The free electron approximation

The Sommerfeld model

Javier Junquera

Basic references, where most of the information is taken from

Charles Kittel
"Introduction to Solid-State Physics"
John-Wiley & Sons, New York, 1996
ISBN 0-471-11181-3

Chapter 6 (7th Edition)
Chapter 7 (in other Editions)

Harald Ibach and Hans Lüth
"Solid-State Physics"
Springer-Verlag, Berlin, 1993
ISBN 3-540-56841-7

Chapter 6

N. W. Ashcroft and N. D. Mermin
"Solid State Physics"
Saunders College Publishers, Fort Worth, 1976
ISBN 0-03-083993-9

Chapter 2

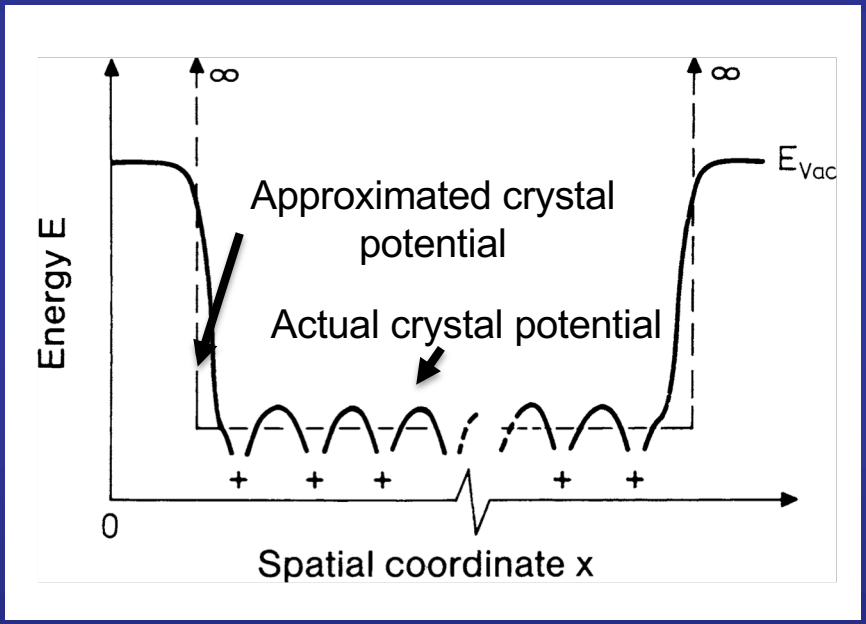
The free electron approximation (Sommerfeld and Bethe 1933)

A. Sommerfeld
(1868-1951)

H. Bethe
(1906-2005)

One extra approximation, beyond the one-particle approximation

The periodic potential will be replaced by a constant potential



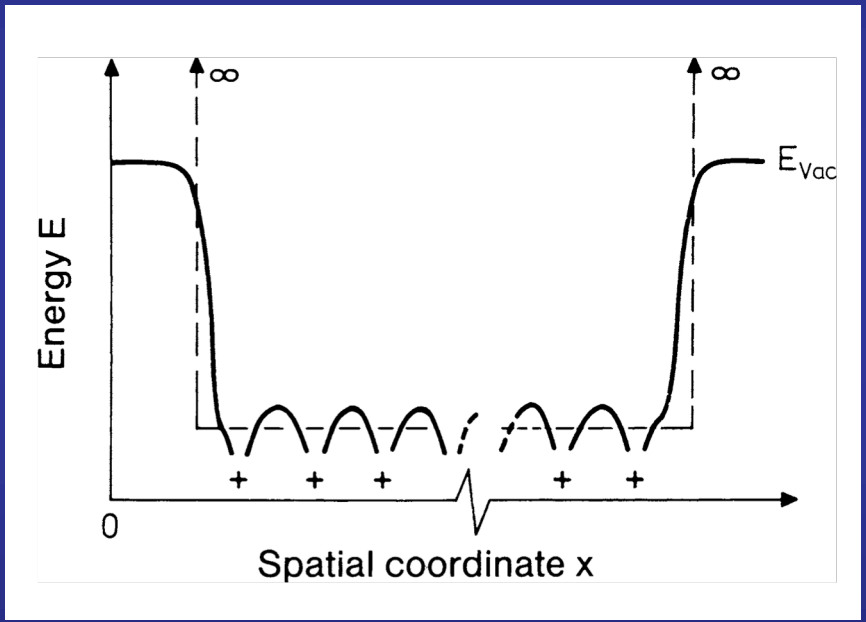
The electrons do not interact neither between themselves nor with the nuclei

The electrons confined within the boundaries of the solid, behave as an ideal gas
(we shall consider only the Pauli exclusion principle)

The free electron gas in an infinite square well potential

Model

A metal crystal is modeled as a cube of side L,
described by a three-dimensional potential box with an infinite barrier at the surface



Within this model, an electron is unable to leave the cristal
(oversimplification: the work functions are finite, of the order of 5 eV)

The free electron gas in an infinite square well potential (1D)

Goal:

Compute the ground state of a gas of:

- N **free electrons (no interaction between themselves nor with the lattice)**
- **In 1-dimension**
- **Keeping only the Pauli exclusion principle**

One electron of mass m is confined in an infinite square quantum well of length L.
The time independent Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

Kinetic energy **Energy levels of one electron in the wave function ψ_n**

Boundary conditions

Due to the infinite barrier, the electrons cannot leave the crystal

$$\psi_n(x=0) = \psi_n(x=L) = 0$$

Normalization conditions

The electron is somewhere within the potential box

$$\int_{\text{box}} \psi_n^*(x)\psi_n(x)dx = 1$$

The free electron gas in an infinite square well potential (1D)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

Solution: similar to the stationary waves propagating in a string

$$\psi_n(x) = A\sin\left(\frac{2\pi}{\lambda_n}x\right) \qquad \frac{1}{2}n\lambda_n = L$$

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

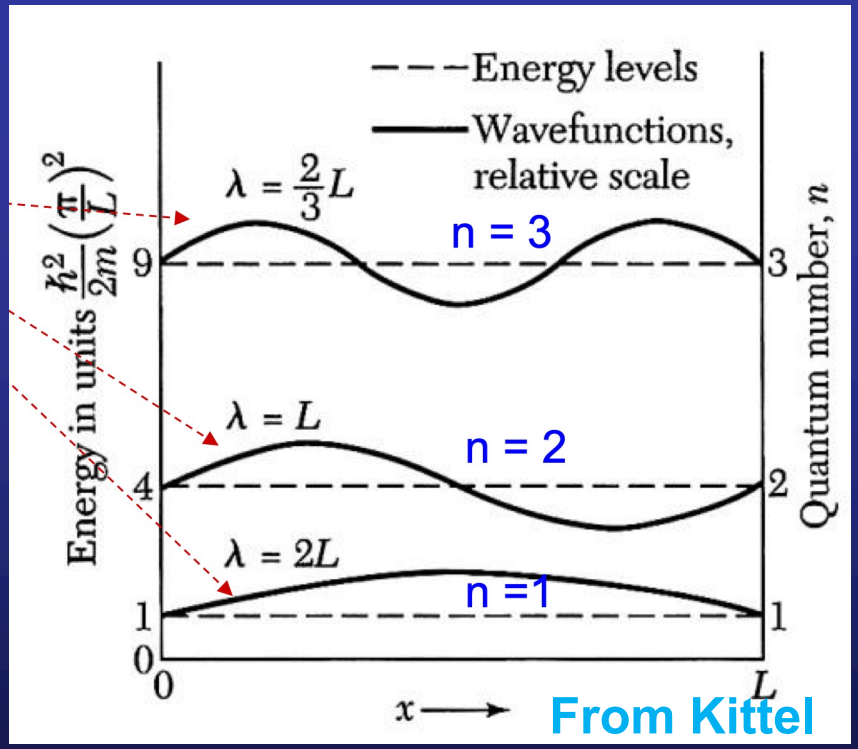
Normalization constant

$$A = \sqrt{\frac{2}{L}}$$

One electron energy levels

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

The energy is a quadratic function of the quantum number n



From Kittel

Eigenfunctions and eigenvalues of the TISE for the free electron gas in an infinite square well potential

Eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalues

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

Possible outcomes of energy measurements

The wavenumbers associated with the energy eigenfunctions within the infinite rectangular well are *quantized*

They have a discrete set of possible values
the energy difference between adjacent wavefunctions increases with increasing *n*

The wavefunction must have zero amplitude at both edges of the well,
the only allowed wavefunctions are
those with an integer number of half-wavelengths within the well.

Fundamental differences with classical mechanics

Eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{a}\right)$$

Eigenvalues

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

Possible outcomes of energy measurements

Classical mechanics

All positive values of the energy are allowed

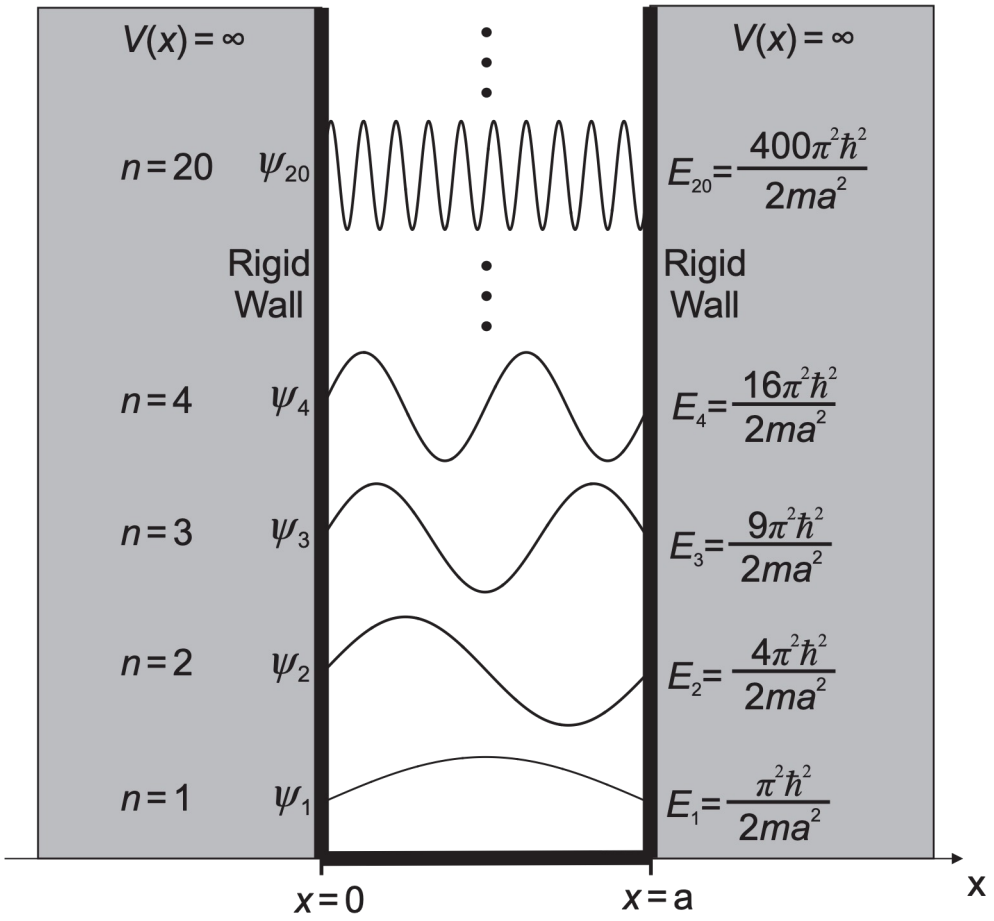
At zero temperature, the lowest energy state has zero energy

Quantum mechanics

The particle can take only certain values

At zero temperature, the lowest energy state has a non zero energy "zero point energy"

Wave functions in an infinite quantum well



Excited states

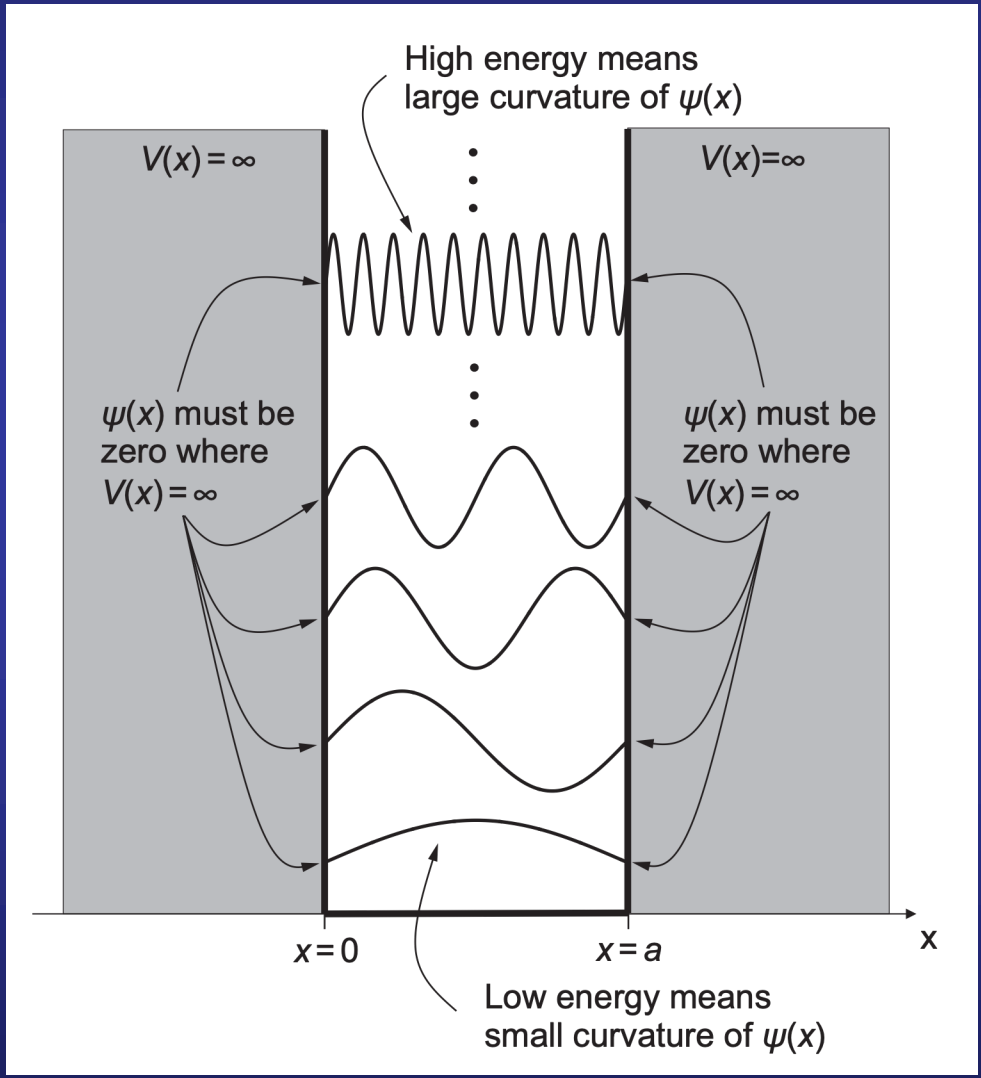
Each step up in energy level adds another half-cycle to the wavefunction across the well and another node within the well

