

Bussei Kenkyu (1975)

**Introduction of A New Principle
in the Theory of Magnetism II.**

**New Statistical Thermodynamics for
Magnetizable Materials and Superconductors**

Shuichi IIDA

Department of Physics, The University
of Tokyo, Tokyo, Japan

(6月18日受理)

Synopsis

A rigorous verification is made that the Meissner state has the minimum magnetostatic energy. The tricky structure of the magnetic energy is analyzed for a system comprised of two doubly connected superconductors, clarifying the profound meaning of the Zeeman energy and the Meissner state. Through emphasizing the correct way of treating the magnetic energy of an externally applied field, a new thermodynamics for Curie-Langevin-Debye paramagnetism, for Larmor diamagnetism, and for superconductor has been developed. Since the thermodynamical energy of a many electron system cannot be identical to the Hamiltonian of the system, Miss. Van Leeuwen's theorem on the absence of diamagnetism in classical systems is wrong. The new thermodynamics allows easy derivation of the London equation and it gives a new way of understanding thermodynamically the normal-superconducting transition in a magnetic field.

§1. Introduction

In the process of reorganizing classical electromagnetism in the framework of modern physics¹⁾, it has been found that the superconductor in magnetism just corresponds to the conductor in electricity. In a stationary field, the former assumes a surface current state producing $\mathbf{H}=0$ inside, just like as the latter of the surface charge state with $\mathbf{E}=0$ inside. We have succeeded in proving rigorously that the surface current state or the Meissner state of the superconductor has the minimum magnetic energy locally, just as the surface charge state of the conductor has the minimum electric energy.

Encouraged by this simple correspondence we have tried to réinterpret the physics of the superconductor within the framework of Maxwell-Lorentz electromagnetism. We found that there has been in the past a complicated mixture of detours and misunderstandings. We believe that Miss Van Leeuwen's theorem is correct mathematically but is wrong physically. There has been no adequate thermodynamics for diamagnetism and especially for perfect diamagnetism. The understanding of boundary effects in the physics of a Fermi gas has been inadequate and the difference between classical physics and quantum physics has been also misunderstood. There is a definite reason for the presence of such a confusion, because magnetism and magnetic energy are very tricky

subjects, the physics of which, especially, of the energy transfer in the Maxwell-Lorentz equations, has not been well understood before.

It should be pointed out that, although all the description in this paper are made in terms of classical physics, the method of analysis and the conclusion should be identical quantum mechanically. We believe that quantum mechanics is necessary to get perfect conduction, but once perfect conduction can be assumed, the Meissner effect is a classical property of the perfect conductor.

Paper I of our study has been published in "Bussei Kenkyu" in English²⁾ already. From our experience, we preferred to publish this more detailed first paper in this no-referee Journal. Although in this paper, we frequently summarize the result of paper I, it is strongly recommended that the readers should read paper I before trying to understand this paper II.

It should be noted that all the physics in this paper stand on the postulate that magnetization always comes from persistent currents. We have succeeded in obtaining a very accurate persistent current model of the electron³⁾, which, of course, presents one of the necessary supports to this paper. The more rigorous explanation of the meaning of magnetic energy will be given in paper III soon²⁸⁾.

§2. Magnetic Energy of A System of Superconductors

Let us assume that there are 1, 2,, N superconductors with stationary persistent currents. Then the macroscopic total magnetic energy of the system, U_m , is

$$U_m = \sum_{i,j} \frac{1}{2} L_{ij} \Delta I_i \Delta I_j = \sum_i \frac{1}{2C} \Phi_i \Delta I_i \quad (1)$$

$$\Phi_i = C \sum_j L_{ij} \Delta I_j \quad (2)$$

in which ΔI_i and L_{ij} are the total current of a closed circuit C_i , and the mutual inductance of the circuits i and j . Here we use the MKS rationalized symmetrical unit system (MKS rationalized Gauss system, or, MKS Heaviside-Lorentz system)* for convenience. We call this system the MKSP system, in which P stands for physical. We have subdivided all the currents into a number of closed loop circuits i with infinitesimally small cross

* We recommend that this system be used for research and education, and that the MKSA system be used for the electrical engineering. Since the two systems are both MKS and rationalized, the compatibility is extremely good.

sections. Φ_i is the total magnetic flux in the loop C_i . There is no requirement on each C_i , so that C_i and C_j may cross or the shape of C_k may be quite artificial, but is still allowable if ΔI_k is assumed to be zero initially.

