Dependence of Diamagnetic Susceptibility on Surface Potential

R. B. Thomas, Jr.
Lockheed Research Laboratory, Palo Alto, California 94304
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The dependence of the diamagnetic susceptibility on the surface potential is investigated for a collection of independent electrons confined within a slab by a harmonic potential barrier perturbed by a small fourth-order anharmonic term. Taking the magnetic field perpendicular to the slab, the partition function and susceptibility are found to first order in the perturbing potential using classical statistics. The susceptibility is examined in the small-size or weak-magnetic-field limit at high temperature. Here it is found that no surface-structure-dependent corrections to the diamagnetic susceptibility exist which vary inversely with temperature and therefore the well-known Landau result remains valid for the assumed surface potential.

I. INTRODUCTION

Following Landau's[1] initial work which proved the existence and quantum-mechanical nature of the diamagnetic susceptibility of a system of independent but confined charges, the problem of precisely how the surface structure or wall potential affects the susceptibility has received attention from several authors.[2-6] Notwithstanding the considerable efforts of these investigators, the results which bear on the question of just how if at all the wall potential alters the Landau value for the susceptibility remains inconclusive. This is probably due in good measure to the unique nature of the interaction, the necessity for employing fairly detailed models, where results are not readily comparable, and certainly not least to the rather formidable analytical difficulties encountered.

There is, however, some evidence that the Landau value for the susceptibility is actually model independent at sufficiently high temperature and that no temperature-independent corrections exist which depend on either the physical dimensions of the system or the detailed structure of the wall potential.[7] The results presented here support this point of view.

In treating the problem of steady diamagnetism of free electrons it is found necessary to provide for their confinement by means of a potential barrier of some kind. In his original treatment Landau assumed the electrons to be contained within a box having infinite potential walls. Landau obtained his well-known result for the susceptibility by simply requiring that the classical center of gyration of each electron remain within the confines of the box. Implicit here is the assumption that the radius of gyration is small compared with the dimensions of the box. For this reason it is not surprising that Landau's result turns out to be independent of the box dimensions.

When the radius of gyration is comparable with the linear dimensions of the volume in which the electrons are confined, it is reasonable to expect contributions to the susceptibility which do depend on the ratio of these characteristic lengths. Similarly one might expect corrections which depend upon structural details of the potential wall itself, involving in this instance the ratio of the radius of gyration to the distance over which the surface potential energy changes by an amount comparable with the energy-level separation of an electron in a uniform magnetic field.

Effects of this kind do indeed exist and are evident in the results of several authors[4,7,8] as well as in those presented here. While the actual expression obtained for the susceptibility is of some interest because of the somewhat improved form of the surface potential employed, the problem of primary concern is the determination of the limiting form of the diamagnetic susceptibility at high temperature. Do corrections to the susceptibility depending on the physical dimensions of the system or the surface-potential structure exist which have an inverse temperature variation as does the Landau susceptibility? Is the Landau susceptibility, which is itself independent of system size and surface potential, the principal part of the diamagnetic susceptibility of any system at sufficiently high temperature?

With respect to these questions the work of Friedman appears significant.[7] In his investigation of the susceptibility of small systems, he considered in detail the confinement of electrons by an infinite potential well. Treating the magnetic field terms as perturbations, he took explicit account of the discrete energy levels resulting from the small size of the system by evaluating the sums themselves rather than replacing them by integrals as is ordinarily done. Using Boltzmann statistics Friedman convincingly shows that the susceptibility of electrons confined within a small infinite square well has, at high temperature, the Landau value without size corrections, the same as found for arbitrarily large systems. Additional information is provided

by his approximate treatment of electrons confined by a harmonic potential. In this case the possibility exists for effects of both size and potential structure to make their appearance. Here again the Landau susceptibility is found to be the leading term at elevated temperature. Thus two rather dissimilar systems, the infinite potential well and the harmonic potential, give rise to the same susceptibility without apparent size or potential structure effects at high temperature.

