The Sommerfeld Theory of Metals

Outline

1. Ground-state properties of the free electron gas
2. Thermal properties of the free electron gas
3. The Sommerfeld theory of conduction in metals
4. Density of States (DOS)
5. Failures of the free electron model

1. Ground-state properties of the free electron gas
2. Thermal properties of the free electron gas
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4. Density of States (DOS)
5. Failures of the free electron model

Ground-state properties of the free electron gas

General remarks

Maxwell-Boltzmann velocity distribution

- Drude assumed the validity of the Maxwell-Boltzmann velocity distribution (at thermal equilibrium)

$$f_{MB}(\mathbf{v}) = n\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_B T}}$$

- normalized such that $\int f_{MB}(\mathbf{v}) d\mathbf{v} = n$, $n = \frac{N}{V}$
  - check yourself ($\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$)
- $f_{MB}(\mathbf{v}) d\mathbf{v}$: number of e^- with velocities in the volume element $d\mathbf{v}$ at $\mathbf{v}$
  - per unit volume
- Equipartition theorem follows ($c_v = \frac{3}{2} n k_B$; $\bar{\varepsilon} = \frac{3}{2} k_B T$)

Ground-state properties of the free electron gas

General remarks

Fermi-Dirac velocity distribution

- Valid for Fermions, as a consequence of the Pauli exclusion principle

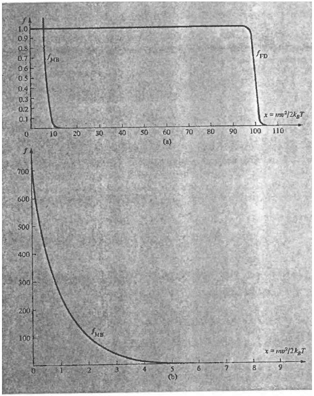
$$f_{FD}(\boldsymbol{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{e^{\frac{(\frac{1}{2}mv^2 - k_B T_0)}{k_B T}} + 1}$$

  - T_0 determined such that $\int f_{FD}(\boldsymbol{v}) d\boldsymbol{v} = n$ (tens of thousands K)
- Sommerfeld theory replaces $f_B(\boldsymbol{v})$ of Drude's theory with $f_{FD}(\boldsymbol{v})$
  - profound consequences on $\bar{\varepsilon}$ and c_v

Ground-state properties of the free electron gas

General remarks

Maxwell-Boltzmann vs Fermi-Dirac velocity distribution



Plot of Maxwell-Boltzmann and Fermi-Dirac distributions for the same n (typical metallic density) and $T = 0.01\,T_0$.

Ground-state properties of the free electron gas

Quantum mechanical solution

Mathematical treatment

- The free electron gas is confined in a cube of edge L ($L = V^{\frac{1}{3}}$)
  - mathematical convenience (shape does not affect bulk properties)
- Assume the independent electron approximation (IEA)
- Particular solutions of the TDSE: $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})e^{-i\frac{\varepsilon t}{\hbar}}$
- Solve the TISE:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

- Apply Born-von Karman periodic boundary conditions (PBCs) to the general solution
- Fill the (one-electron) energy levels by using the Pauli exclusion and auf-bau principles

Ground-state properties of the free electron gas

Quantum mechanical solution

Born-von Karman PBCs

- Needed to have running waves solutions (for charge and energy transport)
- Bulk properties should not be affected

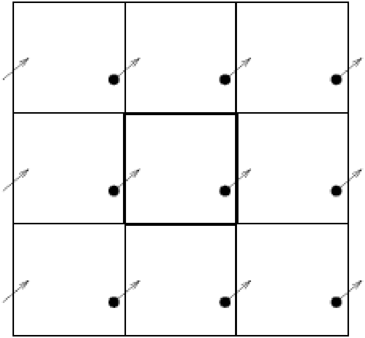
$$\begin{cases} \psi(x, y, z + L) = \psi(x, y, z) \\ \psi(x, y + L, z) = \psi(x, y, z) \\ \psi(x + L, y, z) = \psi(x, y, z) \end{cases}$$

- More complactly: $\psi(\boldsymbol{r} + \boldsymbol{R}) = \psi(\boldsymbol{r}) \quad \forall \boldsymbol{R} \in \mathcal{R}, \quad \forall \boldsymbol{r} \in V$
  - $\psi(\boldsymbol{r})$ is periodic in $\mathcal{R}$: Bravais lattice of which V is the primitive cell (volume of the macroscopic crystal sample)
  - primitive lattice vectors: $\boldsymbol{a}_1 = L\hat{\boldsymbol{x}}$, $\boldsymbol{a}_2 = L\hat{\boldsymbol{y}}$, $\boldsymbol{a}_3 = L\hat{\boldsymbol{z}}$

Ground-state properties of the free electron gas

Quantum mechanical solution

Periodic boundary conditions



PBCs of Born and von Karman applied to the highlighted square

Ground-state properties of the electron gas

Quantum mechanical solution

Separation of variables

- Ansatz $\psi(\boldsymbol{r}) = X(x)Y(y)Z(z)$
- Upon substitution on the TISE:

$$\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) & = \varepsilon_x X(x) \\ -\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y(y) & = \varepsilon_y Y(y) \\ -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}Z(z) & = \varepsilon_z Z(z) \end{cases}$$

- $\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z$

Ground-state properties of the free electron gas

Quantum mechanical solution

Separation of variables

- Ansatz $\psi(\boldsymbol{r}) = X(x)Y(y)Z(z)$
- The boundary conditions are:

$$\begin{cases} Z(z+L) = Z(z) \\ Y(y+L) = Y(y) \\ X(x+L) = X(x) \end{cases}$$

- Three similar homogeneous ODEs of the second order

Ground-state properties of the free electron gas

Quantum mechanical solution

General and particular solutions

$$\begin{cases} \frac{d^2}{dx^2}\phi(x) + k^2\phi(x) & = 0 \\ \phi(x+L) & = \phi(x) \end{cases}$$

- General solution: $\phi(x) = c_1 e^{ikx} + c_2 e^{-ikx}$
  - $k^2 = \frac{2m\varepsilon}{\hbar^2} \Longrightarrow \varepsilon = \frac{\hbar^2 k^2}{2m}$
- Particular (normalized) solution: $\phi(x) = \frac{1}{\sqrt{L}} e^{ikx}$
  - $k = \frac{2n\pi}{L}$, $n = 0, \pm 1, \pm 2, \dots$

Ground-state properties of the free electron gas

Quantum mechanical solution

Eigenfunctions and eigenvalues of the problem

- $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$
  - normalized inside the cube: $\int |\psi_{\boldsymbol{k}}(\boldsymbol{r})|^2 d\boldsymbol{r} = 1$
- allowed wave vectors $\boldsymbol{k}$:
  - $k_x = \frac{2\pi n_x}{L}$; $k_y = \frac{2\pi n_y}{L}$; $k_z = \frac{2\pi n_z}{L}$
  - $n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots$
- $\varepsilon = \varepsilon(|\boldsymbol{k}|) = \frac{\hbar^2 k^2}{2m}$ (dispersion relation)
- Solution of the TDSE: $\Psi(\boldsymbol{r}, t) = \frac{1}{\sqrt{V}} e^{i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)}$
  - running waves ($\lambda = \frac{2\pi}{k}$, $\varepsilon = \hbar\omega$)
- Isoenergetic surfaces are spheres (circles in 2D)

