Intro. to Electro-physics

Sommerfeld's model (3rd)

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Fermi-Dirac statistics (1/3)

Chemical potential

: The change of free energy due to a change of the particle number

$$\mu \triangleq \frac{\partial U}{\partial N}$$

$$f_i = \frac{1}{\exp\frac{\varepsilon_i - \mu}{k_B T} + 1},$$ where μ : chemical potential

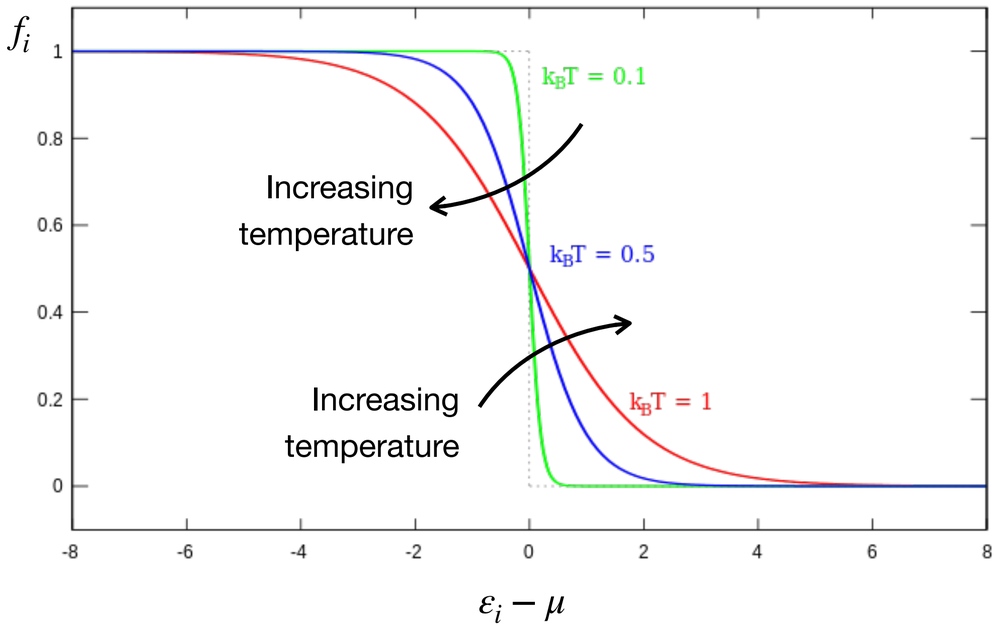
- What is it?

  Quantum statistics that Fermions must obey

  c.f.) Others include Maxwell-Boltzmann, Bose-Einstein statistics

- Meaning
  - The probability (f_i) that a single-Fermion level (ε_i) is occupied
  - The mean number $(\bar{n}_i = f_i)$ of Fermions occupying the level ε_i

    (Always $\bar{n}_i \leq 1$ due to Pauli exclusion principle)



Source: Modello di Sommerfeld (Wikipedia)

Fermi-Dirac statistics (2/3)

Fermi energy

: The kinetic energy of electrons in the highest occupied level in $\boldsymbol{k}-$space at $T = 0$ (K)

$$f_i = \frac{1}{\exp\frac{\varepsilon_i - \mu}{k_B T} + 1}$$

- In the low temperature limit $(T \to 0)$

$$f_i = \begin{cases} 1 & (\varepsilon_i < \mu) \\ 0 & (\varepsilon_i > \mu) \end{cases}$$

$(\varepsilon_i < \mu) \to$ All levels below μ are occupied.

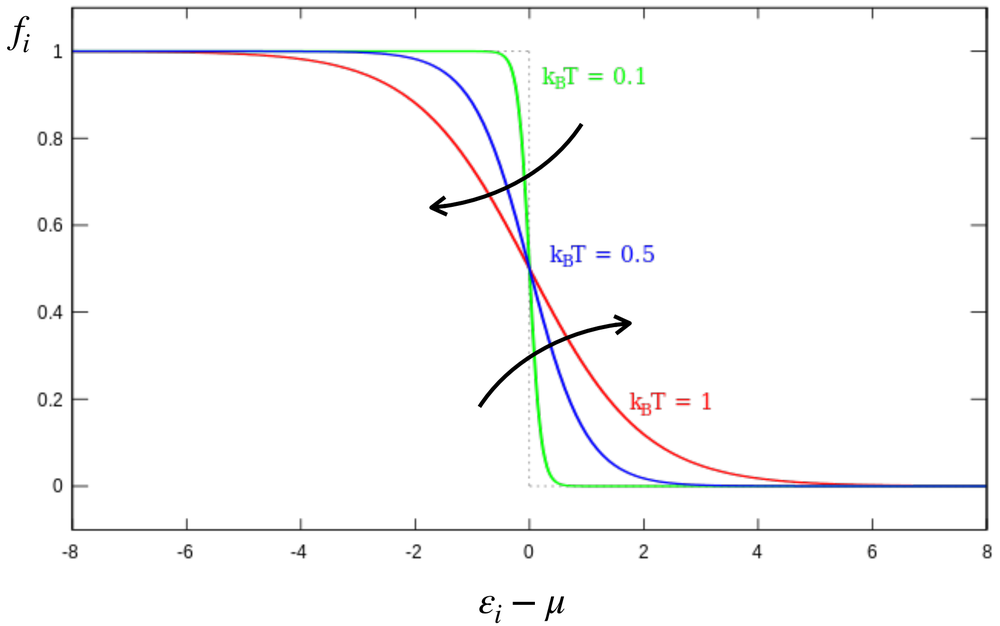
$(\varepsilon_i > \mu) \to$ All levels above μ are NOT occupied.

