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Perimeter corrections to the Landau diamagnetism

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Abstract. If the free electron gas is enclosed in a box of finite volume the Dirichlet boundary condition imposed on the wavefunction modifies the density of states (it increases the energy levels). This is also true in presence of a uniform magnetic field and gives rise to the perimeter corrections χ' to the Landau diamagnetic susceptibility χ_0. We analyse the effect for the zero-field susceptibility by a Green function approach rather than by enumerating the energy levels. The perimeter contribution χ' to the susceptibility is always positive (paramagnetic). The relative correction χ'/χ_0 is given by (apart from a constant of order unity) $l \times$ surface area/volume, where l is a characteristic length and is equal to the thermal de Broglie wavelength at high temperatures and to the Fermi wavelength in another extreme of complete degeneracy. Thus the effect may be observable in small metallic particles of size 10-100 Å, in particular if the electron effective mass is small such as, e.g., in bismuth.

1. Introduction

After Landau's original paper (1930) on the orbital diamagnetism of the free electron gas the effect was studied by Darwin (1931) and van Vleck (1932) confirming Landau's 'surprising' prediction (cf Peierls 1979). (Peierls (1933) discussed the effect for Bloch electrons and also considered the influence of the collisions.) Later the interest was in the boundary effects as studied in papers by Dingle (1952, 1953).

The present paper is concerned with the perimeter corrections to Landau diamagnetism. We will analyse the effect by a method based on the Green function formalism. The idea is to use the fact that the partition function Z can be expressed exactly as the trace of the Green operator with imaginary time $t = -i\hbar\beta$; $\beta = 1/kT$, k is the Boltzmann constant and T is the temperature. The correct Green function can be approximated by the Green function for unrestricted motion (no boundaries) plus the perimeter corrections necessary to account for the imposed Dirichlet boundary condition. The latter are worked out in the next section. This approach avoids the difficult problem of calculating and enumerating the individual energy levels and the summation in the partition function.

First we set up the necessary fundamental relations. The Green function of a given Hamiltonian $\hat{H}$ can be expressed in terms of the orthonormal basis of eigenfunctions $\psi_j(\boldsymbol{r})$,

$$G(\boldsymbol{r}, \boldsymbol{r}', t) = \sum_j \psi_j(\boldsymbol{r})\psi_j^*(\boldsymbol{r}') \exp(-iE_j t/\hbar) \tag{1}$$

where

$$\hat{H}\psi_j = E_j\psi_j. \tag{2}$$

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Clearly, by setting

$$t = -\mathrm{i}\hbar\beta \tag{3}$$

where $\beta = 1/kT$, one finds for the partition function

$$Z = \mathrm{Tr}(\mathrm{e}^{-\beta\hat{H}}) = \int G(\boldsymbol{r}, \boldsymbol{r}, -\mathrm{i}\hbar\beta)\, \mathrm{d}^3\boldsymbol{r}. \tag{4}$$

The free energy F as derived from the canonical partition function (4) is

$$F = -\frac{N_{\mathrm{el}}}{\beta} \log Z \tag{5}$$

where N_{el} is the total number of electrons, while in the case of a degenerate gas one has (see, e.g., Peierls 1955, p 147)

$$F = N_{\mathrm{el}}\eta - \frac{2}{\beta}\int \rho(E) \log\{1+\exp[-\beta(E-\eta)]\}\, \mathrm{d}E \tag{6}$$

where $\rho(E)$ is the density of states (per unit energy) and η is the chemical potential at given temperature. The susceptibility is given by

$$\chi = -\frac{1}{B}\frac{\partial F}{\partial B} \tag{7}$$

and can be obtained at high temperatures from (5). In the degenerate case (6) F can also be expressed explicitly in terms of Z. We note that the density of energy levels $\rho(E)$ is the inverse Laplace transform of Z,

$$\rho(E) = \mathscr{L}_E^{-1}\{Z(\beta)\} = \frac{1}{2\pi\mathrm{i}}\int_{\varepsilon-\mathrm{i}\infty}^{\varepsilon+\mathrm{i}\infty} \mathrm{d}\beta\, Z(\beta)\, \mathrm{e}^{\beta E}. \tag{8}$$

By expanding the logarithm into a power series we obtain

$$F = N_{\mathrm{el}}\eta + \frac{2}{\beta}\sum_{j=0}^{\infty} \frac{(-1)^{j+1}\exp[(j+1)\beta\eta]}{j+1} Z((j+1)\beta). \tag{9}$$

(This series and similar series appearing later on might diverge for $\eta > 0$. The sum is then understood as the analytic continuation of the sum for $\eta < 0$.)

