

Free electron Fermi gas model: specific heat and Pauli paramagnetism
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Abstract

As an example we consider a Na atom, which has an electron configuration of $(1s)^2(2s)^2(2p)^6(3s)^1$. The 3s electrons in the outermost shell becomes conduction electrons and moves freely through the whole system. The simplest model for the conduction electrons is a free electron Fermi gas model. In real metals, there are interactions between electrons. The motion of electrons is also influenced by a periodic potential caused by ions located on the lattice. Nevertheless, this model is appropriate for simple metals such as alkali metals and noble metals. When the Schrödinger equation is solved for one electron in a box, a set of energy levels are obtained which are quantized. When we have a large number of electrons, we fill in the energy levels starting at the bottom. Electrons are fermions, obeying the Fermi-Dirac statistics. So we have to take into account the Pauli's exclusion principle. This law prohibits the occupation of the same state by more than two electrons.

Sommerfeld's involvement with the quantum electron theory of metals began in the spring of 1927. Pauli showed Sommerfeld the proofs of his paper on paramagnetism. Sommerfeld was very impressed by it. He realized that the specific heat dilemma of the Drude-Lorentz theory could be overcome by using the Fermi-Dirac statistics (Hoddeeson et al.).¹

Here we discuss the specific heat and Pauli paramagnetism of free electron Fermi gas model. The Sommerfeld's formula are derived using Mathematica. The temperature dependence of the chemical potential will be discussed for the 3D and 1D cases. We also show how to calculate numerically the physical quantities related to the specific heat and Pauli paramagnetism by using Mathematica, based on the physic constants given by NIST Web site (Planck's constant \hbar , Bohr magneton μ_B , Boltzmann constant k_B , and so on).² This lecture note is based on many textbooks of the solid state physics including Refs. 3 – 10.

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1. Schrödinger equation³⁻¹⁰

A. Energy level in 1D system

We consider a free electron gas in 1D system. The Schrödinger equation is given by

$$H\psi_k(x) = \frac{p^2}{2m}\psi_k(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_k(x)}{dx^2} = \varepsilon_k\psi_k(x), \quad (1)$$

where

$$p = \frac{\hbar}{i} \frac{d}{dx},$$

and ε_k is the energy of the electron in the orbital.

The orbital is defined as a solution of the wave equation for a system of only one electron: ⟨⟨one-electron problem⟩⟩.

Using a periodic boundary condition: $\psi_k(x+L) = \psi_k(x)$, we have

$$\psi_k(x) \sim e^{ikx}, \quad (2)$$

with

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

$$e^{ikL} = 1 \text{ or } k = \frac{2\pi}{L}n,$$

where $n = 0, \pm 1, \pm 2, \dots$, and L is the size of the system.

B. Energy level in 3D system

We consider the Schrödinger equation of an electron confined to a cube of edge L .

$$H\psi_{\mathbf{k}} = \frac{\mathbf{p}^2}{2m}\psi_{\mathbf{k}} = -\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}. \quad (3)$$

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions.

Boundary condition (Born-von Karman boundary conditions).

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

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

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

The wavefunctions are of the form of a traveling plane wave.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (4)$$

with

$$k_x = (2\pi/L) n_x, (n_x = 0, \pm 1, \pm 2, \pm 3, \dots),$$

$$k_y = (2\pi/L) n_y, (n_y = 0, \pm 1, \pm 2, \pm 3, \dots),$$

$$k_z = (2\pi/L) n_z, (n_z = 0, \pm 1, \pm 2, \pm 3, \dots).$$

The components of the wavevector \mathbf{k} are the quantum numbers, along with the quantum number m_s of the spin direction. The energy eigenvalue is

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} \mathbf{k}^2. \quad (5)$$

Here

$$\mathbf{p} \psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar}{i} \nabla_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) = \hbar \mathbf{k} \psi_{\mathbf{k}}(\mathbf{r}). \quad (6)$$

So that the plane wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenfunction of \mathbf{p} with the eigenvalue $\hbar \mathbf{k}$. The ground state of a system of N electrons, the occupied orbitals are represented as a point inside a sphere in \mathbf{k} -space.

Because we assume that the electrons are noninteracting, we can build up the N -electron ground state by placing electrons into the allowed one-electron levels we have just found.

((The Pauli's exclusion principle))

The one-electron levels are specified by the wavevectors \mathbf{k} and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\pm \hbar/2$. Therefore associated with each allowed wave vector \mathbf{k} are two levels:

$$|\mathbf{k}, \uparrow\rangle, |\mathbf{k}, \downarrow\rangle.$$

In building up the N -electron ground state, we begin by placing two electrons in the one-electron level $k = 0$, which has the lowest possible one-electron energy $\varepsilon = 0$. We have

$$N = 2 \frac{L^3}{(2\pi)^3} \frac{4\pi}{3} k_F^3 = \frac{V}{3\pi^2} k_F^3, \quad (7)$$

where the sphere of radius k_F containing the occupied one-electron levels is called the Fermi sphere, and the factor 2 is from spin degeneracy. The electron density n is defined by

$$n = \frac{N}{V} = \frac{1}{3\pi^2} k_F^3. \quad (8)$$

The Fermi wavenumber k_F is given by

$$k_F = (3\pi^2 n)^{1/3}. \quad (9)$$

The Fermi energy is given by

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}. \quad (10)$$

The Fermi velocity is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3}. \quad (11)$$

The Fermi temperature T_F is defined by

$$T_F = \frac{\varepsilon_F}{k_B}.$$

In this model, these quantities is dependent only on the electron density n .

We define the radius r_s (the radius of a sphere that contains one electron) as

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi}{3} r_s^3$$

or

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3}$$

The dimensionless radius parameter is defined as

$$r_s/a_0$$

where a_0 is the first Bohr radius, $a_0 = 0.52917721092 \text{ \AA}$.

((Note))

The Fermi energy ε_F can be estimated using the number of electrons per unit volume (the electron density) as

$$\varepsilon_F = 3.64645 \times 10^{-15} n^{2/3} [\text{eV}] = 1.69253 n_0^{2/3} [\text{eV}],$$

where n and n_0 is in the units of (cm^{-3}) and $n = n_0 \times 10^{22}$. The Fermi wave number k_F is calculated as

$$k_F = 6.66511 \times 10^7 n_0^{1/3} [\text{cm}^{-1}].$$

The Fermi velocity v_F is calculated as

$$v_F = 7.71603 \times 10^7 n_0^{1/3} [\text{cm/s}].$$

((Example-1))

The Fermi energy of Au

Atomic molar mass $M_0 = 196.9666 \text{ g/mol}$

Density $\rho = 19.30 \text{ g/cm}^3$

There is one conduction electron per Au atom; $p = 1$.

$$n = \frac{N}{V} = p \frac{N_0}{V} = p \frac{M}{V} \frac{N}{M} = p \rho \frac{N_A}{M_0} = 5.901 \times 10^{22} / \text{cm}^3.$$

where N_0 is the total number of atoms. Since $n_0 = 5.901$, we have

$$\varepsilon_F = 1.69253 n_0^{2/3} = 5.526 [\text{eV}].$$

$$k_F = 6.66511 \times 10^7 n_0^{1/3} = 1.20442 \times 10^8 [\text{cm}^{-1}].$$

$$v_F = 7.71603 \times 10^7 n_0^{1/3} = 1.39433 \times 10^8 [\text{cm/s}].$$

$$T_F = \varepsilon_F/k_B = 6.4136 \times 10^4 \text{ K}$$

((Example-2)) The Fermi energy of Cu

Cu has a fcc structure with the lattice constant $a = 3.615 \text{ \AA}$ (conventional cell). There are 4 Cu atoms per unit volume for the conventional cell. Then the number electron density n is

$$n = p \frac{4}{a^3} = 8.50234 \times 10^{22} / \text{cm}^3$$

where p ($= 1$) is the number of conduction electron per Cu atom.

The Fermi energy is

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = 1.12964 \times 10^{-11} \text{ erg} = 7.051 \text{ eV}$$

The Fermi velocity is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3} = 1.575 \times 10^8 \text{ cm/s}$$

The Fermi wavenumber

$$k_F = (3\pi^2 n)^{1/3} = 1.3604 \times 10^8 / \text{cm}$$

The Fermi temperature is

$$T_F = \frac{\varepsilon_F}{k_B} = 8.1819 \times 10^4 \text{ K.}$$

The radius r_s is

$$r_s = \left(\frac{3}{4\pi n} \right)^{1/3} = 1.4108 \text{ \AA.}$$

or

$$\frac{r_s}{a_0} = 2.66598.$$

((Table)) Ashcroft and Mermin

FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS^a

ELEMENT	Z	n ($10^{22}/\text{cm}^3$)	$r_s(\text{\AA})$	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (x)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

((Table)) Kittel

(Except for Na, K, Rb, Cs at 0 K and Li at 78 K.)

Valency	Metal	Electron concentration, in cm^{-3}	Radius* parameter r_n	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^6	1.29×10^5	4.72	5.48×10^4
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
	2	Be	24.2	1.88	1.93	2.23	14.14
Mg		8.60	2.65	1.37	1.58	7.13	8.27
Ca		4.60	3.27	1.11	1.28	4.68	5.43
Sr		3.56	3.56	1.02	1.18	3.95	4.58
Ba		3.20	3.69	0.98	1.13	3.65	4.24
Zn		13.10	2.31	1.57	1.82	9.39	10.90
Cd		9.28	2.59	1.40	1.62	7.46	8.66
3		Al	18.06	2.07	1.75	2.02	11.63
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(<i>w</i>)	14.48	2.23	1.62	1.88	10.03	11.64

*The dimensionless radius parameter is defined as $r_n = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

((Mathematica))

Fermi energy ϵ_F (eV) vs the number of electrons ($n = n_0 \times 10^{22} [\text{cm}^{-3}]$).

