Phonons as excitations

THE PROBLEM OF QUANTUM MELTING

Second quantization:

Recall from quantum mechanics:

\[ [x, p] = xp - px = i\hbar \]

Based on this, let's introduce 2 operators, which create and annihilate an excitation when applied to the ground state or vacuum.

\[
\begin{align*}
    b &= \frac{1}{\sqrt{2\hbar m \omega}} (M \omega x + i p) \\
    b^+ &= \frac{1}{\sqrt{2\hbar m \omega}} (M \omega x - i p)
\end{align*}
\]

Let's verify that anticommutator is

\[ [b, b^+] = 1 \]
\[ [bb^+] = \frac{1}{2\hbar m \omega} \left( (M \omega^2) [xx] + i M \omega [px] - i M \omega [xp] + [pp] \right) = \frac{1}{2\hbar} i M \omega [px] = \frac{1}{2\hbar} \left( -2i [xp] \right) = -\frac{i}{\hbar} \]

Inversely we can express \( x \) and \( p \) as

\[ x = \sqrt{\frac{\hbar}{2M \omega}} (b^+ + b) \quad p = i \sqrt{2\hbar M \omega} (b^+ - b) \]

Recall these \( x \), \( p \) are operators here!

Just a different representation.

For the harmonic oscillator:

\[ H = \frac{p^2}{2M} + \frac{\beta}{2} x^2 = \frac{\hbar^2}{2M} \omega (b^+ b)^2 + \frac{\beta \hbar}{2M} (b^+ b)^2 = -\frac{\hbar}{\omega} (b^+ b)^2 + \frac{\beta \hbar}{2M \omega} (b^+ b)^2 \]

\[ \Rightarrow \lambda = \omega \sqrt{b} \]
\[ H = \frac{1}{2} \hbar \omega \left( b b^+ + b^+ b \right) = \hbar \omega \]

\[ = \hbar \omega b^+ b + \frac{1}{2} \hbar \omega = \frac{1}{2} \hbar \omega (n + \frac{1}{2}) \]

where \( n = b^+ b \) is the occupation number (the number of excitations in the particle ground state).

For the states with excitations present:

\[ b | n > = \sqrt{n} | n - 1 > \]

\[ b^+ | n > = \sqrt{n+1} | n+1 > \]

the amplitude grows as \( \sqrt{n+1} \).

\[ b^- \text{ annihilation} \]

\[ b^+ \text{ creation operators} \]

They increase (decrease) the # of bosons by \( +(-1) \).

For \( n = b^+ b \) \( \Rightarrow \)

\[ b^+ b | n > = b^+ b | n > = \sqrt{n} \cdot \sqrt{n} | n - 1 > \]

\[ = \sqrt{n} \cdot \sqrt{n} | n > = n | n > \]

For the ground state \( b^0 > = 0 \)

\[ 1 | 0 > = \frac{1}{\sqrt{n!}} (b^+) \cdot | 0 > \]

Now we are ready for something interesting.

Quantum Melting.
Recall that vibration amplitude
\[ U = 5x = \sqrt{\frac{k}{2M\omega}} (b^+ + b) \text{ for 1 phonon mode} \]

The average shift from eq. is \( U^2 = 0 \)

but for:
\[ \langle U^2 \rangle = \frac{\hbar}{2M\omega} \left( \langle b^+ b + b b^+ \rangle - \hbar b^+ b + b b^+ \right) \]

\[ \langle b^+ b + b b^+ \rangle = \frac{\hbar}{2M\omega} (2 \langle b^+ b \rangle + 1) = \frac{\hbar}{2M\omega} (n + \frac{1}{2}) \]

and for the highest energy phonons
\[ \omega = \omega_0 \quad \theta_0 = \frac{\hbar}{4M\omega_0} \]

\[ \langle U^2 \rangle = \frac{\hbar^2}{2M\omega_0} (n + \frac{1}{2}) \]

So for
\[ T \to 0 \quad \langle U^2 \rangle \sim \frac{\hbar^2}{2M\omega_0} \text{ (zero point oscillations)} \]

\[ T \gg \theta_0 \quad \langle U^2 \rangle \sim \frac{\hbar^2}{8M\theta_0^2} \]

