Orbital magnetic susceptibility of electrons confined in a rectangular box*†

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The orbital magnetic susceptibility of a gas of noninteracting electrons confined by hard walls to a rectangular box has been calculated in the low-magnetic-field limit. The result for the size-corrected susceptibility in the high-temperature limit is $\chi = \chi_L[1-\lambda_T(L_x^{-1}+L_y^{-1})/16\pi^{1/2}]$ where χ_L is the Landau diamagnetism, λ_T is the thermal de Broglie wavelength, and L_x and L_y are the dimensions of the box perpendicular to the direction of the magnetic field. A slightly more complicated formula for the case of Boltzmann statistics is accurate for the range $\lambda_T \leq 2L$. A similar expression is found for Fermi-Dirac statistics valid for high values of the Fermi energy. The result corrects an error by Papapetrou, and agrees with the recent results of Angelescu, Nenciu, and Bundaru. When applied to the case of infinite slabs ($L_y \to \infty$), it agrees with the results of several previous authors. The result, however, indicates that calculations by Dingle and Osborne for spherical and cylindrical volumes are in error. Numerical calculations for the case of Fermi-Dirac statistics at temperatures a few percent of the Fermi level give results which agree reasonably well with the size-corrected susceptibility formula even for a very few electrons in the box ($\lambda_F \lesssim 2L$, where λ_F is the de Broglie wavelength at the Fermi level).

I. INTRODUCTION

The question of size effects upon the diamagnetic susceptibility of noninteracting electrons confined to fixed volume is an old one. Bohr's argument[1] that there is no diamagnetism in classical mechanics examined the orbits of electrons colliding with the surface, and seemed to require that the radius of the cyclotron orbit, $r \equiv (2mE)^{1/2}c/eB$, be small compared to the dimensions of the container L. However, Van Leeuwen's theorem[2] does not require such a condition. In his quantum-mechanical calculation Landau[3] treated the surface in an approximate way and obtained for the magnetic susceptibility per electron

$$\chi_L = -\mu_B^2/2\zeta \tag{1.1a}$$

for $T=0$, and

$$\chi_L = -\mu_B^2/3kT = -\tfrac{1}{3}\mu_B^2\beta\,, \tag{1.1b}$$

in the high-temperature limit. In the above, $\mu_B = e\hbar/2mc$ is the Bohr magneton and ζ is the energy of the Fermi level. Though Teller[4] and Van Vleck[5] constructed treatments of the surface effect, based on the correspondence principle, that also gave Landau's result, the question is quite subtle and several authors have published works indicating important size corrections.

In the present work, we treat only the low-magnetic-field case, where both the cyclotron radius and the radius of gyration $l = (\hbar c/eB)^{1/2}$, become infinite, so that any finite sample is in the "size-effect regime." We shall comment on the finite-field case in Sec. IV. We shall treat only hard-wall containers: i.e., the electrons under consideration are confined by infinite square-well-type potentials. In this regime the important lengths are the sample size L and the characteristic de Broglie wavelength: $\lambda_F = 2\pi\hbar/(2m\zeta)^{1/2}$ for $T=0$ or $\lambda_T = 2\pi\hbar(\beta/2m)^{1/2}$ for high temperature.

In 1937 Papapetrou[6] calculated the magnetic susceptibility at $T=0$ for a thick slab, whose short dimension is perpendicular to the field direction, and obtained the Landau result. In 1939 he calculated[7] the susceptibility for a rectangular box at $T=0$ and found the Landau result when the ratio of the lengths of the box perpendicular to the magnetic field is irrational, but found a very different result, $\chi \sim \chi_L(L/\lambda_F)$, when the lengths are equal! Friedman[8] calculated χ for the thick slab in the high-temperature limit and for $T=0$. He found the Landau result in the high-temperature limit. His result at $T=0$ differed from Landau's by a constant factor, but Denton[9] has pointed out that the correction of an error yields the Landau result. Nedorezov[10] has calculated for a thin slab at low temperatures. He finds the Landau result plus a correction proportional to $\chi_L(\lambda_F/L)$ and an oscillatory term. Moriya, Ohtaka, and Yanagawa[11] and Ohtaka and Moriya[12] have calculated the surface current and correction to diamagnetism due to one plane surface at both high and low temperatures. Their results are in harmony with Nedorezov's. Very recently, Angelescu *et al.*[13] have calculated the susceptibility for a rectangular box for high and low temperatures. They obtained the Landau result plus correction terms proportional to λ/L. Their result is in harmony with those for the slab. In contrast Dingle[14] and Osborne[15] found results of the order of $\chi_L(L/\lambda_F)^{1/3}$ for cylindrical and spherical volumes.