The wavefunctions alternate between even and odd parity if the center of the well is taken as the origin

Ground state

Has a node (location of zero amplitude) at each boundary of the well, but no nodes within the well

Relation between shape of the wavefunction and energy



The free electron gas in an infinite square well: filling the one-electron levels with N electrons

Now, we have to accomodate N electrons according to the Pauli exclusion principle

There cannot be two electrons that have all their quantum numbers identical

Each orbital can be occupied by a maximum of one electron

Quantum numbers for our electrons in a 1D infinite square well

n

Positive integer

The state with $n=0$ cannot be normalized over the volumen and must be excluded

States with negative n give no new linearly independent solutions

m_s

Magnetic quantum number

$$m_s = \pm\frac{1}{2}$$

According to spin orientation

The free electron gas in an infinite square well: filling the one-electron levels with N electrons

Example:

Filling of the one-energy levels if we have six electrons
Gound state would be

n	m_s	Electron occupancy	n	m_s	Electron occupancy
1	↑	1	3	↑	1
1	↓	1	3	↓	1
2	↑	1	4	↑	0
2	↓	1	4	↓	0

From Kittel

Important magnitudes in the free electron gas: The Fermi level energy and Fermi energy

Fermi level (n_{F}): the highest occupied energy level

Since N is usually an extremely large number,
we can assume without major consequences that it is an even number

The condition $2n_{\mathrm{F}} = N$ determines n_{F}

Fermi energy (ϵ_{F}): the energy of the Fermi level

(the energy of the uppermost filled energy level of
the ground state of the system with N electrons)

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2}{2m}\left(\frac{n_{\mathrm{F}}\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$$

Order of magnitude in metallic systems: 1-10 eV
Relatively high: $k_{\mathrm{B}}T$ at room temperature ≈ 0.025 eV

Degeneracy: number of orbitals with the same energy

Important magnitudes in the free electron gas: The total energy

The total energy can be estimated summing over all the orbital energies, upto the Fermi level

$$E_0 = 2\sum_{n=1}^{n_F} \epsilon_n = 2\sum_{n=1}^{N/2} \epsilon_n = 2\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \sum_{n=1}^{N/2} n^2 \approx \frac{\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 \frac{1}{3}\left(\frac{N}{2}\right)^3$$

$$= \frac{1}{3}\frac{\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 \left(\frac{N}{2}\right)^2 \frac{N}{2} = \frac{1}{3} N \epsilon_F$$

$$\sum_{n=1}^{\text{large } s} n^2 = \frac{1}{6} s\left(2s^2 + 3s + 1\right) \approx \frac{s^3}{3}$$

For the one-dimensional problem, the average kinetic energy in the ground state is one third of the Fermi energy

The free electron gas in an infinite square well potential (3D)

Goal:

Generalization of the previous reasoning to a three dimensional case

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r}) = \epsilon_n\psi_n(\vec{r})$$

Boundary conditions

$$\psi_n(\vec{r}) = 0 \qquad \begin{array}{l} \text{for } x = 0 \text{ and } L; \quad \text{for } y, z \text{ between } 0 \text{ and } L \\ \text{for } y = 0 \text{ and } L; \quad \text{for } x, z \text{ between } 0 \text{ and } L \\ \text{for } z = 0 \text{ and } L; \quad \text{for } x, y \text{ between } 0 \text{ and } L \end{array}$$

Normalization conditions

The electron is somewhere within the potential box

$$\int_{\text{box}} d\vec{r}\ \psi_n^*(\vec{r})\psi_n(\vec{r}) = 1$$

The free electron gas in an infinite square well potential (3D)

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r}) = \epsilon_n\psi_n(\vec{r})$$

Solution

$$\psi_n(\vec{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi}{L}n_x x\right)\sin\left(\frac{\pi}{L}n_y y\right)\sin\left(\frac{\pi}{L}n_z z\right)$$

With $n_x, n_y,$ and n_z **positive integers**

The origin is located at a vertex of the cube

Defining $\vec{k} = (k_x, k_y, k_z) = \left(\frac{\pi n_x}{L}, \frac{\pi n_y}{L}, \frac{\pi n_z}{L}\right)$

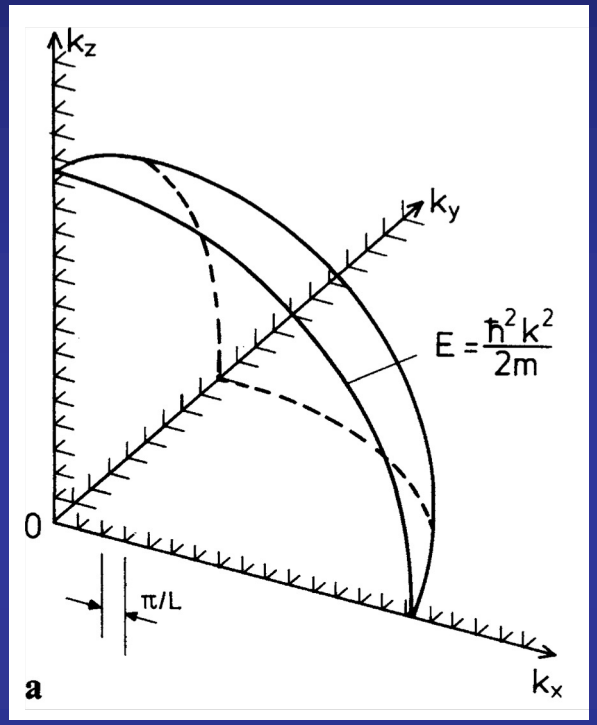
$$\psi_n(\vec{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(k_x x\right)\sin\left(k_y y\right)\sin\left(k_z z\right)$$

The posible states of an electron in a three-dimensional infinite square well of side L and volume L^3 can be listed according to their quantum numbers

$$(n_x, n_y, n_z) \quad \text{or} \quad (k_x, k_y, k_z)$$

The posible energy states are $\epsilon(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2\ k^2}{2m}$

In the ground state of a system of N free electrons with fixed boundary conditions, the occupied orbitals occupy an octant



From Ibach-Lüth

For the fixed boundary conditions, the possible $\vec{k}$ values are confined to the positive octant of the sphere

The choice of the boundary conditions

Problem: represent the confinement of the electron
(by the attraction of the ions)
to the volume V by a boundary condition

In problems where we are not explicitly concerned
by the effect of metallic surfaces

If the metal is sufficiently large we should expect its bulk properties to be unaffected by the detailed configuration of its surface

Then, the choice of the boundary conditions is at one's disposal

The boundary conditions can be determined by mathematical convenience.
We first select the shape of the metal to suit our analytic convenience

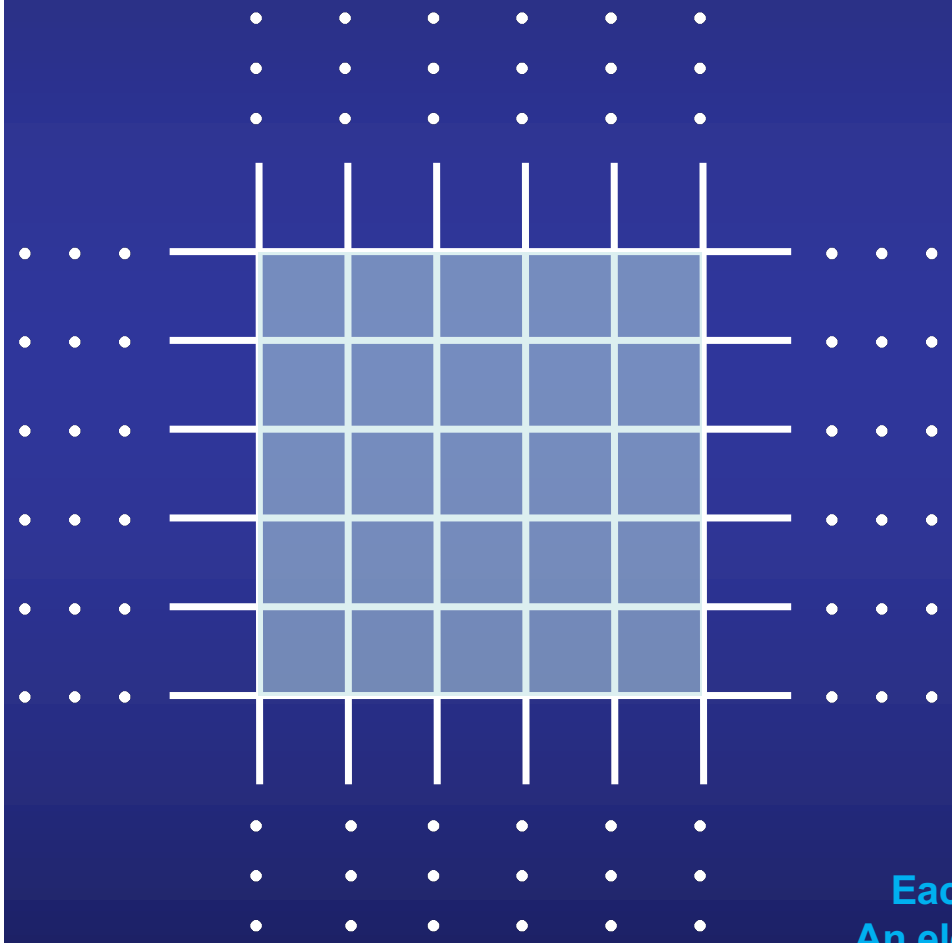
Standard one: a cube of side $L = V^{1/3}$

with periodic boundary conditions
(this illustrates the inconsecuence of the
surface by disposing of it altogether)

Periodic (Born-von Karman) boundary conditions

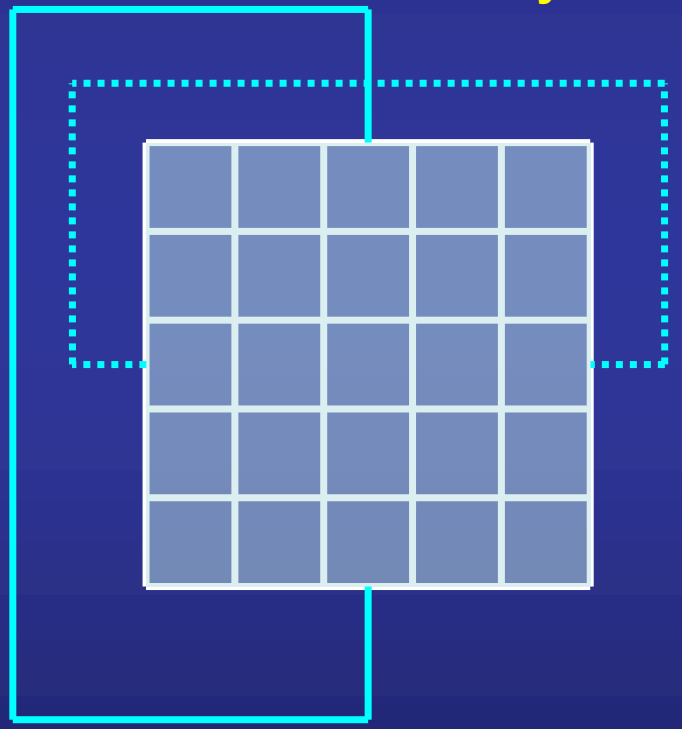
We should expect that the bulk properties to be unaffected by the presence of its surface.

