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.

Content:

9. Conclusion

1. Schrödinger equation[3-10]

A. Energy level in 1D system

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

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

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

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

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 $n = 0, \pm1, \pm2, \ldots$, 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.

$$H\psi_{\boldsymbol{k}} = \frac{\boldsymbol{p}^2}{2m}\psi_{\boldsymbol{k}} = -\frac{\hbar^2}{2m}\nabla^2\psi_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}}\psi_{\boldsymbol{k}}. \tag{3}$$

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

Boundary condition (Born-von Karman boundary conditions).

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

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

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

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

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

with

$k_x = (2\pi/L)\, n_x$, ($n_x = 0, \pm1, \pm2, \pm3, \ldots..$),

$k_y = (2\pi/L)\, n_y$, ($n_y = 0, \pm1, \pm2, \pm3, \ldots..$),

$k_z = (2\pi/L)\, n_z$, ($n_z = 0, \pm1, \pm2, \pm3, \ldots..$).

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

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

Here

$$\boldsymbol{p}\psi_k(\boldsymbol{r}) = \frac{\hbar}{i}\nabla_{\boldsymbol{k}}\psi_k(\boldsymbol{r}) = \hbar\boldsymbol{k}\psi_k(\boldsymbol{r}). \tag{6}$$

So that the plane wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenfunction of $\boldsymbol{p}$ 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 $\boldsymbol{k}$-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 $\boldsymbol{k}$ 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 k are two levels:

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

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

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

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

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

The Fermi wavenumber k_F is given by

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

The Fermi energy is given by

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

The Fermi velocity is

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

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 number density n.

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

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

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

$$k_F = 6.66511\times10^7\ n_0^{1/3}\ [\text{cm}^{-1}].$$

The Fermi velocity v_F is calculated as

$$v_F = 7.71603\times10^7\ n_0^{1/3}\ [\text{cm/s}].$$

((**Example**))
The Fermi energy of Au

Atomic molar mass M_0 = 196.9666 g/mol
Density ρ = 19.30 g/cm^3

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

Since n_0 = 5.901, we have

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

$$k_F = 6.66511\times10^7\ n_0^{1/3} = 1.20442 \text{ x } 10^8 \text{ [cm}^{-1}\text{]}.$$

$$v_F = 7.71603\times10^7\ n_0^{1/3} = 1.39433 \text{ x } 10^8 \text{ [cm/s]}.$$

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

((Mathematica))

Fermi energy ε_F (eV) vs the number of electrons ($n = n_0\times10^{22}$ [cm^{-3}]).

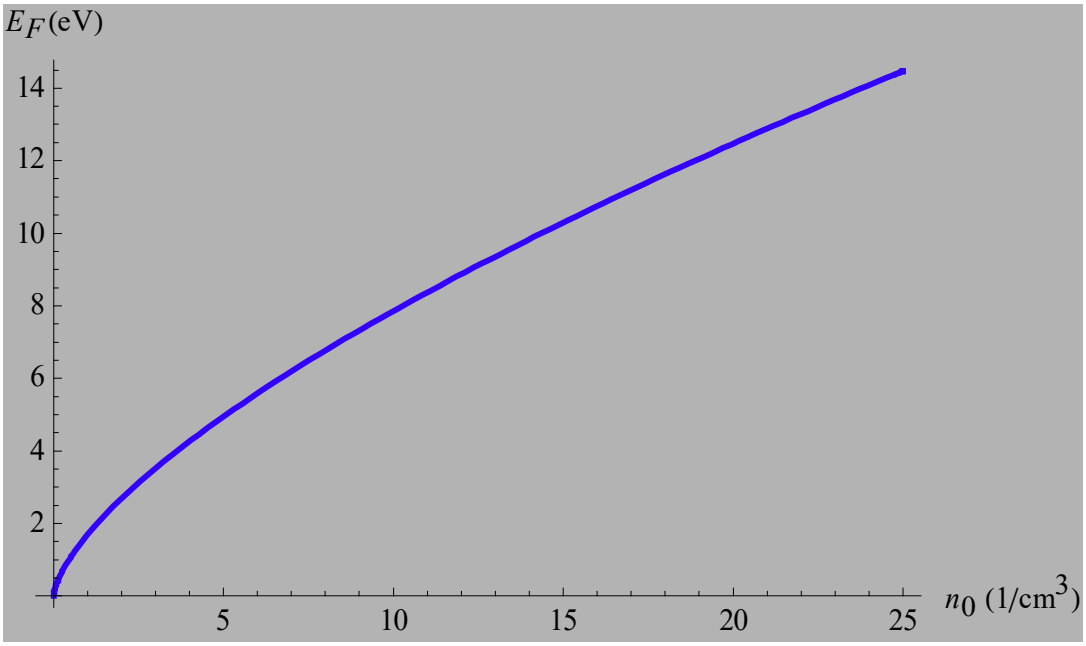

Fig.1 Fermi energy vs number density n (= $n_0\times10^{22}$ [cm^{-3}]).

2. Fermi-Dirac distribution function[3-10]

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

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

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

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

(ii) $f(\varepsilon) = 1/2$ at $\varepsilon = \mu$.

(iii) For $\varepsilon - \mu >> k_B T$, $f(\varepsilon)$ is approximated by $f(\varepsilon) = e^{-\beta(\varepsilon-\mu)}$. This limit is called the Boltzmann or Maxwell distribution.

