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.).

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 \(\mu_B\), Boltzmann constant \(k_B\), and so on). This lecture note is based on many textbooks of the solid state physics including Refs. 3 – 10.

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1. Schrödinger equation\textsuperscript{3-10}

\subsection*{A. Energy level in 1D system}

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

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

(1)

where

\[ p = \frac{\hbar}{i} \frac{d}{dx}, \]

and $\varepsilon_k$ 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

\[ \psi_k(x) \sim e^{ikx}, \]

(2)

with

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

\[ e^{ikx} = 1 \text{ or } k = \frac{2\pi}{L} n, \]

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

\subsection*{B. Energy level in 3D system}

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

\[ H \psi_k = \frac{p^2}{2m} \psi_k = -\frac{\hbar^2}{2m} \nabla^2 \psi_k = \varepsilon_k \psi_k. \]

(3)

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

Boundary condition (Born-von Karman boundary conditions).

\[ \psi_k(x + L, y, z) = \psi_k(x, y, z), \]
\[ \psi_k(x, y + L, z) = \psi_k(x, y, z), \]
\[ \psi_k(x, y, z + L) = \psi_k(x, y, z). \]
The wavefunctions are of the form of a traveling plane wave.
\[ \psi_k(r) = e^{ix} \]

with
\[ k_x = \frac{2\pi}{L} n_x, \quad (n_x = 0, \pm 1, \pm 2, \pm 3, \ldots), \]
\[ k_y = \frac{2\pi}{L} n_y, \quad (n_y = 0, \pm 1, \pm 2, \pm 3, \ldots), \]
\[ k_z = \frac{2\pi}{L} n_z, \quad (n_z = 0, \pm 1, \pm 2, \pm 3, \ldots). \]

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
\[ \varepsilon(k) = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2}{2m} \mathbf{k}^2. \]

Here
\[ \mathbf{p} \psi_k(r) = \frac{\hbar}{i} \nabla_k \psi_k(r) = \hbar \mathbf{k} \psi_k(r). \]

So that the plane wave function \( \psi_k(r) \) 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.

\((\text{The Pauli’s exclusion principle})\)

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
\[ N = 2 \frac{L^3}{(2\pi)^3} 4\pi k_F^3 = V \frac{V}{3\pi^2} k_F^3, \]

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
\[ n = \frac{N}{V} = \frac{1}{3\pi^2} k_F^3. \]
The Fermi wavenumber $k_F$ is given by

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

The Fermi energy is given by

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

The Fermi velocity is

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

**((Note))**

The Fermi energy $\epsilon_F$ can be estimated using the number of electrons per unit volume as

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

where $n$ and $n_0$ is in the units of $(\text{cm}^3)$ 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

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

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

**2. Fermi-Dirac distribution function**

The Fermi-Dirac distribution gives the probability that an orbital at energy $\epsilon$ will be occupied in an ideal gas in thermal equilibrium

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

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

---
(i) \[ \lim_{T \to 0} \mu = \varepsilon_F . \]

(ii) \[ f(\varepsilon) = 1/2 \text{ at } \varepsilon = \mu. \]

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

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

![Fig.2 Fermi-Dirac distribution function \( f(\varepsilon) \) at various \( T \) (= 0.002 – 0.02). \( k_B = 1 \). \( \mu(T = 0) = \varepsilon_F = 1 \).](image1)

![Fig.3 Derivative of Fermi-Dirac distribution function \(-d f(\varepsilon)/d\varepsilon\) at various \( T \) (= 0.002 – 0.02). \( k_B = 1 \). \( \mu(T = 0) = \varepsilon_F = 1 \).](image2)

3. Density of states

A. 3D system

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 \( \varepsilon \) to \( \varepsilon + d\varepsilon \), \( D(\varepsilon)d\varepsilon \)

\[
D(\varepsilon)d\varepsilon = 2\frac{L^3}{(2\pi)^3} 4\pi k^2 dk ,
\]

(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

$$D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}.$$  \hspace{1cm} (14)

