Engineering Physics (2025)
Course code 25PY101
Module 2 Unit 1: Quantum theories of solids

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Unit 2 Plan

1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram

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Specific heat capacity

Definition

- Specific heat capacity [a] C is defined as the rate of change of energy E with temperature T per unit mole of material.

$$C = \frac{\mathrm{d}E}{\mathrm{d}T} \qquad \text{SI unit} \quad [C] = \left[\frac{E}{T} \cdot \frac{1}{\text{mole}}\right] = \mathrm{J\,K^{-1}\,mol^{-1}}.$$

[a] It is also called simply as specific heat.

- Metals heat "quickly". When we heat a metal, the heat energy is transferred to electrons. The quickness is measured in terms of heat capacity.

Problem

Specific heat of mercury is $0.14\,\mathrm{J\,g^{-1}\,K^{-1}}$, *water is* $1\,\mathrm{cal\,g^{-1}\,{}^\circ C^{-1}}$, *ethanol is* $2.44\,\mathrm{J\,g^{-1}\,{}^\circ C^{-1}}$. *Which has more specific heat? Which better material for thermometer?* [$^{200}_{80}Hg$, $1\,\mathrm{cal}=4.2\,\mathrm{J}$, *ethanol* $= CH_3CH_2OH$]

Specific heat capacity – CFET

- Energy of electron at temperature T is $E_{\mathrm{el}} = \frac{3}{2} k_B T$.
- Energy of a mole of electrons is

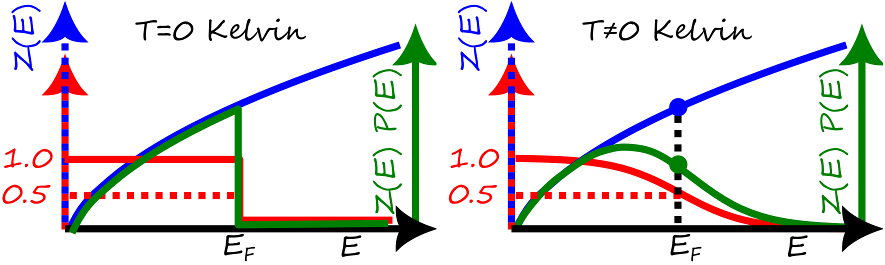
$$E = E_{\mathrm{el}} N_A = \frac{3}{2} k_B N_A T = \frac{3}{2} RT. \qquad \left[R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}\right]$$

- Therefore, specific heat capacity is

$$C^{\text{classical}}_{\mathrm{theory}} = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{3}{2} R \sim 12\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

- But experimental values of specific heat capacity $C_{\text{experiment}}$ are **smaller by two orders** of magnitude.

Specific heat capacity – QFET



- For the derivation of specific heat capacity, only the **form** of density of states functions is necessary and not the exact expression. For 3D metal, $Z(E) \propto \sqrt{E}$ so that

$$Z(E) = \alpha\sqrt{E}, \qquad \text{where } \alpha \text{ is a constant}$$

Specific heat capacity – Form of $Z(E)$

- At $T = 0\,\text{K}$, electron has energy less than or equal to Fermi energy level.
- The number of electrons per unit volume n_c at $T = 0\,\text{K}$ is given by

$$
\begin{aligned}
n_c &= \int_0^{E_F} Z(E)P(E)\,\mathrm{d}E \\
&= \int_0^{E_F} Z(E)\,\mathrm{d}E \\
&= \int_0^{E_F} \alpha\sqrt{E}\,\mathrm{d}E \\
&= \frac{2}{3}\alpha E_F^{3/2}
\end{aligned}
$$

$$
\boxed{\therefore\ n_c = \tfrac{2}{3}\alpha E_F^{3/2}.}
$$

Specific heat capacity – Conduction electron density n_c

- At $T \neq 0\,\mathrm{K}$, due to thermalization, some of the electrons vacate the lower energy levels and occupy the higher energy levels.
- The number of electrons per unit volume n_c at $T \neq 0\,\mathrm{K}$ is given by

