

Chapter 6 Free-Electrons in Solids: Fermi Gas

The free electron model is the simplest possible model for a metal. We shall make two fundamental assumptions that are much more reasonable than they look: (i) the interactions between the electrons are irrelevant and can be ignored (the independent electron approximation); (ii) the electrons move in a constant potential and we can ignore everything about the structure of the material. These are heroic assumptions but they do give a fair representation of a simple metal.

For the exam you should

- be familiar with the free electron model where the potential energy of the electrons is zero and the electron-electron interactions are ignored.
- be familiar with the solutions to the Schrodinger equation for the free electron model and know that the dispersion relation in this case.
- be able to calculate the density of states for free electrons $D(k)$ and $D(E)$ in 1, 2, and 3 dimensions.
- be familiar with the fermi function.
- be able to start from the density of states and calculate the thermodynamic properties such as the heat capacity of electrons.

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6.1 Fermi gas and free electron model

What is a Fermi gas? Fermi gas is a gas that consists of particles with half-integral spin and obeys Fermi-Dirac statistics. Fermi gas that consists of noninteracting particles is called ideal Fermi gas. Fermi gases include electrons in metals and semiconductors, electrons in atoms with large atomic numbers, nucleons in heavy atomic nuclei, and gases consisting of quasiparticles with half-integral spin.

What is the Free electron (Fermi) gas model? Free electron (Fermi) gas is the simplest model of a metal that was proposed by Fermi. For this model, we make the following assumptions: (i) The crystal comprises a fixed background of N identical positively charge nuclei and N electrons, which can move freely inside the crystal without seeing any of the nuclei (monovalent case); and (ii) Coulomb interactions are negligible because the system is neutral overall.

A free electron model is the simplest way to represent the electronic structure of metals. Although the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals. According to this model, the valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal. Therefore, within this model we neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons. In this sense we are talking about a free electron gas. However, there is a principle difference between the free electron gas and ordinary gas of molecules. First, electrons are charged particles. Therefore, in order to maintain the charge neutrality of the whole crystal, we need to include positive ions. This is done within the jelly model, according to which the positive charge of ions is smeared out uniformly throughout the crystal. This positive background maintains the charge neutrality but does not exert any field on the electrons. Ions form a uniform jelly into which electrons move. Second important property of the free electron gas is that it should meet the Pauli exclusion principle, which leads to important consequences.

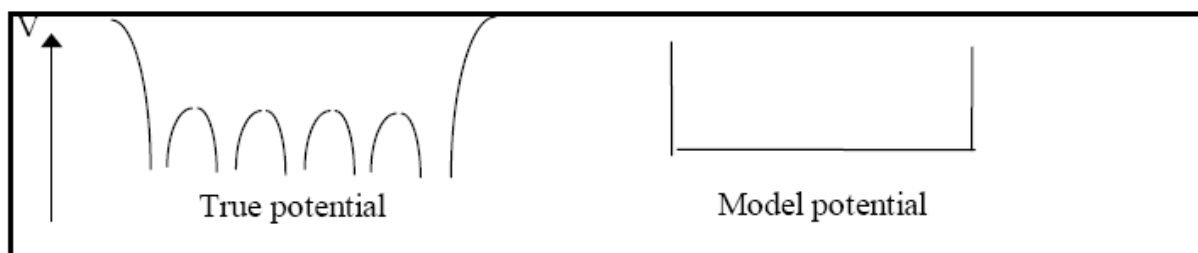


Figure 1. Schematic illustration of the free electron model.

This model works relatively well for alkali metals (Group 1 elements), such as Na, K, Rb and Cs. We would like to understand why electrons are only weakly scattered as they migrate through a metal. This model transfers the ideas of electron orbitals in atoms into a macroscopic object. Thus, the fundamental behaviour of a metal comes from the Pauli exclusion principle. For now, we will ignore the crystal lattice. By a free electron Fermi gas, we mean a gas of free electrons subject to the Pauli principle.

One of the successes of free electron model is the verification of the Heat capacity functional form correct.

6.2 Free electrons in one Dimension

6.2.1 Energy Levels in One Dimension

Consider a free electron gas in one dimension. An electron of mass m is confined to a length L by infinite barriers. We consider first a free electron gas in one dimension. The wavefunction $\psi_n(x)$ of the electron is a solution of the Schrödinger equation $H\psi_n(x) = E_n\psi_n(x)$, where E_n is the energy of electron orbital. Since we can assume that the potential lies at zero, the Hamiltonian H includes only the kinetic energy so that

$$H\psi_n(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) = E_n \psi_n(x).$$

Note that this is a one-electron equation, which means that we neglect the electron-electron interactions. We use the term *orbital* to describe the solution of this equation. Since the $\psi_n(x)$ is a continuous function and is equal to zero beyond the length L , the boundary conditions for the wave function are $\psi_n(0) = \psi_n(L) = 0$. The solution of Eq.(6.1) is therefore

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right)$$

where A is a constant and n is an integer. Substituting (6.2) into (6.1) we obtain for the eigenvalues

$$E_n(x) = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2.$$

These solutions correspond to standing waves with a different number of nodes within the potential well as is shown in Fig.1.

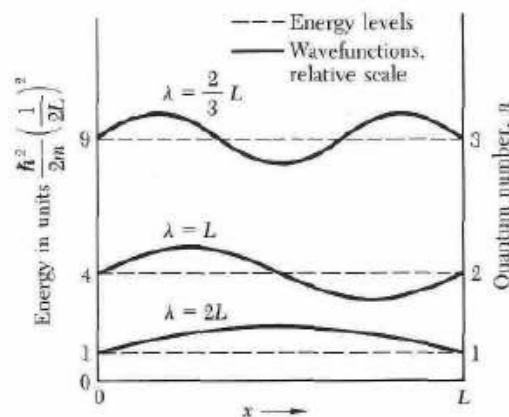


Figure 2. First three energy levels and wave-functions of a free electron of mass m confined to a

line of length L . The energy levels are labeled according to the quantum number n which gives the number of half-wavelengths in the wavefunction. The wavelengths are indicated on the wavefunctions.

6.2.2 Dispersion relations of one dimension

The energy of the confined electron is related to its wavevector k .

$$E_n(k) = \frac{\hbar^2 k^2}{2m}$$

So the dispersion relation of the confined electron is displayed below.

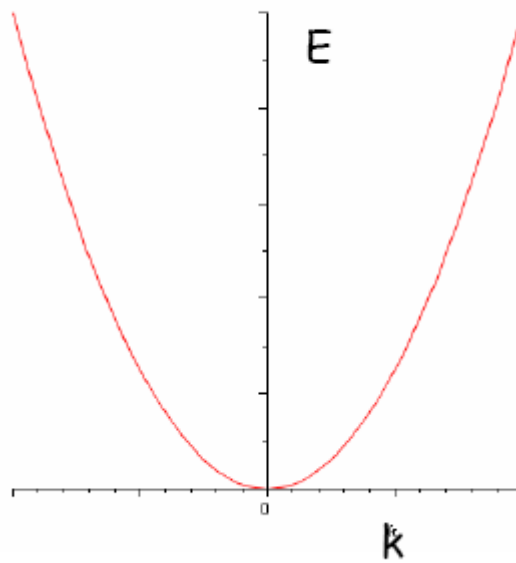


Figure 3. Dispersion relation for one-dimensional electron system.

