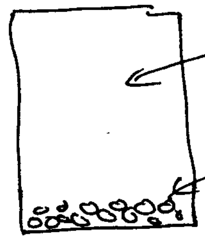
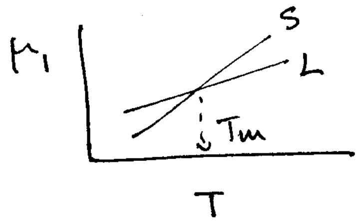
§14.2 - Solid-Liquid Equil, C=2



$$\mu_1^S(T,P) = \mu_1^L(T,P) + k_B T \ln x_1$$

$$\Rightarrow \Delta\mu = -k_B T \ln x_1 \quad (1)$$

$$\left.\frac{\partial(\Delta\mu/T)}{\partial T}\right)_P = -\frac{\Delta h}{T^2} \quad (2)$$



Earlier, we assume $\Delta h = \text{const}$.

More realistically $\rightarrow$ $\Delta h = \Delta h_m + \Delta c_p \cdot (T - T_m)$

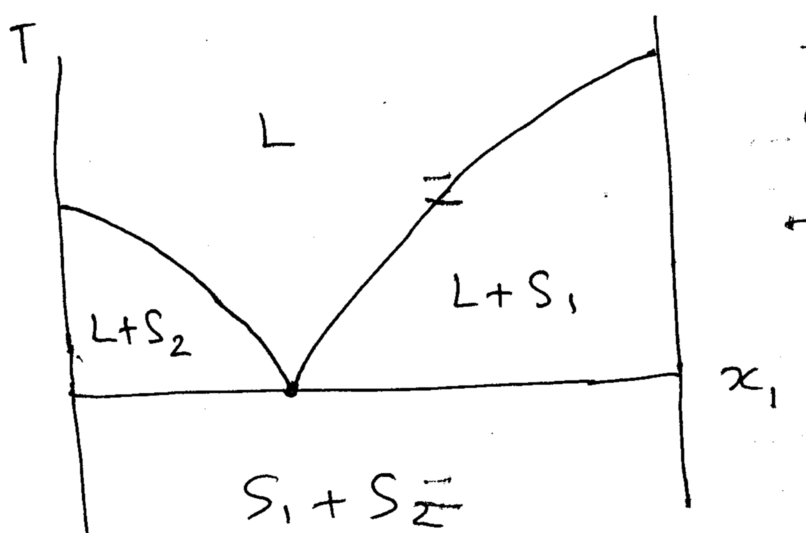
Integrating (2)

$$\int_{T_m}^{T} d\left(\frac{\Delta\mu}{T}\right) = -\int_{T_m}^{T} \frac{\Delta h_m + (T-T_m)\Delta c_p}{T^2}\, dT$$

$$\Rightarrow \frac{\Delta\mu}{T} = \left(\Delta h_m - T_m \Delta c_p\right)\left[\frac{1}{T} - \frac{1}{T_m}\right] - \Delta c_p \ln\frac{T}{T_m}$$

$$\overset{(1)}{\Rightarrow} k_B T \ln x = -\left(\Delta h_m - T_m \Delta c_p\right)\left(1 - \frac{T}{T_m}\right) + T \Delta c_p \ln\frac{T}{T_m}$$

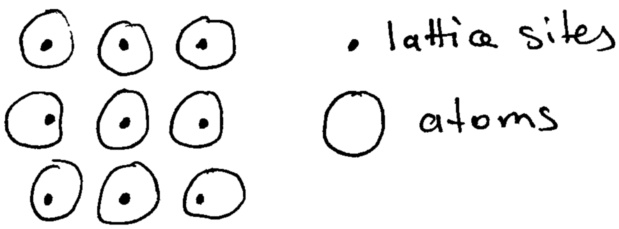
$$\Rightarrow x = \exp\left[-\left(\frac{\Delta h_m}{k_B T_m} - \frac{\Delta c_p}{k_B}\right)\left(\frac{T_m}{T} - 1\right) + \frac{\Delta c_p}{k_B}\ln\frac{T}{T_m}\right]$$