Ground-state properties of the free electron gas

Quantum mechanical solution

Another look at the quantization of the wave number

- Apply the Born-von Karman PBCs to the solution $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$:
  - $\psi(\boldsymbol{r}+\boldsymbol{R}) = \psi(\boldsymbol{r}) \longrightarrow e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = 1 \longrightarrow \boldsymbol{k}\cdot\boldsymbol{R} = 2\pi n \;\; \forall \boldsymbol{R} \in \mathcal{R}, \quad n \in \mathbb{Z}$
  - $\boldsymbol{k} \in \mathcal{R}^*$, the reciprocal Bravais lattice of $\mathcal{R}$
- allowed wave vectors $\boldsymbol{k}$ are all the reciprocal lattice vectors $\boldsymbol{k} \in \mathcal{R}^*$
  - primitive lattice vectors of $\mathcal{R}^*$: $\boldsymbol{b}_1 = \frac{2\pi}{L}\hat{\boldsymbol{x}}$; $\boldsymbol{b}_2 = \frac{2\pi}{L}\hat{\boldsymbol{y}}$; $\boldsymbol{b}_3 = \frac{2\pi}{L}\hat{\boldsymbol{z}}$
  - if $\mathcal{R}$ is SC $\longrightarrow \mathcal{R}^*$ is SC
- Therefore: $\boldsymbol{k} = n_x\boldsymbol{b}_1 + n_y\boldsymbol{b}_2 + n_z\boldsymbol{b}_3 = \frac{2\pi}{L}(n_x, n_y, n_z) \; \forall n_x, n_y, n_z \in \mathbb{Z}$
- Allowed states are indexed by the wave vector $\boldsymbol{k}$
  - infinite set but countable

Ground-state properties of the free electron gas

Quantum mechanical solution

Eigenfunctions and eigenvalues of the problem

- $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ is eigenfunction of the momentum operator $\boldsymbol{p} = \frac{\hbar}{i}\nabla$
  - $\frac{\hbar}{i}\nabla\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \boldsymbol{p}\psi_{\boldsymbol{k}}(\boldsymbol{r})$; $\boldsymbol{p} = \hbar\boldsymbol{k}$
- Its velocity is $\boldsymbol{v} = \frac{\boldsymbol{p}}{m} = \frac{\hbar\boldsymbol{k}}{m}$
- Its energy is $\varepsilon = \frac{p^2}{2m}$
- its wavelength is $\lambda = \frac{2\pi}{k}$ (de Broglie wavelength)

Ground-state properties of the free electron gas

Quantum mechanical solution

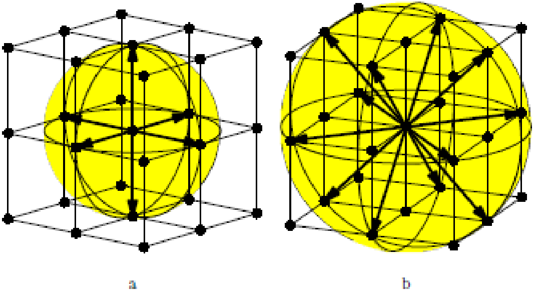
Eigenfunctions and eigenvalues of the problem

- Degenerate states corresponds to $\boldsymbol{k}$ points laying on the surface of a sphere
  - $k_x^2 + k_y^2 + k_z^2 = \frac{2m\varepsilon}{\hbar^2}$
  - centered at the origin of $\mathcal{R}^*$
- Lowest energy corresponds to $\boldsymbol{k} = 0$ ($\varepsilon_0 = 0$)
- ε_1 is 6-fold degenerate
  - $\boldsymbol{k}$ points at: $\frac{2\pi}{L}(\pm 1, 0, 0)$; $\frac{2\pi}{L}(0, \pm 1, 0)$; $\frac{2\pi}{L}(0, 0 \pm 1)$
- ε_2 is 12-fold degenerate
  - $\boldsymbol{k}$ points at: $\frac{2\pi}{L}(\pm 1, 0, 1)$; $\frac{2\pi}{L}(0, \pm 1, 1)$; $\frac{2\pi}{L}(\pm 1, 1, 0)$; $\frac{2\pi}{L}(\pm 1, -1, 0)$; $\frac{2\pi}{L}(\pm 1, 0, -1)$; $\frac{2\pi}{L}(0, \pm 1, -1)$
- degeneracy increases very quickly with distance from $\boldsymbol{O}$
- $\varepsilon_2 - \varepsilon_1 = \frac{\hbar^2}{2m}(\frac{2\pi}{L})^2 = 1.5 \times 10^{-14}$eV for $L = 1$cm
  - very small spacing (approaching a continuum)

Ground-state properties of the free electron gas

Quantum mechanical solution

Eigenfunctions and eigenvalues of the problem



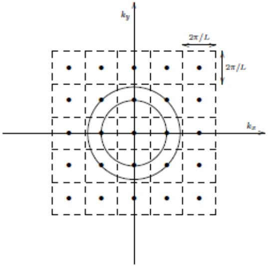
degenerate $\boldsymbol{k}$ points corresponding to ε_1 (left) and ε_2 (right)

Ground-state properties of the free electron gas

Quantum mechanical solution

Counting the quantum mechanical solutions

- Volume per allowed wave vector in k-space: $(\frac{2\pi}{L})^3 = \frac{8\pi^3}{V}$
- For a region Ω, the number is $\frac{\Omega V}{8\pi^3}$
  - must be very large on the scale of $\frac{2\pi}{L}$
  - not too irregularly shaped
- k-space density of levels: $\frac{V}{8\pi^3}$



Ground-state properties of the free electron gas

Quantum mechanical solution

Occupation of the ground-state ($T = 0$K)

- Place a maximum of two e^- on each level, starting with the lowest
  - $\boldsymbol{k} = 0 \Longrightarrow \varepsilon_{\boldsymbol{k}} = 0$
  - $\psi \equiv \psi_{\boldsymbol{k}\sigma}$, $\sigma = \pm\frac{1}{2}$
- $\varepsilon_{\boldsymbol{k}}$ varies with the distance squared from O
- The occupied region is a sphere (Fermi sphere)
  - for very large N
  - radius k_F: Fermi wave vector
  - volume: $\Omega = \frac{4\pi}{3}k_F^3$
- $N = 2\frac{\Omega V}{8\pi^3} = 2(\frac{4\pi k_F^3}{3})(\frac{V}{8\pi^3}) = \frac{k_F^3}{3\pi^2}V$

Ground-state properties of the free electron gas

Quantum mechanical solution

Occupation of the ground-state ($T = 0$K)

- Given a density $n = \frac{N}{V}$, the ground-state is formed by:
  - occupying all levels with $k < k_F$
  - all levels with $k > k_F$ are empty
  - $k_F = (3\pi^2 n)^{\frac{1}{3}}$
- Some nomenclature:
  - region Ω: Fermi sphere
  - k_F: Fermi wave vector
  - surface of Ω: Fermi surface (solution of $\varepsilon(\boldsymbol{k}) = \varepsilon_F$)
  - $p_F = \hbar k_F$: Fermi momentum
  - $v_F = \frac{p_F}{m}$: Fermi velocity
  - $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$: Fermi energy
  - $T_F = \frac{\varepsilon_F}{k_B}$: Fermi temperature
- The Fermi surface separates occ. and unocc. states at T=0 K
- The above quantities can be estimated from n