Next we need the Green function for an electron in a uniform magnetic field. For the enclosure we choose a cylinder formed by a parallel transport of its base (of arbitrary shape, area $\mathscr{A}$ and perimeter $\mathscr{L}$) along a distance L parallel to the magnetic field. We use the fact that the motions parallel and transverse to the field are decoupled so that the wavefunctions factorise, and so does the Green function (1). Thus

$$G(x, y, z, x', y', z', t) = G_1(z, z', t)G_2(x, y, x', y', t) \tag{10}$$

where G_1 is the Green function for the one-dimensional motion on the interval of length L (coordinate z), while G_2 is the Green function for the two-dimensional motion in a plane enclosure (the base of the cylinder) with the uniform magnetic field pointing perpendicularly. In absence of boundaries these Green functions are well known (see, e.g., Feynman and Hibbs 1965):

$$G_{10} = \left(\frac{m}{2\pi\hbar\tau}\right)^{1/2} \exp\left(-\frac{m}{2\hbar\tau}(z-z')^2\right) \tag{11}$$

$$G_{20} = \frac{m}{2\pi\hbar\tau}\frac{\omega\tau}{\sinh(\omega\tau/2)} \exp\left[-\frac{m}{2\hbar}\left(\frac{\omega}{2}[(x-x')^2+(y-y')^2]\coth\frac{\omega\tau}{2} - \mathrm{i}\omega(xy'-yx')\right)\right] \tag{12}$$

where $\omega = eB/mc$ is the cyclotron frequency and $\tau = \mathrm{i}t$, so that (11) and (12) are actually Green functions for the diffusion equation with τ playing the role of time.

By applying (4) with $\tau = \hbar\beta$ and integrating over the domains of definition one gets for the partition functions corresponding to (11) and (12),

$$Z_{10} = L(m/2\pi\hbar^2\beta)^{1/2} \tag{13}$$

$$Z_{20} = \frac{\mathscr{A}m}{2\pi\hbar^2\beta} \frac{\hbar\omega\beta/2}{\sinh(\hbar\omega\beta/2)}. \tag{14}$$

2. The perimeter corrections to the Green function and the partition function

The exact wavefunctions and the exact Green function (1) must obey the Dirichlet boundary condition. The Green functions (11) and (12) for the unrestricted motion give a good approximation to the exact result if τ is sufficiently small *and* if (x, y, z) and (x', y', z') do not lie too close to the boundary, so that the boundary condition may be ignored. They can be regarded as the lowest terms (bulk terms) in an expansion of the exact Green function. The next term, called perimeter correction, must account for the Dirichlet boundary condition. Such systematic expansions have been studied by Balian and Bloch (1970) for the free particles in enclosures with zero magnetic field. We shall generalise the results to the case of plane enclosures with uniform magnetic field.

So let us consider a charged particle in a scalar potential $V(\boldsymbol{r})$ and uniform magnetic field B in a plane domain D with boundary ∂D. (By $\boldsymbol{r}$ we denote the position vector, $\boldsymbol{r} = (x, y)$.) Let $\hat{H}$ denote the Hamilton operator in the absence of the boundaries, i.e.

$$\hat{H} = \frac{1}{2m}\left(\hat{\boldsymbol{p}} - \frac{e}{c}\boldsymbol{A}\right)^2 + V(\boldsymbol{r}) \tag{15}$$

where $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r} = \frac{1}{2}(-By, Bx, 0)$ is the vector potential. The Green function G_0 for the unrestricted motion (no boundaries) satisfies

$$\hat{H}G_0(\boldsymbol{r}, \boldsymbol{r}', t) = \mathrm{i}\hbar\frac{\partial}{\partial t} G_0(\boldsymbol{r}, \boldsymbol{r}', t) \qquad G_0(\boldsymbol{r}, \boldsymbol{r}', 0) = \delta(\boldsymbol{r} - \boldsymbol{r}') \tag{16}$$

and is assumed to be known. Now, how can we construct the Green function G for the restricted motion (G vanishes on ∂D) in terms of G_0? Obviously, we must have

$$G(\boldsymbol{r}, \boldsymbol{r}', t) = G_0(\boldsymbol{r}, \boldsymbol{r}', t) + G'(\boldsymbol{r}, \boldsymbol{r}', t) \tag{17}$$

such that G' also satisfies the Schrödinger equation for all $\boldsymbol{r} \in D$ and

$$G'(\boldsymbol{r}, \boldsymbol{r}', t) = -G_0(\boldsymbol{r}, \boldsymbol{r}'t) \qquad \text{if } \boldsymbol{r} \text{ or } \boldsymbol{r}' \text{ on } \partial D. \tag{18}$$

Following the related ideas by Balian and Bloch (1970) we attempt the ansatz

$$G'(\boldsymbol{r}, \boldsymbol{r}', t) = \int_0^t \mathrm{d}\tau \int_{\partial D} \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha}, t-\tau)}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}', \tau) \tag{19}$$

where $\partial G_0/\partial n_\alpha$ denotes the normal derivative of G_0 at the point $\boldsymbol{\alpha}$ on the boundary ∂D with the normal oriented towards the interior region and $\mathrm{d}s_\alpha$ is the differential of the arc length s_α. The expression (19) does indeed obey the Schrödinger equation