A natural choice to emphasize the inconsequence of the surface by disposing of it altogether



Supercell +

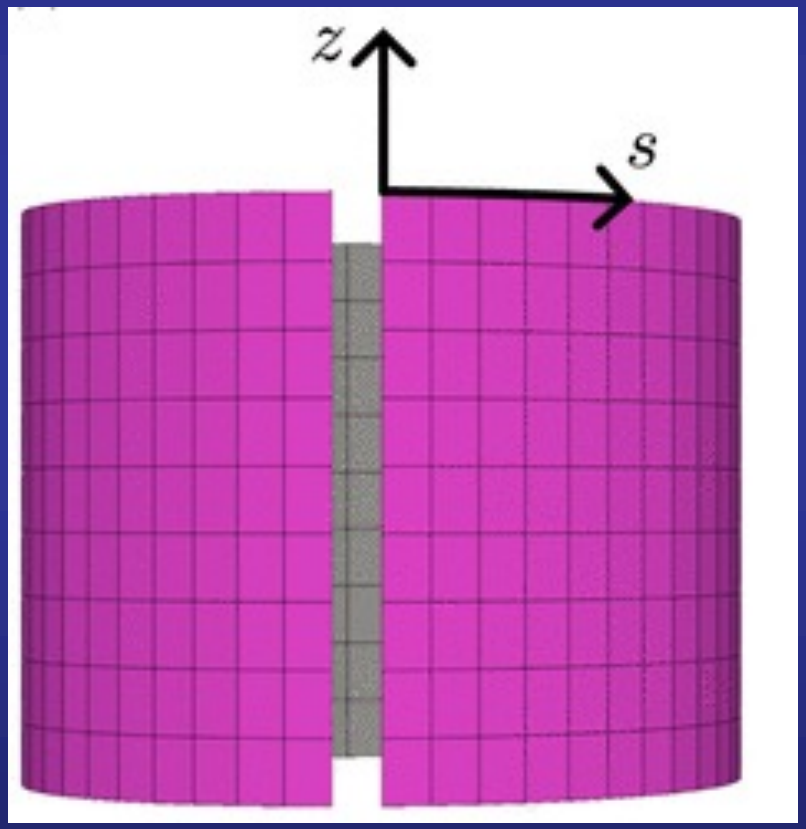
Born-von Karman boundary conditions



Each face of the cube is joined to the face opposite to it.
An electron coming to the "surface" is not reflected back in.
It leaves the metal, simultaneously reentering at the corresponding point on the opposite surface

Periodic (Born-von Karman) boundary conditions

Like playing “origami”



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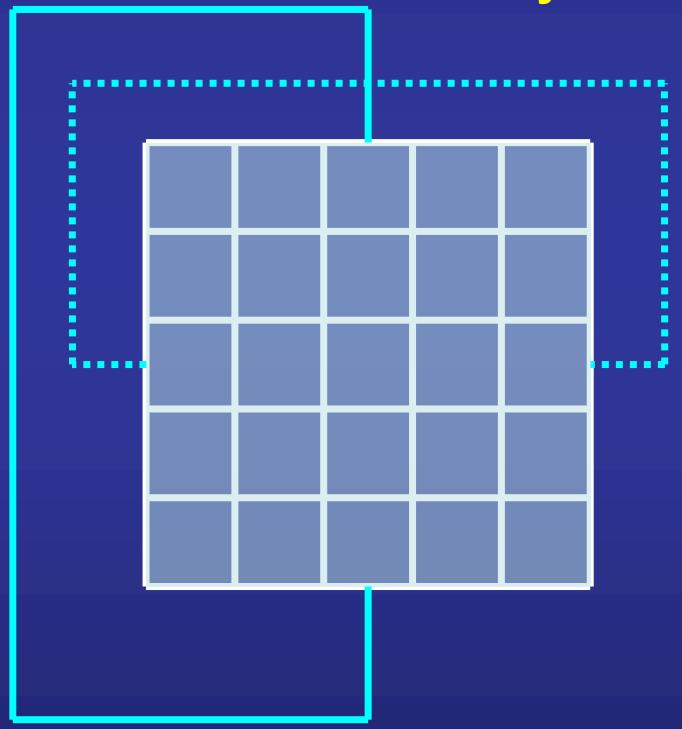

Each face of the cube is joined to the face opposite to it.
An electron coming to the “surface” is not reflected back in.
It leaves the metal, simultaneously reentering at the corresponding point on the opposite surface

What happens with periodic boundary conditions?

Goal:

Solve again the three dimensional time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k})\psi_{\vec{k}}(\vec{r})$$

Boundary conditions
(Born-von Karman)

$$\psi_{\vec{k}}(x+L,y,z) = \psi_{\vec{k}}(x,y+L,z) = \psi_{\vec{k}}(x,y,z+L) = \psi_{\vec{k}}(x,y,z)$$

Normalization conditions

The electron is somewhere
within the potential box

$$\int_{\text{box}} d\vec{r}\ \psi^*_{\vec{k}}(\vec{r})\psi_{\vec{k}}(\vec{r}) = 1$$

What happens with periodic boundary conditions?

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k})\psi_{\vec{k}}(\vec{r})$$

$$\psi_{\vec{k}}(x,y,z+L) = \psi_{\vec{k}}(x,y,z),$$
$$\psi_{\vec{k}}(x,y+L,z) = \psi_{\vec{k}}(x,y,z),$$
$$\psi_{\vec{k}}(x+L,y,z) = \psi_{\vec{k}}(x,y,z).$$

Solution: travelling plane waves

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}}$$

These travelling waves,
in contrast with the stationary waves of the infinite well,
represent better the trasport of electronic charge

They look like plane waves with wave vector $\vec{k}$

Normalization condition $1 = \int_V |\psi_{\vec{k}}(\vec{r})|^2 d\vec{r}$

What happens with periodic boundary conditions?

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k})\psi_{\vec{k}}(\vec{r})$$

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They look like plane waves with wave vector $\vec{k}$

The posible energy states are $\epsilon(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2\ k^2}{2m}$

The momentum operator

The wave vector $\vec{k}$ adquires an special significance

The travelling plane waves are also eigenstates of the linear momentum operator with eigenvalue $\hbar\vec{k}$

$$\hat{\vec{p}} = \frac{\hbar}{i}\nabla = -i\hbar\nabla; \qquad p_x = -i\hbar\frac{\partial}{\partial x}, \ldots$$

$$\hat{\vec{p}}\psi_{\vec{k}}(\vec{r}) = -i\hbar\nabla\psi_{\vec{k}}(\vec{r}) = -i\hbar\nabla\left(\frac{1}{\sqrt{L^3}}e^{i\vec{k}\cdot\vec{r}}\right) = \hbar\vec{k}\left(\frac{1}{\sqrt{L^3}}e^{i\vec{k}\cdot\vec{r}}\right) = \hbar\vec{k}\psi_{\vec{k}}(\vec{r})$$

Related observables

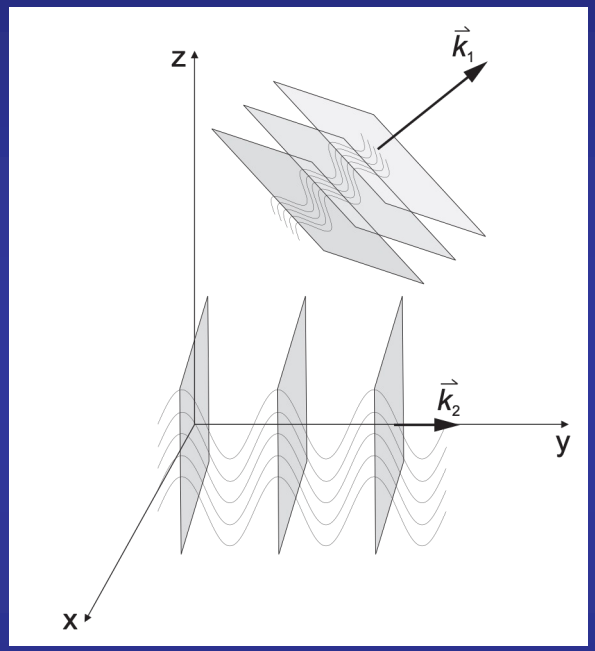
The electron will have a momentum $\vec{p} = \hbar\vec{k}$

…a velocity $\vec{v} = \frac{\vec{p}}{m} = \frac{\hbar\vec{k}}{m}$

…and an energy $\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = \frac{1}{2}mv^2$

Three dimensional plane waves

The plane wave $e^{i\vec{k}\cdot\vec{r}}$ will be constant in any plane perpendicular to $\vec{k}$ and periodic in the direction parallel to $\vec{k}$ with a wave length λ



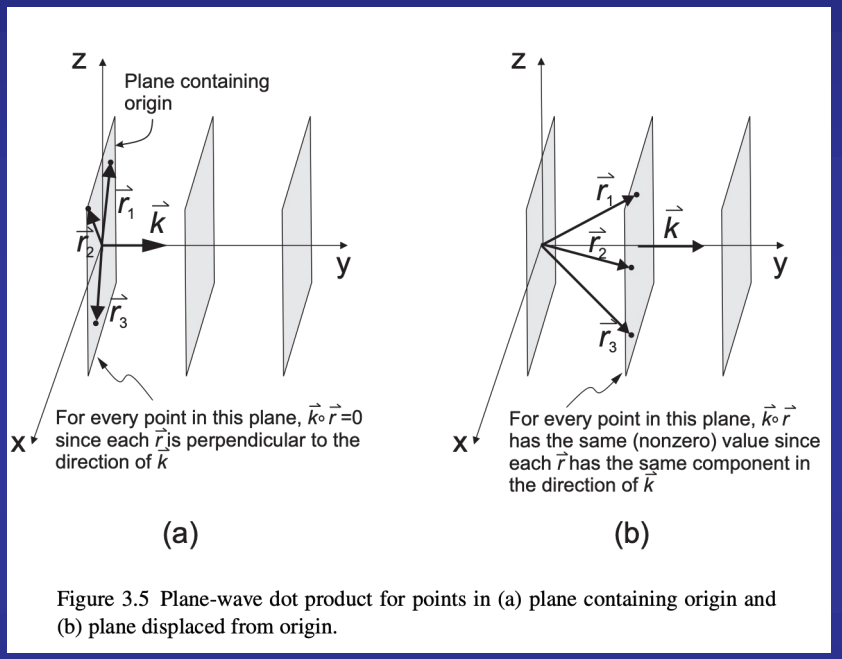


Figure 3.5 Plane-wave dot product for points in (a) plane containing origin and (b) plane displaced from origin.

The module of the wave vector is related with the wave length

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

de Broglie's wave length

A Student's Guide to the Schrödinger equation
Daniel A. Fleisch
Cambridge University Press, Cambridge, 2020
ISBN:978-1-108-81978-7

Quantization of the wave vector $\vec{k}$

To accomplish with the periodic boundary conditions,
not all the values of $\vec{k}$ are allowed
They are quantized

$$k_x = 0 \;\; ; \;\; k_x = \pm\frac{2\pi}{L} \;\; ; \;\; k_x = \pm\frac{4\pi}{L} \;\; ; \;\; \ldots$$

The same for the y and z directions

Any component of the wave vector with the form $k = 2n\pi/L$
with n a positive or negative integer

Proof

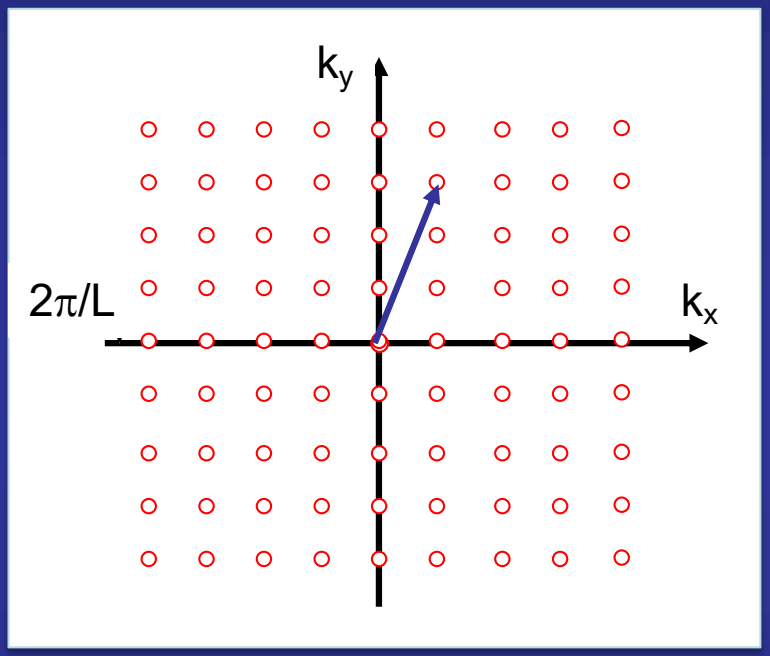
$$e^{ik_x(x+L)} = e^{i\frac{2n\pi}{L}(x+L)} = e^{i\frac{2n\pi x}{L}} e^{i2n\pi} = e^{i\frac{2n\pi x}{L}} = e^{ik_x x}$$

The components of the wave vector, together with the magnetic quantum number m_s, are the quantum numbers of the system

The $\vec{k}$ space

We define a 3D space with Cartesian coordinates $k_x, k_y,$ and k_z, where we represent the allowed wave vectors, which are those with coordinates along the three axes that are multiples of $2\pi/L$

In 2D



Due to the quantization conditions for the allowed wave vectors, there is one allowed wave vector (one with a distinct triplet of quantum numbers $k_x, k_y,$ and k_z) for the volume element $(2\pi/L)^3$ of $\vec{k}$-space

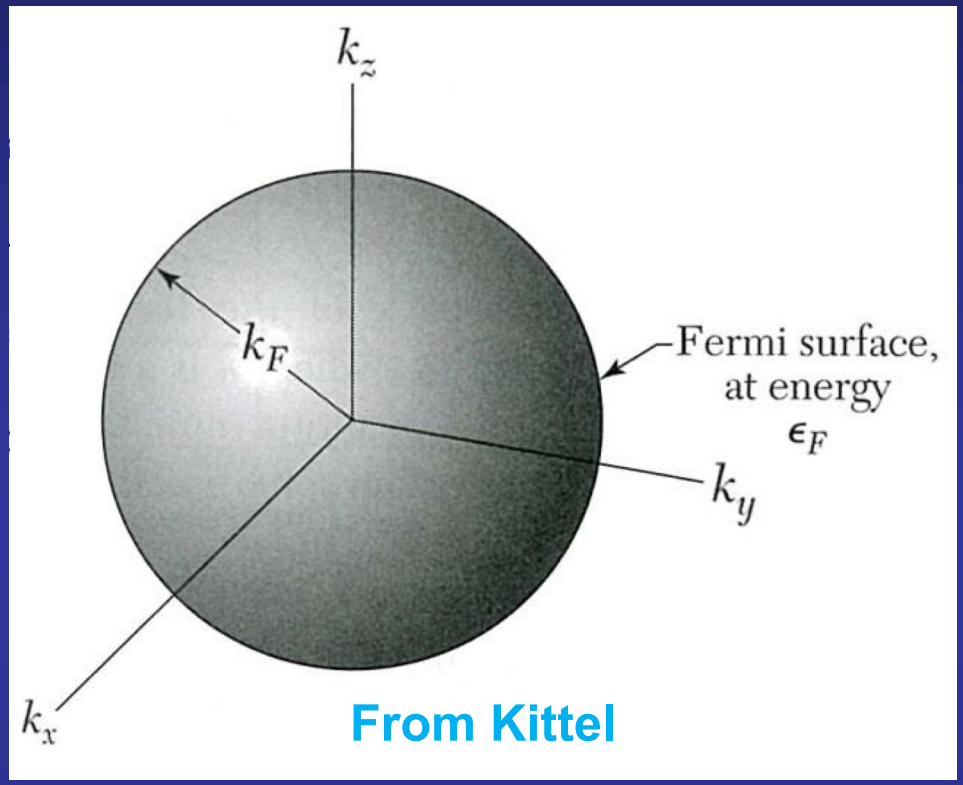
$$V_{\vec{k}} = d^3\vec{k} = \frac{2\pi}{L_x}\frac{2\pi}{L_y}\frac{2\pi}{L_z} = \frac{8\pi^3}{L_x L_y L_z}$$