6.2.3 Fermi Energy in One Dimension

Now we need to accommodate N valence electrons in these quantum states. According to the Pauli exclusion principle no two electrons can have their quantum number identical. That is, each electronic quantum state can be occupied by at most one electron. The electronic state in a 1D solid is characterized by two quantum numbers that are n and m_s , where n describes the orbital $\psi_n(x)$, and m_s describes the projection of the spin momentum on a quantization axis. Electron spin is equal to $S=1/2$, so that there $(2S+1)=2$ possible spin states with $m_s = \pm 1/2$. Therefore, each orbital labeled by the quantum number n can accommodate two electrons, one with spin up and one with spin down orientation.

Let n_F denote the highest filled energy level, where we start filling the levels from the bottom ($n = 1$) and continue filling higher levels with electrons until all N electrons are accommodated. It is convenient to suppose that N is an even number. The condition $2n_F = N$ determines n_F , the value of n for the uppermost

filled level. The energy of the highest occupied level is called the Fermi energy E_F . For the one dimensional system of N electrons we find, using Eq. (6.3),

$$E_F = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2.$$

In metals the value of the Fermi energy is of the order of 5 eV. The ground state of the N electron system is illustrated in Fig.x: All the electronic levels are filled up to the Fermi energy. All the levels above are empty.

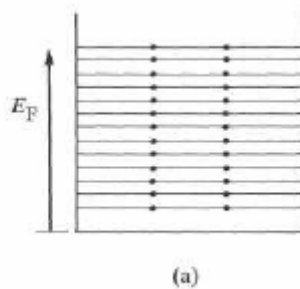


Figure 6. Occupation of energy levels according to the Pauli exclusion principle.

6.2.4 Density of states in one dimension

To calculate various optical properties such as the rate of absorption or emission and how electrons and holes distribute themselves within a solid, we need to know the [number of available states per unit volume per unit energy](#). We first calculate the available states in k -space and then use the energy-momentum relation in parabolic bands to give the density of states in terms of energy.

In one dimensional case, we have derived its discrete wavevector k_n

$$k_n = \frac{\pi n}{L}$$

This equation suggests that there is one quantum state within the momentum interval π/L . Consequently the number of quantum states dN in the momentum interval dk is

$$dN = \frac{dk}{\pi/L} = \frac{L}{\pi} dk$$

Multiplying by 2 for spin degeneracy, the number of states within the interval dk in 1-d,

$$dN = 2 \times \frac{dk}{\pi/L} = \frac{2L}{\pi} dk$$

For one dimensional quantum wires, we have

$$E = \frac{\hbar^2 k^2}{2m}$$

$$dk = \sqrt{\frac{m}{2\hbar^2 E}} dE$$

Therefore the density of states per unit length in 1-d and multiplying by 2 for spin degeneracy,

$$dN = \frac{2L}{\pi} dk = \frac{2L}{\pi} \sqrt{\frac{m}{2\hbar^2 E}} dE$$

$$DOS = \frac{dN}{dE} = \frac{L}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\sqrt{E}}$$

For one dimension, the density of states per unit volume at energy E is given by

$$DOS = \frac{dN}{dE} = \frac{L}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\sqrt{E}}$$

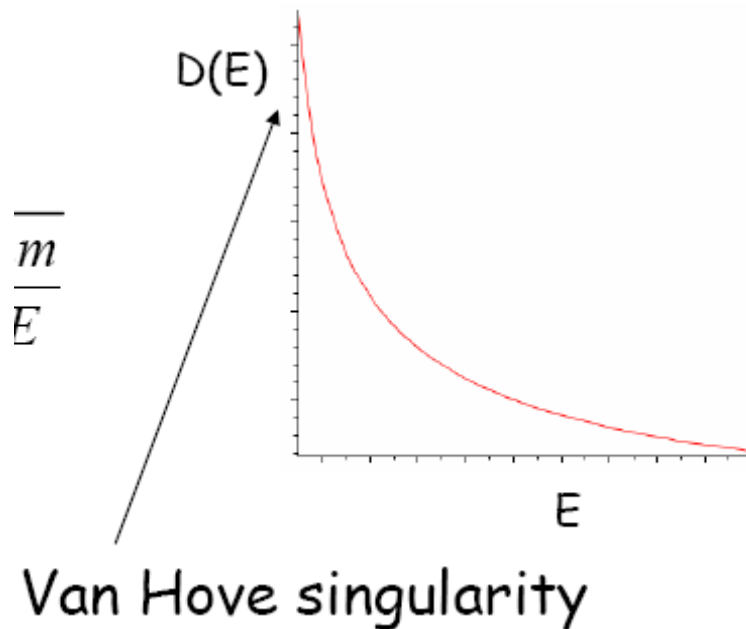


Figure 5. DOS of one dimensional system.

Using more than the first energy level, the density of states function becomes

$$DOS = \frac{L}{\pi} \sqrt{\frac{2m}{\hbar^2}} \sum_i \frac{n_i H(E - E_i)}{\sqrt{E - E_i}}$$

where once again, $H(E-E_i)$ is the Heaviside function and n_i is the degeneracy factor. For quantum structures with dimensions lower than 2, it is possible for the same energy level to occur for more than one arrangement of confined states. To account for this, a second factor $n_i(E)$ is introduced.

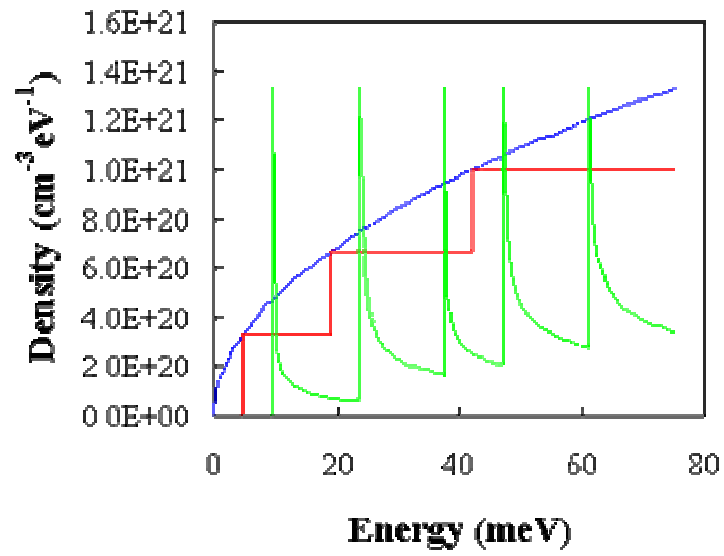


Figure 6. Density of states for quantum wire (1D green) which has multiple states.

6.3 The Fermi-Dirac distribution

6.3.1 Fermi-Dirac distribution at $T=0$ Kelvin

Electrons are Fermions. Two electrons can occupy a state, one with spin up and one with spin down. Fermi function $f(E)$ is the probability that a state at energy E is occupied. Electrons obey the Fermi-Dirac distribution

$$f(E) = \frac{1}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1},$$

where μ is the chemical potential.

At a temperature $T = 0^\circ\text{K}$, an ideal Fermi gas is in the ground state, and the particles of the gas occupy all quantum states with energy up to a certain maximum value, which depends on the gas density and is called the Fermi level (E_F). Quantum states with energy $E > E_F$ are empty; such a distribution of occupied and empty states corresponds to complete degeneracy of the Fermi gas. This is the ground state of the N electron system at absolute zero.