(iv) For $k_B T << \varepsilon_F$, the derivative $-df(\varepsilon)/d\varepsilon$ corresponds to a Dirac delta function having a sharp positive peak at $\varepsilon = \mu$.

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

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

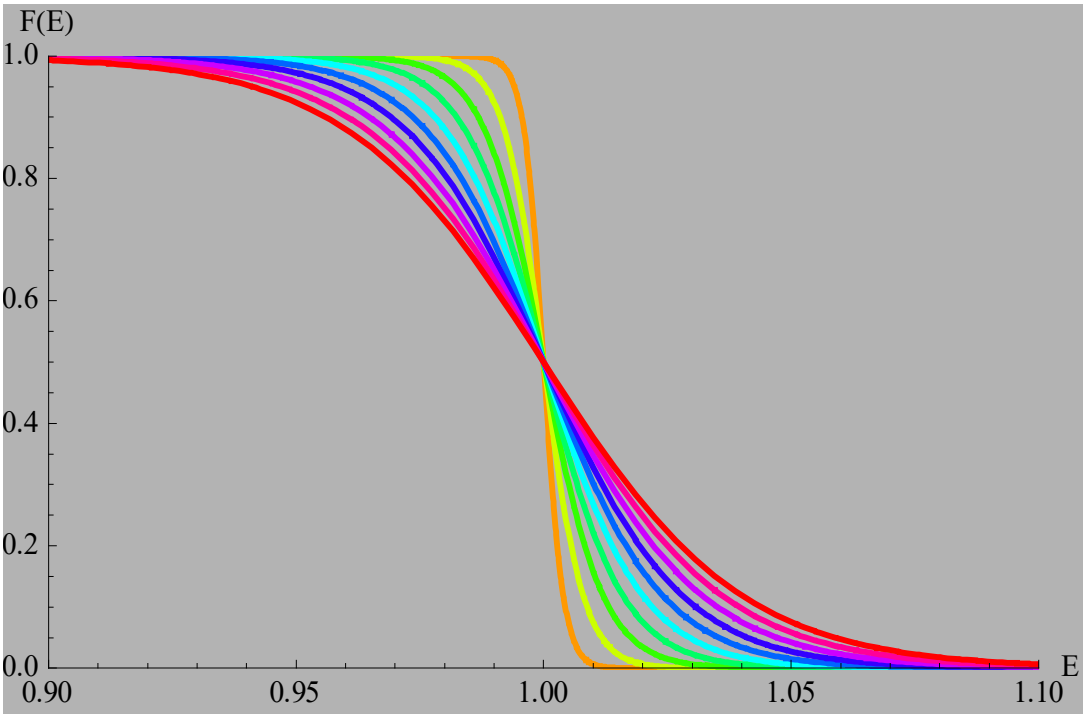

Fig.2 Fermi-Dirac distribution function $f(\varepsilon)$ at various T (= 0.002 – 0.02). $k_B = 1$. $\mu(T = 0) = \varepsilon_F = 1$.

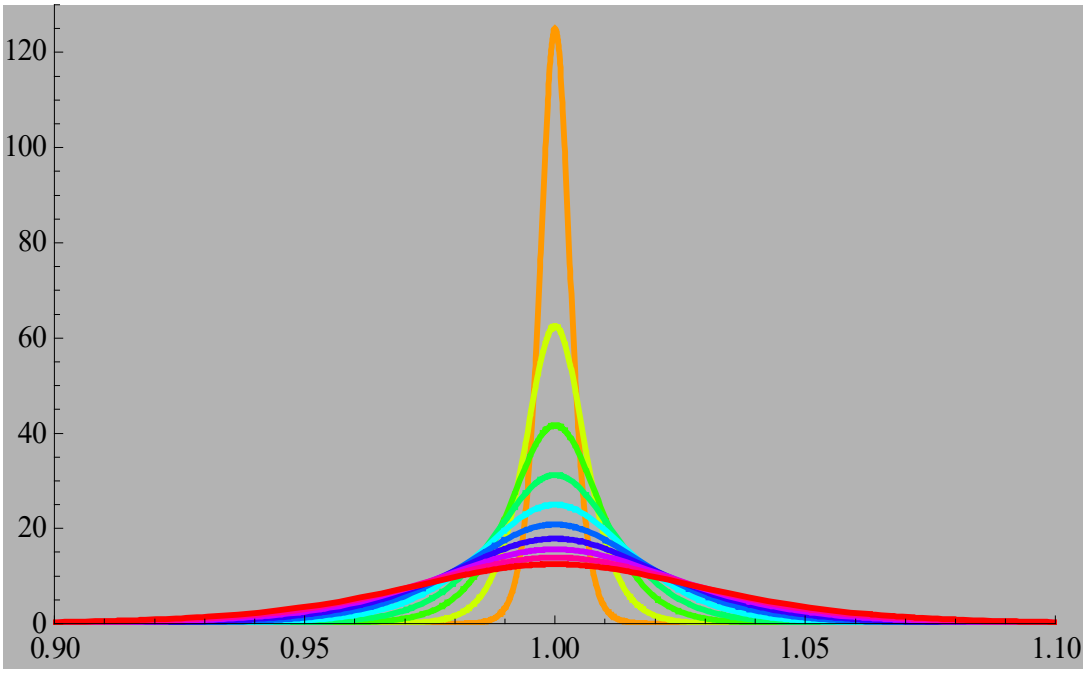

Fig.3 Derivative of Fermi-Dirac distribution function $-df(\varepsilon)/d\varepsilon$ at various T (= 0.002 – 0.02). $k_B = 1$. $\mu(T = 0) = \varepsilon_F = 1$.