Let us make the variation of U_m with respect to $\delta(\Delta I_i)$. Then

$$\begin{aligned}\delta U_m &= \sum_{i,j} L_{i,j} \Delta I_j \delta(\Delta I_i) \\ &= \sum_i \frac{1}{C} \Phi_i \delta(\Delta I_i)\end{aligned}\quad (3)$$

From Eq. (3), in the minimum energy state, we must have the relation

$$\Phi_i = 0$$

When we have no further requirement, Eq. (3) leads to a trivial solution in which no current remains. Let us impose one more physical condition to the variation of Eq. (3). Namely, in the minimization procedure we require that only the variations which are confined to a small micro region are allowable.

This requirement comes from two physical reasons. One reason is thermodynamical, which states that the change in a system occurs always locally so as to reduce the total free energy of the system. The other reason is related to the requirements for interfacing between microscopic Maxwell-Lorentz electromagnetism and macroscopic Maxwell electromagnetism. From the Maxwell equations, on any path C_{λ_i} , the relation

$$\oint_{C_{\lambda_i}} \mathbf{E} \cdot d\mathbf{l} = -\frac{1}{C} \frac{\partial \Phi_{\lambda_i}}{\partial t}\quad (4)$$

is present. The assumption of perfect conductor does not necessarily indicate that

$$\mathbf{E} = 0\quad (5)$$

inside, since there are kinetic energy phenomena. Nevertheless, when we assume further that the mass of the current carriers is infinitesimally small, macroscopically we cannot allow the change of the flux in the perfect conductor. But, microscopically, in the Maxwell-Lorentz electromagnetism, it is theoretically quite possible to assume a small change of the flux Φ_{λ_i} , because this is accomplished by only a small successive change of the route of each current carrier in the Maxwell-Lorentz world. Then, the condition stated in Eq. (3) is only required for the loop C_i 's that can converge to a point with a continuous deformation of the loop inside of the conductor. Therefore, in the minimum magnetic energy state, all the persistent currents should be on the surface and

there is no magnetic field inside the perfect conductor. Such a condition simply corresponds to the Meissner state. Of course the minimum energy state is important in thermodynamics, because, when the corresponding state is not associated with an appreciable decrease in the entropy the state must be realized and we believe that such is the case for our problem. A similar conclusion has been reached before from a different approach⁴⁾.

What we hope to emphasize here is the expectation that the Meissner effect is a classical phenomenon and that, since the electric current in conductors in general is known to be a drift current, there must be a general classical principle which maintain the surface drift current dynamically.

§3. Tricky Dynamical Structure of the Magnetic Energy

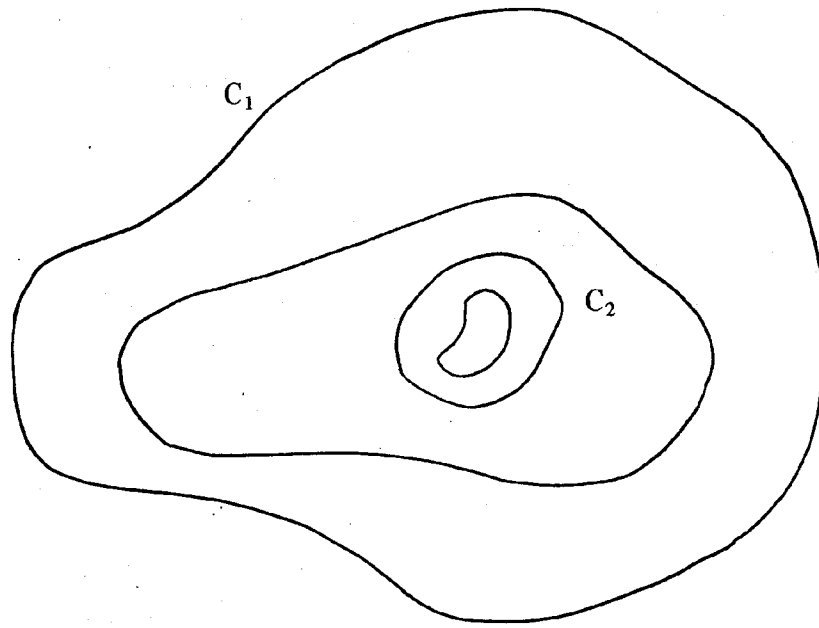
Although it is well known that the statistical physics for the magnetism of a magnetic entity which has permanent magnetic moments, and, for an entity which has no permanent magnetic moments must be different^{5),6)}, there has been no detailed analysis of the difference. Let us start our analysis from the case of two doubly connected superconductors, C_1 and C_2 with purely surface persistent currents I_1 and I_2 (Fig. 1). Here we assume the presence of an idealized superconductor from the first. After certain long classically strict calculations²⁾ we have finally

$$\begin{aligned} U_m &= \frac{1}{2C} (\Phi_1 I_1 + \Phi_2 I_2) \\ &= \frac{1}{2} (L_{11} I_1^2 + 2L_{12} I_1 I_2 + L_{22} I_2^2) \\ &= \frac{1}{2C^2 \Delta_L} (L_{22} \Phi_1^2 - 2L_{12} \Phi_1 \Phi_2 + L_{11} \Phi_2^2) \end{aligned} \quad (6)$$