$\hat{H}G' = i\hbar\,\partial G'/\partial t$ for all $\boldsymbol{r} \in D$ and for all t. By an appropriate choice of the density μ we can obtain G' so that it will satisfy the boundary condition (18). It is easy to show (see Balian and Bloch 1970) that if $\boldsymbol{\beta} \in \partial D$ then

$$\tfrac{1}{2}\mu(\boldsymbol{\beta}, \boldsymbol{r}', t) = -G_0(\boldsymbol{\beta}, \boldsymbol{r}', t) - \int_0^t d\tau \int_{\partial D} ds_\alpha \frac{\partial G_0(\boldsymbol{\beta}, \boldsymbol{\alpha}, t-\tau)}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}', \tau). \tag{20}$$

Notice that this is just the Fourier transform of the similar formula in Balian and Bloch (1970), who deal with the time-independent Green function. Their Green function is assumed real, while ours is complex, but the formula holds for that case as well. The essential point in deriving the integral equation for the time-independent but complex case is that the singular part of the Green function as $\boldsymbol{r} \to \boldsymbol{r}'$ is real. By applying the Fourier transformation we then obtain (20). See the appendix for details. This integral equation for μ can be solved iteratively resulting in a *multiple reflection expansion* (Balian and Bloch 1970). But the lowest approximation is simply

$$\mu(\boldsymbol{\beta}, \boldsymbol{r}', t) = -2G_0(\boldsymbol{\beta}, \boldsymbol{r}', t). \tag{21}$$

Inserting (21) in (19) yields the perimeter correction

$$G'(\boldsymbol{r}, \boldsymbol{r}', t) = -2 \int_0^t d\tau \int_{\partial D} ds_\alpha \frac{\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha}, t-\tau)}{\partial n_\alpha} G_0(\boldsymbol{\alpha}, \boldsymbol{r}', \tau). \tag{22}$$

Including the higher terms of the multiple reflection expansion for G' would give rise to curvature corrections, corner corrections, etc, which we ignore at present. It is easy to verify explicitly that (22) does satisfy the Schrödinger equation $\hat{H}G' = i\hbar\,\partial G'/\partial t$ everywhere in the interior of D and that it has the correct symmetry: according to (1) any Green function is Hermitian, and in particular we must find $G(\boldsymbol{r}, \boldsymbol{r}', t) = G^*(\boldsymbol{r}', \boldsymbol{r}, t)$. This can be easily verified by using the Hermitian property for G_0 and $\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha}, t-\tau)/\partial n_\alpha = -\partial G_0^*(\boldsymbol{\alpha}, \boldsymbol{r}, t-\tau)/\partial n_\alpha$, together with the change of variables $t - \tau \to \tau$ in (22). The quantity we need is the trace of the Green operator,

$$\begin{aligned} Z'(t) &= \int_D G'(\boldsymbol{r}, \boldsymbol{r}, t)\, d^2\boldsymbol{r} \\ &= -2 \int_0^t d\tau \int_D d^2\boldsymbol{r} \int_{\partial D} ds_\alpha \frac{\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha}, t-\tau)}{\partial n_\alpha} G_0(\boldsymbol{\alpha}, \boldsymbol{r}, \tau). \end{aligned} \tag{23}$$

This is obviously a real number, due to the Hermitian symmetry of the Green operator G'. Let us now evaluate (23) for the specific case of vanishing potential $V(\boldsymbol{r}) \equiv 0$ and uniform magnetic field B. From (12) one sees that G_0 can be written as follows:

$$G_0(\boldsymbol{r}, \boldsymbol{r}', t) = \exp[i\boldsymbol{\omega}\cdot(\boldsymbol{r} \times \boldsymbol{r}')] f_0(|\boldsymbol{r} - \boldsymbol{r}'|, t) \tag{24}$$

where f_0 is a real function and $\boldsymbol{\omega} = (0, 0, \omega) = (0, 0, eB/mc)$. From (23) we get

$$Z'(t) = -2 \int_0^t d\tau \int_D d^2\boldsymbol{r} \int_{\partial D} ds_\alpha \frac{\partial f_0(|\boldsymbol{r} - \boldsymbol{\alpha}|, t-\tau)}{\partial n_\alpha} f_0(|\boldsymbol{r} - \boldsymbol{\alpha}|, \tau) \tag{25}$$

so that the complex ('magnetic') phase factor is completely eliminated in this trace formula. This allows us to arrive at the important conclusion that the perimeter corrections Z' to the partition function Z_0 in the case of the uniform magnetic field are exactly the same as for the real Green function $f_0(|\boldsymbol{r} - \boldsymbol{r}'|, t)$. But the perimeter corrections of the latter can be obtained (to the same degree of accuracy) by employing the method of images (Baltes and Hilf 1976, Balian and Bloch 1970). This method is