3. Density of states[3-10]

A. 3D system

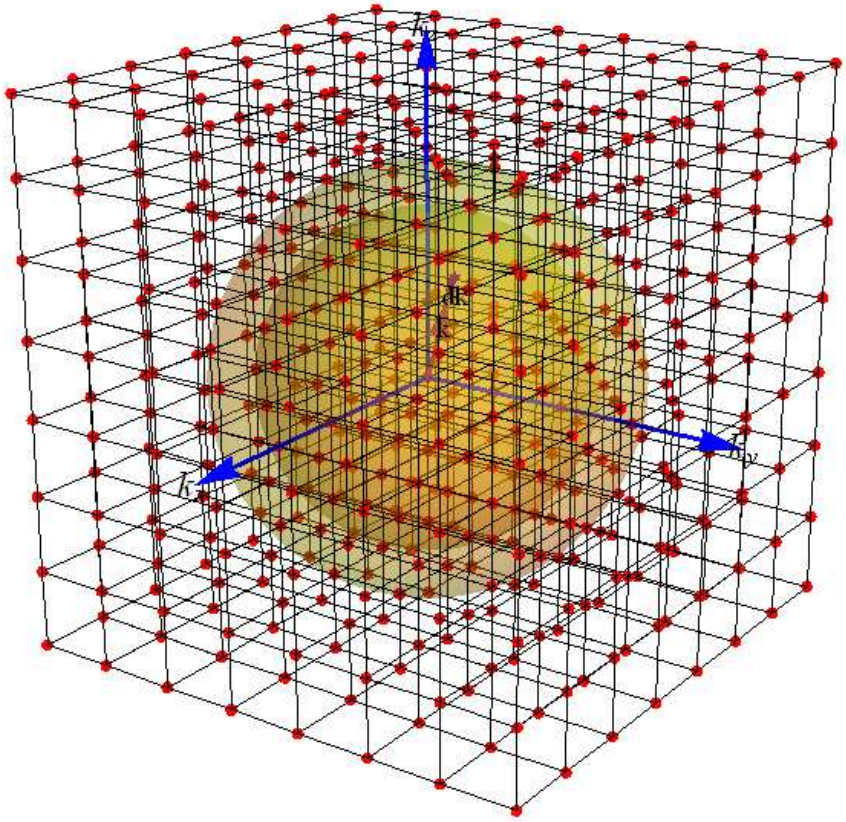

Fig. Density of states in the 3D ***k***-space. There is one state per $(2\pi/L)^3$.

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 $\varepsilon+d\varepsilon$; $D(\varepsilon)d\varepsilon$

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

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

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

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

$$D_A(\varepsilon_F) = \frac{D(\varepsilon_F)}{N}, \tag{15}$$

where

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

Then we have

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

This is the case when each atom has one conduction electron. When there are n_v electrons per atom, $D^A(\varepsilon_F)$ is described as[9]

$$D_A(\varepsilon_F) = \frac{3n_v}{2\varepsilon_F}. \tag{18}$$

For Al, we have ε_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.

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

where

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

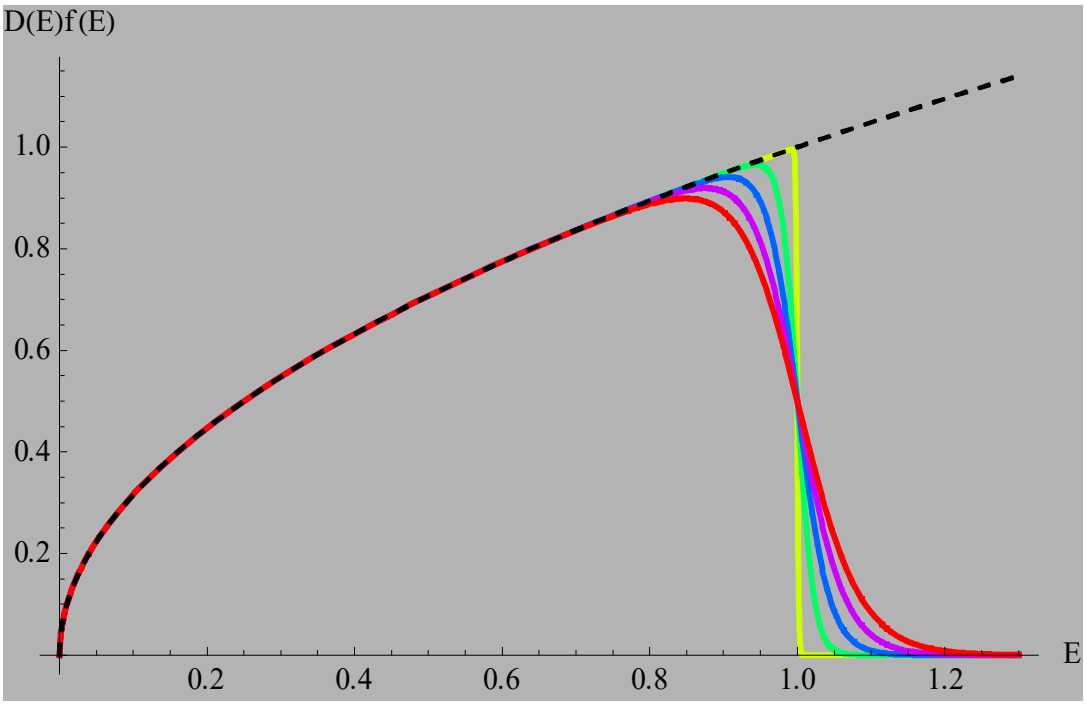

Fig.4 $D(\varepsilon)f(\varepsilon)$ at various T (= 0.001 – 0.05). k_B = 1. $\mu(T = 0) = \varepsilon_F$ = 1. The constant a of $D(\varepsilon)$ (= $a\sqrt{\varepsilon}$) is assumed to be equal to 1. The dashed line denotes the curve of $D(\varepsilon)$.