- Previously in the ground state $(T = 0)$ of the electron gas

$$f_i = \begin{cases} 1 & (\varepsilon_i < \varepsilon_F) \\ 0 & (\varepsilon_i > \varepsilon_F) \end{cases}, \quad \text{where } \varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

The Fermi energy

$$\therefore \lim_{T \to 0} \mu(T) = \varepsilon_F$$



Source: Modello di Sommerfeld (Wikipedia)

Fermi-Dirac statistics (3/3)

- The Fermi energy and Fermi temperature

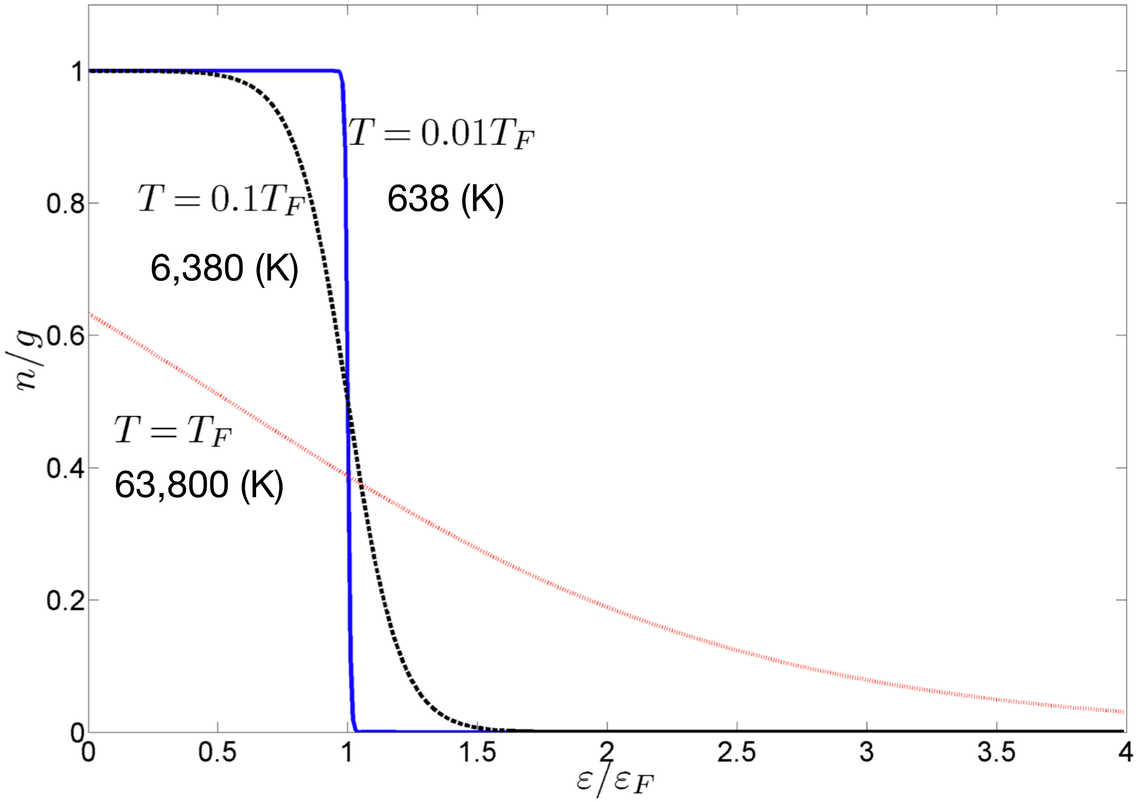
$$\varepsilon_F \triangleq \frac{\hbar^2 k_F^2}{2m} = \frac{50.1}{\left(r_s/a_0\right)^2} \text{ (eV)} \quad \text{and} \quad \varepsilon_F \triangleq k_B T_F$$