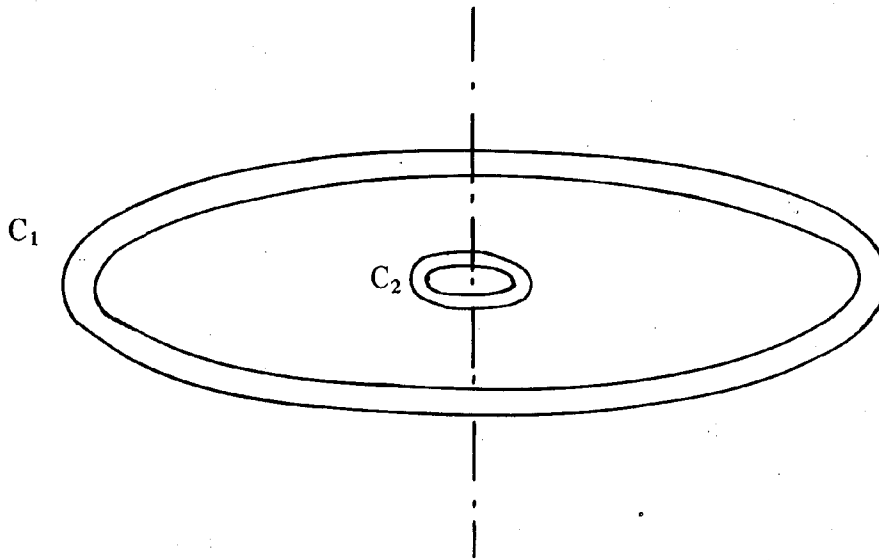
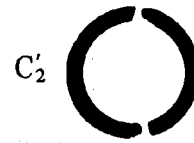
$$\Delta_L = L_{11} L_{22} - L_{12}^2 \quad (7)$$

Here, L_{11} , L_{22} and L_{12} are the effective self- and mutual- inductances of the total circuits C_1 and C_2 , and, Φ_1 and Φ_2 are the total magnetic flux confined in the circuits C_1 and C_2 respectively. Eq. (6) is quite rigorous and the only assumption needed is the superposition principle.

We regard Eq. (6) as the fundamental equation for the magnetic energy for analyzing our problem.



(a)



(b)

Fig. 1 Two doubly connected idealized superconductors C_1 and C_2 . C_2 's is the cross section of a spherical shell C_2 with holes in its two poles.

Now from Eq. (6), we get in general

$$\begin{aligned} \delta U_m &= L_{11} I_1 \delta I_1 + L_{12} (I_1 \delta I_2 + I_2 \delta I_1) + L_{22} I_2 \delta I_2 \\ &+ \frac{I_1^2}{2} \delta L_{11} + I_1 I_2 \delta L_{12} + \frac{I_2^2}{2} \delta L_{22} \\ &= I_1 \frac{\delta \Phi_1}{C} + I_2 \frac{\delta \Phi_2}{C} - I_1 I_2 \delta L_{12} - \frac{I_1^2}{2} \delta L_{11} - \frac{I_2^2}{2} \delta L_{22} \end{aligned} \quad (8)$$

First we shall analyze the case where a permanent magnetic moment, such as electron spin³⁾, is present. Then C_2 represents this microscopic entity with a permanent magnetic moment and C_1 represents a macroscopic current loop. Since, in this case, the main current distribution in C_2 and C_1 are determined separately and independently*, it is reasonable to assume²⁾

$$\delta L_{22} = 0, \quad \delta L_{11} = 0 \quad (9)$$

Then we have

$$\delta U_m - I_2 \frac{\delta \Phi_2}{C} - I_1 \frac{\delta \Phi_1}{C} = - I_1 I_2 \delta L_{12} \quad (10)$$

