Vibrations in a solid

Consider energy states as a set of harmonic oscillators (atoms vibrating back and forwards) about a potential energy minimum E_0 Expect 3N vibrational modes.

The atoms are localized, therefore distinguishable.

α labels the mode. Energy states $E_i = E_o + \hbar\omega_\alpha$

Partition function

$$Z_{\{\alpha\}} = e^{-\beta E_0}\left[1 + e^{-\beta\hbar\omega_\alpha} + e^{-2\beta\hbar\omega_\alpha} + \cdots ..\right]$$

$$Z_{\{\alpha\}} = e^{-\beta E_0}\frac{1}{1 - e^{-\beta\hbar\omega_\alpha}}$$

For N particles ${Z_{\{\alpha\}}}^N = e^{-\beta N E_0}\prod_{n=1}^{N}\frac{1}{1-e^{-\beta\hbar\omega_\alpha}}$

Free energy $F = -k_B T lnZ = NE_0 + Nk_B T\sum_\alpha ln\left(1 - e^{-\beta\hbar\omega_\alpha}\right)$

Einstein's model. One fixed value for $\omega = \omega_E$.   3 modes, x, y, z

$$F = NE_0 + 3Nk_B T ln\left(1 - e^{-\beta\hbar\omega_E}\right)$$

We measure heat capacities

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

Result

$$C_V = 3Nk_B\left(\frac{\hbar\omega_E}{k_B T}\right)^2\frac{e^{-\beta\hbar\omega_E}}{(1 - e^{-\beta\hbar\omega_E})^2}$$

At high T approaches $3Nk_B$. Low T decays exponentially as $e^{-\beta\hbar\omega_E}$. not accurate at low T as the low frequency part of the spectrum should dominate. Solid has wide spectrum of oscillations as recognized by Debye but should have an upper limit.

Debye Model

Low frequency sound modes important. Let s =speed of sound

$\lambda = \frac{s}{f}$ $k = \frac{2\pi}{\lambda} = \frac{\omega}{s}$ But care: two transverse modes and one longitudinal mode with different speeds, s_L and s_T.

Density of states $D(k)dk = \frac{V}{2\pi^2}k^2 dk$ Thus $D(\omega)d\omega = \frac{V}{2\pi^2}\omega^2\left(\frac{1}{s_L^3} + \frac{2}{s_T^3}\right)d\omega$

Take average s_a defined by $\frac{3}{s_a^3} = \frac{1}{s_L^3} + \frac{2}{s_T^3}$

Then take density of states as

$$D(\omega)d\omega = \frac{3V}{2\pi^2 s_a^3}\omega^2 d\omega$$

Helmholtz free energy

$F = NE_0 + \frac{3k_B T}{2\pi^2 {s_a}^3}\int_0^\infty \omega^2 ln\left(1 - e^{-\beta\hbar\omega}\right)d\omega$ Note upper limit only valid at low T

Result

$$F = NE_0 - \frac{\pi^2 (k_B T)^4 V}{30\hbar^3\, {s_a}^3}$$

Entropy $S = -\frac{\partial F}{\partial T} = \frac{2\pi^2 k_B^4 T^3 V}{15\hbar^3\, {s_a}^3}$ at low temperature

Heat capacity

$$C_V = T\frac{\partial S}{\partial T} = \frac{2\pi^2 k_B^4 T^3 V}{5\hbar^3\, {s_a}^3}$$

Agrees with low T behavior

High T Behavior

Debye introduced a cutoff frequency for frequency of vibration, the Debye frequency ω_D

For $\omega < \omega_D$, $D(\omega)d\omega = \frac{3V}{2\pi^2 s_a^3}\omega^2 d\omega$

$\omega > \omega_D$ $D(\omega) = 0$

Can estimate ω_D noting that the total no. of modes is 3N

$$3N = \frac{3V}{2\pi^2 s_a^3}\int_0^{\omega_D} \omega^2\, d\omega = \frac{V\omega_D^2}{2\pi^2 s_a^3}$$

or $\quad \omega_D = \bar{s}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$ F

Gives remarkably good description of heat capacities despite the approximations.