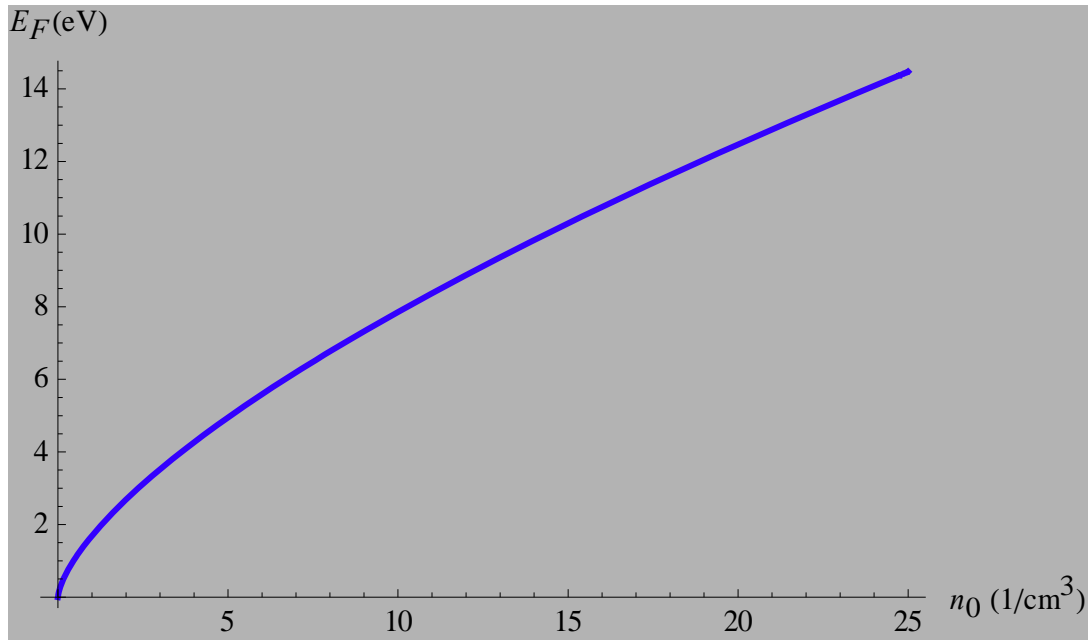


Fig.1 Fermi energy vs number density $n (= n_0 \times 10^{22} [\text{cm}^{-3}])$.

2. Fermi-Dirac distribution function³⁻¹⁰

The Fermi-Dirac distribution gives the probability that a state at energy ε will be occupied in an ideal gas in thermal equilibrium

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (12)$$

where μ is the chemical potential and $\beta = 1/(k_B T)$.

- (i) $\lim_{T \rightarrow 0} \mu = \varepsilon_F$.
- (ii) $f(\varepsilon) = 1/2$ at $\varepsilon = \mu$.
- (iii) For $\varepsilon - \mu \gg k_B T$, $f(\varepsilon)$ is approximated by $f(\varepsilon) = e^{-\beta(\varepsilon-\mu)}$. This limit is called the Boltzmann or Maxwell distribution.
- (iv) For $k_B T \ll \varepsilon_F$, the derivative $-df(\varepsilon)/d\varepsilon$ corresponds to a Dirac delta function having a sharp positive peak at $\varepsilon = \mu$.

$$-\frac{\partial f(\varepsilon)}{\partial \varepsilon} = \beta \frac{e^{\beta(\varepsilon-\mu)}}{[e^{\beta(\varepsilon-\mu)} + 1]^2}$$

$$\int_0^{\infty} \left[-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right] d\varepsilon = [-f(\varepsilon)]_0^{\infty} = 1$$

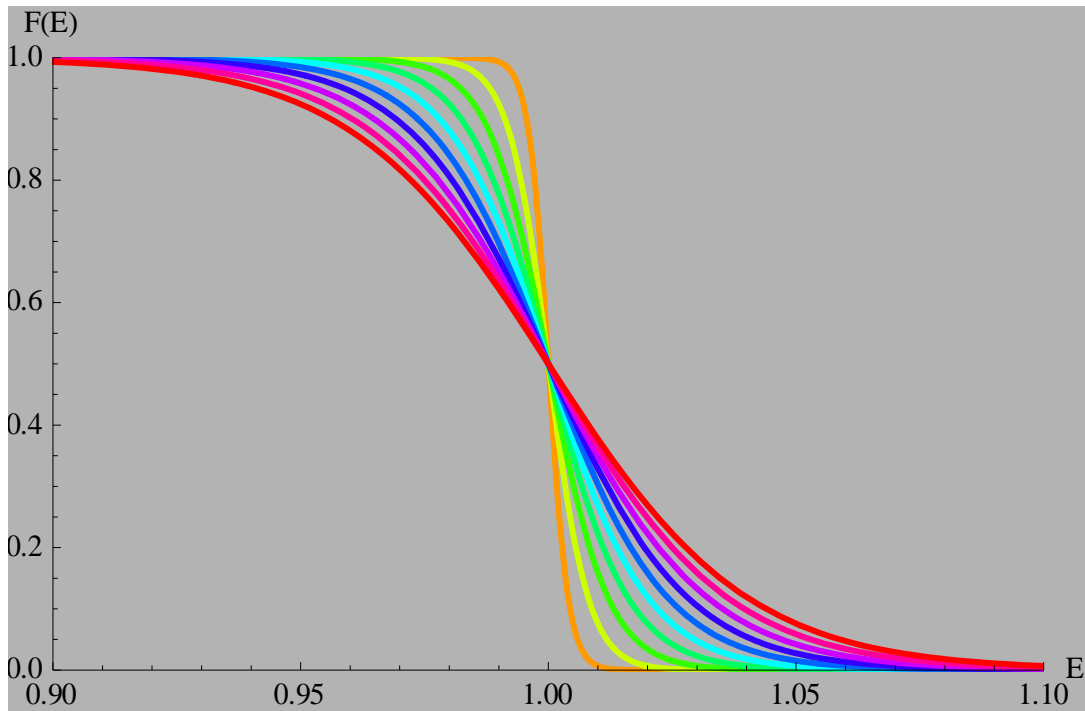


Fig.2 Fermi-Dirac distribution function $f(\varepsilon)$ at various T ($= 0.002 - 0.02$). $k_B = 1$. $\mu(T = 0) = \varepsilon_F = 1$.

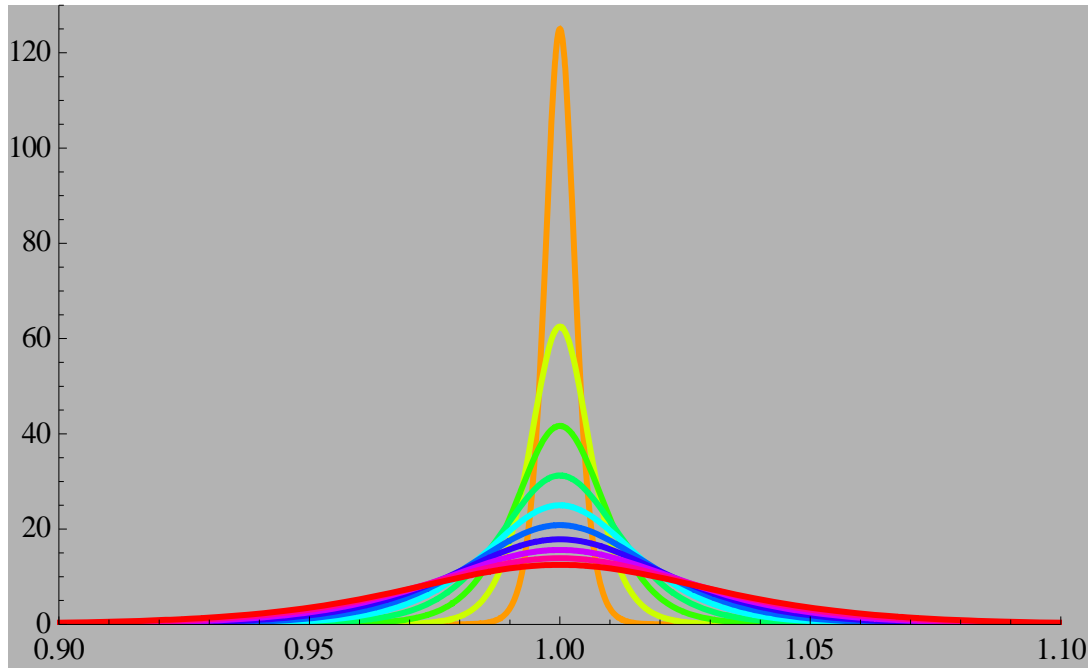


Fig.3 Derivative of Fermi-Dirac distribution function $-df(\varepsilon)/d\varepsilon$ at various T ($= 0.002 - 0.02$). $k_B = 1$. $\mu(T = 0) = \varepsilon_F = 1$.

