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Surface effects on the diamagnetic susceptibility and other properties of a low-temperature electron gas

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A general formulation is developed for determining the free energy of a Fermi gas contained in an arbitrary smooth external potential barrier and in a weak magnetic field, in the low-temperature limit. The Wigner phase-space formalism of quantum mechanics is used as a calculational tool. Explicit formulas are given, which enable one to compute surface and temperature effects on various physical properties (susceptibility, specific heat, etc.) of the system. Some simple examples are constructed for the diamagnetic-susceptibility calculation, which show that the corrections depend on the form of the surface potential barrier and the size of the material, but, in general, they are small in comparison with the dominant Landau result when the size is much larger than ~100 Å. The general formalism that we present can also be applied to other kinds of Fermi gas (for example, nucleons) contained in an external potential. For example, we show how the modified Thomas-Fermi theory may be extended to include temperature effects.

I. INTRODUCTION

The Landau diamagnetic susceptibility was obtained[1] by considering an electron gas confined in a very large box. Analytic expressions for this quantity were derived for a zero-temperature degenerate gas and for a high-temperature Boltzmann gas.[1] Later the same system was reinvestigated by Dingle[2] and formulas were obtained for a Fermi gas in both low- and high-temperature limits. In general, since the electrons are confined by some kind of surface potential barrier, one may expect changes from the Landau values due to the surface effect. The investigations of this question have been carried out by many authors in the past few decades.[3-5] The common point of those investigations is the consideration of simple specific models for the potential barrier. For example, Friedman used a one-dimensional finite well potential and also a harmonic potential.[4] In both cases he found that the surface effects were small. Here we shall pay particular attention to the work of Jennings and Bhaduri.[5] They obtained a general expression for the diamagnetic susceptibility of electrons moving in a smooth potential barrier of arbitrary shape, for both a high-temperature Boltzmann gas and a *zero-temperature* degenerate gas. At the high-temperature limit, they were able to separate the Landau diamagnetic term from the surface—barrier-dependent correction terms and the latter decreased to zero faster than the Landau term as the temperature increases. For a zero-temperature degenerate gas, they also claimed a similar separation and a small surface correction but, as we shall see, this is not possible.

The results for a *Fermi gas* confined in a smooth arbitrary potential both (i) at high-temperature and (ii) at low-temperature *(but nonzero)* limits are still lacking. It is our purpose here to redress this situation.

Jancovici[6] pointed out that when the one-component electron plasma (jellium) is considered the exchange effect can be very small when $(b/\lambda)^2 \gg 1$, where $b=e^2/kT$ and $\lambda=(2\pi\hbar^2/kTm)^{1/2}$ are the average distance of closest approach and the thermal de Broglie wavelength, respectively. The quantitative physical reason for this is that free particles can exchange only when they approach one another at a distance of the order of the de Broglie wavelength λ, which is small in the classical limit, and also the Coulomb repulsion inhibits such encounters. After explicit calculations by the path-integral method, and in the absence of a magnetic field, he was able to obtain analytic expressions for two-body exchange effects, which turned out to be indeed exponentially small when $T \ll 5\times10^4$ K. Similar methods were then employed in the low- and strong-magnetic field limits and the same conclusions were drawn.[7] Thus we conclude that question (i) does not need to be considered and so we shall confine our attention to question (ii).

As we will see, at zero- and low-temperature limits the separation between the Landau term and the surface-barrier-dependent term cannot be achieved in general. In fact, the surface corrections to magnetic susceptibility and specific heat can be as large as those of free-electron gas when the size of the material is small. We consider only weak magnetic fields ($\hbar\omega_c \ll kT$, where ω_c is the cyclotron frequency).

The problem discussed above can be generalized to other kinds of Fermi gas (for example, nucleons) contained in an external potential. It is well known that[8,9] the dominant contribution of shell effects to nuclear masses can be extracted by considering the nucleons moving in a one-body shell potential. To calculate the sum of the occupied single-particle energies, the Strutinsky[9] and Bohr-Mottelson[10] methods are widely used. An alternative approach, the modified Thomas-Fermi (MTF) theory, was developed by Jennings *et al.*[11] They assumed $T=0$.

At room temperature the thermal energy is of order 10^{-2} eV whereas the nuclear energy scale is approximately MeV, which shows that the zero-temperature approximation for the calculations in nuclear physics is very accurate at room temperature. But in some cases the thermal energy can become comparable with the nuclear energy. Examples include artificial nuclear fusions or very hot stars ($T \gtrsim 10^9$ K). Furthermore, the TF theory has also been widely used in atomic physics in which the energy scale is of the order eV. For these reasons we wish to consider the extension of the modified TF theory to nonzero temperatures.

In summary, the above motivates us to develop the formation for a noninteracting[12] Fermi gas in a weak magnetic field and confined in an arbitrary external potential.

In Sec. II, we present the general formalism in the low-temperature limit, which is then applied to the calculation of the diamagnetic susceptibility for an arbitrary potential and next for certain choices of the surface potential. The validity of the MTF theory is also discussed. We then discuss the temperature effect on the MTF theory in Sec. III. The surface effect on the specific heat is determined in Sec. IV. Finally, discussions and conclusions are given in Sec. V. More detailed analysis of MTF is presented in the Appendix.

