We present a pedagogical overview, accessible to the university students of physics, of an intriguing topic of diamagnetism. The treatment touches upon some basic ideas of classical electrodynamics, quantum mechanics, thermodynamics and statistical mechanics. The specific role of the boundary in determining diamagnetism, even in the so-called thermodynamic limit, is underscored.

Keywords: Diamagnetism; Bohr-van Leeuwen Theorem; Landau Levels; Boundary Effects
will occupy our attention in this paper. Because the boundary of enclosure has a special effect, our focus will be the orbital magnetism arising from the cyclotron motion of electric point charges such as electrons due to the presence of an external magnetic field, but constrained to move within an enclosure (van Vleck, 1932). Magnetism due to the intrinsic spin of the electron yielding paramagnetism, ferromagnetism, etc., will be ignored in the present discussion. Instead, we will concentrate on diamagnetism — the collective effect of the orbital motion of a bunch of electrons, assumed to be sufficiently far apart that their Coulomb interactions can be neglected. We will also ignore effects due to the Pauli Exclusion Principle, since the de Broglie wavelength of an electron is smaller than the mean inter-electron spacing, at the dilution considered. Thus, we shall employ Boltzmann statistics, even when quantum effects are significant (Huang, 1967).

Having laid down the scope of this overview the plan of the paper is as follows. In the next section we shall recapitulate the basic classical mechanics of cyclotron motion in terms of the Lagrangian and the concomitant Hamiltonian (Goldstein, 1980). A striking feature will be the occurrence of a velocity-dependent potential, another ubiquity of orbital magnetism. Because our interest is in the collective behaviour of electrons we will also recollect the thermodynamic definition of the macroscopic magnetization in terms of the free energy and how the latter can be computed from an underlying partition function of statistical mechanics (Huang, 1967). Next, we will familiarize the reader with exactly what the enigma of diamagnetism is, thus inter alia bringing to the fore the role of the boundary (Peierls, 1979; Dattagupta, 2010)). The subsequent section is devoted to a quantum statistical treatment (Landau, 1930) that cleverly by-passes the issue of the boundary. The boundary though is there and what it does is elaborated upon next, through an elegant quantum mechanical formulation (Darwin, 1931) in which the effect of the enclosure is simulated by a contrived two-dimensional parabolic well, normal to the direction of the applied magnetic field, in which the electrons are constrained to move. The Darwin method does not take recourse to the degeneracy factor of Landau as it treats the full two-dimensional problem. Yet it is instructive to do away with the ‘artificial’ parabolic well and consider the original problem and closely examine the sensitivity to the boundary. This was done by van Vleck (1932) who formulated the underlying Schroedinger equation in cylindrical coordinates and demonstrated how the quantization of the angular motion very naturally leads to the degeneracy factor and where the difficulty in the direct calculation of \( M \) lies. The resultant analysis helps delineate the particular contribution of the boundary to diamagnetism and further illuminates the Landau result. Our concluding remarks are presented in the last section.

Classical Mechanics and Thermodynamics of Cyclotron Motion

Classical Mechanics

The Lorentz force on an electron of charge ‘\(-e\)’ and mass \(m\) due to the combined presence of an electric field \(\vec{E}\), and a magnetic field \(\vec{B}\) — both taken to be space-time independent, is given by (Goldstein, 1980).

\[
\vec{F} = -e \left[ \vec{E} + (\vec{v} \times \vec{B}) \right]
\]

(1)

Throughout we will take \(\vec{B}\) to be along the \(z\)-axis of the laboratory frame. Notice already one peculiarity of the ‘magnetic force’ — it is velocity-dependent! Such velocity-dependence is unknown in the parlour of Newtonian physics unless one encounters friction, such as in the Stokes force on a ball falling under gravity through a liquid medium. In the absence of \(\vec{B}\) the force is ‘conservative’, derivable from the gradient of a potential \(-e\phi(\vec{r})\), \((\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z)\).

