Lecture 18 Brief Review 13 November 2008

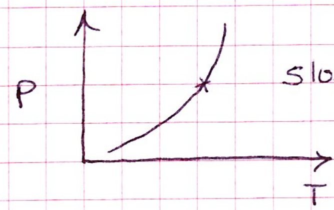
Phase Equilibrium Clausius Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T\Delta V}$$

ΔS, ΔV take for same amount of substance so that ratio not affected

Vaporization of liquid

$$\ln P = \alpha + \frac{\beta}{T}$$



slope of curve is Clausius-Claperyon Equation.

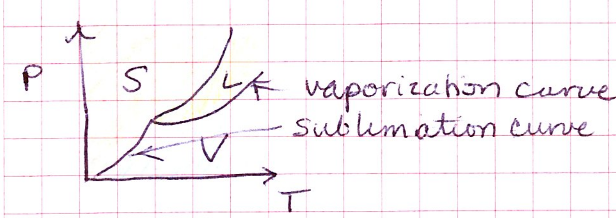
$$\frac{1}{P}\frac{dP}{dT} = -\frac{\beta}{T^2}$$

$$\frac{dP}{P} = -\frac{\beta\, dT}{T^2}$$

assume vapor is classical gas $PV = RT$ for 1 mole

$$\frac{P}{T} = \frac{R}{V} \Rightarrow -\frac{\beta}{T}\frac{R}{V} = \frac{dP}{dT}$$

can approximate as $\frac{dP}{dT} \sim \frac{-\beta R}{T\Delta V}$ $L_{12} = -\beta R$ = molar latent heat

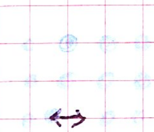


$\ln P = \alpha' + \frac{\beta'}{T}$ triple point from

$$\ln P = \alpha' + \frac{\beta'}{T_{tr}} = \alpha + \frac{\beta}{T_{tr}}$$

Heat Capacity of Solids

N atoms 3N vibrational states 3 normal modes ω_α
Sum the energies of 3N 1D SHO's each SHO corresponds to 1 normal mode
The spatial position that an atom can vibrate that way
1DOF = 1ω 2DOF = 2ω 3DOF = 3ω p. 157 - 158
The equations are coupled in a rather complicated way



Each displacement is subject to forces of neighboring atoms

linear $\dot{q}_i$ uncouple, every normal mode is a SHO

Energy Hamiltonian $H = \sum_{\alpha=1}^{3N}\left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 q_\alpha^2\right)$ general result from classical

$E_\alpha = \hbar\omega_\alpha(n_\alpha + 1/2)$ $n_\alpha \geq 0$ quantum result

Take one SHO a system and the rest as a heat bath.

$$Z_\alpha = \sum_{n_\alpha} e^{-\hbar\omega_\alpha(n_\alpha + 1/2)/kT} = \frac{1}{(1 - e^{-\hbar\omega_\alpha/kT})}$$

$$\bar{E}_\alpha = -\frac{\partial \ln Z_\alpha}{\partial \beta} = \frac{\hbar\omega_\alpha}{e^{\hbar\omega_\alpha/kT} - 1}$$

$$\bar{E} = \sum_{\alpha=1}^{3N} \frac{\hbar\omega_\alpha}{e^{\hbar\omega_\alpha/kT} - 1}$$

Einstein's Heat Capacity Model: $\omega_\alpha = \omega_E$ for all α $\quad \bar{E} = 3N\left(\frac{\hbar\omega_E}{e^{\hbar\omega_E/kT}-1}\right)$

$C_v = \frac{\partial \bar{E}}{\partial T}$ in $kT \gg 1$ $\quad C_v \to 3Nk_B$ $\quad$ low T limit is a deviation

$\omega_E = \frac{a}{mY} = \frac{N_0^{1/3} Y^{1/2}}{\rho^{1/6} M^{1/3}} = f(\text{density, atomic weight, Young's modulus})$ $\quad \omega \gg \log$ $\to$ deviation

Can modify Einstein's model 2NDOF $\omega_\parallel$, 1NDOF $\omega_\perp$ better results.

Debye's Heat Capacity Model: Assume the normal modes are the standing elastic waves.

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

debye: $\int_0^{\omega_D} f(\omega)d\omega = \frac{3V}{2\pi^2\bar{V}^3}\int_0^{\omega_D}\omega^2 d\omega = \frac{3V\omega_D^3}{6\pi^2\bar{V}^3} = 3N \Rightarrow f(\omega)d\omega = \frac{9N\omega^2 d\omega}{\omega_D^3}$

$$\bar{E} = \int_0^{\omega_D} \mathcal{E}(\omega) f(\omega) d\omega = \int_0^{\omega_D}\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\frac{9N\omega^2 d\omega}{\omega_D^3} \propto T^4$$

know $\boxed{\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}}$

$C_v = \frac{\partial \bar{E}}{\partial T} \propto T^3$

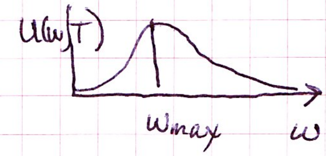
Blackbody Radiation: $f(\omega)d\omega = \frac{V\omega^2 d\omega}{\pi c^3}$ $\quad (v_L = 0, v_T = c)$ cavity radiation

the energy is for ∞ SHO's ∞ DOF to specify E/m energy

$\bar{\mathcal{E}} = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$ $\quad \bar{E} = \int_0^\infty\left(\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\left(\frac{V\omega^2 d\omega}{\pi^2 c^3}\right) \propto T^4$ $\quad u = \frac{E}{V} \propto T^4 = aT^4$

$I = \frac{caT^4}{4} = \sigma T^4$ (proof in folder) $\quad \sigma_B = \frac{ca}{4}$ = Stefan-Boltzmann constant

integrated intensity $u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/kT}-1}$



$\omega_{max} = bT$, $\quad b = 2.822\frac{k}{\hbar}$

@ 6000 K λ_{max} is visible most intense radiation

Cosmic background radiation 2.73 K microwave radiation
Temperature cools as gas expands.

Earth is in thermal equilibrium with the Sun
mostly in the IR, Sun is visible