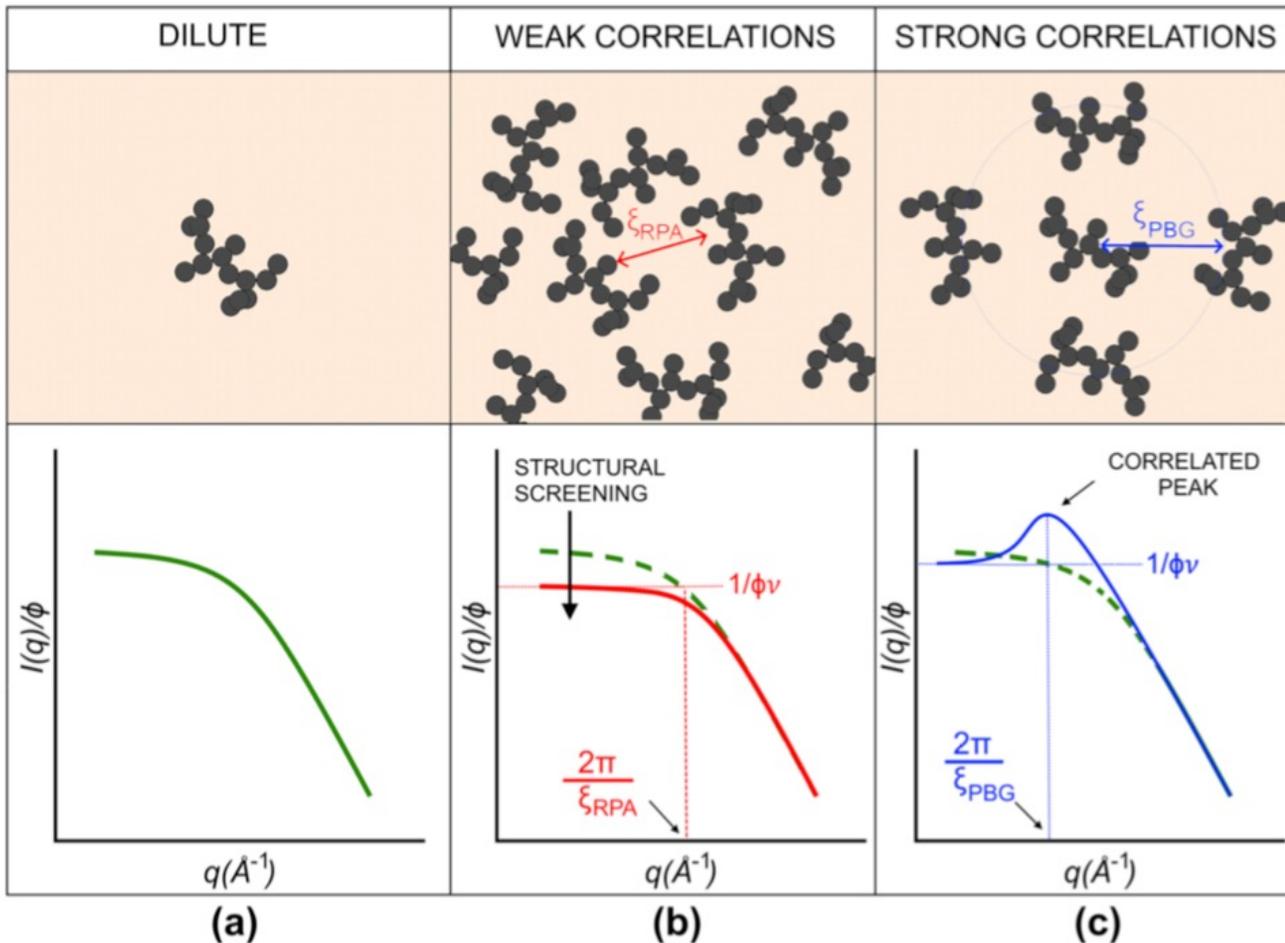
$$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = zLx_{\text{A}}x_{\text{B}}(\omega_{\text{AB}} - T\eta_{\text{AB}})$$

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

$$\Delta_{\text{mix}}^{\text{exc}} G_{\text{m}} = x_{\text{A}}x_{\text{B}}\Omega_{\text{AB}}\left(1 - \frac{T}{\tau}\right)$$

τ 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

$$S(\mathbf{k}) = 1 + \rho \int d\mathbf{r} (g(\mathbf{r}) - 1) \exp(i\mathbf{k} \cdot \mathbf{r}).$$

