

«Original» Partition Function of Electrons in Liquid Metals*

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Abstract

A method of obtaining the partition function for a system of electrons is developed by defining a new density matrix, in which the Fermi statistics is explicitly incorporated. The corresponding Bloch equation is formulated and a practical method of solving the equation is obtained for weak potential. This theory is applied to structurally disordered systems which might be reasonable models for liquid metals.

요 약

Fermi 통계를 도입한 새로운 밀도행렬을 정의함으로써 전자들의 Partition 함수를 구하는 방법이 마련되었다. 새 밀도행렬에 대응하는 Bloch 방정식이 형성되었고 약한 Potential에 대하여 이것을 푸는 방법이 얻어졌다. 이 이론은 액체금속의 모델이 될 수 있는 구조적 불규칙계에 적용되었다.

1. Introduction

One of the most conventional approach to the theoretical investigation for the electronic states in liquid metal is to determine the averaged single particle Green function by various approximations.¹⁻³⁾ More recently, another approach to the liquid metal problem has been developed by Rousseau *et al.*⁴⁾ using the density matrix method. In this approach, one determines the partition function of the system instead of directly determining the density of states. The density of states is related to the partition function by a form of integral transformation, although the inverse transform to obtain the density of states may not be trivial.

Consider a structurally disordered system

such as liquid metals for which the one-electron potential due to the ionic configuration $\{R_i\}$ is described by

$$V(\vec{r}) = \sum_i v(\vec{r} - \vec{R}_i) \quad (1)$$

where $v(\vec{r} - \vec{R}_i)$ is the localized potential centered on an ionic site \vec{R}_i . The one-electron Hamiltonian for this system is written as

$$H = [-\nabla^2 + V(\vec{r})] \quad (2)$$

Here, we employ the atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$) and, for the convenience of expression, we take the volume of the system to be unity.

In the usual density matrix theory⁵⁾, the canonical density matrix $C(\vec{r}, \vec{r}_0, \beta)$ is defined in terms of the eigenstates $\psi_i(\vec{r})$ and eigenvalues E_i of the Hamiltonian H by

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$$C(\vec{r}, \vec{r}_0, \beta) = \sum_i \Psi_i^*(\vec{r}) \Psi_i(\vec{r}_0) e^{-\beta E_i} \quad (3)$$

where $\beta = (k_B T)^{-1}$. The canonical density matrix C then satisfies the Bloch equation

$$HC = -\frac{\partial C}{\partial \beta} \quad (4)$$

with the boundary condition $C(\vec{r}, \vec{r}_0, \beta) = \delta(\vec{r} - \vec{r}_0)$.

For the solution of this Bloch equation, Hilton *et al*⁵⁾ suggested the form

$$C = C_0 e^{-\beta U(\vec{r}, \vec{r}_0, \beta)} \quad (5)$$

where C_0 is the free particle density matrix. Bloch equation (4) then reduces to a differential equation for $U(\vec{r}, \vec{r}_0, \beta)$, and they obtained a solution for U in closed form neglecting a term nonlinear in U . Rousseau *et al*⁴⁾ applied this theory to the disordered system and, in particular, obtained a convenient form for the calculation of partition function in liquid metals, using a simplified form of Kirkwood approximation for higher order correlation functions. Pant *et al*⁶⁾ applied this theory to evaluated the density of states of electrons in liquid aluminum.

The partition function they obtained, however, does not have the usual physical significance such that various thermodynamic quantities can be derivable from it, since it is essentially based on the Maxwell-Boltzmann statistics.

In the present work, we incorporate the Fermi statistics in the density matrix theory such that a partition function with correct statistics can be obtained for the electrons in liquid metals.

2. Modified Density Matrix Theory

We define a new density matrix, in which the Fermi statistics is incorporated, by

$$D(\vec{r}, \vec{r}_0, \alpha, \beta) = \sum_i \Psi_i^*(\vec{r}) \Psi_i(\vec{r}_0) \ln(1 + e^{\alpha - \beta E_i}) \quad (6)$$

where α is a quantity related to the chemical potential μ by $\alpha = \beta\mu$. The logarithm of the

grand partition function Q is then represented by the trace of D :

$$\ln Q = \int D(\vec{r}, \vec{r}, \alpha, \beta) d\vec{r} \quad (7)$$

It is easily verified that, in place of the Bloch equation (4), we obtain a similar equation satisfied by D as

$$H \frac{\partial D}{\partial \alpha} = -\frac{\partial D}{\partial \beta} \quad (8)$$

with the Hamiltonian H given in (2). From the definition of D in (6), we have a boundary condition for $\beta = 0$ as