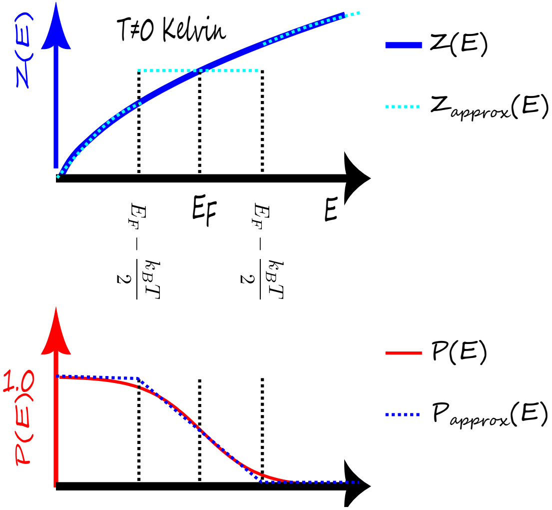
$$\begin{aligned} n_c &= \int_0^\infty Z(E)P(E)\,\mathrm{d}E \\ &= \int_0^\infty \frac{\alpha\sqrt{E}}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}\,\mathrm{d}E \end{aligned}$$

  Note that integration limits are 0 to ∞!
- We observe that because of the strong variation of Fermi Dirac distribution only near the Fermi level, the electron with energy belonging to range $E_F - \frac{k_B T}{2}$ to E_F jumps to energy in the range E_F to $E_F + \frac{k_B T}{2}$. Let us use this to **approximate** the integral.

Key Insight

Electrons with energy very much less than Fermi energy level do not participate in the thermalization process.

Specific heat capacity – Approximations to $Z(E), P(E)$

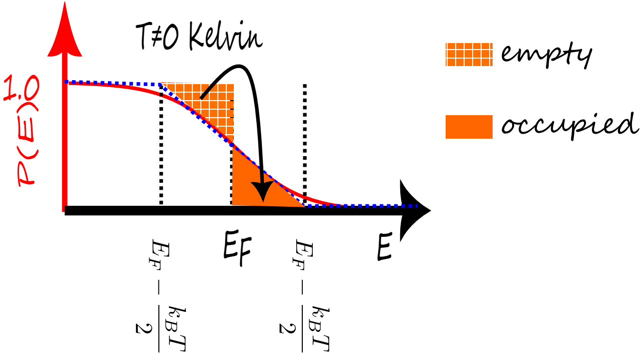


- Let us approximate the density of states in the neighbourhood of E_F as

$$Z(E) \simeq Z(E_F)$$

- Let us approximate probability distribution as piece-wise straight line function.

Specific heat capacity – Fraction of thermalized electrons



- The number of thermalized electrons is equal to area of the filled triangle multiplied by the density of states in the neighbourhood.
- Area of the filled triangle is

$$A = \frac{1}{2}\frac{k_B T}{2}\frac{1}{2} = \frac{1}{8}k_B T$$

$$\therefore n_{\text{thermal}} = \frac{1}{8}k_B T \cdot Z(E_F) = \frac{1}{8}\alpha k_B T\sqrt{E}$$

Specific heat capacity – Fraction of thermalized electrons

- The fraction of thermalized electrons is given by ratio of thermalized electrons to total electrons

$$
\begin{aligned}
f_{\text{thermalized}} &= \frac{n_{\text{thermal}}}{n_c} \\
&= \frac{1}{8} k_B T \frac{\alpha\sqrt{E}}{\frac{2}{3}\alpha E_F^{3/2}} \\
&= \frac{3}{16} \frac{k_B T}{E_F}
\end{aligned}
$$

Problem

The Fermi level of silver is 5.5 eV. *Calculate the fraction of free electrons at room temperature.*

Key Insight

The fraction of thermalized electrons is of the order of $\frac{k_B T}{E_F}$.

