# The Sommerfeld Theory of Metals

# Outline

# Ground-state properties of the electron gas

## General remarks

### Maxwell-Boltzmann velocity distribution

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

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

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

# Ground-state properties of the electron gas

## General remarks

### Fermi-Dirac velocity distribution

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

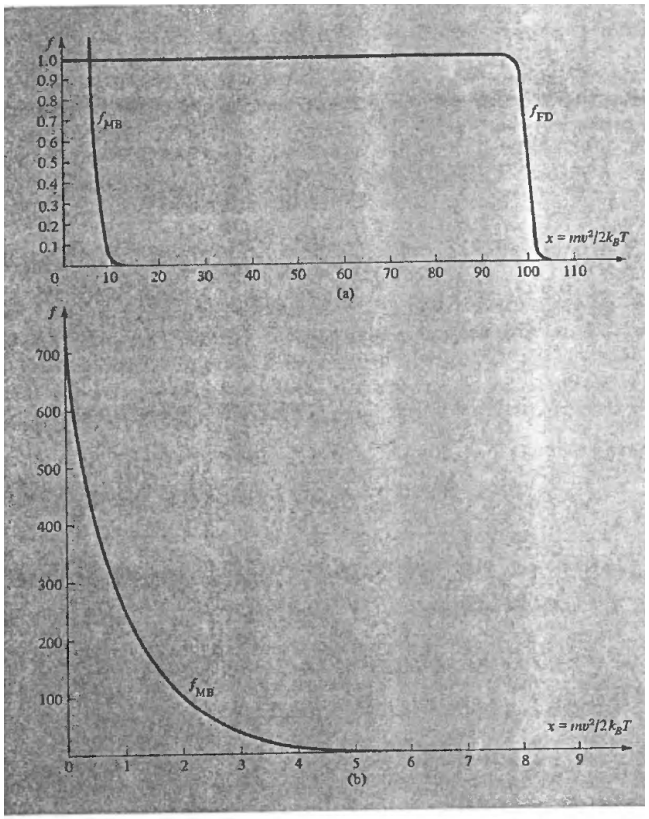
$$f(\boldsymbol{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{e^{\frac{(\frac{1}{2}mv^2 - k_B T_0)}{k_B T}} + 1}$$

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

# Ground-state properties of the electron gas

## General remarks

### Maxwell-Boltzmann vs Fermi-Dirac velocity distribution




Plot of Maxwell-Boltzmann and Fermi-Dirac distributions for the same $n$ given by $T = 0.01\,T_0$.

# Ground-state properties of the electron gas

## Quantum mechanical solution

### Mathematical treatment

- The free electron gas is confined in a cube of edge $L$ ($L = V^{\frac{1}{3}}$)
- Assume the independent electron approximation
- Solve the TISE (separation of variables)

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

- Apply Born-von Karman boundary conditions to the general solution

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

- Fill the energy levels by using the Pauli exclusion principle

# 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 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 electron gas

## Quantum mechanical solution

### General and particular solutions

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

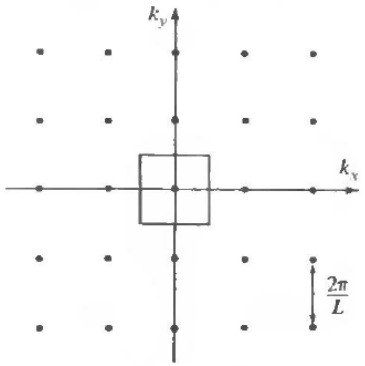
- General solution: $\phi(x) = c_1 e^{ikx} + c_2 e^{-ikx}$
  - $k^2 = \frac{2m\varepsilon}{\hbar^2} \Longrightarrow \varepsilon = \frac{\hbar^2 k^2}{2m}$
- Particular (normalized) solution: $\phi(x) = \frac{1}{\sqrt{L}} e^{ikx}$
  - $k = \frac{2n\pi}{L}$, $n = 0, \pm 1, \pm 2, \ldots$

# Ground-state properties of the 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 $\boldsymbol{k}$:
  - $k_x = \frac{2\pi n_x}{L}$; $k_y = \frac{2\pi n_y}{L}$; $k_z = \frac{2\pi n_z}{L}$
  - $n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots$
- $\varepsilon = \varepsilon(|\boldsymbol{k}|) = \frac{\hbar^2 k^2}{2m}$ (depends only on $k = |\boldsymbol{k}|$)