One arbitrary region of volume Ω in the $\vec{k}$ space contains a number of $\vec{k}$ points equal to

$$\frac{\Omega}{V_{\vec{k}}} = \frac{\Omega}{\left(\frac{2\pi}{L}\right)^3} = \frac{\Omega L^3}{8\pi^3}$$

$\vec{k}$ space density: number of states per unit volume $\frac{L^3}{8\pi^3}$

In the ground state of a system of N free electrons, the occupied orbitals of the system fill a sphere



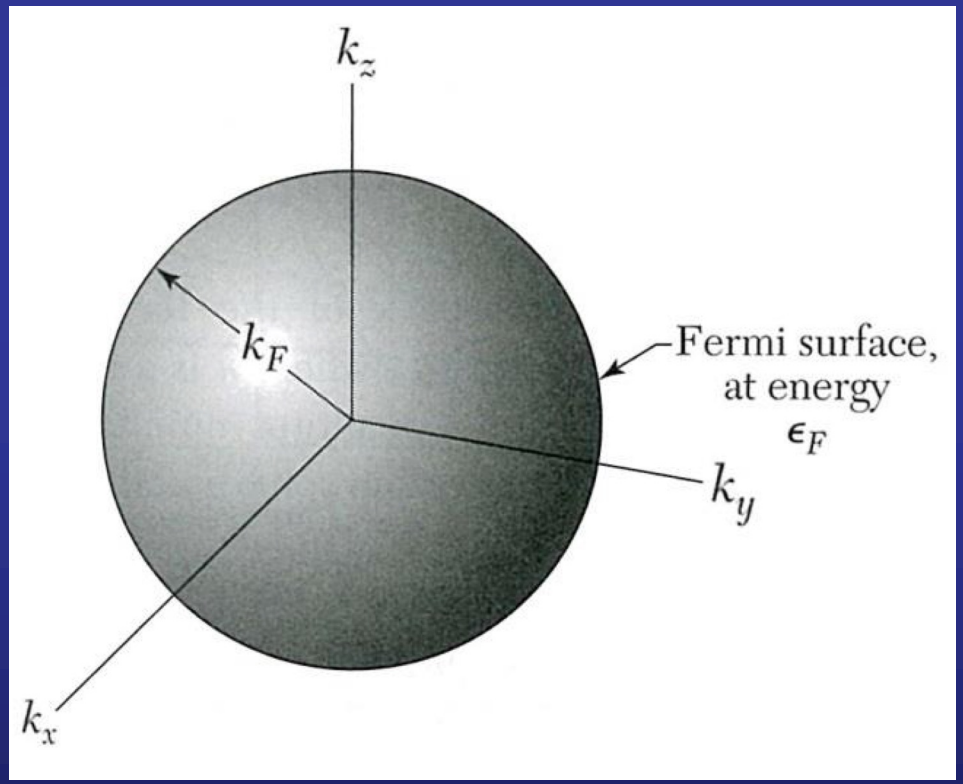
From Kittel

A representation of the allowed values in a three-dimensional wave-vector space yields constant energy surfaces $\epsilon(\vec{k}) = \dfrac{\hbar^2 k^2}{2m}$ that are spherical

Important magnitudes in the free electron gas: The Fermi wave vector, sphere, surface and energy

In the ground state of a system with N free electrons the occupied states may be represented as points inside a sphere in $\vec{k}$ space

When N is very large, the volume of the region of occupied states in $\vec{k}$ space is a sphere



The energy at the surface of the sphere is the **Fermi energy**

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2}{2m} k_{\mathrm{F}}^2$$

Fermi wave vector k_{F}

radius of the sphere of states with

$$E \leq E_{\mathrm{F}}$$

Fermi sphere

Sphere of radius k_{F}

$$\Omega_{\mathrm{F}} = \frac{4}{3}\pi k_{\mathrm{F}}^3$$

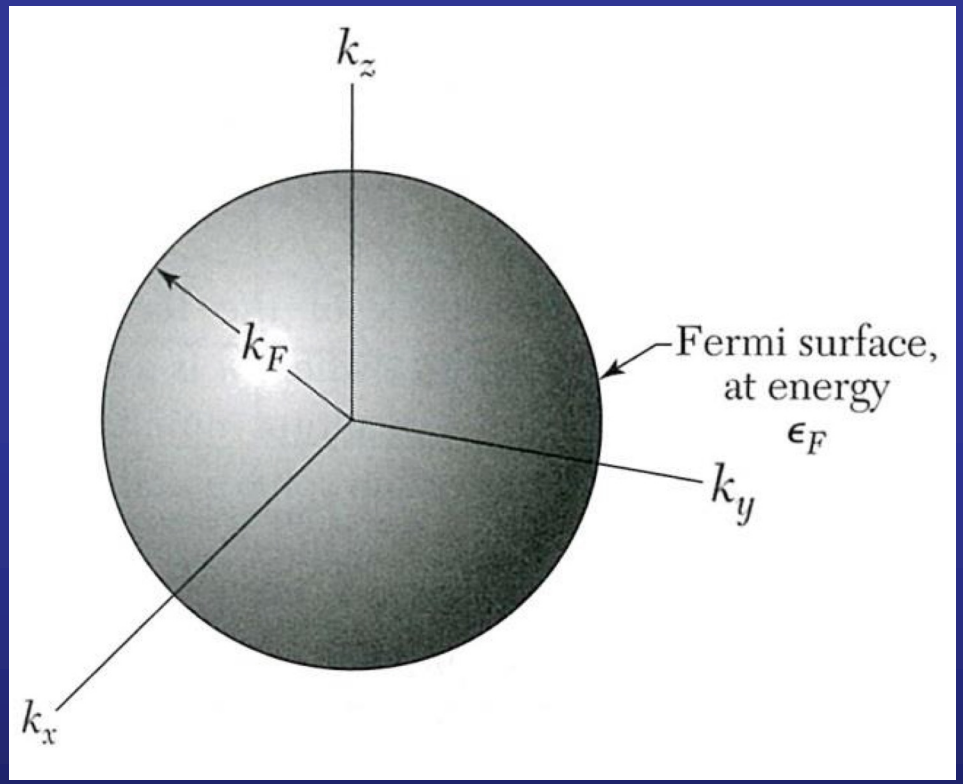
Fermi surface

Surface of the Fermi sphere

Important magnitudes in the free electron gas: The Fermi momentum and velocity

In the ground state of a system with N free electrons the occupied states may be represented as points inside a sphere in $\vec{k}$ space

When N is very large, the volume of the region of occupied states in $\vec{k}$ space is a sphere



Fermi momentum

$$p_{\mathrm{F}} = \hbar k_{\mathrm{F}}$$

Fermi velocity

$$v_{\mathrm{F}} = \frac{p_{\mathrm{F}}}{m} = \frac{\hbar k_{\mathrm{F}}}{m}$$

≈10^8 cm/s (1% of speed of light)

As important as the thermal velocity in a classical gas

$$v = \left(\frac{3 k_{\mathrm{B}} T}{m} \right)^{1/2}$$

Fermi energy as a function of the electron density

In the Fermi sphere of volume $\frac{4}{3}\pi k_{\mathrm{F}}^3$

The total allowed number of states is

$$2 \times \frac{\frac{4}{3}\pi k_{\mathrm{F}}^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{3\pi^2} k_{\mathrm{F}}^3 = \frac{V}{3\pi^2} k_{\mathrm{F}}^3 = N$$

spin

Below the Fermi energy, all the states are occupied,
so the number of states is the same as the number of electrons.
Then

$$k_{\mathrm{F}} = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = \left(3\pi^2 n\right)^{1/3}$$

$$\epsilon_{\mathrm{F}} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

Orders of magnitude of all the Fermi magnitudes

Table 9.4 Fermi Energies (T = 300 K), Fermi Temperatures, and Fermi Velocities for Selected Metals

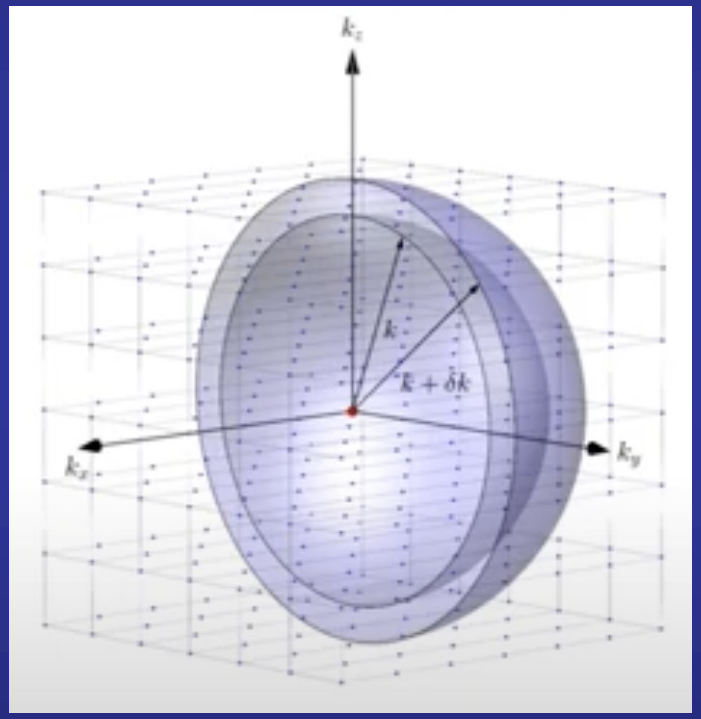
Element	E_F (eV)	T_F ($\times 10^4$ K)	u_F ($\times 10^6$ m/s)	Element	E_F (eV)	T_F ($\times 10^4$ K)	u_F ($\times 10^6$ m/s)
Li	4.74	5.51	1.29	Fe	11.1	13.0	1.98
Na	3.24	3.77	1.07	Mn	10.9	12.7	1.96
K	2.12	2.46	0.86	Zn	9.47	11.0	1.83
Rb	1.85	2.15	0.81	Cd	7.17	8.68	1.62
Cs	1.59	1.84	0.75	Hg	7.13	8.29	1.58
Cu	7.00	8.16	1.57	Al	11.7	13.6	2.03
Ag	5.49	6.38	1.39	Ga	10.4	12.1	1.92
Au	5.53	6.42	1.40	In	8.63	10.0	1.74
Be	14.3	16.6	2.25	Tl	8.15	9.46	1.69
Mg	7.08	8.23	1.58	Sn	10.2	11.8	1.90
Ca	4.69	5.44	1.28	Pb	9.47	11.0	1.83
Sr	3.93	4.57	1.18	Bi	9.90	11.5	1.87
Ba	3.64	4.23	1.13	Sb	10.9	12.7	1.96
Nb	5.32	6.18	1.37				

From N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Philadelphia: Saunders College (1976).

Density of states per unit volumen in 3D

We build multielectron states by filling available energy levels one at a time, considering two spin orientations per level.

Let us consider two energy surfaces (spheres) of radii k and $k + dk$, corresponding to the energies ϵ and $\epsilon + d\epsilon$



$$\epsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow \frac{d\epsilon}{dk} = \frac{\hbar^2 k}{m} \Rightarrow d\epsilon = \frac{\hbar^2 k}{m} dk$$

Number of allowed wave vectors between the two spheres?

First, compute the volume of the spherical crust

$$\Omega = 4\pi k^2 dk$$

Second, divide by the volume per allowed $\vec{k}$ point

$$\frac{4\pi k^2 dk}{\frac{8\pi^3}{L^3}}$$

Then, the number of electrons with energies between ϵ and $\epsilon + d\epsilon$

$$N_{3D}(\epsilon)d\epsilon = \underset{\text{spin}}{2} \times \frac{4\pi k^2 dk}{8\pi^3/V} = V\left(\frac{k}{\pi}\right)^2 \frac{m}{\hbar^2 k} d\epsilon$$

$$N_{3D}(\epsilon) = V\frac{mk}{\pi^2\hbar^2}$$

Density of states per unit volumen in 3D

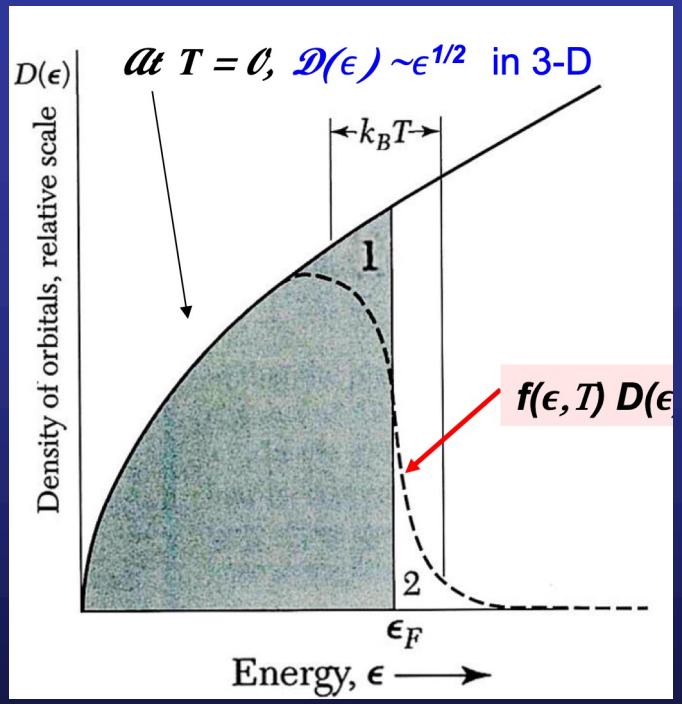
$$N_{3D}(\epsilon)d\epsilon = 2 \times \frac{4\pi k^2 dk}{8\pi^3/V} = V\left(\frac{k}{\pi}\right)^2 \frac{m}{\hbar^2 k} d\epsilon \qquad N_{3D}(\epsilon) = V\frac{mk}{\pi^2\hbar^2}$$

spin

To define the density of states
(number of states per unit volume with energy between ϵ and $\epsilon + d\epsilon$)

$$n_{3D}(\epsilon) \equiv \frac{N_{3D}(\epsilon)}{V} = \frac{mk}{\pi^2\hbar^2} = \frac{m}{\pi^2\hbar^3}\sqrt{2m\epsilon}$$

$$\epsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2m\epsilon}}{\hbar}$$



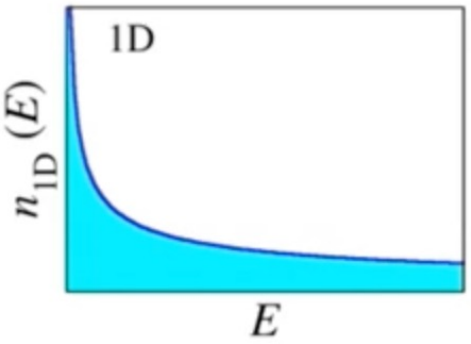
A dimensionally more transparent way of writing it

$$n_{3D}(\epsilon) = \frac{3}{2}\frac{n}{\epsilon_F}\left(\frac{\epsilon}{\epsilon_F}\right)^{1/2}$$