Same treatment for Comp. 2 solid

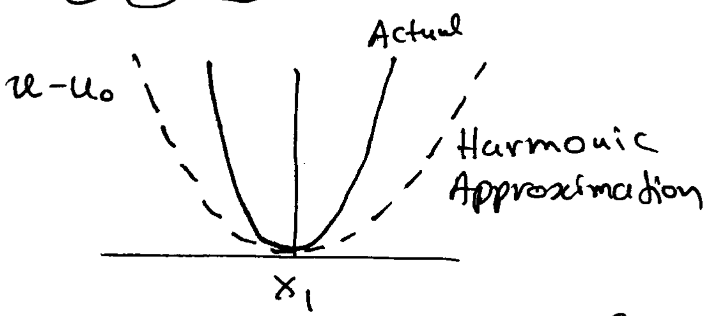
$\longleftrightarrow$ eutectic point

§14.4-6 Microscopic View



→ Atoms vibrate around equilibrium lattice positions

→ Simple, atomic solids (spherically symmetric, no directional bonds)



$$\Delta u = \underbrace{\cancel{\frac{\partial \Delta u}{\partial x_1}} \Delta x_1}_{\text{0 at equilibrium position}} + \underbrace{\frac{1}{2}\frac{\partial^2 \Delta u}{\partial x_1^2}(\Delta x_1)^2}_{\text{harmonic term}} + \underbrace{\cdots}_{\text{higher order terms}}$$

Classical harmonic oscillator frequency $\nu = \frac{1}{2\pi}\sqrt{\frac{1}{m}\frac{\partial^2 u}{\partial x_1^2}}$ (1)

Einstein Model

Assumes → Each atom oscillates independently
→ All frequencies are equal to ν

$$\Delta u = 2\pi^2 m \nu^2 \left(\Delta x_1^2 + \Delta y_1^2 + \Delta z_1^2 + \Delta x_2^2 + \cdots + \Delta z_N^2\right)$$

Quantum mechanical harmonic oscillator, 1D

$$-\frac{\hbar}{2m}\left(\frac{\partial^2 \psi}{\partial x^2}\right) + (2\pi^2 m \nu^2) x^2 \psi = \varepsilon \psi$$

gives solutions for $\varepsilon = \left(n + \frac{1}{2}\right) h\nu$, $n = 0, 1, 2, \ldots$

$$E = \sum_{i=1}^{3N} \varepsilon_i = \sum_{i=1}^{3N} \left(n_i + \frac{1}{2}\right) h\nu = \left[n_t + \frac{3N}{2}\right] h\nu$$

where $n_t = \sum_i n_i$

what is $\Omega(E,V,N)$? Need to find ways of assigning $3N$ integers so that $\sum_{i=1}^{3N} n_i = n_t$,

where $n_t = \frac{E}{h\nu} - \frac{3N}{2}$

n_t objects, $3N$ bins, indistinguishable, can have more than one object per bin:

$$\Omega(E,V,N) = \frac{(n_t + 3N - 1)!}{(3N-1)!\; n_t!}$$

(see Example 2.3 case d – no proof!)

$$S(E,V,N) = k_B \ln \Omega \approx k_B \ln\left[\frac{(n_t+3N)!}{(3N)!\, n_t!}\right] = -k_B\left[3N \ln\frac{3N}{n_t+3N} + n_t \ln\frac{n_t}{n_t+3N}\right]$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial S}{\partial n_t}\frac{\partial n_t}{\partial E} = -\frac{k_B}{h\nu}\left[\frac{-3N}{n_t+3N} + \ln n_t + 1 - \ln(n_t+3N) - \frac{n_t}{n_t+3N}\right] = -\frac{k_B}{h\nu}\ln\frac{n_t}{n_t+3N}$$

Rearranging: $$E(T,V,N) = 3Nh\nu\left(\frac{1}{2} + \frac{1}{e^{h\nu/k_BT} - 1}\right)$$

as $T \to 0$ $\quad E \to \frac{3Nh\nu}{2}$

$$C_V = \left.\frac{\partial E}{\partial T}\right)_V = 3N(h\nu)^2 \cdot \left(+\frac{1}{k_BT^2}\right) \cdot \frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT} - 1)^2} =$$

$$= 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \cdot e^{h\nu/k_BT} \Big/ (e^{h\nu/k_BT} - 1)^2 \Rightarrow \frac{C_V}{3Nk_B} = \left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

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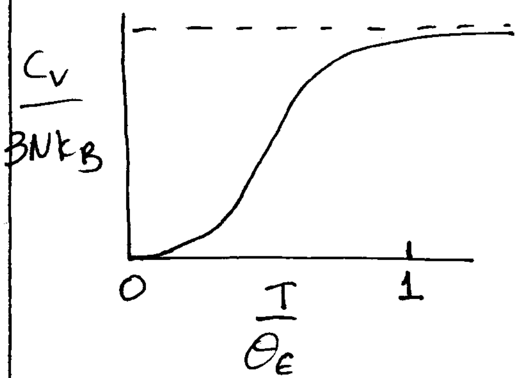

$C_v \to 3Nk_B \qquad T \gg \theta_E$

$$A = E - TS \Rightarrow A = -3Nk_BT \ln \frac{e^{-\theta_E/2T}}{1-e^{-\theta_E/2T}}$$

low-T behavior does not match experiment!