  - For silver, $\boxed{\varepsilon_F = 5.49 \text{ (eV)} \longrightarrow T_F = 63{,}800 \text{ (K)}}$

- Temperature-dependence of Fermi-Dirac distribution

$$f = \frac{1}{\exp\frac{\varepsilon - \mu}{k_B T} + 1}$$

  - At $T \ll T_F$: Nearly a step function
    - At $\varepsilon = \mu \quad \rightarrow \quad f = \frac{1}{2}$ regardless of T
  - At $T \gg T_F$: the F-D distribution approaches the M-B distribution (**HW!**)



Source: Prof. Williams at Univ. of Liverpool [Thermal Physics]

Chemical potential

Chemical potential

: The change of free energy due to a change of the particle number

$$\mu \triangleq \frac{\partial U}{\partial N}$$

$gd\varepsilon$: Number of single-electron levels in the energy range from ε to $\varepsilon + d\varepsilon$

- Temperature-dependence of chemical potential μ
  - Derivation of μ (considering the degeneracy)

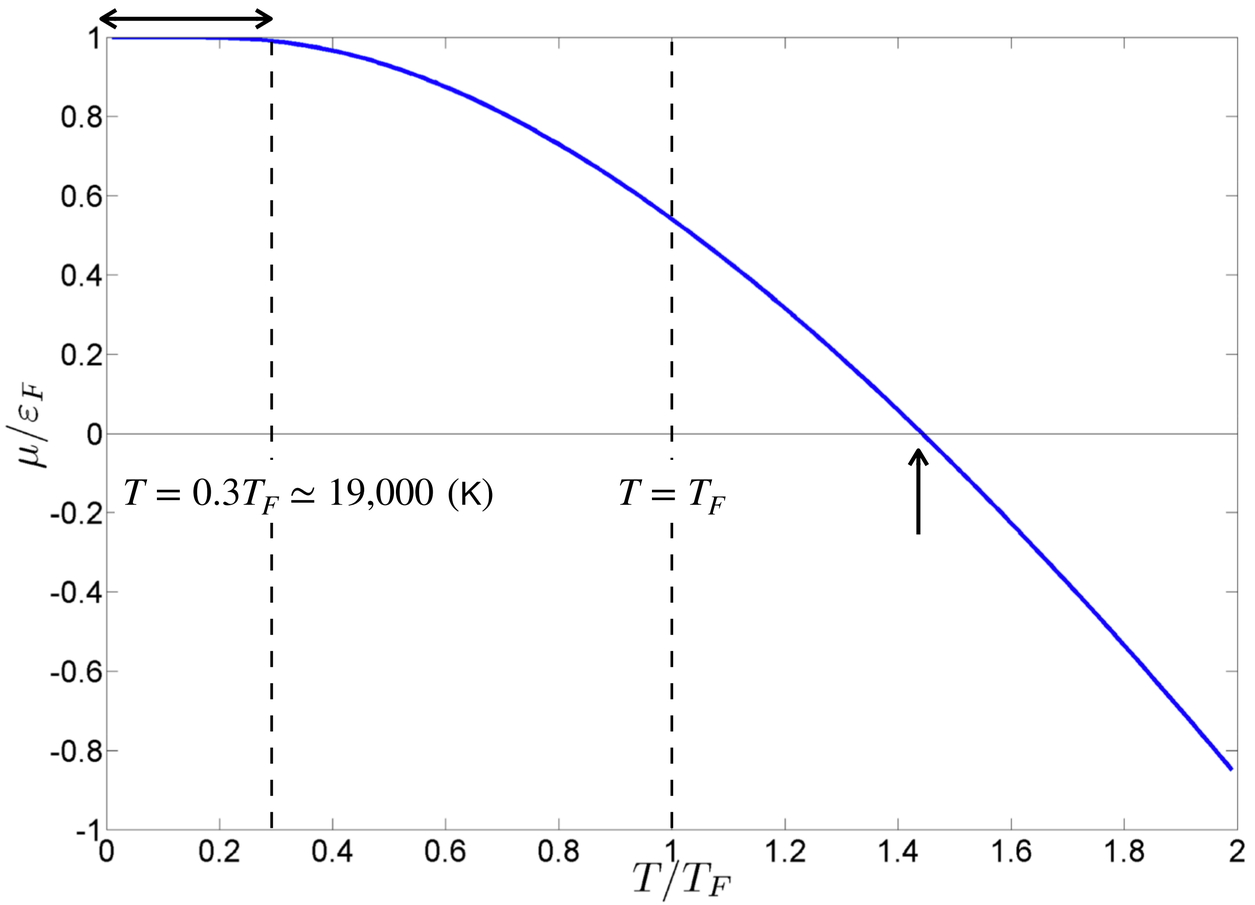
    $\bar{n}_i = f_i \cdot g_i$, where g_i : # of levels with an energy ε_i