based on the idea of replacing a piece of the boundary by its local tangent and setting $f_1 = -f_0(|\boldsymbol{r} - \boldsymbol{r}'_R|, t)$, where $\boldsymbol{r}'_R$ is the mirror image (across the tangent) of $\boldsymbol{r}'$. Clearly, $f = f_0 + f_1$ vanishes if $\boldsymbol{r}$ or $\boldsymbol{r}'$ is on the boundary. The approximation hinges upon the assumption that the Green function decays rapidly with $|\boldsymbol{r} - \boldsymbol{r}'_R|$ so that its value soon becomes negligible as $\boldsymbol{r}$ moves away from the boundary. It is assumed that the typical decay length is much less than the local radius of curvature. The conclusion is that it is not necessary to calculate Z' using the formula (25) but simply

$$Z'(t) = -\int_D d^2\boldsymbol{r} f_0(\boldsymbol{r}, \boldsymbol{r}_R, t) \tag{26}$$

where $\boldsymbol{r}_R$ is the mirror image of $\boldsymbol{r}$ across the boundary. We identify f_0 in (12) and, when integrating in (26), we change the coordinates to the arclength s and the distance R along the normal from the boundary, and finally invoking the rapid decay of f_0 to allow for the extension of the R integration limit to ∞, we find

$$Z_{21} = -\frac{m\mathscr{L}}{2\pi\hbar\tau}\frac{\omega\tau/2}{\sinh(\omega\tau/2)}\int_0^\infty dR \exp\left(-\frac{m\omega R^2}{\hbar}\coth\frac{\omega\tau}{2}\right). \tag{27}$$

The integration is trivial and we obtain, after inserting $\tau = \hbar\beta$,

$$Z_{21} = -\frac{\mathscr{L}}{8}\left(\frac{2m}{\pi\hbar^2\beta}\right)^{1/2}\left(\frac{\hbar\omega\beta}{\sinh(\hbar\omega\beta)}\right)^{1/2}. \tag{28}$$

The perimeter correction to the Green function G_{10} for the one-dimensional free motion, given in (11), can be obtained trivially by the method of images. The result for the partition function is

$$Z_{11} = -\tfrac{1}{2}. \tag{29}$$

Consequently we have for the partition functions

$$Z_1(\beta) = L\left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2}\left[1 - \frac{1}{2L}\left(\frac{2\pi\hbar^2\beta}{m}\right)^{1/2}\right] \tag{30}$$

and

$$Z_2(\beta) = \frac{\mathscr{A}m}{2\pi\hbar^2\beta}\frac{\hbar\omega\beta/2}{\sinh(\hbar\omega\beta/2)} - \frac{\mathscr{L}}{8}\left(\frac{2m}{\pi\hbar^2\beta}\right)^{1/2}\left(\frac{\hbar\omega\beta}{\sinh(\hbar\omega\beta)}\right)^{1/2}. \tag{31}$$

The total partition function is

$$Z(\beta) = Z_1(\beta)Z_2(\beta). \tag{32}$$

3. The perimeter correction to the Landau susceptibility

The result for the susceptibility (7) at high temperatures (using (5)) follows immediately by noting that Z_1 is independent of the field and does not contribute to (7). The substitution of (31) into the expression (5) followed by the differentiation (7) yields

$$\chi = -\frac{N_{el}\mu_B^2}{3kT}\frac{1 - \frac{3}{2}(l\mathscr{L}/\mathscr{A})}{1 - (l\mathscr{L}/2\mathscr{A})} \simeq -\frac{N_{el}\mu_B^2}{3kT}\left(1 - \frac{l\mathscr{L}}{\mathscr{A}}\right) \tag{33}$$

where $l = (\pi\hbar^2/2mkT)^{1/2}$ is the thermal de Broglie wavelength. As $l\mathscr{L}/\mathscr{A} \to 0$ the paramagnetic (perimeter) correction vanishes and we recover the high temperature Landau susceptibility as given by Darwin (1931) (see also Peierls 1979) (μ_B is the Bohr magneton $\mu_B = e\hbar/2mc$).

In case of degeneracy one has to use the expression (9) with Z as given by (30)–(32). We need to know the chemical potential η which is determined by the implicit equation

$$\frac{\partial F}{\partial \eta}=0 \tag{34}$$

whence from (6)

$$N_{\mathrm{el}}=2\int_0^\infty \frac{\rho(E)\,\mathrm{d}E}{1+\exp[\beta(E-\eta)]}. \tag{35}$$

At zero temperature ($\beta=\infty$) the bulk value for the Fermi energy η_0 is equal to

$$\eta_0=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_{\mathrm{el}}}{V}\right)^{2/3} \tag{36}$$

where $V=L\mathscr{A}$ is the volume of the cylinder enclosure. When the perimeter corrections are included in the density of states $\rho(E)$ (cf Balian and Bloch 1970)

$$\rho(E)=\frac{V\sqrt{E}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}-\frac{S}{16\pi}\frac{2m}{\hbar^2} \tag{37}$$

where $S=L\mathscr{L}+2\mathscr{A}$ is the surface of the cylinder, we find

$$\begin{aligned}\eta &= \eta_0\left(1+\frac{\pi\hbar S}{4V(2m\eta_0)^{1/2}}\right)\\ &= \eta_0\left[1+\frac{\pi\hbar}{4(2m\eta_0)^{1/2}}\left(\frac{\mathscr{L}}{\mathscr{A}}+\frac{2}{L}\right)\right].\end{aligned} \tag{38}$$