II. GENERAL FORMULATION IN THE LOW-TEMPERATURE LIMIT

In Fermi statistics the free energy of N noninteracting electrons is given by

$$F = N\mu - \frac{g_s}{\beta} \sum_i \ln(1+e^{\beta(\mu-E_i)}) , \tag{1}$$

where μ is the chemical potential, determined by

$$N = g_s \sum_i (e^{\beta(E_i-\mu)}+1)^{-1} , \tag{2}$$

g_s is the spin degeneracy, $\beta = 1/kT$ is the inverse temperature, and E_i is the energy of the ith level.[13]

The general relationship between the free energy in Fermi statistics and the Boltzmann partition function $Z(\beta)$ has been established by Sondheimer and Wilson[13,14] for arbitrary temperature. If one defines a function $\phi(E)$ by

$$\frac{Z(\beta)}{\beta^2} = \int_0^\infty \phi(E) e^{-\beta E} dE$$
$$\equiv L_\beta(\phi(E)) , \tag{3}$$

where L_β denotes the Laplace transform, then it follows that

$$F = N\mu + \int_0^\infty \phi(E) \frac{\partial f_0}{\partial E} dE , \tag{4}$$

where f_0 is the Fermi function

$$f_0 = (e^{\beta(E-\mu)}+1)^{-1} . \tag{5}$$

Evaluations of Eqs. (3) and (4) often involve analytic or numerical solutions of the Schrödinger equation and summation of infinite series, which is, in most cases, very difficult. In order *to avoid the direct computation of the energy levels* of the system, Wigner[15] pioneered the development of the phase-space formulation of quantum mechanics, so as to provide a framework for the treatment of quantum-mechanical problems in terms of classical concepts. For example, in the high-temperature limit, the Wigner-Kirkwood expansion[16] is a very powerful tool to evaluate the Boltzmann partition function[8]

$$Z(\beta) = g_s \sum_i e^{-\beta E_i} . \tag{6}$$

In the absence of a magnetic field, to order $\hbar^4$ (apart from the overall phase factor, $\hbar^{-3}$, in front) the expansion reads

$$Z_0^{(2)}(\beta) = 2 \left[\frac{m}{2\pi\beta\hbar^2} \right]^{3/2} \times \int d^3r\, e^{-\beta U} \left[1 - \frac{\hbar^2\beta^2}{24m} \nabla^2 U \right] , \tag{7}$$

where U is the external potential. The superscript "2" denotes order $\hbar^2$ and the subscript "0" denotes the absence of a magnetic field (which will be considered below). We should notice that the definition of $Z(\beta)$, given by Eq. (6), is larger than the usual definition by a factor of g_s, which explains the shift differences of Eqs. (4) and (7) from the original ones.[13,14]

The essential feature of the modified Thomas-Fermi theory is to use the Wigner-Kirkwood expansion and Eqs. (3) and (4) to obtain an approximation for the free energy.[11] It has been shown[11] that this MTF theory is closely related to the Strutinsky method in nuclear physics, and also to the three-dimensional Wentzel-Kramers-Brillouin (WKB) method.[17]

One would notice that the Wigner-Kirkwood expansion is valid only for small β, but the Laplace inverse in Eq. (3) in principle involves the values of the partition function for all values of β. We wish to present the following arguments on the validity of MTF.

Suppose that a typical energy-level spacing of the system is ΔE and the number of electrons is N. At low temperatures, the energy of the system is on the order of $N^2 \Delta E$, for a large N. The energy fluctuation of the system, e.g., when the external magnetic field or temperature varies, is about the order of ΔE, which is a reasonable estimate for the amplitude of the oscillatory part of the energy. In general, the singularity of the Boltzmann partition function at $\beta = 0$ gives rise to the steady part of the energy, whereas the singularities along the imaginary axis of β plane accounts for the oscillatory part (a mathematical proof of this conclusion and more discussions on it are presented in the Appendix). A small-β (Wigner-Kirkwood) expansion of the Boltzmann partition function therefore will enable one to obtain the steady part of the free energy, and to ignore the oscillatory part. Hence the error of the MTF theory is on the order of N^{-2}, which is usually very small. In this paper we are only interested in the (steady) Landau diamagnetism, so MTF provides us with a good approximation. Needless to say that when one is concerned with the oscillatory behavior of the system, such as the de Haas—van Alphen effect, MTF is no longer valid.

By expressing $\phi(E)$ is a Taylor series in powers of $(E-\mu)$,

$$\phi(E)=\sum_{n=0}^{\infty}\frac{\phi^{(n)}(\mu)}{n!}(E-\mu)^n\,, \tag{8}$$

it has been shown that [Ref. 13, p. 331 and Eqs. (A6) and (A8)]

$$\int_0^{\infty}\phi(E)\frac{\partial f_0}{\partial E}dE=-\phi(\mu)-2\sum_{n=1}^{\infty}\phi^{(2n)}(\mu)(kT)^{(2n)}\times(1-2^{1-2n})\zeta(2n)\,, \tag{9}$$

where $\zeta(Z)$ is Riemann's zeta function.

The combination of Eqs. (4) and (9) gives the free energy at the low-temperature limit, with an arbitrary potential built in $\phi(\mu)$ [by virtue of Eqs. (3) and (7)],

$$F=N\mu-\phi(\mu)-2\sum_{n=1}^{\infty}\phi^{(2n)}(\mu)(kT)^{2n}(1-2^{1-2n})\zeta(2n)\,. \tag{10}$$

Here the Fermi energy μ is determined by [Ref. 13, p. 329 and Eq. (A2.9)]

$$\frac{\partial F}{\partial\mu}=0=N-\phi^{(1)}(\mu)-2\sum_{n=1}^{\infty}\phi^{(2n+1)}(\mu)(kT)^{2n}\times(1-2^{1-2n})\zeta(2n)\,. \tag{11}$$