    Let's assume $g_i = g$ for simplicity. Then,

$$N = \sum_i \bar{n}_i \simeq \int_0^\infty g f(\varepsilon)\, d\varepsilon = \int_0^\infty \frac{g d\varepsilon}{\exp\left[\frac{\varepsilon - \mu}{k_B T}\right] + 1}$$

$$\mu(T) = k_B T \ln\left(\exp\left(\frac{N}{g k_B T}\right) - 1\right)$$

  - At low temperatures $\left(T \ll T_F\right)$: $\mu(T) \simeq \varepsilon_F$



Source: Prof. Williams at Univ. of Liverpool [Thermal Physics]

Total energy of an electron gas (1/3)

Conversion of sum to integral:

$$\sum_{\boldsymbol{k}} = \int \frac{d\boldsymbol{k}}{\Delta \boldsymbol{k}}, \text{ where } \Delta k = \frac{8\pi^3}{V}$$

$$\rightarrow \frac{1}{V}\sum_{\boldsymbol{k}} = \int \frac{d\boldsymbol{k}}{8\pi^3}$$

$$f(\varepsilon) = \frac{1}{\exp\frac{\varepsilon - \mu}{k_B T} + 1}$$

- **Electron gas:** A collection of weakly interacting electrons that are free to move within a bounded volume V, but are unable to move beyond the boundary
  - Energy of the single electron in the gas

    $\varepsilon\left(\boldsymbol{k}\right) = \frac{\hbar^2 k^2}{2m}$, for whose wavevector being $\boldsymbol{k}$

  - Total number of electrons in the gas and Total energy of the gas

    And their conversion in an integral form

$$N = 2\sum_{\boldsymbol{k}} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) \longrightarrow \boxed{\frac{N}{V} \triangleq n = \int \frac{d\boldsymbol{k}}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right)}$$

Number of electrons in the gas of unit volume

$$U = 2\sum_{\boldsymbol{k}} \varepsilon\left(\boldsymbol{k}\right) f\left(\varepsilon\left(\boldsymbol{k}\right)\right) \longrightarrow \boxed{\frac{U}{V} \triangleq u = \int \frac{d\boldsymbol{k}}{4\pi^3} \varepsilon\left(\boldsymbol{k}\right) f\left(\varepsilon\left(\boldsymbol{k}\right)\right)}$$

Total energy of the gas of unit volume

Total energy of an electron gas (2/3)

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

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

- Total energy of an Fermi gas (contd.)
  - Expression for n and u in terms of ε (i.e., conversion of $\boldsymbol{k} \rightarrow \varepsilon$)

    (The integrand depends on $\boldsymbol{k}$ only through $\varepsilon\left(\boldsymbol{k}\right)$)

$$n = \int \frac{d\boldsymbol{k}}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) = \int_0^\infty \frac{4\pi k^2 dk}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) \longrightarrow \int_0^\infty g\left(\varepsilon\right) f\left(\varepsilon\right) d\mathscr{E}$$

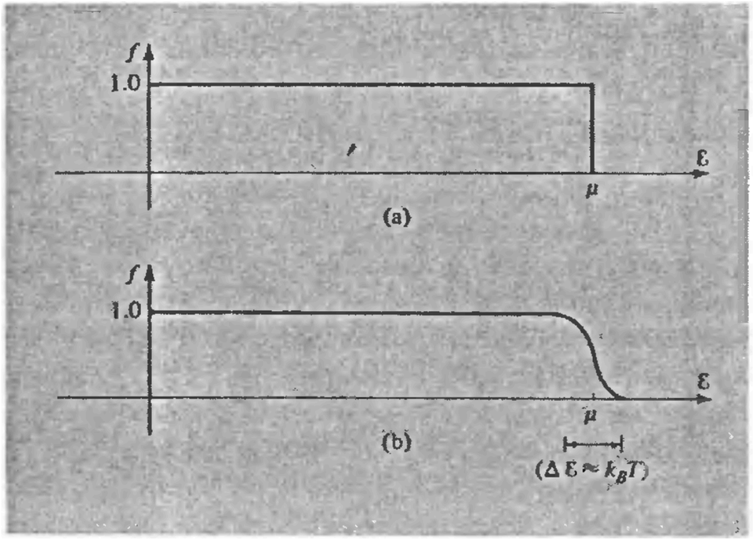
$$k^2 = \frac{2m\mathscr{E}}{\hbar^2},\ 2kdk = \frac{2m}{\hbar^2} d\mathscr{E} \rightarrow kdk = \frac{m}{\hbar^2} d\mathscr{E}$$