Ground-state properties of the free electron gas

Quantum mechanical solution

Some numbers

- $k_F = \frac{\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}}{r_s} = \frac{1.92}{r_s} = \frac{3.63}{\frac{r_s}{a_0}}\text{Å}^{-1}$
  - $r_s \sim$2–6 Å $\Longrightarrow k_F \sim \text{Å}^{-1}$ $(\lambda \sim \text{Å})$
- $v_F = \frac{\hbar}{m}k_F = \frac{4.20}{\frac{r_s}{a_0}} \times 10^8 \text{cm/s}$
  - 1% of c, (classical estimate at room temperature $v \sim 10^7$cm/s)
- $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right)(k_F a_0)^2 = \frac{50.1}{\left(\frac{r_s}{a_0}\right)^2}$ eV
  - $\varepsilon_F \in$ 1.5–15 eV
- $T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{\left(\frac{r_s}{a_0}\right)^2} \times 10^4\text{K}$
  - energy per electron of a classical ideal gas vanishes at $T = 0\text{K}$ $(\bar{\varepsilon} = \frac{3}{2}k_B T)$

Ground-state properties of the free electron gas

Quantum mechanical solution

Some numbers

FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS[a]

ELEMENT	r_s/a_0	$\mathcal{E}_F$	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	1.12×10^8 cm^{-1}	1.29×10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

Ground-state properties of the free electron gas

Quantum mechanical solution

Total energy of the ground-state ($T = 0$K)

- $E = 2 \times \sum_{k<k_F} \varepsilon_{\boldsymbol{k}} = \sum_{k<k_F} 2 \times \frac{\hbar^2 k^2}{2m}$
- Standard way of treating summations:

$$\sum_{\boldsymbol{k}} F(\boldsymbol{k}) = \frac{V}{8\pi^3} \sum_{\boldsymbol{k}} F(\boldsymbol{k}) \Delta \boldsymbol{k}$$

$$\lim_{V\to\infty} \frac{1}{V} \sum_{\boldsymbol{k}} F(\boldsymbol{k}) = \int \frac{F(\boldsymbol{k})}{8\pi^3} d\boldsymbol{k}$$

- Therefore:

$$\frac{E}{V} = 2 \int_{k<k_F} \frac{d\boldsymbol{k}}{8\pi^3} \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$$

Ground-state properties of the free electron gas

Quantum mechanical solution

Total energy of the ground-state ($T = 0$K)

- $\frac{E}{V} = \frac{1}{\pi^2}\frac{\hbar^2 k_F^5}{10m}$
  - energy density of the electron gas
- $\frac{E}{N} = \frac{3}{5}\varepsilon_F = \frac{3}{5}k_B T_F$
  - for a classical particle $\frac{E}{N} = \frac{3}{2}k_B T \Longrightarrow T = \frac{2}{5}T_F \sim 10^4$K

Ground-state properties of the free electron gas

Quantum mechanical solution

Bulk properties of the ground-state

- $dU = TdS - pdV + \mu dN \longrightarrow dE = -pdV + \mu dN$ at T=0K
- Electronic pressure: $P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3}\frac{E}{V}$
  - exerted by the electron gas
- Compressibility: $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$
- Bulk modulus: $B = \frac{1}{K} = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2}{3}n\varepsilon_F$
  - $B = \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10}$dynes/cm^2

Ground-state properties of the free electron gas

Quantum mechanical solution

Bulk properties of the ground-state

BULK MODULI IN 10^{10} DYNES/CM² 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

- Electronic contribution cannot completely determine the resistance of a metal to compression
  - electronic contribution as important as other effects

1 Ground-state properties of the free electron gas

2 Thermal properties of the free electron gas

3 The Sommerfeld theory of conduction in metals

4 Density of States (DOS)

5 Failures of the free electron model

Thermal properties of the free-electron gas

The Fermi-Dirac distribution

The partition function

- If T$\neq$ 0, N-electron excited states become populated
  - thermal equilibrium is assumed
- Boltzmann distribution law:

$$P_N(E) = \frac{e^{-\frac{E}{k_B T}}}{\sum_\alpha e^{-\frac{E_\alpha^N}{k_B T}}}$$

- $P_N(E)$: probability of finding the system in the N-electron state of energy E
- $Z = \sum_\alpha e^{-\frac{E_\alpha^N}{k_B T}}$ is the partition function
  - the sum is over all N-electron states

Thermal properties of the free-electron gas

The Fermi-Dirac distribution

Derivation

- Consider a N-electron system at constant volume V and at thermal equilibrium at a T
- The N-electron state is specified by a list of the one-electron levels occupied
  - states $\psi_{\boldsymbol{k}\sigma}(\boldsymbol{r})$
- Define $f_i^N = \sum_\alpha P_N(E_\alpha^N)$
  - α runs over all N-electron states with level i occupied
  - $0 \leq f_i^N \leq 1$ (Pauli exclusion principle)
- f_i^N: probability that the one-electron level i is occupied
  - average occupation of level i
  - we will find an explicit expression for f_i^N

Thermal properties of the free-electron gas

The Fermi-Dirac distribution

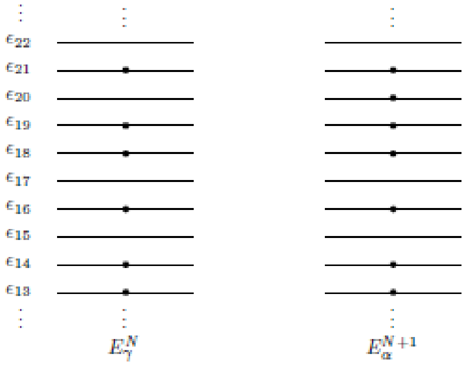
Derivation

- Helmholtz free energy: $F_N = U - TS = -k_B T \ln(Z)$
  - $Z = e^{-\frac{F_N}{k_B T}} \longrightarrow P_N(E) = e^{-\frac{E-F_N}{k_B T}}$
- $f_i^N = 1 - \sum_\gamma P_N(E_\gamma^N)$
  - γ labels N-electron states where i is not occupied
- $f_i^N = 1 - \sum_\gamma P_N(E_\alpha^{N+1} - \varepsilon_i)$
  - $E_\gamma^N = E_\alpha^{N+1} - \varepsilon_i$
  - $N+1$-electron states obtained from γ's by placing an electron in level i
- $\mu = F_{N+1} - F_N \Longrightarrow f_i^N = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} \sum_\alpha P_{N+1}(E_\alpha^{N+1})$
- $f_i^N = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} f_i^{N+1}$

Thermal properties of the free-electron gas

The Fermi-Dirac distribution

Bijective map $E_\gamma^N \iff E_\alpha^{N+1}$



Thermal properties of the free-electron gas

The Fermi-Dirac distribution

Derivation

- Assuming that $f_i^N = f_i^{N+1}$ for $N \sim 10^{22}$

$$f_i^N = \frac{1}{e^{\frac{(\varepsilon_i - \mu)}{k_B T}} + 1}$$

- $N = \sum_i f_i^N = \sum_i \frac{1}{e^{\frac{(\varepsilon_i - \mu)}{k_B T}} + 1}$
  - N (or $n = \frac{N}{V}$) as a function of T and μ
  - We can express μ as a function of n and T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Limiting form of f_i^N

- In the ground-state:

$$\begin{cases} f_{\boldsymbol{k}\sigma} = 1 & \varepsilon(\boldsymbol{k}) < \varepsilon_F \\ f_{\boldsymbol{k}\sigma} = 0 & \varepsilon(\boldsymbol{k}) > \varepsilon_F \end{cases}$$