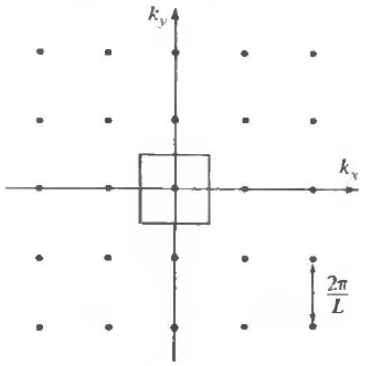

allowed wave vectors in a 2D $k$ space

# Ground-state properties of the 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 $\boldsymbol{v} = \frac{\boldsymbol{p}}{m} = \frac{\hbar\boldsymbol{k}}{m}$



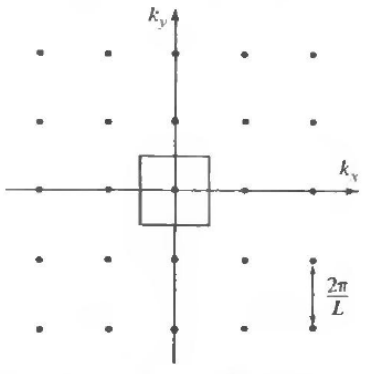

allowed wave vectors in a 2D $k$ space

# Ground-state properties of the 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 $\Omega$, 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: $\frac{V}{8\pi^3}$




allowed wave vectors in a 2D $k$ space

# Ground-state properties of the 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 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 $\Omega$: Fermi sphere
  - $k_F$: Fermi wave vector
  - surface of $\Omega$: Fermi surface
  - $p_F = \hbar k_F$: 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 above quantities can be estimated from $n$

# Ground-state properties of the electron gas

## Quantum mechanical solution

### Some numbers

- $k_F = \frac{(\frac{9\pi}{4})^{\frac{1}{3}}}{r_s} = \frac{1.92}{r_s} = \frac{3.63}{\frac{r_s}{a_0}}\text{Å}^{-1}$
  - $r_s \sim$2–6 Å $\Longrightarrow k_F \sim$ Å$^{-1}$ ($\lambda \sim$ 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)
- $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = (\frac{e^2}{2a_0})(k_F a_0)^2 = \frac{50.1}{(\frac{r_s}{a_0})^2}$ eV
  - $\varepsilon_F \in$ 1.5–15 eV
- $T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{(\frac{r_s}{a_0})^2} \times 10^4\text{K}$
  - energy per electron of a classical ideal gas vanishes at $T = 0$K ($\bar{\varepsilon} = \frac{3}{2}k_B T$)

# Ground-state properties of the 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 | $5.51 \times 10^4$ K | $1.12 \times 10^8$ cm$^{-1}$ | $1.29 \times 10^8$ 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 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 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
- $\frac{E}{N} = \frac{3}{5}k_B T_F$
  - 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 electron gas

## Quantum mechanical solution

### Bulk properties of the ground-state

- Electronic pressure: $P = \frac{2}{3}\frac{E}{V}$
  - exerted by the electron gas
- Compressibility: $K = -\frac{1}{V}(\frac{\partial V}{\partial P})$
- Bulk modulus: $B = \frac{1}{K} = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2}{3}n\varepsilon_F$
- Numerically: $B = (\frac{6.13}{r_s/a_0})^5 \times 10^{10}\text{dynes/cm}^2$

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 |

# 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 state of energy $E$
- $Z = \sum_\alpha e^{-\frac{E_\alpha^N}{k_B T}}$ is the partition function

# Thermal properties of the free-electron gas

## The Fermi-Dirac distribution

### The partition function

- $F_N = U - TS = -k_B T \ln(Z) \Longrightarrow Z = e^{-\frac{F_N}{k_B T}}$
  - Helmholtz free energy
- $P_N(E) = e^{-\frac{E - F_N}{k_B T}}$