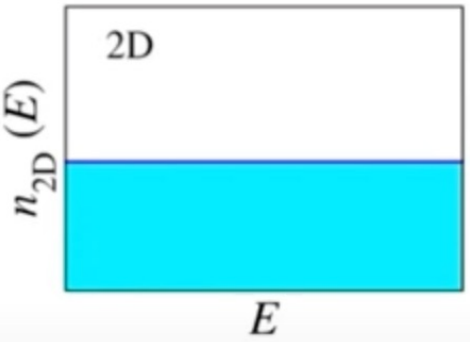
so

$$n_{3D}(\epsilon_F) = \frac{3}{2}\frac{n}{\epsilon_F}$$

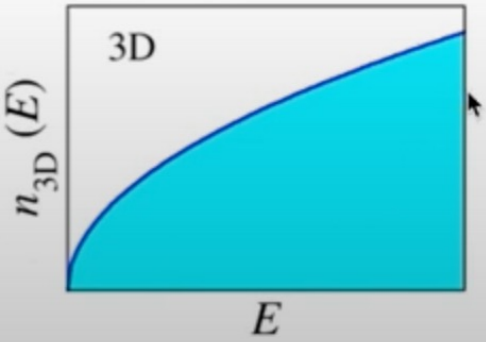
Density of states in different dimensions



$$n_{1D}(E) = \frac{1}{\pi \mathrm{h}} \sqrt{\frac{2m}{E}}$$



$$n_{2D}(E) = \frac{m}{\pi \mathrm{h}^2}$$



$$n_{3D}(E) = \frac{m}{\pi^2 \mathrm{h}^3} \sqrt{2mE}$$

$$n_d(E): \; E^{(d-2)/2}$$

Computing the energy density of the electron gas

To calculate the ground-state energy of N electrons in a volume V we must add the energies of all the one-electron levels inside the Fermi sphere

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

We can multiply and divide by the volume allowed per $\vec{k}$ point

$$E = 2 \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} \frac{\Delta k}{\Delta k} = \frac{2}{\Delta k} \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} \Delta k = \frac{2}{\left(\frac{2\pi}{L}\right)^3} \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} \Delta k = \frac{V}{4\pi^3} \sum_{k \leq k_F} \frac{\hbar^2 k^2}{2m} \Delta k$$

Now, we take the macroscopic limit of the side of the cube $L \to \infty$

$$L \to \infty \Rightarrow V \to \infty \Rightarrow \Delta k = \left(\frac{2\pi}{L}\right)^3 \to 0$$

$$\sum_k F(\vec{k}) \Delta k \to \int d^3k \; F(\vec{k})$$

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k \leq k_F} \frac{\hbar^2 k^2}{2m} d^3k = \frac{1}{4\pi^3} \int_0^{k_F} dk \; k^2 \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \frac{\hbar^2 k^2}{2m}$$

Computing the energy density of the electron gas

Performing the integral in polar variables

$$\frac{E}{V} = \frac{1}{4\pi^3}\int_{k\leq k_\mathrm{F}} \frac{\hbar^2 k^2}{2m} d^3k = \frac{1}{4\pi^3}\int_0^{k_\mathrm{F}} dk\ k^2 \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \frac{\hbar^2 k^2}{2m}$$

The angular part is trivial. The remaining radial part takes the form

$$\frac{E}{V} = \frac{4\pi}{4\pi^3}\int_0^{k_\mathrm{F}} dk\ k^2 \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2}\frac{\hbar^2}{2m}\frac{k_\mathrm{F}^5}{5} = \frac{1}{\pi^2}\frac{\hbar^2 k_\mathrm{F}^5}{10m}$$

From this, we can compute the energy per electron

$$\frac{E}{N} = \frac{E}{V}\frac{V}{N} = \frac{E}{V}\frac{1}{n} = \frac{1}{\pi^2}\frac{\hbar^2 k_\mathrm{F}^5}{10m}\frac{3\pi^2}{k_\mathrm{F}^3} = \frac{3}{10}\frac{\hbar^2 k_\mathrm{F}^2}{m} = \frac{3}{5}\epsilon_\mathrm{F}$$

$$n = \frac{k_\mathrm{F}^3}{3\pi^2}$$

Interesting consequence of the Pauli exclusion principle:
A Fermi gas of free particles, in contrast to a classical gas, has a non-vanishing internal energy at T=0 K

The Fermi temperature

$$\frac{E}{N} = \frac{3}{5}\epsilon_{\mathrm{F}} \equiv \frac{3}{5}k_{\mathrm{B}}T_{\mathrm{F}}$$

Where we have introduced the Fermi temperature as

$$T_{\mathrm{F}} = \frac{\epsilon_{\mathrm{F}}}{k_{\mathrm{B}}}$$

In contrast to this, the energy per electron in a classical gas amounts to $\frac{3}{2}k_{\mathrm{B}}T$

and vanishes at zero temperature

In the classical gas, to get a value as large as the one in the quantum gas, we need temperatures of the order of 10^4 K

Pressure and the bulk module

Once we know the ground state energy, one can calculate the pressure exerted by the electron gas

$$P = -\left.\frac{\partial E}{\partial V}\right|_N$$

Expressing the energy as a function of the volume

$$E = \frac{3}{5}N\epsilon_{\rm F} = \frac{3}{5}N\frac{\hbar^2 k_{\rm F}^2}{2m} = \frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} = \frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

Taking the partial derivative

$$-\frac{\partial E}{\partial V} = -\left(-\frac{2}{3}\right)\left[\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}N^{2/3}\right]V^{-5/3} = -\left(-\frac{2}{3}\right)\left[\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}\right]\left(\frac{1}{V}\right) = \frac{2}{3}\frac{E}{V}$$

The bulk module is defined as $B = -V\dfrac{\partial P}{\partial V}$

$$B = -V\frac{\partial}{\partial V}\left(\frac{2}{3}\frac{E}{V}\right) = -V\frac{\partial}{\partial V}\left[\frac{2}{3}\frac{1}{V}\left(\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}\right)\right] = -V\frac{\partial}{\partial V}\left[\frac{2}{3}\left(\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}N^{2/3}\right)V^{-5/3}\right]$$

$$= -\left(-\frac{5}{3}\right)\left[\frac{2}{3}\left(\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}N^{2/3}\right)V^{-5/3}\right] = \frac{10}{9}\left[\left(\frac{3}{5}N\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}\right)\frac{1}{V}\right] = \frac{10}{9}\frac{E}{V}$$

$$B = \frac{10}{9}\frac{E}{V} = \frac{10}{9}\frac{E}{N}\frac{N}{V} = \frac{10}{9}n\frac{E}{N} = \frac{10}{9}n\left(\frac{3}{5}\epsilon_{\rm F}\right) = \frac{2}{3}n\epsilon_{\rm F} \qquad \Rightarrow B = \frac{\hbar^2}{9\pi^2 m}k_{\rm F}^5$$

Pressure and the bulk module

$$P = \frac{2}{3}\frac{E}{V} \qquad B = \frac{2}{3} n \epsilon_{\mathrm{F}}$$

Bulk Moduli in 10^{10} dynes/cm^2 for Some Typical Metals[a]

Metal	Free Electron B	Measured B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

From Ashcroft and Mermin

The Fermi-Dirac distribution at 0 K

The ground state is the state of the system at absolute zero temperature

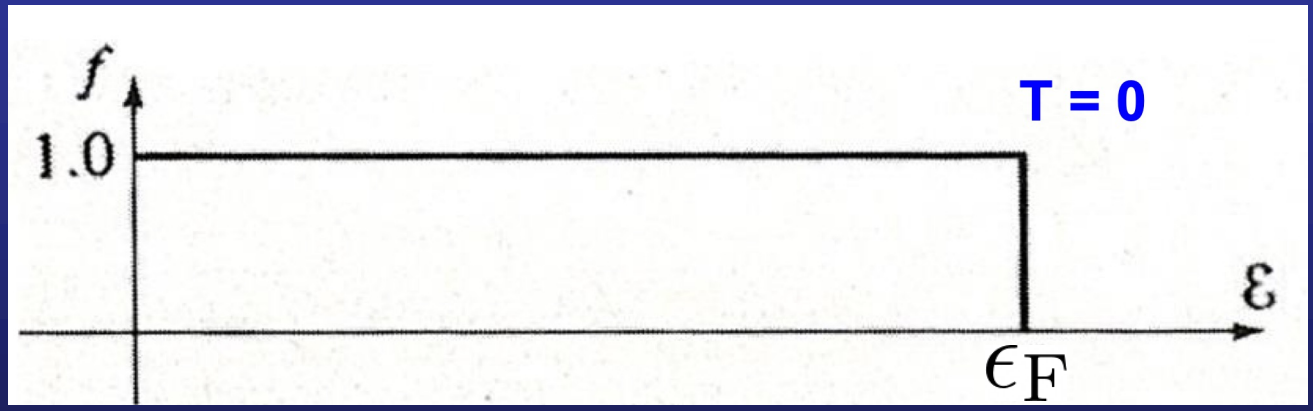
At the time of filling the energy levels with our N electrons:

- all the **levels below the Fermi energy were filled**,
- all the **levels above the Fermi energy were empty**

Let us define a probability function that a state at a given energy ϵ will be occupied in an ideal electron gas in thermal equilibrium

(the probability that a state is occupied by an electron is the average number of electrons in the state)

At 0 K, the probability function will take the form of a step function



What does happen at finite temperature?

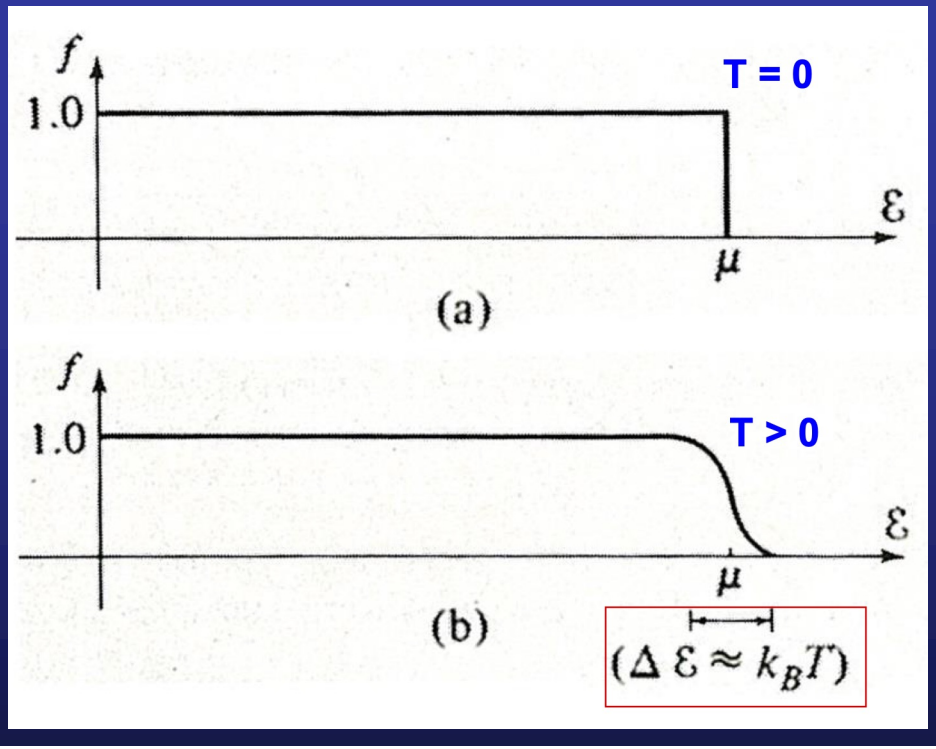
The Fermi-Dirac distribution at finite temperature

As temperature increases:

- some energy levels are occupied which were vacant at absolute zero
- some levels are vacant which were occupied at absolute zero

This is described by the Fermi-Dirac distribution function

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon-\mu}{k_{\mathrm{B}}T}} + 1}$$



μ **is called the chemical potential**

- It is temperature dependent
- Must be chosen in such a way that the total number of particles in the system comes out correctly
- At zero temperature, $\mu = \epsilon_{\mathrm{F}}$
- At all finite temperatures,