B. 2D system

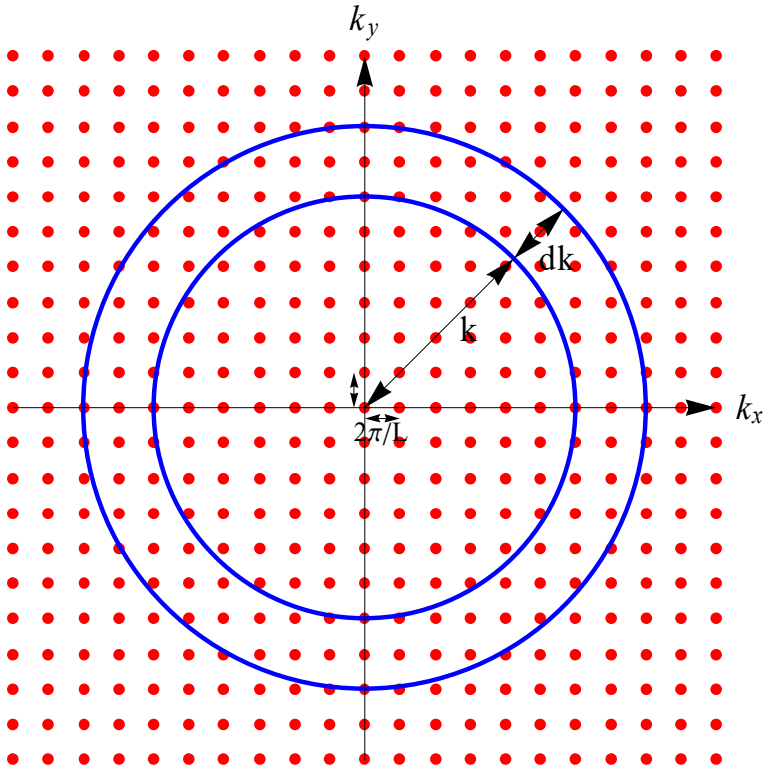

Fig. Density of states for the 2D ***k***-space. There is one state per area $\left(\frac{2\pi}{L}\right)^2$ of the reciprocal lattice plane.

For the 2D system, we have

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

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

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

which is independent of ε.

C. 1D system

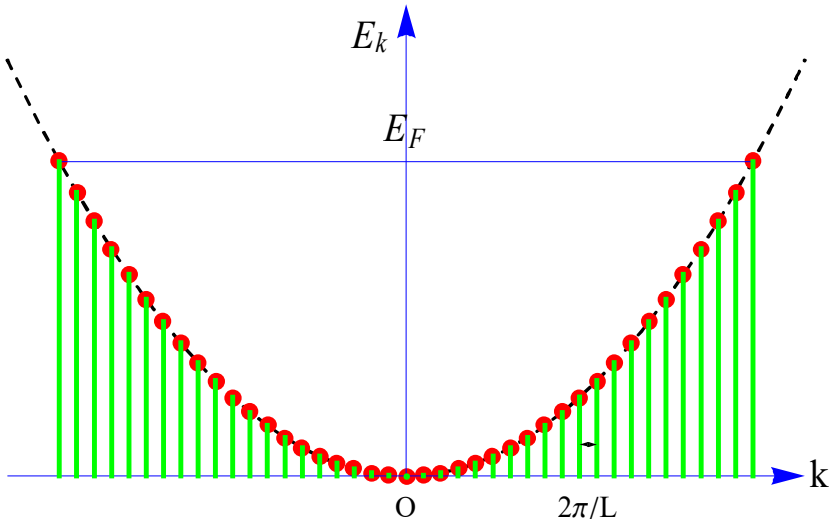

Fig. Energy ε_k vs k for the one dimensional case. The discrete states are described $|k,\uparrow\rangle$ and $|k,\downarrow\rangle$ with $k = (2\pi/L)n$. ($n_x = 0, \pm1, \pm2,...$). All the states below the Fermi energy ε_F are occupied at $T = 0$ K.

For the 1D system we have

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

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

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

which decreases with increasing ε.

4. Sommerfeld's formula

When we use a formula

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

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

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

and

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

First we prove that

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

using Mathematica.