Specific heat capacity – Energy of thermalized electron

- The net increase in energy of thermalized electron is

$$\Delta E_{\text{thermalized}} = E_F + \frac{k_B T}{2} - \left(E_F - \frac{k_B T}{2} \right) = k_B T$$

- Since only a fraction of the electrons are thermalized, the net increase in energy of 1 electron is

$$\begin{aligned} \Delta E_{1\text{ el}} &= \Delta E_{\text{thermalized}} \cdot f_{\text{thermalized}} \\ &= \frac{3}{16} k_B T \cdot \frac{k_B T}{E_F} \end{aligned}$$

- Therefore, the net increase in energy of 1 mole of electrons is

$$\begin{aligned} \Delta E_{1\text{ mole}} &= \Delta E_{1\text{ el}} \cdot N_A \\ &= \frac{3}{16} (k_B N_A) T \cdot \frac{k_B T}{E_F} \\ &= \frac{3}{16} R \frac{k_B T^2}{E_F} \end{aligned}$$

Specific heat capacity – Electronic contribution

- The specific heat capacity is given by

$$\begin{aligned} C_{\text{theory}}^{\text{quantum}} &= \frac{\mathrm{d}E_{1\ \text{el}}}{\mathrm{d}T} \\ &= \frac{3}{8}R\frac{k_B T}{E_F} \\ &= \frac{3}{2}R \cdot \left(\frac{1}{4}\frac{k_B T}{E_F}\right) \\ &= C_{\text{theory}}^{\text{classical}} \cdot \left(\frac{1}{4}\frac{k_B T}{E_F}\right) \end{aligned}$$

$$\boxed{\therefore\ C_{\text{theory}}^{\text{quantum}} \simeq \left(\frac{k_B T}{E_F}\right) \cdot C_{\text{theory}}^{\text{classical}}.}$$

- Therefore, quantum theory corrects the classical expression by the fraction $\frac{k_B T}{E_F}$. At room temperature, specific heat capacity is given by

$$C_{\text{theory}}^{\text{quantum}} = C_{\text{theory}}^{\text{classical}} \cdot \frac{k_B T_{300\,\text{K}}}{E_F} \simeq 0.01\, C_{\text{theory}}^{\text{classical}} \simeq C_{\text{experiment}}$$

This validates Quantum Free Electron Theory.

Specific heat capacity – Phonon contribution

- Electronic contribution to specific heat at low T is **linear**.
- In addition to electrons, phonons i.e. quanta of lattice vibrations also contribute to specific heat capacity C_{phonon}.
- The contribution from phonons has cubic form.

$$\begin{aligned} \therefore C_{\text{theory}}^{\text{quantum}} &= C_{\text{electron}} + C_{\text{phonon}} \\ &= AT + BT^3 \end{aligned}$$

Key Insight

Phonon contribution is significant compared to electronic contribution to the specific heat capacity of metals.

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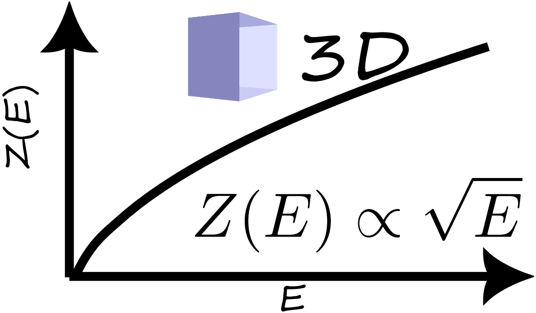
Density of states (3D)

- The form of the DOS in 3D is $Z(E) \propto \sqrt{E}$

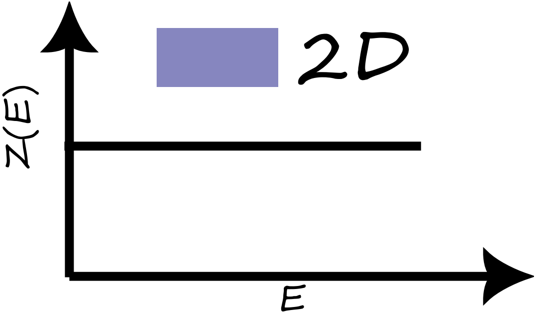


Problem

If $Z_{3D}(E) = k\sqrt{E}$, where k is a constant, find the expression for conduction electron number density n_c in terms of Fermi level E_F at $T = 0\,\mathrm{K}$ in a 3D material.