Here we define $D^4(\varepsilon_F) \left[1/(\text{eV atom})\right]$ which is the density of states per unit energy per unit atom.

$$D_A(\varepsilon_F) = \frac{D(\varepsilon_F)}{N},$$  \hspace{1cm} (15)

where

$$N = \int_0^{\varepsilon_F} D(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} \sqrt{\varepsilon}d\varepsilon = \frac{2}{3} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_F^{3/2}. \hspace{1cm} (16)$$

Then we have

$$D_A(\varepsilon_F) = \frac{3}{2\varepsilon_F}. \hspace{1cm} (17)$$

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

$$D_A(\varepsilon_F) = \frac{3n_v}{2\varepsilon_F}. \hspace{1cm} (18)$$

For Al, we have $\varepsilon_F = 11.6 \text{ eV}$ and $n_v = 3$. Then $D^A(\varepsilon_F) = 0.39/(\text{eV atom})$.

((Note)) \hspace{1cm} \textbf{Average energy}

$$E = \int_0^{\varepsilon_F} \varepsilon D(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2}d\varepsilon = \frac{2}{5} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_F^{5/2}.$$  \hspace{1cm}

Then we have

$$\frac{E}{N} = \frac{2}{5} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_F^{5/2} = \frac{3}{5} \varepsilon_F.$$  \hspace{1cm}
Here we make a plot of $f(\varepsilon)D(\varepsilon)$ as a function of $\varepsilon$ using Mathematica.

![Graph of $f(\varepsilon)D(\varepsilon)$](image)

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.

**B. 2D system**

For the 2D system, we have

$$D(\varepsilon)d\varepsilon = 2\frac{L^2}{(2\pi)^2} 2\pi k d\varepsilon.$$  \hspace{1cm} (19)

Since $d\varepsilon = (\hbar^2 / 2m)2kd\varepsilon$, we have the density of states for the 2D system as

$$D(\varepsilon) = \frac{mL^2}{\pi\hbar^2},$$  \hspace{1cm} (20)

which is independent of $\varepsilon$.

**C. 1D system**

For the 1D system we have

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

Thus the density of states for the 1D system is

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

**4. Sommerfeld’s formula**

When we use a formula
\[ \sum_k F(k) \to \frac{L^3}{(2\pi)^3} \int d\mathbf{k} F(\mathbf{k}) . \] (23)

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

\[ N = 2 \sum_k f(\varepsilon_k) = \frac{2L^3}{(2\pi)^3} \int d\mathbf{K} f(\varepsilon_k) = \int d\varepsilon D(\varepsilon) f(\varepsilon) , \] (24)

and

\[ E = 2 \sum_k \varepsilon_k f(\varepsilon_k) = \frac{2L^3}{(2\pi)^3} \int d\mathbf{K} \varepsilon K f(\varepsilon_k) = \int d\varepsilon D(\varepsilon) \varepsilon f(\varepsilon) . \] (25)

First we prove that

\[ \int \limits_{-\infty}^{\infty} g(\varepsilon) \left[ - \frac{\partial f(\varepsilon)}{\partial \varepsilon} \right] d\varepsilon = g(\mu) + \frac{1}{6} k_B^2 T^2 \pi^2 g^{(2)}(\mu) + \frac{7}{360} k_B^4 T^4 \pi^4 g^{(4)}(\mu) + \frac{31}{15120} k_B^6 T^6 \pi^6 g^{(6)}(\mu) + \frac{127}{604800} k_B^8 T^8 \pi^8 g^{(8)}(\mu) + \frac{73}{3421440} k_B^{10} T^{10} \pi^{10} g^{(10)}(\mu) + \ldots \] (26)

Here we note that

\[ \int \limits_{0}^{\infty} g(\varepsilon) \left[ - \frac{\partial f(\varepsilon)}{\partial \varepsilon} \right] d\varepsilon = -f(\varepsilon)g(\varepsilon) \bigg|_{0}^{\infty} + \int \limits_{0}^{\infty} g'(\varepsilon)f(\varepsilon) d\varepsilon = \int \limits_{0}^{\infty} g'(\varepsilon)f(\varepsilon) d\varepsilon . \] (27)