But because of the presence of the magnetic term a ‘generalized potential’ will have to be introduced (Goldstein, 1980). Consequently Eq. (1) is generalized to

\[
\vec{F} = -\nabla \phi(\vec{r}, \vec{v}) + \left( \frac{d}{dt} \right) \nabla \phi(\vec{r}, \vec{v}),
\]

(2)

where,

\[
\phi(\vec{r}, \vec{v}) = -e\phi(\vec{r}) + \frac{e}{c} (\vec{v} \cdot \vec{A}(\vec{r}))
\]

(3)

c being the speed of light and \(\vec{A}(\vec{r})\) the position-dependent vector potential such that its curl yields
the constant magnetic field. Because \( \nabla \times \chi(\mathbf{r}) \) is identically zero, \( \chi(\mathbf{r}) \) being an arbitrary scalar field, the vector potential \( \mathbf{A}(\mathbf{r}) \) enjoys ‘gauge-freedom’ which implies that to \( \mathbf{A}(\mathbf{r}) \) one can add \( \nabla \chi(\mathbf{r}) \) without altering the physical field \( \mathbf{B} \). The gauge-freedom allows several choices for the \( \mathbf{A} \)-field, the two most prominent ones being (Tonomura, 2000)

(a) The symmetric gauge, in which

\[
\mathbf{A}(\mathbf{r}) = \left( -\frac{yB}{2}, \frac{xB}{2}, 0 \right),
\]

(4)

and

(b) The Landau gauge, in which

\[
\mathbf{A}(\mathbf{r}) = (0, xB, 0),
\]

(5)

which can be obtained from Eq. (4) by adding to it \( \nabla \left( \frac{Bxy}{2} \right) \). It can be easily verified that either of these two choices leads to, via Eqs. (2) and (3), to Eq. (1) for the force which, of course, would have to be gauge-independent.

With the aid of the generalized potential the Lagrangian can be written as

\[
L = \frac{1}{2} m \mathbf{\dot{r}} \cdot \mathbf{\ddot{r}} - \phi (\mathbf{r}, \mathbf{v}) + \mathcal{E}.
\]

(6)

The corresponding Lagrange equations then yield the Newtonian equation of motion:

\[
m \frac{dv}{dt} = F,
\]

(7)

as expected. Indeed the choice of generalized potential in the Lagrangian in Eq. (6) is dictated by the requirement that Lagrange equations must lead to the equation of motion, as given by (7).

Associated with \( L \) is the Hamiltonian defined by (Goldstein, 1980)

\[
H = \mathbf{\dot{p}} \cdot \mathbf{\dot{r}} - L = \mathbf{\dot{r}} \cdot \frac{\partial L}{\partial \mathbf{\dot{r}}} - L
\]

(8)

where \( \mathbf{\dot{p}} \) is the canonical momentum. Using Eqs. (3) and (6) we obtain

\[
H = \frac{1}{2m} (\mathbf{\dot{p}} + e\mathbf{A}/c)^2 - e\phi(\mathbf{r}).
\]

(9)

The canonical momentum \( \mathbf{\dot{p}} \) is related to the so-called ‘kinematic’ momentum by

\[
\mathbf{\dot{p}}_{\text{kin}} = m \mathbf{\ddot{r}} = (\mathbf{\dot{p}} + e\mathbf{A}/c).
\]

(10)

It is interesting to observe that the Poisson brackets of the different Cartesian components of the kinematic momentum do not vanish. This has important consequences in quantum mechanics as will appear below.

**Thermodynamics**

In the presence of a magnetic field the first law of thermodynamics is modified as (Bhattacharjee and Banerjee, 2017)

\[
dQ = T dS = dE + P dV - B dM,
\]

(11)

where, \( Q \) is the heat, \( T \) the temperature, \( S \) the entropy, \( E \) the internal energy, \( P \) the pressure, \( V \) the volume and \( M \) the magnetization. It may be noted that the macroscopic magnetization is an extensive variable like the volume \( V \) unlike the magnetic field \( B \), which like the pressure \( P \), is an intensive variable. In the theory of phase transitions \( M, V, S... \) (divided by the total volume) are called density variables, as they undergo changes across phase transitions, while \( B, P, T \) are called the field variables which remain the same for co-existing phases (Griffiths, 1974). The magnetization \( M \) plays the same role as \( V \), while \( B \) plays the same role as \(-P\). Given this we may introduce the ‘enthalpy’ \( \varepsilon \) as

\[
\varepsilon = E - BM.
\]