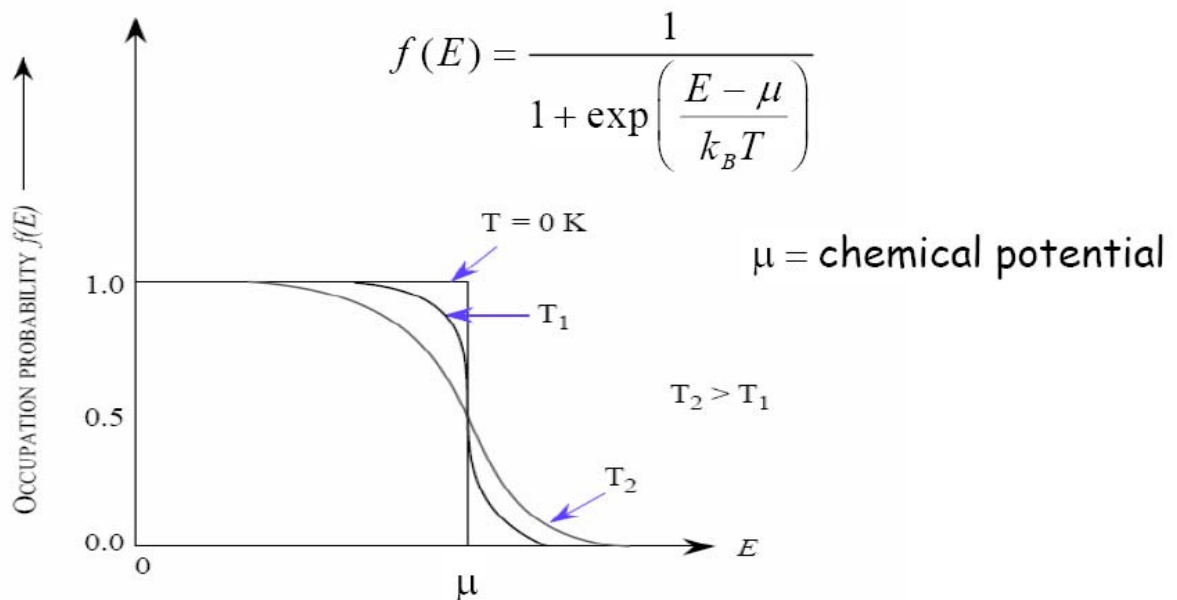


Figure 7. Fermi distribution at zero temperature.

It follows from the preceding discussion that the distribution function for electrons at $T = 0^\circ\text{K}$ has the form

$$f(E) = \begin{cases} 1, & E < \mu \\ 0, & E > \mu \end{cases}$$

That is, all levels below E_F are completely filled, and all those above E_F are completely empty. This function is plotted in Fig. 2 (b), which shows the discontinuity at the Fermi energy.

6.3.2 Fermi-Dirac distribution at $T > 0$ Kelvin

What happens if the temperature is increased? The kinetic energy of the electron gas increases with temperature. Therefore, some energy levels become occupied which were vacant at zero temperature, and some levels become vacant which were occupied at absolute zero. The distribution of electrons among the levels is usually described by the distribution function, $f(E)$, which is defined as the probability that the level E is occupied by an electron. Thus if the level is certainly empty, then, $f(E) = 0$, while if it is certainly full, then $f(E) = 1$. In general, $f(E)$ has a value between zero and unity.

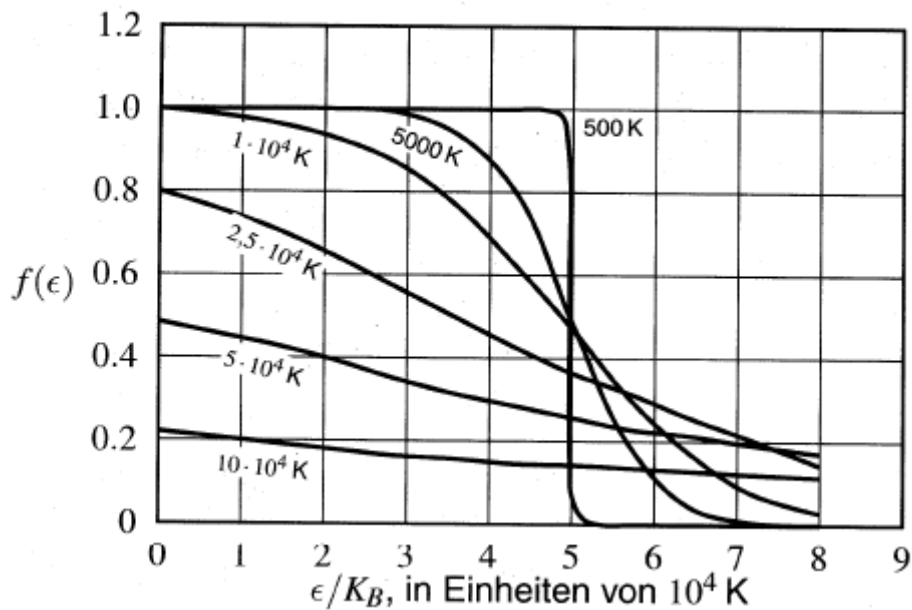


Figure 8. Fermi-Dirac distribution function at various temperatures, for $E_F/k_B = 50000$ K. The results apply to a gas in three dimensions. The total number of particles is constant, independent of temperature. The chemical potential at each temperature may be read from the graph as the energy at which $f = 0.5$.

At $T \neq 0^\circ$ K, the mean occupation number for a quantum state of an ideal Fermi gas is described by the Fermi-Dirac distribution function. When the system is heated ($T > 0^\circ$ K), thermal energy excites the electrons. However, all the electrons do not share this energy equally, as would be the case in the classical treatment, because the electrons lying well below the Fermi level E_F cannot absorb energy. If they did so, they would move to a higher level, which would be already occupied, and hence the exclusion principle

would be violated. Recall in this context that the energy which an electron may absorb thermally is of the order $k_B T$ ($=0.025$ eV at room temperature), which is much smaller than E_F , this being of the order of 5 eV.

Therefore only those electrons close to the Fermi level can be excited, because the levels above E_F are empty, and hence when those electrons move to a higher level there is no violation of the exclusion principle. Thus only these electrons - which are a small fraction of the total number - are capable of being thermally excited. The distribution function at non-zero temperature is given by the Fermi distribution function. The Fermi distribution function determines the probability that an orbital of energy E is occupied at thermal equilibrium.

This function is also plotted in Fig. 2(b), which shows that it is substantially the same as the distribution at $T = 0^\circ\text{K}$, except very close to the Fermi level, where some of the electrons are excited from below E_F to above it. The quantity m is called the chemical potential. The chemical potential can be determined in a way that the total number of electrons in the system is equal to N . At absolute zero $\mu = E_F$.