From Eq. (4)^{7),2)},

$$- I_\xi \frac{\delta \Phi_\xi}{C} = \iiint_{V_\xi} \mathbf{E} \cdot \mathbf{j} \delta t dV_\xi = \delta A_\xi \quad (11)$$

where δA_ξ is the work given to the current I_ξ through the induced electric field \mathbf{E} . When the current is supplied by a source, this energy is given to the source, and, when the current is a persistent current and the current has another mechanism of keeping the energy, then

$$\delta A_\xi = \delta U_{k\xi} \quad (12)$$

i. e., it transforms into the increase of the potential-like energy of the persistent current system ξ , $U_{k\xi}$. (k is taken from the word "kinetic") On the other hand,²⁾

$$- I_1 I_2 L_{12} = - \oint_{\lambda_1} \oint_{\mu} \frac{dl_\alpha \cdot dl_\beta}{4\pi c^2 r_{\alpha\beta}} I_1 I_2 = - \oint_{\mu_2} \frac{\mathbf{A}(r_\alpha)}{c} \cdot I_2 dl_\alpha$$

* Rigorous comparison of the order of the magnitudes of these independent and dependent current intensities are given in Ref. (2).

$$= - \iint_{S_2} \nabla \times \mathbf{A}(\mathbf{r}_\alpha) \frac{I_2}{c} \cdot d\mathbf{s}_\alpha = -\mathbf{H}_{21} \cdot \frac{I_2 \mathbf{s}_2}{c} = -(\mathbf{H}_{21} \cdot \boldsymbol{\mu}_2) \quad (13)$$

Here, \mathbf{H}_{21} is the magnetic field supplied from C_1 to C_2 and $\boldsymbol{\mu}_2$ is the magnetic moment of C_2 . In deriving Eq. (13), we have made a few reasonable approximations.²⁾ Now we get

$$\delta^* [- (\boldsymbol{\mu}_2 \cdot \mathbf{H}_{21})] = \delta [U_m + U_{k2} + U_{k1}] \quad (14)$$

Here* indicates that the variation should be performed only for the mutual location of $\boldsymbol{\mu}_2$ and C_1 .

Eq. (14) represents the fundamental origin of the famous Zeeman energy expression and we believe that the Zeeman expression is just an effective Hamiltonian, the variation of which represents the change of the total energy of the system.

In order to understand the implication of Eq. (14), we need one more structure of the problem. In this case, when the current of C_1 is maintained constant, then after a lengthy calculation we can get

$$\delta U_{k1} = \delta U_{k2} = -\delta U_m$$

so that

$$\delta [U_{k1} + U_m] = 0$$

$$\delta [U_m + U_{k2} + U_{k1}] = \delta U_{k1} = \delta^* [- (\boldsymbol{\mu}_2 \cdot \mathbf{H}_{21})] .$$

When, C_1 is an idealized superconductor for which no electromagnetic energy can be received through induction,

$$\delta U_{k1} = 0, \quad \delta U_m = 0$$

and again

$$\delta [U_{k1} + U_m] = 0$$

$$\delta [U_m + U_{k2} + U_{k1}] = \delta U_{k1} = \delta^* [- (\boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_{21})]$$

can be obtained. This means, that the usual treatment for an atom using the usual Hamiltonian is effectively all right, and the excess energy may be radiated from the considered atom, just according to the usual way of understanding. The analytical

procedure to obtain this result will, however, be left to a paper in near future.²⁸⁾ In these processes, however, δU_{k_1} is definitely involved and this transfer of energy can have a certain serious meaning in the thermodynamics of some magnetizable materials.

Next let us extend the analysis to the case where no rigid permanent magnetic moment can be assumed. From Eq. (4), we get

$$U_m = \frac{1}{2} (L_{11} I_1^2 + 2L_{12} I_1 I_2 + L_{22} I_2^2) \quad I_1, I_2 \quad (15)$$

$$= \frac{1}{2c^2 \Delta L} (L_{22} \Phi_1^2 - 2L_{12} \Phi_1 \Phi_2 + L_{11} \Phi_2^2) \quad \Phi_1, \Phi_2 \quad (16)$$

$$= \frac{1}{2} \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) I_1^2 + \frac{1}{2L_{22}} \frac{\Phi_2^2}{c^2} \quad I_1, \Phi_2 \quad (17)$$

$$= \frac{1}{2L_{11}} \frac{\Phi_1^2}{c^2} + \frac{1}{2} \left(L_{22} - \frac{L_{12}^2}{L_{11}} \right) I_2^2 \quad \Phi_1, I_2 \quad (18)$$

Now, let us fix the locations of the two conductors in their most symmetric configuration such as shown in Fig. 1(b), and consider only the change induced by the change in the two independent variable taken from I_1, I_2, Φ_1 and Φ_2 . Then

$$L_{11}, L_{22}, L_{12} > 0 \quad (19)$$

and L_{11}, L_{12} , and L_{22} are the fixed quantities. (20)

From Eqs. (15)–(18), we see

	Fixed Quantities,	Min. U_m Conditions,	Type only from U'_m	Final Type
I	I_1	$\Phi_2 = 0$	Meissner	Meissner
II	Φ_1	$I_2 = 0$	Normal conductor	Meissner
III	$I_1, I_2 $	$I_1 \uparrow \downarrow I_2$	Meissner	Zeeman
IV	$I_1, \Phi_2 $	$\pm \Phi_2$	No dependence	Zeeman
V	$\Phi_1, \Phi_2 $	$\Phi_1 \uparrow \downarrow \Phi_2$	Zeeman	Zeeman

(21)

Here, in the third column we show the minimum magnetic energy condition under the given restrictions. In the fourth and fifth columns, Meissner or Zeeman mean that the corresponding state has parallel or antiparallel magnetic moments of the two conductors.