A distinction is usually made between effects resulting from the small size of the system and the structure or form of the wall potential. It is not at all clear that such a distinction can actually be made between these effects. If, however, these effects can be separated in a meaningful way, the example of the infinite potential well treated by Friedman would seem to offer the most advantageous model for investigation. Here the wall structure assumes probably its most simple physical form. In comparing Friedman's results with those obtained by other authors there appear to be some areas of disagreement. In particular there seems to be some reason to question the validity of Ham's[6] conclusions about surface effects arrived at through the use of the WKB approximation. Alternatively it is not readily apparent that any error at all exists in Dingle's[4] finding that the Landau susceptibility is enhanced by a factor depending on the ratio of the radius of his cylindrically shaped system to the electron wavelength at the Fermi energy. Still, it should be remembered that the systems dealt with by these authors are not identical nor are the approximations quite the same; consequently one must exercise caution in attempting to draw conclusions from such comparisons.

The results for parabolic and infinite square-well potential confinement of electrons are noteworthy and lend themselves to interpretation in two possible ways: first, that no size or surface-potential effects in the susceptibility exist at high temperature for any form of charge confinement and that the results for these two potentials are simply exhibiting this general behavior; second, that the two examples chosen are fortuitously possessed of special properties which can be attributed to the analytical form of the potentials selected and are responsible for the absence in the susceptibility of size and surface effects. Initially the second explanation seemed most likely and the possibility of demonstrating it provided the motivation for the present work.

In the case of the infinite potential well it may be argued that the system is perhaps equivalent to a juxtaposition of similar systems where outermost as well as internal boundaries can be considered equivalent in their analytical representation to the assumption of periodic boundary conditions. This seems quite plausible when we recall that the arbitrary division of an electron orbit by a plane representing an infinitely high separation potential can as well be viewed as parts of two completely separate and independent systems having electron orbits which are perfectly reflected from the interposed wall. This argument is in fact sufficient to show that in the classical limit a system of free charges exhibits no diamagnetism, the reflected charge current exactly canceling the effect of the net circulation of those electrons not coming in contact with the walls.[9] However, this argument appears to break down in situations where the radius of the classical orbit is larger than the characteristic dimensions of the system but then the very meaning of magnetic susceptibility would itself seem to become a concept that is less than well defined.

The case of a harmonic potential has also a special character in that the analytical form of the potential, quadratic in the spatial variable, is identical with that of the well-known diamagnetic terms originating in the vector potential appearing in the kinetic-energy term of the Hamiltonian. By the device of completing the square, the harmonic potential can be combined with the small diamagnetic term and the resulting equation solved exactly.

In view of these possible special characteristics of both the square-well and harmonic potentials it appears useful to investigate the susceptibility of a system of electrons confined by a potential of substantially different analytical form from either of these. Unfortunately when a magnetic field is included, the Schrödinger equation cannot easily be solved for other potentials of interest, say, those expressible as a polynomial in the spatial variables. For our purpose, however, an exact solution does not appear necessary; the inclusion of a small additional perturbing potential which is at least in part linearly independent of both the harmonic and square-well potentials should be sufficient to settle the question of the existence of a structure-dependent correction to the Landau diamagnetic susceptibility varying inversely with temperature.

In an attempt to answer this question and at the same time to determine more precisely the dependence of the diamagnetic susceptibility on surface potential and temperature, we investigate here the magnetic properties of a system of electrons confined within an infinite slab by a parabolic potential perturbed by a fourth-order anharmonic term. Without approximation in the magnetic field the partition function and susceptibility of the system are found to first order in the perturbing potential. The expression for the susceptibility is expanded in inverse powers of the temperature and compared with the Landau value. Finally the significance of the results and possible extensions of the work are discussed.

II. ENERGY EIGENVALUES

Consider a collection of independent electrons of mass m and charge e moving in the presence of a uniform magnetic field and confined by a potential of the form

$$U(\vec{r}) = V(x) + V(y) + V(z) , \tag{2.1}$$

where

$$V(x) = 0, \quad -\infty \leq x \leq \infty ,$$
$$V(y) = V_0 \sum_{m=1} b_{2m} y^{2m} , \tag{2.2}$$
$$V(z) = 0, \quad -\infty \leq z \leq \infty .$$