In calculating the susceptibility (7) we may ignore the dependence of η on ω, because of (34). So in using (9) we only have to take the derivative of Z at $\omega=0$,

$$\frac{1}{\omega}\frac{\partial Z}{\partial \omega}=\frac{Z_1}{\omega}\frac{\partial Z_2}{\partial \omega} \tag{39}$$

where

$$\frac{1}{\omega}\frac{\partial Z_2}{\partial \omega}=-\frac{\mathscr{A}m\beta}{24\pi}+\frac{\mathscr{L}\beta^2\hbar^2}{48}\left(\frac{2m}{\pi\hbar^2\beta}\right)^{1/2}. \tag{40}$$

In (39) we shall only keep terms linear in the perimeter corrections, i.e. we shall neglect the term $Z_{11}\partial Z_{21}/\partial\omega$. In this way we obtain at last

$$\chi=\chi_0+\chi_1 \tag{41}$$

$$\chi_0=-\frac{\mathscr{A}Lm}{12\pi}\frac{e^2}{m^2c^2}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2}\sum_{j=0}^{\infty}\frac{(-1)^j\exp[(j+1)\beta\eta]}{(j+1)^{1/2}} \tag{42}$$

$$\chi_1=\frac{e^2}{24\pi mc^2}\frac{L\mathscr{L}+\mathscr{A}}{1+\mathrm{e}^{-\beta\eta}}. \tag{43}$$

In absence of surface effects when η has just its bulk value, (42) is equal to the (bulk) Landau diamagnetic susceptibility. Its value at zero temperature is (see, e.g., Peierls 1955)

$$\chi_{\mathrm{Landau}}=-\frac{L\mathscr{A}}{12\pi^2}\frac{e^2k_0}{mc^2} \tag{44}$$

where

$$k_0 = (2m\eta_0)^{1/2}/\hbar = (3\pi^2 N_{el}/V)^{2/3} \tag{45}$$

is the Fermi wavenumber. The correction χ_1 as given by (43) is always finite, only χ_1/χ_0 vanishes as $S/k_0 V \to 0$. But (43) is *not* the complete perimeter correction to the Landau diamagnetism, because η itself in (42) has surface corrections, which at zero temperature are given by (38). When this is taken into account we obtain the susceptibility at zero temperature as follows:

$$\chi = \chi_{\text{Landau}}\left(1 - \frac{\pi}{4k_0 L} - \frac{3\pi\mathscr{L}}{8k_0\mathscr{A}}\right) \tag{46}$$

where χ_{Landau} is the bulk Landau susceptibility as given in (44) and k_0 is the (bulk) Fermi wavenumber as given by (45). Thus the perimeter correction to the Landau diamagnetism at zero temperature is equal to

$$\chi_{\text{surface}} = -\frac{\pi}{4k_0}\left(\frac{1}{L} + \frac{3\mathscr{L}}{2\mathscr{A}}\right)\chi_{\text{Landau}} \tag{47}$$

and is *always paramagnetic*. We will explain this in the next section. It is interesting that the surface paramagnetism at zero temperature as given in (47) is independent of $\hbar$: substituting (44) in (47) we obtain

$$\chi_{\text{surface}} = \frac{e^2}{48\pi mc^2}(\mathscr{A} + \tfrac{3}{2}L\mathscr{L}) \tag{48}$$

which indicates an apparently classical effect in contradiction with the Miss-van Leeuven theorem (Peierls 1979). This is, however, no more paradoxical than the fact that the Landau susceptibility (44) is independent of $\hbar$ (the Fermi wavenumber (45) does not depend on $\hbar$). The behaviour of the susceptibility at zero temperature as a function of $\hbar$, in the limit of $\hbar \to 0$, is obviously non-analytic: at any $\hbar \neq 0$ we have a discrete energy spectrum and the complete degeneracy as a consequence of the Pauli exclusion principle, which give rise to (44). When $\hbar = 0$ the spectrum is continuous. Since there is no classical analogy of the exclusion principle all electrons are in the lowest energy state, i.e. they are at rest, implying zero magnetic moments and non-existence of the magnetism. On the other hand, the susceptibility does behave analytically as a function of $\hbar$ as $\hbar \to 0$ for finite temperatures and in the absence of the degeneracy: according to (33) the bulk term vanishes as $\chi \sim \hbar^2$ when $\hbar \to 0$, and the surface term goes to zero as $\chi \sim \hbar^3$.