- For the f_i^N distribution we have

$$\begin{cases} f_{\boldsymbol{k}\sigma} = 1 & \varepsilon(\boldsymbol{k}) < \mu \\ f_{\boldsymbol{k}\sigma} = 0 & \varepsilon(\boldsymbol{k}) > \mu \end{cases}$$

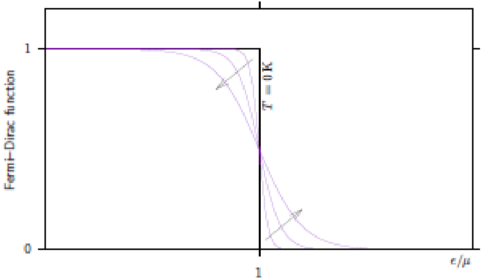
- Therefore $\lim_{T\to 0} \mu = \varepsilon_F$
- $\mu \sim \varepsilon_F$ also at room T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

properties

- $f(\varepsilon, T) = \frac{1}{1+e^{\frac{(\varepsilon-\mu)}{k_B T}}} = \frac{1}{1+e^{\frac{(\frac{\varepsilon}{\mu}-1)}{\frac{k_B T}{\mu}}}} = f(\frac{\varepsilon}{\mu}, \frac{k_B T}{\mu})$
- $\lim_{\frac{\varepsilon}{\mu}\to-\infty} f = 1$ (finite T)
- $\lim_{\frac{\varepsilon}{\mu}\to\infty} f = 0$ (finite T)

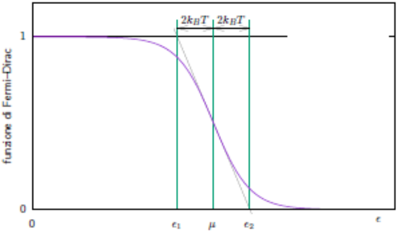


Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

properties

- $(\varepsilon = \mu, \frac{1}{2})$ is an inflection point
- consider the tangent to it and its intersections with $f = 0$ (ε_2) and $f = 1$ (ε_1)
- $\varepsilon_2 - \varepsilon_1 = 4k_B T$
  - $k_B T = 0.026\text{eV}$ at room T



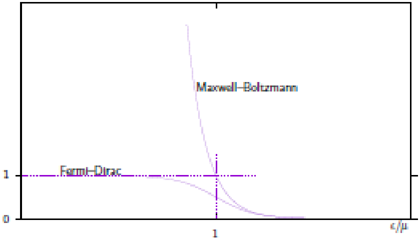
Broadening of the Fermi function as a function of T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Comparison with the Maxwell-Boltzmann distribution

- Maxwell-Boltzmann distribution: $b(\varepsilon, T) = e^{-\frac{\varepsilon-\mu}{k_B T}}$
  - Average occupation of state at energy ε
- The two distributions overlap for $\frac{\varepsilon-\mu}{k_B T} >> 1$



Comparison of the Maxwell-Boltzmann and Fermi-Dirac distribution functions

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Total energy of the electron gas

- At any T, $U = 2\sum_{\boldsymbol{k}} \varepsilon(\boldsymbol{k}) f(\varepsilon(\boldsymbol{k}))$

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

- Defining $u = \frac{U}{V}$

$$u = \int \frac{d\boldsymbol{k}}{4\pi^3} \varepsilon(\boldsymbol{k}) f(\varepsilon(\boldsymbol{k}))$$

- From $N = 2\sum_{\boldsymbol{k}} f(\varepsilon(\boldsymbol{k}))$

$$n = \frac{N}{V} = \int \frac{d\boldsymbol{k}}{4\pi^3} f(\varepsilon(\boldsymbol{k}))$$

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Density of states (DOSs

- Working in spherical coordinates:

$$\int \frac{d\boldsymbol{k}}{4\pi^3} f(\varepsilon(\boldsymbol{k})) = \int_0^\infty \frac{k^2 dk}{\pi^2} F(\varepsilon(\boldsymbol{k})) = \int_{-\infty}^\infty d\varepsilon g(\varepsilon) f(\varepsilon)$$

- Integral evaluation of $\frac{1}{V}\sum_{\boldsymbol{k}\sigma} f(\varepsilon(\boldsymbol{k}))$
- $g(\epsilon)$: density of levels (per unit volume)

$$g(\varepsilon) = \begin{cases} \frac{m}{\hbar^2\pi^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}} & \varepsilon > 0 \\ 0 & \varepsilon < 0 \end{cases}$$

- At the Fermi level: $g(\varepsilon_F) = \frac{mk_F}{\hbar^2\pi^2}$

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Density of levels

- Alternatively:

$$g(\varepsilon) = \begin{cases} \frac{3}{2}\frac{n}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2} & \varepsilon > 0 \\ 0 & \varepsilon < 0 \end{cases}$$

- At the Fermi level: $g(\varepsilon_F) = \frac{3}{2}\frac{n}{\varepsilon_F}$

Total energy and density of the electron gas

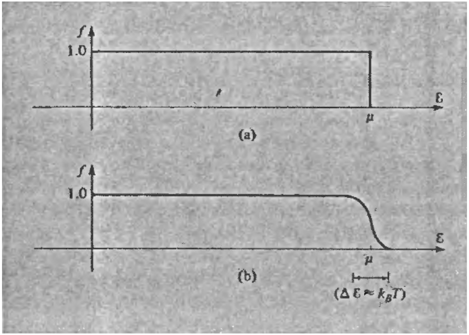
- $u = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon)\varepsilon f(\varepsilon)$
- $n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon)$
- valid for any non-interacting electron systems

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

The Sommerfeld expansion

- For metals, $T << T_F$ even at room T
- For $T \neq 0$ $f(\varepsilon)$ differs little from its T=0 form
  - region $\Delta\varepsilon \sim k_B T$ around μ



Fermi function f for given μ at $T = 0\,\mathrm{K}$ (top) and room temperature (bottom)

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

The Sommerfeld expansion

- Applied to integrals of the type $\int_{-\infty}^{\infty} H(\varepsilon)f(\varepsilon)d\varepsilon$
- If $H(\varepsilon)$ does not vary much for $\Delta\varepsilon \sim k_B T$ around μ
  - Taylor expansion of $H(\varepsilon)$ around μ
  - assumed to converge rapidly for well-behaved $H(\varepsilon)$

$$
\begin{aligned}
\int_{-\infty}^{\infty} H(\varepsilon)f(\varepsilon)d\varepsilon &= \int_{-\infty}^{\mu} H(\varepsilon)d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) \\
&+ \frac{7\pi^4}{360}(k_B T)^4 H'''(\mu) + O\left(\frac{k_B T}{\mu}\right)^6
\end{aligned}
$$

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Specific heat of the electron gas

- Apply the Sommerfeld expansion to both u and n:

$$u = \int_0^{\mu} \varepsilon g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \left[\mu g'(\mu) + g(\mu)\right] + O(T^4)$$

$$n = \int_0^{\mu} g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) + O(T^4)$$

- Also, to order T^2:

$$\int_0^{\mu} H(\varepsilon)\, d\varepsilon = \int_0^{\varepsilon_F} H(\varepsilon)\, d\varepsilon + (\mu - \varepsilon_F) H(\varepsilon_F)$$

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Specific heat of the electron gas

- Therefore:

$$u = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\, d\varepsilon + \varepsilon_F \left\{ (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right\} + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)$$

$$n = \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon + \left\{ (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \right\}$$