In particular, at zero temperature, we have the usual results

$$F_0=N\mu_0-\phi(\mu_0)\,, \tag{12}$$

and

$$N=\frac{\partial\phi(E)}{\partial E}\Big|_{E=\mu_0}\equiv\phi^{(1)}(\mu_0)\,. \tag{13}$$

The Fermi energy μ, which is defined by Eq. (11) and used in Eq. (10), is temperature dependent. We shall now reduce Eq. (10) to a form that contains μ_0 only by first solving Eq. (11) for μ. To the order of $(kT/\mu_0)^4$, the Fermi energy is

$$\mu=\mu_0-\frac{\pi^2}{6}\frac{\phi^{(3)}(\mu_0)}{\phi^{(2)}(\mu_0)}(kT)^2-\left[\frac{\pi^2}{6}\left[\frac{\phi^{(3)}(\mu_0)}{\phi^{(2)}(\mu_0)}\right]^3-\frac{\pi^4}{36}\left[\frac{\phi^{(3)}(\mu_0)}{\phi^{(2)}(\mu_0)}\right]\left[\frac{\phi^{(4)}(\mu_0)}{\phi^{(2)}(\mu_0)}\right]\right](kT)^4\,. \tag{14}$$

Substituting Eq. (14) back into Eq. (10), we finally obtain the free energy at the low-temperature limit,

$$F=F_0-\frac{\pi^2}{6}\phi^{(2)}(\mu_0)(kT)^2+\frac{\pi^4}{72}\frac{[\phi^{(3)}(\mu_0)]^2}{\phi^{(2)}(\mu_0)}(kT)^4\,, \tag{15}$$

where $F_0=N\mu_0-\phi(\mu_0)$ is the zero-temperature result. The magnetic susceptibility immediately follows from $\chi=-B^{-1}(\partial F/\partial B)_{\mu,V,T}$. Since $\chi_0=B^{-1}\partial\phi(\mu_0)/\partial B$, it is easy to verify that, using Eq. (15),

$$\chi=\chi_0+\frac{\pi^2}{6}\chi_0^{(2)}(kT)^2-\frac{\pi^4}{72}\left[\frac{2\phi^{(3)}(\mu_0)}{\phi^{(2)}(\mu_0)}\chi_0^{(3)}-\left[\frac{\phi^{(3)}(\mu_0)}{\phi^{(2)}(\mu_0)}\right]^2\chi_0^{(2)}\right](kT)^4\,, \tag{16}$$

where χ_0 is the magnetic susceptibility at zero temperature $\chi_0^{(n)}\equiv\partial^n\chi_0/\partial\mu_0^n$. Using Eq. (25) of Ref. 5, but including spin degeneracy, we have

$$\chi_0=-\frac{e^2\hbar^2}{12m^2c^2}\left[g_0(\mu_0)-\frac{1}{240\pi^2}\left[\frac{2m}{\hbar^2}\right]^{1/2}\frac{\partial}{\partial\mu_0}\times\int d^3r(\nabla_1^2U)\Theta(\mu_0-U)\times(\mu_0-U)^{-1/2}\right]\,, \tag{17}$$

where $\Theta(\chi)$ is the Heaviside unit step function and

$$g_0(\mu)=\frac{1}{2\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\left[\int d^3r(\mu-U)^{1/2}\Theta(\mu-U)-\frac{\hbar^2}{24m}\left[\frac{\partial^2}{\partial\mu^2}\int d^3r(\mu-U)^{1/2}\nabla^2U\Theta(\mu-U)+\delta(\mu)\frac{\partial}{\partial\epsilon'}\times\int d^3r(\epsilon'-U)^{1/2}\nabla^2U\Theta(\epsilon'-U)\Big|_{\epsilon'=0^+}\right]\right] \tag{18}$$

is the density of states of an electron gas with Fermi energy μ in the absence of magnetic field. By setting U to be zero, the last two terms in Eq. (18) vanish, while the first term gives the density of states for the free-electron gas.

In general, in contrast to the conclusion of Ref. 5, we point out that the first term in Eq. (17) is not the well-known Landau term, the reason being that the density of state differs from that of the free-electron gas when a nonzero confining potential barrier is considered. We will illustrate this point more clearly below by choosing a simple form for the potential.

Substituting Eq. (17) into Eq. (16), we obtain the lowest-order temperature correction to the magnetic susceptibility,

$$\Delta_T\chi=-\frac{\pi^2e^2\hbar^2}{72m^2c^2}(kT)^2\left[g_0''(\mu_0)-\frac{1}{240\pi^2}\left[\frac{2m}{\hbar^2}\right]^{1/2}\times\frac{\partial^3}{\partial\mu_0^3}\int d^3r(\nabla_1^2U)\Theta(\mu_0-U)\times(\mu_0-U)^{-1/2}\right]. \quad (19)$$

To proceed further we need a more explicit form for the relation between the Fermi energy μ_0 and the number of electrons, which can be obtained by using Eq. (13) for N in terms of the first derivative of $\phi(\mu)$. We now turn to the evaluation of the latter quantity.

In a weak magnetic field limit, the corresponding Wigner-Kirkwood expansion has been derived by Jennings and Bhaduri.[5] To order B^2, where B is the magnetic field, it reads as follows:

$$Z_B^{(2)'}(\beta)=Z_0^{(2)'}(\beta)-\frac{e^2B^2\hbar^2B^2}{24m^2c^2}Z_0^{(0)'}(\beta), \quad (20)$$

where

$$Z_0^{(0)'}=2\left[\frac{m}{2\pi\beta\hbar^2}\right]^{3/2}\int d^3r\,e^{-\beta U}, \quad (21)$$

and $Z_0^{(2)'}(\beta)$ is given by Eq. (7).