Choosing the Landau gauge for the vector potential, $\vec{A}(\vec{r}) = (-By, 0, 0)$, corresponding to a uniform magnetic field $\vec{B}$ in the z direction, the wave function $\psi_\nu(\vec{r})$ of an electron within the finite potential region satisfies the equation

$$\frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}(\vec{r})\right)^2 \psi_\nu(\vec{r}) + V_0 \sum_{m=1} b_{2m} y^{2m} \psi_\nu(\vec{r}) = E_\nu \psi_\nu(\vec{r}) , \tag{2.3}$$

in which ν stands for the set of quantum numbers used to describe an electronic state. Now assume periodic boundary conditions in the x and z directions over large but finite distances L_x and L_z, respectively. Taking $\psi_\nu(\vec{r})$ to be of the form

$$\psi_\nu(\vec{r}) = N_{xy} e^{i(k_x x + k_z z)} \varphi_n(y) \tag{2.4}$$

and setting

$$E_\nu = E_{k_x k_z} + E_n , \tag{2.5a}$$

we find from (2.3) that

$$E_{k_x k_z} = (\hbar^2/2m)(k_x^2 + k_z^2) \tag{2.5b}$$

with the normalization $N_{xz} = (L_x L_z)^{-1/2}$.

$\varphi_n(y)$ then satisfies the equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \hbar\omega k_x y + \tfrac{1}{2} m\omega^2 y^2 + V_0 \sum_{m=1} b_{2m} y^{2m}\right) \varphi_n(y) = E_n \varphi_n(y) , \tag{2.6}$$

where $\omega = eB/mc$ is the cyclotron frequency.

With a proper choice of the coefficients b_{2m} a good representation of most potentials of physical interest can be found but ordinarily the resulting equation can be solved only with difficulty. However, an exact solution to Eq. (2.6) can be obtained if the potential sum is limited to its initial term for which $m = 1$. In order to make possible an analytical treatment of the problem, it is arbitrarily assumed that the first term provides the principal contribution to $V(y)$ and that the remaining terms can be included by means of Rayleigh–Schrödinger perturbation theory. Setting $V_0 b_2 = \frac{1}{2} m\Omega^2$, the zero-order solution $\varphi_n^{(0)}(y)$ can be shown to satisfy the equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \tfrac{1}{2} m(\omega^2 + \Omega^2) \times \left(y + \frac{\hbar\omega k_x}{m(\omega^2 + \Omega^2)}\right)^2\right] \varphi_n^{(0)}(y) = \left(E_n^{(0)} + \frac{\hbar^2\omega^2 k_x^2}{2m(\omega^2 + \Omega^2)}\right) \varphi_n^{(0)}(y) \tag{2.7}$$

by completing the square in the variable y. This equation, which involves no approximation in the magnetic field, is identical in form with that for the displaced harmonic oscillator and has the solution[10]

$$\varphi_n^{(0)}(y) = N_n H_n\left(\alpha\left(y + \frac{\hbar k_x \omega}{m(\omega^2 + \Omega^2)}\right)\right) \times \exp\left[-\frac{1}{2}\alpha^2\left(y + \frac{\hbar k_x \omega}{m(\omega^2 + \Omega^2)}\right)^2\right] \tag{2.8}$$

with energy eigenvalues

$$E_n^{(0)} = \hbar\Omega\left(1 + \frac{\omega^2}{\Omega^2}\right)^{1/2}(n + \tfrac{1}{2}) - \frac{\hbar^2}{2m} k_x^2 \frac{\omega^2}{\omega^2 + \Omega^2} . \tag{2.9}$$

Here $H_n(x)$ is the Hermite polynomial of order n,

$$N_n = (\alpha/\pi^{1/2} 2^n n!)^{1/2} ,$$
$$\alpha^2 = (m\Omega/\hbar)(1 + \omega^2/\Omega^2)^{1/2} .$$

As a further simplification we limit consideration of the remaining terms in $V(y)$ to a single term, the second or quartic term given by $V_0 b_4 y^4$. From Rayleigh–Schrödinger perturbation theory the first-order energy correction is just

$$E_\nu^{(1)} = V_0 b_4 \int \psi^*(\vec{r}) y^4 \psi(\vec{r})\, d\vec{r} . \tag{2.10}$$