- Note:
  - $n = \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon$ (number density)
  - $u_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\, d\varepsilon$ (GS energy density)

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Deviation of μ from ε_F

- From:

$$0 = (\mu - \varepsilon_F) g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F)$$

- We get:

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} = \varepsilon_F \left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right]$$

- Shift of order T^2: difference is $\sim 0.01\%$ even at room T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

heat capacity, c_v

- From:

$$u = u_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F)$$

- We get:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{\pi^2}{3} k_B^2\, T g(\varepsilon_F) = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$$

  - varies linearly with T
  - compare with the classical result $c_v = \frac{3}{2} n k_B \left(\frac{\pi^2}{3}\frac{k_B T}{\varepsilon_F} \sim 10^{-2}\right)$
  - electronic contribution is negligible even at room T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Specific heat capacity, c_v: qualitative considerations

- From the T-dependence of the Fermi function $f(\varepsilon)$:
  - nr. of electrons excited (per unit volume): $\sim g(\varepsilon_F) \times k_B T$
  - excitation energy: $\sim k_B T$
  - energy density: $\sim (k_B T)^2 g(\varepsilon_F) \rightarrow c_v \sim k_B^2 T g(\varepsilon_F)$

Fermi function at non-zero T

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Experimental verification of $c_v = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$

- At room T c_v is determined by the ionic contribution ($\propto T^3$ for $T \to 0$)
  - $c_v = \gamma T + AT^3$
- Experimental data (of c_p) are fitted to the equation: $\frac{c_v}{T} = \gamma + AT^2$
  - electronic contribution is comparable to the ionic at T of few K
  - extrapolate at $T \to 0$
- Experimentally $[C] = \left[\frac{\text{cal}}{\text{K mol}}\right]$. Multiply by $\frac{ZN_A}{n}$:
  - $C = \frac{\pi^2}{3} ZR \frac{k_B T g(\varepsilon_F)}{n}$
  - $\implies \gamma = \frac{1}{2}\pi^2 R \frac{Z}{T_F} = 0.169\, Z \left(\frac{r_s}{a_0}\right)^2 \times 10^{-4}\, \text{cal mol}^{-1}\text{K}^{-2}$

Thermal properties of the free-electron gas

Applications of the Fermi-Dirac distribution

Experimental verification of $c_v = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$

SOME ROUGH EXPERIMENTAL VALUES FOR THE COEFFICIENT OF THE LINEAR TERM IN T OF THE MOLAR SPECIFIC HEATS OF METALS, AND THE VALUES GIVEN BY SIMPLE FREE ELECTRON THEORY

ELEMENT	FREE ELECTRON γ (in 10^{-4} cal-mole^{-1}-K^{-2})	MEASURED γ (in 10^{-4} cal-mole^{-1}-K^{-2})	RATIO[a] (m^*/m)
Li	1.8	4.2	2.3
Na	2.6	3.5	1.3
K	4.0	4.7	1.2
Rb	4.6	5.8	1.3
Cs	5.3	7.7	1.5
Cu	1.2	1.6	1.3
Ag	1.5	1.6	1.1
Au	1.5	1.6	1.1
Be	1.2	0.5	0.42
Mg	2.4	3.2	1.3
Ca	3.6	6.5	1.8
Sr	4.3	8.7	2.0
Ba	4.7	6.5	1.4
Nb	1.6	20	12
Fe	1.5	12	8.0
Mn	1.5	40	27
Zn	1.8	1.4	0.78
Cd	2.3	1.7	0.74
Hg	2.4	5.0	2.1
Al	2.2	3.0	1.4
Ga	2.4	1.5	0.62
In	2.9	4.3	1.5
Tl	3.1	3.5	1.1
Sn	3.3	4.4	1.3
Pb	3.6	7.0	1.9
Bi	4.3	0.2	0.047
Sb	3.9	1.5	0.38

- good agreement for the alkali metals
- gross discrepancies for Fe, Mn, Bi, Sb

1 Ground-state properties of the free electron gas

2 Thermal properties of the free electron gas

3 The Sommerfeld theory of conduction in metals

4 Density of States (DOS)

5 Failures of the free electron model

Sommerfeld theory of conduction in metals

Fermi-Dirac velocity distribution

Velocity distribution for electrons in a metal

- Consider an element of volume $d\boldsymbol{k}$ around $\boldsymbol{k}$
  - number of one-electron levels: $2 \times \left(\frac{V}{(2\pi)^3}\right) = \frac{V}{(4\pi^3)}\, d\boldsymbol{k}$
  - probability of occupation: $f(\varepsilon(\boldsymbol{k}))$
  - total number of electrons: $f(\varepsilon(\boldsymbol{k}))\frac{V}{(4\pi^3)}\, d\boldsymbol{k}$
  - with velocity $\boldsymbol{v} = \dfrac{\hbar\boldsymbol{k}}{m} \to d\boldsymbol{k} = \left(\frac{m}{\hbar}\right)^3 d\boldsymbol{v}$
- therefore the number of electrons with velocity $\in (\boldsymbol{v}, \boldsymbol{v} + d\boldsymbol{v})$ is:

$$f(\boldsymbol{v})\, d\boldsymbol{v} = \frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3} \frac{1}{e^{\frac{1/2\, mv^2 - \mu}{k_B T}} + 1} d\boldsymbol{v}$$

  - probability density (per unit volume)

Sommerfeld theory of conduction in metals

Validity of the classical description

$\Delta x \, \Delta p \sim \hbar$

- Sommerfeld used the Fermi-Dirac velocity distribution in an otherwise classical theory
- Classical description of electron dynamics is valid if:
  - $\boldsymbol{r}$ and $\boldsymbol{p}$ can be specified as accurately as necessary
  - without violating the uncertainty principle ($\Delta x \, \Delta p \sim \hbar$)
- The classical description is valid if:
  - $\Delta p << \hbar k_F \sim p$
  - $\Delta x \sim \frac{\hbar}{\Delta p} >> \frac{1}{k_F} \sim r_s \sim 2\text{–}6\,\text{Å}$

Sommerfeld theory of conduction in metals

Validity of the classical description

$\Delta x \, \Delta p \sim \hbar$

- Electronic position must be specified in some instances:
  - for applied electromagnetic fields ($\Delta x << \lambda$)
  - for applied T gradients
- Conclusions of the models were valid if $\boldsymbol{E}$ or T vary negligibly in the scale of Δx
  - valid for UV-vis radiation, not X-rays (QM must be used)
  - usually valid for normal ∇T's
- We assumed $\Delta x << l$, the mean free path
  - $l \sim 100\,\text{Å}$ at room T

Sommerfeld theory of conduction in metals

Improvements over Drude's theory

The use of Fermi-Dirac velocity distribution

- Affected properties:
  - mean free path
  - thermal conductivity
  - thermopower
- Properties not affected:
  - magnetoresistance
  - Hall coefficient
  - DC and AC conductivities

Sommerfeld theory of conduction in metals

Improvements over Drude's theory

Mean free path

- From $l = v_F \tau \rightarrow l = \dfrac{(r_s/a_0)^2}{\rho_\mu} \times 92\,\text{Å}$
  - $l \sim 100\,\text{Å}$ are possible at room T

Thermal conductivity

- From $\kappa = \dfrac{1}{3} v^2 \tau c_v$

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8}\,\text{watt} \cdot \text{ohm}/\text{K}^2$$

  - excellent agreement with exp.