6.3.3 Temperature-dependent chemical potential

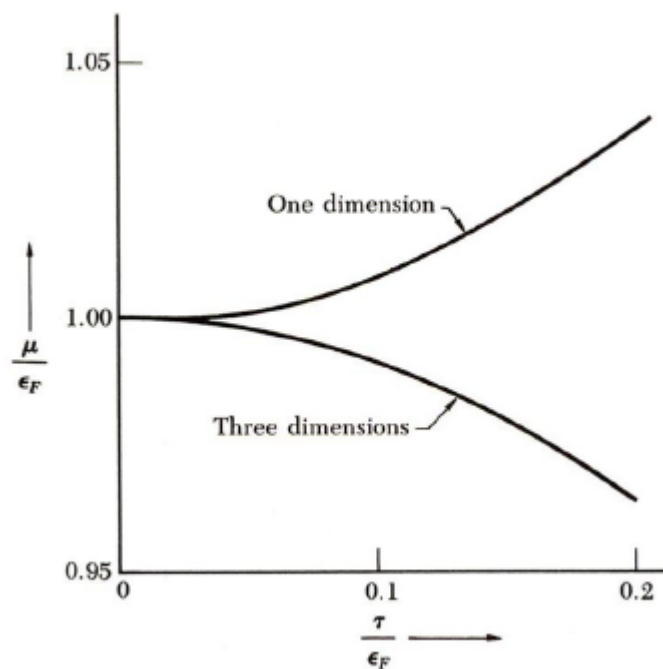


Figure 9. Variation of the chemical potential with temperature for free electron Fermi gases in one and three dimensions.

A Fermi level also exists for a nonideal Fermi gas, although the particles of such a gas do not occupy specific quantum states. In a nonideal Fermi gas consisting of electrons in a metal, the formation of pairs of correlated electrons (the Cooper effect) and the transition of the metal to the superconducting state may

occur at very low temperatures because of the attraction of electrons with equal but oppositely directed momenta and spins. A Fermi gas consisting of electrons in heavy atoms is described by the Thomas-Fermi model.

6.4 Electrons in three dimensions

6.4.1 Energy levels in 3D

The Schrödinger equation in the three dimensions takes the form

$$H\psi_n(x, y, z) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n(x, y, z) = E_n \psi_n(x, y, z)$$

If the electrons are confined to a cube of edge L , the solution is the standing wave

$$\psi_n(x, y, z) = A \sin\left(\frac{n\pi}{L} x\right) \sin\left(\frac{n\pi}{L} y\right) \sin\left(\frac{n\pi}{L} z\right)$$

where n_x , n_y , and n_z are positive integers.

In many cases, however, it is convenient to introduce periodic boundary conditions, as we did for lattice vibrations. The advantage of this description is that we assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution. We require then that our wavefunction is periodic in x , y , and z directions with period L , so that

$$\psi(x + L, y, z) = \psi(x, y, z)$$

and similarly for the y and z coordinates. The solution of the Schrödinger equation (6.7) which satisfies these boundary conditions has the form of the traveling plane wave:

$$\psi_{\vec{k}}(\vec{r}) = A \exp(i\vec{k} \cdot \vec{r})$$

provided that the component of the wavevector \vec{k} are determined from

$$k_x = \frac{\pi n_x}{L}, k_y = \frac{\pi n_y}{L}, k_z = \frac{\pi n_z}{L}$$

where n_x , n_y , and n_z are positive or negative integers.

6.4.2 Dispersion relations in 3D

If we now substitute this solution to Eq.(6.7) we obtain for the energies of the orbital with the wavevector \vec{k}

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

The dispersion relation is

$$E_{\vec{k}} = \frac{\hbar^2}{2m} k^2$$

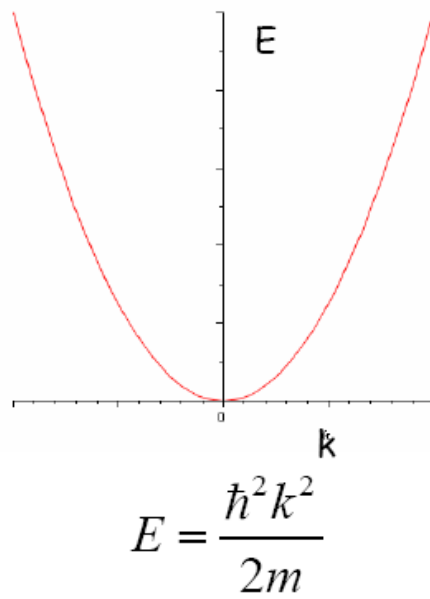


Figure10. Dispersion relation for 3D.

6.4.3 Density of states in 3D case

In three dimensional case, wavevector k has discrete values.

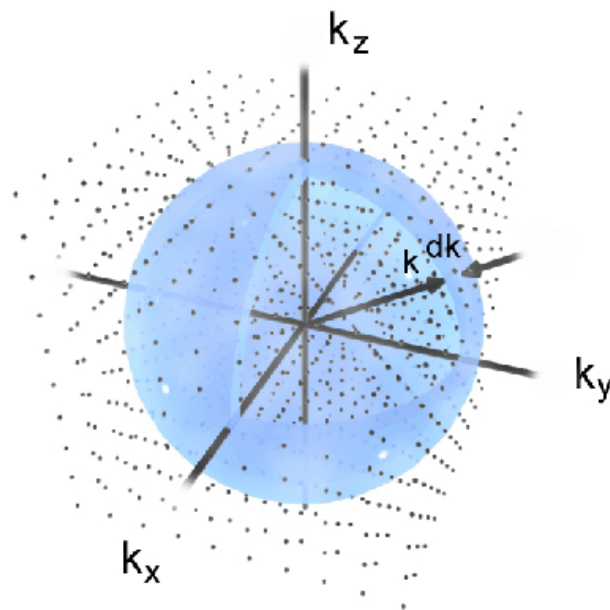


Figure 11. Visualisation of k -space showing values of k as points. The number of allowed states is the number of these points contained in the shell of radius k and thickness dk .

The diagram shows the spherical shells. The problem of finding the number of allowed states amounts to finding the number of these allowed states between spheres of radius k and $k + dk$. In 3-dimensions, the volume between the two shells is given by:

$$d\vec{k} = dk_x dk_y dk_z = 4\pi k^2 dk$$

Therefore, the number of states is given simply by dividing this volume by the volume of a single energy state. At this point it is convenient to introduce an additional factor of two to account for the intrinsic angular momentum of the electrons or spin states.

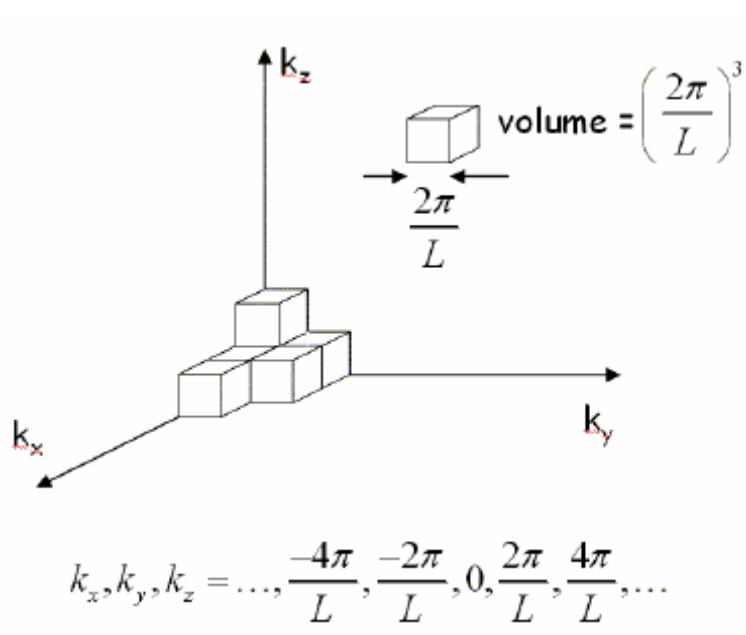


Figure 12. Discrete k values for 3D

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$$

This equation suggests that there is one quantum state within the momentum interval $(2\pi/L)^3$.

