Problem set 12

(1.) The expression for C_V in question (using the entropy S) is

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

The entropy S can be calculated from the Helmholtz free energy F via

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

and F can be calculated using

$$F = -k_B T \ln Z$$

where Z is the canonical partition function of the whole system.

In the Debye model (in 3D), consisting of N atoms, the "system" refers to $3N$ harmonic oscillator modes

(N longitudinal and $2N$ transverse modes)

The available oscillation frequencies are

$$\omega_n = \frac{\pi C_s}{L} n \qquad \text{where } n = \sqrt{n_x^2 + n_y^2 + n_z^2}, \quad n_{x,y,z} = 1, 2, 3, \ldots$$

except that there is a constraint, that

$$n < n_{max} \qquad \text{(so that the upper limits of } n_x, n_y, n_z \text{ are not } \infty)$$

or the available oscillation frequencies are bounded from above by some maximum frequency ω_{max} :

$$0 < \omega_{\underline{n}} \leq \omega_{max}$$

The value of $n = |\underline{n}|$ correspondng to ω_{max} is defined as n_{max}

$$\omega_{max} = \frac{\pi c_s}{L} n_{max} \quad , \text{ so that } \quad 0 < n \leq n_{max}$$

In addition, we have to take into account that each mode $\vec{n} = (n_x, n_y, n_z)$ $(\underline{n})$ – or each triplet of integers (n_x, n_y, n_z) – has a "spin" or "polarization" <u>multiplicity of 3</u> – 1 longitudinal and 2 transverse modes

<u>3 polarization states for each $\vec{n}$</u>

Before we proceed, need to find ω_{max} (or n_{max}) in terms of the given total number of atoms N.

This is done in $\vec{n} = (n_x, n_y, n_z)$ – space, from the requirement that the sum over all modes

$$\sum_{\text{all modes}} 1 = 3 \sum_{\underline{n}}^{n < n_{max}} 1$$

adds up to the known total number of atoms N times 3 (total of $3N$ linear harmonic oscillator modes for N atoms)

$$3N = 3 \sum_{\underline{n}}^{n < n_{max}} 1 \longrightarrow 3 \, \frac{1}{8} \cdot 4\pi \int_0^{n_{max}} dn \, n^2 = \frac{\pi}{2} n_{max}^3$$

Solving for n_{max}, we find

$$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

and therefore

$$\omega_{max} = \frac{\pi c_s}{L} n_{max} = \frac{\pi c_s}{L}\left(\frac{6N}{\pi}\right)^{1/3}$$

[n_{max} - in terms of the given number of atoms N is needed for calculating the total energy of the system U as

$$U = \underbrace{3\sum_n}_{\text{all modes}} E_n f_p(E_n) = 3\sum_n \hbar\omega_n f_p(\hbar\omega_n)$$

need to know what this upper limit is.

$$\rightarrow 3\cdot\frac{1}{8}4\pi\int_0^{n_{max}} dn\, n^2 \frac{\hbar\omega_n}{e^{\hbar\omega_n/k_BT}-1} = \cdots$$

[see Lecture notes].

Here, we are not calculating U, but instead have to calculate F, from Z, and n_{max} is going to be needed here as well.

The partition function of the total system Z is calculated (using the factorizability property) as a product of partition functions of all individual harmonic ocillator modes (3N modes)

For __one__ mode of an elastic wave (either longitudinal or transverse) at frequency $\omega_{\underline{n}}$, the partition function $Z_{\underline{n}}$ is the same as for a mode of electromagnetic radiation:

$$Z_{\underline{n}} = \sum_{S_{\underline{n}}=0}^{\infty} e^{-E_{S_{\underline{n}}}/k_B T} = \sum_{S_{\underline{n}}=0}^{\infty} e^{-S_{\underline{n}} \hbar \omega_{\underline{n}}/k_B T} =$$

$$= \underbrace{\sum_{S_{\underline{n}}=0}^{\infty} \left(e^{-\hbar\omega_{\underline{n}}/k_B T}\right)^{S_{\underline{n}}}}_{\rightarrow \text{ geometric series}} = \frac{1}{1-e^{-\hbar\omega_{\underline{n}}/k_B T}}$$

where $S_{\underline{n}} = 0, 1, 2, 3, \ldots \infty$ is the number of excitation quanta ("phonons" instead of photons) in the mode.