3. Density of states³⁻¹⁰

A. 3D system

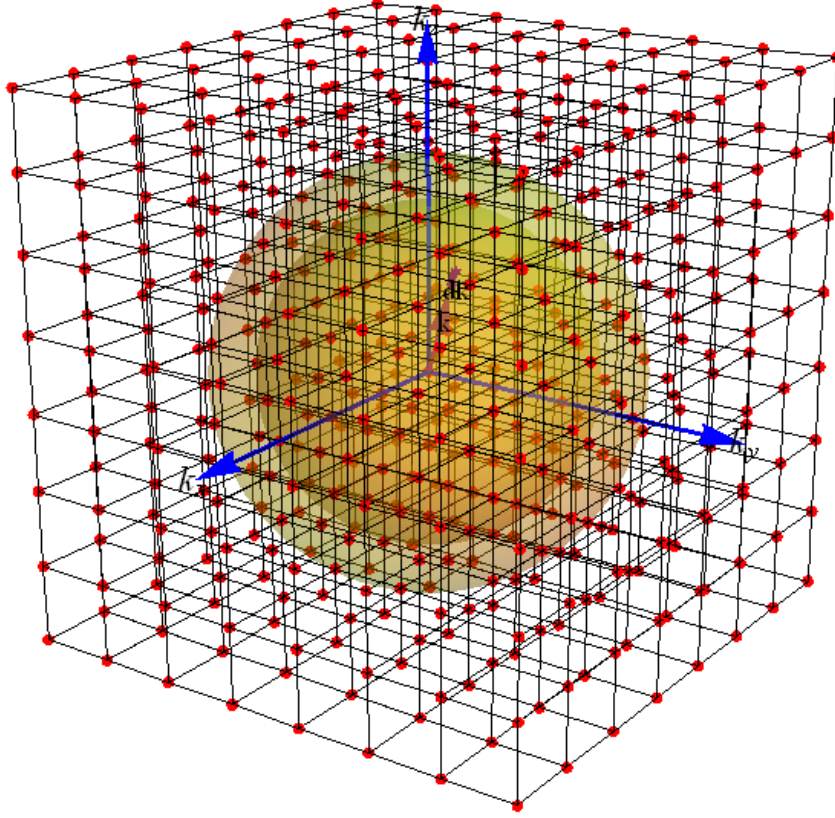


Fig. Density of states in the 3D k -space. There is one state per $(2\pi/L)^3$.

There is one state per volume of k -space $(2\pi/L)^3$. We consider the number of one-electron levels in the energy range from ε to $\varepsilon+d\varepsilon$; $D(\varepsilon)d\varepsilon$

$$D(\varepsilon)d\varepsilon = 2 \frac{L^3}{(2\pi)^3} 4\pi k^2 dk, \quad (13)$$

where $D(\varepsilon)$ is called a density of states. Since $k = (2m/\hbar^2)^{1/2} \sqrt{\varepsilon}$, we have

$$dk = (2m/\hbar^2)^{1/2} d\varepsilon / (2\sqrt{\varepsilon}).$$

Then we get the density of states

$$D(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon}. \quad (14)$$

((Definition))

So far we assume that there are N free electrons in the volume V . We consider the case when each atom in metals has n_v conduction electrons. If there are N_0 atoms in the volume V , the number of the total free electrons N is expressed by

$$N = n_v N_0$$

Here we define $D_A(\varepsilon_F)$ [1/(eV atom)] which is the density of states per unit energy per atom.

$$D_A(\varepsilon_F) = n_v \frac{D(\varepsilon_F)}{N} = \frac{D(\varepsilon_F)}{N_0}, \quad (15)$$

where $D(\varepsilon_F)/N$ corresponds to the density of states per unit energy per electron. Noting that

$$N = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{2}{3} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{3/2}. \quad (16)$$

we have

$$D_A(\varepsilon_F) = \frac{3}{2\varepsilon_F} n_v. \quad (17)$$

For Al, we have $\varepsilon_F = 11.6$ eV and $n_v = 3$. Then $D_A(\varepsilon_F) = 0.39$ /(eV atom).

Here we make a plot of $f(\varepsilon)D(\varepsilon)$ as a function of ε using Mathematica.

$$f(\varepsilon)D(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} + 1} = a \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (18)$$

where

$$a = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}$$

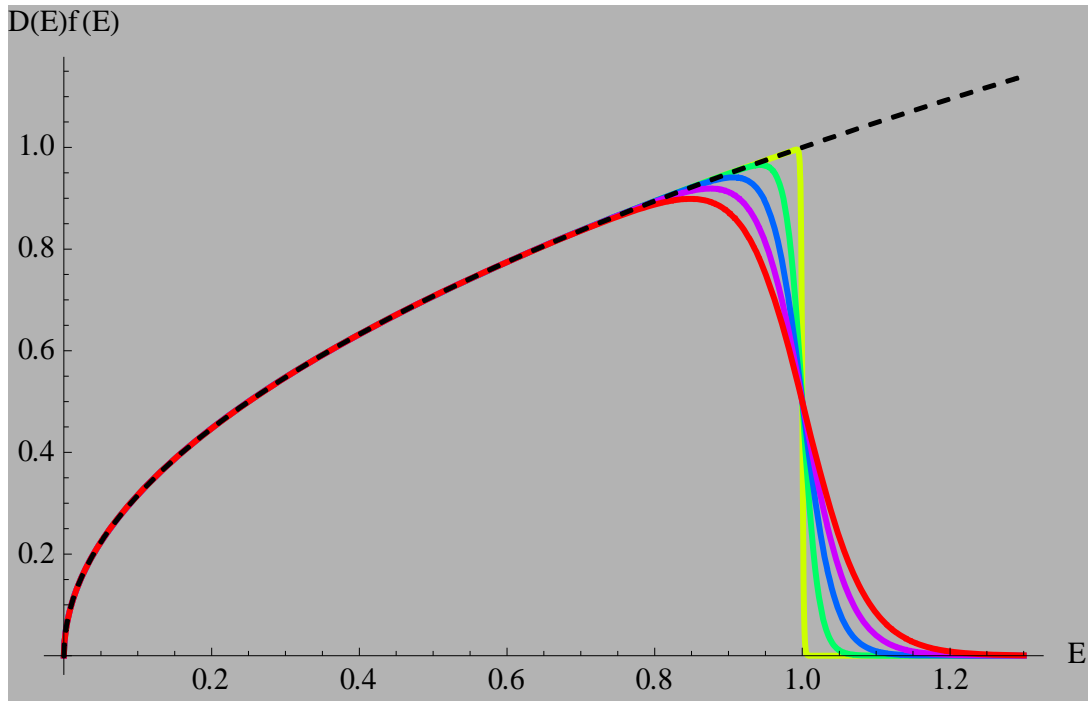


Fig.4 $D(\varepsilon)f(\varepsilon)$ at various T ($= 0.001 - 0.05$). $k_B = 1$. $\mu(T = 0) = \varepsilon_F = 1$. The constant a of $D(\varepsilon)$ ($= a\sqrt{\varepsilon}$) is assumed to be equal to 1. The dashed line denotes the curve of $D(\varepsilon)$.

B. 2D system

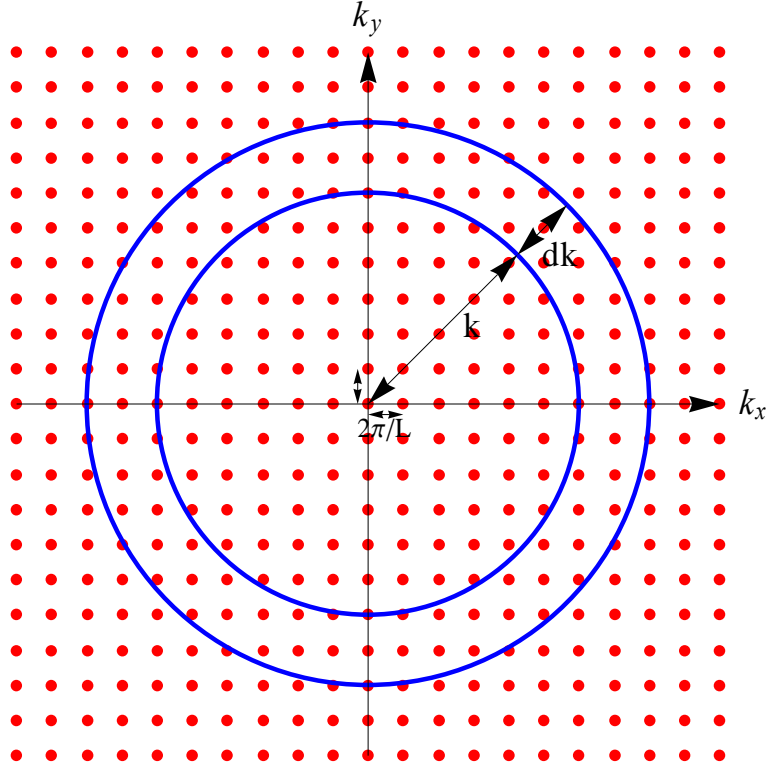


Fig. Density of states for the 2D \mathbf{k} -space. There is one state per area $\left(\frac{2\pi}{L}\right)^2$ of the reciprocal lattice plane.