In Sec. II we derive results for the case $L \gg \lambda$

which agree with those of Angelescu *et al.*,[13] but go to higher order in λ/L. In Sec. III we present numerical calculations in the opposite limit ($\lambda_F \lesssim 2L$), where only a few electrons are in the box. The results for a temperature a few percent of the Fermi energy agree well with the formula from Sec. II. Discussion of the results, and of the effect of using a self-consistent surface potential, is presented in Sec. IV.

II. CALCULATION OF THE SUSCEPTIBILITY FOR $\lambda \ll L$

We first calculate the orbital magnetic susceptibility in the high-temperature limit, for which Boltzmann statistics may be used. We then use the Laplace transform method of Sondheimer and Wilson[16] to obtain results for Fermi-Dirac statistics. We obtain the partition function by calculating the trace of the operator $\exp(-\beta\mathcal{H})$, where

$$\mathcal{H} = \mathcal{H}_0 + B(e\vec{a}\cdot\vec{p}/mc) + e^2a^2B^2/2mc^2 , \tag{2.1}$$

and we write the vector potential $\vec{A} = \vec{a}B$. We ignore the effect of electron spin, which has been treated for the thin slab by Nedorezov.[10] We use the method of Goldberger and Adams[17] to expand the partition function to order B^2, and use the standard low-field definition of the susceptibility, $\chi = -\beta^{-1}\partial^2 \ln Z/\partial B^2\big|_{B=0}$. The result for the susceptibility per particle is

$$\chi = -\frac{e^2}{Z_0 mc^2} \times \mathrm{Tr}\left(a^2 e^{-\beta\mathcal{H}_0} - \frac{\beta}{m}\int_0^1 ds\ \vec{a}\cdot\vec{p}e^{-(1-s)\beta\mathcal{H}_0}\vec{a}\cdot\vec{p}e^{-s\beta\mathcal{H}_0}\right), \tag{2.2a}$$

where

$$Z_0 = \mathrm{Tr}(e^{-\beta\mathcal{H}_0}) . \tag{2.2b}$$

In the derivation, we have used the result that $\mathrm{Tr}(\vec{a}\cdot\vec{p}e^{-\beta\mathcal{H}_0}) = 0$. This vanishing can be proven in several ways,[18] and without it there would be a permanent magnetic moment in the system at high temperatures. The formula (2.2a) is very close to those derived by Kubo[19] using the Wigner distribution function. In our treatment $\mathcal{H}_0$ is the kinetic energy of the electron, and the effect of the confining potential is in the boundary condition which requires that the wave functions over which the trace is taken vanish on the boundaries. Even though one takes traces over a set of functions which already obey the boundary conditions imposed by the potential, one must not assume that the potential V is zero thereafter. The full Hamiltonian $\mathcal{H}_0 = T + V$ must be used when evaluating commutators of $\vec{p}$ and $\vec{a}$ with $\mathcal{H}_0$. However, our calculation does not involve any commutations.

We shall evaluate (2.2a) by using the complete set of unperturbed eigenstates, and express the products as matrix multiplications. If the integration on s is carried out before the summation in the trace, then we would obtain the same results as from applying nondegenerate perturbation theory to find the changes in the energy eigenvalues, except that the energy denominators would appear in factors such as $(e^{-\beta\mathcal{E}_n} - e^{-\beta\mathcal{E}_m})/(\mathcal{E}_n - \mathcal{E}_m)$. Thus degeneracy or near degeneracy would not cause any difficulties.[20] This explains why Papapetrou[7] obtained the correct result for the case of an irrational ratio of lengths of the sides. However for the case of equal lengths he treated some degeneracies explicitly, but ignored others and obtained a spurious result. Our point of view concerning this error differs somewhat from Denton's.[9] We shall perform the summations before the integrations on s, as then the sum is the product of simpler sums associated with the x and y directions.

Before carrying out the summation, we modify the formula for χ by combining the results for three different gauges with the magnetic field in the z direction,

$$\vec{a}_1 = (0, x, 0) , \tag{2.3a}$$

$$\vec{a}_2 = (-y, 0, 0) , \tag{2.3b}$$

$$\vec{a}_3 = \tfrac{1}{2}(-y, x, 0) = \tfrac{1}{2}(\vec{a}_1 + \vec{a}_2) . \tag{2.3c}$$

The final susceptibility must be the same in any gauge. By taking twice the result for gauge 3 and subtracting one-half each of the results for gauges 1 and 2, we obtain

$$\chi = -\frac{e^2\beta}{2Z_0 m^2c^2}\int_0^1 ds\ \mathrm{Tr}(xp_y e^{-(1-s)\beta\mathcal{H}_0} y p_x e^{-\beta\mathcal{H}_0} + y p_x e^{-(1-s)\beta\mathcal{H}_0} x p_y e^{-\beta\mathcal{H}_0}) . \tag{2.4}$$