Since each triplet $\underline{n} = (n_x, n_y, n_z)$ has a multiplicity of 3 – one longitudinal and two transverse modes of the same frequency – the total partition function corresponding to these 3 modes is

$$\left(Z_{\underline{n}}\right)^3$$

– using the factorizability property for 3 independent modes ("systems"):

$$Z_{\underline{n},\text{longitudinal (say } z)} \times Z_{\underline{n},\text{transverse}(x)} \times$$

$$\times Z_{\underline{n},\text{transverse}(y)}$$

The total partition function Z for <u>all</u> available modes (with $0 < \omega_{\underline{n}} < \omega_{max}$) will be given by a product of these $(Z_{\underline{n}})^3$ taken over all triplets of positive integers $\underline{n} = (n_x, n_y, n_y)$ – with the upper limit of $n = |\underline{n}| = n_{max}$

$$Z = \prod_{\underline{n}}^{n<n_{max}} (Z_{\underline{n}})^3$$

$\prod_{\underline{n}}$ means $\prod_{n_x} \prod_{n_y} \prod_{n_z}$

Then

$$F = -k_B T \ln Z = -k_B T \ln \left(\prod_{\underline{n}}^{n<n_{max}} (Z_{\underline{n}})^3 \right)$$

$$= -k_B T \cdot \sum_{\underline{n}}^{n<n_{max}} \ln (Z_{\underline{n}})^3 = -3 k_B T \sum_{\underline{n}}^{n<n_{max}} \ln Z_{\underline{n}}$$

(all triplets with $n = |\underline{n}| < n_{max}$)

$$= -3 k_B T \sum_{\underline{n}}^{n<n_{max}} \ln \frac{1}{1 - e^{-\hbar\omega_{\underline{n}}/k_B T}}$$

$$= 3 k_B T \sum_{\underline{n}}^{n<n_{max}} \ln \left(1 - e^{-\hbar\omega_{\underline{n}}/k_B T}\right)$$

Thus

$$\boxed{F = 3 k_B T \sum_{\underline{n}}^{n<n_{max}} \ln \left(1 - e^{-\hbar\omega_{\underline{n}}/k_B T}\right)}, \quad \omega_{\underline{n}} = \frac{\pi c_s}{L} n$$

$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$ ↳ function of T, N, and L

This general expression can not be simplified further for all temperatures, and has to be calculated numerically.

However, simple analytic results can be obtained in 2 limiting cases: low temperatures,

(a) $T \ll T_D = \dfrac{\hbar\omega_{max}}{k_B}$; and high temperatures

(b) $T \gg T_D = \dfrac{\hbar\omega_{max}}{k_B}$ – (T_D – Debye temperature)

(a). $T \ll T_D = \dfrac{\hbar\omega_{max}}{k_B}$

means

$$x_{max} \equiv \frac{\hbar\omega_{max}}{k_B T} \gg 1$$

In $F = 3k_B T \sum_{\underline{n}}^{n<n_{max}} (\cdots)$

can convert to (approximate by) an integral in spherical coordinates

$$\sum_{\underline{n}}^{n<n_{max}} \longrightarrow \frac{1}{8}\, 4\pi \int_0^{n_{max}} n^2\, dn$$

Then

$$F = 3k_B T \cdot \frac{1}{8} \cdot 4\pi \int_0^{n_{max}} dn\; n^2 \ln\left(1 - e^{-\hbar\omega_{\underline{n}}/k_B T}\right) \qquad \omega_{\underline{n}} = \frac{\pi c_s}{L} n$$

$$= \frac{3k_B T\pi}{2} \cdot \int_0^{n_{max}} dn\; n^2 \ln\left(1 - e^{-\frac{\hbar\pi c_s n}{L k_B T}}\right)$$

introduce (variable change) $x \equiv \dfrac{\hbar\pi c_s n}{L k_B T}$

$$= \frac{3\pi k_B T}{2}\left(\frac{k_B T L}{\hbar\pi c_s}\right)^3 \int_0^{x_{max}} dx\ x^2 \ln\left(1-e^{-x}\right)$$

where $x_{max} = \dfrac{\hbar\pi c_s n_{max}}{L k_B T} = \dfrac{\hbar\omega_{max}}{k_B T} \gg 1$