# Thermal properties of the free-electron gas

## The Fermi-Dirac distribution

### Derivation

- The $N$-electron state is specified by a list of the one-electron levels occupied
  - states $\psi_{\boldsymbol{k}\sigma}(\boldsymbol{r})$
- Define $f_i^N = \sum P_N(E_\alpha^N)$
  - probability that the one-electron level $i$ is occupied in the N-electron state
  - Pauli exclusion principle requires $0 \leq f_i^N \leq 1$
  - mean occupation of the level $i$
- We will find an explicit expression for $f_i^N$

# Thermal properties of the free-electron gas

## The Fermi-Dirac distribution

### Derivation

- $f_i^N = 1 - \sum P_N(E_\gamma^N)$
  - $\gamma$ labels $N$-electron states where $i$ is not occupied
- $f_i^N = 1 - \sum P_N(E_\alpha^{N+1} - \varepsilon_i)$
  - $E_\gamma^N = E_\alpha^{N+1} - \varepsilon_i$
  - $N+1$-electron states obtained from $\gamma$'s by placing an electron in level $i$
- Defining $\mu = F_{N+1} - F_N \Longrightarrow f_i^N = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} \sum P_{N+1}(E_\alpha^{N+1})$
- $f_i^N = 1 - e^{\frac{\varepsilon_i - \mu}{k_B T}} f_i^{N+1}$

# Thermal properties of the free-electron gas

## The Fermi-Dirac distribution

### 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 $\mu$
  - We can express $\mu$ 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 temperature

# 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 $N = 2\sum_{\boldsymbol{k}} f(\varepsilon(\boldsymbol{k}))$:

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

# Thermal properties of the free-electron gas

## Applications of the Fermi-Dirac distribution

### Density of levels

- Working in spherical coordinates:

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

- $g(\epsilon)$: 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: $g(\varepsilon_F) = \frac{3}{2}\frac{n}{\varepsilon_F}$

# Thermal properties of the free-electron gas

## Applications of the Fermi-Dirac distribution

### Total energy and density of the electron gas

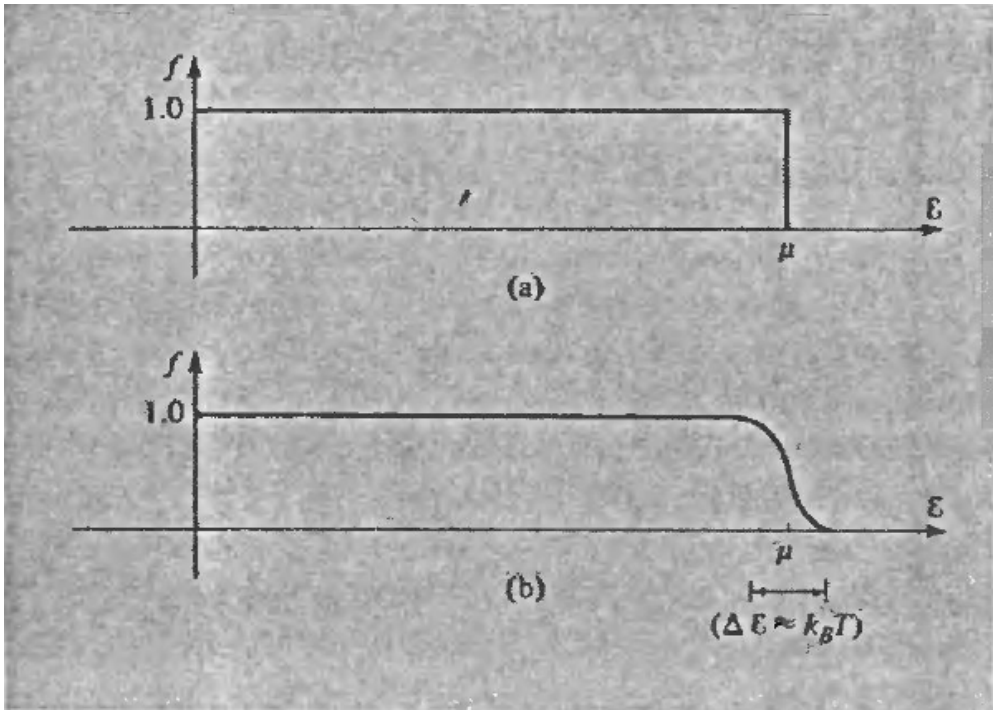
- $u = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon)\varepsilon f(\varepsilon)$
- $n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon)$
- valid for any non-interacting electron systems