Making use of (2.4) and (2.8) one finds

$$E_\nu^{(1)} = V_0 b_4 N_n^2 \int_{-\infty}^{\infty} H_n^2(\alpha y) e^{-\alpha^2 y^2} \times \left[y^4 + 6y^2\left(\frac{\hbar k_x \omega}{m(\omega^2 + \Omega^2)}\right)^2 + \left(\frac{\hbar k_x \omega}{m(\omega^2 + \Omega^2)}\right)^4\right] dy , \tag{2.11}$$

since all odd powers of y integrate to zero. Carrying out the integrations with the aid of well-known matrix relations for the harmonic-oscillator wave functions, we finally obtain

$$E_\nu^{(1)} = V_0 b_4\left[\frac{3}{2}\frac{1}{\alpha^4}\left[(n + \tfrac{1}{2})^2 + \tfrac{1}{4}\right] + \frac{6}{\alpha^2}\left(\frac{\hbar k_x \omega}{m(\Omega^2 + \omega^2)}\right)^2 (n + \tfrac{1}{2}) + \left(\frac{\hbar k_x \omega}{m(\omega^2 + \Omega^2)}\right)^4\right] , \tag{2.12}$$

which is seen to be a function only of the quantum number n but depends on the magnetic field through both ω and α.

III. PARTITION FUNCTION

If terms to first order in the perturbation potential are retained, the partition function for a system obeying classical statistics can be expanded and written

$$Z=\sum_{\nu} e^{-\beta E_\nu(0)} - \beta \sum_{\nu} e^{-\beta E_\nu^{(0)}} E_\nu^{(1)} , \tag{3.1}$$

where $\beta = 1/kT$. Letting $Z = Z^{(0)} + Z^{(1)}$ and making use of the expression for $E_\nu^{(0)}$ given by (2.5) and (2.9) we find

$$Z^{(0)} = \sum_{k_x=-\infty}^{\infty} \exp\left[-\beta \frac{\hbar^2}{2m} \left(1 - \frac{\omega^2}{\omega^2+\Omega^2}\right) k_x^2 \right] \times \sum_{k_z=-\infty}^{\infty} \exp\left(-\beta \frac{\hbar^2}{2m} k_z^2\right) \times \sum_{n=0}^{\infty} \exp[-\beta\hbar(\omega^2+\Omega^2)^{1/2}(n+\tfrac{1}{2})] . \tag{3.2}$$

Approximating the sums over k_x and k_z by integrals according to the transformation

$$\sum_{k=-\infty}^{\infty} = \frac{L}{2\pi} \int_{-\infty}^{\infty} dk \tag{3.3}$$

and recognizing the sum over n as a geometrical progression, we obtain

$$Z^{(0)} = \tfrac{1}{2} L_x L_z \frac{m}{2\pi\beta\hbar^2} \left(1 + \frac{\omega^2}{\Omega^2}\right)^{1/2} \times \operatorname{csch}\left[\frac{\beta\hbar\Omega}{2}\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2}\right]. \tag{3.4}$$

Using the result (2.12) for $E_\nu^{(1)}$, $Z^{(1)}$, the first-order correction to the partition function takes the form

$$Z^{(1)} = -\beta V_0 b_4 \sum_{k_x=-\infty}^{\infty} \sum_{k_z=-\infty}^{\infty} \exp\left\{ -\beta \frac{\hbar^2}{2m} \left[k_x^2 \left(1 - \frac{\omega^2}{\omega^2+\Omega^2}\right) + k_z^2 \right] \right\} \sum_{n=0}^{\infty} \exp[-\beta\hbar(\omega^2+\Omega^2)^{1/2}(n+\tfrac{1}{2})] \times \left[\frac{3}{2} \frac{1}{\alpha^4} [(n+\tfrac{1}{2})^2 + \tfrac{1}{4}] + \frac{6}{\alpha^2} \left(\frac{\hbar\omega}{m(\omega^2+\Omega^2)}\right)^2 k_x^2 (n+\tfrac{1}{2}) + \left(\frac{\hbar\omega}{m(\omega^2+\Omega^2)}\right)^4 k_x^4 \right] . \tag{3.5}$$