For the 2D system, we have

$$D(\varepsilon)d\varepsilon = 2 \frac{L^2}{(2\pi)^2} 2\pi k dk . \quad (19)$$

The factor 2 comes from the spin weight. Since $d\varepsilon = (\hbar^2/2m)2kdk$, we have the density of states for the 2D system as

$$D(\varepsilon) = \frac{mL^2}{\pi\hbar^2}, \quad (20)$$

which is independent of ε .

C. 1D system

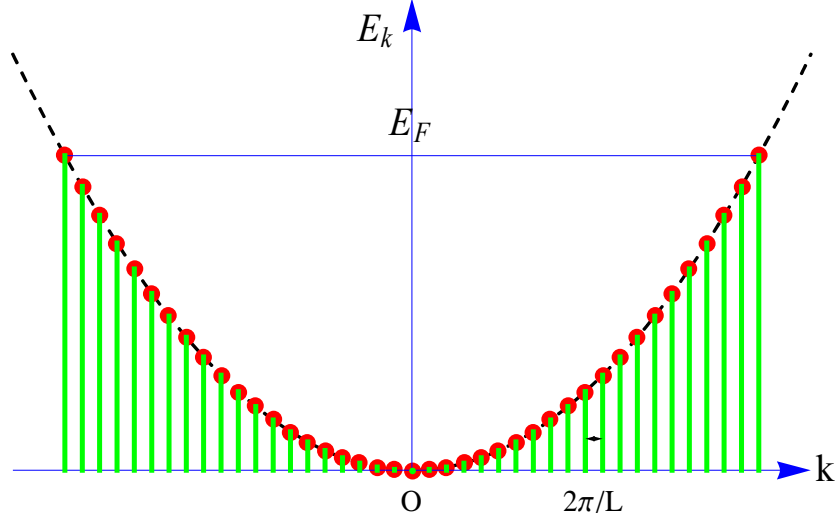


Fig. Energy ε_k vs k for the one dimensional case. The discrete states are described $|k, \uparrow\rangle$ and $|k, \downarrow\rangle$ with $k = (2\pi/L)n$. ($n_x = 0, \pm 1, \pm 2, \dots$). All the states below the Fermi energy ε_F are occupied at $T = 0$ K.

For the 1D system we have

$$D(\varepsilon)d\varepsilon = 2 \frac{L}{2\pi} 2dk = \frac{2L}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2} \varepsilon^{-1/2} d\varepsilon \quad (21)$$

The factor 2 before dk arises from the two states of k and $-k$. Thus the density of states for the 1D system is

$$D(\varepsilon) = \frac{L}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} \varepsilon^{-1/2}. \quad (22)$$

which decreases with increasing ε .

4. Sommerfeld's formula

When we use a formula

$$\sum_{\mathbf{k}} F(k) \rightarrow \frac{L^3}{(2\pi)^3} \int d\mathbf{k} F(\mathbf{k}). \quad (23)$$

the total particle number N and total energy E can be described by

$$N = 2 \sum_k f(\varepsilon_k) = \frac{2L^3}{(2\pi)^3} \int d\mathbf{k} f(\varepsilon_k) = \int d\varepsilon D(\varepsilon) f(\varepsilon), \quad (24)$$

and

$$E = 2 \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} f(\varepsilon_{\mathbf{k}}) = \frac{2L^3}{(2\pi)^3} \int d\mathbf{k} \varepsilon_{\mathbf{k}} f(\varepsilon_{\mathbf{k}}) = \int d\varepsilon D(\varepsilon) \varepsilon f(\varepsilon). \quad (25)$$

First we prove that

$$\begin{aligned} \int_{-\infty}^{\infty} g(\varepsilon) \left[-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right] d\varepsilon &= \int_{-\infty}^{\infty} g'(\varepsilon) f(\varepsilon) d\varepsilon \\ &= g(\mu) + \frac{1}{6} k_B^2 T^2 \pi^2 g^{(2)}(\mu) + \frac{7}{360} k_B^4 T^4 \pi^4 g^{(4)}(\mu) \\ &\quad + \frac{31}{15120} k_B^6 T^6 \pi^6 g^{(6)}(\mu) + \frac{127}{604800} k_B^8 T^8 \pi^8 g^{(8)}(\mu) \\ &\quad + \frac{73}{3421440} k_B^{10} T^{10} \pi^{10} g^{(10)}(\mu) + \frac{1414477}{653837184000} k_B^{12} T^{12} \pi^{12} g^{(12)}(\mu) + \dots \end{aligned} \quad (26)$$

using Mathematica.

((Mathematica))

Sommerfeld's formula

```
Clear["Global`*"]; f[x_] := 1 / (Exp[x/(k_B T)] + 1); h[x] = -D[f[x], x] // Simplify;
g1 = Series[g[x], {x, μ, 14}] // Normal; G1 = k_B T (g1 h[x]) /. {x -> μ + k_B T y} // Expand;
K[n_] := Integrate[G1[[n]], dy];
G2 = Sum[K[n], {n, 1, 13}]
g[μ] + 1/6 k_B^2 π^2 T^2 g''[μ] + 7/360 k_B^4 π^4 T^4 g^{(4)}[μ] + 31 k_B^6 π^6 T^6 g^{(6)}[μ] / 15120 +
127 k_B^8 π^8 T^8 g^{(8)}[μ] / 604800 + 73 k_B^{10} π^{10} T^{10} g^{(10)}[μ] / 3421440 + 1414477 k_B^{12} π^{12} T^{12} g^{(12)}[μ] / 653837184000
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So we get a final result

$$\begin{aligned} \int_{-\infty}^{\infty} g(\varepsilon) \left(-\frac{df}{d\varepsilon} \right) d\varepsilon &= g[\mu] + \frac{1}{6} k_B^2 T^2 \pi^2 g''[\mu] + \frac{7}{360} k_B^4 T^4 \pi^4 g^{(4)}[\mu] + \frac{31 k_B^6 T^6 \pi^6 g^{(6)}[\mu]}{15120} + \\ &\quad \frac{127 k_B^8 T^8 \pi^8 g^{(8)}[\mu]}{604800} + \frac{73 k_B^{10} T^{10} \pi^{10} g^{(10)}[\mu]}{3421440} + \frac{1414477 k_B^{12} T^{12} \pi^{12} g^{(12)}[\mu]}{653837184000} \end{aligned}$$

Here we note that

$$\int_0^{\infty} g(\varepsilon) \left[-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right] d\varepsilon = -f(\varepsilon)g(\varepsilon) \Big|_0^{\infty} + \int_0^{\infty} g'(\varepsilon) f(\varepsilon) d\varepsilon$$

$$= \int_0^{\infty} g'(\varepsilon) f(\varepsilon) d\varepsilon$$
(27)

We define

$$\varphi(\varepsilon) = g'(\varepsilon) \quad \text{and} \quad g(\varepsilon=0) = 0,$$

or

$$g(\varepsilon) = \int_0^{\varepsilon} \varphi(\varepsilon') d\varepsilon'.$$
(28)

Then we have a final form (Sommerfeld's formula).

$$\int_0^{\infty} f(\varepsilon) \varphi(\varepsilon) d\varepsilon = \int_0^{\mu} \varphi(\varepsilon') d\varepsilon' + \frac{1}{6} k_B^2 T^2 \pi^2 \varphi'(\mu) + \frac{7}{360} k_B^4 T^4 \pi^4 \varphi^{(3)}(\mu)$$

$$+ \frac{31}{15120} k_B^6 T^6 \pi^6 \varphi^{(5)}(\mu) + \frac{127}{604800} k_B^8 T^8 \pi^8 \varphi^{(7)}(\mu)$$

$$+ \frac{73}{3421440} k_B^{10} T^{10} \pi^{10} \varphi^{(9)}(\mu) + \frac{1414477}{653837184000} k_B^{12} T^{12} \pi^{12} \varphi^{(11)}(\mu) + \dots$$
(29)

5. T dependence of the chemical potential

We start with

$$N = \int d\varepsilon D(\varepsilon) f(\varepsilon),$$

where

$$D(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} = a \sqrt{\varepsilon},$$

and

$$a = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}$$

$$N = \int_0^{\infty} f(\varepsilon)D(\varepsilon)d\varepsilon \approx \int_0^{\mu} D(\varepsilon')d\varepsilon' + \frac{1}{6}k_B^2 T^2 \pi^2 D'(\mu) = \frac{2a}{3}\mu^{3/2} + \frac{1}{6}k_B^2 T^2 \pi^2 \frac{a}{2\sqrt{\mu}}.$$

But we also have $\varepsilon_F = \mu(T = 0)$. Then we have

$$N = \int_0^{\varepsilon_F} D(\varepsilon)d\varepsilon = \frac{2a}{3}\varepsilon_F^{3/2}.$$

Thus the chemical potential is given by

$$\frac{2a}{3}\varepsilon_F^{3/2} = \frac{2a}{3}\mu^{3/2} + \frac{1}{6}k_B^2 T^2 \pi^2 \frac{a}{2\sqrt{\mu}},$$

or

$$1 = \left(\frac{\mu}{\varepsilon_F}\right)^{3/2} + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2 \left(\frac{\mu}{\varepsilon_F}\right)^{-1/2}.$$

which is valid for the order of $\left(\frac{k_B T}{\varepsilon_F}\right)^2$ in the above expansion formula. The ContourPlot of μ/ε_F and $k_B T/\varepsilon_F$ can be obtained by using the Mathematica .