The inverse Laplace transform of Eq. (20) divided by β^2 gives

$$\phi(\mu)=\phi_0(\mu)-\frac{e^2B^2\hbar^2}{24m^2c^2}g_0(\mu), \quad (22)$$

where $g_0(\mu)$ is given by Eq. (18), and where

$$\begin{aligned}\phi_0(\mu)&\equiv L_\mu^{-1}(Z_0(\beta)/\beta^2)\\&=\frac{1}{2\pi i}\int_{C-i\infty}^{C+i\infty}\frac{Z_0(\beta)}{\beta^2}e^{\beta\mu}d\beta\\&=\frac{1}{3\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{\mathbf{r}_\mu}d^3r\left[\tfrac{2}{5}(\mu-U)^{5/2}-\frac{\hbar^2}{16m}\nabla^2U(\mu-U)^{1/2}\right],\end{aligned} \quad (23)$$

where L_μ^{-1} is the Laplace inverse, and the real number C is chosen such that every singular point of $Z_0(\beta)/\beta^2$ stays on the left-hand side of C.

The integrals in Eq. (23) cut off at the classical turning point $U(\mathbf{r}_\mu)=\mu$. The relation

$$L_\mu^{-1}\left[\frac{e^{-\beta U}}{\beta^{n+1/2}}\right]=\frac{2^n}{[\pi(2n-1)!!]^{1/2}}(\mu-U)^{n-1/2}\times\Theta(\mu-U),\quad n=1,2,\ldots, \quad (24)$$

has been used to establish Eq. (23).

Then Eq. (13) reads

$$N=\phi_0'(\mu_0)-\frac{e^2B^2\hbar^2}{24m^2c^2}g_0'(\mu_0). \quad (25)$$

We should mention that in the zero-potential limit our formulas lead to Landau[1] and Dingle's[2] results (including the de Haas–van Alphen effect).

We shall now apply Eqs. (17) and (19) to evaluate the diamagnetic susceptibility for some simple choices of potential barrier.

A. Isotropic harmonic-oscillator potential

In this case

$$U=\tfrac{1}{2}m\omega^2r^2. \quad (26)$$

It has been shown that[5]

$$\chi_0=-\frac{e^2\hbar^2}{12m^2c^2}\left[g_0(\mu_0)-\frac{1}{15\hbar\omega}\right], \quad (27)$$

where the density of states is[18]

$$g_0(\mu_0)=\frac{\mu_0^2}{(\hbar\omega)^3}-\frac{1}{4\hbar\omega}. \quad (28)$$

Making use of Eq. (19), to order T^2,

$$\Delta_T\chi=\frac{\pi^2}{3}\frac{(kT)^2}{(\hbar\omega)^2}\frac{1}{\hbar\omega}\frac{e^2\hbar^2}{12m^2c^2}. \quad (29)$$

Also

$$\phi_0(\mu_0)=\frac{\mu_0^4}{12(\hbar\omega)^3}-\frac{\mu_0^2}{8(\hbar\omega)}. \quad (30)$$

Consider now, for example, a small metallic ball with radius r_0 and let E_0 be the work function of the metal. If one uses the isotropic-oscillator potential to describe the surface effect, one will have

$$\mu_0+E_0=\tfrac{1}{2}m\omega^2r_0^2 \quad (31)$$

or

$$\hbar\omega=\hbar\left[\frac{2E_0+\mu_0}{mr_0^2}\right]^{1/2}. \quad (32)$$

For a typical metal, $E_0+\mu_0\sim$eV. Thus, even for r_0 as small as 100 Å one finds that $\hbar\omega$ is no greater than about 0.1 eV. So it is a good approximation to retain the first terms in Eqs. (28) and (30). Then by making use of Eqs. (13), (27), (28), and (30), we have the following relations:

$$\chi_0\approx-\frac{\mu_B^2N}{\mu_0}, \quad (33)$$

$$N\approx\frac{1}{3}\left[\frac{\mu_0}{\hbar\omega}\right]^3, \quad (34)$$

where $\mu_B=e\hbar/2mc$ is the Bohr magneton. The combination of Eqs. (32) and (34) gives an explicit expression for the Fermi energy,

$$\mu_0=b\sqrt{E_0}\left\{\frac{b}{2\sqrt{E_0}}+\left[\left[\frac{b}{2\sqrt{E_0}}\right]^2+1\right]^{1/2}\right\}, \quad (35)$$

with $n = N/V = 3N/4\pi r_0^3$, the number of electrons per unit volume, $b = (2/m)^{1/2}(4\pi n)^{1/3}\hbar$.

We note that Eq. (33) has the same form as the Landau diamagnetic susceptibility, except that the latter has the Fermi energy of free-electron gas

$$\varepsilon_F = \frac{(2\pi\hbar)^2}{2m}\left[\frac{3n}{8\pi}\right]^{2/3} \tag{36}$$

instead of μ_0 given by Eq. (35).