((Mathematica))

Sommerfeld's formula

```
Clear["Global`*"]; f[x_] := 1/(Exp[(x-μ)/(kB T)] + 1); h[x] = -D[f[x], x] // Simplify;
g1 = Series[g[x], {x, μ, 14}] // Normal; G1 = kB T (g1 h[x]) /. {x → μ + kB T y} // Expand;
K[n_] := ∫_-∞^∞ G1[[n]] dy;
G2 = Sum[K[n], {n, 1, 13}]
```

$$g[\mu] + \frac{1}{6}\,kB^2\,\pi^2\,T^2\,g''[\mu] + \frac{7}{360}\,kB^4\,\pi^4\,T^4\,g^{(4)}[\mu] + \frac{31\,kB^6\,\pi^6\,T^6\,g^{(6)}[\mu]}{15\,120} + \frac{127\,kB^8\,\pi^8\,T^8\,g^{(8)}[\mu]}{604\,800} + \frac{73\,kB^{10}\,\pi^{10}\,T^{10}\,g^{(10)}[\mu]}{3\,421\,440} + \frac{1\,414\,477\,kB^{12}\,\pi^{12}\,T^{12}\,g^{(12)}[\mu]}{653\,837\,184\,000}$$

So we get a final result

$$\int_{-\infty}^{\infty} g(E)\left(-\frac{df}{dE}\right)dE = g[\mu] + \frac{1}{6}\,kB^2\,T^2\,\pi^2\,g''[\mu] + \frac{7}{360}\,kB^4\,T^4\,\pi^4\,g^{(4)}[\mu] + \frac{31\,kB^6\,T^6\,\pi^6\,g^{(6)}[\mu]}{15\,120} + \frac{127\,kB^8\,T^8\,\pi^8\,g^{(8)}[\mu]}{604\,800} + \frac{73\,kB^{10}\,\pi^{10}\,T^{10}\,g^{(10)}[\mu]}{3\,421\,440} + \frac{1\,414\,477\,kB^{12}\,\pi^{12}\,T^{12}\,g^{(12)}[\mu]}{653\,837\,184\,000}$$

Here we note that

$$\int_0^\infty g(\varepsilon)[-\frac{\partial f(\varepsilon)}{\partial \varepsilon}]d\varepsilon = -f(\varepsilon)g(\varepsilon)|_0^\infty + \int_0^\infty g'(\varepsilon)f(\varepsilon)]d\varepsilon$$
$$= \int_0^\infty g'(\varepsilon)f(\varepsilon)]d\varepsilon \quad . \tag{27}$$

We define

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

or

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

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

$$\int_0^\infty f(\varepsilon)\varphi(\varepsilon)d\varepsilon = \int_0^\mu \varphi(\varepsilon')d\varepsilon' + \frac{1}{6}{k_B}^2T^2\pi^2\varphi'(\mu) + \frac{7}{360}{k_B}^4T^4\pi^4\varphi^{(3)}(\mu)$$
$$+ \frac{31}{15120}{k_B}^6T^6\pi^6\varphi^{(5)}(\mu) + \frac{127}{604800}{k_B}^8T^8\pi^8\varphi^{(7)}(\mu)$$
$$+ \frac{73}{3421440}{k_B}^{10}T^{10}\pi^{10}\varphi^{(9)}(\mu) + \frac{1414477}{653837184000}{k_B}^{12}T^{12}\pi^{12}\varphi^{(11)}(\mu) + ... \tag{29}$$