```

Clear["Global`*"]; eq1 =  $y^{1/2} = y^2 + \frac{\pi^2}{8} x^2$ ;
f1 = ContourPlot[Evaluate[eq1], {x, 0, 0.1},
  {y, 0.99, 1.00}, ContourStyle -> {Red, Thick}];
f2 =
Graphics[
  {Text[Style[" $k_B T / E_F$ ", Black, 12], {0.09, 0.99}],
  Text[Style[" $\mu / E_F$ ", Black, 12], {0.004, 0.999}],
  Text[Style["3D system", Black, 15],
  {0.07, 0.9995}]}];
Show[f1, f2, PlotRange -> All]

```

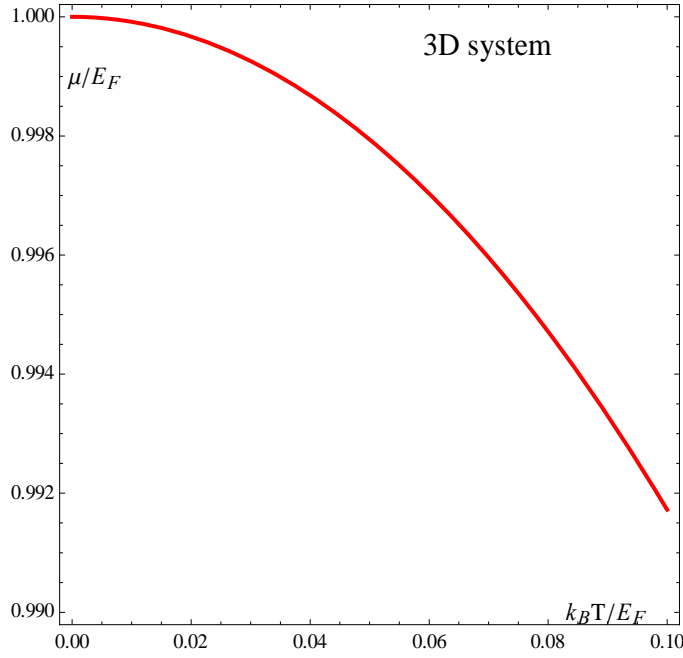


Fig. ContourPlot of μ/ε_F and $k_B T/\varepsilon_F$ for small values of $k_B T/\varepsilon_F$

The chemical potential μ is approximated by the forms,

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \text{ (3D case).} \quad (30)$$

For the 1D case, similarly we have

$$\mu = \varepsilon_F \left[1 + \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 \right] \text{ (1D case).} \quad (31)$$

((**Mathematica**))

We now discuss the T dependence of μ by using the Mathematica. The higher order terms (proportional to T^4 , T^6 , ..) are also taken into account. The results are as follows.

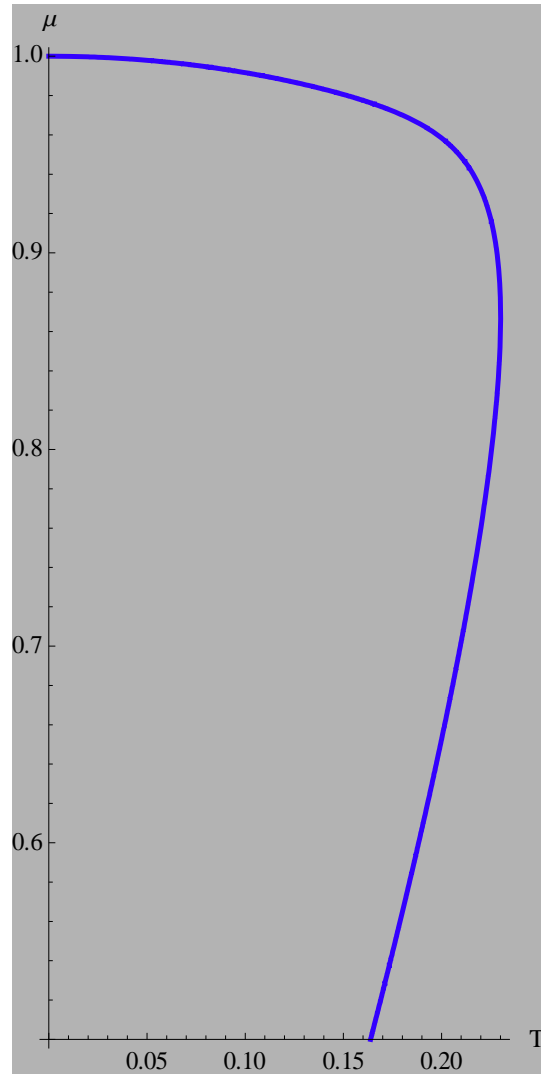


Fig.5 T dependence of chemical potential μ for the 3D system. $k_B = 1$. $\varepsilon_F = \mu(T = 0) = 1$.

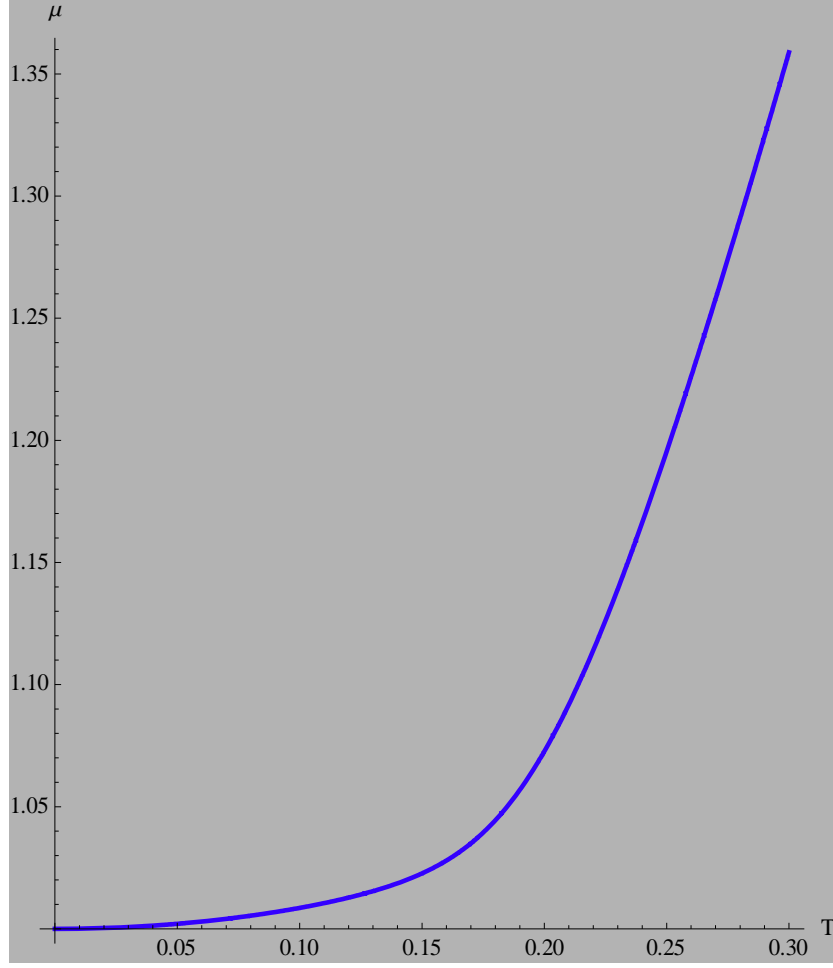


Fig.6 T dependence of chemical potential μ for the 1D system. $k_B = 1$. $\varepsilon_F = \mu(T = 0) = 1$.

6. Total energy and specific heat

Using the Sommerfeld's formula, the total energy U of the electrons is approximated by

$$U = \int_0^{\infty} f(\varepsilon) \varepsilon D(\varepsilon) d\varepsilon = \int_0^{\mu(T)} \varepsilon D(\varepsilon) d\varepsilon + \frac{1}{6} \pi^2 (k_B T)^2 \{D[\mu(T)] + \mu(T) D'[\mu(T)]\}.$$

The total number of electrons is also approximated by

$$N = \int_0^{\infty} f(\varepsilon) D(\varepsilon) d\varepsilon = \int_0^{\mu(T)} D(\varepsilon) d\varepsilon + \frac{1}{6} \pi^2 (k_B T)^2 D'[\mu(T)].$$

Since $\partial N / \partial T = 0$ (N is independent of T), we have

$$\mu'(T)D[\mu(T)] + \frac{1}{3}\pi^2k_B^2TD'[\mu(T)] \approx 0,$$

or

$$\mu'(T) = -\frac{1}{3}\pi^2k_B^2T \frac{D'[\mu(T)]}{D[\mu(T)]}.$$

The specific heat C_{el} is defined by

$$C_{el} = \frac{dU}{dT} = \frac{1}{3}\pi^2k_B^2TD[\mu(T)] + \left\{ \frac{1}{3}\pi^2k_B^2TD'[\mu(T)] + \mu'(T)D[\mu(T)] \right\} \mu(T).$$

The second term is equal to zero. So we have the final form of the specific heat

$$C_{el} = \frac{1}{3}\pi^2k_B^2TD[\mu(T)].$$

When $\mu(T) \approx \varepsilon_F$,

$$C_{el} = \frac{1}{3}\pi^2k_B^2D(\varepsilon_F)T. \quad (32)$$

7. The heat capacity of electrons per mol atom

From the above discussion, we have

$$D(\varepsilon_F) = a\sqrt{\varepsilon_F},$$

$$N = \frac{2a}{3}\varepsilon_F^{3/2},$$

and

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

The heat capacity of N electrons is given by

$$C_{el} = \frac{1}{3}\pi^2k_B^2D(\varepsilon_F)T$$

So the heat capacity per electron is given by

$$\frac{C_{el}}{N} = \frac{1}{3} \pi^2 k_B^2 \frac{D(\varepsilon_F)}{N} T.$$

Using the expression of $D(\varepsilon_F)/N = 3/(2\varepsilon_F)$, we have

$$\frac{C_{el}}{N} = \frac{1}{3} \pi^2 k_B^2 \frac{3}{2\varepsilon_F} T = \frac{\pi^2 k_B^2}{2\varepsilon_F} T$$

Suppose that each atom has n_v conduction electrons. The total number of electrons is N ;

$$N = n_v N_0.$$

So each atom has the heat capacity as

$$\begin{aligned} n_v \frac{C_{el}}{N} &= \frac{C_{el}}{N_0} = \frac{n_v}{N} \frac{1}{3} \pi^2 k_B^2 D(\varepsilon_F) T \\ &= \frac{1}{3} \pi^2 k_B^2 \frac{D(\varepsilon_F)}{N_0} T \\ &= \frac{1}{3} \pi^2 k_B^2 D_A(\varepsilon_F) T \end{aligned}$$

where

$$D_A(\varepsilon_F) = \frac{D(\varepsilon_F)}{N_0}$$

or

$$D_A(\varepsilon_F) = n_v \frac{D(\varepsilon_F)}{N} = \frac{3n_v}{2\varepsilon_F}$$

The heat capacity per mol atom is

$$C_{el}^{(M)} = \frac{1}{3} \pi^2 k_B^2 D_A(\varepsilon_F) N_A T$$

where N_A is the Avogadro number.

$$\frac{1}{3} \pi^2 N_A k_B^2 = 2.35715 \text{ mJ eV/K}^2.$$

γ is related to $D_A(\varepsilon_F)$ as

$$\gamma = \frac{1}{3} \pi^2 N_A k_B^2 D_A(\varepsilon_F),$$

or

$$\gamma (\text{mJ/mol K}^2) = 2.35715 D_A(\varepsilon_F). \quad (33)$$

We now give the physical interpretation for Eq.(32). When we heat the system from 0 K, not every electron gains an energy $k_B T$, but only those electrons in orbitals within a energy range $k_B T$ of the Fermi level are excited thermally. These electrons gain an energy of $k_B T$. Only a fraction of the order of $k_B T D(\varepsilon_F)$ can be excited thermally. The total electronic thermal kinetic energy E is of the order of $(k_B T)^2 D(\varepsilon_F)$. The specific heat C_{el} is on the order of $k_B^2 T D(\varepsilon_F)$.

((Note))

For Pb,	$\gamma = 2.98,$	$D_A(\varepsilon_F) = 1.26/(\text{eV at})$
For Al	$\gamma = 1.35,$	$D_A(\varepsilon_F) = 0.57/(\text{eV at})$
For Cu	$\gamma = 0.695,$	$D_A(\varepsilon_F) = 0.29/(\text{eV at})$

Table The value of γ for typical metals (H.P. Myers, Introductory Solid State Physics (Taylor & Francis, London, 1990).

TABLE 6.2
 γ (mJ mol⁻¹ K⁻²)

Na	1.38	Ti	3.35
K	2.08	V	9.26
Mg	1.3	Cr	1.4
Al	1.35	Mn	9.2
Pb	2.98	Fe	4.98
Cu	0.7	Co	4.73
Ag	0.65	Ni	7.02
Au	0.73	Pt	7.0

((Mathematica))

Heat capacity for the 3D case. We use the Sommerfeld's formula for the calculation of the total energy and the total number