$\therefore$ the upper limit can be extended to ∞ [the integrand $\to 0$ as $x \to \infty$]

$$\simeq \frac{3\pi k_B T}{2}\left(\frac{k_B T L}{\hbar\pi c_s}\right)^3 \underbrace{\int_0^{\infty} dx\ x^2 \ln\left(1-e^{-x}\right)}_{\text{by parts}}$$

$$= \frac{\cancel{3}\pi k_B T}{2}\left(\frac{k_B T L}{\hbar\pi c_s}\right)^3 \frac{1}{\cancel{3}}\int_0^{\infty} \underbrace{d(x^3)}_{u}\ \underbrace{\ln\left(1-e^{-x}\right)}_{v}$$

$$= \frac{\pi k_B T}{2}\left(\frac{k_B T L}{\hbar\pi c_s}\right)^3 \left\{\left[\cancel{x^3 \ln\left(1-e^{-x}\right)}\Big|_0^{\infty}\right]^{0} - \int_0^{\infty} dx\ x^3 \frac{d}{dx}\left[\ln\left(1-e^{-x}\right)\right]\right\}$$

$$= -\frac{\pi k_B T}{2}\left(\frac{k_B T L}{\hbar\pi c_s}\right)^3 \cdot \int_0^{\infty} dx\ \frac{x^3 e^{-x}}{1-e^{-x}}$$

$$= -\frac{\pi L^3 (k_B T)^4}{2\pi^3\hbar^3 c^3} \cdot \underbrace{\int_0^{\infty} dx\ \frac{x^3}{e^x - 1}}_{=\ \frac{\pi^4}{15}}$$

$$= -\frac{\pi^2 V}{30\hbar^3 c^3}(k_B T)^4$$

Thus, for $T \ll T_D$: $\boxed{F = -\dfrac{\pi^2 V}{30\hbar^3 c^3}(k_B T)^4}$

Then, the entropy S is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4\pi^2 V}{30\hbar^3 c^3} k_B^4 T^3 = \frac{2\pi^2 V}{15\hbar^3 c_s^3} k_B^4 T^3$$

[Can check that $U = F + TS = \frac{\pi^2 V}{10\hbar^3 c_s^3}(k_B T)^4$ –

– same as in lecture notes]

Finally, the heat capacity:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{2\pi^2 V}{\cancel{15}_{\,5}\hbar^3 c_s^3} k_B^4 \cdot \cancel{3} T^2$$

$$= \frac{2\pi^2 V k_B^4}{5\hbar^3 c_s^3} T^3$$ – Debye T^3 law (at low T)

– same as in lecture notes.

(b) High temperature limit

$$T \gg T_D \equiv \frac{\hbar\omega_{max}}{k_B}$$

means $$\frac{\hbar\omega_{max}}{k_B T} \ll 1.$$

Since all $\omega_n < \omega_{max}$, we have

$$\frac{\hbar\omega_n}{k_B T} \ll 1$$ for all mode frequencies

$\therefore$ in

$$F = 3k_BT\sum_{\underline{n}}^{n<n_{max}} \ln\left(1 - e^{-\overbrace{\hbar\omega_n/k_BT}^{\ll 1}}\right)$$

can expand $e^{-\hbar\omega_n/k_BT}$ in Taylor series and keep the lowest order term

$$F \simeq 3k_BT\sum_{\underline{n}}^{n<n_{max}} \ln\left(1 - 1 + \frac{\hbar\omega_n}{k_BT} + \dots\right)$$

$$F = 3k_BT\sum_{\underline{n}}^{n<n_{max}} \ln\frac{\hbar\omega_n}{k_BT}$$

Then

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -3k_B\sum_{\underline{n}}^{n<n_{max}} \ln\frac{\hbar\omega_n}{k_BT} -$$

$$-3k_BT\sum_{\underline{n}}^{n<n_{max}} \frac{\partial}{\partial T}\left(\ln\frac{\hbar\omega_n}{k_BT}\right)$$

$$= -3k_B\sum_{\underline{n}}^{n<n_{max}} \ln\frac{\hbar\omega_n}{k_BT} - 3k_BT\sum_{\underline{n}}^{n<n_{max}} \frac{1}{\frac{\hbar\omega_n}{k_BT}}\cdot\frac{\hbar\omega_n}{k_B}\left(-\frac{1}{T^2}\right)$$

$$= -3k_B\sum_{\underline{n}}^{n<n_{max}} \ln\frac{\hbar\omega_n}{k_BT} + 3k_B\underbrace{\sum_{\underline{n}}^{n<n_{max}} 1}_{=3N}$$