According to the Lindemann criterion

when \( \langle U^2 \rangle \sim a \)

m elting occurs,

(\text{precisely} \ \langle U^2 \rangle \sim 0.2a)\)

so one can introduce the melting parameter
\[ \Lambda = \frac{\langle U^2 \rangle}{a} < \text{De Boer parameter} \]

at \( T = 0 \)

\[ \langle U^2 \rangle \sim \frac{\hbar^2}{4M\omega} \text{ where } \omega = \sqrt{\frac{E_{\text{bulk}}}{M}} \]

the stiffness of the lattice
If we shift an atom from the equilibrium by a there will be a change in the potential energy of a pair \( w \sim V(a) \) 

\[ w \sim \frac{V(a)}{a^2} \Rightarrow \lambda \in \frac{\hbar}{a} \sqrt{\frac{m e^2}{\hbar}} \sim \frac{1}{\sqrt{a}} \]

and if \( \lambda > 0.2 - 0.3 \) the system is unstable against the zero point motion and the crystal "melts"!!!

Q: Does it really happen? We need small \( \lambda \) and weak \( V(a) \)

That's why He is liquid down to \( 200 \) K.

What do you think about \( H \) (hydrogen)?

Another way to encourage quantum melting is to apply pressure \( P \)

but of course \( \lambda^2 \) but \( V(a) \) goes up and then \( \lambda = V(a)/a^2 \) may change either way. For He \( V(a) \) goes up quickly and it becomes solid. For electronic liquid it is opposite:

\[ V(a) = \frac{e^2}{a} \text{ and } \lambda = \frac{\hbar}{a} \sqrt{\frac{m e^2}{\hbar}} \sim \frac{1}{\sqrt{a}} \]

so as \( P \uparrow a \downarrow \lambda \uparrow \Rightarrow \text{cold melting of an electronic crystal (Wigner)} \)
\[ P \]

\[ \text{He I} \]

\[ \text{Solid} \quad \text{Liquid} \quad \text{supersolid} \quad \text{He II} \]

\[ T_c \quad T \]

\[ \text{Wigner xtal} \]

\[ T \]

\[ \text{Metal (electronic liquid)} \]

\[ \text{(Wigner)} \quad \text{electronic solid} \]

\[ P \]

\[ \text{LIS} \]
PHYSICAL QUANTITIES IN SEMICLASSICAL MODEL

[Phonons]: The 1st force: collective excitations

Consider a chain of identical atoms
\[ x \rightarrow \text{motion along the chain} \]

Define the position of atoms as:
\[ x_n \text{ in the equilibrium } x_n^{eq} = \text{a} \]

If we allow the motion of the atoms:
\[ \delta x_n = x_n - x_n^{eq} \]

Note since it's 1D we allow only longitudinal

Let us also assume the potential is quadratic:

Now it's getting strange. We technically describe the motion of balls, connected with springs!

\[ V_{total} = \sum_j V(x_j - x_j') = \sum_j \frac{1}{2} k (x_j - x_j')^2 \]

\[ = \frac{1}{2} k \sum_j (\delta x_{j+1} - \delta x_j) \]

The force on the mass \( n \) is

\[ F_n = -\frac{dV_{total}}{dx_n} = -\frac{\partial}{\partial x_n} \left( \frac{k}{2} (x_{n+1} - x_n - a)^2 \right) = \]

\[ \delta x_n = x_n - x_n^{eq} \]

\[ = k (\delta x_{n+1} - \delta x_n) + k (\delta x_n - \delta x_n) = m \delta \ddot{x}_n \]

Newtonian Law.