This formula has the advantage that the cancellation between the large a^2 and $(\vec{a}\cdot\vec{p})^2$ terms in Eq. (2.2a) has been eliminated, though we have verified that our method gives the same answers as putting the Landau gauge $\vec{a}_2$ in Eq. (2.2a). Papapetrou[7] obtained an equivalent result by manipulating the specific sums. We now choose the same normalized eigenstates as Papapetrou[7] and Friedman[8]

$$\psi_{lmn}(x, y, z) = \varphi_l(x)\varphi_m(y)\varphi_n(z) , \tag{2.5a}$$

$$\varphi_l(x) = (2/L_x)^{1/2}\begin{cases}\cos(l\pi/L_x), & l \text{ odd},\\ \sin(l\pi/L_x), & l \text{ even},\end{cases} \tag{2.5b}$$

$$\mathcal{E}_{lmn} = (\hbar^2\pi^2/2m)[(l/L_x)^2 + (m/L_y)^2 + (n/L_z)^2] , \tag{2.5c}$$

where the origin is in the center of the box of sides L_x, L_y, and L_z. The matrix elements needed are then

$$\langle l|x|l'\rangle = (4/\pi)L_x ll'/(l'^2 - l^2)\,, \tag{2.6a}$$

$$\langle l|p_x|l'\rangle = (8i\hbar/\pi L_x)ll'/(l'^2 - l^2)^2\,, \tag{2.6b}$$

if $l - l'$ is odd and zero otherwise, in agreement with Friedman and Papapetrou. Substituting the matrix elements and energy into Eq. (2.4), and using Friedman's notation

$$a_x^2 = \pi^2\hbar^2\beta/2mL_x^2 = (\lambda_T/2L_x)^2\,,$$

we find

$$\chi = -4\frac{\mu_B^2\beta}{Z_0'}\int_0^1 ds\, J[(1-s)a_x^2, sa_x^2]J[(1-s)a_y^2, sa_y^2]\,, \tag{2.7a}$$

where

$$J(x,y) = \frac{32}{\pi^2}\sum_l{}'\sum_{l'}{}'\frac{l^2 l'^2}{(l'^2 - l^2)^3}e^{-(l^2x + l'^2y)}\,. \tag{2.7b}$$

In the above, the sum on l' is over odd values if l is even, and over even values if l is odd. We have used the result that the summation on n (involving the z coordinate) cancels against the same term in Z_0; Z_0' includes the summation on l and m only (x and y coordinates). The double sum $J(x,y)$ is evaluated in Appendix A for high temperatures (small a). With an accuracy of better than 0.5% up to $a = 1$, we have

$$J[(1-s)a^2, sa^2] = [\pi^{1/2}(1-2s)/4a] - [\sin^{-1}(1-2s) + 2(1-2s)s^{1/2}(1-s)^{1/2}]/2\pi. \tag{2.8}$$

Friedman's evaluation of Z_0 is good to better than 0.004% up to $a_x = 1$,

$$z_x = \sum_l \exp(-l^2a_x^2) = \pi^{1/2}/2a_x - \tfrac{1}{2}\,, \tag{2.9}$$

where $Z_0 = z_x z_y z_z$ and $Z_0' = z_x z_y$. Substituting the results for the summations into Eq. (2.7a) and integrating on s we have

$$\chi = -\tfrac{1}{3}\mu_B^2\beta\frac{1 - (9/8\pi^{1/2})(a_x + a_y) + (3 - 256/15\pi^2)a_x a_y/\pi}{1 - \pi^{-1/2}(a_x + a_y) + a_x a_y/\pi}\,. \tag{2.10}$$

The result is the high-temperature expression for χ, but it has an accuracy better than 0.5% up to $a = 1$, for which $\lambda_T = 2L$. We see that the leading term is the Landau term, for all ratios of L_x and L_y. In order to compare with other work, we Taylor expand the denominator, though this will reduce the accuracy, to obtain

$$\chi = \chi_L[1 - \tfrac{1}{8}(a_x + a_y)\pi^{-1/2} - \tfrac{1}{8}(a_x + a_y)^2\pi^{-1} + (2 - 256/15\pi^2)a_x a_y \pi^{-1}]\,. \tag{2.11}$$

The result through order a is exactly that of Angelescu *et al.*[13] and that given by applying Ohtaka and Moriya's[12] formula to the four faces parallel to the magnetic field. We can obtain the result for a slab by letting $L_y \to \infty, a_y \to 0$. The result then agrees with a result to second order in a_x which can be found by making a trivial extension of Friedman's[8] sum formula (2.6).