These results differ from those of Dingle (1952, 1953), who does not obtain (as a lowest term) a field-independent perimeter correction to the Landau diamagnetic susceptibility. From (33) or (46) we see that the relative perimeter contribution to the susceptibility of the free electron gas has the order of magnitude l/d, where d is a typical macroscopic dimension and l is the thermal de Broglie wavelength, or in another extreme the Fermi wavelength. Thus the effect may be observable in small metallic particles of size 10–100 Å. A more convenient geometry would be that of thin layers (thickness 10–100 Å), with magnetic field parallel to their plane, in which case one can control the geometry more reliably, eliminating the statistical effects. Another interesting effect is expected when each electron 'sees' an effective enclosure smaller than that given by the macroscopic boundaries. This is the case of localised states in a sufficiently disordered system. (The existence of localisation in multidimensional systems has been recently proved by Delyon *et al* (1985).) Qualitatively one expects paramagnetic corrections of relative order l/d, where d is now the localisation length.

4. Certain aspects of Landau condensation: why the perimeter corrections are always paramagnetic

From the formalism which we have employed to calculate the susceptibility it is clear that the perimeter corrections to the susceptibility are paramagnetic if $dZ/d\omega$ is less than $dZ_{\text{Landau}}/d\omega$, where Z is the partition function of an electron in the plane enclosure with uniform field, while Z_{Landau} is the partition function in which the surface corrections are neglected. Hence we must show that imposing the Dirichlet boundary conditions implies

$$\frac{dZ}{d\omega} < \frac{dZ_{\text{Landau}}}{d\omega}. \tag{49}$$

A free electron in a magnetic field has the Landau energy spectrum

$$E_n = (n+\tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \ldots \tag{50}$$

where each Landau level is infinitely degenerate. The effect of an enclosure is, to the lowest approximation, in lifting the infinite degeneracy, so that there are then only

$$g = \frac{\mathcal{A}eB}{2\pi\hbar c} \tag{51}$$

levels per Landau level. Hence the corresponding partition function is equal to

$$Z_{\text{Landau}} = \sum_j \exp(-\beta E_j) = g \sum_{n=0}^{\infty} \exp[-(n+\tfrac{1}{2})\hbar\omega\beta]$$
$$= \frac{\mathcal{A}m}{2\pi\hbar^2\beta} \frac{(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)} \tag{52}$$

which was also given in (14).

There are a few critical remarks. The degeneracy is not exact, but one finds exponentially small ($\exp(-\text{constant}\times\omega)$) splitting of levels instead. Some of the levels lie very close to the Landau level. Such Landau condensation is less pronounced the higher the energy. Therefore, the degeneracy number g has, as $n\to\infty$, merely the meaning of the average number of levels per one Landau level and in this asymptotic limit there is no Landau condensation at all. Figure 1 illustrates aspects of Landau condensation for low levels for the circular enclosure (integrable), in which case the spectrum can be analysed exactly. In figure 2 we show Landau condensation for the rectangular enclosure, which is a classically non-integrable system (Robnik 1986). (I plan to offer in a separate paper a more detailed discussion with a general semiclassical theory of Landau condensation.) Thus the spectrum can be written as

$$E_{nj} = (n+\tfrac{1}{2})\hbar\omega + f_{nj}(\omega) \tag{53}$$

where $n = 0, 1, 2, \ldots$, is the Landau level quantum number, while $f_{nj}(\omega)$ is the field-dependent correction, where the second quantum number $j = 1, 2, \ldots, g$.

Now there is one universal aspect of Landau condensation (in hard walled potentials), namely that for any ω

$$f_{nj}(\omega) > 0 \tag{54}$$

and for sufficiently large ω

$$\frac{df_{nj}}{d\omega}(\omega) < 0. \tag{55}$$

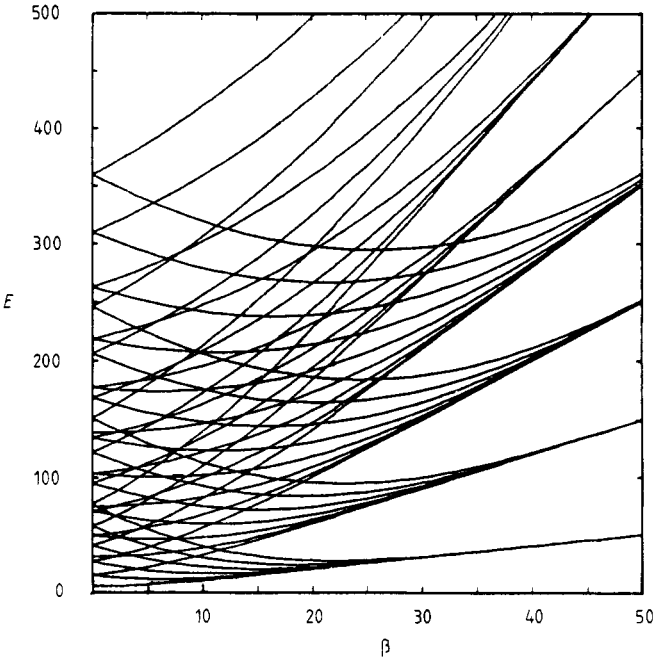

Figure 1. Landau condensation for the low lying states of a circular enclosure. $\beta = eB\mathscr{A}/\pi\hbar c$, where $\mathscr{A}$ is the area of the circular disc, is a dimensionless measure of the magnetic field strength B, while the energy E is in units of $\pi\hbar^2/2m\mathscr{A}$.