where $g\left(\varepsilon\right) \triangleq \frac{\sqrt{2}}{\pi^2}\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon}$ **density of energy levels per unit volume**

$$u = \int \frac{d\boldsymbol{k}}{4\pi^3} \varepsilon\left(\boldsymbol{k}\right) f\left(\varepsilon\left(\boldsymbol{k}\right)\right) \longrightarrow u = \int_0^\infty \varepsilon g\left(\varepsilon\right) f\left(\varepsilon\right) d\varepsilon$$

$$n = \int \frac{d\boldsymbol{k}}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) \longrightarrow n = \int_0^\infty g\left(\varepsilon\right) f\left(\varepsilon\right) d\varepsilon$$

Total energy of an electron gas (3/3)



- Method of evaluating the form $\int_0^\infty H(\varepsilon) f(\varepsilon)\, d\varepsilon$
  - $f(\epsilon)$ differs from its zero-temp value only in a small region about μ $\left(\Delta\varepsilon \approx k_B T\right)$
  - Integration of $H(\varepsilon) f(\varepsilon)$ near $\left(\varepsilon = \mu\right)$ matters → Use **Taylor's expansion! (HW)**

- Total energy of the electron gas $\left(T \ll T_F\right)$

$$u = \int_0^\infty \varepsilon g(\varepsilon) f(\varepsilon)\, d\varepsilon \simeq \frac{3}{5} n\varepsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right] \triangleq U_0 + \Delta U$$

→ Ground-state energy at $T = 0$ (K)

→ Excited-state energy at $T > 0$ (K)

- **Specific heat capacity** at constant volume $\left(T \ll T_F\right)$

$$c_V = \frac{1}{V}\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V = \frac{\pi^2}{2} n k_B \frac{T}{T_F} = \boxed{\frac{3}{2} n k_B \cdot \left(\frac{\pi^2}{3}\frac{k_B T}{\varepsilon_F}\right)}$$

Specific heat capacity (1/2)

- Specific heat capacity at constant volume $\left(T \ll T_F\right)$

$$c_V = \frac{3}{2} n k_B \cdot \left(\frac{\pi^2}{3} \frac{k_B T}{\varepsilon_F} \right)$$

- Example: c_V for **Silver** at $T = 298$ (K)

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}, \quad \text{where } n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} = \frac{\rho N_A}{A}$$

$$\varepsilon_F = 5.49 \text{ (eV)}, \quad T_F = \frac{\varepsilon_F}{k_B} \simeq 63{,}900 \text{ (K)}$$

$$\therefore c_V = \frac{3}{2} n k_B \left(\frac{\pi^2}{3} \frac{k_B T}{\varepsilon_F} \right) \simeq 1.74 \ \left(J/kg \cdot K \right).$$

c.f.) measured c_V for silver at constant pressure $\simeq 235 \ \left(J/kg \cdot K \right)$

Parameters for silver

Mass density	ρ	10,500 (kg/m^3)
Relative atomic mass	A	0.108 (kg/mol)
Planck's constant	$\hbar$	1.055 x 10^{-34} (J·s)
Electron mass	m	9.11 x 10^{-31} (kg)
Boltzmann's constant	k_B	1.38 x 10^{-23} (J/K)
Avogadro's number	N_A	6.023 x 10^{23} (/mol)

Specific heat capacity (2/2)

- In reality
  - The specific heat = Ionic contribution + Electronic contribution

$$C_{V,m} = \gamma T + AT^3$$

- Associated with atomic vibrations
- **Dominant at high T**
- Associated with conduction electrons
- **Dominant at low T**

$$C_{V,m} = \frac{\pi^2}{2} N_A k_B \frac{T}{T_F}$$

$$\longrightarrow \quad \gamma = \lim_{T \to 0} \frac{\partial C_{V,m}}{\partial T} = \frac{\pi^2}{2} \frac{N_A k_B}{T_F} \simeq 0.643 \ \left(\text{mJ/mol-K}^2\right) \text{ for silver}$$