Consequently the number of quantum states dN in the momentum interval dk is

$$dN = \frac{d\vec{k}}{(2\pi/L)^3} = \left(\frac{L}{2\pi}\right)^3 d\vec{k} = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk$$

Multiplying by 2 for spin degeneracy, the number of states within the interval dk ,

$$dN = 2 \times \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk$$

For 3 dimensional quantum case, we have

$$E = \frac{\hbar^2 k^2}{2m}$$

$$dk = \sqrt{\frac{m}{2\hbar^2 E}} dE$$

Therefore the density of states per unit length in 1-d and multiplying by 2 for spin degeneracy,

$$dN = 4\pi \times \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE$$

For 3 dimension, the density of states per unit volume at energy E is given by

$$DOS = \frac{dN}{dE} = 4\pi \times \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

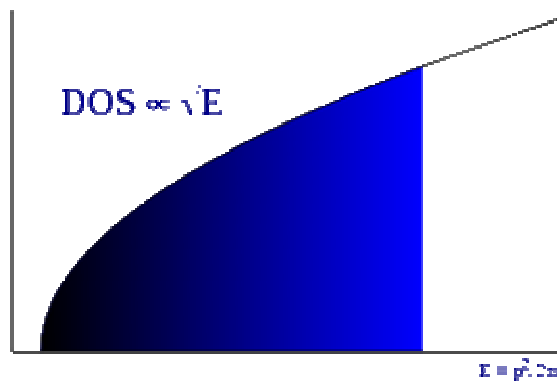


Figure 13 Density of states of three dimensional case.

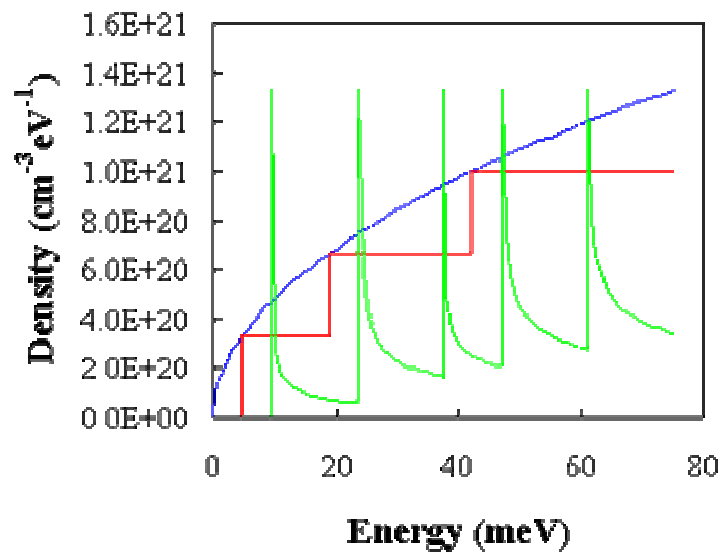


Figure 14. Density of states for bulk (3D blue).

6.4.4 Fermi energy in 3D case

From the equation of DOS, we have

$$dN = 4\pi \times \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE$$

$$N = \int dN = \int_0^{\infty} 4\pi \times \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE = \frac{L^3}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F} E^{1/2} dE = \frac{L^3}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{L^3}\right)^{2/3} = \frac{\hbar^2}{2m} \left[(3n\pi^2)^{1/3}\right]^2,$$

where n is the electron density. Comparison to the equation.

$$E = \frac{\hbar^2}{2m} k^2$$

leads to the Fermi wavevector

$$k_F = (3n\pi^2)^{1/3}$$

Because the linear momentum of an electron is

$$\vec{p} = m\vec{v} = \hbar\vec{k},$$

We can derive the Fermi velocity for an electron as

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3n\pi^2)^{1/3}$$

An alternative way to understand the Fermi energy is list as below.

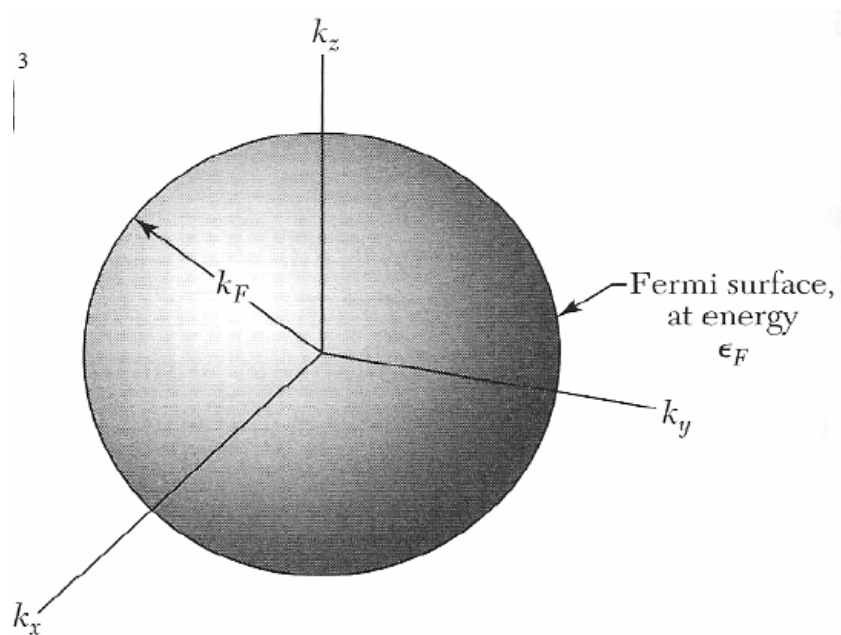


Figure 15. Fermi surface.

$$N = 2 \times \frac{4\pi k_F^3 / 3}{(2\pi / L)^3}$$

We can get the same expressions of the Fermi wavevector and Fermi energy level.

6.4.5 Example

Calculate the Fermi energy, Fermi wavevector, Fermi velocity and Fermi temperature for metal Li, whose electron density is $4.70 \times 10^{22} \text{ cm}^{-3}$.

$$\text{Solution: } E_F = \frac{\hbar^2}{2m} \left[(3n\pi^2)^{1/3} \right]^2 = 4.32 \text{ eV},$$

where n is the electron density.

The Fermi wavevector is given by

$$k_F = (3n\pi^2)^{1/3} = (3 \times 4.7 \times 10^{28} \times 3.14^2)^{1/3} = 1.12 \times 10^{10} \text{ m}^{-1} = 1.12 \times 10^8 \text{ cm}^{-1}$$

We can derive the Fermi velocity for an electron as

$$v_F = \frac{\hbar k_F}{m} = \frac{1.05 \times 10^{-34}}{0.91 \times 10^{-30}} \times 1.12 \times 10^{10} = 1.29 \times 10^6 \text{ m/s}$$

The Fermi temperature is given by

$$T_F = E_F / k = 4.32 \times 1.6 \times 10^{-19} / 1.38 \times 10^{-23} = 5.0086 \times 10^4 \text{ K}$$

Example 2. Calculate the number of states per unit energy in a 100 by 100 by 10 nm piece of silicon ($m^* = 1.08 m_0$) 100 meV above the conduction band edge. Write the result in units of eV^{-1} .