To find the expression for Fermi-Dirac statistics, we follow the Sondheimer-Wilson[16] prescription of applying the transformation

$$\chi_{FD} = -i\pi^{-1}\int d\mathcal{E}\frac{-\partial f}{\partial\mathcal{E}}\int_{c-i\infty}^{c+i\infty} d\beta\, Z_0(\beta)\chi_B(\beta)e^{\beta\mathcal{E}}\beta^{-1}\,, \tag{2.12}$$

where $\chi_B(\beta)$ is the susceptibility for Boltzmann statistics, $Z_0(\beta)$ is the trace of the Boltzmann distribution function, χ_{FD} is the susceptibility for Fermi-Dirac statistics, and f is the Fermi-Dirac distribution function. This expression gives the total susceptibility of all the electrons in the volume and includes the spin degeneracy. The total number of electrons is given by $N = -\partial\Omega/\partial\zeta$, where

$$\Omega = -i\pi^{-1}\int d\mathcal{E}\frac{-\partial f}{\partial\mathcal{E}}\int_{c-i\infty}^{c+i\infty} d\beta\, Z_0(\beta)e^{\beta\mathcal{E}}\beta^{-2}\,, \tag{2.13}$$

which also includes the spin degeneracy.

For high temperatures, the correction to χ for use of Fermi-Dirac statistics is proportional to $\chi_L\beta^{3/2}$ for the three-dimensional case, so that the correction is of higher order than is kept in Eq. (2.10). For a two-dimensional case (appropriate to a layer structure) this correction is proportional to $\chi_L\beta$.

For $T = 0$ we find for the Fermi-Dirac case

$$\chi = (\mu_B^2 m/3\pi^2\hbar^3)(2m\zeta)^{1/2}L_x L_y L_z \times[1 - \tfrac{1}{2}\alpha_z - \tfrac{9}{16}(\alpha_x + \alpha_y) + \tfrac{1}{2}(3 - 256/15\pi^2)\alpha_x\alpha_y\pi^{-1} + 9\alpha_z(\alpha_x + \alpha_y)/16\pi]\,, \tag{2.14}$$

where

$$\alpha_x^2 = \hbar^2\pi^2/2mL_x^2\zeta = (\lambda_F/2L_x)^2\,.$$

The leading term is the total Landau susceptibility of an electron gas at $T = 0$ in the volume $L_x L_y L_z$ and with Fermi level ζ. Note that in contrast to the case of Boltzmann statistics, there are corrections associated with the face of the box perpendicular to the field direction (involving α_z). For the slab case, $\alpha_y = \alpha_z = 0$, the first-order correction in α_x agrees with the nonoscillatory term of Nedorezov,[10] but does not reproduce his term which is oscillatory in L_x/λ_F. This is because our result is an expansion in inverse powers of ζ. The effect of the Sondheimer-Wilson transform on the neglected terms in $Z_0(\beta)\chi_B(\beta)$ presumably would produce the oscillatory terms. Note that there is

no error from Taylor expanding a denominator as $Z_0(\beta)\chi_B(\beta)$ is the numerator of (2.10) times z_z. The correction linear in α_z is in agreement with that of Allen[21] for a thick slab perpendicular to the magnetic field, when specialized to our potential model.

The relation between the number of electrons and the Fermi energy is (including spin degeneracy)

$$N=(3\pi^2)^{-1}(2m\zeta/\hbar^2)^{3/2}L_xL_yL_z \times[1-\tfrac{3}{4}(\alpha_x+\alpha_y+\alpha_z)-(3/4\pi)\alpha_x\alpha_y\alpha_z +3(\alpha_x\alpha_y+\alpha_y\alpha_z+\alpha_z\alpha_x)/2\pi]. \quad (2.15)$$

Angelescu *et al.*[13] express their susceptibility in terms of carrier density $\rho=N/L_xL_yL_z$ and Ohtaka and Moriya[12] express their results in terms of ζ_0, the Fermi level which would correspond to the same carrier density $\rho=(2m\zeta_0/\hbar^2)^{1/2}/3\pi^2$ if there were no surface effects. The relationship is

$$\zeta\cong\zeta_0[1+\tfrac{1}{2}(\alpha_x^0+\alpha_y^0+\alpha_z^0)], \quad (2.16)$$

where

$$\alpha_x^0=(\hbar^2/2m\zeta_0)^{1/2}\pi/L_x=\lambda_0/2L_x.$$

With this substitution we find to first order in α

$$\chi=-N(\mu_B^2/2\zeta_0)[1-\tfrac{1}{4}\alpha_z^0-\tfrac{5}{16}(\alpha_x^0+\alpha_y^0)]. \quad (2.17)$$

This expression agrees exactly with that found by applying Ohtaka and Moriya's results to all six faces of the box, and with the result of Angelescu *et al.* when one takes into account the fact that they do not include the spin degeneracy. Our formulas, Eqs. (2.14) and (2.15), should be more accurate