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 + π^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_BT/E_F", Black, 12], {0.09, 0.99} ],
   Text[Style["μ/E_F", Black, 12], {0.004, 0.999}],
   Text[Style["3D system", Black, 15],
    {0.07, 0.9995}]}];
Show[f1, f2, PlotRange → All]
```

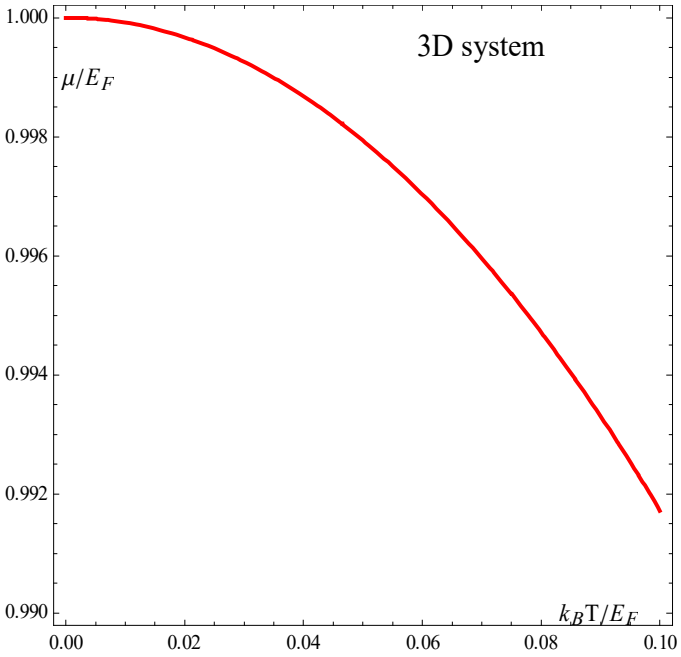

Fig. ContourPlot of μ/ε_F and k_BT/ε_F for small values of k_BT/ε_F

The chemical potential μ is approximated by the forms,

$$\mu = \varepsilon_F[1-\frac{\pi^2}{12}(\frac{k_BT}{\varepsilon_F})^2] \text{ (3D case).} \tag{30}$$

For the 1D case, similarly we have

$$\mu = \varepsilon_F[1+\frac{\pi^2}{12}(\frac{k_BT}{\varepsilon_F})^2] \text{ (1D case).} \tag{31}$$

((**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.

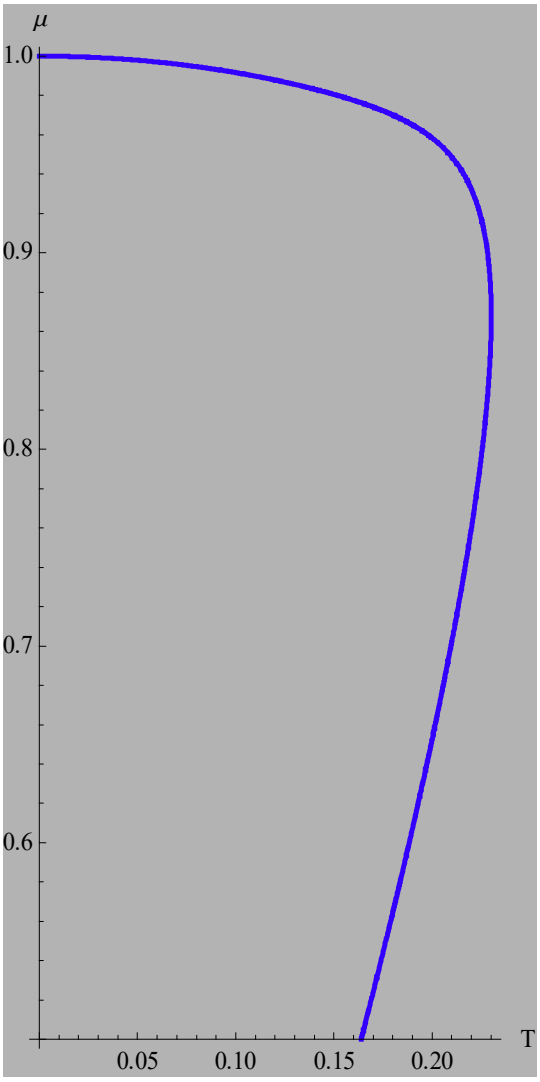

Fig.5 T dependence of chemical potential μ for the 3D system. $k_B = 1$. $\varepsilon_F = \mu(T = 0) = 1$.

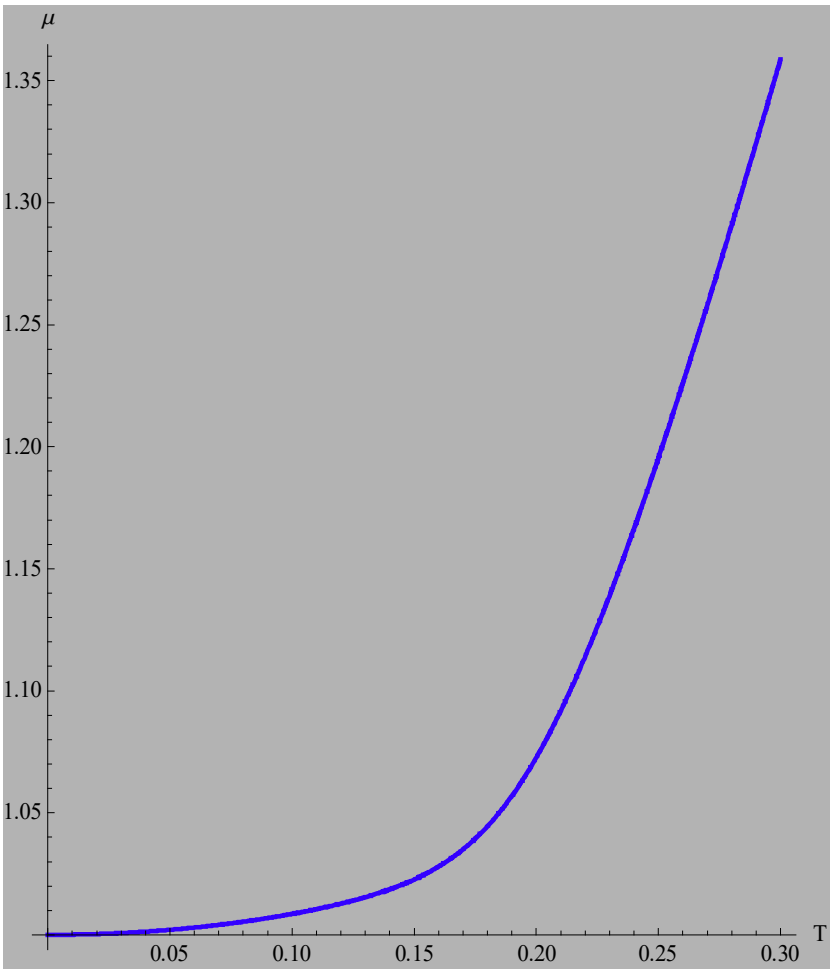

Fig.6 T dependence of chemical potential μ for the 1D system. $k_B = 1$. $\varepsilon_F = \mu(T=0) = 1$.

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

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

or

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

The specific heat $C_{\rm el}$ is defined by

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

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

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

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

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

In the above expression of $C_{\rm el}$, we assume that there are N electrons inside volume V (= L^3). The specific heat per mol is given by

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

where $N_{\rm A}$ is the Avogadro number and $D^A(\varepsilon_F)$ [1/(eV at)] is the density of states per unit energy per unit atom. Note that

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

((**Note**)) The heat capacity of free electron

$$\frac{D(\varepsilon_F)}{N}=\frac{a\sqrt{\varepsilon_F}}{\frac{2a}{3}{\varepsilon_F}^{3/2}}=\frac{3}{2\varepsilon_F}=\frac{3}{2k_BT_F}$$

The electronic heat capacity per mol is

$$\frac{1}{3}\pi^2 \frac{D(\varepsilon_F)}{N} N_A k_B{}^2 T = \frac{1}{3}\pi^2 \frac{3}{2k_B T_F} R k_B T = \frac{\pi^2}{2} R \frac{T}{T_F}$$

Then 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

$$\gamma(\text{mJ/mol K}^2) = 2.35715\ D^A(\varepsilon_F). \qquad (33)$$

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,	$\gamma = 2.98$,	$D^A(\varepsilon_F) = 1.26$/(eV at)
For Al	$\gamma = 1.35$,	$D^A(\varepsilon_F) = 0.57$/(eV at)
For Cu	$\gamma = 0.695$,	$D^A(\varepsilon_F) = 0.29$/(eV at)

((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[ζ[x], {x, 0, μ[T]}] + 1/6 (kB T)^2 π^2 D[ζ[μ[T]], {μ[T], 1}] + 7/360 (kB T)^4 π^4 D[ζ[μ[T]], {μ[T], 3}];
replace = {ζ → (# De[#] &)}; U1 = U /. replace;
Ce = D[U1, T] // Expand
```