Debye model

Instead of independent oscillators, consider coupled perturbations away from equilibrium:

$$\Delta u = \underbrace{\frac{\Delta x_1^2}{2}\frac{\partial^2 u}{\partial x_1^2} + \frac{\Delta x_1 \Delta y_1}{2}\frac{\partial^2 u}{\partial x_1 \partial y_1} + \cdots + \frac{\Delta z_N^2}{2}\frac{\partial^2 u}{\partial z_N^2}}_{9N^2 \text{ terms}} .$$

$$\Delta u = \frac{1}{2}\left[\Delta x_1\ \Delta y_1\ \Delta z_1 \cdots \Delta z_N\right] \cdot \begin{bmatrix} \frac{\partial^2 u}{\partial x_1^2} & \frac{\partial^2 u}{\partial x_1 \partial y_1} & \cdots & \frac{\partial^2 u}{\partial x_1 \partial z_N} \\ \frac{\partial^2 u}{\partial y_1 \partial x_1} & \cdots & & \\ \vdots & & & \\ \frac{\partial^2 u}{\partial z_N \partial x_1} & \cdots & & \frac{\partial^2 u}{\partial z_N^2} \end{bmatrix} \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \vdots \\ \Delta z_N \end{bmatrix}$$

or $\Delta u = \frac{1}{2}\vec{q}^{\,T} \underline{\underline{H}}\, \vec{q}$ $\quad \underline{\underline{H}}$: symmetric matrix

Eigen decomposition of $\underline{\underline{H}} = \underline{\underline{P}}^T \underline{\underline{D}}\, \underline{\underline{P}}$ $\quad \underline{\underline{D}}$: diagonal matrix of eigenvalues

$\underline{\underline{P}}$: eigenvector matrix

$$\Delta u = \frac{1}{2}\vec{q}^{\,T}\underline{\underline{P}}^T \underline{\underline{D}}\, \underline{\underline{P}}\vec{q} = \frac{1}{2}(\underline{\underline{P}}\vec{q})^T \underline{\underline{D}} (\underline{\underline{P}}\vec{q})$$: "normal mode" decomposition

$$= \frac{1}{2}\sum_{i=1}^{3N} \lambda_i \Delta\vec{S}_i^{\,2}$$ $\quad \Delta\vec{S}_i$: displacement along ith eigenvector (normal mode)

$$= 2\pi^2 m \sum_{i=1}^{3N} \nu_i^2 \Delta S_i^2$$

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The key difference from the Einstein model is that the frequencies ν_i are not equal.

Debye suggested $\rho(\nu) = 3\nu^2/\nu_m^3$ for $\nu < \nu_m$
[based on ideas from continuous mechanics] "cutoff" frequency
where $\rho(\nu)d\nu$ counts frequencies between ν and $\nu+d\nu$

The heat capacity per particle from the Einstein model:

$$C_v^{Einst} = 3k_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{\exp(h\nu/k_BT)}{[\exp(h\nu/k_BT)-1]^2}$$

$$C_v^{Debye}(T) = \int_0^{\nu_m} C_v^{Einst}\rho(\nu)\,d\nu = 3k_B\int_0^{\nu_m}\left(\frac{h\nu}{k_BT}\right)^2 \frac{\exp\left(\frac{h\nu}{k_BT}\right)}{\left[\exp\left(\frac{h\nu}{k_BT}\right)-1\right]^2}\frac{3\nu^2}{\nu_m^3}\,d\nu$$

Change of variables: $x = \frac{h\nu}{k_BT}$ $\quad d\nu = k_BT\frac{dx}{h}$; $\Theta_D \equiv \frac{h\nu_m}{k_B}$

$$C_v^{Debye}(T) = 9k_B\int_0^{\Theta_D/T}\frac{x^2e^x}{(e^x-1)^2}\frac{(k_BT)^3x^2}{h^3\nu_m^3}\,dx \Rightarrow$$

$$C_v^{Debye}(T) = 9k_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\,dx$$

The major result is that, as $T\to 0$

The heat capacity $C_v^{Debye} \propto T^3$

versus $C_v^{Einst} \propto T^{-2}e^{-\Theta_E/T}$

Experiments at low T confirm the Debye model.