Solution: The density of states equals:

$$DOS = \frac{dN}{dE} = \left(\frac{1}{2\pi^2} \right) \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

$$DOS = \left(\frac{8\pi\sqrt{2}}{h^3} \right) m^{*3/2} (E - E_c)^{1/2} = 1.51 \times 10^{56} \text{ m}^{-3} \text{ J}^{-1}$$

So that the total number of states per unit energy equals:

$$g(E)V = 1.51 \times 10^{56} \times 10^{-22} \text{ J}^{-1} = 2.41 \times 10^5 \text{ eV}^{-1}$$

$$DOS = 1.51 \times 10^{56} \times 10^{22} \text{ J}^{-1} = 2.41 \times 10^5 \text{ eV}^{-1}$$

6.5 Electron heat capacity

6.5.1 Qualitative Representation of Electron Specific Heat

At $T=0$, the Fermi-Dirac distribution function drops precisely at $E=E_F$. At low temperatures, the function remains roughly symmetric around $E=E_F$. The number of electrons promoted is proportional to the area between the $T=0$ and finite temperature curves, which is proportional to T .

The average increase of their energy is also proportional to T . So the finite- T system has an excess energy proportional to T^2 , giving $C_V \propto T$.

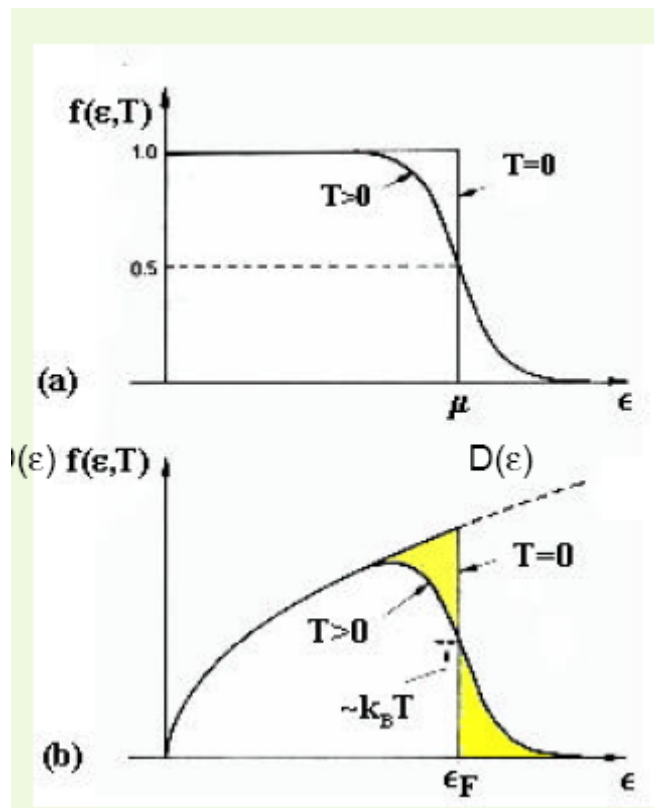


Figure 16. Fermi-Dirac distribution for various temperatures, where $T_F \equiv F/k_B = 50,000\text{K}$. This result applies at a gas in three dimensions. The chemical potential at each temperature is the value at $f=0.5$.

Only the electrons near the Fermi surface are excited by thermal energy kT . The number of excited electrons is roughly of the order of

$$N' \approx N \frac{kT}{E_F}$$

The energy absorbed by the electrons is

$$U \approx N'kT \approx N \frac{(kT)^2}{E_F}$$

The specific heat capacity of electrons is given by the following equation

$$C_{el} = \frac{\partial U}{\partial T} \approx Nk \frac{T}{T_F}$$

In general, the Fermi temperature is about 50,000 K. For classic thermodynamics, the specific heat of a particle is

$$C_{classic} = \frac{\partial U}{\partial T} = \frac{3}{2} Nk .$$

So the electronic heat of electrons is two orders less than expected in classic thermodynamics. Because $T/T_F \sim 0.01$, therefore usually electron specific is much smaller than phonon specific heat. In general,

$$C = C_{el} + C_{ph} = \gamma T + AT^3$$

C_{el} becomes more important at very low T .

6.5.2 Experimental Result of Electron Specific Heat

We expect the total specific heat to be of the form:

$$C = C_{el} + C_{ph} = \gamma T + AT^3$$

Dividing both sides by T gives:

$$\frac{C_V}{T} = \underbrace{\gamma}_{(C_V)_{\text{electrons}}} + \underbrace{AT^2}_{(C_V)_{\text{phonons}}}$$

where the latter (phonon) term is from the Debye model. So if we plot C_V/T as a function of T^2 , the intercept gives γ , whilst the gradient gives A .

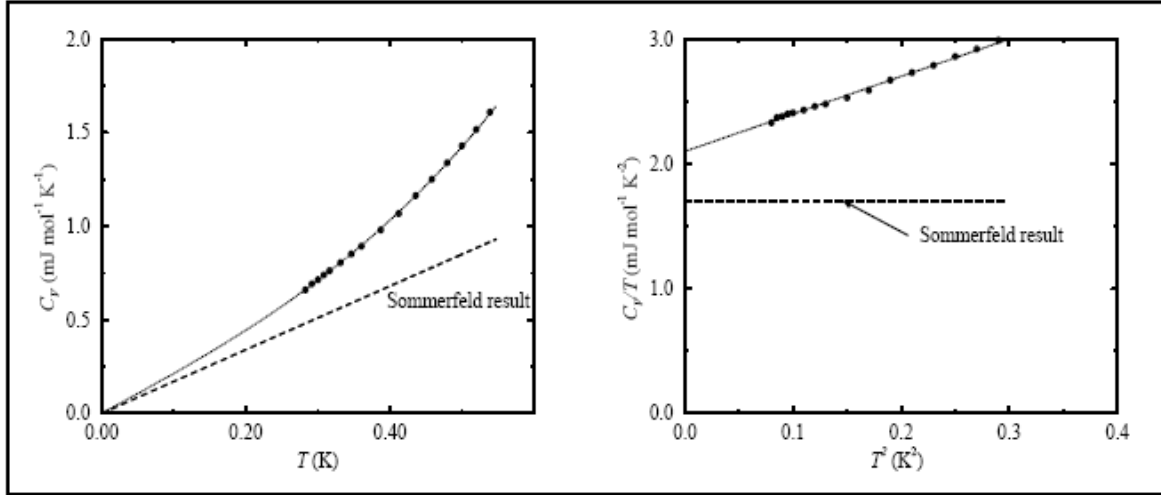


Figure 17. The specific heat of metal potassium at low temperatures.

6.5.3 Quantitative Representation of Electron Specific Heat

A major success of Fermi's consideration of electrons in metals is that it could explain the “excess” heat capacity in metals (beyond that given by the phonons). Combine DOS and thermal distribution, the total electron energy is given by the sum over all energies:

$$U = \int_0^{\infty} D(E) f(E, T) E dE$$

For $T = 0$, the Fermi function becomes a step, so we can define E_F implicitly as:

$$N = \int_0^{\infty} D(E) f(E, T) dE = \int_0^{E_F} D(E) dE$$

We need a few approximations. In general, $T \ll T_F$, where T_F is the Fermi temperature. In other words, $k_B T \ll E_F$. In this case, $T \ll T_F$ we can approximate N as in equation. This also allows us to approximate the occupation number as:

$$f(E) \approx \frac{1}{\exp[(E - \mu)/k_B T] + 1}$$

Let $x = (E - E_F)/k_B T$, then $f = 1/(e^x + 1)$.