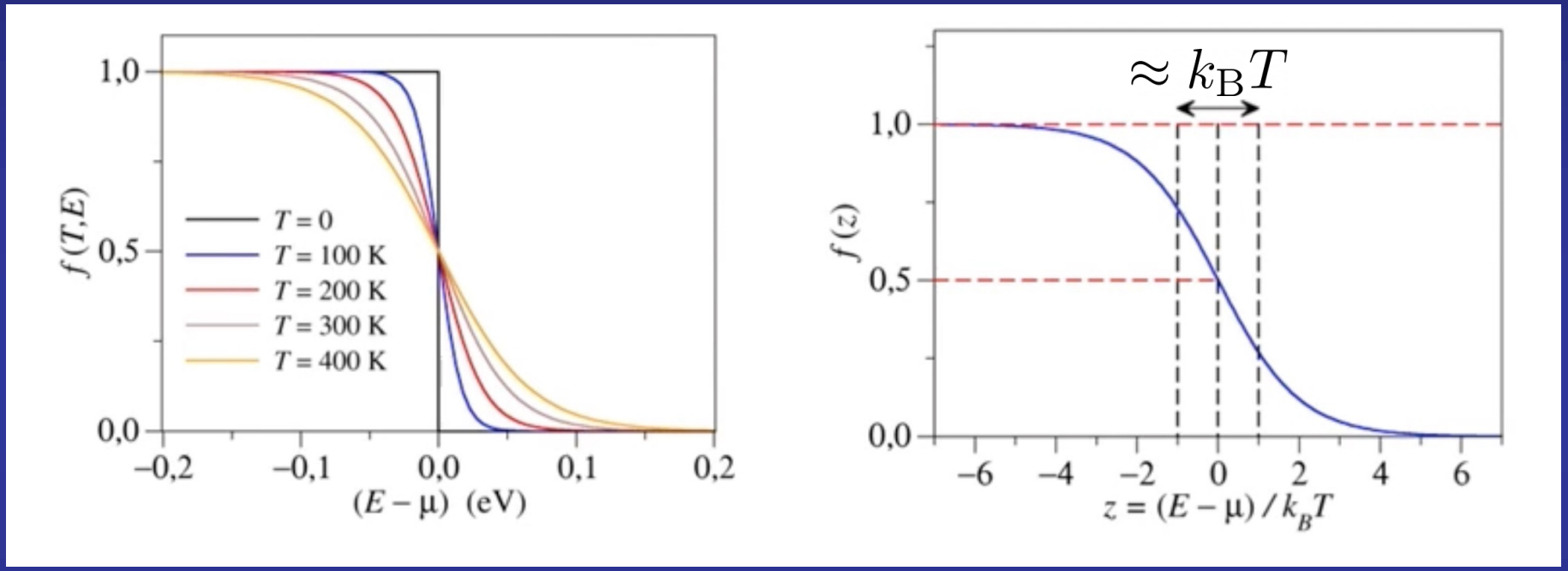
$$f(\epsilon = \mu) = 1/2$$

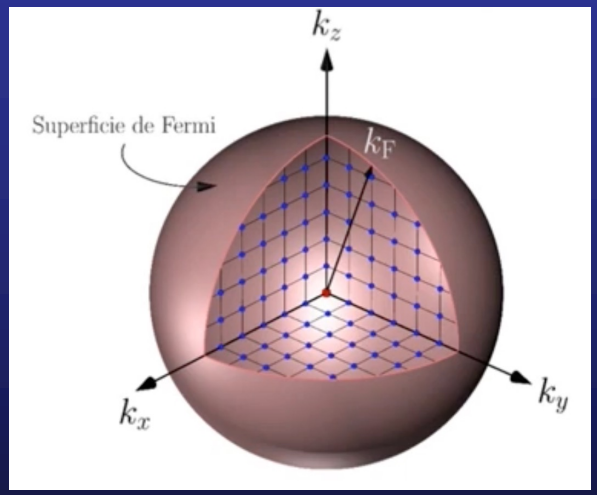
The two curves differ only in a region of the order of $k_{\mathrm{B}}T$ about μ

The Fermi-Dirac distribution at finite temperature

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon-\mu}{k_B T}} + 1}$$

The width increases when T increases





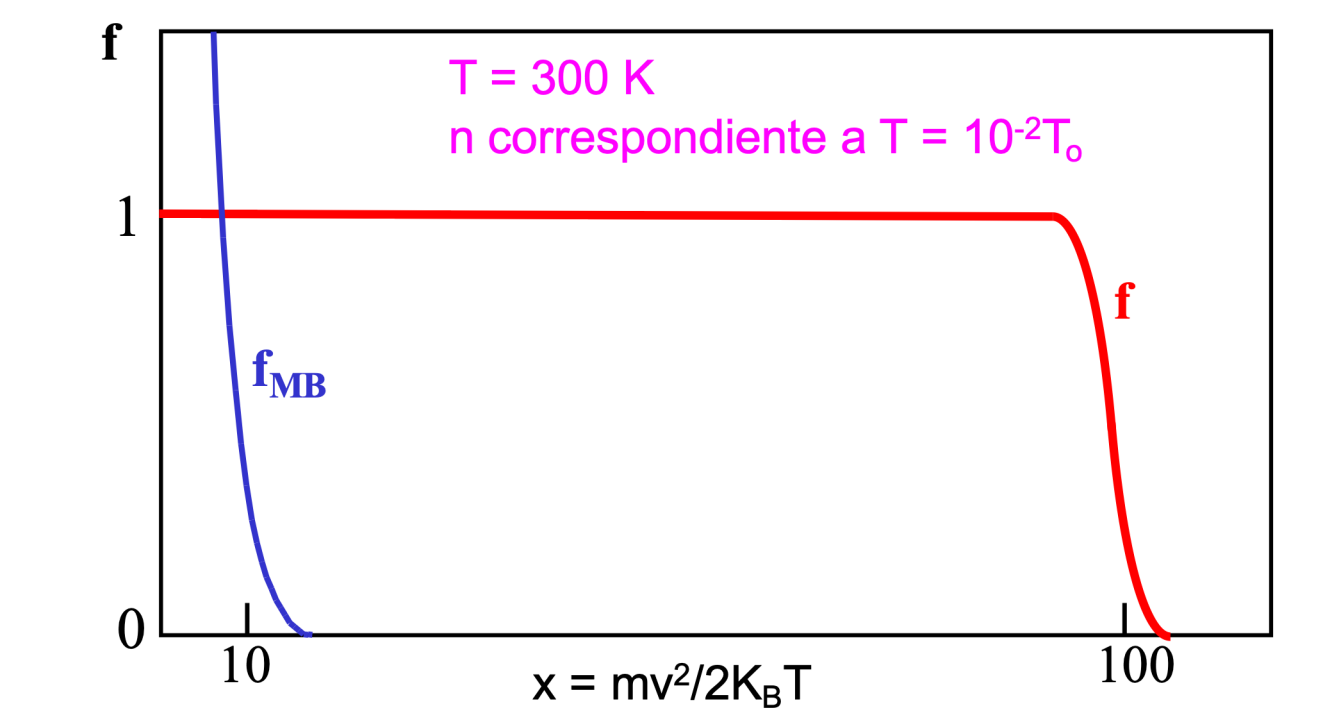
Only the electrons close to the Fermi energy are able to promote (there are empty states close in energy)

Fermi-Dirac versus Boltzmann distribution

The high-energy tail of the distribution $\dfrac{\epsilon - \mu}{k_{\mathrm{B}}T} >> 1$

$$f(\epsilon) \approx e^{-\frac{\epsilon-\mu}{k_{\mathrm{B}}\mathrm{T}}}$$

That is essentially the Boltzmann distribution

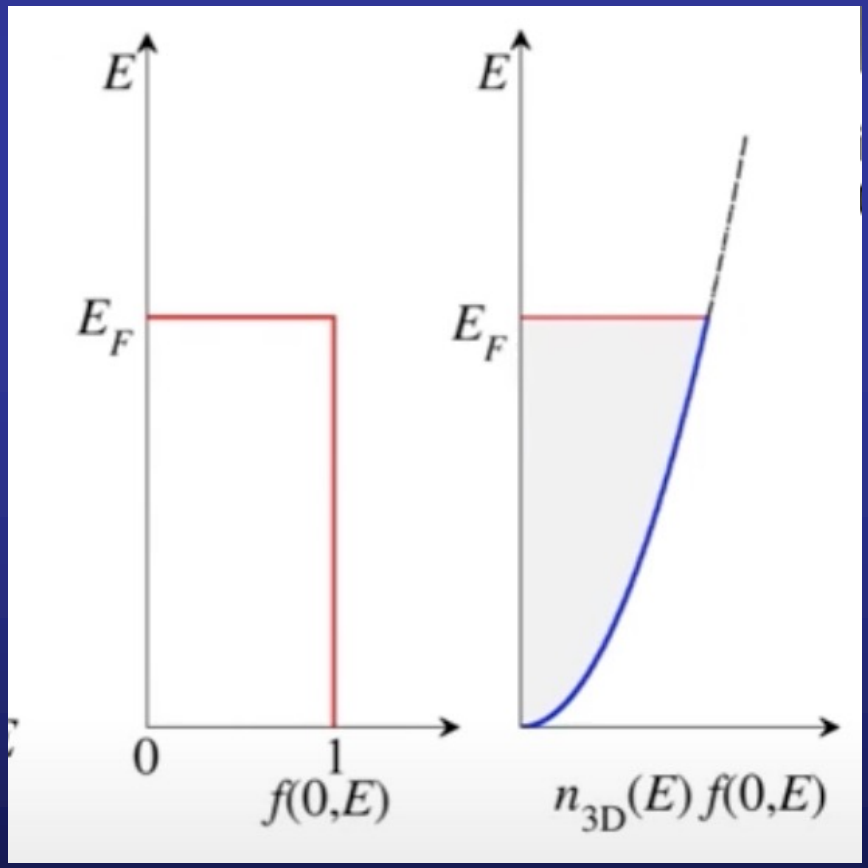


Computing the density of particles as a product of density of states and Fermi distribution

$$n = \int_0^\infty d\epsilon \; n_{3D}(\epsilon) f(T=0,\epsilon) = \int_0^{\epsilon_F} d\epsilon \; n_{3D}(\epsilon) = \frac{m}{\pi^2\hbar^3}\sqrt{2m}\int_0^{\epsilon_F} d\epsilon \; \sqrt{\epsilon} = \frac{m}{\pi^2\hbar^3}\sqrt{2m}\frac{\epsilon_F^{3/2}}{\frac{3}{2}}$$

Probability of occupation

Number of levels per volume with energies between ϵ and $d\epsilon$



From the previous equation

$$n = \frac{m}{\pi^2\hbar^3}\sqrt{2m}\frac{\epsilon_F^{3/2}}{\frac{3}{2}} = \frac{(2m)^{3/2}}{3\pi^2\hbar^3}\epsilon_F^{3/2}$$

So, the Fermi energy will take the value

$$\epsilon_F^{3/2} = \frac{3\pi^2\hbar^3}{(2m)^{3/2}}n \Rightarrow \epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

Since

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

Computing the energy density as a product of density of states and Fermi distribution

$$u = \frac{E}{V} = \frac{U}{V} = \int_{-\infty}^{\infty} d\epsilon \; n_{3\mathrm{D}}(\epsilon) f(T=0,\epsilon)\epsilon = \frac{3}{5} n \epsilon_{\mathrm{F}}$$

Number of levels per volume with energies between ϵ and $d\epsilon$

Probability of occupation

Energy

The density of states is defined as

$$n_{3\mathrm{D}}(\epsilon) = \begin{cases} \dfrac{m}{\pi^2 \hbar^3} \sqrt{2m\epsilon}, & \epsilon > 0 \\ 0, & \epsilon < 0 \end{cases}$$

So the integral can be extended between $-\infty$ and $+\infty$

Dependence of the chemical potential with temperature

The density of particles does not change with temperature

$$\int_0^\infty n_{3D}(\epsilon) f(T,\epsilon) d\epsilon = \int_0^\infty n_{3D}(\epsilon) f(T=0,\epsilon) d\epsilon = \int_0^{\epsilon_F} n_{3D}(\epsilon) d\epsilon$$

Replacing the shape of the density of states in 3D

$$\frac{m}{\pi^2\hbar^3}\sqrt{2m}\int_0^{\epsilon_F}\sqrt{\epsilon}d\epsilon = \frac{m}{\pi^2\hbar^3}\sqrt{2m}\int_0^{\infty}\sqrt{\epsilon}\frac{d\epsilon}{e^{\frac{\epsilon-\mu}{k_B T}}+1}$$

$$\int_0^{\epsilon_F}\sqrt{\epsilon}d\epsilon = \int_0^{\infty}\sqrt{\epsilon}\frac{d\epsilon}{e^{\frac{\epsilon-\mu}{k_B T}}+1}$$

Change the variables to make the integrals adimensional

$$y = \frac{\epsilon}{k_B T} \qquad y_0 = \frac{\epsilon_F}{k_B T} \qquad x = \frac{\mu}{k_B T}$$

$$\int_0^{y_0}\sqrt{y}dy = \int_0^{\infty}\frac{\sqrt{y}}{e^{y-x}+1}dy$$

Dependence of the chemical potential with temperature

$$\int_0^{y_0} \sqrt{y} dy = \int_0^{\infty} \frac{\sqrt{y}}{e^{y-x}+1} dy$$

$$\frac{2}{3} y_0^{3/2} \approx \frac{2}{3} x^{3/2} \left(1 + \frac{\pi^2}{8x^2}\right) \Rightarrow x \approx y_0 \left(1 - \frac{\pi^2}{12 y_0^2}\right)$$

To get this, follow the next two slides

Solution of $\frac{2}{3}y_0^{3/2} \approx \frac{2}{3}x^{3/2}\left(1+\frac{\pi^2}{8x^2}\right) \Rightarrow x \approx y_0\left(1-\frac{\pi^2}{12y_0^2}\right)$

Multiplying the two terms by 3/2

$$y_0^{3/2} = x^{3/2}\left(1+\frac{\pi^2}{8x^2}\right)$$

Taking the power of 2/3

$$y_0 = x\left(1+\frac{\pi^2}{8x^2}\right)^{2/3} = x\left(1+z\right)^{2/3} \approx x\left(1+\frac{2}{3}z\right)$$

$$z = \frac{\pi^2}{8x^2} \qquad (1+z)^n \approx 1+nz \text{ if } z \to 0$$

The previous approach is valid, since the chemical potential is much larger than the thermal energy

$$\mu >> k_B T \Rightarrow x >> 1 \Rightarrow z << 1$$

Then

$$y_0 = x\left(1+\frac{2}{3}z\right) = x\left(1+\frac{2}{3}\frac{\pi^2}{8x^2}\right) = x\left(1+\frac{\pi^2}{12x^2}\right)$$

Solution of $\frac{2}{3}y_0^{3/2} \approx \frac{2}{3}x^{3/2}\left(1+\frac{\pi^2}{8x^2}\right) \Rightarrow x \approx y_0\left(1-\frac{\pi^2}{12y_0^2}\right)$