Density of states (2D)

- The form of the DOS in 2D is $Z(E) = \text{const}$



Problem

If $Z_{2D}(E) = k$, where k is a constant, find the expression for conduction electron number density n_c in terms of Fermi level E_F at $T = 0\,\text{K}$ in a 2D material.

Unit 2 Plan

Merits and demerits of QFET

Merits

- Electrical conductivity
- Thermal conductivity
- Heat capacity

Demerits

- Cannot explain classification of condensed matter into metals, semiconductors and insulators
- Occurence of positive Hall coefficient in some metals like Zn.

Unit 2 Plan

$E - k$ diagram – 1D case

- In a 1D metal, the electron is free as well as independent.
- For a free electron, the energy is related to the momentum p by

$$E = \frac{p^2}{2m}.$$

- However, since the electron behaves also as a wave, its wavelength λ is related to the momentum by the de Broglie relation

$$\lambda = \frac{h}{p} \quad \Rightarrow \quad p = \frac{h}{\lambda}.$$

- By definition, the wavevector k of the electron is inversely related to the wavelength as

$$k = \frac{2\pi}{\lambda}$$

- Therefore, the energy is related to the wavevector by

$$E = \frac{1}{2m}\left(\frac{h}{\lambda}\right)^2 = \frac{1}{2m}\left(\frac{hk}{2\pi}\right)^2 = \frac{\hbar^2 k^2}{2m}.$$

$E - k$ diagram – 3D case

- The analysis for 1D case can be extended to the 3D case by considering the components of momentum p_x, p_y, p_z

$$\vec{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$$

so that

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

- The wavevector has three components k_x, k_y, k_z so that

$$\vec{k} = k_x\hat{i} + k_y\hat{j} + k_z\hat{k}.$$

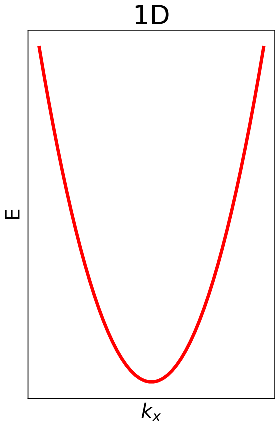
- The energy of the free electron is given by

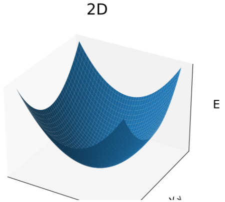
$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$$

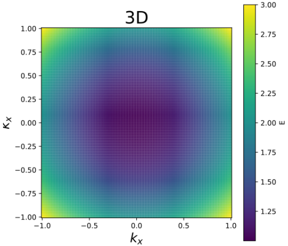
Problem

Fermi wavector k_F If the Fermi energy is $E_F = 5\,\mathrm{eV}$, find the Fermi wavevector.

Form of $E - k$ diagram – 1D, 2D, 3D







Key Insight

Form of $E - k$ is parabolic.

Summary of Quantum free electron theory (QFET)

- Derived density of states function $Z(E)$.
- Quantum free electron theory addressed the electronic contribution to specific heat of metals
- However, the theory has drawbacks. Some of them are
  - Cannot explain anomalous sign of Hall coefficient in some metals.
  - Cannot explain classification of materials into conductors. semi-conductors and insulators.

Reason for drawbacks

- Invalidity of free electron approximation.
- Drawbacks addressed by Bloch's quantum band theory.