Multiplying equation (6.17) by E_F and subtract from equation (6.16) gives:

$$\Delta U = U - N E_F = \int_0^{\infty} (E - E_F) D(E) F(E) dE$$

Taking the partial differential over equation (6.19) with respect to temperature, and noticing that N and E_F are independent of temperature gives an expression for the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \int_0^{\infty} (E - E_F) D(E) \frac{\partial f}{\partial T} dE$$

where

$$\frac{\partial f}{\partial T} = \frac{e^x}{(1 + e^x)^2} \frac{(E - E_F)}{k_B T^2}.$$

This only becomes larger near $E = E_F$, corresponding to $-1 < x < 1$, so we can approximate $D(E) \approx D(E_F) = \text{const.}$ Thus

$$C_V = D(E_F) \int_0^{\infty} \frac{e^x}{(1 + e^x)^2} \frac{(E - E_F)^2}{k_B T^2} dE$$

And using the definition of x : $dx = dE/k_B T$, gives:

$$C_V = k_B^2 T D(E_F) \int_{-\frac{E_F}{k_B T}}^{\infty} \frac{e^x x^2}{(1 + e^x)^2} dE$$

But, $E_F \gg k_B T$, leads to $-\frac{E_F}{k_B T} \rightarrow -\infty$, so the integral becomes

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}$$

Thus the specific heat becomes:

$$C_V = \frac{\pi^2}{3} k_B T D(E_F) = \frac{\pi^2}{2E_F} N k_B^2 T$$

To derive above equation we should have DOS expressed in N and E . As proven in previous problems,

$$D(E) = A E^{1/2},$$

where $A = \frac{3}{2} N E_F^{-3/2}$.

$$D(E) = \frac{3}{2} N E_F^{-3/2} E^{1/2}$$

$$D(E_F) = \frac{3N}{2E_F}$$

References

- 1 <http://lamp.tu-graz.ac.at/~hadley/ss1/fermigas/fermigas.php>
- 2 For DOS, see http://ecee.colorado.edu/~bart/book/book/chapter2/ch2_4.htm#fig2_4_4
- 3 For DOS, see http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/basics/b2_1_8.html
- 4 For semiconductors, see http://www.tf.uni-kiel.de/matwis/amat/semi_en/index.html
- 5 For DOS, see http://ecee.colorado.edu/~bart/book/book/chapter2/ch2_4.htm#fig2_4_4
- 6 For DOS, see http://en.wikipedia.org/wiki/Density_of_states

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Appendix

In solid-state and condensed matter physics, the density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. Unlike isolated systems, like atoms or molecules in gas phase, the density distributions are not discrete like a spectral density but continuous. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level. In general a DOS is an average over the space and time domains occupied by the system. Local variations, most often due to distortions of the original system, are often called local density of states (LDOS). If the DOS of a undisturbed system is zero, the LDOS can locally be non-zero due to the presence of a local potential.

A: 2-D Density of States

Energy levels in 2D

The Schrödinger equation in the two dimensions takes the form

$$H\psi_n(x, y) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi_n(x, y) = E_n \psi_n(x, y)$$

If the electrons are confined to a rectangle of edge L , the solution is the standing wave

$$\psi_n(x, y) = A \sin\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}y\right)$$

where n_x and n_y are positive integers.

In many cases, however, it convenient to introduce periodic boundary conditions, as we did for lattice vibrations. The advantage of this description is that we assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution. We require then that our wavefunction is periodic in x , y , and z directions with period L , so that

$$\psi(x + L, y) = \psi(x, y)$$

and similarly for the y and z coordinates. The solution of the Schrödinger equation (6.7) which satisfies these boundary conditions has the form of the traveling plane wave:

$$\psi_k(\vec{r}) = A \exp(i\vec{k} \cdot \vec{r})$$

provided that the component of the wavevector \mathbf{k} are determined from

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}$$

where n_x and n_y are positive or negative integers.

Dispersion relations in 2D

If we now substitute this solution to Eq.(6.7) we obtain for the energies of the orbital with the wavevector \mathbf{k}

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

The dispersion relation is

$$E_k = \frac{\hbar^2}{2m}k^2$$

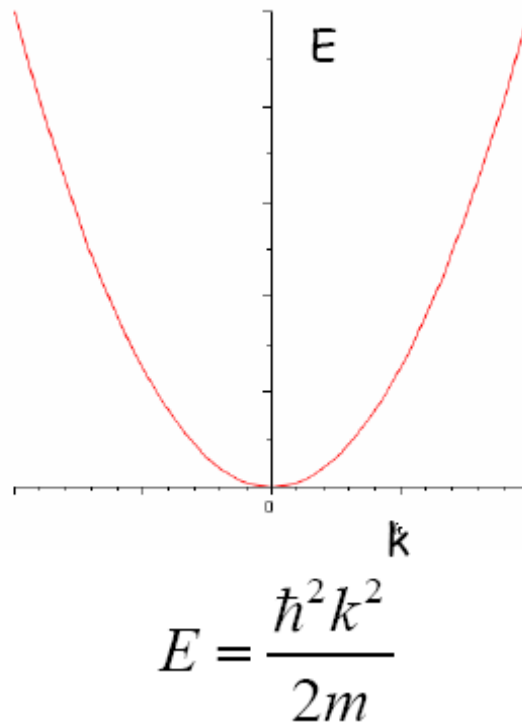


Figure 18. Dispersion relation for 2D

Density of states in 2D case

In two dimensional case, wavevector k has discrete values.

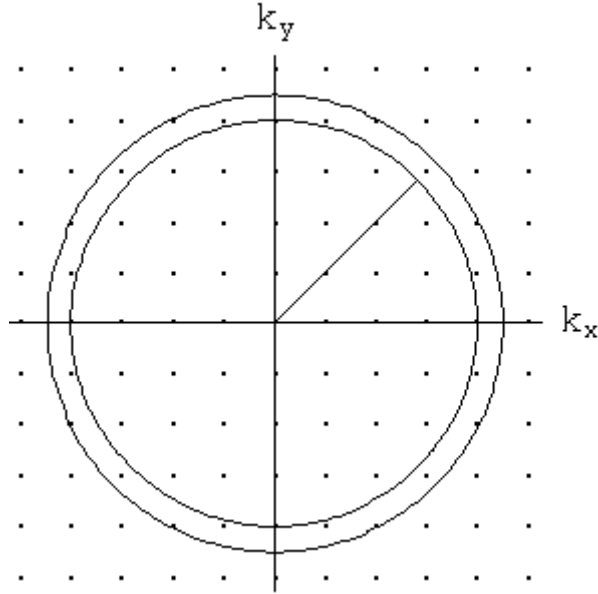


Figure 19. k-space in 2D. The density of states at an energy E is the number of k-states per unit volume contained within the annulus of radius k and thickness dk .

The diagram shows the spherical shells. The problem of finding the number of allowed states amounts to finding the number of these allowed states between areas of radius k and $k + dk$. In 2-dimensions, the area between the two shells is given by:

$$d\vec{k} = dk_x dk_y = 2\pi k dk$$

Therefore, the number of states is given simply by dividing this volume by the volume of a single energy state. At this point it is convenient to introduce an additional factor of two to account for the intrinsic angular momentum of the electrons or spin states.

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}$$

This equation suggests that one quantum state occupies the area $(\pi/L)^2$ in the momentum space.