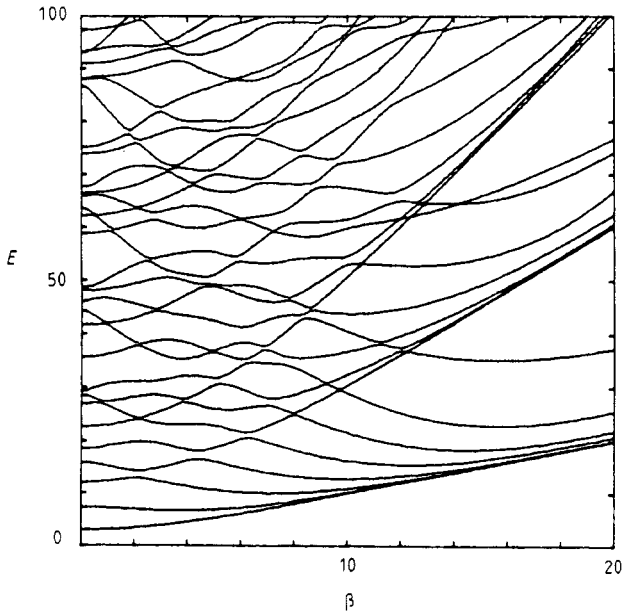

Figure 2. Landau condensation of the positive-parity states for the non-integrable case of the rectangular enclosure of sides $2a$ and $2b$, where $a = 1$ and $b = \pi - 1$. The unit of energy E is $\hbar^2/2ma^2$, while $\beta = eBa^2/\hbar c$.

Indeed, $f_{nj}(\omega)$ must be positive for the very general reason that imposing a more restrictive boundary condition on an eigenfunction raises the corresponding energy (cf Courant and Hilbert 1953). The order of magnitude of $f_{nj}(\omega)$ follows from the observation that a Landau orbital (eigenfunction of a free electron in a magnetic field) decays as $\exp[-(eB/\hbar c)r^2]$ with distance r, so by a perturbation analysis $f_{nj}(\omega) \propto \exp(-\text{constant} \times \omega)$. We can also conclude that the correction $f_{nj}(\omega)$ is larger the more extended the Landau orbitals are, i.e. the larger the Larmor radii or the smaller the magnetic field. This explains the inequality (55). It follows trivially, by using (54) and (55), that

$$Z = \sum_{n=0}^{\infty} \sum_{j=1}^{g} \exp[-(n+\tfrac{1}{2})\beta\hbar\omega - \beta f_{nj}(\omega)] \tag{56}$$

satisfies (49). Therefore the perimeter corrections must be paramagnetic for sufficiently large ω, at least. In case of cylinder enclosure (integrable) one can show that this applies strictly down to $\omega = 0$, as (55) holds for all ω. A more general theory of Landau condensation will be given in a separate paper.

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Appendix. Derivation of the integral equation (20) for the double layer density μ

Equation (20) can be obtained trivially from the corresponding equation for the time-independent Green function

$$\tfrac{1}{2}\mu(\boldsymbol{\beta}, \boldsymbol{r}', E) = -G_0(\boldsymbol{\beta}, \boldsymbol{r}', E) - \int \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{\beta}, \boldsymbol{\alpha}, E)}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}', E) \qquad \boldsymbol{\beta} \in \partial D \tag{A1}$$

by applying the Fourier transform to (A1), and taking into account the causality requirements that both $G_0(\boldsymbol{r}, \boldsymbol{r}', t)$ and $\mu(\boldsymbol{r}, \boldsymbol{r}', t)$ are zero if $t < 0$. Hence our task is to derive (A1) for the case of the complex time-independent Green function for the Hamiltonian (15). (In the following we omit explicit writing of the energy E, so $G_0(\boldsymbol{r}, \boldsymbol{r}')$ stands for $G_0(\boldsymbol{r}, \boldsymbol{r}', E)$, etc.) By definition we have

$$(\hat{H} - E)G_0(\boldsymbol{r}, \boldsymbol{r}') = -\frac{\hbar^2}{2m}\delta(\boldsymbol{r} - \boldsymbol{r}') \tag{A2}$$

where $\hat{H}$ is given in (15). It follows that the singular part of $G_0(\boldsymbol{r}, \boldsymbol{r}')$ as $\boldsymbol{r} \to \boldsymbol{r}'$ must be real; more precisely

$$G_0(\boldsymbol{r}, \boldsymbol{r}') \to \frac{1}{2\pi} f(\boldsymbol{r}, \boldsymbol{r}') \ln|\boldsymbol{r} - \boldsymbol{r}'| \qquad \text{as } \boldsymbol{r} \to \boldsymbol{r}' \tag{A3}$$

where $f(\boldsymbol{r}, \boldsymbol{r}')$ may be complex but must obey

$$f(\boldsymbol{r}, \boldsymbol{r}') \to 1 \qquad \text{as } \boldsymbol{r} \to \boldsymbol{r}'. \tag{A4}$$

Indeed, by inserting (A3) into (A2) and integrating both the LHS and RHS over a small disc around $\boldsymbol{r}'$ we correctly obtain the identity $1 = 1$. (Clearly, the delta function on the RHS of (A2) is produced by the action of the Laplace operator on (A3).)