```

Clear["Global`*"];
U = Integrate[ξ[x] dx, {x, 0, μ[T]} + 1/6 (kB T)^2 π^2 D[ξ[μ[T]], {μ[T], 1}] + 7/360 (kB T)^4 π^4 D[ξ[μ[T]], {μ[T], 3}];
replace = {ξ -> (# De[#] &)}; U1 = U /. replace;
Ce = D[U1, T] // Expand
1/3 kB^2 π^2 T De[μ[T]] + 1/3 kB^2 π^2 T μ[T] De'[μ[T]] + De[μ[T]] μ[T] μ'[T] +
1/3 kB^2 π^2 T^2 De'[μ[T]] μ'[T] + 7/30 kB^4 π^4 T^3 De''[μ[T]] + 1/6 kB^2 π^2 T^2 μ[T] μ'[T] De''[μ[T]] +
7/90 kB^4 π^4 T^3 μ[T] De^(3)[μ[T]] + 7/90 kB^4 π^4 T^4 μ'[T] De^(3)[μ[T]] + 7/360 kB^4 π^4 T^4 μ[T] μ'[T] De^(4)[μ[T]]

```

The chemical potential $\mu[T]$ can be estimated from the expression of N

```

N1 = U /. {ξ -> (De[#] &)}; N2 = D[N1, T] // Expand
1/3 kB^2 π^2 T De'[μ[T]] + De[μ[T]] μ'[T] + 1/6 kB^2 π^2 T^2 μ'[T] De''[μ[T]] +
7/90 kB^4 π^4 T^3 De^(3)[μ[T]] + 7/360 kB^4 π^4 T^4 μ'[T] De^(4)[μ[T]]

```

For simplicity we use the approximation to the order of 0 (T^2) for the total energy and number.
Note that $D[N1, T]=0$ since N is independent of T.