$$D(\vec{r}, \vec{r}_0, \alpha, 0) = \ln(1 + e^\alpha) \delta(\vec{r} - \vec{r}_0) \quad (9)$$

independently of potential V . As an auxiliary relation which would eventually relate α to β , we have the condition

$$\int \frac{\partial D}{\partial \alpha}(\vec{r}, \vec{r}, \alpha, \beta) d\vec{r} = \sum_i \frac{1}{1 + e^{-\alpha + \beta E_i}} = N \quad (10)$$

where N is the total number of the electrons in the system. We here observe the fact that even though the density matrix D and grand partition function Q are functions of formally independent variables α and β , they are related in a specific equation $\alpha = \mu(\beta)\beta$ for a system of fixed number of electrons N . This relation, however, is not predetermined but should be determined by the condition (10) after D is obtained. In actual calculation, therefore, it is imperative to go through a self-consistent procedure to determine the relation $\alpha = \mu(\beta)\beta$.

The free particle density matrix D_0 can be obtained directly from the definition (6) as

$$D_0(\vec{r}, \vec{r}_0, \alpha, \beta) = \sum_i e^{i\vec{k} \cdot (\vec{r} - \vec{r}_0)} \ln(1 + e^{\alpha - \beta \epsilon_k}) \quad (11)$$

and the diagonal element $D_0(\alpha, \beta)$ is independent of \vec{r} and can be conveniently separated into a function of β and a function of α as

$$\begin{aligned} D_0(\alpha, \beta) &= \frac{4\pi}{(2\pi)^3} \int_0^\infty \ln(1 + e^{\alpha - \beta \epsilon_k}) k^2 dk \\ &= \frac{1}{2\pi^2} \beta^{-\frac{3}{2}} \int_0^\infty \ln(1 + e^{\alpha - \beta x^2}) x^2 dx \end{aligned} \quad (12)$$

We try a solution in the form

$$D(\vec{r}, \vec{r}_0, \alpha, \beta) = D_0(\vec{r}, \vec{r}_0, \alpha, \beta) e^{-U(\vec{r}, \vec{r}_0, \alpha, \beta)} \quad (13)$$

assuming that the potential $V(\vec{r})$ in (1) is sufficiently weak. Substituting (13) into (8), we obtain an equation satisfied by U as

$$\begin{aligned} \nabla^2 U - (\nabla U)^2 - \frac{\gamma_1}{\beta} \frac{\partial U}{\partial \alpha} + \gamma_2 \nabla^2 \frac{\partial U}{\partial \alpha} \\ - 2\gamma_2 (\nabla \frac{\partial U}{\partial \alpha}) \nabla U - \gamma_2 \frac{\partial U}{\partial \alpha} \nabla^2 U \\ + \gamma_2 \frac{\partial U}{\partial \alpha} (\nabla U)^2 + V + \gamma_2 \frac{\partial U}{\partial \alpha} V = \gamma_2 \frac{\partial U}{\partial \beta} \end{aligned} \quad (14)$$

where γ_1 and γ_2 are functions of α defined by

$$\gamma_1(\alpha) = \int_0^\infty \ln(1 + e^{\alpha-x}) x^4 dx / \int_0^\infty \frac{x^2 dx}{1 + e^{-\alpha+x}} \quad (15)$$

$$\gamma_2(\alpha) = \int_0^\infty \ln(1 + e^{\alpha-x}) x^2 dx / \int_0^\infty \frac{x^2 dx}{1 + e^{-\alpha+x}} \quad (16)$$

For small $V(\vec{r})$, we assume that

$$\gamma_2 \frac{\partial U}{\partial \alpha} \ll 1 \text{ and } (\nabla U)^2 \ll \nabla^2 U \quad (17)$$

which amounts to neglecting the second and higher order terms in U and V . We then get a linear differential equation of U as

$$\begin{aligned} \nabla^2 U - \frac{\gamma_1}{\beta} \frac{\partial U}{\partial \alpha} + \gamma_2 \nabla^2 \frac{\partial U}{\partial \alpha} \\ + V = \gamma_2 \frac{\partial U}{\partial \beta} \end{aligned} \quad (18)$$

This is the central equation to be investigated in the present theory. Since it is a formidable task to seek a solution directly from this equation, we deliberately leave out the most troublesome term $\gamma_2 \nabla^2 \frac{\partial U}{\partial \alpha}$ for a while. We then try to solve a simpler equation

$$\nabla^2 U + V = \frac{\gamma_1}{\beta} \frac{\partial U}{\partial \alpha} + \gamma_2 \frac{\partial U}{\partial \beta} \quad (19)$$