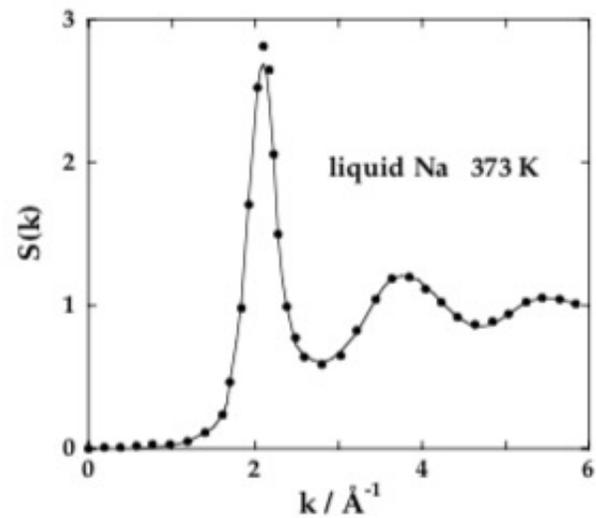


FIG. 3.2. Structure factor of liquid sodium near the normal melting temperature. The points are experimental x-ray scattering results⁸ and the curve is obtained from a Monte Carlo calculation⁹ for the r^{-4} potential under the same thermodynamic conditions.

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

acidity parameter, α , and basicity parameter, β .

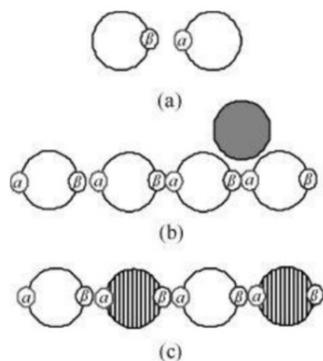


Figure 11.7. Observations about complexation. (a) A mixture of acid with base suggests favorable interactions, as in acetone + chloroform. (b) Hydrogen bonding leads to unfavorable interactions when one component associates strongly and the other is inert, as in isooctane + water. (c) Hydrogen bonding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

Hildebrand Model

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

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

Table 11.1. Acidity (α) and Basicity (β) Parameters in $(\text{J}/\text{cm}^3)^{1/2}$ and Molar Volumes (cm^3/mol) for Various Substances as liquids at 298 K^a

Compound	α	β	V^L
Acetone	0	11.14	73.4
Benzene	0.63	2.24	89.7
Chloroform	5.80	0.12	80.5
Ethanol	12.58	13.29	58.2
<i>n</i> -Hexane	0	0	130.3
Isooctane	0	0	162.9
Isopropanol	9.23	11.86	76.8
Methanol	17.43	14.49	40.5
MEK	0	9.70	90.1
Water	50.13	15.06	18.0

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);