Recap: A normal mode is a collective oscillation where all particles move at the same frequency.
Let's attempt to solve it by assuming that we have a wave propagating through the chain
\[ \Delta x_n = A e^{i\omega t - ikx_n} = Ae^{i\omega t - ikx_n} \]

\( A \) is the amplitude of the wave,
\[ \omega^2 A e^{i\omega t - ikx_n} = \alpha A e^{i\omega t - ikx_{n+1}} + e^{-(k\alpha x - i) - 2i\omega t} \]

\[ m\omega^2 = 2\kappa \left[ 1 - \cos(k\alpha) \right] = 4\kappa \sin^2(k\alpha/2) \]

or
\[ \omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin \left( \frac{k\alpha}{2} \right) \right| \]

Not too surprising again b/c of the periodicity of the crystal we end up with the same physics.
\[ \beta \cdot x = 1 \quad \text{where} \quad \beta = \frac{2\pi}{a}. \]

Again the same issue as for electrons

\( k \) is defined up to \( k + 2\pi \nabla \)

But what \( k \) we should use say is

\[ \frac{\omega}{k} = ? = \frac{\omega}{k+\epsilon} ? \]

or do we say \( \frac{2\pi}{\alpha} \) or \( \frac{2\pi}{k+\epsilon} ? \)
The resolution to this puzzle comes from the fact that:

We can define the wave only at the lattice points $x_n$.

So $k + \frac{2\pi}{a} n$ and $k$ are the same.

This is also known as aliasing of waves.

Properties of 1D chains.

Sound wave: always has $\lambda$ much larger than $a$ (e.g. $\text{harn} = 10^{-3}$ m).

Large $\lambda$, small $k$ so the dispersion $w = \frac{\omega}{\text{sound}} k$.

$$w = 2 \sqrt{\frac{k}{m}} / \sin \left(\frac{ka}{2}\right) \approx 2 \sqrt{\frac{k}{m}} \cdot \frac{ka}{ka}$$

$$\text{sound} = \frac{\omega}{k} \approx \sqrt{\frac{k}{m}}.$$}

Large $\lambda$, short $k$: We define the group velocity:

$$v_{\text{group}} = \frac{dw}{dk},$$

$$v_{\text{phase}} = \frac{\omega}{k}.$$

How individual maxima and minima move.

If the dispersion is linear $v_{\text{group}} = v_{\text{phase}}$.

Non-linear they are different.

Note at $2\pi/a$: $v_{\text{group}} = 0$! the dispersion is flat.
Two atoms per unit cell. - Phonon modes.

Let's for simplicity assume that \( m_1 = m_2 \). We are about to repeat the same algebra as for the 1D chain with 1-type of atoms where we found that the system will have the energy dispersion \( \omega(k) = \sqrt{\frac{k^2}{2m} + \frac{\hbar^2}{2m} k'^2} \).

\[
\begin{align*}
\int m \delta x_n &= k_2 (\delta y_n - \delta x_n) + k_1 (\delta y_{n-1} - \delta x_n) \\
\int m \delta y_n &= k_1 (\delta x_{n+1} - \delta y_n) + k_2 (\delta x_n - \delta y_n)
\end{align*}
\]

Again we will be looking for a solution of this kind:

\[
\begin{align*}
\delta x_n &= A_x e^{i \omega t - i k x}, \\
\delta y_n &= A_y e^{i \omega t - i k x}
\end{align*}
\]

We focus our attention on the 1st BZ, \(-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}\), with \( N \) unit cells \( L = N a \). \( k \) will be quantized:

\[
k = \frac{2 \pi}{N a} = \frac{2 \pi}{L}
\]

Here we mean \( N \) the number of U.C. Not the number of atoms.
If we decide the range of \( k \) values in the 1st BZ \( \frac{2\pi}{a} \) by the spacing between neighboring \( k \)'s \( \frac{2\pi}{N_2} \), we obtain \( N \) possible values of \( k \) or 1 value of \( k \) per unit cell. But Debye states that there is only one more normal mode per degree of freedom and here we have 2 atoms but seemingly one mode!

What to do? Let's go ahead and solve the equations:

\[
\begin{align*}
-w^2 m A_x e^{-i\omega t} - i\kappa A_x &= -k_1 A_y e^{-i\omega t} - i\kappa A_x - (k_1 + k_2) A_x e^{-i\omega t} - i\kappa A_x \\
-w^2 m A_y e^{-i\omega t} - i\kappa A_y &= -k_2 A_y e^{-i\omega t} + k_1 A_y e^{-i\omega t} - (k_1 + k_2) A_y e^{-i\omega t} - i\kappa A_y \\
-w^2 m A_x &= k_2 A_y + k_1 A_y e^{i\kappa a} - (k_1 + k_2) A_x \\
-w^2 m A_y &= k_1 A_x e^{-i\kappa a} + k_2 A_x - (k_1 + k_2) A_y
\end{align*}
\]