To evaluate $Z^{(1)}$ rewrite the sums over n as appropriate derivatives of the exponential with respect to the temperature parameter β and again make use of (3.3). After some algebra we find

$$Z^{(1)} = -\frac{3}{16\pi} L_x L_z \frac{V_0 b_4}{m\Omega^2} \left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2} \operatorname{csch}\left[\frac{\beta\hbar\Omega}{2}\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2}\right] \left\{ \exp\left[-\frac{\beta\hbar\Omega}{2}\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2}\right] \times \operatorname{csch}\left[\frac{\beta\hbar\Omega}{2}\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2}\right] + \frac{2}{\beta\hbar\Omega} \frac{\omega^2}{\Omega^2} \left(1+\frac{\omega^2}{\Omega^2}\right)^{3/2} + 1 \right\}^2 . \tag{3.6}$$

In order to represent the partition function by the partial expansion (3.1) some limitation must be placed on the size of the product $V_0 b_4$. If the usual condition that the perturbation energy be small compared with the zero-order energy level separation is applied, we must have

$$\hbar\Omega\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2} \gg V_0 b_4 \left[\frac{3}{2} \frac{1}{\alpha^4} (n^2+n+\tfrac{1}{2}) + \frac{6}{\alpha^2} \left(\frac{\hbar k_x \omega}{m(\omega^2+\Omega^2)}\right)^2 (n+\tfrac{1}{2}) + \left(\frac{\hbar k_x \omega}{m(\omega^2+\Omega^2)}\right)^4 \right] , \tag{3.7}$$

according to (2.9) and (2.12) for all possible values of n and k_x. It is apparent that the required inequality (3.7) in which the right-hand side increases with both n and k_x no longer holds for sufficiently large values of either n or k_x regardless of the choice of $V_0 b_4$. However, because of the exponential factor $e^{-\beta E_\nu^{(0)}}$ appearing in terms of the partition function expansion, only energies near or less than kT contribute appreciably to the partition function. This places the effective limits

$$\frac{\hbar^2 k_x^2}{2m}\left(1-\frac{\omega^2}{\omega^2+\Omega^2}\right) \lesssim kT , \tag{3.8a}$$

$$\hbar\Omega\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2} n \lesssim kT \tag{3.8b}$$

on the sizes of k_x and n insofar as the condition (3.7) is concerned. With these restrictions $V_0 b_4$ need only be chosen in conformity with the inequality[11]

$$\hbar\Omega\left(1+\frac{\omega^2}{\Omega^2}\right)^{1/2} \gg \tfrac{3}{2} V_0 b_4 \left(\frac{kT}{m}\right)^2 (\omega^2+\Omega^2)^{-2}$$

$$\times\left[1+8\left(\frac{\omega}{\Omega}\right)^2+\frac{8}{3}\left(\frac{\omega}{\Omega}\right)^4\right] \qquad (3.9)$$

to obtain a valid perturbation expansion for Z as represented by Eq. (3.1). The inequality (3.9) shows that as the temperature is increased $V_0 b_4$ must be reduced in size as expected since at higher temperaures states with large n are favored.

IV. MAGNETIC SUSCEPTIBILITY

The complete expression for the magnetic susceptibility of a system can be found from the formula

$$\chi=-\frac{1}{B}\left(\frac{\partial F}{\partial B}\right)_{NVT}, \qquad (4.1)$$

where F is the Helmholtz free energy defined by

$$F=kT\ln Z \qquad (4.2)$$

in terms of the partition function Z. From the form of our expression for Z, the sum of (3.4) and (3.6), it is evident that with no further simplification, the resulting χ will depend explicitly on the magnetic field and the structure of the confining potential through Ω and $V_0 b_4$.

The general expression for the susceptibility is not, however, of immediate concern to us and is not given explicitly. As has already been explained at some length in the introduction the purpose here is to determine whether or not the inclusion of new linearly independent terms in the confining potential, such as the quartic perturbation, leads at high temperature to the introduction of a purely structure-dependent correction to the Landau diamagnetic susceptibility having its characteristic inverse first-power temperature variation. Because the Landau susceptibility is itself independent of the magnetic field, it is sufficient to examine χ in the weak-magnetic-field limit where it can be assumed[12]

$$\omega \ll \Omega , \qquad (4.3)$$

a condition which allows expansions in the small dimensionless ratio ω/Ω.