(sum over all modes)

$$\boxed{S = -3k_B\sum_{\underline{n}}^{n<n_{max}} \ln\frac{\hbar\omega_n}{k_BT} + 3k_BN}$$

Finally

$$C_V = T \cdot \left(\frac{\partial S}{\partial T}\right)_V = -3k_B \sum_{\underline{n}}^{n<n_{max}} \frac{\partial}{\partial T}\left[\ln \frac{\hbar\omega_n}{k_B T}\right]_V$$

$$= -3k_B \cdot \sum_{\underline{n}}^{n<n_{max}} \frac{1}{\frac{\hbar\omega_n}{k_B T}} \cdot \frac{\hbar\omega_n}{k_B}\left(-\frac{1}{T^2}\right)$$

$$= k_B \cdot \underbrace{3\sum_{\underline{n}}^{n<n_{max}} 1}_{=3N} = 3N$$

(sum over all modes)

$$\boxed{C_V = 3Nk_B}$$

same as in Lecture notes

↳ at high temperatures;
classical regime;
agrees with equipartition theorem:

3N linear harmonic oscillators, each having <u>two</u> degrees of freedom

$$\left(\tfrac{1}{2}k_B + \tfrac{1}{2}k_B\right) \times 3N = 3Nk_B$$

(2) Debye solid in 2D

All approximations and arguments are the same as in 3D (see lecture notes), except that the total number of independent modes is now $2N$ (for N atoms) and

$$\omega_{max} = \frac{\pi c_s}{L} n_{max} \quad \text{or} \quad n_{max} \text{ is found}$$

from

$$2N = \underbrace{2 \sum_{\underline{n}}^{n<n_{max}} 1}_{\text{sum over all modes}}$$

Where $\underline{n} = (n_x, n_y)$ – pair of positive integers $n_x, n_y = 1, 2, 3 \ldots$ with $n = |\underline{n}| = \sqrt{n_x^2 + n_y^2}$ defining the available frequencies $\omega_n = \frac{\pi c_s}{L} n$ with $0 < \omega_n < \omega_{max}$.

"Spin" or "polarization" multiplicity is now 2: each $\underline{n} = (n_x, n_y)$ comes in 2 "polarizations" (one longitudinal and one transverse mode)

In polar coordinates:

$$2N = 2 \sum_{\underline{n}}^{n<n_{max}} 1 \longrightarrow 2 \cdot \frac{1}{4} \int_0^{2\pi} d\varphi \int_0^{n_{max}} n \, dn =$$

$$= 2 \cdot \frac{1}{4} \cdot 2\pi \int_0^{n_{max}} n \, dn = \frac{\pi n_{max}^2}{2}$$

$$\Rightarrow \quad n_{max} = \sqrt{\frac{4N}{\pi}} \quad \Rightarrow \quad \omega_{max} = \frac{\pi c_s}{L} \left(\frac{4N}{\pi} \right)^{1/2}$$

This gives a Debye temperature of

$$T_D = \frac{\hbar \omega_{max}}{k_B} = \frac{\hbar \pi c_s}{k_B L} \left(\frac{4N}{\pi} \right)^{1/2}$$

Total average energy

$$U = 2 \sum_{\underline{n}}^{n<n_{max}} \underbrace{\langle s_{\underline{n}} \rangle}_{} \hbar \omega_{\underline{n}}$$

↳ Planck distribution $f_P(E_{\underline{n}})$
[thermal average number of phonons in the mode of frequency $\omega_{\underline{n}}$, energy $E_{\underline{n}} = \hbar\omega_{\underline{n}}$.]