The fourth column indicates the situation deduced if only the magnetic energy is

considered and the fifth indicates the situation deduced from all the energies involved, the actual situation expected physically.

As we see, the situation is very delicate and tricky. We regard that the most important are cases I and III. Since the entity 2 can see only the magnetic field from C_1 , this physical situation corresponds to constant I_1 . Case I tells us that, if there is no other condition, the $\Phi_2 = 0$ state has the minimum magnetic energy. It will be easy to see that this state just corresponds to the Meissner state of a simply connected superconductor. In case IV when we require that the magnitude of Φ_2 is constant, then, from Eq. (17), the energy has no dependence on the sign of Φ_2 . In case III, although the magnetic energy U_m becomes minimum when the magnetic moment by I_2 is antiparallel to the magnetic field by I_1 , we know from Eq. (14) that the total energy becomes minimum in the Zeeman state. When there is a current I_2 in a magnetic field, H_{21} , then the current must receive a Lorentz force which exerts a torque upon C_2 . When there is another energy and momentum reservoir, such as the lattice, in C_2 , then the system release the Zeeman energy of Eq. (14) to this reservoir, and C_2 will start a rotation. When, however, there is no such reservoir, then C_2 will start Larmor precession, keeping the Zeeman energy constant, which, of course, cannot maintain eternally. This is the reason that we conclude the Zeeman state will be its final type. The same principle cannot work in case I, because the presence of I_2 is not guaranteed. Case II as compared case I demonstrates tricky structure of the magnetic energy showing that a slight change in the fixed conditions results in a completely different mathematical result. Of course we know from the general principle of physics that, as the requirement for C_2 , case I is physically simple but case II is not, although we can construct case II by using a superconductor for C_1 ^{2),7)}. Case III, IV and V are quite similar. The difference between cases IV and V corresponds to the difference between case I and II. The spin magnetic moment of the electron will be close to case III³⁾. Although there are slight differences in these case, there is a definite torque exerting towards the minimum Zeeman energy state.

In conclusion, we can say that the case with a permanent magnetic moment and the case with no permanent magnetic moment must be distinguished. The Zeeman state is for the former, but, for the latter, the Meissner state will be realized because this state definitely has the minimum magnetic energy and there is no further dynamical requirement.

Introduction of A New Principle in the Theory of Magnetism II

In these analyses, we have assumed that the processes are quasi-static, i. e., C_1 and C_2 are assumed to couple electromagnetically tightly, and we have neglected the time for the electromagnetic wave to travel from C_2 to C_1 or from C_1 to C_2 . At first glance, it looks that this may not be the case when the diameter of C_2 is extremely large. Careful analysis, however, has shown⁷⁾ that, even in the latter case, the changing electromagnetic field constructs a local mode which couples tightly with the change of the electromagnetic quantities of the source and there are no appreciable radiating electromagnetic waves. In both these situations, since C_2 can see only the magnetic field at the location of C_2 , we can conclude that the major physical phenomena for C_2 must be not different in the two cases. In the following calculations, although we frequently use the idealized electromagnetically tightly coupled superconductor as the source of the applied magnetic field, this is just for the purpose of simplification and general applicability of the results must still be present.

§4. New Statistical Thermodynamics of Magnetizable Materials.

In order to reorganize the physics of materials in a magnetic field taking into account the role of the magnetic energy correctly, the obvious procedure is to find out the material function which is to be minimized. We found that this can be done by exploring the statistical thermodynamics of the system. Now, the thermodynamics of ferromagnets, and diamagnets has been believed to be well understood^{8),9),10),11)}. However, there are some different opinion¹²⁾ and different approaches¹³⁾, and we believe that the thermodynamics has not been well understood.

Let us present our analysis. For simplicity we assume as the specimen a unit volume material taken from a very long cylindrical specimen, 2, which is immersed in a magnetic field of a similar long coaxial cylindrical superconducting coil, 1, which maintains a supercurrent for supplying the magnetic field to the specimen. In this way we can neglect the boundary or shape effect of the problem. In order to avoid unnecessary complications, we shall make every kind of simplification hereafter.