(12)

Correspondingly, the Gibbs free energy \( G \) is

\[
G = E - BM - TS,
\]

(13)

and hence,

\[
dG = -SdT - P dV - M dB,
\]

(14)

which leads to the defining equation for the magnetization:
In order to reflect on this point it is useful to rewrite the law of thermodynamics in Eq. (11) as (Bhattacharjee and Banerjee, 2017)

$$T \, dS = d\varepsilon + P \, dV + M dB.$$  \hspace{1cm} (16)

The enthalpy $\varepsilon$ is the average (indicated by angular brackets below) of the kinetic energy plus the generalized potential energy, thus

$$\varepsilon = \langle (p_{\text{kin}})^2 / 2m + \phi (r, p_{\text{kin}}) \rangle.$$  \hspace{1cm} (17)

Note, however the intriguing fact that $\varepsilon$ is not the average of the Hamiltonian: $\langle H \rangle$, as is usually the case. Instead (cf. Eq. (9))

$$\langle H \rangle = E,$$  \hspace{1cm} (18)

where,

$$\langle H \rangle = \text{Tr} \{ H \exp [-H/(kT)] \}/Z,$$  \hspace{1cm} (19)

$Z$ being the canonical partition function:

$$Z = \text{Tr} \{ \exp [-H/(kT)] \}.$$  \hspace{1cm} (20)

The symbol $\text{Tr}$ denotes an integral over the phase space of coordinates and momenta in classical physics, whereas it implies a sum over all eigenstates of the Hamiltonian $H$ in quantum physics. It may be noted that because the pressure $P$ and the volume $V$ do not play any role in the present discussion on diamagnetism there is no difference between the Gibbs free energy and the Helmholtz energy, the latter being directly related to $Z$. Because of Eq. (14) and the fact that

$$G = -kT \log (Z),$$  \hspace{1cm} (21)

it is clear that

$$M = -\left( \frac{\partial H}{\partial B} \right)_{T,V} = -\frac{\partial E}{\partial B}.$$  \hspace{1cm} (22)

**Diamagnetism – The Peierls View**

Peierls calls diamagnetism one of the ‘surprises in theoretical physics’ – Why (Peierls, 1979; Dattagupta, 2010)? The answer is embedded in the simple (non-rigorous) argument given below.

A point charge under the Lorentz force of a magnetic field $B$ moves in a circle. Since a moving charge constitutes an electric current $I$ the consequent magnetic moment would be given by (Semat, 1966)

$$\mu = I \pi (a)^2,$$  \hspace{1cm} (23)

where, the radius $a$ of the circle can be derived by balancing the centripetal force with the Lorentz force, thus

$$a = (mvc)/(eB) = v/(\omega_c),$$  \hspace{1cm} (24)

$v$ being the velocity of the orbiting electron and $\omega_c = eB/mc$ is the cyclotron frequency. The current $I$, on the other hand, is the amount of charge circulating under one revolution, and hence

$$I = -e v/(2\pi a).$$  \hspace{1cm} (25)

Combining with Eqs. (23) and (24), we find

$$\mu = -m (v)^2 c/(2B).$$  \hspace{1cm} (26)

This is patently a ridiculous answer as it is not only independent of the electron’s charge but is also indicative of a divergence as $B \to 0$. The fallacy in the above estimate for $\mu$, as was pointed out by van Vleck (1932) and Peierls (1979), lies in the fact that it counts only those orbits whose centres lie within the enclosure (see Fig. 1). However, there are electrons, near but within the boundary, whose centres fall outside the enclosure. This is especially true of those electrons under very small magnetic fields whose paths are almost straight because $a$ is inversely proportional to $B$ (See Eq. (24)). These boundary electrons, though small in number, can cause a huge contribution to the magnetic moment, especially for low magnetic fields, as is evident from Eq. (26). They form a counter ‘edge current’, opposite to the direction of circulation of the