$\underline{n} = (n_x, n_y)$

$$= 2 \sum_{\underline{n}}^{n<n_{max}} \frac{\hbar \omega_{\underline{n}}}{e^{\hbar\omega_{\underline{n}}/k_B T} - 1} \qquad \left[\omega_{\underline{n}} = \frac{\pi c}{L} n\right]$$

(a) Low T limit : $T \ll T_D \equiv \frac{\hbar \omega_{max}}{k_B}$

Transform $\sum_{\underline{n}} (\cdots) \longrightarrow \frac{1}{4} 2\pi \int_0^{n_{max}} n \, dn \, (\cdots)$

$$U = 2 \cdot \frac{1}{4} \cdot 2\pi \int_0 dn \cdot n \cdot \frac{\hbar \omega_n}{e^{\hbar\omega_n/k_B T} - 1}$$

[2π comes from $\int_0^{2\pi} d\varphi = 2\pi$]

$$= \pi \int_0^{n_{max}} dn \cdot n \, \frac{\frac{\hbar \pi c_s}{L} n}{e^{\frac{\hbar \pi c_s n}{L k_B T}} - 1}$$

def $\quad x \equiv \dfrac{\hbar \pi c_s n}{L k_B T}$

$$= \pi \cdot (k_B T) \left(\frac{L k_B T}{\hbar \pi c_s}\right)^2 \cdot \int_0^{x_{max}} dx \, \frac{x^2}{e^x - 1}$$

where $x_{max} = \frac{\hbar \pi c_s}{L k_B T} n_{max} = \frac{\hbar \omega_{max}}{k_B T} \gg 1$

The integrand $\frac{x^2}{e^x - 1} \ll 1$ at $x \sim x_{max}$

$$\Rightarrow \quad \int_0^{x_D} dx \, (\cdots) \simeq \int_0^{\infty} dx \, (\cdots)$$

$$\simeq \pi (k_B T) \left(\frac{L k_B T}{\hbar \pi c_s}\right)^2 \underbrace{\int_0^{\infty} dx \, \frac{x^2}{e^x - 1}}_{\simeq 2.404}$$

$$\simeq \frac{2.404 \, \pi \, L^2 (k_B T)^3}{\pi \, \hbar^2 c_s^2}$$

def. $L^2 \equiv A$ area

$$\boxed{U = \frac{2.404 \cdot A}{\pi \hbar^2 c_s^2} (k_B T)^3} \quad , \text{ at } T \ll T_D$$

$$C_A = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3 \times 2.404 \cdot A}{\pi \hbar^2 c_s^2} k_B^3 T^2$$

$\hookrightarrow$ $A = L^2$ is the area (instead of C_V, with V-volume in 3D)

$\boxed{C_A \propto T^2}$ in 2D at low T ($\propto T^3$ in 3D)

(b) high temperature limit:

$$T \gg T_D = \frac{\hbar \omega_{max}}{k_B}$$

$\therefore$ $\frac{\hbar \omega_{max}}{k_B T} \ll 1$ and since

$\omega_{\underline{n}} < \omega_{max} \implies \frac{\hbar \omega_{\underline{n}}}{k_B T} \ll 1$ for all modes

Then, from

$$U = 2 \sum_{\underline{n}}^{n < n_{max}} \frac{\hbar \omega_{\underline{n}}}{\underbrace{e^{\hbar \omega_n / k_B T}}_{\text{expand in Taylor series and keep the lowest order term}} - 1}$$

$$\simeq 2 \sum_{\underline{n}}^{n < n_{max}} \frac{\hbar \omega_n}{\cancel{1} + \frac{\hbar \omega_n}{k_B T} + \cdots \cancel{-1}} =$$

$$= 2 k_B T \sum_{\underline{n}}^{n < n_{max}} 1 = k_B T \cdot 2N$$

sum over all modes

$$\implies \boxed{U = 2N k_B T}$$

(agrees with equipartition theorem: 2N linear harmonic oscillators, each having 2 degrees of freedom, and contributing $\frac{1}{2} k_B T + \frac{1}{2} k_B T$ energy, so the total is $2N \cdot k_B T$

$$\implies \boxed{C_A = \left(\frac{\partial U}{\partial T}\right)_A = 2N k_B}$$

3. Debye solid in 1D (reading quiz question)

In 1D, the total number of modes is N

$$\left[N = \sum_{n=1}^{n_{max}} 1 = n_{max} \right]$$

$$\omega_{max} = \frac{\pi c_s}{L} n_{max} = \frac{\pi c_s}{L} N$$

Debye temperature

$$T_D = \frac{\hbar \omega_{max}}{k_B} = \frac{\hbar \pi c_s}{k_B L} N$$

For $N = 3.5 \times 10^8$ and $L = 10$ cm, and $c_s = 5000$ m/s

$$T_D = \text{sub in} = 418 \text{ K}$$