```

eq1=N2[[1]]+N2[[2]]==0; eq2=Solve[eq1, μ'[T]]
{{μ'[T] -> -kB^2 π^2 T De'[μ[T]] / (3 De[μ[T]])}}
Ce1=Ce[[1]]+Ce[[2]]+Ce[[3]]; Ce2=Ce1/.eq2[[1]]//Simplify
1/3 kB^2 π^2 T De[μ[T]]

```

8. The relation between effective mass and the value of γ

The value of γ is expressed by

$$\gamma = \frac{1}{3} \pi^2 k_B^2 D(\varepsilon_F) = \frac{1}{3} \pi^2 k_B^2 \frac{3N}{2\varepsilon_F} = \frac{1}{3} \pi^2 k_B^2 \frac{3N}{\hbar^2 k_F^2} m$$

So the value of γ is proportional to the mass m . It is common practice to express the ratio of the observed to the free electron values of the electronic heat capacity as a ratio of a thermal effective mass to the electron mass m , is defined by the relation,

$$\frac{m_{th}}{m} = \frac{\gamma(observed)}{\gamma(free)}.$$

9. Pauli paramagnetism

The magnetic moment of spin is given by

$$\hat{\mu}_z = -\frac{2\mu_B\hat{S}_z}{\hbar} = -\mu_B\hat{\sigma}_z \quad (\text{quantum mechanical operator}).$$

Then the spin Hamiltonian (Zeeman energy) is described by

$$\hat{H} = -\hat{\mu}_z B = -\left(-\frac{2\mu_B\hat{S}_z}{\hbar}\right)B = \mu_B\hat{\sigma}_z B, \quad (34)$$

in the presence of a magnetic field, where the Bohr magneton μ_B is given by

$$\mu_B = \frac{e\hbar}{2mc}. \quad (e>0)$$

with

$$\mu_B = 9.27400915(23) \times 10^{-24} \text{ J/T} \quad (\text{S.I. unit})$$

$$\mu_B = 9.27400915(23) \times 10^{-21} \text{ erg/Oe} \quad (\text{cgs unit})$$

$$\text{erg/Oe} = \text{emu}$$

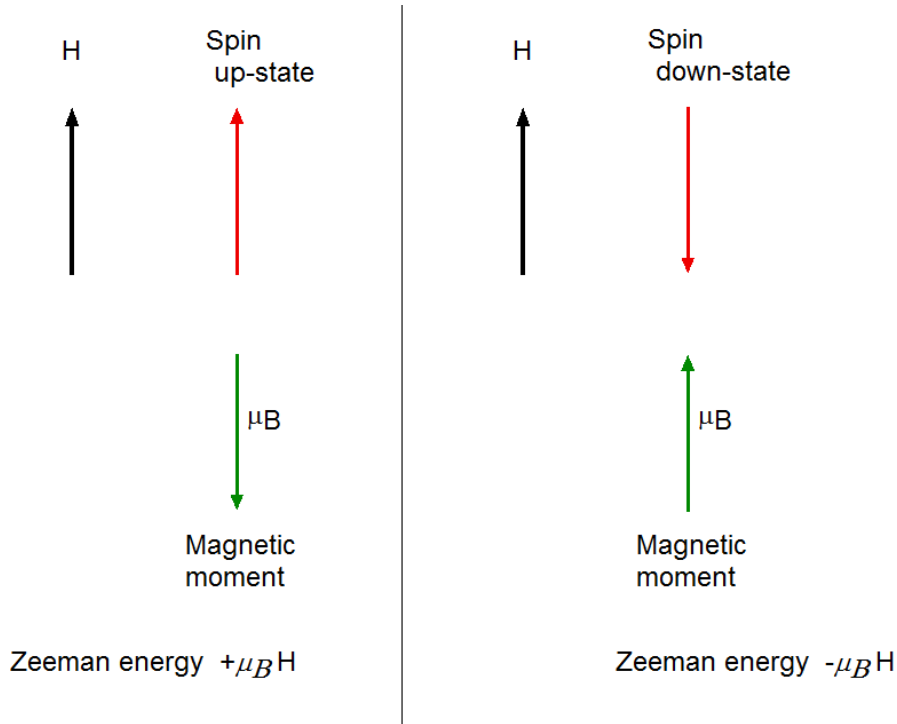


Fig. The magnetic field is applied along the z axis. (a) Spin-up state $|\sigma_z\rangle = |+\rangle$. The spin magnetic moment is antiparallel to the magnetic field. The Zeeman energy is $+\mu_B H$.

(b) Spin-down state $|\sigma_z\rangle = |-\rangle$. The spin magnetic moment is parallel to the magnetic field. The Zeeman energy is $-\mu_B H$.

(i) **The magnetic moment antiparallel to H .**

Note that the spin state is given by a up-state,

$$|\sigma_z\rangle = |+\rangle.$$

The energy of electron is given by

$$\varepsilon = \varepsilon_k + \mu_B H,$$

with $\varepsilon_k = (\hbar^2/2m)k^2$. The density of state for the **spin-up state** (the down-state of the magnetic moment) is

$$D_-(\varepsilon)d\varepsilon = \frac{L^3}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon - \mu_B H} d\varepsilon,$$

or

$$D_-(\varepsilon) = \frac{1}{2} D(\varepsilon - \mu_B H). \quad (35)$$

The factor $1/2$ comes from the fact that $D_-(\varepsilon)$ is the density of states per spin. Then we have

$$N_- = \int_{\mu_B H}^{\infty} \frac{1}{2} D(\varepsilon - \mu_B H) f(\varepsilon) d\varepsilon. \quad (36)$$

(ii) **The magnetic moment parallel to H .** Note that the spin state is given by

$$|\sigma_z\rangle = |-\rangle.$$

The energy of electron is given by

$$\varepsilon = \varepsilon_k - \mu_B H,$$

The density of state for the **spin down-state** (the up-sate of the magnetic moment) is

$$D_+(\varepsilon)d\varepsilon = \frac{L^3}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon + \mu_B H} d\varepsilon,$$

or

$$D_+(\varepsilon) = \frac{1}{2}D(\varepsilon + \mu_B H). \quad (37)$$

Then we have

$$N_+ = \int_{-\mu_B H}^{\infty} \frac{1}{2}D(\varepsilon + \mu_B H)f(\varepsilon)d\varepsilon. \quad (38)$$

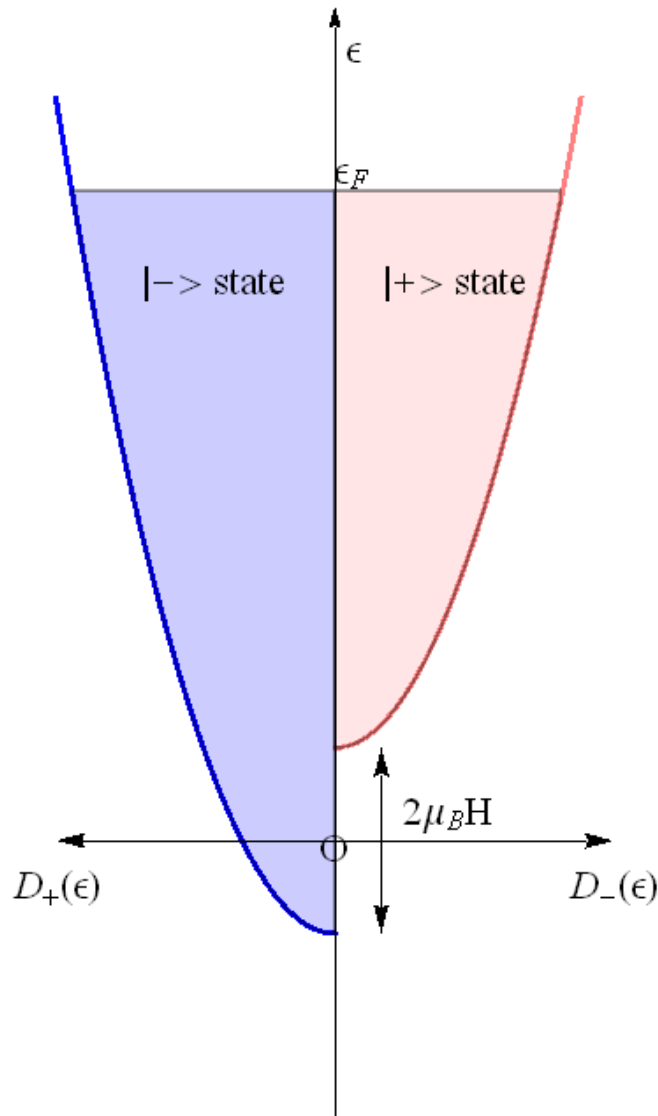


Fig. Density of states for the Pauli paramagnetism of free electron. Left: $(D_+(\varepsilon))$ for the $|\sigma_z\rangle = |-\rangle$, the direction of the spin magnetic moment is parallel to

that of magnetic field). Right: ($D(\varepsilon)$ for $|\sigma_z\rangle = |+\rangle$); the direction of the spin magnetic moment is antiparallel to that of magnetic field).

The magnetic moment M is expressed by

$$M = \mu_B(N_+ - N_-) = \frac{\mu_B}{2} \left[\int_{-\mu_B H}^{\infty} D(\varepsilon + \mu_B H) f(\varepsilon) d\varepsilon - \int_{\mu_B H}^{\infty} D(\varepsilon - \mu_B H) f(\varepsilon) d\varepsilon \right], \quad (39)$$

or

$$\begin{aligned} M &= \frac{\mu_B}{2} \int_0^{\infty} D(\varepsilon) [f(\varepsilon - \mu_B H) - f(\varepsilon + \mu_B H)] d\varepsilon \\ &= \mu_B^2 H \int_0^{\infty} D(\varepsilon) \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) d\varepsilon = \mu_B^2 H D(\varepsilon_F) \end{aligned} \quad (40)$$

Here we use the relation;

$$\left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) = \delta(\varepsilon - \varepsilon_F)$$

(see **Fig.3**).

The susceptibility (M/H) thus obtained is called the Pauli paramagnetism.

$$\chi_p = \mu_B^2 D(\varepsilon_F). \quad (41)$$

10. Pauli susceptibility per atom mol

Each atom has the Pauli susceptibility as

$$\begin{aligned} n_v \frac{\chi_{Pauli}}{N} &= \frac{n_v}{N} \chi_{Pauli} \\ &= \frac{\chi_{Pauli}}{N_0} = \mu_B^2 \frac{D(\varepsilon_F)}{N_0} = \mu_B^2 D_A(\varepsilon_F) \end{aligned}$$

where each atom has n_v conduction electrons;

$$N = n_v N_0$$

and

$$D_A(\varepsilon_F) = \frac{D(\varepsilon_F)}{N_0}$$

Then the Pauli susceptibility per atom mol is given by

$$\chi_P^M = N_A \mu_B^2 D_A(\varepsilon_F)$$

where N_A is the Avogadro number.

11. Experimental values of Pauli susceptibility

Experimentally we measure the susceptibility per mol, χ_P (emu/mol)

$$\chi_P^M = \mu_B^2 \frac{D(\varepsilon_F)}{N} N_A = \mu_B^2 N_A D_A(\varepsilon_F), \quad (42)$$

where $\mu_B^2 N_A = 3.23278 \times 10^{-5}$ (emu eV/mol) and $D_A(\varepsilon_F)$ [1/(eV atom)] is the density of states per unit energy per atom. Since

$$\gamma = \frac{1}{3} \pi^2 N_A k_B^2 D_A(\varepsilon_F), \quad (43)$$

we have the following relation between χ_P (emu/mol) and γ (mJ/mol K²),

$$\chi_P^M = 1.37148 \times 10^{-5} \gamma. \quad (44)$$

where

$$\gamma = \frac{1}{3} \pi^2 N_A k_B^2 D_A(\varepsilon_F)$$

((Exempl-1)) Rb atom has one conduction electron.

$$\begin{aligned} \gamma &= 2.41 \text{ mJ/mol K}^2, \chi_P = (1.37 \times 10^{-5}) \times 2.41 \text{ (emu/mol)} \\ 1 \text{ mol} &= 85.468 \text{ g} \\ \chi_P &= 0.386 \times 10^{-6} \text{ emu/g (calculation)} \end{aligned}$$

((Exempl-2)) K atom has one conduction electron.

$$\begin{aligned} \gamma &= 2.08 \text{ mJ/mol K}^2, \chi_P = (1.37 \times 10^{-5}) \times 2.08 \text{ (emu/mol)} \\ 1 \text{ mol} &= 39.098 \text{ g} \\ \chi_P &= 0.72 \times 10^{-6} \text{ emu/g (calculation)} \end{aligned}$$

((Exempl-3)) Na atom has one conduction electron.

$$\begin{aligned}\gamma &= 1.38 \text{ mJ/mol K}^2, \chi_P = (1.37 \times 10^{-5}) \times 1.38 \text{ (emu/mol)} \\ 1 \text{ mol} &= 29.98977 \text{ g} \\ \chi_P &= 0.8224 \times 10^{-6} \text{ emu/g (calculation)}\end{aligned}$$

The susceptibility of the conduction electron is given by

$$\chi = \chi_P + \chi_L = \chi_P - \chi_P/3 = 2\chi_P/3, \quad (45)$$

where χ_L is the Landau diamagnetic susceptibility due to the orbital motion of conduction electrons.

Using the calculated Pauli susceptibility we can calculate the total susceptibility:

$$\begin{aligned}\text{Rb: } \chi &= 0.386 \times (2/3) \times 10^{-6} = 0.26 \times 10^{-6} \text{ emu/g} \\ \text{K: } \chi &= 0.72 \times (2/3) \times 10^{-6} = 0.48 \times 10^{-6} \text{ emu/g} \\ \text{Na: } \chi &= 0.822 \times (2/3) \times 10^{-6} = 0.55 \times 10^{-6} \text{ emu/g}\end{aligned}$$

These values of χ are in good agreement with the experimental results.⁶

12. Physical quantities related to specific heat and Pauli paramagnetism

Here we show how to evaluate the numerical calculations by using Mathematica. To this end, we need reliable physics constant. These constants are obtained from the NIST Web site: <http://physics.nist.gov/cuu/Constants/index.html>

Planck's constant,	$\hbar = 1.05457168 \times 10^{-27} \text{ erg s}$
Boltzmann constant	$k_B = 1.3806505 \times 10^{-16} \text{ erg/K}$
Bohr magneton	$\mu_B = 9.27400949 \times 10^{-21} \text{ emu}$
Avogadro's number	$N_A = 6.0221415 \times 10^{23} \text{ (1/mol)}$
Velocity of light	$c = 2.99792458 \times 10^{10} \text{ cm/s}$
electron mass	$m = 9.1093826 \times 10^{-28} \text{ g}$
electron charge	$e = 1.60217653 \times 10^{-19} \text{ C}$
	$e = 4.803242 \times 10^{-10} \text{ esu (this is from the other source)}$
1 eV	$= 1.60217653 \times 10^{-12} \text{ erg}$
1 emu	$= \text{erg/Gauss}$
1mJ	$= 10^4 \text{ erg}$

Using the following program, one can easily calculate many kinds of physical quantities. Here we show only physical quantities which appears in the previous sections.

((**Mathematica**)) Physics constants

Use the physical constants to calculate the physical quantities (in the units of cgs)