Consequently the number of quantum states dN in the momentum interval dk is

$$dN = \frac{d\vec{k}}{(2\pi/L)^2} = \left(\frac{L}{2\pi}\right)^2 d\vec{k} = \left(\frac{L}{2\pi}\right)^2 2\pi k dk$$

Multiplying by 2 for spin degeneracy, the number of states within the interval dk ,

$$dN = 2 \times \left(\frac{L}{2\pi}\right)^2 2\pi k dk$$

For 2 dimensional quantum case, we have

$$E = \frac{\hbar^2 k^2}{2m}$$

$$kdk = \frac{m}{\hbar^2} dE$$

Therefore the density of states per unit area in 2-d and multiplying by 2 for spin degeneracy,

$$dN = 4\pi \times \left(\frac{1}{2\pi}\right)^2 \left(\frac{m}{\hbar^2}\right) dE$$

For 2 dimension, the density of states per unit area at energy E is given by

$$DOS = \frac{dN}{dE} = \frac{1}{\pi} \left(\frac{m}{\hbar^2}\right)$$

It is significant that the 2-d density of states does not depend on energy. Immediately, as the top of the energy-gap is reached, there is a significant number of available states. Taking into account the other energy levels in the quantum well, the density of states takes on a staircase like function given by:

$$DOS = \frac{dN}{dE} = \frac{1}{\pi} \left(\frac{m}{\hbar^2}\right) \sum_i H(E - E_i) dE$$

where $H(E-E_i)$ is the Heaviside function. It takes the value of zero when E is less than E_i and 1, when E is equal to or greater than E_i . E_i is the i -th energy level within the quantum well.

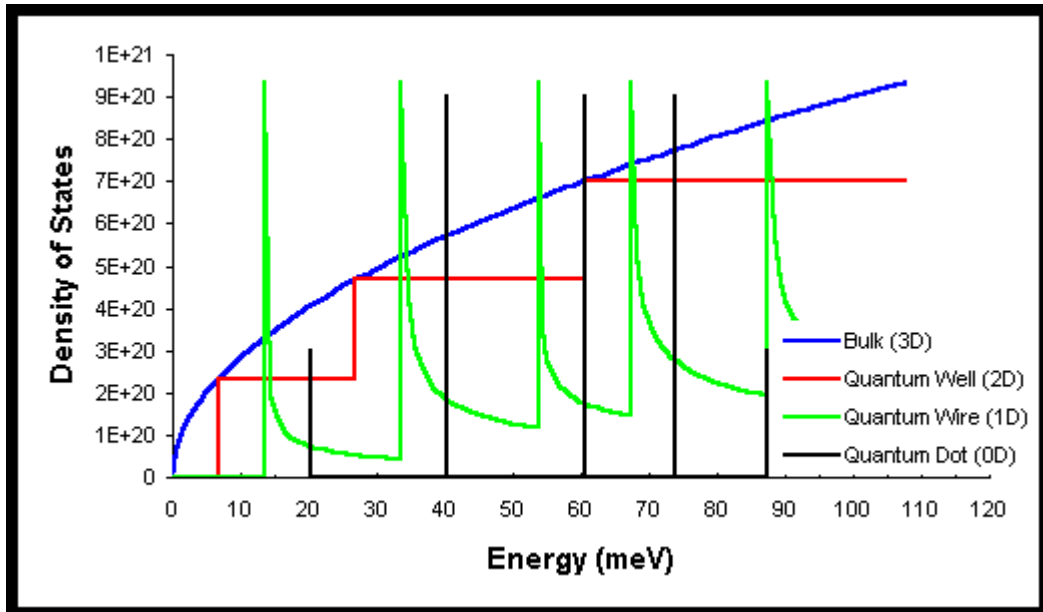


Figure 20. Density of states for bulk (3D blue), quantum well (2D red), quantum wire (1D green) and quantum Dot (0D black)

B: 0-D Density of States

Finally we consider the density of states in a zero-dimensional system, the quantum box. No free motion is possible in such a quantum box, since the electron is confined in all three spatial dimensions. Consequently there is no k-space available which could be filled up with electrons. Each quantum state of a 0D system can therefore be occupied by two electrons. The density of states is therefore described by a delta function.

$$DOS(E) = 2\delta(E - E_0)$$

For more than one quantum state the density of states is given by

$$DOS(E) = \sum_n 2\delta(E - E_n)$$

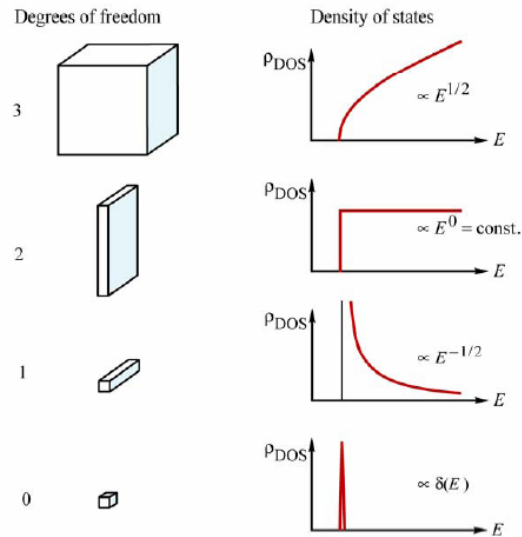


Figure 21. Electronic density of states of semiconductors with 3, 2, 1, and 0 degrees of freedom for electron propagation. Systems with 2, 1, and 0 degrees of freedom are referred to as quantum wells, quantum wires, and quantum boxes, respectively.

The density of states for one quantized level for 3D, 2D, 1D, and 0D electron system are schematically illustrated in Fig. 21.

Questions

- 1 Calculate the kinetic energy of N electrons in 3D system zero temperature $U_0 = \frac{3}{5}NE_F$.
- 2 Calculate the Fermi energy of a metal. What is the relationship between the electron density and the Fermi energy in the free electron model? Explain how this relationship would be derived. Hint: The volume in k -space corresponding to one allowed k -state is $((2\pi)/L)^3$, where L is the length of the crystal. The total volume of the crystal is L^3 . There are twice as many electrons states as k -states due to spin.
- 3 Derive the relationship connecting pressure and volume of an electron gas at 0 K. The result may be written as $p = 2(U_0/V)/3$. Show that the bulk modulus $B = -V(dp/dV)$ of an electron gas at $T = 0$ is $B = 5p/3 = 10U_0/9V$.
- 4 Average electron energy in 2-D. For a metal at a temperature of $T = 0$ K, the conduction electrons at the bottom of the band have an energy $E = 0$ and the conduction electrons with the highest energy have an energy $E = E_F$. For free electrons in two-dimensions, what is the average energy of the conduction electrons?
- 5 Find the density of states as a function of energy for a non-interacting free electron gas in two dimensions. For this system it is possible to find an analytic expression for the temperature dependence of the chemical potential. Show that

$$\mu(T) = kT \ln \left[\exp\left(\frac{\pi m \hbar^2}{mkT}\right) - 1 \right] = kT \ln \left[\exp\left(\frac{E_F}{kT}\right) - 1 \right],$$

here n is the number of electrons per unit area.

- 6 Thermodynamic properties of a metal. A monovalent metal has a simple cubic Bravais lattice and a lattice constant of $a = 0.15$ nm. Calculate the chemical potential, the specific heat, the entropy, and the Helmholtz free energy of the electrons at temperatures of 10 K and 300 K assuming that the free electron model can be used.
- 7 Derive the density of states $D(k)$ in two dimensions. The density of states for a free electron gas in two dimensions is, $D(E) = m/(\hbar^2 \pi)$. What is the heat capacity for a free electron gas in two dimensions?