We define

\[ \varphi(\varepsilon) = g'(\varepsilon) \quad \text{or} \quad g(\varepsilon) = \int \limits_{0}^{\varepsilon} \varphi(\varepsilon') d\varepsilon' . \] (28)

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

\[ \int \limits_{0}^{\infty} f(\varepsilon)\varphi(\varepsilon) d\varepsilon = \int \limits_{0}^{\mu} \varphi(\varepsilon')d\varepsilon' + \frac{1}{6} k_B^2 T^2 \pi^2 \varphi'(\mu) + \frac{7}{360} k_B^4 T^4 \pi^4 \varphi^{(3)}(\mu) + \frac{31}{15120} k_B^6 T^6 \pi^6 \varphi^{(5)}(\mu) + \frac{127}{604800} k_B^8 T^8 \pi^8 \varphi^{(7)}(\mu) + \frac{73}{3421440} k_B^{10} T^{10} \pi^{10} \varphi^{(9)}(\mu) + \frac{1414477}{6538718400} k_B^{12} T^{12} \pi^{12} \varphi^{(11)}(\mu) + \ldots \] (29)
5. \( T \) dependence of the chemical potential

We start with

\[
N = \int d\epsilon D(\epsilon) f(\epsilon)
\]

where

\[
D(\epsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} = a\sqrt{\epsilon}
\]

and

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

\[
N = \int_0^\epsilon f(\epsilon) D(\epsilon) d\epsilon = \int_0^\mu D(\epsilon') d\epsilon' + \frac{1}{6} k_B^2 T^2 \pi^2 D'(\mu) = \frac{2a}{3} \mu^{3/2} + \frac{1}{6} k_B^2 T^2 \pi^2 \frac{a}{2\sqrt{\mu}}
\]

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

\[
N = \int_0^{\epsilon_F} D(\epsilon) d\epsilon = \frac{2a}{3} \epsilon_F^{3/2}.
\]

Thus the chemical potential is given by

\[
\frac{2a}{3} \epsilon_F^{3/2} = \frac{2a}{3} \mu^{3/2} + \frac{1}{6} k_B^2 T^2 \pi^2 \frac{a}{2\sqrt{\mu}},
\]

or

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

(30)

For the 1D case, similarly we have

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

(31)

We now discuss the \( T \) dependence of \( \mu \) by using the Mathematica.
6. **Total energy and specific heat**

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

$$U = \int_0^\infty f(\varepsilon)\varepsilon D(\varepsilon) d\varepsilon = \mu(T) + \frac{1}{6} \pi^2 (k_B T)^2 \{ D[\mu(T)] + \mu(T) D'[\mu(T)] \}. $$
The total number of electrons is also approximated by

\[ N = \int_{0}^{\infty} f(\varepsilon) D(\varepsilon) d\varepsilon = \frac{\mu^{(T)}}{0} D(\varepsilon) d\varepsilon + \frac{1}{6} \pi^{2} (k_{B} T)^{2} D'[\mu(T)] . \]

Since \( \partial N / \partial T = 0 \), we have

\[ \mu'(T) D[\mu(T)] + \frac{1}{3} \pi^{2} k_{B}^{2} T D'[\mu(T)] = 0 , \]

or

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

The specific heat \( C_{\text{el}} \) is defined by

\[ C_{\text{el}} = \frac{dU}{dT} = \frac{1}{3} \pi^{2} k_{B}^{2} T D[\mu(T)] + \frac{1}{3} \pi^{2} k_{B}^{2} T D'[\mu(T)] + \mu'(T) D(\mu(T))\mu(T) . \]

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

\[ C_{\text{el}} = \frac{1}{3} \pi^{2} k_{B}^{2} T D[\mu(T)] . \]