![Fig. 1:](image-url)
cyclotron orbits in the bulk of the enclosure (Fig. 1). As it turns out, in the classical limit of what is fully a quantum problem, the edge contribution exactly cancels the bulk contribution. Thus, we are faced with an intriguing situation in which the boundary or surface effects cannot be ignored, even for a macroscopic thermodynamic quantity such as the magnetization. Normally the surface-to-bulk ratio of the number of electrons is proportional to \((N)^{-1/3}\) and unless one is dealing with a nano-system, this ratio goes to zero for an infinitely large \(N\), the total number. Therefore, in the so-called thermodynamic limit, the boundary should not matter – but not for diamagnetism!

One way to circumvent the boundary issue, as was demonstrated by van-Leeuwen (1921), was to recognize that in order to calculate the macroscopic magnetization one ought to resort to \(Z\), and then compute \(M\) via Eqs. (14) and (21). The partition function \(Z\) is not as sensitive to the boundary as the underlying phase space integrals simply end at the boundary. This is not true if one follows the route of Eq. (22) and differentiates inside the integrals and then carries out the integrations. Hence, when treating diamagnetism, differentiation and integration do not commute! This subtle point will be further elaborated upon, in the quantum calculation of \(M\), in Sec. 6.

van Leeuwen however encountered another roadblock in calculating the magnetization from the classical partition function. Recall that the latter is given by (cf. Eq. (20)).

\[
Z = \int \exp \left[ -\frac{H}{kT} \right] d^3 r d^3 \mathbf{p},
\]  

(27)

where, the Hamiltonian \(H\) is given by Eq. (9). Because the integrals over the momenta run over all space the dependence on the magnetic field can be obliterated by a change in the integration variables. Consequently, the partition function becomes independent of \(B\) and hence the magnetization, being the derivative of the free energy with respect to \(B\), vanishes. This result, now called vanLeeuwen’s theorem, has given rise to a curious remark: The phenomenon of diamagnetism does not exist in classical physics (Huang, 1967)!

The Landau Treatment

Despite the van Leeuwen result, diamagnetism as a phenomenon does, of course, exist though it is often masked by paramagnetism. However in cases where there are no unpaired electrons in the outermost shells of atoms such as in Bi, diamagnetism emerges as the dominant magnetic response. Came Landau to the rescue – he argued that one has to employ quantum mechanics to explain the effect. The analysis runs as follows (Landau, 1930).

Keeping only the magnetic field terms in Eq. (9) the Hamiltonian for two-dimensional motion in the XY-plane normal to \(B\) and in the Landau gauge (Eq. (5)), reduces to

\[
H = \frac{1}{2m} \left( \frac{\hbar}{2\pi} \right)^2 \left( \frac{\partial^2 \psi(x)}{\partial x^2} \right) + \left( \frac{m}{2} \right) \left( \omega_c^2 \right) \left( x + X \right)^2 \psi(x) = \lambda \psi(x).
\]  

(31)

It is evident from Eq. (29) that \(p_y\) commutes with \(H\) and is therefore a good quantum that can be expressed as \(2\pi q_y\). This prompts an ansatz for the Schroedinger wave function as

\[
\psi(x,y) = \exp[iq_y y] \psi(x),
\]  

(30)

where, the x-dependent wave function satisfies just a one-dimensional Schroedinger equation, which is familiar in the context of a one-dimensional quantum harmonic oscillator (Sakurai, 1985):

\[
- \left( \frac{1}{2m} \right) \left( \frac{\hbar}{2\pi} \right)^2 \left( \frac{\partial^2 \psi(x)}{\partial x^2} \right) + \left( \frac{m}{2} \right) \left( \omega_c^2 \right) \left( x + X \right)^2 \psi(x) = \lambda \psi(x).
\]  

Here,

\[
X = q_y(hc)/(2\pi eB), \quad \text{and} \quad \lambda \quad \text{is the energy eigenvalue which, for a one-dimensional oscillator, is given by}
\]  

\[
\lambda = (j + \frac{1}{2}) (h\omega_c^2)/(2\pi), \quad j = 0,1,2,3,... .
\]  