In terms of the mass density ρ, the molecular weight M, the number of valence electrons Z, and Avogadro's constant N_0, one has $N = ZN_0/M$ and $N/V = \rho N$, so that

$$\begin{aligned} d &\equiv \frac{b}{2\sqrt{E_0}} \\ &= \frac{1}{2}\frac{\hbar}{\sqrt{E_0}m}\left[4\pi\frac{\rho Z N_0}{M}\right]^{1/3} \\ &= 3.84(E_0 R)^{-1/2}(\rho Z M^{-1})^{1/3} , \end{aligned} \tag{37}$$

and

$$\begin{aligned} p &\equiv \frac{\varepsilon_F}{b\sqrt{E_0}} \\ &= 1.71(E_0 R)^{-1/2}(\rho Z M^{-1})^{1/3} , \end{aligned} \tag{38}$$

where E_0 is in eV, ρ in g/cm^3, Z, M are pure numbers, and R is the ratio of the effective electron mass and the free-electron mass. If one puts $Z = 1$, $\rho = 0.97$ g cm^{-3}, $M = 23$, $E_0 = 2.35$ eV, and $R = 1.3$ for Na, one obtains

$$\begin{aligned} \frac{\chi_0}{\chi_L} &= 2\left[\frac{\varepsilon_F}{\mu_0}\right] \\ &= 2p[d + (d^2+1)^{1/2}]^{-1} \\ &= 0.62, \text{ for Na} . \end{aligned} \tag{39}$$

From these results and Eq. (29), we find that the temperature effect is smaller than the free-electron gas case

$$\begin{aligned} \frac{\Delta_T\chi}{\chi_L} &= \frac{\pi^2}{3}\left[\frac{kT}{\mu_0}\right]^2\left[\frac{\varepsilon_F}{\mu_0}\right] \\ &\sim 10^{-5} \end{aligned} \tag{40}$$

at room temperature. The corresponding ratio in the case of the free-electron gas is about 10^{-4}.

B. Thomas potential

Now we choose the one-dimensional perturbed harmonic potential, originally introduced by Thomas,[3]

$$U(y) = \tfrac{1}{2}m\omega^2 y^2 + \lambda y^4 . \tag{41}$$

The high-temperature case has been considered by Thomas[3] and Jennings *et al.*[5]

We are interested in getting the correction to the harmonic case to first order in λ in the low-temperature limit.

From Eq. (18), the density of states is

$$\begin{aligned} g_0(\mu_0) = &\frac{1}{(2m\omega^2)^{1/2}}\left[\frac{S}{4\pi}\right]\left[\frac{2m}{\hbar^2}\right]^{3/2} \\ &\times\left[2\mu_0 + \frac{\mu_0^2\lambda}{(m\omega^2)^2}\right] , \end{aligned} \tag{42}$$

where S is the surface area of the slab.

To obtain the second term in Eq. (17), we need to calculate the integral

$$I(\lambda) = 2\int_0^{y'} dy \frac{\partial^2 U}{\partial y^2}(\mu_0 - U)^{-1/2} , \tag{43}$$

where y' is given by $U(y') = \mu$. We obtain

$$\begin{aligned} I(\lambda) = 2&\int_0^{y'}(m\omega^2)(\mu_0 - \tfrac{1}{2}m\omega^2 y^2 - \lambda y^4)^{-1/2}dy \\ &+ 24\lambda\int_0^{y_0} y^2(\mu_0 - \tfrac{1}{2}m\omega^2 y^2)^{-1/2}dy , \end{aligned} \tag{44}$$

where $y_0 = (2\mu_0/m\omega^2)^{1/2}$. The second term can be easily obtained, while the first one turns out to be a complete elliptic integral. The result, to first order in λ, is

$$I(\lambda) = \pi(2m\omega^2)^{1/2} + \frac{13\sqrt{2}\pi\mu_0\lambda}{(m\omega^2)^{3/2}} . \tag{45}$$

Substituting Eq. (42) and (45) into Eq. (17), we obtain the diamagnetic susceptibility at zero temperature,

$$\begin{aligned} \chi_0 = -&\frac{e^2\hbar^2}{12m^2c^2}\left[\frac{S}{4\pi}\right]\left[\frac{2m}{\hbar^2}\right]^{1/2} \\ &\times\left[\left[\frac{4m\mu_0}{\hbar^2(2m\omega^2)^{1/2}}\right]\right. \\ &\left.+\lambda\left[\frac{2m\mu_0^2}{\hbar^2(m\omega^2)^{5/2}} - \frac{13\sqrt{2}}{60(m\omega^2)^{3/2}}\right]\right] . \end{aligned} \tag{46}$$

The temperature correction to order T^2 is

$$\begin{aligned} \Delta_T\chi &= -\frac{\lambda^2}{6}(kT)^2\frac{\partial^2\chi_0}{\partial\mu_0^2} \\ &= \frac{e^2 S\lambda}{12\pi mc^2(m\omega^2)^{5/2}}\left[\frac{2m}{\hbar^2}\right]^{1/2} . \end{aligned} \tag{47}$$

From Eqs. (46) and (47) we conclude that temperature-dependent corrections due to surface effects arise only from the anharmonic part of the potential.

III. TEMPERATURE EFFECT ON THE MODIFIED THOMAS-FERMI THEORY

By taking the inverse of Eq. (3) and using Eq. (7), Jennings *et al.*[11] found that the first classical term in the Wigner-Kirkwood expansion led to the energy given by the Thomas-Fermi (TF) theory, while the quantum correction terms gave the corrections to the TF theory. By explicit calculation, using the Woods-Saxon potential, they were able to show that those higher-order terms tended to zero very fast and the results involving the first correction agreed fairly well with the values evaluated through the Strutinsky method.

This modified Thomas-Fermi theory is valid only for zero temperature. For the reasons explained in Sec. I, we need to extend this theory to include the temperature effect. With the help of our general results derived in Sec. II, it can be done in a straightforward fashion.