When \( \mu(T) \approx \varepsilon_{F} \),

\[ C_{\text{el}} = \frac{1}{3} \pi^{2} k_{B}^{2} D(\varepsilon_{F}) T . \] (32)

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

\[ \frac{C_{\text{el}}}{N} N_{A} = \frac{1}{3} \pi^{2} \frac{D(\varepsilon_{F})}{N} N_{A}, k_{B}^{2} T = \frac{1}{3} \pi^{2} D^{4}(\varepsilon_{F}) N_{A}, k_{B}^{2} T . \]

where \( N_{A} \) is the Avogadro number and \( D^{4}(\varepsilon_{F}) [1/(\text{eV at})] \) is the density of states per unit energy per unit atom. Note that

\[ \frac{1}{3} \pi^{2} N_{A}, k_{B}^{2} = 2.35715 \text{ mJ eV/K}^{2} . \]

Then \( \gamma \) is related to \( D^{4}(\varepsilon_{F}) \) as
\[ \gamma = \frac{1}{3} \pi^2 N_s k_B^2 D^4(\epsilon_F), \]

or

\[ \gamma (\text{mJ/mol K}^2) = 2.35715 \ D^4(\epsilon_F). \]  

(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 \( k_B T D(\epsilon_F) \) can be excited thermally. The total electronic thermal kinetic energy \( E \) is of the order of \((k_B T)^2 D(\epsilon_F)\). The specific heat \( C_{el} \) is on the order of \( k_B^2 T D(\epsilon_F) \).

((Note))

For Pb, \[ \gamma = 2.98, \quad D^4(\epsilon_F) = 1.26/(\text{eV at}) \]

For Al \[ \gamma = 1.35, \quad D^4(\epsilon_F) = 0.57/(\text{eV at}) \]

For Cu \[ \gamma = 0.695, \quad D^4(\epsilon_F) = 0.29/(\text{eV at}) \]

7. Pauli paramagnetism

The magnetic moment of spin is given by

\[ \hat{\mu}_z = -\frac{2 \mu_B \hat{S}_z}{\hbar} = -\mu_B \hat{\sigma}_z \]  

(quantum mechanical operator). Then the spin Hamiltonian (Zeeman energy) is described by

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

(34)

in the presence of a magnetic field, where the Bohr magneton \( \mu_B \) is given by \( \mu_B = \frac{e \hbar}{2mc} \) \((e>0)\).

(i) The magnetic moment antiparallel to \( H \): Note that the spin state is \( |\sigma_z\rangle = |+\rangle \).

The energy of electron is given by

\[ \epsilon = \epsilon_k + \mu_B H \]

with \( \epsilon_k = (\hbar^2 / 2m)k^2 \). The density of state for the down-state

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

or
\[ D_-(\varepsilon) = \frac{1}{2} D(\varepsilon - \mu_b H). \] 

Then we have

\[ N_- = \int_{\mu_b H}^{\infty} \frac{1}{2} D(\varepsilon - \mu_b H) f(\varepsilon) d\varepsilon. \] 

(ii) The magnetic moment parallel to \( H \). Note that the spin state is \( |\sigma_z\rangle = |\uparrow\rangle \).

The energy of electron is given by

\[ \varepsilon = \varepsilon_k - \mu_b H, \]

\[ D_+(\varepsilon) d\varepsilon = \frac{L^2}{(2\pi)^3} 4\pi k^2 d\kappa = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon + \mu_b H} d\varepsilon, \]

or

\[ D_+(\varepsilon) = \frac{1}{2} D(\varepsilon + \mu_b H). \] 

Then we have

\[ N_+ = \int_{-\mu_b H}^{\infty} \frac{1}{2} D(\varepsilon + \mu_b H) f(\varepsilon) d\varepsilon. \] 

The magnetic moment \( M \) is expressed by

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

or

\[ M = \frac{\mu_b}{2} \int_{0}^{\infty} D(\varepsilon) [f(\varepsilon - \mu_b H) - f(\varepsilon + \mu_b H)] d\varepsilon \]

\[ = \mu_b^2 \hbar \int_{0}^{\infty} D(\varepsilon) \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) d\varepsilon = \mu_b^2 \hbar D(\varepsilon_F) \]
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.