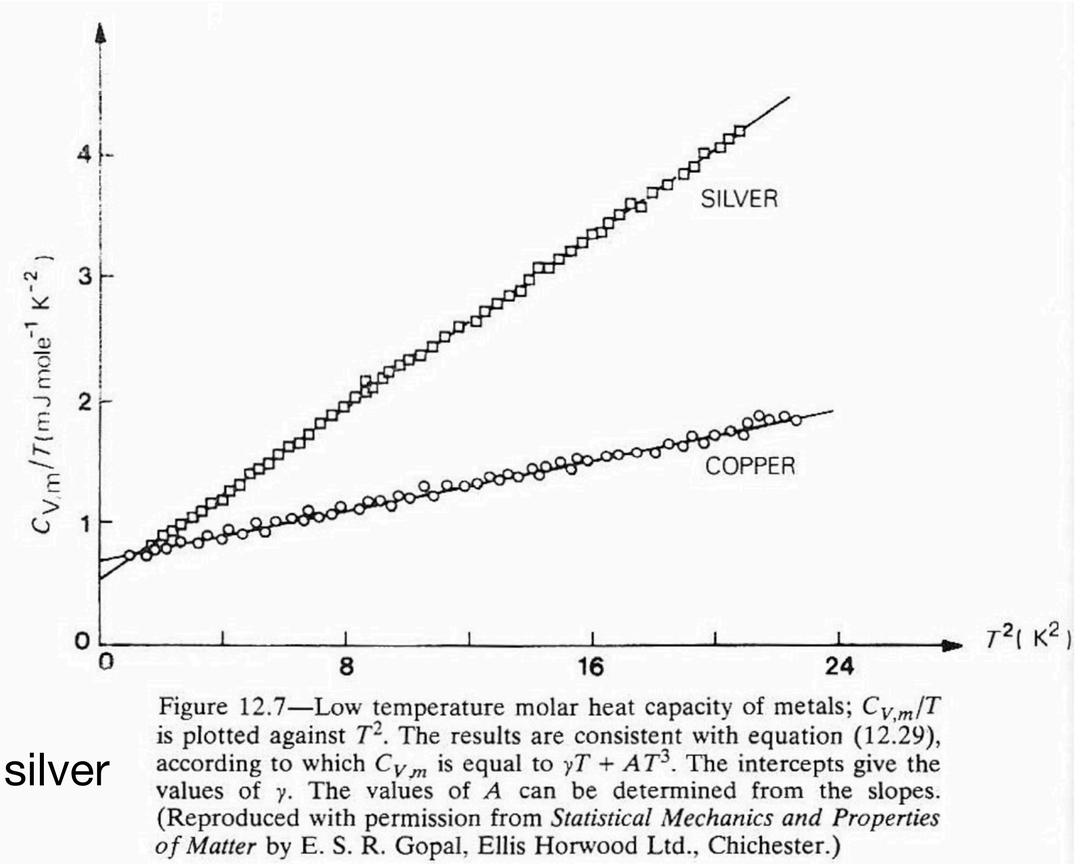


Figure 12.7—Low temperature molar heat capacity of metals; $C_{V,m}/T$ is plotted against T^2. The results are consistent with equation (12.29), according to which $C_{V,m}$ is equal to $\gamma T + AT^3$. The intercepts give the values of γ. The values of A can be determined from the slopes. (Reproduced with permission from *Statistical Mechanics and Properties of Matter* by E. S. R. Gopal, Ellis Horwood Ltd., Chichester.)

  - γ obtained as an intercept of the curve of $C_{V,m}/T$ vs. T^2 (or T)!

classic vs. quantum mechanics

- The specific heat of the electron gas

	Classcial	Quantum mechanical
Electronic velocity distribution	$f_{MB}(\boldsymbol{v}) = n\left(\frac{m}{2k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}$	$f_{FD}(\boldsymbol{v}) = \frac{1}{4}\left(\frac{m}{\pi\hbar}\right)^3 \frac{1}{\exp\left(\frac{\frac{1}{2}mv^2 - E_0}{k_BT}\right) + 1}$
The specific heat of the electron gas	$c_V = \frac{3}{2}nk_B$	$c_V = \frac{3}{2}nk_B \cdot \left(\frac{\pi^2}{3}\frac{k_BT}{\mathscr{E}_F}\right)$ **~0.01 at** $T = 298$ **(K)**

What **Drude** predicted

What **Sommerfeld** revised

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Sommerfeld's model (4th)

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Velocity distribution for electrons in metals (1/2)

- Conversion of F-D dist. from $\varepsilon\left(\boldsymbol{k}\right)$ to $\boldsymbol{v}$

  - The number of single-electron levels in a small volume element $d\boldsymbol{k}$:

$$n_{d\boldsymbol{k}} = 2 \times \frac{1}{(2\pi/L)^3} \times d\boldsymbol{k} = \frac{V}{4\pi^3} d\boldsymbol{k}$$

The volume of interest

# of available $\boldsymbol{k}$-values per unit volume

Twofold spin degeneracy

  - The probability of each energy level (associated with $\boldsymbol{k}$) is being occupied: $f\left(\varepsilon\left(\boldsymbol{k}\right)\right)$

  - Total number of electrons in the volume element $d\boldsymbol{k}$:

$$N_{d\boldsymbol{k}} = n_{d\boldsymbol{k}} \cdot f\left(\varepsilon\left(\boldsymbol{k}\right)\right) = \frac{V}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) d\boldsymbol{k}$$

