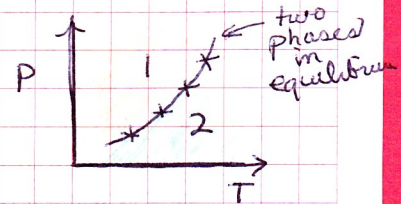## Phase Equilibrium

$$g_1(T,P) = g_2(T,P) \quad \text{\Large *} \text{ most important thing}$$

slope of equilibrium curve
$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T\Delta V} \quad \text{units of 1 mole or 1 gram, etc.}$$

$$\ln P = \alpha - \frac{B}{T} \quad \text{pressure of vapor}$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{B}{T^2} \Rightarrow \frac{dP}{dT} = \frac{BP}{T^2} \Rightarrow \frac{P}{T} = \frac{R}{V} \text{ for 1 mole} \Rightarrow \frac{dP}{dT} = \frac{BR}{TV}$$

Can approximate ΔV for vaporization curve
$V = $ volume of vapor much greater than volume of liquid $V_g \gg V_L$
$\therefore V_g \sim \Delta V$

$$\frac{dP}{dT} = \frac{B}{T}\frac{R}{\Delta V} \Leftrightarrow \frac{L_{12}}{T\Delta V} = \frac{dP}{dT} \Rightarrow L_{12} = BR$$

The point where the two curves meet is the triple point
Equate the right-hand sides of the two

Heat Capacities of Solids
Two important experimental results:
① Molar $C_V \sim 3NR$ at room temperature Dulong-Petit's Rule; Exceptions Carbon/Diamond
② At low T, $C_V \propto T^3$ goes to zero, vibrational energy of the atoms
conduction e^-'s go to zero as $T \to 0$

Theoretical
The vibrational energy of solids can be written as the sum of SHO in
normal coordinates = $3N$. Write the Hamiltonian as:

$$H = \sum_{\alpha=1}^{3N}\left(\frac{P_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha W_\alpha^2 q_\alpha^2\right) \qquad \varepsilon_\alpha = \hbar w_\alpha(n+\tfrac{1}{2}) = -\frac{\partial}{\partial\beta}\ln Z_\alpha$$

Partition Function:

$$Z_\alpha = \sum_n e^{-E_n/kT} = \sum_{n=0}^{\infty} e^{-\hbar w_\alpha(n+\frac{1}{2})/kT} = \sum_{n=0}^{\infty}x^n = \frac{1}{1-x} = \frac{1}{1-e^{-\hbar w_\alpha/kT}}$$

$$\overline{\varepsilon_\alpha} = \frac{\hbar w_\alpha}{e^{\hbar w_\alpha/kT}-1} \qquad \overline{E} = \sum_{\alpha=1}^{3N}\overline{\varepsilon_\alpha} = \sum_{\alpha=1}^{3N}\frac{\hbar w_\alpha}{(e^{\hbar w_\alpha/kT}-1)}$$

$$C_V = \frac{\partial\overline{E}}{\partial T} \sim P_P = k\sum_{\alpha=1}^{3N}\left(\frac{\hbar w_\alpha}{kT}\right)^2\frac{e^{\hbar w_\alpha/kT}}{(e^{\hbar w_\alpha/kT}-1)^2}$$

Einstein model: $W_\alpha = W_E$ all α $\quad C_V = 3Nk\left(\frac{\hbar w}{kT}\right)^2\frac{e^{\hbar w/kT}}{(e^{\hbar w/kT}-1)^2}$

$\boxed{\Theta}_E = \hbar w_E/k$ we can get from young's modulus,
Can't take high T limit of this   etc. for diamond it is quite large
$C_V \to 3Nk$ he could explain deviation from Dulong-Petit as Θ_E
But low T limit doesn't have $C_V \propto T^3$

Debye's model: Assumes the solid was a continuous "standing elastic waves" mostly low frequency with an upper frequency cutoff. Two transverse elastic waves per degree of freedom

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2}\left(\frac{1}{V_L^3} + \frac{2}{V_T^3}\right) = \frac{V\omega^2 d\omega}{2\pi^2}\left(\frac{3}{V^3}\right)$$

✓ ω_D needed because ω diverges

for solid $f(\omega)d\omega = V\omega^2 d\omega/(2\pi^2 V_T^3)$

The total number of normal modes is 3N $\qquad \int_0^{\omega_D} f(\omega)d\omega = 3N$

$$\frac{2\cancel{3}V}{2\pi^2 V^3}\left(\frac{\omega_D^3}{3}\right) = 3N \rightarrow f(\omega)d\omega = \frac{9N\omega^2 d\omega}{\omega_D^3}$$

dimensionless number

The vibrational energy of the solid

$$\Xi = \int_0^{\omega_D}\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)f(\omega)d\omega = \frac{9N\hbar}{\omega_D^3}\left(\frac{kT}{\hbar}\right)^4\int_0^{\omega_D}\frac{x^3 dx}{e^x-1} \quad \text{if } \omega_D \to \infty \int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15} \rightarrow$$

debye's model explains the low temp limit
ultimately you need quantum theory to explain heat capacity.

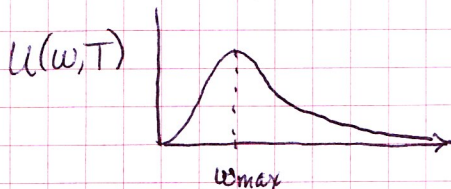Blackbody Radiation: E/m in thermal equilibrium with matter

$$f(\omega)d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3} \qquad \bar{E}(\omega) = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} \rightarrow kT \text{ in classical limit}$$

$$E = \int_0^\infty \bar{E}(\omega)f(\omega)d\omega = \frac{V\hbar}{\pi c^3}\int_0^\infty \frac{\omega^3 d\omega}{e^{\hbar\omega/kT}-1} = \frac{V\hbar\omega^3}{\pi^2 c^3(e^{\hbar\omega/kT}-1)}$$

spectral energy for a particular ω

$$U(\omega,T) = \frac{\bar{E}(\omega,T)}{V} = \frac{\hbar\omega^3}{\pi c^3(e^{\hbar\omega/kT}-1)} = \text{Planck's expression agreed well with experimental data}$$

$U(\omega,T)$

ω_{max}

$\frac{dU}{d\omega} = 0$ to get max

$\omega_{max} \propto T$ Wein's displacement law

$$\omega_{max} = \left(\frac{2.822 k_B}{\hbar}\right)T$$

To get all total energy density, integrate over all ω

$$U(T) = \int_0^\infty \frac{\hbar\omega^3 d\omega}{\pi^2 c^3(e^{\hbar\omega/kT}-1)} = aT^4 \quad \text{before planck this was known experimentally}$$

$I = \frac{c}{4}U$ plane E/m wave only ¼ goes thru hole $\quad I = \sigma T^4$

Stefan-Boltzmann constant $5.67 \cdot 10^{-8} Jm^{-2}s^{-1}K^{-4}$

can also calculate partition function

$\sum \ln \rightarrow \ln \sum \rightarrow \ln \int$ to get Helmholtz Free Energy for the cavity

then can get from the Helmholtz Free Energy $S \propto T^3$ ⅓ energy density

2.73K microwave background radiation approximate the Sun's BBR Surface of Sun, though, is between 5000K & 6000K