(32)

Simple as it looks, Eq. (32) has a caveat – it is derived from solving the equation of a ‘displaced’ harmonic oscillator, the centre of motion of which (given by \(-X\), can however take innumerably large number of values corresponding to the allowed values of \(q_y\). This means that for each \(j\) we can have a large number of quantum states, each of which corresponds to the centre of the cyclotron orbit being found...
anywhere within the two-dimensional area of the XY-plane given by \( S \). The consequent degeneracy \( \eta \) is roughly given by the total number of cyclotron orbits that can be accommodated within the area \( S \). A pictorial description of how free (i.e., for \( B = 0 \)) electron states coalesce into discrete Landau levels giving rise to the degeneracy factor \( \eta \), independent of the level-index \( j \), is shown schematically in Fig. 2 (Huang, 1967). Hence,

\[
\eta = S / (2\pi \xi^2), \quad (33)
\]

where, the so-called ‘magnetic length’ \( \xi \) is given by the ‘quantized’ cyclotron radius. From Eq. (24),

\[
(\xi)^2 = \eta \cdot (h/2\pi)/(eB), \quad (34)
\]

where, we have replaced \((mva)\) by the Planck quantum \((h/2\pi)!\) Thus

\[
\eta = eBS/(hc). \quad (35)
\]

Interestingly, because (BS) is the magnetic flux \( \phi \) through the area \( S \), \( \eta \) can be expressed as the ratio of two fluxes: \((\phi/\phi_0)\), where the quantum of flux \( \phi_0 \) is defined by

\[
\phi_0 = (hc)/e. \quad (36)
\]

We are now all set to calculate \( Z \). From Eq. (20)

\[
Z = \{ (hc/2eSB) \text{ Sinh} [h\omega_c/(4\pi kT)] \}^{-N}. \quad (38)
\]

The Helmholtz (or the Gibbs) free energy \( G \) is then (cf. Eq. (21))

\[
G = NkT \{ \log(hc/2eSB) + \log \text{ Sinh} [h\omega_c/(4\pi kT)] \}. \quad (39)
\]

Finally, the magnetization is given from Eq. (15) as

\[
M = (ehN/4\pi mc) \{ 4\pi kT/h\omega_c \} – \text{ Coth} [h\omega_c/(4\pi kT)]. \quad (40)
\]

Evidently, in the classical limit, in which the Plank constant goes to zero, \( M \) vanishes in accordance with the Bohr-van Leeuwen result. The Landau treatment, therefore, craftily skirts around the boundary issue by dealing directly with the partition function. The role of the boundary is amplified in the scheme presented below.

### The Darwin Method

As mentioned earlier Darwin introduced a parabolic potential well which constrains the electron motion in two dimensions, in order to simulate the boundary effects (Darwin, 1921). Ignoring the electric field and adding the parabolic term, the Hamiltonian can be obtained by modifying Eq. (9), in the symmetric gauge of Eq. (4), as

\[
H = (1/2m) (p_x^2 + p_y^2) + (m/2). (\omega')^2 (x^2 + y^2) - \omega_c (yp_x - xp_y)/2, \quad (41)
\]

where,

\[
\omega' = [(\omega_0)^2 + (\omega_c/2)^2]^{1/2}. \quad (42)
\]

In what follows we will provide a different scheme from Darwin’s and work out first the equations of motion. Introducing a variable \( \zeta \) defined as

\[
\zeta = x + iy, \quad (43)
\]

the Hamilton’s equations for canonical coordinates and momenta can be combined to yield

\[
(d/dt)^2 \zeta + \omega_\zeta (d/dt) \zeta + \omega_0^2 \zeta = 0, \quad (44)
\]

the solution of which reads
\[ \zeta(t) = \frac{1}{2} \omega' \cdot \zeta(t = 0) \left\{ (\omega' - \omega / 2) \exp \left[ -i t (\omega' + \omega / 2) \right] \right. \right. \] 
\[ \left. \left. + i \left( \frac{1}{2} \omega' \right) \cdot (d/dt) \zeta(t) \right|_{t=0} \{ \exp \left[ -i t (\omega' + \omega / 2) \right] \right. \right. \] 
\[ \left. \left. - \exp \left[ -i t (\omega' - \omega / 2) \right] \} \right. \right. \] 
\[ ](45) \]