\[
\chi_p = \mu_\text{B}^2 D(\varepsilon_F).
\]

(41)

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

\[
\chi_p = \mu_\text{B}^2 \frac{D(\varepsilon_F)}{N} = \mu_\text{B}^2 N_A D(\varepsilon_F),
\]

(42)

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

\[
\gamma = \frac{1}{3} \pi^2 N_A k_\text{B}^2 D(\varepsilon_F),
\]

(43)

we have the following relation between \(\chi_p\) (emu/mol) and \(\gamma\) (mJ/mol K²),

\[
\chi_p = 1.37148 \times 10^{-5} \gamma.
\]

(44)

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

\[
y = 2.41\text{ mJ/mol K}^2, \quad \chi_p = (1.37 \times 10^{-5}) \times 2.41 \text{ (emu/mol)}
\]

1 mol = 85.468 g

\[
\chi_p = 0.386 \times 10^{-6}\text{ emu/g (calculation)}
\]

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

\[
y = 2.08\text{ mJ/mol K}^2, \quad \chi_p = (1.37 \times 10^{-5}) \times 2.08 \text{ (emu/mol)}
\]

1 mol = 39.098 g

\[
\chi_p = 0.72 \times 10^{-6}\text{ emu/g (calculation)}
\]

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

\[
y = 1.38\text{ mJ/mol K}^2, \quad \chi_p = (1.37 \times 10^{-5}) \times 1.38 \text{ (emu/mol)}
\]

1 mol = 29.98977 g

\[
\chi_p = 0.8224 \times 10^{-6}\text{ emu/g (calculation)}
\]

The susceptibility of the conduction electron is given by

\[
\chi = \chi_p + \chi_L = \chi_p - \chi_p / 3 = 2\chi_p / 3,
\]

(45)

where \(\chi_L\) is the Landau diamagnetic susceptibility due to the orbital motion of conduction electrons.

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

\[
\text{Rb: } \chi = 0.386 \times (2/3) \times 10^{-6} = 0.26 \times 10^{-6}\text{ emu/g}
\]

\[
\text{K: } \chi = 0.72 \times (2/3) \times 10^{-6} = 0.48 \times 10^{-6}\text{ emu/g}
\]
These values of $\chi$ are in good agreement with the experimental results.\textsuperscript{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 constants. These constants are obtained from the NIST Web site: http://physics.nist.gov/cuu/Constants/index.html

- Planck’s constant, $h = 1.05457168 \times 10^{-27}$ 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
- Velocity of light, $c = 4.803242 \times 10^{-10}$ esu (this is from the other source)

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.

9. Liquid $^3$He

A $^3$He refrigerator uses $^3$He to achieve temperatures of 0.2 to 0.3 K. A dilution refrigerator uses a mixture of $^3$He and $^4$He to reach cryogenic temperatures as low as a few thousandths of a K.