# Thermal properties of the free-electron gas

## Applications of the Fermi-Dirac distribution

### The Sommerfeld expansion

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




Fermi function $f$ for given $\mu$ at $T = 0$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 $\mu$
  - Taylor expansion of $H(\varepsilon)$ around $\mu$
  - 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 $n$:

$$\begin{aligned} u &= \int_0^\mu \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 [\mu g'(\mu) + g(\mu)] + O(T^4) \\ n &= \int_0^\mu g(\varepsilon) d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) + O(T^4) \end{aligned}$$

- 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:

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

- Note:
  - $n = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon$
  - $u_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon$

# Thermal properties of the free-electron gas

## Applications of the Fermi-Dirac distribution

### Deviation of $\mu$ from $\varepsilon_F$

- From:

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

- We get:

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

- The difference is $\sim 0.01\%$ even at room T

# Thermal properties of the free-electron gas

## Applications of the Fermi-Dirac distribution

### Specific heat capacity, $c_v$

- From:

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

- We get:

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

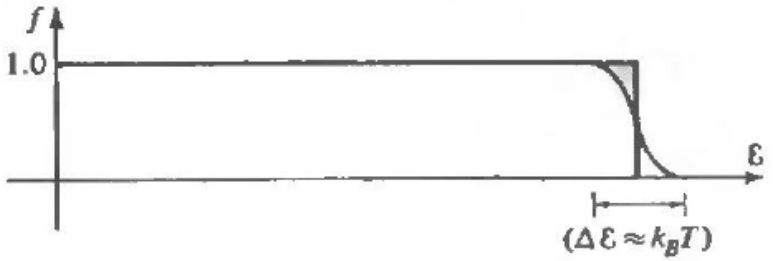
  - varies linearly with T
  - compare with the classical result $c_v = \frac{3}{2} n k_B$ $(\frac{k_B T}{\varepsilon_F} \sim 10^{-2})$
  - electronic contribution is negligible even at room T

# 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 $T \neq 0$

# 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 $T \to 0$)
  - $c_v = \gamma T + A T^3$
- Experimental data (of $c_p$) are fitted to the equation: $\frac{c_v}{T} = \gamma + A T^2$
  - electronic contribution is comparable to the ionic at T of few K
  - extrapolate at $T \to 0$
- Experimentally $[C] = [\frac{\text{cal}}{K\,\text{mol}}]$. Multiply by $\frac{ZN_A}{n}$:

$$\begin{aligned} C &= \frac{\pi^2}{3} ZR \frac{k_B T g(\varepsilon_F)}{n} \\ \Longrightarrow \quad \gamma &= \frac{1}{2}\pi^2 R \frac{Z}{T_F} = 0.169 Z \left(\frac{r_s}{a_0}\right)^2 \times 10^{-4} \text{cal mol}^{-1} K^{-2} \end{aligned}$$

# 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 $\gamma$ (in $10^{-4}$ cal-mole$^{-1}$-K$^{-2}$) | MEASURED $\gamma$ | 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 |

# 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: $2 \times (\frac{V}{(2\pi)^3}) = \frac{V}{(4\pi^3)} d\boldsymbol{k}$
  - 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 $\boldsymbol{v} = \frac{\hbar \boldsymbol{k}}{m} \rightarrow d\boldsymbol{k} = (\frac{m}{\hbar})^3 d\boldsymbol{v}$
- therefore the number of electrons with velocity $\in (\boldsymbol{v}, \boldsymbol{v} + d\boldsymbol{v})$ is:

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

  - 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:
  - $\Delta p << \hbar k_F \sim p$
  - $\Delta x \sim \frac{\hbar}{\Delta p} >> \frac{1}{k_F} \sim r_s \sim$ 2–6Å

# 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 $\Delta x$
  - valid for UV-vis radiation, not X-rays (QM must be used)
  - usually valid for normal $\nabla T$'s
- We assumed $\Delta x << l$, the mean free path
  - $l \sim 100$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 $l = v_F \tau \rightarrow l = \frac{(r_s/a_0)^2}{\rho_\mu} \times 92$ Å
  - $l \sim 100$ Å are possible at room T

### Thermal conductivity

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

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

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