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

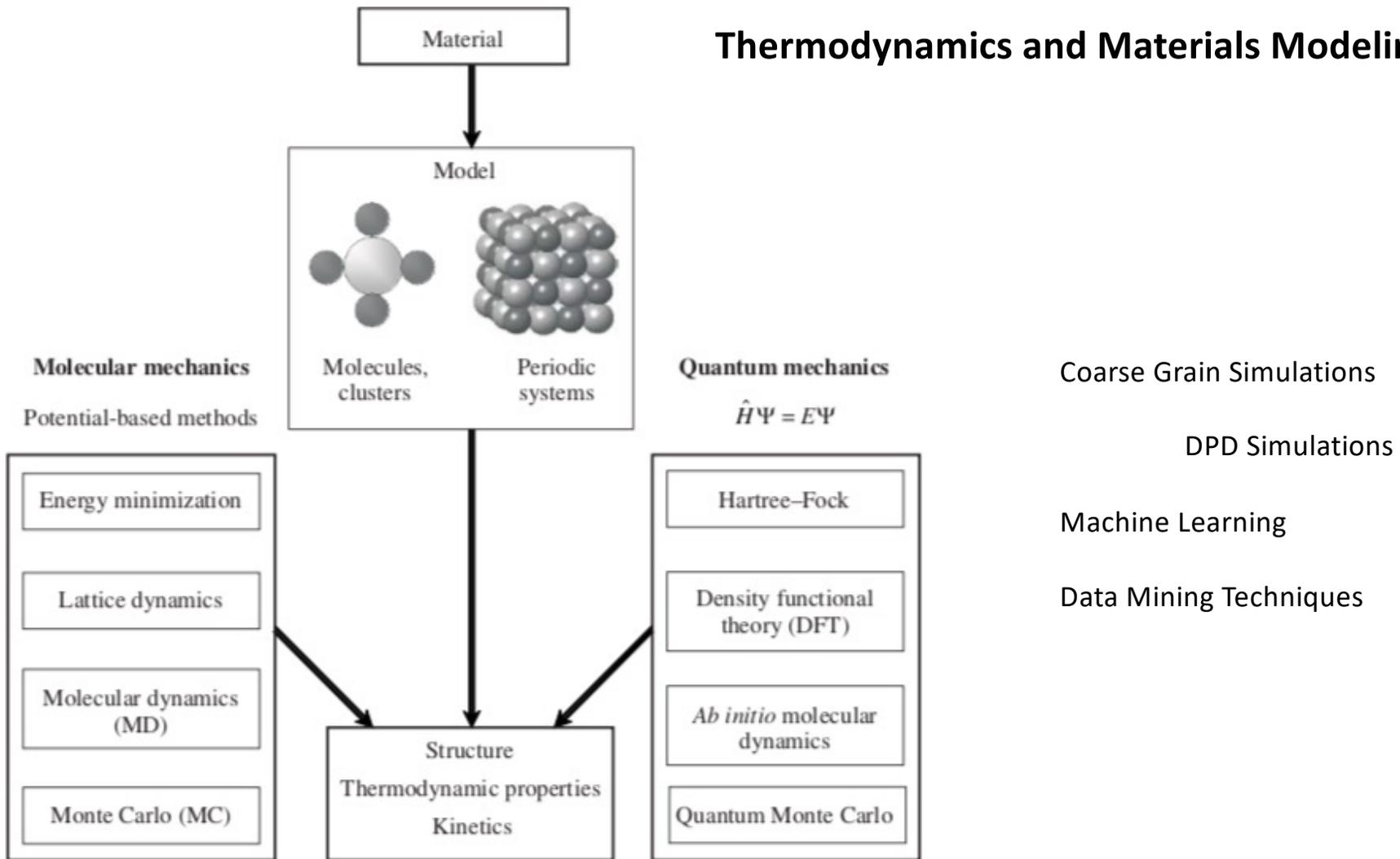


Figure 11.1

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 Schrodinger equation

$$\hat{H}\Psi = E\Psi$$

Hamiltonian in atomic units:

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

r_i electron positions; d_{α} nuclear positions, Z_{α} 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 $\rho(\mathbf{r})$
- 2) Parallel non-interacting system (NIS)

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

- 3) Write the energy functional as

$$\begin{aligned} E[\rho] &= T_S[\rho] + V_{\text{nuc}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \\ &= -\frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} - \sum_{\alpha} \int \rho(\mathbf{r}) \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{d}_{\alpha}|} d\mathbf{r} \\ &\quad + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho] \end{aligned}$$