Substituting Eq. (23) into Eq. (15) we obtain

$$F=F_0+\Delta_T F\ , \tag{48}$$

where F_0 is the energy given by Jennings *et al.*,[11]

$$F_0=N\mu_0-\frac{1}{3\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\times\int_0^{r_{\mu_0}}d^3r\left\{\tfrac{2}{5}(\mu_0-U)^{5/2}-\frac{\hbar^2}{16m}\nabla^2U(\mu_0-U)^{1/2}\right\}, \tag{49}$$

and we obtain, to the order of $(kT/\mu_0)^4$,

$$\begin{aligned}\Delta_T F={}&-\frac{1}{18}\left[\frac{2m}{\hbar^2}\right]^{3/2}\left[\tfrac{3}{2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}+\frac{\hbar^2}{64m}\int_0^{r_{\mu_0}}d^3r\,\nabla^2U(\mu_0-U)^{-3/2}\right](kT)^2\\&+\frac{1}{324}\left[\frac{2m}{\hbar^2}\right]^{3/2}\left\{\frac{9}{16}\frac{\left[\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{-1/2}\right]^2}{\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}}\right.\\&-\frac{\hbar^2}{32m}\left[\tfrac{1}{3}\int_0^{r_{\mu_0}}d^3r\,\nabla^2U(\mu_0-U)^{-3/2}\left[\frac{\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{-1/2}}{\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}}\right]^2\right.\\&\left.\left.+\frac{9}{8}\frac{\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{-1/2}\int_0^{r_{\mu_0}}d^3r\,\nabla^2U(\mu_0-U)^{-5/2}}{\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}}\right]\right\}(kT)^4\ ,\end{aligned} \tag{50}$$

which is the sought-after temperature effect on the MTF theory. Usually it is sufficient to consider only a few terms of the lowest orders in temperature.

The Fermi energy at zero temperature can be determined by Eq. (13), i.e.,

$$N=\frac{1}{(3\pi^2)}\left[\frac{2M}{\hbar^2}\right]^{3/2}\times\int_0^{r_{\mu_0}}d^3r\left\{(\mu_0-U)^{3/2}-\frac{\hbar^2}{32M}(\mu_0-U)^{-1/2}\nabla^2U\right\}. \tag{51}$$

IV. SURFACE EFFECT ON THE SPECIFIC HEAT

The specific heat of a Fermi gas in the absence of an external potential has been discussed by many authors.[2] We now compute the correction terms due to the surface potential.

First, we obtain the internal energy by $\partial(\beta F)/\partial\beta$, which gives

$$\begin{aligned}U&=\partial(\beta F)/\partial\beta\\&=F_0+\frac{\pi^2}{6}\phi^{(2)}(\mu_0)(kT)^2-\frac{\pi^4}{72}\frac{[\phi^{(3)}(\mu_0)]^2}{\phi^{(2)}(\mu_0)}(kT)^4\ .\end{aligned} \tag{52}$$

Then

$$C_v=\left[\frac{\partial U}{\partial T}\right]_v$$

$$=\frac{\pi^2}{3}\phi^{(2)}(\mu_0)k^2T-\frac{\pi^4}{18}\frac{[\phi^{(3)}(\mu_0)]^2}{\phi^{(2)}(\mu_0)}k^4T^3\;. \tag{53}$$

Again we shall discuss the model for a small metallic ball ($r_0 \lesssim 100$ Å) with a harmonic potential barrier. For simplicity we retain the lowest-order term in Eq. (51) only. With the help of Eqs. (22), (28), and (30), the heat capacity can be written as follows:

$$C_v=\pi^2Nk(kT/\mu_0)\left[1-\tfrac{1}{12}(3N)^{-1/3}-\frac{1}{24}\left[\frac{\omega_c}{\omega}\right]^2(3N)^{-1/3}\right], \tag{54}$$

where $\omega_c=eB/mc$ is the cyclotron frequency. The last two terms are negligible. Recalling that the specific heat for free-electron gas, $C_v^{(0)}$, say, at low temperature is

$$C_v^{(0)}=\frac{\hbar^2}{2}Nk(kT/\varepsilon_F)\;, \tag{55}$$

we obtain

$$\frac{C_v}{C_v^{(0)}}=2\left[\frac{\varepsilon_F}{\mu_0}\right]=0.62 \text{ for Na}\;. \tag{56}$$

V. CONCLUSIONS AND DISCUSSIONS

We have obtained analytic expressions for the free energy of a Fermi gas in the presence of an arbitrary smooth potential and a weak magnetic field in low-temperature limit. The formulas derived were then applied to calculate the surface and temperature corrections to the diamagnetic susceptibility. Detailed discussions for the susceptibility problem were given for various special choices of surface potential barrier.

In the harmonic barrier model, we have essentially assumed that every electron in the system is influenced by such a surface potential. This is true only when the size of the material is very small (~ 100 Å). In this case, the Fermi energy is measurably enhanced with respect to that of free electrons. Surface corrections to the physical properties (magnetic susceptibility, specific heat, etc.) are expected to be of the same order of magnitude as those of free-electron gas. To obtain quantitative results, one needs to use a more realistic surface potential barrier.

In the case where the size of the material is much larger than 100 Å, the above assumption is no longer valid. One can then separate the total number of electrons N into two parts: there are N_1 electrons near the surface and $N-N_1$ well inside the surface. It is those electrons near the surface that give rise to the surface corrections. Since $N_1 \ll N$ when the size is large, one would then expect the surface corrections to be small.

The general formulation developed can be readily used to compute the surface effects on other physical quantities. To show this, we have briefly discussed the specific heat for the system. More detailed calculations, like these we did for the diamagnetic susceptibility, can be carried out following the outline given by us.