To reduce the equation further, it is convenient to define a function $\lambda(\alpha, \beta)$ which would satisfy

$$\frac{\gamma_1}{\beta} \frac{\partial \lambda}{\partial \alpha} + \gamma_2 \frac{\partial \lambda}{\partial \beta} = 1 \quad (20)$$

Assuming that such a λ can be obtained and regarding U as a function of \vec{r} , \vec{r}_0 , and λ , we can write (19) as

$$\nabla^2 U - \frac{\partial U}{\partial \lambda} = -V \quad (21)$$

The Green function for the last equation is found to be⁷⁾

$$\begin{aligned} G(\vec{r}, \vec{r}_0, \vec{r}_1, \lambda) \\ = \frac{1}{4\pi} \frac{(|\vec{r}-\vec{r}_1| + |\vec{r}_1-\vec{r}_0|)}{(|\vec{r}-\vec{r}_1| \cdot |\vec{r}_1-\vec{r}_0|)} \\ e^{-\frac{1}{4\lambda} [(|\vec{r}-\vec{r}_1| + |\vec{r}_1-\vec{r}_0|)^2 - (\vec{r}-\vec{r}_0)^2]} \end{aligned} \quad (22)$$

It is easily verified that G satisfies (21) with $V=0$ at $\vec{r} \neq \vec{r}_1$ and becomes $(4\pi|\vec{r}-\vec{r}_1|)^{-1}$ as $\vec{r} \rightarrow \vec{r}_1$. The exact solution for (21) is then given by

$$U(\vec{r}, \vec{r}_0, \lambda) = \int G(\vec{r}, \vec{r}_0, \vec{r}_1, \lambda) V(\vec{r}_1) d\vec{r}_1 \quad (23)$$

We now consider the boundary condition in connection with the form of the solution we are seeking here. Comparing (9) and (13), we find that $U \rightarrow 0$ as $\beta \rightarrow 0$. On the other hand, the Green function given in (22) satisfies the condition $G \rightarrow 0$ as $\lambda \rightarrow 0$ and thus U in (23) also satisfies $U \rightarrow 0$ as $\lambda \rightarrow 0$. These two conditions dictate therefore that λ should satisfy the condition $\lambda \rightarrow 0$ as $\beta \rightarrow 0$.

With this boundary condition for λ , we return to the problem of finding the function $\lambda(\alpha, \beta)$ which would satisfy (20). Consider a particular path in α - β plane

$$\beta(\alpha, c) = c \exp\left[\int_0^\alpha \frac{\gamma_2}{\gamma_1} d\alpha\right] \quad (24)$$

for which $d\beta = \beta \frac{\gamma_2}{\gamma_1} d\alpha$, where c is an arbitrary constant. Along the path (24),

$$\begin{aligned} d\lambda &= \left(\frac{\partial \lambda}{\partial \alpha}\right) d\alpha + \left(\frac{\partial \lambda}{\partial \beta}\right) d\beta \\ &= \left[\frac{\gamma_1}{\beta} \frac{\partial \lambda}{\partial \alpha} + \gamma_2 \frac{\partial \lambda}{\partial \beta}\right] \frac{\beta}{\gamma_1} d\alpha \end{aligned} \quad (25)$$

and using (20) we obtain

$$d\lambda = \frac{\beta}{\gamma_1} d\alpha \quad (26)$$

If the point (α_1, β_1) , for which we are trying to find the value of λ , lies on the path (24), we can determine the corresponding value λ from (26). We therefore adjust the constant c such that the path (24) passes through (α_1, β_1) by

$$c = \beta_1 \exp\left[-\int_0^{\alpha_1} \frac{\gamma_2}{\gamma_1} d\alpha\right] \quad (27)$$

Then integrating (26), we obtain

$$\lambda = \beta_1 e^{-\gamma_3(\alpha)} \int_{\alpha_0}^{\alpha_1} \frac{1}{\gamma_1} e^{\gamma_3(\alpha)} d\alpha \quad (28)$$

where

$$\gamma_3(x) = \int_0^x \frac{\gamma_2}{\gamma_1} d\alpha \quad (29)$$

and the lower integral limit α_0 should be determined by the boundary condition that $\lambda=0$ for $\beta=0$. Since the integral (28) is performed along the path (24), the value of α corresponding to $\beta=0$ is $\alpha=-\infty$. We therefore have the explicit solution of λ as

$$\lambda(\alpha, \beta_1) = \beta_1 e^{-\gamma_3(\alpha)} \int_{-\infty}^{\alpha_1} \frac{1}{\gamma_1} e^{\gamma_3(\alpha)} d\alpha \quad (30)$$