Sommerfeld theory of conduction in metals

Improvements over Drude's theory

Thermopower

- With Sommerfeld estimate of the specific heat:

$$Q = -\frac{\pi^2}{6}\frac{k_B}{e}\left(\frac{k_B T}{\varepsilon_F}\right) = -1.42\left(\frac{k_B T}{\varepsilon_F}\right) \times 10^{-4}\,\text{volt/K}$$

  - smaller by $O\left(\frac{k_B T}{\varepsilon_F}\right) \sim 0.01$ at room T

1. Ground-state properties of the free electron gas
2. Thermal properties of the free electron gas
3. The Sommerfeld theory of conduction in metals
4. Density of States (DOS)
5. Failures of the free electron model

Density of States

Motivation

Density of States

- The number of accessible electronic states in a macroscopically large solid is enormous $\Rightarrow$ individual state-by-state treatment is impossible
- In contrast, atoms/molecules (finite systems) have few electrons $\Rightarrow$ state-by-state analysis is standard
- density of states: number of allowed states per unit energy interval and unit volume
    - the number of states depends linearly on V
- $g(\varepsilon)d\varepsilon$: number of electronic states in the energy interval $[\varepsilon, \varepsilon + d\varepsilon]$ per unit V

Density of States

DOS from the cumulative number of allowed states

- Let $N(\epsilon)$ be the total number of allowed states with energy $\leq \epsilon$:

$$g(\epsilon) = \frac{1}{V} \lim_{\Delta\epsilon \to 0} \frac{N(\epsilon + \Delta\epsilon) - N(\epsilon)}{\Delta\epsilon} = \frac{1}{V} \frac{dN(\epsilon)}{d\epsilon}$$

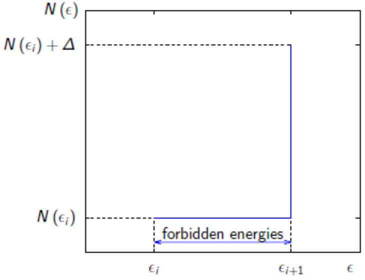
- Number of states in a finite interval:

$$N(\epsilon + \Delta\epsilon) - N(\epsilon) = V \int_{\epsilon}^{\epsilon+\Delta\epsilon} g(\epsilon')\, d\epsilon'$$

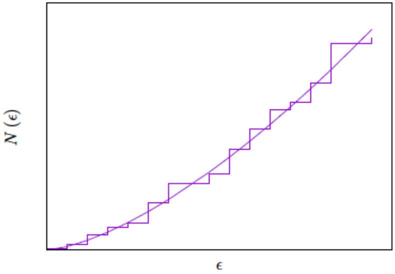
- Warning: $N(\epsilon)$ is a step function $\Rightarrow$ $\frac{dN}{d\varepsilon}$ diverges at each step
  - need a continuous approximation to $N(\varepsilon)$
  - good approximation since $\Delta\varepsilon$ is tiny
  - the formally correct approach uses the Dirac delta function

Density of States

DOS from the cumulative number of allowed states



$N(\varepsilon)$ is a step function



$N(\varepsilon)$ for the first 15 states of the free electron gas

Density of States

DOS from the cumulative number of allowed states

$N(\varepsilon)$ for the 3D Fermi gas

$$N(\varepsilon) = \frac{\text{volume of isosphere at } \varepsilon}{\text{volume per } \boldsymbol{k} \text{ point}} = \frac{\frac{4}{3}\pi k_\varepsilon^3}{\frac{8\pi^3}{V}}$$

- From the dispersion relation $\epsilon = \hbar^2 k_\varepsilon^2/2m \longrightarrow k_\varepsilon^3 = \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{3/2}$

$$N(\epsilon) = \frac{V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{3/2}$$

- a continuous approximation to $N(\varepsilon)$
  - the volume of a sphere divided by the volume of a cube is generally not an integer

Density of States

DOS from the cumulative number of allowed states

$g(\varepsilon)$ for the 3D Fermi gas

$$g(\varepsilon) = \frac{1}{V}\frac{d}{d\varepsilon}N(\varepsilon) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}$$

- Each level can host two electrons $\rightarrow$ multiply by two the expression above (density of monoelectronic states)

$g(\varepsilon)$ for the 2D and 1D Fermi gas

- In 2D: $N(\varepsilon) = \frac{mL^2\varepsilon}{2\pi\hbar^2} \longrightarrow g(\varepsilon) = \frac{m}{2\pi\hbar^2}$ (independent of ε)
- In 1D: $N(\varepsilon) = \frac{L}{\pi}\sqrt{\frac{2m\varepsilon}{hbar^2}} \longrightarrow g(\varepsilon) = \frac{1}{2\pi}\sqrt{\frac{2m}{\varepsilon}}$

Density of States

DOS from the cumulative number of allowed states

Density of states vs density of occupied states

- The density of states is T-independent
- The density of occupied states is T-dependent:

$$g_{\mathrm{occ}}(\varepsilon) = g(\varepsilon) f_{FD}(\varepsilon)$$

- at T=0K:

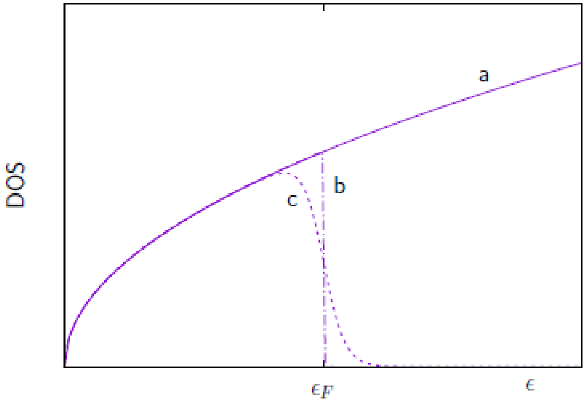
$$\begin{cases} g_{\mathrm{occ}}(\varepsilon) = g(\varepsilon) & \varepsilon \leq \varepsilon_F \\ g_{\mathrm{occ}}(\varepsilon) = 0 & \varepsilon > \varepsilon_F \end{cases}$$

- at finite T the sharp edge is smoothed by $f_{FD}(\varepsilon)$

Density of States

DOS from the cumulative number of allowed states

Density of states vs density of occupied states



a) $g(\varepsilon)$; b) $g_{\rm occ}(\varepsilon)$ at T=0K; c)$g_{\rm occ}(\varepsilon)$ at T¿ 0K

Density of States

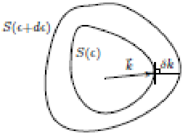
DOS from a dispersion relation $\varepsilon = \varepsilon(\boldsymbol{k})$

- Starting from $g(\varepsilon)d\varepsilon = \frac{1}{V}dN(\varepsilon)$
  - $dN(\varepsilon)$: number of states in the interval $[\varepsilon, \varepsilon + d\varepsilon]$
- Let's consider two isoenergetic surfaces at ε and $\varepsilon + d\varepsilon$:

$$dN(\varepsilon) = \frac{\delta V}{\frac{(2\pi)^3}{V}} = \frac{V}{(2\pi)^3}\delta V$$

- δV is the volume between surfaces:

$$\delta V = \int_{\delta V} d\boldsymbol{k} = \int_{S(\varepsilon)} dS \delta_{k_{\boldsymbol{k}}}$$