or

\[
\begin{align*}
mw^2 (A_x) &= (k_1 + k_2) - k_1 - i\kappa (k_1 + k_2) (A_x) \\
mw^2 (A_y) &= k_2 - i\kappa (k_1 + k_2) (A_y)
\end{align*}
\]
The solution is:

\[ 0 = \begin{vmatrix} \left(k_1 + k_2\right) - m \omega^2 & -k_2 - k_1 e^{i \kappa a} \\ -k_2 - k_1 e^{-i \kappa a} & \left(k_1 + k_2\right) + m \omega^2 \end{vmatrix} = 0 \]

\[ m \omega^2 = \left(k_1 + k_2\right) \pm \sqrt{k_1 + k_2} e^{i \kappa a} \]

\[ |k_1 + k_2 e^{i \kappa a}| = \sqrt{(k_1 + k_2 e^{i \kappa a}) (k_1 + k_2 - e^{-i \kappa a})} = \]

\[ = \sqrt{k_1^2 + k_2^2 + 2k_1 k_2 \cos k_2 a} \]

So finally

\[ \omega_k^\pm = \sqrt{\frac{k_1 + k_2}{m} \pm \frac{1}{m} \sqrt{k_1^2 + k_2^2 + 2k_1 k_2 \cos k_2 a}} \]

\[ = \sqrt{\frac{k_1 k_2}{m} \pm \frac{1}{m} \sqrt{(k_1 + k_2)^2 - 4 k_1 k_2 \sin^2 \left(\frac{k_2 a}{2}\right)}} \]

For each \( k \) we have 2 solutions \( \pm \), or 2 branches of the dispersion.

Since there are 2 branches, or we have \( 2N \) modes. Exactly as Debye predicted one excitation mode per degree of freedom.
Long wavelength show linear dispersion

\[ \omega_{-}(k) \]

Def: any mode which \( \omega = \omega_{0} \) for \( k \to 0 \)
is called acoustical

and if we assume \( \sin \frac{k \alpha}{2} \sim \frac{k \alpha}{2} \) and \( \sqrt{1 + \frac{k^{2}}{k^{2}}} \)

we get \( \omega_{-} = \sqrt{\frac{k_{1} + k_{2}}{2m}} \phi - \frac{1}{2} \sqrt{(k_{1} + k_{2})^{2} - \frac{k_{2} k_{2}}{4}} \)

\[ \omega_{\text{sound}} = \frac{d \omega_{-}}{dk} = \sqrt{\frac{a^{2} k_{1} k_{2}}{2m (k_{1} - k_{2})}} \]

The high energy branch is more interesting:

for \( k = 0 \) \( \omega_{+} = \sqrt{\frac{2(k_{1} + k_{2})}{m}} \)

and

\[ \omega_{\text{group}} = \frac{d \omega_{+}}{dk} = 0 \text{ at } k = 0 \]

This branch is called optical.

Here is why.

during the light absorption energy and momentum must be conserved, i.e.

\( \omega = \omega_{0} \) so as is very large but phonons have \( k \to \frac{\omega}{c} \) as maximum and cannot absorb the photon with anything rather than this small value.

But for \( \omega_{+} \), even for \( k \to 0 \) \( \omega_{+} \) is finite and can match \( \omega = \omega_{0} \).

So whenever light and phonons interact we involve optical phonons.
Let's look a little more carefully at the optical and acoustic modes for $k \to 0$

$$\begin{pmatrix} \frac{\omega^2}{m} A_x \\ \frac{\omega^2}{m} A_y \end{pmatrix} = \begin{pmatrix} k_1 + k_2 & -k_2 - k_1 \\ -k_2 - k_1 & k_1 k_2 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

or

$$\begin{pmatrix} \frac{\omega^2}{m} A_x \\ \frac{\omega^2}{m} A_y \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \cdot \frac{k_1 + k_2}{m}$$

for the acoustic mode $\omega = 0$ at $k = 0$

$$\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} = 0 \Rightarrow \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} \cdot \\ \cdot \end{pmatrix}$$

masses at position $x$ and $y$ move together.