A. Curie-Langevin-Debye's Paramagnetism

Let us first assume that the magnetic elements in the specimen have freely rotatable permanent magnetic moments and they are present independently, or well separated.

Then the important microscopic energy relation is Eq. (14) and we know from a general principle in physics that the energy released from the system is present initially at the place where the change has been generated. The the total entropy S of the system will be represented by

$$S = S(U_L, M) \quad (22)$$

where M is the magnetization and U_L is the energy of the lattice or the energy which is not related directly to the electromagnetism. The magnetism related energies of

$$U_m + U_{k1} + \sum_i U_{k2}^i \quad (23)$$

where i means individual magnetic moment, are first left out of the consideration.

Then

$$ds = \left(\frac{\partial S}{\partial U_L} \right)_M dU_L + \left(\frac{\partial S}{\partial M} \right)_{U_L} dM \quad (24)$$

From Eq. (24), the equation

$$dU_L = TdS + HdM \quad (25)$$

should apply. Eq. (25) can be justified from the following two considerations.

1), when the heat dQ is given to the system, then

$$\begin{aligned} dU_L &= TdS_L = TdS - TdS_M \\ &= TdS - dQ_M = TdS + HdM \end{aligned} \quad (26)$$

where S_L and S_M are the entropies of the lattice and the paramagnetic system, respectively. From Eq. (14), it is obvious that

$$HdM = -dQ_M = -TdS_M \quad (27)$$

is the energy or the heat released from the paramagnetic system to the lattice.

2), when $dQ = 0$, and $dM \neq 0$, then

$$dS = 0 \quad (28)$$

and

$$dU_L = HdM = TdS_L = -TdS_M \quad (29)$$

Since Eq. (25) has been justified in these two cases, it should be correct generally.

We know that there is a radiation energy equation¹⁴⁾

$$\begin{aligned}
 -c \iiint \mathbf{E} \times \mathbf{H} \cdot \delta \mathbf{t} d\mathbf{s} &= \iiint (\mathbf{E} \cdot \delta \mathbf{D} + \mathbf{H} \cdot \delta \mathbf{B} + \mathbf{E} \cdot \mathbf{j} \delta t) dV & (30) \\
 &\rightarrow \iiint (\mathbf{H} \cdot \delta \mathbf{H} + \mathbf{H} \cdot \delta \mathbf{M}) dV.
 \end{aligned}$$

Eq. (27) tells that, in this case, the energy expressed by $\mathbf{H} \cdot \delta \mathbf{M}$ is transformed exclusively into the increase of the energy U_L .

The Halmholtz free energy, enthalpy, and Gibbs free energy, F^I , \mathcal{A}^I , and G^I , are

$$F^I = U_L - TS \quad , \quad dF^I = -SdF + HdM \quad (31)$$

$$\mathcal{A}^I = U_L - HM \quad , \quad d\mathcal{A}^I = TdS - MdH \quad (32)$$

$$G^I = U_L - TS - HM \quad , \quad dG^I = -SdT - MdH \quad (33)$$

From thermodynamics, we can conclude that at constant temperature and constant magnetic field, G^I should be minimized. When we can assume that U_L is not dependent on M , we get the usual Zeeman energy type statistics from Eq. (33). It should be noted that we can use

$$HdB \quad (34)$$

in Eq. (25) if we add

$$\frac{H^2}{2} \quad (35)$$

to the internal energy U_L . This is strictly allowed physically also from Eq. (30).

Then we have

$$U^{II} = U_L + \frac{H^2}{2} \quad (36)$$

$$dU^{II} = TdS + HdB \quad (37)$$

$$F^{II} = U^{II} - TS \quad , \quad dF^{II} = -SdT + HdB \quad (38)$$

$$\mathcal{A}^{II} = U^{II} - HB \quad , \quad d\mathcal{A}^{II} = TdS - BdH \quad (39)$$

$$G^{II} = U^{II} - HB - TS$$

$$\begin{aligned}
&= U_L + \frac{M^2}{2} - \frac{B^2}{2} - TS \\
&= U_L - \frac{H^2}{2} - HM - TS \quad , \quad dG^{II} = -SdT - BdH \quad (40)
\end{aligned}$$

At constant temperature T and applied magnetic field H , G^{II} should be minimized and the result is identical to the case of Eq. (33).

It should be noted that in this treatment we do not regard the Zeeman energy as a part of the internal energy, because, from Eq. (14), it is definitely related to the external world. $(H^2/2)$ will also be related to the external world. But, mathematically, we can add it to the internal energy without introducing any different result. This is because, from Eqs. (29) and (30), in this idealized Curie-Langevin-Debye paramagnetism, this part can be regarded as a strictly reversible magnetic potential energy.