Density of States

Gradient of a function, ∇f

- Given $f = f(\boldsymbol{r})$ a function of the space variables (x,y,z):

$$\nabla f = \frac{\partial f}{\partial x}\hat{\boldsymbol{i}} + \frac{\partial f}{\partial y}\hat{\boldsymbol{j}} + \frac{\partial f}{\partial z}\hat{\boldsymbol{k}}$$

- Directional derivative:

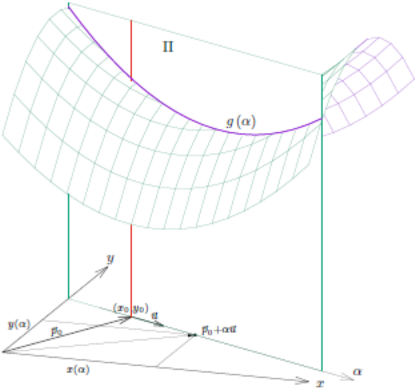
$$\frac{\partial f}{\partial \hat{\boldsymbol{u}}} = \lim_{h\to 0}\frac{f(\boldsymbol{r}+h\hat{\boldsymbol{u}}) - f(\boldsymbol{r})}{h} = \nabla f \cdot \hat{\boldsymbol{u}} = D_{f,\hat{\boldsymbol{u}}}$$

  - variation of f along the direction $\hat{\boldsymbol{u}}$
  - generalization to arbitrary directions of the partial derivatives $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$, $\frac{\partial f}{\partial z}$

Density of States

Gradient of a function, ∇f

The directional derivative $D_{f,\hat{\boldsymbol{u}}}$



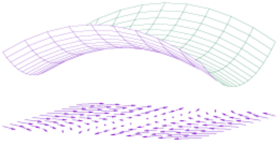
$D_{f,\hat{\boldsymbol{u}}}$ for a function of two variables at point (x_0, y_0)

Density of States

Gradient of a function, ∇f

Properties

- $\nabla f = 0$ on stationary points ($df = 0$)
- When $\nabla f \neq 0$, the vector points to the direction of maximum variation of f
  - $D_{f,\hat{\boldsymbol{u}}} = \nabla f \cdot \hat{\boldsymbol{u}} = |\nabla f| \cos\theta \Longrightarrow D_{f,\hat{\boldsymbol{u}}}$ max. when $\theta = 0$
  - $D_{f,\frac{\nabla f}{|\nabla f|}} = |\nabla f|$
- In a point ∇f is always $\perp$ to a isosurface of f. If $\hat{\boldsymbol{v}}$ is tangent to the isosurface, $D_{f,\hat{\boldsymbol{v}}} = \nabla f \cdot \hat{\boldsymbol{v}} = 0$



gradient of the $f(x, y) = x^2 - y^2$ in the neighborhood of the saddle point

Density of States

DOS from a dispersion relation $\varepsilon = \varepsilon(\boldsymbol{k})$

- Since $\nabla\varepsilon(\boldsymbol{k}) \perp S(\varepsilon) \implies$ oriented along $\delta_{k_{\boldsymbol{k}}}$:
  - $d\varepsilon = |\nabla\varepsilon(\boldsymbol{k})|\delta_{k_{\boldsymbol{k}}}$
  - $d\varepsilon = S(\varepsilon + d\varepsilon) - S(\varepsilon)$ is independent of the path taken
- Therefore: $\delta V = \int_{S(\varepsilon)} \frac{dS}{|\nabla\varepsilon(\boldsymbol{k})|} d\varepsilon = d\varepsilon \int_{S(\varepsilon)} \frac{dS}{|\nabla\varepsilon(\boldsymbol{k})|}$
- From: $dN(\varepsilon) = \frac{V}{(2\pi)^3}\delta V = \frac{V}{(2\pi)^3} d\varepsilon \int_{S(\varepsilon)} \frac{dS}{|\nabla\varepsilon(\boldsymbol{k})|}$
- One gets:

$$g(\varepsilon) = \frac{1}{V}\frac{dN}{d\varepsilon} = \frac{1}{(2\pi)^3}\int_{S(\varepsilon)} \frac{dS}{|\nabla\varepsilon(\boldsymbol{k})|}$$

Density of States

DOS from a dispersion relation $\varepsilon = \varepsilon(\boldsymbol{k})$

- $g(\varepsilon)$ depends on ε through the isosurface $S(\varepsilon)$
  - In practical calculations one needs to find the isosurfaces $S(\varepsilon)$
- The density of monoelectronic states would be $2 \times g(\varepsilon) = \frac{1}{4\pi^3} \int_{S(\varepsilon)} \frac{dS}{|\nabla\varepsilon(\boldsymbol{k})|}$
- $g(\varepsilon)$ is higher in points where $\varepsilon(\boldsymbol{k})$ varies slowly and viceversa
- The argument of the integral diverges at the stationary points of $\varepsilon(\boldsymbol{k})$ (cusps in the DOS profile known as van Hove singularities)
  - the presence of a finite number of these points does not limit the existence of the integral

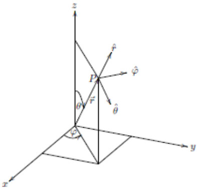
Density of States

DOS from a dispersion relation $\varepsilon = \varepsilon(\boldsymbol{k})$

Application to the 3D Fermi gas

- Integral is best evaluated in spherical coordinates:
  - $\nabla f = \frac{\partial f}{\partial r}\hat{\boldsymbol{r}} + \frac{1}{r}\frac{\partial f}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial f}{\partial \varphi}\hat{\boldsymbol{\varphi}}$
  - $|\nabla\varepsilon(\boldsymbol{k})| = \frac{\hbar^2 k}{m}$
  - $S(\varepsilon)$ is the surface of a sphere

$$g(\varepsilon) = \frac{1}{(2\pi)^3}\frac{m}{\hbar^2 k}\int_{S(\varepsilon)} dS = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\varepsilon^{1/2}$$



spherical coordinates are an orthogonal set of coordinates

Density of States

Mathematically rigorous definition

The Dirac Delta Function

- It is not an ordinary function (distribution or generalized function)
- defined as:

$$\begin{cases} \int_{-\infty}^{+\infty} \delta(x)\, dx = 1 \\ \delta(x) = 0 \quad \text{for } x \neq 0 \end{cases}$$

- $\delta(x)$ is null everywhere except at $x = 0$, where it is undefined.
- Intuitively: a spike of zero width at $x = 0$
  - useful for counting discrete objects

Density of States

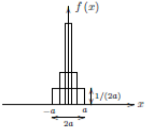
Mathematically rigorous definition

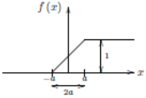
The Dirac Delta Function

- limit of some ordinary function: $\delta(x) = \lim_{a \to 0} f_a(x)$

$$f_a(x) = \begin{cases} 0 & |x| > a \\ \dfrac{1}{2a} & |x| < a \end{cases}$$

- $\delta(x) = \lim_{\sigma \to 0} \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/(2\sigma^2)}$
- Derivative of Heaviside $H(x)$ function: $\delta(x) = \frac{dH(x)}{dx}$





Density of States

Mathematically rigorous definition

Selected properties of the Dirac Delta Function

- $\delta(x-a)$ shoots its spike at $x=a$ (null everywhere except at $x=a$)
  - $\int_{-\infty}^{+\infty} \delta(x-a)dx = 1$
- localisation:

$$\int_{x_1}^{x_2} \delta(x-a)\, dx = \begin{cases} 1 & a \in [x_1, x_2] \\ 0 & \text{otherwise} \end{cases}$$