$$\frac{1}{3}\,kB^2\,\pi^2\,T\,De[\mu[T]] + \frac{1}{3}\,kB^2\,\pi^2\,T\,\mu[T]\,De'[\mu[T]] + De[\mu[T]]\,\mu[T]\,\mu'[T] + \frac{1}{3}\,kB^2\,\pi^2\,T^2\,De'[\mu[T]]\,\mu'[T] + \frac{7}{30}\,kB^4\,\pi^4\,T^3\,De''[\mu[T]] + \frac{1}{6}\,kB^2\,\pi^2\,T^2\,\mu[T]\,\mu'[T]\,De''[\mu[T]] + \frac{7}{90}\,kB^4\,\pi^4\,T^3\,\mu[T]\,De^{(3)}[\mu[T]] + \frac{7}{90}\,kB^4\,\pi^4\,T^4\,\mu'[T]\,De^{(3)}[\mu[T]] + \frac{7}{360}\,kB^4\,\pi^4\,T^4\,\mu[T]\,\mu'[T]\,De^{(4)}[\mu[T]]$$

The chemical potential μ[T] can be estimated from the expression of N

```
N1 = U /. {ζ → (De[#] &)}; N2 = D[N1, T] // Expand
```

$$\frac{1}{3}\,kB^2\,\pi^2\,T\,De'[\mu[T]] + De[\mu[T]]\,\mu'[T] + \frac{1}{6}\,kB^2\,\pi^2\,T^2\,\mu'[T]\,De''[\mu[T]] + \frac{7}{90}\,kB^4\,\pi^4\,T^3\,De^{(3)}[\mu[T]] + \frac{7}{360}\,kB^4\,\pi^4\,T^4\,\mu'[T]\,De^{(4)}[\mu[T]]$$

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]]
```

$$\left\{\left\{\mu'[T] \to -\frac{kB^2\,\pi^2\,T\,De'[\mu[T]]}{3\,De[\mu[T]]}\right\}\right\}$$