Equations (37) and (56) give rise to the following question: Are these relations true for an arbitrary potential? The answer would be yes, but with a factor which depends on the form of potential. To see this point, we compare Eqs. (18), (23), and (25) with only the first terms retained, i.e.,

$$g_0(\mu_0)=\frac{1}{2\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}\;, \tag{57}$$

$$\phi_0(\mu_0)=\frac{2}{15\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{5/2}\;, \tag{58}$$

and

$$N=\frac{1}{3\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{3/2}\;. \tag{59}$$

Then we cast Eq. (59) into the following form:

$$N=\frac{\mu_0}{3\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\left[1-\frac{U(r_1)}{\mu_0}\right]\times\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}\;, \tag{60}$$

by defining the integral mid value of $U(r)$ by

$$\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}U=U(r_1)\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}\;. \tag{61}$$

The diamagnetic susceptibility, Eq. (17), takes the form

$$\chi_0=-\frac{\mu_B^2}{3}\frac{1}{2\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}$$

$$=-\frac{\mu_B^2}{2}\frac{N}{\mu_0}\left[1-\frac{U(r_1)}{\mu_0}\right]^{-1}, \tag{62}$$

which is

$$\frac{\chi_0}{\chi_L}=\left[\frac{\varepsilon_F}{\mu_0}\right]\left[1-\frac{U(r_1)}{\mu_0}\right]^{-1}. \tag{63}$$

Similarly, the specific heat can be written as follows:

$$C_v=\frac{\pi^2}{2}\frac{k^2T}{3\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}\int_0^{r_{\mu_0}}d^3r(\mu_0-U)^{1/2}\;. \tag{64}$$

Again we find that

$$\left[\frac{C_v}{C_v'}\right]=\left[\frac{\varepsilon_F}{\mu_0}\right]\left[1-\frac{U(r_1)}{\mu_0}\right]^{-1}. \tag{65}$$

In the case we have considered, $U=\frac{1}{2}m\omega^2r^2$, it is readily verified that

$$U(r_1)=\tfrac{1}{2}\mu_0\;. \tag{66}$$

Equations (64) and (65) then reduce to Eqs. (37) and (56).

The modified Thomas-Fermi theory has now been extended to include the temperature effect, which may provide one with a useful method of evaluating the thermal fluctuations in nuclear and atomic physics. However, in the latter cases, one must choose more realistic potentials (as, for example, the Woods-Saxon potential). The formulas given here can form the basis of such calculations but integrations, such as appears in Eq. (60), will have to be performed numerically.

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APPENDIX: SOME GENERAL PROPERTIES OF THE BOLTZMANN PARTITION FUNCTION AND THE FUNCTION $\phi(E)$ DEFINED BY EQ. (3).

In this appendix, we wish to gain more insight on the modified Thomas-Fermi theory by first discussing some general properties of the Boltzmann partition function and its Laplace inverse. Then we shall illustrate our results further with a simple special case, one-dimensional harmonic-oscillator system.

The Boltzmann partition function $Z(\beta)$ is defined by Eq. (6) for an arbitrary system. If we consider $Z(\beta)$ as a function of complex variable β, definition Eq. (6) is obviously not proper for the left half β plane. We now define $Z(\beta)$ in the entire β plane by the sum function obtained by performing the summation in Eq. (6) in the right half β plane. For example, let us consider one-dimensional harmonic-oscillator potential. The eigenenergies are $E_n=(n+\frac{1}{2})\hbar\omega$.

$$g_s\sum_{n=0}^{\infty}\exp(-\beta E_n)$$

does not exist in the left-hand β plane. After performing the summation, we obtain a sum function $[\sinh(\beta\hbar\omega/2)]^{-1}$ (with $g_s=2$), which is then the definition for $Z(\beta)$ in the entire β plane.

Lemma 1. If β_l is a nonzero singular point of $Z(\beta)$, β_l must be a purely imaginary number, i.e., $\beta_l=i\lambda_l$, where λ_l is real.

Proof. Suppose $\beta_l=\alpha_l+i\lambda_l$ with real α_l and λ_l, and $|Z(\beta_l)|=+\infty$. We shall consider first the right half of β plane, i.e., $\alpha_l>0$,

$$\begin{aligned}|Z(\beta_l)|&=g_s\left|\sum_j e^{-(\alpha_l+i\lambda_l)E_j}\right|\\&<g_s\sum_j\left|e^{-(\alpha_l+i\lambda_l)E_j}\right|<g_s\sum_j e^{-\alpha_lE_j}\\&=Z(\alpha_l)<+\infty\ .\end{aligned}\tag{A1}$$

Contradiction. Hence $\alpha_l=0$, i.e., there is no singularities of $Z(\beta)$ in the right half β plane. By definition, it is also true for the left half β plane.

Lemma 2. If $\beta_l=i\lambda_l$ is a singular point of $Z(\beta)$, so is $\beta_l^*=-i\lambda_l$.

Proof. Suppose $|Z(\beta_l)|=\infty$, hence

$$[Z(\beta_l)]^{-1}=\left[\sum_j g_se^{-\lambda_lE_j}\right]^{-1}=0\ .$$

Taking the complex conjugate, one has

$$\left[\sum_j g_se^{+i\lambda_lE_j}\right]^{-1}=0\ ,\tag{A2}$$

which is $|Z(\beta_l^*)|=+\infty$.

Lemma 3. $\beta=0$ is always a singular point of $Z(\beta)$.

Proof. $|Z(\beta=0)|=+\infty$. (A3)

Hence we conclude that all the singularities of $Z(\beta)$ lie symmetrically along the imaginary axis of the β plane.