We now take care of the term $\gamma_2 \nabla^2 \frac{\partial U}{\partial \alpha}$, which has been deliberately ignored in the solution of (18). It might be possible that there are a number of ways to deal with this problem. We propose here a convenient method to get the solution of (18) by modifying the Green function (22). We assume that the Green function for (18) have the form

$$G'(\mathbf{r}, \mathbf{r}_0, \mathbf{r}_1, \lambda) = G(\mathbf{r}, \mathbf{r}_0, \mathbf{r}_1, \lambda) F(\mathbf{r}, \mathbf{r}_0, \mathbf{r}_1, \lambda) \quad (31)$$

where G is the Green function for (19) given by (22). Defining new functions ξ and f as

$$\begin{aligned} \xi(\mathbf{r}, \mathbf{r}_0, \mathbf{r}_1, \lambda) &= \frac{1}{4\lambda} [(|\mathbf{r}-\mathbf{r}_1| + |\mathbf{r}_1-\mathbf{r}_0|)^2 - (\mathbf{r}-\mathbf{r}_0)^2] \\ f &= 1 - e^{-\xi} \end{aligned} \quad (32)$$

$$f = 1 - e^{-\xi} \quad (33)$$

We let

$$F = a_0 + a_1 f + a_2 f^2 + a_3 f^3 + \dots \quad (34)$$

which would converge for all the possible values \mathbf{r} . From the definition of G' it is evident that

$$\lim_{\mathbf{r} \rightarrow \mathbf{r}_1} G' = \lim_{\mathbf{r} \rightarrow \mathbf{r}_1} G = \frac{1}{4\pi |\mathbf{r}-\mathbf{r}_1|} \quad (35)$$

and U would satisfy the same boundary condition, that is $U=0$ for $\beta=0$. To satisfy another criterion for Green function, G' should satisfy

$$\nabla^2 G' - \frac{\partial}{\partial \lambda} G' + \gamma_2 \nabla^2 \frac{\partial G'}{\partial \alpha} = 0 \quad (36)$$

for $\mathbf{r} \neq \mathbf{r}_1$. Substituting (31) and (34) into (36), we can determine the coefficients a_0, a_1, a_2, \dots by requiring that the coefficient of each power of $|\mathbf{r}-\mathbf{r}_1|$ should vanish separately. Finally, the determined G' should replace G in (33) and this completes the solution of our central equation (18).

Once U is determined, the grand partition function is expressed as

$$\ln Q(\alpha, \beta) = D_0(\alpha, \beta) \int e^{-U(\mathbf{r}, \mathbf{r}_0, \alpha, \beta)} d\mathbf{r} \quad (37)$$

and we can evaluate many interesting thermodynamic quantities, such as Helmholtz free energy, using this partition function. The density of states $n(E)$, in particular, is related to $\ln Q$ by a form of integral transformation

$$\ln Q(\alpha, \beta) = \int n(E) \ln(1 + e^{\alpha - \beta E}) dE \quad (38)$$

Although the inverse transform is not analytically possible, we can investigate some interesting properties of $n(E)$ using this relation.

Finally, we observe that the density of electrons can be evaluated by

$$\frac{\partial D}{\partial \alpha}(\mathbf{r}, \mathbf{r}) = \sum_i \Psi_i^*(\mathbf{r}) \Psi_i(\mathbf{r}) \frac{1}{1 + e^{-\alpha + \beta E_i}} \quad (39)$$

3. Application to Liquid Metals

We apply the general theory developed in the previous section to the electrons in liquid metals. The potential for this system is described by (1) and the function U for this potential can be written as

$$U(\mathbf{r}, \mathbf{r}, \lambda) = \sum_i u(\mathbf{r} - \mathbf{R}_i, \lambda) \quad (40)$$

with

$$\begin{aligned} u(\mathbf{r} - \mathbf{R}_i, \lambda) &= \int G'(\mathbf{r} - \mathbf{R}_i, \mathbf{r} - \mathbf{R}_i, \mathbf{r}', \lambda) v(\mathbf{r}') d\mathbf{r}' \\ &= \int G'(\mathbf{r} - \mathbf{R}_i, \mathbf{r} - \mathbf{R}_i, \mathbf{r}', \lambda) v(\mathbf{r}') d\mathbf{r}' \end{aligned} \quad (41)$$