An important property of $^3$He, which distinguishes it from the more common $^4$He, is that its nucleus is a fermion since it contains an odd number of spin 1/2 particles. $^4$He nuclei are bosons, containing an even number of spin 1/2 particles. This is a direct result of the addition rules for quantized angular momentum. At low temperatures (about 2.17 K), $^4$He undergoes a phase transition: A fraction of it enters a superfluid phase that can be roughly understood as a type of Bose-Einstein condensate. Such a mechanism is not available for $^3$He atoms, which are fermions. However, it was widely speculated that $^3$He could also become a superfluid at much lower temperatures, if the atoms formed into pairs analogous to Cooper pairs in the BCS theory of superconductivity. Each Cooper pair, having integer spin, can be thought of as a boson. During the 1970s, David Lee, Douglas Osheroff and Robert Coleman Richardson discovered two phase transitions along the melting curve, which were soon realized to be the two superfluid phases of helium-3. The transition to a superfluid occurs at 2.491 mK on the melting curve. They were awarded the 1996 Nobel Prize in Physics for their discovery. Tony Leggett won the 2003 Nobel Prize in Physics for his work on refining understanding of the superfluid phase of helium-3.\textsuperscript{23}
In zero magnetic field, there are two distinct superfluid phases of $^3$He, the A-phase and the B-phase. The B-phase is the low-temperature, low-pressure phase which has an isotropic energy gap. The A-phase is the higher temperature, higher pressure phase that is further stabilized by a magnetic field and has two point nodes in its gap. The presence of two phases is a clear indication that $^3$He is an unconventional superfluid (superconductor), since the presence of two phases requires an additional symmetry, other than gauge symmetry, to be broken. In fact, it is a $p$-wave superfluid, with spin one, $S=1$, and angular momentum one, $L=1$. The ground state corresponds to total angular momentum zero, $J=S+L=0$ (vector addition). Excited states are possible with non-zero total angular momentum, $J>0$, which are excited pair collective modes. Because of the extreme purity of superfluid $^3$He (since all materials except $^4$He have solidified and sunk to the bottom of the liquid $^3$He and any $^4$He has phase separated entirely, this is the most pure condensed matter state), these collective modes have been studied with much greater precision than in any other unconventional pairing system.


The atom $^3$He has spin 1/2 and is a fermion. Here we calculate the Fermi velocity, Fermi energy, and Fermi temperature for $^3$He at $T = 0 \text{ K}$, viewed as a gas of noninteracting fermions. The density of the liquid is 0.081 g/cm$^3$. We also calculate the heat capacity at low temperatures for $T<<T_F$. The experimental value is given as

$$C_V = 2.89 \, N k_B T.$$  

Liquid $^3$He as a fermion

spin $I = 1/2$.

density $\rho = 0.081 \text{ g/cm}^3$,

$\rho = 3.160293 \text{ u}$

The number density $n$;
\[ \rho = \frac{Nm}{V} \quad n = \frac{N}{V} = \frac{\rho}{m} = 1.543 \times 10^{28}/m^3 \]

The Fermi energy is given by
\[ \varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = 0.3924 \text{ meV} \]

The Fermi temperature is defined as
\[ T_F = \frac{\varepsilon_F}{k_B} = 4.55 \text{ K} \]

The Fermi velocity is given by
\[ v_F = \sqrt{\frac{2\varepsilon_F}{m}} = 154.79 \text{ m/s} \]

The heat capacity is given by
\[ C = \frac{1}{2} \pi^2 Nk_B \frac{T}{T_F} = 1.0837 Nk_B T \]

((Mathematica)) Liquid $^3$He
Clear["Global`*"];

rule1 = {NA -> 6.02214179 \times 10^{23}, \ u -> 1.660538782 \times 10^{-27},
        eV -> 1.602176487 \times 10^{-19}, \ kB -> 1.3806504 \times 10^{-23},
        h -> 6.62606896 \times 10^{-34}, \ \hbar -> 1.05457162853 \times 10^{-34}, \ gram -> 10^{-3},
        cm -> 10^{-2}, \ mol -> NA, \ \rho -> 0.081 \ gram/ cm^3, \ m -> 3.160293 \ u};

n1 = \frac{\rho}{m} // . rule1
1.54351 \times 10^{28}

\epsilon_F = \frac{\hbar^2}{2m} \left(3 \pi^2 n_1\right)^{2/3} // . rule1
6.28684 \times 10^{-23}

\frac{\epsilon_F}{\epsilon_F} // . rule1
\epsilon_F
0.000392394

TF = \frac{\epsilon_F}{kB} // . rule1
4.55353

v_F = \sqrt{\frac{2\epsilon_F}{m}} // . rule1
154.79

1 \ \frac{\pi^2}{2} \frac{1}{\epsilon_F} // . rule1
1.08373

10. 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 $\gamma$ 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 $\gamma$ 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.

REFERENCES