Theorem. The function $\phi(E)$ defined by Eq. (3) has the following general form:

$$\begin{aligned}\phi(E)&=\phi_{\rm st}(E)+\sum_{l=1}^{\infty}[\theta_{\rm os}^{(1)}(E)\cos(\lambda_lE)+\theta_{\rm os}^{(2)}(E)\sin(\lambda_lE)]\\&\equiv\phi_{\rm st}(E)+\phi_{\rm os}(E)\ ,\end{aligned}\tag{A4}$$

where $\phi_{\rm st}(E)$ is determined by the singularity at $\beta=0$, whereas the oscillatory parts, $\theta_{\rm os}^{(1)}(E)$ and $\theta_{\rm os}(2)(E)$ are determined by the singularities at $\beta_{\pm l}=\pm i\lambda_l$, with λ_l real and positive. The free energy at zero temperature is given by

$$\begin{aligned}F_0&=[N\mu_0-\phi_{\rm st}(\mu_0)]+[-\phi_{\rm os}(\mu_0)]\\&\equiv F_{\rm st}+F_{\rm os}\ ,\end{aligned}\tag{A5}$$

where $F_{\rm st}=N\mu_0-\phi_{\rm st}(\mu_0)$ and $F_{\rm os}=-\phi_{\rm os}(\mu_0)$.

Proof. $\phi(E)$ can be obtained by an inverse Laplace transform [see Eq. (23)] through a standard semicircle in the β plane, $\phi(E)$ can then be expressed as a sum over all the residues of the integrand $Z(\beta)e^{E\beta}/\beta^2$. All residues at nonzero singular points have the form $G_n(E)\exp(i\lambda_nE)$ or $Q_n(E)i\exp(i\lambda_nE)$, where $G_n(E)$, $Q_n(E)$ are real functions of E. If we notice the fact that $\phi(E)$ is always real [see Eq. (12)], we conclude that the sum over all residues at nonzero singularities can be written as the second term of Eq. (A4). Hence the steady part of $\phi(E)$ is determined only by the residue at $\beta=0$. Combining Eqs. (12) and (A4) we obtain Eq. (A5).

As an illustration of the above general results, we shall consider an N-electron (noninteracting) system confined in a one-dimensional harmonic-oscillator potential, where exact results can be easily obtained without any help of MTF.

The Boltzmann partition function in this case is

$$Z(\beta)=\frac{1}{\sinh(\beta\hbar\omega/2)}\ .\tag{A6}$$

The nonzero singular points are purely imaginary and come in pairs,

$$\beta_{\pm l}=\pm\frac{2\pi li}{\hbar\omega},\quad l=1,2,3,\ldots\ .\tag{A7}$$

We shall now evaluate

$$\phi(E)=\frac{1}{2\pi i}\int_{C-i\infty}^{C+i\infty}\frac{e^{E\beta}}{\beta^2\sinh(\beta\hbar\omega/2)}d\beta$$

$$=\gamma_0+\sum_{l=1}^{\infty}(\gamma_l+\gamma_{-l}) , \tag{A8}$$

where the residue at $\beta_{\pm l}$ is

$$\gamma_{\pm l}=\frac{(-1)^{l-1}\exp(\pm 2\pi i l E/\hbar\omega)}{2(l\pi)^2}(\hbar\omega) . \tag{A9}$$

Hence the oscillatory part of $\phi(E)$ is

$$\phi_{\rm os}(E)=\sum_{l=1}^{\infty}(\gamma_l+\gamma_{-l})$$

$$=\hbar\omega\sum_{l=1}^{\infty}\frac{(-1)^{l-1}\cos(2\pi l E/\hbar\omega)}{(l\pi)^2} . \tag{A10}$$

Similarly the steady part of $\phi(E)$ is determined by the residue at $\beta=0$,

$$\phi_{\rm st}(E)=\gamma_0$$

$$=\frac{E^2}{\hbar\omega}-\frac{\hbar\omega}{12} . \tag{A11}$$

It is of interest to see that MTF instead gives the steady part of the function $\phi(E)$. The Wigner-Kirkwood expansion for the present system is obtained by Eq. (7) and $U=\frac{1}{2}m\omega^2x^2$,

$$Z(\beta)=\frac{2}{\beta\hbar\omega}\left[1-\frac{\beta^2\hbar^2\omega^2}{24}\right] . \tag{A12}$$

The function $\phi(E)$ is evaluated by a Laplace inverse

$$\phi(E)=L_E^{-1}(Z(\beta)/\beta^2)$$

$$=\frac{E^2}{\hbar\omega}-\frac{\hbar\omega}{12} , \tag{A13}$$

which is exactly Eq. (A11).

The Fermi energy μ_0 can be determined by Eq. (13),

$$N=\frac{2\mu_0}{\hbar\omega}-2\sum_{l=1}^{\infty}\frac{(-1)^{l-1}\sin(2\pi l\mu_0/\hbar\omega)}{l\pi} , \tag{A14}$$

which is equivalent to

$$\mu_0=(N\hbar\omega)/2 . \tag{A15}$$

Substituting Eq. (A15) into Eq. (A5), we obtain $F_0=N^2\hbar\omega/4$. But here we are interested in comparing the two parts of the free energy,

$$F_{\rm st}=\frac{N^2\hbar\omega}{4}+\frac{\hbar\omega}{12} \tag{A16}$$

and

$$F_{\rm os}=-\hbar\omega\sum_{l=1}^{\infty}\frac{(-1)^{l-1}\cos(2\pi l\mu_0/\hbar\omega)}{(l\pi)^2}$$

$$=-\frac{\hbar\omega}{12} . \tag{A17}$$

We can see that when $N \ll 1$, $F_{\rm os} \sim N^{-2}F_{\rm st}$.

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