B. Larmor Diamagnetism

Two physically identical treatments I and II are also possible in this case. Now there is an important difference between diamagnetism and paramagnetism. In paramagnetism, it is at least theoretically possible to take off the magnetic field from the specimen adiabatically while keeping the magnetization practically constant. Maxwell's demon can do this work without consuming energy theoretically. But in diamagnetism, this is not possible because the magnetization is due to the Larmor precession, which can exist only in the presence of a magnetic field. We have to admit that magnetic field and magnetization are inseparable in diamagnetism.

Now, let us assume an idealized non-conductive diamagnet such as the molecular crystal. The total energy in this case is

$$U^{\text{total}} = U_m + U_{k1} + \sum_i U_{k2}^i + U_L \quad (42)$$

Let us define the internal energy

$$U^I = U_L + \sum_i U_{k2}^i \quad (43)$$

or

$$U^I = U^{\text{total}} - U_{k1} - U_m \quad (44)$$

Then

$$S = S(U^I, B) \quad (45)$$

and we have concluded that

$$dU^I = TdS - MdB \quad (46)$$

The second term of Eq. (46) is quite important and is based on the energy transfer relation of the Maxwell equations and the Maxwell-Lorentz equations⁷⁾. In this case, the magnetic energy of the Maxwell-Lorentz world, u_m , can be classified as

$$u_m = \iiint \frac{h^2}{2} dV = \iiint \frac{B^2}{2} dV + \iiint \frac{(h')}{2} dV \quad (47)$$

where

$$\bar{h} = B, \quad h' = h - B, \quad \bar{h}' = 0. \quad (48)$$

we should regard the first term as the macroscopic long range magnetic energy, U_m , in the Maxwell world and the second term as a part of the internal energy

$$\sum_i U_{k2}^i \quad (49)$$

because, in the Larmor diamagnetism, the short range magnetic energy must couple inseparably with the motion of the electrons²⁸⁾. This classification of the magnetic energy is not possible in the Curie-Langevin-Debye paramagnetism, because one of the component of B , i. e., M is concentrated in very small regions where the permanent magnetic moments are present, and, as shown in Eqs. (36) and (37), H is more important than B there. Now in the present case, in terms of Eq. (30), we get

$$H \cdot dB = d\left(\frac{B^2}{2}\right) - M \cdot dB \quad (50)$$

Then, $-M \cdot dB$ must be the work given to U^I . This conclusion can be justified from the Maxwell-Lorentz equations also. We have⁷⁾

$$\nabla \times h^\mu = \frac{I^\mu}{c} + \frac{1}{c} \frac{\partial e^\mu}{\partial t} \quad (51)$$

$$\nabla \times e = -\frac{1}{c} \frac{\partial h}{\partial t} \quad (52)$$

$$-c \nabla \cdot (e \times h^\mu) = h^\mu \cdot \frac{\partial h}{\partial t} + e \cdot I^\mu + e \cdot \frac{\partial e^\mu}{\partial t} \quad (53)$$

$$-c \iint_S e \times h^\mu \cdot ds = \iiint_V \left[h^\mu \cdot \frac{\partial h}{\partial t} + e \cdot I^\mu + e \cdot \frac{\partial e^\mu}{\partial t} \right] dV. \quad (54)$$

Here

$$\iiint \mathbf{I}^\mu dV = \sum_i -e_i v_i^\mu \quad (55)$$

is the effective current of the persistent electron movements which are contribution to the Larmor diamagnetism, and \mathbf{h}^μ and \mathbf{e}^μ are the magnetic and electric fields which are associated with these electron movements. \mathbf{h}^μ and \mathbf{e}^μ can be defined in each place locally by taking a small needle volume along the magnetization⁷⁾. Further, it is geometrically reasonable to assume

$$-c \iint_S \mathbf{e} \times \mathbf{h}^\mu \cdot d\mathbf{S} = -c \iint_S \mathbf{e} \cdot \mathbf{h}^\mu \times d\mathbf{S} = 0 \quad (56)$$

at the surface of the specimen volume⁷⁾. Eq. (56) means that \mathbf{e} and \mathbf{h}^μ are not correlated and the energy transfer through magnetomechanical actions such as magnetostriction are neglected. Then,

$$- \iiint_V \mathbf{M} \cdot \frac{\partial \mathbf{B}}{\partial t} dV = \iiint_V \left[\mathbf{e} \cdot \mathbf{I}^\mu + (\mathbf{h}^\mu)' \cdot \frac{\partial \mathbf{h}'}{\partial t} + (\mathbf{E} + \mathbf{e}') \cdot \frac{\partial \mathbf{e}^\mu}{\partial t} \right] dV \quad (57)$$