From the previous slide…

$$y_0 = x\left(1+\frac{2}{3}z\right) = x\left(1+\frac{2}{3}\frac{\pi^2}{8x^2}\right) = x\left(1+\frac{\pi^2}{12x^2}\right)$$

Simplifying the expression

$$y_0 = \left(\frac{12x^2+\pi^2}{12x}\right) \Rightarrow 12y_0x = 12x^2+\pi^2 \Rightarrow x^2 - y_0x + \frac{\pi^2}{12} = 0$$

Solve the equation for x

$$x = \frac{y_0 \pm \sqrt{y_0^2 - \frac{\pi^2}{3}}}{2} = \frac{y_0}{2} \pm \sqrt{\left(\frac{y_0}{2}\right)^2 - \frac{\pi^2}{12}} = \frac{y_0}{2} \pm \frac{y_0}{2}\sqrt{1-\frac{\pi^2}{12}\frac{4}{y_0^2}} = \frac{y_0}{2} \pm \frac{y_0}{2}\sqrt{1-\frac{\pi^2}{3y_0^2}}$$

Taking again the approximation for the power a binomial

$$x \approx \frac{y_0}{2} \pm \frac{y_0}{2}\left(1-\frac{1}{2}\frac{\pi^2}{3y_0^2}\right) = \frac{y_0}{2} \pm \frac{y_0}{2}\left(1-\frac{\pi^2}{6y_0^2}\right) = \frac{y_0}{2} \pm \left(\frac{y_0}{2} - \frac{\pi^2}{12y_0}\right)$$

Only the positive solution has physical meaning
(the other one gives a non-sense negative value for x**)**

$$x \approx y_0 - \frac{\pi^2}{12y_0} = y_0\left(1-\frac{\pi^2}{12y_0^2}\right)$$

Dependence of the chemical potential with temperature

$$\int_0^{y_0} \sqrt{y} dy = \int_0^{\infty} \frac{\sqrt{y}}{e^{y-x}+1} dy$$

$$\frac{2}{3} y_0^{3/2} \approx \frac{2}{3} x^{3/2} \left(1 + \frac{\pi^2}{8x^2}\right) \Rightarrow x \approx y_0 \left(1 - \frac{\pi^2}{12 y_0^2}\right)$$

Undoing the change of variables

$$\frac{\mu}{k_B T} \approx \frac{\epsilon_F}{k_B T} \left[1 - \frac{\pi^2}{12\left(\frac{\epsilon_F^2}{(k_B T)^2}\right)}\right] = \frac{\epsilon_F}{k_B T} \left[1 - \frac{\pi^2 (k_B T)^2}{12 \epsilon_F^2}\right] = \frac{\epsilon_F}{k_B T} \left[1 - \frac{\pi^2 (k_B T)^2}{12 (k_B T_F)^2}\right]$$

Simplifying the expression

$$\mu \approx \epsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right] \approx \epsilon_F \ (\text{if } T << T_F)$$

Number of electrons that can be excited at low temperature

The number of particles in excited states at temperature T can be obtained integrating the corresponding interval around the Fermi energy

$$n_{\mathrm{exc}} = \int_{\epsilon_{\mathrm{F}}-k_{\mathrm{B}}T}^{\epsilon_{\mathrm{F}}+k_{\mathrm{B}}T} n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) d\epsilon$$

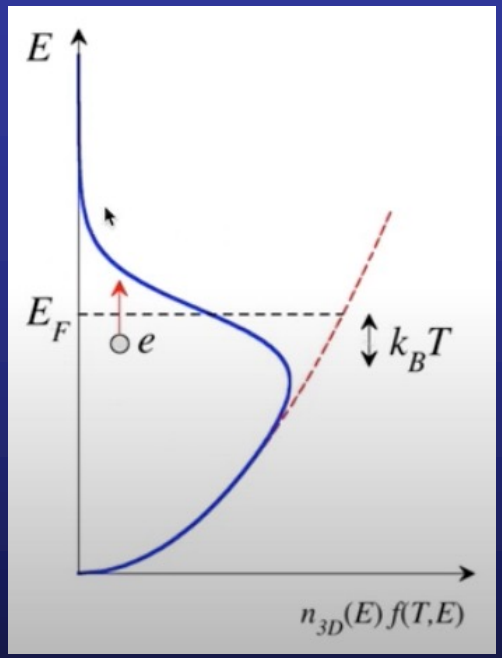
Assuming

$$\epsilon_{\mathrm{F}} >> k_{\mathrm{B}}T$$

$$n_{3\mathrm{D}}(\epsilon) = A\sqrt{\epsilon}$$

Then we can compute

$$n_{\mathrm{exc}} \approx A\sqrt{\epsilon_{\mathrm{F}}} \int_{\epsilon_{\mathrm{F}}-k_{\mathrm{B}}T}^{\epsilon_{\mathrm{F}}+k_{\mathrm{B}}T} f(T,\epsilon) d\epsilon = Ak_{\mathrm{B}}T\sqrt{\epsilon_{\mathrm{F}}}$$



$$z = \frac{\epsilon - \epsilon_{\mathrm{F}}}{k_{\mathrm{B}}T} \Rightarrow \int_{\epsilon_{\mathrm{F}}-k_{\mathrm{B}}T}^{\epsilon_{\mathrm{F}}+k_{\mathrm{B}}T} f(T,\epsilon) d\epsilon = k_{\mathrm{B}}T \int_{-1}^{1} \frac{1}{e^z+1} dz = k_{\mathrm{B}}T$$

$$n = \int_0^{\epsilon_{\mathrm{F}}} n_{3\mathrm{D}}(\epsilon) d\epsilon = A \int_0^{\epsilon_{\mathrm{F}}} \sqrt{\epsilon} d\epsilon = \frac{2}{3} A \epsilon_{\mathrm{F}}^{3/2}$$

$$\frac{n_{\mathrm{exc}}}{n} = \frac{3}{2}\frac{k_{\mathrm{B}}T}{\epsilon_{\mathrm{F}}} = \frac{3}{2}\frac{T}{T_{\mathrm{F}}}$$

Fraction of electrons thermally excited at finite temperatures beyond the Fermi energy

The specific heat capacity of electrons in metals

Due to the Pauli exclusion principle, only a fraction of the electrons of the order of $k_{\mathrm{B}}T/\epsilon_{\mathrm{F}}$ can absorb thermal energy

The energy absorbed per electron is of the order of $k_{\mathrm{B}}T$. Therefore, the increase in the energy density due to the thermally excited electrons is

$$u \sim \frac{T}{T_{\mathrm{F}}} \times k_{\mathrm{B}}T \times n + u(T=0) \Rightarrow C_{\mathrm{el,V}} = \frac{\partial u}{\partial T} \sim n k_{\mathrm{B}} \frac{T}{T_{\mathrm{F}}}$$

Linearly dependent on the temperature

Since the Fermi temperature is very large, the electronic contribution to the specific heat of the solid will be very small compared with the lattice contribution

The specific heat capacity of electrons in metals (more accurate calculation)

The change in the total energy of the system of N electrons on heating from 0 to T

$$\Delta U \equiv U(T) - U(0)$$

$$\Delta U(T) = \int_0^\infty d\epsilon \;\; \epsilon \, n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_\mathrm{F}} d\epsilon \;\; \epsilon \, n_{3\mathrm{D}}(\epsilon)$$

We can multiply the following identity…

$$N = \int_0^\infty d\epsilon \;\; n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) = \int_0^{\epsilon_\mathrm{F}} d\epsilon \;\; n_{3\mathrm{D}}(\epsilon)$$

… by the Fermi energy

$$\left(\int_0^{\epsilon_\mathrm{F}} + \int_{\epsilon_\mathrm{F}}^\infty \right) d\epsilon \;\; \epsilon_\mathrm{F} \, n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) = \int_0^{\epsilon_\mathrm{F}} d\epsilon \;\; \epsilon_\mathrm{F} \, n_{3\mathrm{D}}(\epsilon)$$

Then

$$\int_0^{\epsilon_\mathrm{F}} d\epsilon \;\; \epsilon_\mathrm{F} \;\; n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) + \int_{\epsilon_\mathrm{F}}^\infty d\epsilon \;\; \epsilon_\mathrm{F} \;\; n_{3\mathrm{D}}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_\mathrm{F}} d\epsilon \;\; \epsilon_\mathrm{F} \;\; n_{3\mathrm{D}}(\epsilon) = 0$$

The specific heat capacity of electrons in metals (more accurate calculation)

The change in the total energy of the system of N electrons on heating from 0 to T

$$\Delta U \equiv U(T) - U(0)$$

$$\int_0^\infty d\epsilon\ \epsilon\ n_{3D}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon\ n_{3D}(\epsilon) = \int_0^{\epsilon_F} d\epsilon\ \epsilon\ n_{3D}(\epsilon) f(T,\epsilon) + \int_{\epsilon_F}^\infty d\epsilon\ \epsilon\ n_{3D}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon\ n_{3D}(\epsilon).$$

Since

$$\int_0^{\epsilon_F} d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) f(T,\epsilon) + \int_{\epsilon_F}^\infty d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) = 0,$$

then we can substract the second equation from the first one

$$\begin{aligned}
&\int_0^{\epsilon_F} d\epsilon\ \epsilon\ n_{3D}(\epsilon) f(T,\epsilon) + \int_{\epsilon_F}^\infty d\epsilon\ \epsilon\ n_{3D}(\epsilon) f(T,\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon\ n_{3D}(\epsilon) \\
&\qquad - \int_0^{\epsilon_F} d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) f(T,\epsilon) - \int_{\epsilon_F}^\infty d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) f(T,\epsilon) + \int_0^{\epsilon_F} d\epsilon\ \epsilon_F\ n_{3D}(\epsilon) \\
&= \int_{\epsilon_F}^\infty d\epsilon\ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_0^{\epsilon_F} d\epsilon\ (\epsilon_F - \epsilon) n_{3D}(\epsilon) - \int_0^{\epsilon_F} d\epsilon\ (\epsilon_F - \epsilon) n_{3D}(\epsilon) f(T,\epsilon) \\
&= \int_{\epsilon_F}^\infty d\epsilon\ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_0^{\epsilon_F} d\epsilon\ (\epsilon_F - \epsilon)\left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon).
\end{aligned}$$

Therefore

$$\Delta U = \int_{\epsilon_F}^\infty d\epsilon\ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_0^{\epsilon_F} d\epsilon\ (\epsilon_F - \epsilon)\left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon).$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$\Delta U(T) = \int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon_F - \epsilon) \left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon)$$

The electronic heat capacity (at constant volumen) is defined as

$$C_{el,V} = \frac{\partial U}{\partial T}$$

Taking into account that the only term that depends on Temperature is the Fermi-Dirac distribution

$$\begin{aligned}
C_{el,V} &= \frac{\partial \Delta U}{\partial T} \\
&= \frac{\partial}{\partial T}\left[\int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon_F - \epsilon) \left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon)\right] \\
&= \int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) \frac{\partial f(T,\epsilon)}{\partial T} + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon_F - \epsilon) \left[-\frac{\partial f(T,\epsilon)}{\partial T}\right] n_{3D}(\epsilon) \\
&= \int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) \frac{\partial f(T,\epsilon)}{\partial T} + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon - \epsilon_F) \frac{\partial f(T,\epsilon)}{\partial T} n_{3D}(\epsilon) \\
&= \int_{0}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) \frac{\partial f(T,\epsilon)}{\partial T}
\end{aligned}$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$\Delta U(T) = \int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon_F - \epsilon) \left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon)$$

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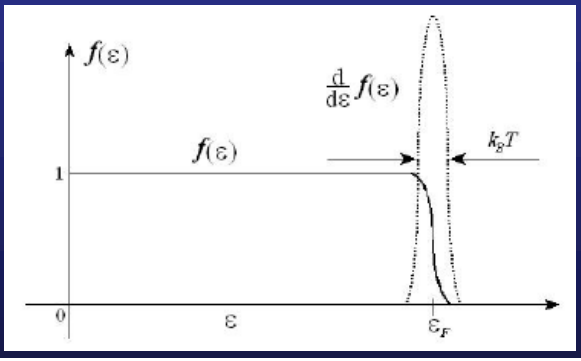
$$C_{el,V} = \frac{\partial U}{\partial T}$$

Taking into account that the only term that depends on Temperature is the Fermi-Dirac distribution

$$C_{el,V} = \frac{\partial U}{\partial T} = \int_{0}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) \frac{\partial f(T,\epsilon)}{\partial T} n_{3D}(\epsilon)$$

At low temperatures ($k_B T/\epsilon_F < 0.01$) of interest the derivative $\partial f(T,\epsilon)/\partial T$ is large only at energies near the Fermi energy.