Velocity distribution for electrons in metals (2/2)

- Derivation (contd.)
  - The velocity of a free electron with a wave vector $\boldsymbol{k}$: $\boldsymbol{v} = \dfrac{\hbar \boldsymbol{k}}{m}$
  - Due to 1 : 1 correspondence between $\boldsymbol{k}$ and $\boldsymbol{v}$,

# of electrons in a volume element $d\boldsymbol{v}$ about $\boldsymbol{v}$ = # of electrons in a volume element $d\boldsymbol{k}$ about $\boldsymbol{k}$

  - [The number of electrons per unit volume of real space] in a velocity space element $d\boldsymbol{v}$:

$$f(\boldsymbol{v})\,d\boldsymbol{v} = \frac{N_{d\boldsymbol{k}}}{V} = \frac{1}{V}\left(\frac{V}{4\pi^3} f\left(\varepsilon\left(\boldsymbol{k}\right)\right) d\boldsymbol{k}\right) = \frac{\left(m/\hbar\right)^3}{4\pi^3} \frac{d\boldsymbol{v}}{\exp\left[\left(\frac{1}{2}mv^2 - \mu\right)/k_B T\right] + 1}$$

$$d\boldsymbol{k} = \left(\frac{m}{\hbar}\right)^3 d\boldsymbol{v}$$

Drude's model vs. Sommerfeld model

	Drude model	Sommerfeld model
Electronic velocity distribution	$f_{MB}(\boldsymbol{v}) = n\left(\frac{m}{2k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}$ Maxwell-Boltzmann dist.	$f_{FD}(\boldsymbol{v}) = \frac{1}{4}\left(\frac{m}{\pi\hbar}\right)^3 \frac{1}{\exp\left(\frac{\frac{1}{2}mv^2-\mu}{k_BT}\right)+1}$ Fermi-Dirac dist.
Assumptions	Free-electron approx. Independent approx. Relaxation-time approx.	
The specific heat of the electron gas	$c_V = \frac{3}{2}nk_B$	$c_V = \frac{3}{2}nk_B \cdot \left(\frac{\pi^2}{3}\frac{k_BT}{\mathscr{E}_F}\right)$
Mean square electronic velocity	$v^2 = \frac{3k_BT}{m}$ ↑ What **Drude model** derived	$v^2 = \frac{3k_BT}{m} \cdot \left(\frac{2}{3}\frac{\varepsilon_F}{k_BT}\right)$ ↑ What **Sommerfeld model** derived

Predictions by Sommerfeld model (1/3)

- The replacement of Maxwell-Boltzmann with Fermi-Dirac distribution affects the predictions of physical quantities that require the electronic velocity distribution
  - (1) Mean-free path, (2) Thermal conductivity (and Widemann-Franz law), (3) Thermopower

(1) Mean-free path

- The average distance an electron travels between collisions, $l = v\tau$ $\begin{cases} v : \text{Average electronic speed} \\ \tau : \text{relaxation time (an average survival time)} \end{cases}$
- Estimated $\tau : 10^{-15} \sim 10^{-14}\,(s)$ at $T = 300\ (K)$

	Drude model	**Sommerfeld model**
Average Electronic speed	$v = \sqrt{\frac{3k_BT}{m}} \simeq 10^{2-3}\,(\text{m/s})$	$v = v_F = \frac{\hbar k_F}{m} = \frac{4.2}{r_s/a_0} \times 10^6\,(\text{m/s})$
Mean-free path	$l = 1 \sim 10\,(\text{Å})$	$l > 100\,(\text{Å})$

Predictions by Sommerfeld model (2/3)

(2) Thermal conductivity (and Wiedemann-Franz law)

- Thermal conductivity (κ) and electrical conductivity (σ)

$$\kappa = \frac{1}{3} v^2 \tau c_V \text{ and } \sigma = \frac{ne^2\tau}{m}$$

- Wiedemann-Franz law

$$\frac{\kappa}{\sigma T} = \frac{m v^2 c_V}{3ne^2 T} = C$$

Element	273 K	373 K
Li	2.22	2.43
Na	2.12	
K	2.23	
Cu	2.20	2.29
Ag	2.31	2.38
Au	2.32	2.36
Mg	2.14	2.25
Fe	2.61	2.88
Zn	2.28	2.30
Cd	2.49	
Al	2.14	2.19
In	2.58	2.60
Sn	2.48	2.54
Pb	2.64	2.53

Kaye and Laby, Table of Physical and Chemical Constants, Longmans Green, Longdon, 1966.