This harmonic oscillator like solution suggests that there exist two characteristic frequencies
\[ \gamma_+ = \omega' + \omega / 2, \quad \gamma_- = \omega' - \omega / 2. \] 
\[ ](46) \]

Physically, the two frequencies represent clockwise and anticlockwise circulations of the electron with respect to the direction of the magnetic field. Quantizing the motion governed by Eq. (45) we may write the energy eigenvalue as
\[ \varepsilon = \frac{h}{2\pi} \left[ \gamma_+ (j_+ + 1/2) + \gamma_- (j_- + 1/2) \right], \] 
\[ ](47) \]

Carrying out the summations over \( j_+ \) and \( j_- \), we find
\[ Z = \left\{ \sum_j \exp \left[ -h \Upsilon_+ (j_+ + 1/2) / 2\pi kT \right] \right. \] 
\[ \left. + \sum_j \exp \left[ -h \Upsilon_- (j_- + 1/2) / 2\pi kT \right] \right\}^N. \] 
\[ ](48) \]

The result in Eq. (49) is in agreement with Darwin’s.

Because we are eventually interested in the limit of vanishing parabolic well (\( \omega_0 \to 0 \)), we write
\[ \gamma_+ \sim \omega' + \omega / 2, \quad \gamma_- \sim |(\omega_0)^2/\omega_c|. \] 
\[ ](50) \]

From Eq. (49)
\[ Z \sim (z_c \cdot z_0)^N, \] 
\[ ](51) \]

where \( z_c \) is the pure ‘magnetic’ contribution to the partition function (per particle) and \( z_0 \) is the contribution arising from the well (i.e., the boundary), given by
\[ z_c = [2 \sinh (h \omega_c / 4\pi kT)]^{-1}, \] 
\[ ](52) \]
\[ z_0 = \{h[(\omega_0)^2/(2\omega_c \cdot kT)]\}^{-1}. \] 
\[ ](53) \]

The Helmholtz free energy is then
\[ G = N k T \left\{ \log \left[ 2 \sinh \left( \frac{h \omega_c}{4\pi kT} \right) \right] \right. \] 
\[ \left. + \log \left[ h \left( \frac{\omega_0^2}{2\pi k T \omega_c} \right) \right] \right\}, \] 
\[ ](54) \]

where, the last term may be viewed to be entirely due to the boundary.

Interestingly, \( \omega_0 \) does not have any influence on the magnetization as the latter is given by a derivative with respect to the magnetic field. Thus \( M \) is again obtained from Eq. (40), the Landau answer!

**Diamagnetism a la van Vleck**

Imagine the enclosure to be a cylinder of radius \( R \) in which the magnetic field is applied along the axis taken to be the \( z \)-direction (Fig. 3). We are concerned with the motion in the plane normal to the axis defined by the radial coordinate \( \rho \) and the azimuthal angle \( \omega \). The corresponding Schrödinger equation can be written as (van Vleck, 1932)
\[ \left( \frac{h^2}{8\pi m} \right)^2 \] 
\[ \left\{ \left( \frac{\partial}{\partial \rho} \right)^2 + \left( \frac{\partial}{\partial \rho} \right)^2 + \left( \frac{1}{\rho} \right)^2 \left( \frac{\partial}{\partial \theta} \right)^2 \right\} \] 
\[ \left\{ -i \left( \frac{h \omega_c}{2\pi} \right) \frac{\partial}{\partial \theta} \left[ \frac{m\omega_c^2}{8} \right] (\rho)^2 - \varepsilon \right\} \] 
\[ \psi(\rho, \theta) = 0, \] 
\[ ](54) \]

which, by a further transformation:
\[ \psi(\rho, \theta) = \chi(\rho) \exp (i\theta), \] 
\[ ](55) \]
(l being positive and negative integers) can be decomposed as

\[ -\left(\frac{\hbar^2}{8m\pi^2}\right)\left(\frac{d}{dp}\right)^2 + \left(\frac{d}{dp}\right) - \left(\frac{l}{p}\right)^2 \]

\[ -\left(m\omega^2/8\right)\rho^2 \chi(p) = \left[\varepsilon - (\hbar\omega/l4\pi)\right] \chi(p) \] (56)