```
Clear["Global`*"];
rule1 = {μB → 9.27400949 × 10-21, kB → 1.3806505 × 10-16, NA → 6.0221415 × 1023,
c → 2.99792458 × 1010, ħ → 1.05457168 × 10-27, m → 9.1093826 × 10-28, e → 4.803242 × 10-10,
eV → 1.60217653 × 10-12, mJ → 104};
```

Fermi energy

$$\frac{\hbar^2}{2m} (3\pi^2 n_0)^{2/3} (1/\text{eV}) /. \text{rule1}$$

$$1.69253 n_0^{2/3}$$

Fermi wavenumber

$$(3\pi^2 n_0)^{1/3} /. \text{rule1} // \text{N}$$

$$6.66511 \times 10^7 n_0^{1/3}$$

Fermi velocity

$$\frac{\hbar}{m} (3\pi^2 n_0)^{1/3} /. \text{rule1}$$

$$7.71603 \times 10^7 n_0^{1/3}$$

heat capacity

$$\frac{1}{3} \pi^2 \text{NA kB}^2 / (\text{eV mJ}) /. \text{rule1}$$

$$2.35715$$

Pauli paramagnetism

$$\mu\text{B}^2 \text{NA} / \text{eV} /. \text{rule1} // \text{ScientificForm}$$

$$3.23278 \times 10^{-5}$$

Relation between Pauli paramagnetism and heat capacity

$$\frac{3\mu\text{B}^2}{\pi^2 \text{kB}^2} \text{mJ} /. \text{rule1} // \text{ScientificForm}$$

$$1.37148 \times 10^{-5}$$

13. Conclusion

The temperature dependence of the specific heat is discussed in terms of the free electron Fermi gas model. The specific heat of electrons is proportional to T . The Sommerfeld's constant γ for Na is 1.38 mJ/(mol K²) and is close to the value [1.094 mJ/(mol K²)] predicted from the free electron Fermi gas model. The linearly T dependence of the electronic specific heat and the Pauli paramagnetism give a direct evidence that the conduction electrons form a free electron Fermi gas obeying the Fermi-Dirac statistics.

It is known that the heavy fermion compounds have enormous values, two or three orders of magnitude higher than usual, of the electronic specific heat. Since γ is proportional to the mass, heavy electrons with the mass of 1000 m (m is the mass of free electron) move over the system. This is due to the interaction between electrons. A moving electron causes an inertial reaction in the surrounding electron gas, thereby increasing the effective mass of the electron.

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APPENDIX

Analysis of the specific heat data of typical metals at low temperatures

H.P. Myer , *Introductory Solid State Physics* (Taylor & Francis, London, 1990).
Problem 6-8

6.8 In an experiment the following values of heat capacity were determined:

$T(K)$	C (mJ mol ⁻¹ K ⁻¹)
0.5	1.38
1.0	5
1.5	13.1
2.0	28
2.5	52
3.0	87
3.5	136

What substance was under study?

((Solution))

The lattice contribution to the heat capacity per mol atom is

$$C_L^M = 233.782 N_A k_B \left(\frac{T}{\Theta} \right)^3 = 233.782 R \left(\frac{T}{\Theta} \right)^3 \quad \text{mJ/(mol K)}$$

where N_A is the Avogadro number and R is the gas constant

$$R = 8,314.4621 \text{ mJ/(mol K)}.$$

The electron contribution to the heat capacity per mol atom is

$$C_{el}^{(M)} = \frac{1}{3} \pi^2 N_A k_B^2 D_A(\varepsilon_F) T = \gamma T \quad \text{mJ/(mol K)}$$

where

$$\gamma = 2.35715 D_A(\varepsilon_F), \quad \text{mJ/(mol.K}^2)$$

where the unit of $D_A(\varepsilon_F)$ is

$$D_A(\varepsilon_F) \text{ [1/eV.at].}$$

Experimentally the specific heat at low temperatures can be expressed by

$$C(\text{mJ / mol.K}) = \gamma T + AT^3. \quad (1)$$

In order to determine the values of γ and A , we make a plot of the specific heat data: C/T vs T^2 .

$$\frac{C(\text{mJ / mol.K})}{T} = \gamma + AT^2 \quad (1)$$

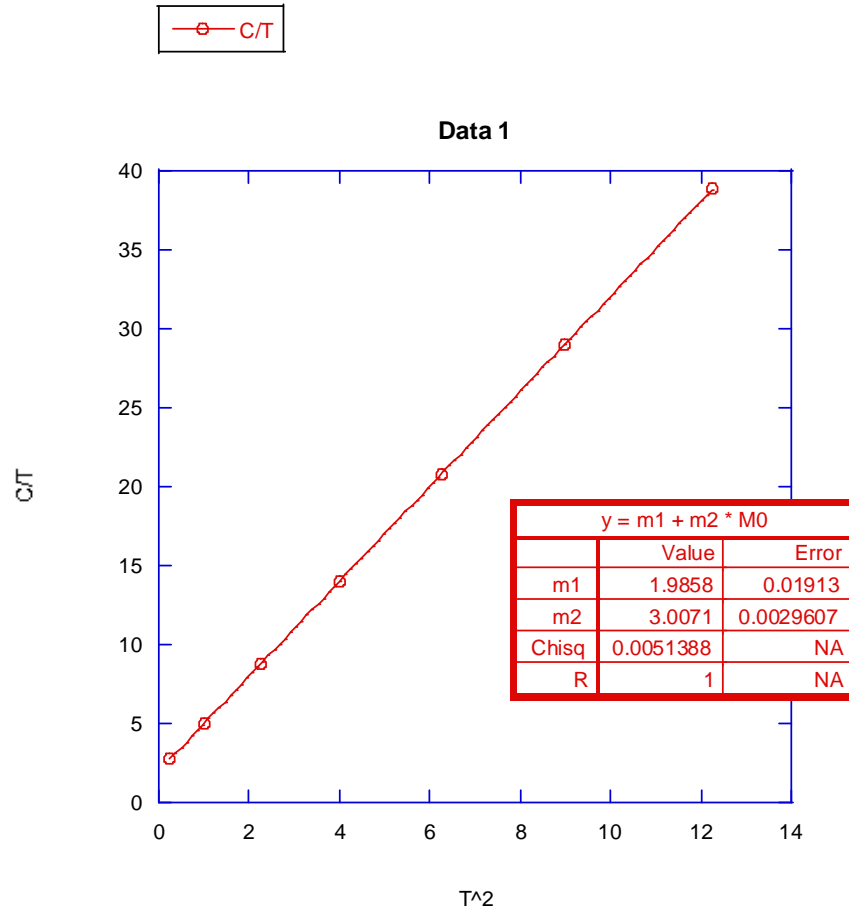


Fig. Plot of C/T vs T^2 for the substance under study.

It is found that C/T is linearly proportional to T^2 . Using the least-squares fit of the data to Eq.(1), we obtain

$$\gamma = 1.986 \pm 0.019 = 2.35715 D_A(\varepsilon_F) \text{ [mJ/(mol K}^2\text{)]}$$

$$A = 3.007 \pm 0.003 = 233.782 \frac{R}{\Theta^3}$$

The values of the Debye temperature Θ is obtained as

$$\Theta = 86.5K .$$

These values of γ and Θ indicate that the substance under study is **K** (potassium)