According to Eqs. (4.1) and(4.2) only terms in the free energy of second order in the magnetic field contribute to the field-independent part of χ in which we are interested. Accordingly we take

$$Z=\sum_{m=0} Z^{(0)}_{(m)}+\sum_{m=0} Z^{(1)}_{(m)} , \qquad (4.4)$$

where the subscript indicates the order in the magnetic field B. Place this in Eq. (4.2) and expand the logarithm, retaining only terms up to second order in B. Substituting the result into (4.1) gives

$$\chi=\frac{1}{\beta B}\left(\frac{1}{Z^{(0)}_{(0)}}\frac{\partial Z^{(0)}_{(2)}}{\partial B}+\frac{1}{Z^{(0)}_{(0)}}\frac{\partial Z^{(1)}_{(2)}}{\partial B}-\frac{Z^{(1)}_{(0)}}{(Z^{(0)}_{(0)})^2}\frac{\partial Z^{(0)}_{(2)}}{\partial B}\right)_{TVN}, \qquad (4.5)$$

since $Z_{(1)}$ will be found to vanish.

Expand (3.4) and (3.6) making use of (4.4). We obtain

$$Z^{(0)}_{(0)}=\frac{L_x L_z}{4\pi}\frac{m}{\beta\hbar^2}\operatorname{csch}\frac{\beta\hbar\Omega}{2} ,$$

$$Z^{(0)}_{(1)}=0 ,$$

$$Z^{(0)}_{(2)}=\frac{1}{8\pi}L_x L_z\frac{m}{\beta\hbar^2}\left(\frac{\omega}{\Omega}\right)^2\frac{\beta\hbar\Omega}{2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}\left(\frac{2}{\beta\hbar\Omega}-\coth\frac{\beta\hbar\Omega}{2}\right),$$

$$Z^{(1)}_{(0)}=-\frac{3}{16\pi}L_x L_z\frac{V_0 b_4}{m\Omega^2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}\left(e^{-\beta\hbar\Omega/2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}+1\right)^2 , \qquad (4.6)$$

$$Z^{(1)}_{(1)}=0 ,$$

$$Z^{(1)}_{(2)}=\frac{3}{32\pi}L_x L_z\frac{V_0 b_4}{m\Omega^2}\left(\frac{\omega}{\Omega}\right)^2\operatorname{csch}\frac{\beta\hbar\Omega}{2}\left(e^{-\beta\hbar\Omega/2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}+1\right)$$

$$\times\left[\left(1+\frac{\beta\hbar\Omega}{2}\coth\frac{\beta\hbar\Omega}{2}\right)\left(e^{-\beta\hbar\Omega/2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}+1\right)+2\left(\frac{\beta\hbar\Omega}{2}e^{-\beta\hbar\Omega/2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}+\frac{\beta\hbar\Omega}{2}e^{-\beta\hbar\Omega/2}\operatorname{csch}\frac{\beta\hbar\Omega}{2}\coth\frac{\beta\hbar\Omega}{2}-\frac{4}{\beta\hbar\Omega}\right)\right] .$$

Inserting the results (4.6) into Eq. (4.5) and setting

$$\chi = \chi^{(0)}_{(0)} + \chi^{(1)}_{(0)} \ , \tag{4.7}$$

we find from the first term of (4.5) that

$$\chi^{(0)}_{(0)} = \frac{kT}{B} \ \frac{1}{Z^{(0)}_{(0)}} \ \frac{\partial Z^{(0)}_{(2)}}{\partial B}$$

$$= \frac{e^2 kT}{m^2 c^2 \Omega^2} \left(1 - \frac{\hbar\Omega}{2kT} \coth \frac{\hbar\Omega}{2kT} \right) , \tag{4.8}$$

which is seen to depend on the form of the confining potential as evidenced by the appearance of Ω.