	Drude model	Sommerfeld model
The specific heat of electron gas	$c_V = \frac{3}{2} n k_B$	$c_V = \frac{3}{2} n k_B \cdot \left(\frac{\pi^2}{3} \frac{k_B T}{\mathscr{E}_F} \right) < \frac{1}{100}$
Mean-square electronic speed	$v^2 = \frac{3 k_B T}{m}$	$v^2 = \frac{3 k_B T}{m} \cdot \left(\frac{2}{3} \frac{\mathscr{E}_F}{k_B T} \right) > 100$
Widemann-Franz law	$\frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 = 1.11 \times 10^{-8} \left(\frac{W \cdot \Omega}{K^2} \right)$	$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \left(\frac{W \cdot \Omega}{K^2} \right)$

Predictions by Sommerfeld model (3/3)

Element	Q [V/K]
Na	-5 x 10^{-6}
K	-12.5 x 10^{-6}
Cu	1.8 x 10^{-6}
Be	1.5 x 10^{-6}
Al	-1.8 x 10^{-6}

(3) Thermopower

$\boldsymbol{E} = Q\nabla T$, where $\boldsymbol{E}$: thermoelectric field, Q : thermopower (V/K)

$$Q = -\frac{1}{3e}\frac{d}{dT}\left(\frac{mv^2}{2}\right) = -\frac{1}{3ne}n\frac{d\mathscr{E}}{dT} = -\frac{c_V}{3ne}$$

	Drude model	Sommerfeld model
The specific heat of electron gas	$c_V = \frac{3}{2}nk_B$	$c_V = \frac{3}{2}nk_B \cdot \left(\frac{\pi^2}{3}\frac{k_BT}{\mathscr{E}_F}\right)$
Thermopower	$Q = -\frac{k_B}{2e} = -0.43 \times 10^{-4}\,(V/K)$	$Q = -\frac{k_B}{2e}\left(\frac{\pi^2}{3}\frac{k_BT}{\mathscr{E}_F}\right) = -1.42\left(\frac{k_BT}{\mathscr{E}_F}\right) \times 10^{-4}\,(V/K)$ $\sim \frac{1}{100}$

Common failures of both models

- Drude vs. Sommerfeld
  - Commonality: **Free-electron approx.**, Independent approx., Relaxation time approx.
  - Difference: Electronic velocity distribution (Maxwell-Boltzmann vs. Fermi-Dirac)

	What aspects cannot be explainable
Hall coefficient	
Magnetoresistance	
Thermoelectric field	**pp. 58 ~ 60 Ashcroft & Mermin**
Widemann-Franz law	
DC electrical conductivity	
AC electrical conductivity	
Specific heat	
Nonmetallic elements	

To move further...

- 3 Key assumptions in the Drude's model

  ① Free-electron approx.: No electron-ion interaction (*except collisions)

  ② Independent approx.: No electron-electron interaction

  ③ Relaxation-time approx.: τ independent of electron's position and velocity

- Revision of ②, ③ leads to only minor improvement in predictions

- Most of the problems in Drude's and Sommerfeld's model stem from ①!

- The details of ① Free-electron approx.:

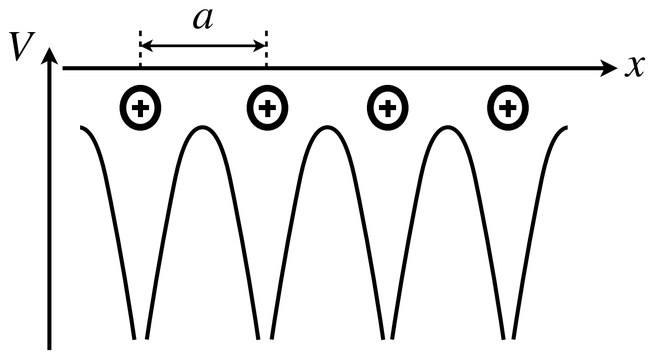
  (i) The effect of the ions on an electron between collisions is ignored

  (ii) How the ions result in collisions is left unexplained

  (iii) The contribution of the ions to physical phenomena (e.g. specific heat, thermal conductivity) is ignored

To move further...

- How free-electron approx. needs to be revised:
  - (i) & (ii) Electrons move in the presence of a static potential due to a periodic array of stationary ions ("Nearly-free electron model")
    - Main topics: Bloch's state and electronic band structure
  - (iii) Consideration of the effects of ionic vibrations in that array
    - Main topic: phonon (→ temp-dependent electric conductivity, cubic term in the specific heat, a source of collisions, etc)



- Crystalline structure
  - The ions in metals are arranged in a regular periodic array (i.e., lattice)
    = A basis for the entire analytic framework of solid-state physics
  - A direct characterization of the periodicity = X-ray diffraction (XRD)