For a particular configuration of ions $\{\mathbf{R}_i\}$, the grand partition function Q can be expressed as

$$\ln Q = D_0 \int \prod_i \exp\{-u(\vec{r}-\vec{R}_i, \lambda)\} d\vec{r} \quad (42)$$

using (40). Following Rousseau *et al.*⁴⁾, we introduce a Mayer function

$$w(\vec{r}-\vec{R}_i) = \exp\{-u(\vec{r}-\vec{R}_i, \lambda)\} - 1 \quad (43)$$

then,

$$\begin{aligned} \ln Q = D_0 \int & [1 + \sum_i w(\vec{r}-\vec{R}_i) \\ & + \frac{1}{2!} \sum_{i,i'} w(\vec{r}-\vec{R}_i) w(\vec{r}-\vec{R}_{i'}) \\ & + \frac{1}{3!} \sum_{i,i',i''} w(\vec{r}-\vec{R}_i) w(\vec{r}-\vec{R}_{i'}) w(\vec{r}-\vec{R}_{i''}) \\ & + \dots] d\vec{r} \end{aligned} \quad (44)$$

the prime on the summation means that any term with same index for $R_i, R_{i'}, R_{i''} \dots$ should be omitted.

To perform an ensemble average of this kind, it is necessary to know the correlation functions between atoms to all order, although only two-body correlation function is directly measurable by neutron or X-ray scattering in systems like liquid metals⁸⁾. Several schemes of approximation are known to get the higher order correlation functions, including the well-known Kirkwood approximation. In the context of present theory, the most convenient one is a simplified version of Kirkwood approximation introduced by Rousseau *et al.*⁴⁾. In this scheme, the approximation to the n -th order correlation function is given by

$$\begin{aligned} g_n(\vec{r}_1 \dots \vec{r}_n) = \frac{1}{n} [& g(r_{12}) g(r_{13}) \dots g(r_{1n}) \\ & + g(r_{21}) g(r_{23}) \dots g(r_{2n}) + \dots \\ & + g(r_{n1}) g(r_{n2}) \dots g(r_{nn-1})] \end{aligned} \quad (45)$$

where $g(r_{12}) = g(|\vec{r}_1 - \vec{r}_2|)$ is the two-body correlation function between atoms located at \vec{r}_1 and \vec{r}_2 .

The ensemble average of $\ln Q$ can then be obtained by

$$\langle \ln Q \rangle = D_0 \int [1 + \frac{w(\vec{r})}{W(\vec{r})} \{e^\rho W(\vec{r}) - 1\}] d\vec{r} \quad (46)$$

where ρ is the density of atoms, and

$$W(\vec{r}_1) = \int w(\vec{r}_2) g(r_{12}) d\vec{r}_2 \quad (47)$$

The auxiliary equation (10) is written as

$$\frac{1}{r_2} \ln Q - \frac{\partial \lambda}{\partial \alpha} D_0 \int \frac{\partial U}{\partial \lambda} e^{-U} d\vec{r} = N \quad (48)$$

where the integral in the second term can be expressed as

$$\begin{aligned} & \int \frac{\partial U}{\partial \lambda} e^{-U} d\vec{r} \\ & = \int \frac{\partial u}{\partial \lambda}(\vec{r}_1) [\rho + \frac{w(\vec{r}_1)}{W(\vec{r}_1)} \{e^\rho W(\vec{r}_1) - 1\}] d\vec{r}_1 \\ & + \rho \int \frac{\partial u}{\partial \lambda}(\vec{r}_1) [\int \frac{w(\vec{r}_2)}{W(\vec{r}_2)} \{e^\rho W(\vec{r}_2) \\ & - 1\} g(r_{12}) d\vec{r}_2] d\vec{r}_1 \end{aligned} \quad (49)$$

for liquid metals.

It might also be very interesting to investigate the space distribution of electrons in liquid metals, which might ultimately be related to the ion-ion interaction, using the relation (39) given in previous section.

For the actual calculation, we suggest that pseudopotentials, which are well known for simple metals⁹⁾ might be very useful. The nonlocality and, in particular, the energy dependence of the pseudopotential might bring in some difficulties which should be examined carefully. Since the density matrix is defined in terms of all the possible energy eigenstates, the inaccuracy of the potential for the higher energy states might lead to inaccurate density matrix. We expect, however, that this effect can be ignored since the probabilities to occupy the higher energy states are very small for electrons in metals at ordinary temperature.

The local pseudopotential, on the other hand, has the well-know property that it is much more slowly varying in the core region than the real potential is. Due to this property, the local pseudopotential is more suitable for the present theory, in which a weak potential is assumed.

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