Here \(\varepsilon\) is the energy eigenvalue which gets shifted thus

\[ \varepsilon' = \left[\varepsilon - (\hbar\omega/l4\pi)\right]. \] (57)

Interestingly, Eq. (57), read with \(E'\) as the energy eigenvalue, is identical to an isotropic two-dimensional harmonic oscillator in the x- and y-directions with a common frequency \(\omega/2\). Such an oscillator is known to have quantized eigenvalues as (Sakurai, 1985)

\[ \varepsilon' = (n_x + \frac{1}{2}) (h\omega/4\pi) + (n_y + \frac{1}{2}) (h\omega/4\pi), \] (58)

where, each quantum number \(n_x\) or \(n_y\) runs over all positive integers. Given that the left hand side of Eq. (56) is symmetric under the interchange \(l \rightarrow -l\), \(\varepsilon'\) can be re-expressed as

\[ \varepsilon' = (2n + |l| + 1) (h\omega/4\pi), \] (59)

where \(n\), like \(n_x\) and \(n_y\), is a positive integer. The actual eigenvalue can then be constructed from Eq. (57) as

\[ \varepsilon_{n,l} = (2n + |l| + 1 + 1) (h\omega/4\pi). \] (60)

Evidently, for \(l > 0\),

\[ \varepsilon_{n,l} = 2(n + l + 1/2)(h\omega/4\pi), \] (61)

whereas, for \(l < 0\),

\[ \varepsilon = 2(n + \frac{1}{2}) (h\omega/4\pi). \] (62)

It remains now to work out the partition function \(Z\), which evidently involves two separate summations: one over \(n\) and the other over \(l\). However, the latter is not an unrestricted one, as is elegantly argued by van Vleck (1932). Note that \(l\) is the quantum number for the azimuthal angular momentum, which can be written in terms of the kinematic angular momentum minus a term arising from \((rxA)\) (cf., Eq. (10):

\[ (h\omega/2\pi) = (xp_{kin})_z - e(r \times A)/c = m\left[x(\text{dy/dt}) - y(\text{dx/dt}) - (\omega/2)(x^2 + y^2)\right]. \] (63)

On the other hand, the classical cyclotron motion can be represented by

\[ x(t) = x_0 + a \cos(\omega_c t/2), \]
\[ y(t) = y_0 + a \sin(\omega_c t/2), \] (64)

where, \(x_0\) and \(y_0\) are the coordinates of the centre of the cyclotron orbit (See Fig. 3). Thus

\[ (h\omega/2\pi) = (1/2)m \omega_c (a^2 - d^2), d^2 = (x_0)^2 + (y_0)^2. \] (65)

Now, positive values of \(l\) would require that \(d < a\), which, however, can be satisfied for a miniscule number of orbits, especially for appreciably large magnetic fields (cf. Eq. (24)). Therefore, we shall ignore \(l > 0\) in the summation for \(Z\).

Thus, from Eq. (65),

\[ |l| = [\pi(m\omega_c)/\hbar]. R^2 = B.S/(hc/e) = (\phi/\phi_0), \] (66)

where \(S\) is the area of the cylinder (Fig. 3), \(\phi\) is the total flux threading the cylinder and \(\phi_0\) is the flux quantum (cf. Eq. (36)).

We are now all set to compute \(Z\):

\[ Z = \sum_{l=-\infty}^{l=\infty} \sum_{n=0}^{\infty} \text{Exp} - \left[ (n + 1/2) h\omega_c/(2\pi kT) \right] = (\phi/\phi_0). \sum \text{Exp} - \left[ (n + 1/2) h\omega_c/(2\pi kT) \right], \] (67)

which again yields the Landau answer given in Eq. (38). The route to this result further clarifies the meaning of the degeneracy factor \(\eta\) introduced earlier.