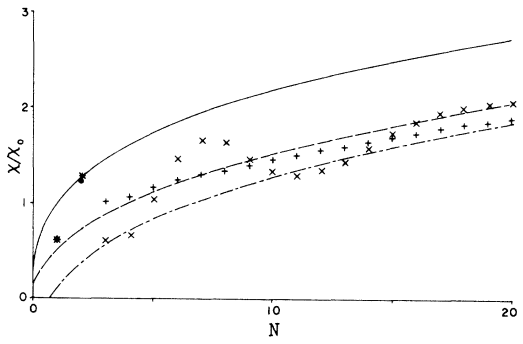

FIG. 1. Total orbital diamagnetism of electrons in a nearly cubical box. The magnetic field is in the z direction and χ_0 is defined by Eq. (3.1). The ratios of the sides of the box are $L_x/L_y=3/\pi$ and $L_x/L_z=1$. The curves, all for $T=0$, are (solid line) Landau diamagnetism; (dash-dot line) size-corrected diamagnetism of Angelescu *et al.*; (dashed line) size-corrected diamagnetism of the present work. The points are exact calculations for different temperatures: •, $T=0$; ×; $kT/\zeta=0.15$; +, $kT/\zeta=0.3$.

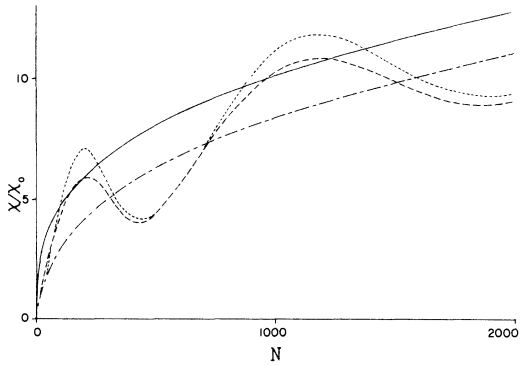

FIG. 2. Total orbital diamagnetism of electrons in a flat box vs the number of electrons in the box. The ratios of the sides of the box are $L_x/L_y=0.3/\pi$ and $L_x/L_z=0.1$. The curves are: (solid line) Landau diamagnetism, $T=0$; (dash-dot line) size-corrected diamagnetism of Angelescu *et al.*, $T=0$; (broken line) exact result, $kT=0.1\zeta$; (dashed line) Nedorezov's approximation for an infinite slab, $kT=0.1\zeta$.

than Eq. (2.17) as α increases. However, we shall see in Sec. III that the difference between the two formulas is not very great.

III. CALCULATION OF THE SUSCEPTIBILITY FOR $\lambda_F \lesssim 2L$

In this section we calculate the diamagnetic susceptibility in the case of Fermi-Dirac statistics when only a few electrons are in the box. We start by expressing the total Landau susceptibility in terms of L_x, L_y, L_z, and N (eliminating the Fermi energy). We obtain

$$\chi_L=-(\mu_B^2m/\hbar^2)(L_xL_yL_z/3\pi^2)^{2/3}N^{1/3}=\chi_0N^{1/3}, \quad (3.1)$$

which is quite similar to the formula for atomic diamagnetism,[22]

$$\chi_A=-(\mu_B^2m/\hbar^2)\langle x^2+y^2\rangle. \quad (3.2)$$

Viewed this way, Landau diamagnetism and atomic diamagnetism do not seem very different, and one may expect that size effects are not large. The Landau susceptibility is plotted in Figs. 1 and 2, for an almost cubical box and for a flat box. Our corrections, Eqs. (2.14) and (2.15), and that of Angelescu *et al.*, Eq. (2.17), are also plotted in Fig. 1.

We now calculate the exact susceptibility. If there are no degenerate unperturbed states connected by matrix elements of xp_y, then the total susceptibility at $T=0$, ignoring spin degeneracy, can be written

$$\chi(\zeta,0)=-(\mu_B^2m/\hbar^2)(L_x^{-2}+L_y^{-2})^{-1}S(R), \quad (3.3a)$$

where

$$S(R)=\frac{2^{15}}{\pi^6}\sum_m\sum_l\sum_n\sum_{l'}{}'\sum_{m'}{}'\frac{l^2m^2l'^2m'^2}{(l'^2-l^2)^3(m'^2-m^2)^3[(l'^2-l^2)(1+R)+(m'^2-m^2)(1-R)]}\,, \tag{3.3b}$$

and $R=(L_y^2-L_x^2)/(L_y^2+L_x^2)$, the sums on l, m, and n are over occupied states such that $\mathcal{E}_{lmn}<\zeta$, the sum on l' is over odd integers if l is even and over even integers if l is odd, and similarly for the sum on m'. Formula (3.3), which can be derived by perturbation theory or by transforming Eq. (2.7), agrees with Eq. (27) of Papapetrou.[7]

We first evaluate $S(R)$ for the ground state, $l=m=n=1$. For the slab case, $R=1$, the sum can be done analytically, yielding $S(1)=\frac{1}{3}(1-6/\pi^2)=0.1307$. The sum decreases slightly as R is reduced; the value found by direct summation for $R=0(L_x=L_y)$ is 0.1276. For the square cross section ($R=0$) the diamagnetic atomic term, Eq. (3.2), corresponds to $S=\frac{1}{3}(1-6/\pi^2)$. The 2.4% decrease to 0.1276 represents the Van Vleck paramagnetism,[23] which is small for this most symmetric case. The Van Vleck paramagnetism is more important for other values of R. The exact susceptibilities at $T=0$ for one electron and two electrons (one spin up and one spin down) are plotted in Fig. 1.