Converted to units on K, Debye constant Θ_D varies from 40 K for elements such as Cs to 647 K for Si.

Free energy in Debye model

$$F = NE_0 + \frac{3k_BTV}{2\pi^2 s_a^3}\int_0^{\omega_D} \omega^2 ln\left(1 - e^{-\frac{\hbar\omega}{k_BT}}\right) d\omega$$

or

$$F = NE_0 + \frac{3k_BTV}{2\pi^2 s_a^3}\left(\frac{k_BT}{\hbar}\right)^3 \int_0^{\omega_D} x^2 ln(1 - e^{-x})\, dx$$

Can use this to calculate thermodynamic properties numerically.

Solid-- vapor equilibrium

N_S solid atoms in equilibrium with N_G atoms.

ONLY sum $N_S + N_G$ is constant $\quad dN_S = -dN_G$

Partition functions (Use Einstein model)

For solid (vibrations) $\quad Z_S = e^{-\beta N_S E_0}\left\{\frac{1}{1-e^{-\beta\hbar\omega_E}}\right\}$

For gas

$$Z_G = \frac{Z_1^{N_G}}{N_G!}$$

Where Z_1 is the single particle gas partition function (de Broglie wavelength)

Total partition function $Z = Z_S Z_G$

Helmholtz free energy

$$F = -k_B T ln(Z_S) - k_B T ln(Z_G)$$

Minimize F with respect to N_G

$$\frac{\partial F}{\partial N_G} = k_B T \frac{\partial}{\partial N_S} ln(Z_S) - k_B T \frac{\partial}{\partial N_G} ln(Z_G) = 0$$

Calculate $\frac{\partial}{\partial N_S} ln(Z_S) = -ln\left[\left(1 - e^{-\beta E_0}\right)^3 e^{-\beta N_S E_0}\right]$

and $\frac{\partial}{\partial N_G} ln(Z_G) = ln \frac{Z_1}{N_G}$

Find $\frac{Z_1}{N_G} = \frac{e^{-\beta E_0}}{\left(1-e^{-\beta E_0}\right)^3}$ and using $PV_G = N_G k_B T$

deduce equilibrium vapor pressure $P = \frac{N_G k_B T Z_1}{V_G} \frac{e^{\beta E_0}}{\left(1-e^{-\beta E_0}\right)^3}$

Can be improved with mire detailed Debye model.

Book Problem

8.1

Ripplons on surface of liquid helium

$$\omega = \left(\frac{\gamma}{\rho}\right)^{\frac{1}{2}} k^{\frac{3}{2}}$$

Find k as function of ω $\hbar\beta\omega = \hbar\beta \left(\frac{\gamma}{\rho}\right)^{\frac{1}{2}} k^{\frac{3}{2}} = z^{\frac{3}{2}}$

$$k = z\left(\frac{\rho}{\gamma}\right)^{\frac{1}{3}}\left(\frac{1}{\hbar\beta}\right)^{\frac{2}{3}}$$

$$kdk = zdz\left(\frac{\rho}{\gamma}\right)^{\frac{2}{3}}\left(\frac{1}{\hbar\beta}\right)^{\frac{4}{3}}$$

New variable

Need 2D density of states $D^2(k)dk = \frac{A}{2\pi}kdk$

Average internal energy

$$\bar{U} = \int D^2(k)dk\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$\bar{U} = k_B T\frac{A}{2\pi}\left(\frac{\rho}{\gamma}\right)^{\frac{2}{3}}\left(\frac{k_B T}{\hbar}\right)^{\frac{4}{3}}\int_0^\infty \frac{z^{5/2}dz}{e^{z^{3/2}} - 1}$$