Once again the direct calculation of the partition function circumvents the ticklish issue of the boundary. To finally address this question we turn, following van Vleck, to a direct calculation of \(M\)

\[ d\varepsilon_{n,l}/dB = \mu_b(2n + |l| + 1 + 1), \] (68)

where, \(\mu_B\) \((= eh/4\pi mc)\) is the Bohr magneton. Using Boltzmann statistics the macroscopic magnetization is given by

\[ M = -\mu_B N. < (2n + |l| + 1 + 1) >= -\mu_B N. \sum\sum_{n=0}^{n=\infty} (2n + 1) \text{Exp} - [E_n/kT]/Z, \] (69)

where, the partition function \(Z\) is given in Eq. (67). Surprisingly, a computation of Eq. (69) leads to just the second term in Eq. (40) of the Landau answer! The catch is, now the contributions from the terms \(l = -\infty\) to \(-\phi/\phi_0\) cannot be omitted. Keeping the latter in the reckoning the additional contribution from
the surface (indicated by the subscript S) can be written as

\[ M_S = -\{ \Sigma l \Sigma_n \left[ d(\varepsilon_S)_{n,l}/dB \right] \}
\]

\[ \exp -\left[ (\varepsilon_S)_{n,l}/(kT) \right] \}/ Z, \]

(70)

where, we have retained the same Z in the denominator of Eq. (70) as the latter may be assumed to be immune to boundary effects, as Landau showed. Here \( E_S \) is the energy of the boundary electrons. Now the trick is to convert the derivative with respect to B to a derivative with respect to \( l \) and replacing the sum over \( l \) by an integral over \( l \). Thus

\[ \Sigma_l \left[ d(\varepsilon_S)_{n,l}/dB \right] \{ \ldots \} \]

\[ \int dl \left( \frac{dl}{dB} \right) d(\varepsilon_S)_{n,l} dl \{ \ldots \}. \]

(71)

The quantity \( (dl/dB) \) is calculated from Eq. (65);

\( (dl/dB) \sim -\phi/\phi_0 \),

(72)

where we have replaced \( (a^2 - d^2) \) by \( R^2 \). The limits of the integral over \( l \) in Eq. (71) are from \( \infty \) to \( -\phi/\phi_0 \). While it is difficult to estimate the surface contribution \( (\varepsilon_S)_{n,l} \) the idea is to rewrite the integrand as a total differential and then compute the contributions from the end points of the integral. The final result is just \( -(NkT/B) \) times \( Z \), and hence

\[ M_S = NkT/B, \]

(73)

which is just the first term in Eq. (43). We have now been able to disentangle the surface and bulk contributions to the magnetization and resolve the question of why in classical physics the two terms simply cancel each other.

**Concluding Remarks**

In this overview, we have made a comprehensive analysis of the phenomenon of diamagnetism. We have argued why the problem is intrinsically quantum mechanical. Further, the role of the boundary has been elaborated on. Our methods of calculation are based on different approaches—that of Landau in directly assessing the magnetization from the partition function; of Darwin’s in which an imagined parabolic potential is employed to mimic the boundary; and finally, that of van Vleck in tackling the complete two-dimensional quantum problem in cylindrical coordinates and delineating the bulk and surface contributions separately. The analysis sheds light on why Peierls calls diamagnetism as one of the surprises in theoretical physics. The present paper can also be viewed as a case study in which the foundational pillars of theoretical physics — classical mechanics, electromagnetism, thermodynamics, statistical mechanics and quantum mechanics — all come together to illuminate what the phenomenon of diamagnetism is. The effect of dissipation on diamagnetism – outside the scope of the present review — but important in the contemporary challenging themes of dissipative quantum systems and stochastic thermodynamics, further throws light on the transition from the Landau to Bohr-van Leeuwen regimes, from coherence to decoherence, etc. (Dattagupta and Singh, 1997; Bandyopadhyay and Dattagupta, 2006; Dattagupta et al., 2010; Dattagupta and Chaturvedi, 2017). The Darwin stratagem of incorporating a fake boundary assumes a critical role in the underlying quantum Langevin equations for the dissipative diamagnetism.

**References**


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