The specific heat capacity of electrons in metals (more accurate calculation)

$$\Delta U(T) = \int_{\epsilon_F}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) n_{3D}(\epsilon) f(T,\epsilon) + \int_{0}^{\epsilon_F} d\epsilon \ (\epsilon_F - \epsilon) \left[1 - f(T,\epsilon)\right] n_{3D}(\epsilon)$$

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$$C_{el,V} = \frac{\partial U}{\partial T} = \int_{0}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) \frac{\partial f(T,\epsilon)}{\partial T} n_{3D}(\epsilon)$$

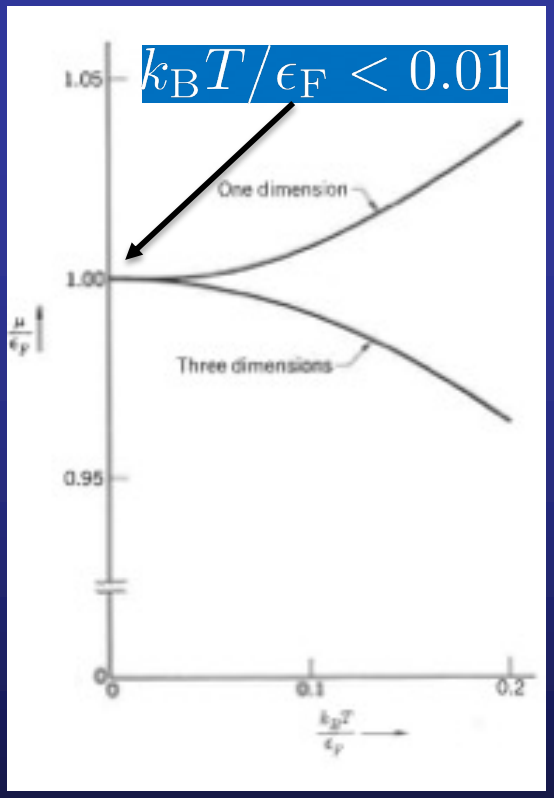
At low temperatures ($k_B T/\epsilon_F < 0.01$) of interest the derivative $\partial f(T,\epsilon)/\partial T$ is large only at energies near the Fermi energy.
We can take the density of states evaluated at the Fermi energy outside of the integral

$$C_{el,V} \approx n_{3D}(\epsilon_F) \int_{0}^{\infty} d\epsilon \ (\epsilon - \epsilon_F) \frac{\partial f(T,\epsilon)}{\partial T}$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$C_{\mathrm{el,V}} \approx n_{\mathrm{3D}}(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{\partial f(T,\epsilon)}{\partial T}$$

Assuming that, to first order in temperature the chemical potential does not depend on T, we can replace in the expression of the Fermi-Dirac distribution the chemical potential by the Fermi energy



$$\mu(T=0) \equiv \epsilon_{\mathrm{F}}$$

From Kittel

The specific heat capacity of electrons in metals (more accurate calculation)

$$C_{\mathrm{el,V}} \approx n_{\mathrm{3D}}(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{\partial f(T,\epsilon)}{\partial T}$$

Assuming that, to first order in temperature the chemical potential does not depend on T, we can replace in the expression of the Fermi-Dirac distribution the chemical potential by the Fermi energy

$$\mu(T=0) \equiv \epsilon_{\mathrm{F}}$$

Then, taking the derivative of the Fermi-Dirac distribution

$$\begin{aligned} f(T,\epsilon) &= \frac{1}{e^{\frac{(\epsilon-\mu)}{k_{\mathrm{B}}T}}+1} \\ &\approx \frac{1}{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1} \end{aligned}$$

$$\begin{aligned} \frac{\partial f(T,\epsilon)}{\partial T} &= \frac{\partial}{\partial T}\left[\frac{1}{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1}\right] \\ &= \frac{-\frac{\partial}{\partial T}\left(e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1\right)}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1\right]^2} \\ &= \frac{-\left(-\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T^2}e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}\right)}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1\right]^2} \\ &= \frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T^2}\frac{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}+1\right]^2} \end{aligned}$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$C_{\mathrm{el,V}} \approx n_{\mathrm{3D}}(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{\partial f(T,\epsilon)}{\partial T}$$

$$\frac{\partial f}{\partial T} = \frac{\epsilon - \epsilon_{\mathrm{F}}}{k_{\mathrm{B}} T^2} \frac{e^{(\epsilon-\epsilon_{\mathrm{F}})/k_{\mathrm{B}}T}}{\left[e^{(\epsilon-\epsilon_{\mathrm{F}})/k_{\mathrm{B}}T} + 1\right]^2}$$

$$C_{\mathrm{el},V} \approx n_{\mathrm{3D}}(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{\partial f(T,\epsilon)}{\partial T}$$

$$= n_{\mathrm{3D}} \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T^2} \frac{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}} + 1\right]^2}$$

$$= n_{\mathrm{3D}} \int_0^\infty d\epsilon \ \frac{k_{\mathrm{B}} T(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T} \frac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T^2} \frac{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}} + 1\right]^2}$$

$$= n_{\mathrm{3D}} \int_0^\infty d\epsilon \ \frac{k_{\mathrm{B}} (\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T} \frac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T} \frac{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}} + 1\right]^2}$$

$$= n_{\mathrm{3D}} k_{\mathrm{B}} \int_0^\infty d\epsilon \ \frac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T} \frac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}} T} \frac{e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}}}{\left[e^{\frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}} + 1\right]^2}$$

Setting $x \equiv \frac{(\epsilon-\epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T} \Rightarrow dx = \frac{d\epsilon}{k_{\mathrm{B}}T} \Rightarrow d\epsilon = k_{\mathrm{B}} T \, dx$,

and when $\epsilon = 0 \Rightarrow x = -\frac{\epsilon_{\mathrm{F}}}{k_{\mathrm{B}}T}$, then

$$C_{\mathrm{el},V} \approx n_{\mathrm{3D}} \left(k_{\mathrm{B}}^2 T\right) \int_{-\frac{\epsilon_{\mathrm{F}}}{k_{\mathrm{B}}T}}^\infty x^2 \frac{e^x}{(e^x+1)^2}$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$C_{\mathrm{el,V}} \approx n_{\mathrm{3D}}(\epsilon_{\mathrm{F}}) \int_0^\infty d\epsilon \ (\epsilon - \epsilon_{\mathrm{F}}) \frac{\partial f(T,\epsilon)}{\partial T}$$

Assuming that, to first order in temperature the chemical potential does not depend on T, we can replace in the expression of the Fermi-Dirac distribution the chemical potential by the Fermi energy

$$\mu(T=0) \equiv \epsilon_{\mathrm{F}}$$

Then, taking the derivative of the Fermi-Dirac distribution

$$\frac{\partial f}{\partial T} = \frac{\epsilon - \epsilon_{\mathrm{F}}}{k_{\mathrm{B}} T^2} \frac{e^{(\epsilon-\epsilon_{\mathrm{F}})/k_{\mathrm{B}}T}}{\left[e^{(\epsilon-\epsilon_{\mathrm{F}})/k_{\mathrm{B}}T}+1\right]^2}$$

Setting $x \equiv \dfrac{(\epsilon - \epsilon_{\mathrm{F}})}{k_{\mathrm{B}}T}$

$$C_{\mathrm{el,V}} = n_{\mathrm{3D}}(\epsilon_{\mathrm{F}})(k_{\mathrm{B}}^2 T) \int_{-\epsilon_{\mathrm{F}}/k_{\mathrm{B}}T}^\infty dx \ x^2 \frac{e^x}{(e^x+1)^2}$$

The specific heat capacity of electrons in metals (more accurate calculation)

$$C_{\mathrm{el,V}} = n_{3\mathrm{D}}(\epsilon_{\mathrm{F}})(k_{\mathrm{B}}^2 T) \int_{-\epsilon_{\mathrm{F}}/k_{\mathrm{B}}T}^{\infty} dx \;\; x^2 \frac{e^x}{(e^x+1)^2}$$

Because the factor e^x in the integrand is negligible at $x = -\epsilon_{\mathrm{F}}/k_{\mathrm{B}}T$ we may replace the lower limit by $-\infty$

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

$$C_{\mathrm{el},V} = \frac{1}{3}\pi^2 n_{3\mathrm{D}}(\epsilon_{\mathrm{F}}) k_{\mathrm{B}}^2 T$$

Since we have proved before that $n_{3\mathrm{D}}(\epsilon_{\mathrm{F}}) = \frac{3}{2}\frac{n}{\epsilon_{\mathrm{F}}}$

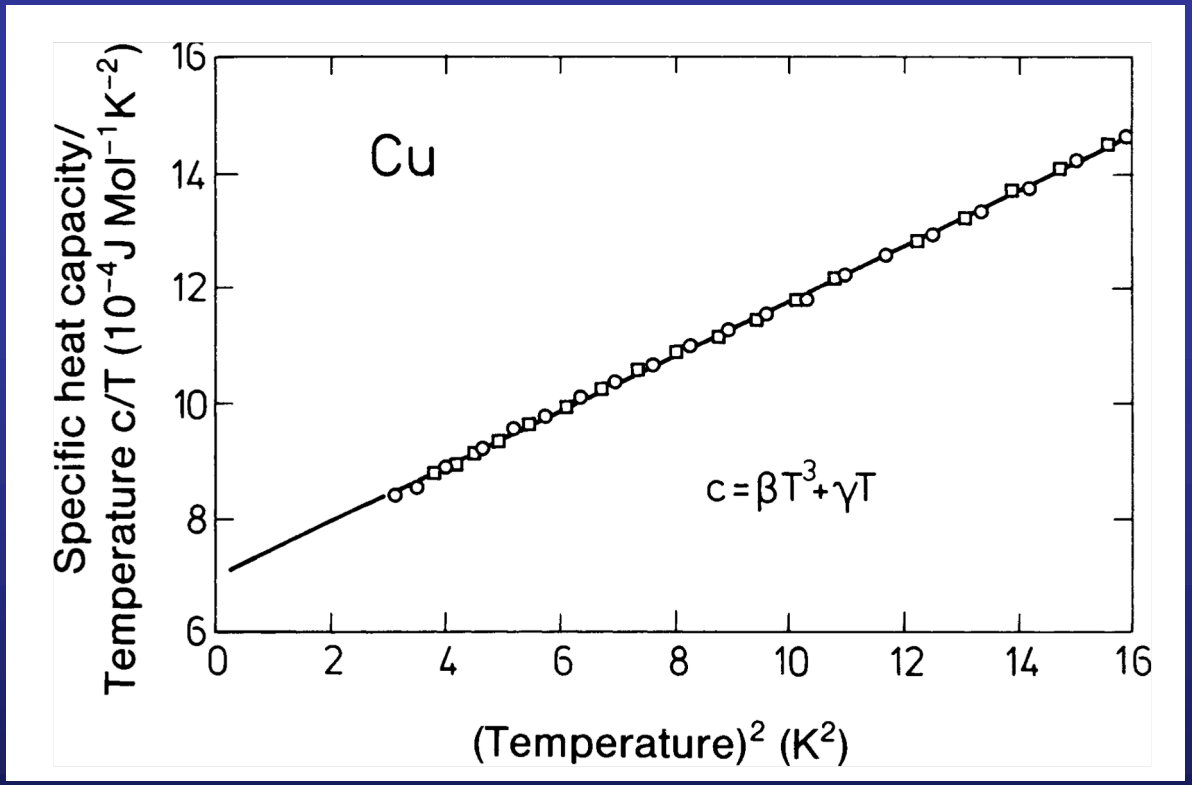
$$C_{\mathrm{el},V} = \frac{1}{2}\pi^2 n k_{\mathrm{B}} \frac{T}{T_{\mathrm{F}}}$$

Essentially the same expression as in the previous rough estimate

Experimental heat capacity of metals

$$C = \gamma T + AT^3$$

Phonon contribution to the specific heat
(Debye contribution)



From
Ibach-Lüth

Experimental heat capacity of metals

$$C = \gamma T + AT^3$$

Phonon contribution to the specific heat (Debye contribution)

Table 6.2. Comparison of experimentally determined values of the coefficient γ of electronic specific heat with values calculated using the free-electron-gas model. At low temperatures one has $c_v = \gamma T + \beta T^3$ for the combined electronic ($\propto T$) and ($\propto T^3$) contributions to the specific heat

Metal	γ_{exp} (10^{-3} J/Mol K^2)	$\gamma_{exp}/\gamma_{theo}$
Li	1.7	2.3
Na	1.7	1.5
K	2.0	1.1
Cu	0.69	1.37
Ag	0.66	1.02
Al	1.35	1.6
Fe	4.98	10.0
Co	4.98	10.3
Ni	7.02	15.3

From Ibach-Lüth

For transition metals the determined values of the electronic contribution to the specific heat bear little resemblance to those calculated from the electron gas

Experimental heat capacity of metals

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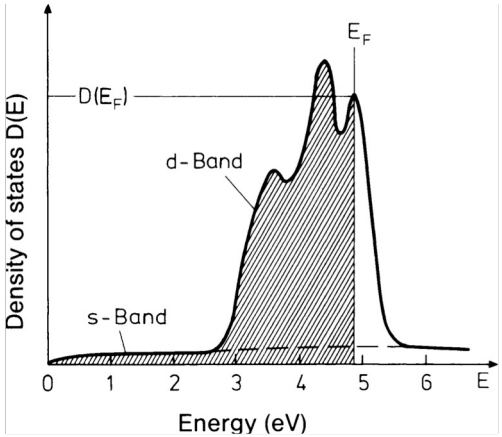

From Ibach-Lüth

Fig. 6.9. Qualitative behavior of the density of states $D(E)$ for the conduction band of a transition metal. The strong contribution of the d-electrons in the vicinity of the Fermi level lies on top of that of the s-band (*partially dashed*)

For transition metals the determined values of the electronic contribution to the specific heat bear little resemblance to those calculated from the electron gas

Fe, Co, Ni: d-electron shell is partially occupied.

The d-bands lie at the Fermi energy

The d-electrons are strongly localized around the atoms, and the overlap of their wave functions is small

Supporting slides

Computing the energy density of the electron gas

To calculate the ground-state energy of N electrons in a volume V we must add the energies of all the one-electron levels inside the Fermi sphere

$$E = 2 \sum_{k<k_{\mathrm{F}}} \frac{\hbar^2 k^2}{2m}$$

We can multiply and divide by the volume allowed per $\vec{k}$ point

$$E = 2 \sum_{k \leq k_{\mathrm{F}}} \frac{\hbar^2 k^2}{2m} \frac{\Delta k}{\Delta k} = \frac{2}{\Delta k} \sum_{k \leq k_{\mathrm{F}}} \frac{\hbar^2 k^2}{2m} \Delta k = \frac{2}{\left(\frac{2\pi}{L}\right)^3} \sum_{k \leq k_{\mathrm{F}}} \frac{\hbar^2 k^2}{2m} \Delta k = \frac{V}{4\pi^3} \sum_{k \leq k_{\mathrm{F}}} \frac{\hbar^2 k^2}{2m} \Delta k$$

Now, we take the macroscopic limit of the side of the cube $L \to \infty$

$$L \to \infty \Rightarrow V \to \infty \Rightarrow \Delta k = \left(\frac{2\pi}{L}\right)^3 \to 0$$

$$\sum_k F(\vec{k}) \Delta k \to \int d^3k \;\; F(\vec{k})$$

$$\lim_{V \to \infty} \frac{1}{V} \sum_k F(\vec{k}) \Delta k = \frac{1}{8\pi^3} \int d^3k \;\; F(\vec{k})$$