In short, the atoms within the unit cell always move together.

For optical branch $k = 0$, $\omega^2(k = 0) = \frac{2(k_1 + k_2)}{m}$

$$\begin{pmatrix} \frac{\omega^2}{2} A_x \\ \frac{\omega^2}{2} A_y \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \cdot \frac{k_1 + k_2}{m} \Rightarrow$$

$$\begin{pmatrix} A_y \\ A_x \end{pmatrix} = \begin{pmatrix} \cdot \\ \cdot \end{pmatrix}$$

describes two modes moving in opposite directions within the unit cell.
Now let's study our nodes close to the zone boundary $\pm \frac{\pi}{a}$.

\[
\begin{align*}
\omega^+ &= \sqrt{\frac{2E}{m}} \\
\omega^- &= \sqrt{\frac{2E}{m}}
\end{align*}
\]

\(\omega^+ \neq \omega^- \) at the Z.B.

when the phonon \( k \) approaches the Z.B., the plane wave turns into a standing wave with anti-phase motion.
For $\hbar = 0$ we get $\beta \hbar (\omega n) / 2$
The lowest energy of excitation for $\beta \hbar (\omega n) \rightarrow n = 1$

For a given $k$

Phonons are discrete quantum of vibration
(photons is a quantum of light)

All known excitations are bosons except for exotics like spinons, monopoles, etc.

Temperature shakes atoms and the phonons can occupy higher and higher energy states.

Based on the Bose statistics:

$$n_B (\beta \hbar \omega) = \frac{1}{e^{\beta \hbar \omega} - 1}, \quad \beta = \frac{1}{k_B T}$$

Thus the energy expectation:

$$E_k = \hbar \omega (n_B + \frac{1}{2})$$ for finite $T$

From this we can calculate many thermodynamical quantities, including say the heat capacity:

$$U_{\text{total}} = \sum_k \hbar \omega (n_B + \frac{1}{2})$$ sum over all normal modes

$$k = \frac{2 \pi n}{N}, \quad \text{for} \quad -\frac{\pi}{a} < k < \frac{\pi}{a}$$

As we did for electrons:

$$\frac{5}{2} \rightarrow \frac{N a}{2 \pi} \int_{-\pi/a}^{\pi/a} du$$

Note the total number of modes is

$$\frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk = N$$
Now let's calculate the total internal energy $U_{\text{total}}$ due to phonons. For a dielectric (with Debye model), we have:

$$U_{\text{total}} = \frac{N_a}{2\pi} \int_{-\Pi/a}^{\Pi/a} \frac{d\omega}{\omega} \left[ \frac{3}{2} \alpha_0 \omega \right]$$

Recall the difference between Debye and what we got in our case. This is what we introduced for Debye case, but in our case, it's just $\omega = \frac{c}{V_{\text{el}}} \sin(kx)$. In fact, what we did was move the Debye term to the left hand side, and what we got in our case for Debye model is even simpler, but since what we did was just move the Debye term to the left hand side, it doesn't affect the final result.
We state without proof that bosons should obey Bose-Einstein statistics, i.e.

\[ n = \frac{1}{e^\frac{\hbar\omega}{k_BT} - 1} \]

and if consider the thermal vibrations of the frequency \( \omega \) (or \( E = \hbar\omega \))

\[ n(\omega, T) = \frac{1}{e^\frac{\hbar\omega}{k_BT} - 1} \]

for high temperatures \( k_BT > \frac{1}{2} \hbar \omega \)

\[ \frac{1}{2} + h = \frac{1}{2} + \frac{1}{e^{\frac{\beta E}{k_BT} - 1}} = \frac{e^{\frac{\beta E}{k_BT}} + 1}{2(e^{\frac{\beta E}{k_BT}} - 1)} \]

\[ \approx \frac{1}{\beta E} = \frac{k_BT}{\hbar \omega} \quad \Rightarrow \text{for high } T \text{ we have} \]

\[ E = \hbar \omega \left( \frac{1}{2} + h(\omega, T) \right) = \hbar \omega \left( \frac{1}{2} + \frac{k_BT}{\hbar \omega} \right) = \frac{\hbar \omega}{2} + \frac{k_BT}{\hbar} \quad \text{(This is for 1D)} \]

for motion

\[ E = \sum \ldots = 3k_BT \quad \text{which is equivalent to the internal energy of a gas.} \]
Heat capacity:

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V = 2 \hbar \frac{2 \hbar}{2T} = \sum k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{-\frac{\hbar \omega}{k_B T}}}{(e^{-\frac{\hbar \omega}{k_B T}} - 1)^2} \]

For the high-T limit \( C_V = 3R \) (J/K)

\[ = \text{Dulong-Petit} \]

What classical stat. phys. cannot explain why the heat capacity \( \to 0 \) \( T \to 0 \)?

\[ C_V \text{ Al}_2\text{SiO}_5 = 2k_B \text{ J/K}^- \text{ per mole (eqs, 8 atoms \text{ per cell})} \]

Density of states for phonons

\[ \text{g}(\omega) \text{ the number of vibration modes between } \omega \text{ and } \omega + d\omega \Rightarrow g(\omega) \, d\omega \]

\[ U = \int \left( \frac{\hbar}{2} \omega \text{g}(\omega) \right) \, d\omega \]

\[ C_V = \int \frac{d\omega}{2 \pi} \, \hbar \omega \text{g}(\omega) \, d\omega \]

Now let's apply the idea of DOS to acoustic phonons:

To determine \( g(\omega) \) we note

\[ g(\omega) \, d\omega = g_{\text{mode}} \, d\omega \]

In the \( \text{BZ} \) with \( N \) unit cells, the volume per cell \( V \)

\[ \frac{V}{N} \text{ and the volume of } BZ = \frac{2\pi^3 N}{V} \]

So in the 1st BZ there will be \( N \) available values of the \( k \)-vector, and hence for the number of \( k \)-values per unit volume of the reciprocal space:

\[ \frac{N}{V_{BZ}} \approx \frac{2\pi^3 N}{V} \]
**THERMODYNAMICS**

Or, in spherical coordinates:

\[
g(\omega) \, d\omega = \frac{V}{(2\pi)^2} \cdot \frac{1}{\pi} \frac{1}{\omega^2} \, d\omega = \frac{V}{(2\pi)^2} \cdot \frac{1}{\omega^2} \, d\omega
\]

This comes from the fact that there are 3 branches of acoustic waves for 3D, so \( g(\omega) \sim \omega^2 \)

**HEAT CAPACITY**

The total energy due to phonons:

\[
E = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 a} \cdot \frac{1}{\omega} \cdot \frac{1}{\hbar \omega/k_B T - 1} \, d\omega
\]

where \( \omega_D \) is called the Debye frequency, a cut-off parameter.

\[
\Rightarrow \frac{dE}{dT} = CV = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 a} \cdot \frac{1}{\hbar \omega/k_B T} \cdot \frac{d\omega}{dT}
\]

1. **Low T limit:** At low T only low \( \omega \) phonons exist since \( g(\omega, T) \rightarrow 0 \) as \( T \rightarrow 0 \).

Also, those \( \omega < \omega_D \) so \( \omega_D \) looks like \( \omega \).

Substituting \( x = \frac{\hbar \omega}{k_B T} \)

\[
E = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 a} \cdot \frac{1}{\hbar \omega/k_B T} \cdot \frac{d\omega}{dT}
\]

\[
E = \frac{3V\pi^2 (k_B T)^4}{10 (\hbar v_F a)^3} \int_0^{\omega_D} x^3 (e^x - 1)^{-1} \, dx
\]

\[
E = \frac{\pi^3}{15} \Rightarrow \frac{dE}{dT} = CV = \frac{dE}{dT}
\]

Or \( CV = \frac{2V\pi^2 k_B T}{(\hbar v_F a k_B)^3} \cdot T^3 \) if we introduce the Debye temperature

\[
\Theta_D = \frac{\hbar \omega_D}{k_B} \Rightarrow \Theta_D = \frac{h v_F a}{k_B} \left( \frac{16 \pi N^2}{\nu} \right)^{1/2} (\text{not shown here and A.M.)}
\]