For more than two electrons, we must reckon with the degeneracies which concerned Papapetrou. For exact degeneracy, a small magnetic field produces Zeeman splittings (found by using degenerate perturbation theory). First suppose that the temperature is put to zero while the field is kept small but finite. Zeeman splittings of states entirely below or above the Fermi level then produce no effect on the magnetic moment. However, if only part of a group of Zeeman levels is occupied, they produce a magnetic moment independent of the field strength. This is the case studied by Denton[9] (for spherical containers) who showed that significant deviations from the Landau susceptibility occur, and who argued that the results could explain the saturating paramagnetic moment found by Meier and Wyder[24] in small indium particles. We shall treat the other limit, putting the field to zero while the temperature is kept small but finite. In this case, the Zeeman levels within a few kT of the Fermi level produce a Curie-type paramagnetism which is proportional to $1/T$. Even if no exact degeneracies occur, the near degeneracies will produce small energy denominators in Eq. (3.3b), causing large paramagnetic excursions at low temperatures.

For simplicity, we have evaluated Eq. (3.3b) for cases without exact degeneracies in the region studied, $L_x/L_y=0.3/\pi, 1.5/\pi, 3/\pi$; $R=0.9802$, 0.6287, 0.046085. Several different values were used for the ratio L_x/L_z: 1, 0.5, 0.1. The summation on m' was done analytically by techniques similar to those used by Friedman.[8] Part of the sum on l' was done analytically. The remaining sum on l', which was done numerically, converged very rapidly. The sums on l, n, and m were performed numerically. For small l and n the results were checked by direct summation. As many as 200 levels (without spin) for fixed m were treated, and the susceptibility was calculated for as many as 3000 levels (including spin). For $L_x/L_y=1.5/\pi$ and $3/\pi$ the fluctuations in χ vs N at $T=0$ were severe, χ rapidly changing from positive to negative, with values more than an order of magnitude greater than χ_L. The paramagnetic peaks are stronger but the diamagnetic peaks are broader with the result that the averaged value is close to the Landau value. The calculations of Denton[9] correspond to starting at $B=0$ at one of our paramagnetic peaks and following the evolution of the magnetic moment as B increases. In order to obtain results to compare with the formulas in Sec. II, we calculated the susceptibility for finite temperature. The calculation of χ and N were carried out using

$$\chi(\zeta,T)=\sum_{lmn}\chi(\mathcal{E}_{lmn},0)[f(\mathcal{E}_{lmn}-\zeta,T)-f(\mathcal{E}_{l'm'n'}-\zeta,T)]\,, \tag{3.4}$$

where $l'n'm'$ is the state with energy just above the state lmn and the sums on l, n, and m go from 1 to ∞. The most presentable curves were prepared by taking the temperature to be a fixed fraction of the Fermi energy. Figure 1 shows the results for the nearly cubical box for $kT/\zeta=0.15$ and 0.3. As kT/ζ is reduced below 0.15 the fluctuations increase rapidly. A variation of $kT\propto\zeta^{2/3}\propto N^{4/9}$ keeps the magnitude of fluctuations roughly constant as a function of N. When the fluctuations die out, the curves agree well with our size-corrected susceptibility curve calculated for the same temperature to Fermi-level ratio. For large N there is very little difference between our size-corrected susceptibility curve and that of Angelescu *et al.* The fluctuations decrease with decrease in both L_x/L_y and L_x/L_z. For example, the curve for $L_x/L_y=1.5/\pi$, $L_x/L_z=0.5$, and $kT/\zeta=0.1$ fluctuates less than the curve for $kT/\zeta=0.15$ in Fig. 1. We also calculated the susceptibility for a flat box, $L_x/L_y=0.3/\pi$, $L_x/L_z=0.1$. The result for a constant temperature is shown in Fig. 2, along with the Landau result, the result of Angelescu *et al.*, and Nedorezov's complete result[10] for the

infinite slab. The smooth oscillations are due to the onset of occupation of levels with new values of l (the change in energy with l is approximately 100 times that with m and n). For $T=0$ the fluctuations are much less than for the other cases, about $\pm 2\%$ of χ_L for the first peak and about $\pm 15\%$ of χ_L for the second peak. For lower temperatures than shown in Fig. 2, Nedorezov's result (which was derived for finite temperatures) deviates from the exact result. For higher temperatures, both approach the size-corrected susceptibility curves. Thus we see that as long as the temperature is not too low, Nedorezov's result for infinite slabs is accurate for a flat box whose ratio of sides is at least 10 to 1.