We now wish to examine the form of $\chi^{(0)}_{(0)}$ in the high-temperature limit[13]

$$\beta\hbar\Omega \ll 1 \ , \tag{4.9}$$

where the energy-level spacing $\hbar\Omega$ is much less than kT. On the basis of the assumption (4.9) expand the right-hand side of Eq. (4.8) in a power series in $\beta\hbar\Omega$. Then at high temperature

$$\chi^{(0)}_{(0)} = \chi_L \left[1 - \frac{1}{15} \left(\frac{\hbar\Omega}{2kT} \right)^2 + \frac{2}{315} \left(\frac{\hbar\Omega}{2kT} \right)^4 + \cdots \right] , \tag{4.10}$$

$$\chi_L = -\frac{1}{12} \ \frac{1}{kT} \ \frac{e^2\hbar^2}{M^2c^2} \tag{4.11}$$

is the well-known Landau diamagnetic susceptibility. Then in the limit of high temperature the susceptibility of a purely parabolic confining potential approaches the Landau value and there exist no structure-dependent corrections to the susceptibility in this approximation having the inverse-temperature variation of the Landau term itself.

Now consider the two remaining terms of (4.5),

$$\chi^{(1)}_{(0)} = \frac{kT}{B} \ \frac{1}{Z^{(0)}_{(0)}} \left(\frac{\partial Z^{(1)}_{(2)}}{\partial B} - \frac{Z^{(1)}_{(0)}}{Z^{(0)}_{(0)}} \ \frac{\partial Z^{(0)}_{(2)}}{\partial B} \right) . \tag{4.12}$$

Performing the indicated differentiations using (4.6) we find

$$\chi^{(1)}_{(0)} = \chi_L \frac{9}{2} \ \frac{V_0 b_4 \hbar}{m^2\Omega^3} \ \frac{1}{\beta\hbar\Omega} \left(e^{-\beta\hbar\Omega/2} \operatorname{csch} \frac{\beta\hbar\Omega}{2} + 1 \right)$$

$$\times \left[e^{-\beta\hbar\Omega/2} \operatorname{csch} \frac{\beta\hbar\Omega}{2} + 1 - \frac{4}{\beta\hbar\Omega} \right.$$

$$\left. + \frac{\beta\hbar\Omega}{2} \ e^{-\beta\hbar\Omega/2} \left(1 + \coth \frac{\beta\hbar\Omega}{2} \right) \right] , \tag{4.13}$$

which also depends on the potential through $V_0 b_4$ and Ω. Again assume $\beta\hbar\Omega \ll 1$ and expand the right-hand side of (4.13) in powers of $\beta\hbar\Omega$. Then in the high-temperature limit

$$\chi^{(1)}_{(0)} = -\chi_L \frac{1}{5} \ \frac{V_0 b_4 \hbar}{m^2\Omega^3} \ \frac{kT}{\hbar\Omega}$$

$$\times \left[\left(\frac{\hbar\Omega}{2kT} \right)^2 + \frac{7}{64} \left(\frac{\hbar\Omega}{2kT} \right)^4 + \cdots \right] . \tag{4.14}$$

This is a series in inverse even integral powers of the temperature since $\chi_L \sim 1/T$. The two separate terms of (4.12) are actually found to begin with order $\beta\hbar\Omega \sim 1/T$ but they turn out to be equal in magnitude and so cancel. The negative sign of (4.14) shows that the susceptibility is increased in magnitude as the temperature is raised.

V. CONCLUSION

On comparing (4.14), the correction to the susceptibility resulting from the addition of the quartic perturbation potential, with the zero-order part given by (4.10), it is seen that in the high-temperature limit the leading term in the diamagnetic susceptibility is still just the Landau susceptibility (4.11), which is entirely independent of the confining potential assumed for the system. The structure-independent part of the susceptibility, varying inversely with temperature comes entirely from $\chi^{(0)}_{(0)}$; the surface-structure-dependent corrections to both $\chi^{(0)}_{(0)}$ and $\chi^{(1)}_{(0)}$ begin with terms linear in $\beta\hbar\Omega$ and form an ascending series in inverse powers of the temperature. They therefore become vanishingly small at high temperature.