- Sifting property: $\int_{-\infty}^{\infty} f(x)\, \delta(x-a)\, dx = f(a)$
- Scaling property: for any $a \in \mathbb{R}$, $\delta(ax) = \frac{1}{|a|}\, \delta(x)$

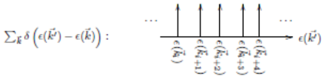
Density of States

Mathematically rigorous definition

Formal definition

$$g(\varepsilon) = \frac{1}{V} \sum_{\boldsymbol{k}} \delta(\varepsilon - \varepsilon(\boldsymbol{k}))$$

- The sum runs over all allowed $\boldsymbol{k}$ points.
- Each term shoots its spike when $\varepsilon = \varepsilon(\boldsymbol{k})$
- Monoelectronic DOS: multiply by two (spin degeneracy)



Density of States

Mathematically rigorous definition

Proof

- $N(\varepsilon + \Delta\varepsilon) - N(\varepsilon) = V \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} g(\varepsilon')\, d\epsilon'$
- Replace g with its Dirac-delta definition:

$$
\begin{aligned}
N(\varepsilon + \Delta\varepsilon) - N(\varepsilon) &= \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} \sum_{\boldsymbol{k}} \delta(\varepsilon - \epsilon(\boldsymbol{k})) d\epsilon \\
&= \sum_{\boldsymbol{k}} \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} \delta(\varepsilon - \varepsilon(\boldsymbol{k}))\, d\epsilon \\
&= \sum_{\substack{\boldsymbol{k}:\, \varepsilon(\boldsymbol{k}) \\ \in[\varepsilon,\, \varepsilon+\Delta\varepsilon]}} \underbrace{\int_{-\infty}^{+\infty} \delta(\varepsilon - \varepsilon(\boldsymbol{k})) d\varepsilon}_{=1} \\
&= \sum_{\substack{\boldsymbol{k}:\, \varepsilon(\boldsymbol{k}) \\ \in[\varepsilon,\, \varepsilon+\Delta\varepsilon]}} 1
\end{aligned}
$$

Density of States

Application to the Fermi gas

- Starting from the formal definition and passing to the thermodynamic limit ($V \to \infty$, sum $\to$ integral):

$$g(\varepsilon) = \frac{1}{8\pi^3} \int_{\boldsymbol{k}} \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) d\boldsymbol{k}$$

- Using spherical symmetry ($d\boldsymbol{k} = 4\pi k^2 dk$), $k^2 dk = \frac{m}{\hbar^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}} d\varepsilon$

$$\begin{aligned} g(\varepsilon) &= \frac{1}{2\pi^2}\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{2} \int_0^\infty \delta(\varepsilon - \varepsilon(\boldsymbol{k}))\, \varepsilon^{1/2} d\varepsilon \\ &= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{1/2} \end{aligned}$$

Density of States

Practical use

- For any property Q which depends on the occupied states:

$$Q = \frac{2}{V} \sum_{\boldsymbol{k}} Q\left(\varepsilon(\boldsymbol{k})\right) f_{FD}\left(\varepsilon(\boldsymbol{k})\right)$$

- Use the sifting property of the Dirac delta function:

$$Q = 2 \int Q(\varepsilon)\, f_{FD}(\varepsilon)\, g(\varepsilon)\; d\varepsilon$$

1 Ground-state properties of the free electron gas

2 Thermal properties of the free electron gas

3 The Sommerfeld theory of conduction in metals

4 Density of States (DOS)

5 Failures of the free electron model

Failures of the free electron model

General remarks

- Free electron theory successfully accounts for a wide range of metallic properties.
- Deficiencies of the Drude model related to the use of classical statistical mechanics
  - predicted thermoelectric fields and heat capacities 100 times too large (even at room T)
  - Deficiencies obscured by a fortuitous cancellation of errors in predicting the Wiedemann-Franz law
- Application of Fermi-Dirac statistics eliminated this class of difficulties
- However:
  - many quantitative predictions do not reproduce experimental measurements
  - leaves many fundamental questions of principle unresolved

Difficulties with the free electron model

Inadequacies in the free electron transport coefficients

- Hall coefficient:
  - $R_H = -1/nec$, independent of: T, relaxation time (τ), strength of the magnetic field (H)
  - contrary to exp. observations (see e.g. Al)
  - good agreement only for alkali metals
- Magnetoresistance:
  - free electron theory predicts that the resistance of a wire $\perp$ to a uniform $\boldsymbol{H}$ should not depend on the strength of the field.
  - experimentally it does in almost all cases (for noble metals it can be made to increase apparently without limit)
  - further dependencies: preparation of the metallic specimen, orientation w.r.t $\boldsymbol{H}$
- Thermoelectric Field:
  - free electron theory cannot always account for its sign (like R_H)
- Wiedemann-Franz law:
  - obeyed at high (room) T, and probably at very low T (few K)
  - at intermediate T, $\frac{\kappa}{\sigma T}$ depends on T

Difficulties with the free electron model

Inadequacies in the free electron transport coefficients

- T dependence of the DC electrical conductivity
  - free electron theory cannot account for its T-dependence
  - described as an ad-hoc T-dependence in τ
- Directional dependence of the DC electrical conductivity
  - In some metals the DC conductivity depends on the orientation of the specimen (if suitably prepared) with respect to the field: $\mathbf{j}$ is not $\parallel$ to $\boldsymbol{E}$
- AC conductivity
  - subtle frequency dependence to the optical properties of metals compared to the free electron dielectric constant

Difficulties with the free electron model

Inadequacies in the static thermodynamic predictions

- Linear term in the specific heat
  - Sommerfeld theory accounts reasonably well for the size of the term linear in T in the low-T specific heat of the alkali metals
  - works less well for the noble metals
  - works poorly for transition metals (too small for Fe and Mn, too large for Bi and Sb)
- Cubic term in the specific heat
  - free electron theory cannot account for it (wrong sign and six order of magnitude too small)
- Compressibility of metals
  - does remarkably well. However ions and electron-electron interactions play a role for an accurate estimate of the equation of state of a metal

Difficulties with the free electron model

Fundamental mysteries

- What determines the number of conduction electrons?
  - we assumed all valence electrons become conduction electrons
  - why elements such as Fe can have more than one chemical valence?
- Why some elements are non metals?
  - free electron theory cannot explain the existence of insulators
  - e.g B is an insulator while Al displays excellent metal properties
  - C(gr) is conductor while C(diamond) is an insulator
  - why Bi and Sb are poor conductors?

Review of basic assumptions

1. Free Electron Approximation
   - metallic ions play a minor role (needed for charge neutrality)
2. Independent electron approximation (IEA)
3. Relaxation time approximation
   - outcome of a collision does not depend on the configuration of the electrons at the moment of the collision

Review of basic assumptions

Relaxing the approximations

- All these oversimplifications must be abandoned for an accurate model of the solid
- Improve some aspects of the free electron approximation while retaining the IE and relaxation time approx
- In many instances IEA does not affect seriously the analysis (major role only in metallic compressibilities)
- The free electron approximation is the major source of the difficulties encountered:
  - the effect of the ions on the dynamics of an electron between collisions is ignored
  - what role the ions play as a source of collisions is left unspecified
  - the possibility that the ions themselves, contribute to physical phenomena (specific heat or thermal conductivity) is ignored
- Need to allow for ionic motion