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

$$\frac{3}{2} Nk_B T = \frac{1}{2} \sum_i m_i v_i^2$$

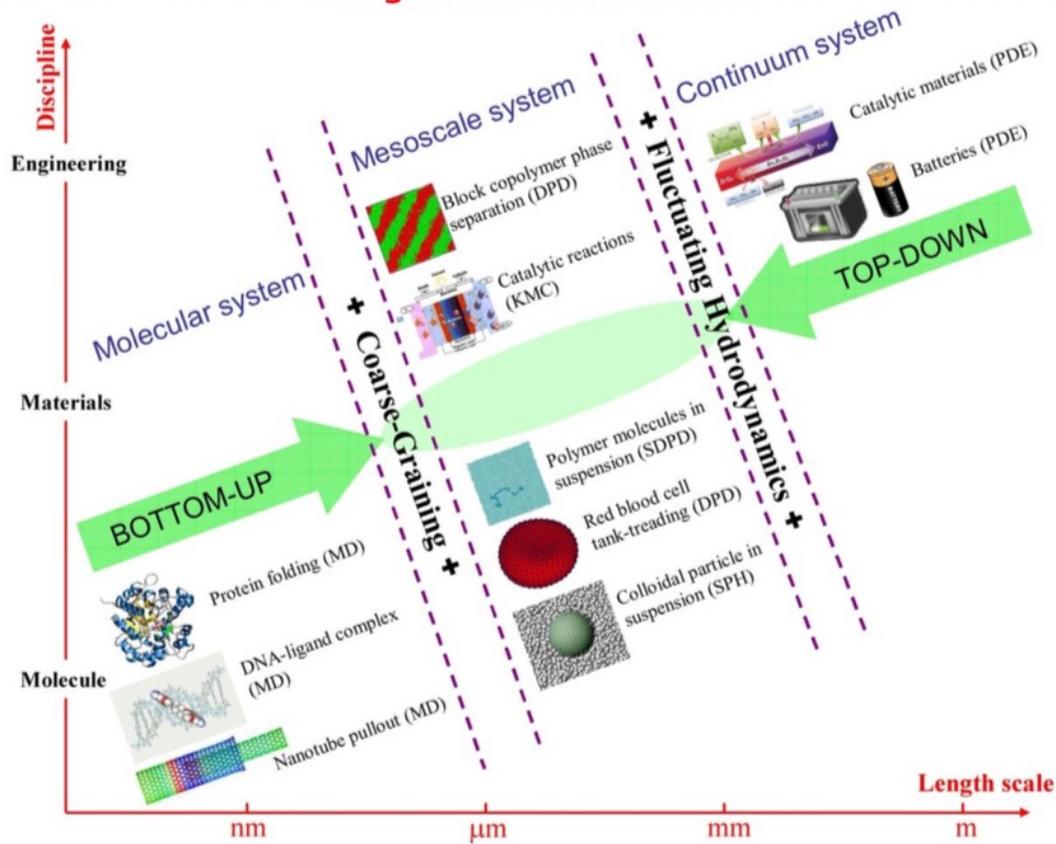
- 5) After steady state record velocities and positions so that $\langle r^2 \rangle = 6Dt$ is found
Time calculation is on the order of nanoseconds.

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

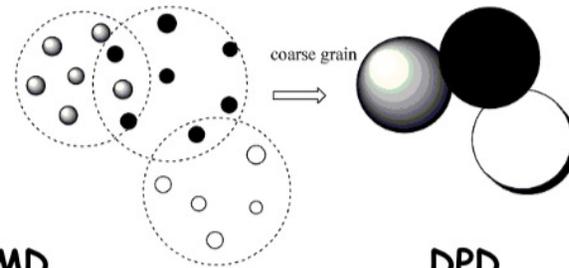
They can calculate differences in free energy for phase diagram construction

Mesoscale Phenomena and Models

Due to wide range of characteristic **lengths - times**, several simulation methods that describe **length and time scales** have been developed:



Dissipative Particle Dynamics (DPD)



MD

DPD

Navier-Stokes

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

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

- continuum fluid mechanics
- **MACRO**scopic modeling

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



Monte Carlo/Metropolis Method

Periodic Boundary Conditions

Fix T, V, N

$$\langle Q \rangle = \int Q(Z)P(Z) dZ \quad P(Z) = \frac{\exp(-U(Z)/k_B T)}{\int \exp(-U(Z)/k_B T) dZ} \quad \text{"Z" is a state of the system}$$

- 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)

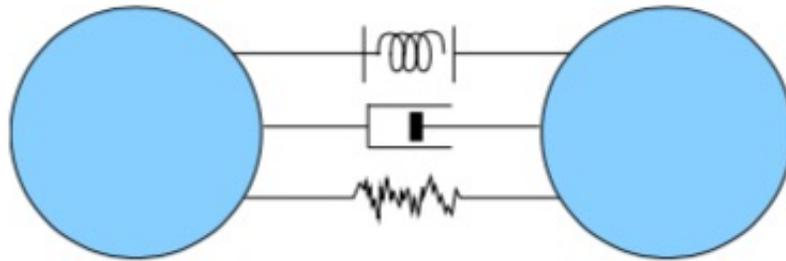


FIG. 1. Dissipative particles interact pair-wise with a conservative linear repulsive force, and a Brownian dashpot made of a friction force that reduces the relative velocity between the particles and a stochastic force that gives kicks of equal size and opposite directions to the particles. These forces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

Course Summary

XI. Experimental Thermodynamics

Calorimetry

Differential Scanning Calorimetry

Modulated DSC

Microcalorimetry

Differential Thermal Analysis

Thermal Gravimetric Analysis

Bomb Calorimetry/Combustion Calorimetry

Didn't cover the other 25 techniques (no time)

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**
- XI. Experimental methods**