The Landau susceptibility (4.11) appears to be the entire contribution to the diamagnetic susceptibility at high temperature; all corrections depending explicitly on the form of the surface potential most probably involve higher than linear inverse powers of temperature and for this reason have little influence on χ in the range of temperature where (4.9) is satisfied.[14] No structure-dependent term having only a simple inverse temperature variation seems to exist beyond the Landau term itself.

Results obtained here are of course based upon perturbation methods and for this reason it cannot be said with certainty that no structure-dependent contribution to the susceptibility of the Landau form exists in the high-temperature limit. Still, for the purpose of deciding whether or not such effects exist, there is no readily apparent objection to the use of ordinary perturbation methods. For however small such effects might be, under conditions where the requirements of the perturbation approximation are satisfied, it should still be capable of settling the question of the effect's existence. The use of a field-theoretical approach[15] involving partial summation, where the perturbation potential need not necessarily be small, would not further the accomplishment of this objective since regardless of the result the question of the contribution of those terms (or diagrams) not actually included would remain unanswered.

In view of these considerations ordinary perturbation techniques appear to be an appropriate and logical means of elucidating the question of the surface potential dependence of the high-tempera-

ture susceptibility. The next step should be the treatment of a system in which the confining potential is represented by a polynomial of higher order in the coordinate variables. By the inclusion of a sufficient number of terms in the series (2.2) any potential single valued at the surface can be well approximated. In this event a collective restriction must be placed on the magnitude of the numerical coefficients to satisfy the requirements of perturbation theory. Unfortunately the accomplishment of this objective is hindered by the circumstance that the higher order matrix elements encountered lead to the introduction of factors of progressively higher power in temperature, making it very difficult to demonstrate explicitly the cancellation (if indeed it takes place) of all but those terms involving only inverse powers of temperature, such as appear in Eqs. (4.10) and (4.14). By a procedure similar to that used here to treat the quartic potential, the temperature dependence of all corrections to the susceptibility resulting from an assumed confining potential of the form $V_0(b_4y^4+b_6y^6)$ was verified after some effort. Although it seems highly probable that all terms in the potential (2.2) would lead to a similar temperature variation for χ, there appears to be no practicable way by which this can be conclusively demonstrated using the present analytical approach.

It is interesting to point out that an appropriately scaled potential having the functional form y^n approaches that of a one-dimensional square well as n becomes large; this is possibly significant in light of the fact that the three-dimensional square-well potential is known to lead to a susceptibility having exactly the Landau form with corrections involving only inverse powers of temperature. This circumstance lends some support to the conjecture that any potential single valued at the surface, or equivalently one expressible as a power series in the spatial coordinates, would have exactly the Landau susceptibility at high temperature.

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[12]The inequality $\omega \gg \Omega$ can also be interpreted to imply a narrow system in the y direction when compared with the electron's radius of gyration.
[13]The inequalities $\omega \ll \Omega$ and $\beta\hbar\Omega \ll 1$ together imply $\hbar\omega \ll kT$, the condition that ensures that oscillatory phenomena relating to the de Haas–van Alphen effect are small.
[14]For a system obeying classical statistics, which has been assumed here, the conclusions correctly apply only in the high-temperature limit where $kT \gg \hbar\Omega$. However, for real metals, classical statistics are not sufficient and Fermi–Dirac statistics must be used. The low-temperature limit $\eta \gg kT \approx \hbar\Omega$ is then appropriate with the Fermi energy η essentially replacing kT in the corresponding conditions and results.
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Theory of Phase Separation in Liquid-Metal Alloys: Li_xNa_{1-x}†

D. Stroud
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
*Department of Physics, Ohio State University, Columbus, Ohio 43210**
(Received 14 August 1972)

The phase separation curves of liquid-metal alloys may be obtained by a variational method which involves no free parameters. The scheme is applied to Li_xNa_{1-x} and yields results in good qualitative agreement with experiment.

I. INTRODUCTION

This is the last in a group of three papers on the subject of phase transformations in liquid and solid metals and alloys. Previous papers have dealt with the origin of the Hume–Rothery rules for the crystal structures of binary alloys,[1] and with the theory of melting of simple metals.[2] The present paper extends the procedures used in these calculations to apply to a second-order phase transition,