IV. DISCUSSION AND CONCLUSIONS

We have confirmed the results of Angelescu *et al.*,[13] that in the limit of high temperatures, or the limit of high Fermi energy at low but finite temperature, the orbital diamagnetism of electrons confined in a rectangular box is given by the Landau value plus a term proportional to the Landau value and proportional to the characteristic de Broglie wavelength divided by a length of the box.[25] We have gone further than Angelescu *et al.*, producing a result for Boltzmann statistics which is accurate for much lower temperatures ($\lambda_T = 2L$) and a result for Fermi-Dirac statistics which is also more accurate. We have also made numerical calculations for the low-Fermi-level case (few electrons in the box) that show that our high-Fermi level result describes the diamagnetism for temperatures of the order of a few percent of the Fermi energy, for which Fermi-Dirac statistics are still required. However, though our formulas, Eqs. (2.14) and (2.15), are more accurate than that of Angelescu *et al.*, Eq. (2.17), the difference is important only for very small particles. For lower temperatures, there are large fluctuations. If any large size corrections exist in the low-field limit, they are due to these fluctuations which for nearly cubical samples are related to the Zeeman splittings studied by Denton,[9] or for flat samples (or films) are given by the work of Nedorezov.[10]

Our high-temperature and high-Fermi-level results agree with all the previous (corrected) results for slabs, and reinforce the interpretation of Ohtaka and Moriya[12]: the total value of the surface current (which by classical electrodynamics is $\vec{j} = \vec{\nabla} \times \vec{M}$) is that appropriate to give the bulk susceptibility. The current flows in a skin depth of thickness of the order of the de Broglie wavelength, giving corrections of the order of $\chi_L(\lambda/L)$. Ohtaka and Moriya have calculated and exhibited the density of this current as a function of depth for both high and low temperatures. As we have observed, the correct result for the box to order λ/L can be obtained by applying Ohtaka and Moriya's results to the six faces of the box. The effects of the square corners appear only in second order in λ/L. Thus we are confident that any geometrical shape, all of whose dimensions are larger than λ, can be treated by using Ohtaka and Moriya's results, and the total susceptibility will be $\chi_L[1+O(\lambda/L)]$. This conclusion disagrees with the results of Dingle[14] and Osborne[15] and thus we believe that these authors' calculations must contain subtle errors.

The hard-wall surface potential used in this work is not self-consistent. A considerable body of work exists which studies the question of self-consistency and calculates its effect upon surface properties.[21,26-28] The hard walls would force the electron density in the interior to be larger than in bulk material,[26] which would be prevented in a real material by the strong electrostatic screening forces. To achieve self-consistency, the charge expands past the original boundary which increases the area of the current loop and thus increases the diamagnetism. We shall estimate the effect by adopting Sugiyama's model[26,28]: the boundary conditions $\psi = 0$ are satisfied on boundaries outside the original boundaries. Specifically, the new boundaries are described by using $L_i' = L_i + \frac{3}{8}\lambda_F$, where $L_x L_y L_z$ is the volume of bulk material containing N electrons. Replacing the L_i in Eq. (2.15) by L_i' causes the first order corrections to vanish, so that the Fermi level and electron density in the interior of the small sample are (to first order) the same as for bulk material.[26,28] To first order, Eq. (2.14) becomes

$$\chi = \chi_L[1 + \tfrac{1}{4}\alpha_z + \tfrac{3}{16}(\alpha_x + \alpha_y)], \tag{4.1}$$

where χ_L is the total susceptibility of N electrons in the bulk material. Compared to Eq. (2.17), we see that the effect of self-consistency is to reverse the sign of the size correction, and to reduce slightly its magnitude. Perfect screening cannot be established for the very small samples treated in Sec. III, as the screening potential has a range of the order of λ_F. Thus the effect of self-consistency should be less important for the small samples, though it would still tend to increase the diamagnetism. The high-temperature size correction is not changed to first order. Thus consideration of self-consistency does not alter our basic conclusion that, with the exceptions noted above, the size effects on the diamagnetism are small and of the order of $(\lambda/L)\chi_L$.