Now the Green function $G(\boldsymbol{r}, \boldsymbol{r}')$ for the restricted problem with Dirichlet boundary conditions is constructed from $G_0(\boldsymbol{r}, \boldsymbol{r}')$ as follows:

$$G = G_0 + G' \tag{A5}$$

where G' is sought in the form

$$G'(\boldsymbol{r}, \boldsymbol{r}') = \int \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha})}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}') \tag{A6}$$

and must satisfy

$$G'(\boldsymbol{r}, \boldsymbol{r}') = -G_0(\boldsymbol{r}, \boldsymbol{r}') \qquad \text{if } \boldsymbol{r} \in \partial D \tag{A7}$$

to ensure that the Dirichlet boundary condition is satisfied. μ is a smooth function, while G_0 has a (real) singularity as given by (A3). The integral (A6) exists if $\boldsymbol{r}$ is a point $\boldsymbol{r}_0$ on the boundary ∂D but its value differs from the limit $\boldsymbol{r} \to \boldsymbol{r}_0$ when $\boldsymbol{r}$ approaches $\boldsymbol{r}_0$ from the interior of D. The jump

$$J = \lim_{\boldsymbol{r} \to \boldsymbol{r}_0} G'(\boldsymbol{r}, \boldsymbol{r}') - G'(\boldsymbol{r}_0, \boldsymbol{r}') \tag{A8}$$

is due to the singularity of G_0 and can be easily calculated using (locally) cartesian coordinates and inserting (A3) into (A6) and further into (A8). Let $\boldsymbol{r}_0 = (0, 0)$, and the y axis be oriented parallel to the boundary. Then we have to calculate

$$G'(\boldsymbol{r}_0, \boldsymbol{r}') = \int \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{r}_0, \boldsymbol{\alpha})}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}') \tag{A9}$$

and

$$\lim_{\boldsymbol{r} \to \boldsymbol{r}_0} G'(\boldsymbol{r}, \boldsymbol{r}') = \lim_{\boldsymbol{r} \to \boldsymbol{r}_0} \int \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{r}, \boldsymbol{\alpha})}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}'). \tag{A10}$$

Since $\mu(\boldsymbol{\alpha}, \boldsymbol{r}')$ is a smooth function, the jump J is a consequence of the singularity (A3). So we can assume μ to be constant and $f = 1$, and we obtain (for the contribution from the singular part; the regular parts do not contribute to J)

$$G'(\boldsymbol{r}_0 = 0, \boldsymbol{r}') = \frac{\mu}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\alpha_y \frac{\alpha_x}{\alpha_x^2 + \alpha_y^2} = 0 \tag{A11}$$

because $\alpha_x = 0$. On the other hand,

$$\lim_{\boldsymbol{r} \to \boldsymbol{r}_0 = 0} G'(\boldsymbol{r}, \boldsymbol{r}') = \frac{\mu}{2\pi} \lim_{\substack{x \to 0 \\ y \to 0}} \int_{-\infty}^{\infty} \mathrm{d}\alpha_y \frac{\alpha_x - x}{(\alpha_x - x)^2 + (\alpha_y - y)^2} = \frac{\mu}{2}. \tag{A12}$$

Thus

$$J = \tfrac{1}{2}\mu(\boldsymbol{r}_0, \boldsymbol{r}') \qquad \boldsymbol{r}_0 \in \partial D. \tag{A13}$$

Recall now that G_0, G' and G are continuous in the interior of D and that

$$\lim_{\boldsymbol{r} \to \boldsymbol{r}_0} G'(\boldsymbol{r}, \boldsymbol{r}') = -G_0(\boldsymbol{r}_0, \boldsymbol{r}') \tag{A14}$$

must be obeyed to satisfy the boundary condition (A7). Therefore (A8), (A13) and (A14) imply

$$\tfrac{1}{2}\mu(\boldsymbol{r}_0, \boldsymbol{r}') = -G_0(\boldsymbol{r}_0, \boldsymbol{r}') - \int \mathrm{d}s_\alpha \frac{\partial G_0(\boldsymbol{r}_0, \boldsymbol{\alpha})}{\partial n_\alpha} \mu(\boldsymbol{\alpha}, \boldsymbol{r}') \qquad \boldsymbol{r}_0 \in \partial D. \tag{A15}$$

This is the desired integral equation (A1) for the double layer density μ.

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