```
Ce1=Ce[[1]]+Ce[[2]]+Ce[[3]];Ce2=Ce1/.eq2[[1]]//Simplify
```

$$\frac{1}{3}\,kB^2\,\pi^2\,T\,De[\mu[T]]$$

7. Pauli paramagnetism

The magnetic moment of spin is given by

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

Then the spin Hamiltonian (Zeeman energy) is described by

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

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

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

with

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

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

erg/Oe = emu

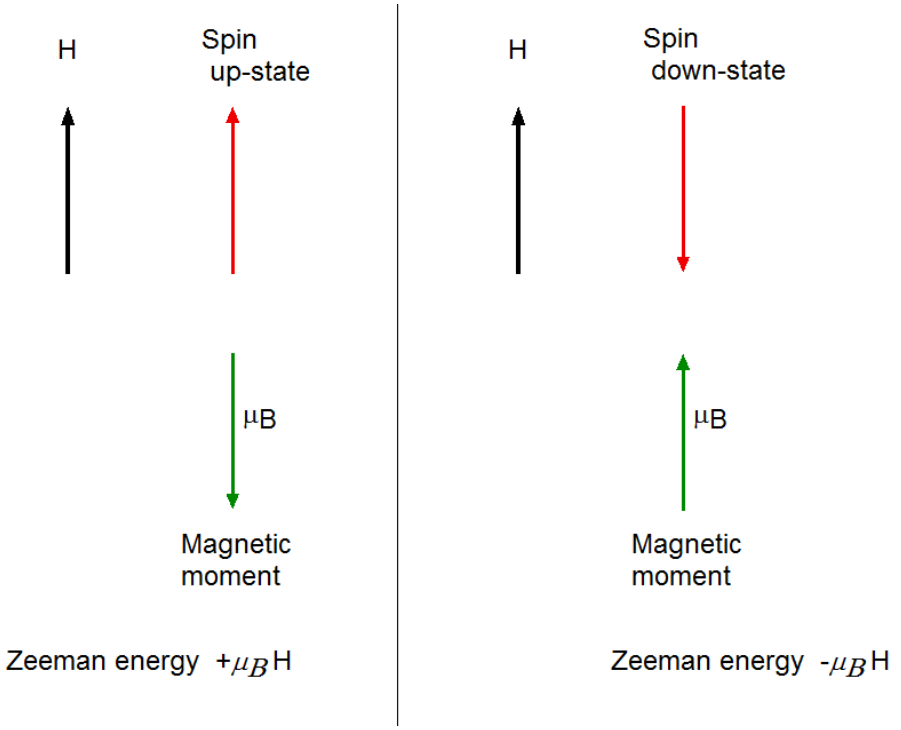

Fig. The magnetic field is applied along the z axis. (a) Spin–up state $|\sigma_z\rangle = |+\rangle$. The spin magnetic moment is antiparallel to the magnetic field. The Zeeman energy is $+\mu_B H$. (b) Spin-down state $|\sigma_z\rangle = |-\rangle$. The spin magnetic moment is parallel to the magnetic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

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

or

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

The factor ½ comes from the fact that $D_{-}(\varepsilon)$ is the density of states per spin. Then we have

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

(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

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

or

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

Then we have

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

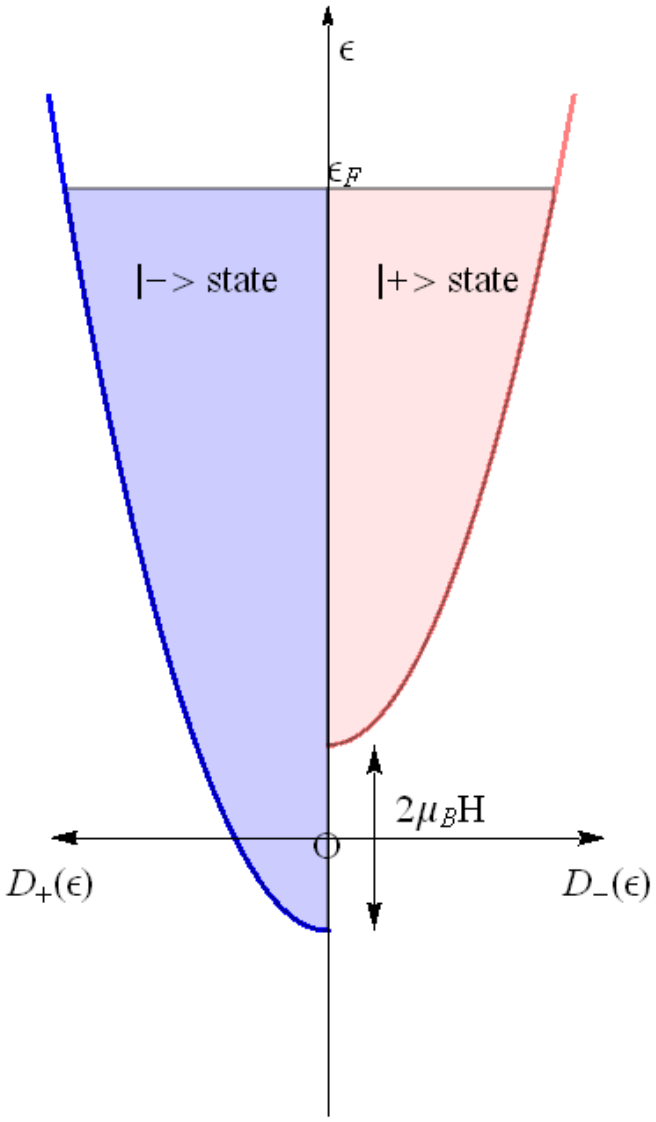

Fig. Density of states for the Pauli paramagnetism of free electron. Left: ($D_+(\varepsilon)$ for the $|\sigma_z\rangle = |-\rangle$, the direction of the spin magnetic moment is parallel to that of magnetic field). Right: ($D_-(\varepsilon)$ for $|\sigma_z\rangle = |+\rangle$; the direction of the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

The magnetic moment M is expressed by

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

or

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

Here we use the relation;

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

(see **Fig.3**).

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

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

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

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

where $\mu_B^2 N_A$ = 3.23278×10^{-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 K^2),

$$\chi_P = 1.37148\times10^{-5}\gamma. \quad (44)$$

((**Exampl-1**)) Rb atom has one conduction electron.

γ = 2.41 mJ/mol K^2, χ_P = (1.37x10^{-5})×2.41 (emu/mol)
1 mol = 85.468 g
χ_P =0.386×10^{-6} emu/g (calculation)

((**Exampl-2**)) K atom has one conduction electron.

γ = 2.08 mJ/mol K^2, χ_P = (1.37x10^{-5})×2.08 (emu/mol)
1 mol = 39.098 g
χ_P =0.72x10^{-6} emu/g (calculation)

((**Exampl-3**)) Na atom has one conduction electron.

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

The susceptibility of the conduction electron is given by

$$\chi = \chi_P + \chi_L = \chi_P - \chi_P/3 = 2\chi_P/3, \tag{45}$$

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:

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

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

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

Fermi energy

```
ℏ^2/(2 m) (3 π^2 10^22 n0)^(2/3) (1 / eV) /. rule1
```

$$1.69253\, n0^{2/3}$$

Fermi wavenumber

```
(3 π^2 10^22 n0)^(1/3) /. rule1 // N
```

$$6.66511 \times 10^{7}\, n0^{1/3}$$

Fermi velocity

```
ℏ/m (3 π^2 10^22 n0)^(1/3) /. rule1
```

$$7.71603 \times 10^{7}\, n0^{1/3}$$

heat capacity

```
1/3 π^2 NA kB^2 / (eV mJ) /. rule1
```

$$2.35715$$

Pauli paramagnetism

```
μB^2 NA / eV /. rule1 // ScientificForm
```

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

Relation between Pauli paramagnetism and heat capacity

```
3 μB^2/(π^2 kB^2) mJ /. rule1 // ScientificForm
```

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

9. 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 K^2) and is close to the value [1.094 mJ/(mol K^2)] 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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