We now wish to consider the application of these results to real systems. If we consider small par-

ticles of a metal such as indium[24] with an electron density of about 0.9×10^{23}, the free-electron Fermi level is about 9 eV, which corresponds to a temperature of about 10^4 °K. Thus any small particle of a good metal will be in the range of large fluctuations. In a real experiment the particles would probably not be of uniform size, so that the average susceptibility may still be close to that given by the size-corrected formulas. Meier and Wyder's[24] particles of 20 Å diameter contain about 400 electrons. For this number of electrons we find that the paramagnetic fluctuations are suppressed for kT/ζ greater than 0.04. The half-width of the derivative of the Fermi function is about $3.5\,kT$, so a distribution of Fermi levels of width 0.14 of the average Fermi level will damp out the paramagnetism at zero magnetic field. This corresponds to a half width of the diameter distribution of about 7% of the average diameter. Although Meier and Wyder state that the distribution of diameters falls monatonically from 20 to 100 Å, they do not give further information on the size distribution. We feel it is very important to obtain good size distribution information in this kind of experiment.

In contrast, small particles of a semimetal such as bismuth, with a Fermi energy[29] for electrons of about 0.03 eV ≃ 350 °K, could be in the regime of the thermally smoothed curves shown in Fig. 1. The electron density in pure bismuth is about[29,30] $10^{18}\,\mathrm{cm}^{-3}$ ($3\times10^{17}\,\mathrm{cm}^{-3}$ at 4 °K to approximately 3×10^{18} at 300 °K), which means that a cubical particle containing 20 free electrons would be about 100 Å on each side. The diamagnetism of bismuth is dominated by the interband effect, but for pure bismuth roughly one-third of the measured susceptibility is given by a Landau-like term[30].

We now wish to speculate about size effects at higher fields. A number of authors have claimed[31] that for $L\gg r$, χ is proportional to $\chi_L r^{4/3}/\lambda_F^{1/3}L \propto B^{-4/3}$ for various geometrical shapes. However, Nedorezov[32] states that these calculations are in error, and the χ is proportional to[10,32] $\chi_L[1+O(l/L)]$. In Nedorezov's view the steady susceptibility is close to the Landau value at high and low magnetic fields, but there is an important paramagnetic contribution in the region $l\simeq L$. This seems unreasonable to us by the following argument. In classical mechanics there is no diamagnetism[1,2] for any field strength, so that there is no current near the surface. In quantum mechanics the cancellation of current due to different orbits cannot take place in a region near the surface. The depth of this region in the low-field case is the characteristic de Broglie wavelength, the distance between nodes of the important wavefunctions.[33] At all fields the characteristic internodal distance is the de Broglie wavelength, and $\lambda<l<r$ for all fields up to the quantum limit. However, this problem is full of subtle points and the archives contain many erroneous papers on the subject, so that our speculation is no substitute for rigorously careful calculafions. However, in the case of slab geometry with the electrons confined by a harmonic potential, Childers and Pincus[34] do not find important size effects in the steady susceptibility for any field range at $T=0$.

In this paper we have ignored the electron spin paramagnetism. This has been treated by Nedorezov[10] for the thin slab, and his results can easily be adapted to the case of the rectangular box. We have not discussed the effect of sample size upon the de Haas–van Alphen effect, which has been treated by several authors.[35] We must also recognize that band structure effects can produce very different size dependencies, as shown by the work of Chausse and Hoarau[36] on infinite ribbons of graphite.

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APPENDIX A: CALCULATION OF THE SUM J

We evaluate $J(x,y)$, Eq. (2.7b), by noting that

$$\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)^3 J(x,y)=\frac{32}{\pi^2}\sum_m{\sum_{m'}}' m^2m'^2e^{-(m^2x+m'^2y)} \equiv I(x,y)\,. \tag{A1}$$

The sum I can be found from the sum (2.9) which was evaluated by Friedman.[8] A little manipulation is called for because of the restriction on m', but it is easily found for small x and y that

$$I(x,y)=(2\pi x^{3/2}y^{3/2})^{-1}\,. \tag{A2}$$

J will be a function whose third derivative of the type in Eq. (A1) gives $I(x,y)$ plus $(x-y)$ times any function of $(x+y)$. Other possible terms whose third derivative is zero are eliminated as $J(x,y)$ is odd on interchange of x and y. The extra term is found by evaluating $J(x,0)$, which is easily done using the same technique as Friedman,[8]

$$J(x,0)=\tfrac{1}{2}\sum_m e^{-m^2x}=\pi^{1/2}/4x^{1/2}-\tfrac{1}{4}\,. \tag{A3}$$

The desired result is

$$J(x,y)=[\pi^{1/2}(x-y)/4(x+y)^{3/2}] - \{\sin^{-1}[(x-y)/(x+y)] + 2x^{1/2}y^{1/2}(x-y)/(x+y)^2\}/2\pi . \quad \text{(A4)}$$

The original sum is rapidly convergent for finite x or y. We have evaluated it numerically for $x+y=1$ and find the error in (A4) is always less than 0.5% and for $x+y=0.5$, where the error is less than 0.023%.

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