where

$$(\mathbf{h}^\mu)' = \mathbf{h}^\mu - \overline{\mathbf{h}^\mu} = \mathbf{h}^\mu - \mathbf{M} \quad (58)$$

$$\mathbf{h}' = \mathbf{h} - \overline{\mathbf{h}} = \mathbf{h} - \mathbf{H} - \mathbf{M} \quad (59)$$

$$\mathbf{e}' = \mathbf{e} - \overline{\mathbf{e}} = \mathbf{e} - \mathbf{E}$$

When we assume that, in a small needle region, the only origin of the magnetic moment related fluctuation is due to the change in \mathbf{h}^μ , we can derive from Eq. (57)

$$- \iiint_V \mathbf{M} \cdot \frac{\partial \mathbf{B}}{\partial t} dV = \iiint \left[\mathbf{e} \cdot \mathbf{I}^\mu + \frac{\partial}{\partial t} \left\{ \frac{(\mathbf{h}')^2 + (\mathbf{e}')^2}{2} \right\} \right] dV \quad (60)$$

Obviously $\mathbf{e} \cdot \mathbf{I}^\mu$ is the work given to $\sum_i U_{k2}^i$ and, from the argument of Eqs. (47), (48), and (49), we can conclude that,

$$- \mathbf{M} \cdot \delta \mathbf{B} = \delta \left(\sum_i U_{k2}^i \right) \quad (61)$$

which is in excellent agreement with the interpretation of Eq. (50). It is to be noted, however, that there is a question whether the usual Hamiltonian does include the term

$$\iiint \frac{(\mathbf{h}')^2}{2} dV$$

Introduction of A New Principle in the Theory of Magnetism II

of Eq. (47), or not. This is one of the essential parts of our study, for which an important analysis will be given in §'s 5 and 6. The conclusive analysis will be given in paper III²⁸⁾. From Eq. (44) U_m is not included in U^I and we have the relation (46). Then

$$T = \left(\frac{\partial U^I}{\partial S} \right)_B, \quad M = - \left(\frac{\partial U^I}{\partial B} \right)_S \quad (62)$$

$$F^I = U^I - TS, \quad dF^I = -SdT - MdB \quad (63)$$

$$\mathcal{A}^I = U^I + MB, \quad d\mathcal{A}^I = TdS + BdM \quad (64)$$

$$G^I = U^I - TS + MB, \quad dG^I = -SdT + BdM \quad (65)$$

Now, in the actual experiment, we have to fix T and H . Therefore, let us introduce

$$I = U^I + \frac{M^2}{2}, \quad dI = TdS - MdH \quad (66)$$

Then,

$$F' = I - TS = U_L + \sum_i U_{k2}^i + \frac{M^2}{2} - TS$$

$$dF' = -SdT - MdH \quad (67)$$

$$S = - \left(\frac{\partial F'}{\partial T} \right)_H, \quad M = - \left(\frac{\partial F'}{\partial H} \right)_T \quad (68)$$

Therefore the free energy F' should be minimized. Now it becomes large when $|M|$ increases. As we see, $M^2/2$ seems to play the rôle of the intrinsic internal energy of the diamagnet. This situation will be analyzed more in detail in §6.

In this case also it is possible to make another treatment in which the magnetic energy, U_m ⁷⁾.

$$U_m = \frac{B^2}{2} \quad (69)$$

is included in U . When this has been done, then

$$U^{II} = U_L + \sum_i U_{k2}^i + \frac{B^2}{2}$$

$$dU^{II} = TdS + HdB \quad (70)$$

$$F^{II} = U^{II} - TS, \quad dF = HdB - SdT \quad (71)$$

$$\mathcal{A}^{II} = U^{II} - HB, \quad d\mathcal{A} = TdS - BdH \quad (72)$$

$$G^{\text{II}} = U^{\text{II}} - TS - HB = U_L + \sum_i U_{k2}^i + \frac{M^2}{2} - \frac{H^2}{2} - TS \quad (73)$$

$$dG^{\text{II}} = -SdT - BdH \quad (74)$$

The equilibrium condition at constant T and H is to minimize the Gibbs free energy G^{II} . Now from Eqs. (74) or (67),

$$B = - \left(\frac{\partial G^{\text{II}}}{\partial H} \right)_T \quad (75)$$

$$M = - \left(\frac{\partial}{\partial H} \right)_T (U_L + \sum_i U_{k2}^i) - M \left(\frac{\partial M}{\partial H} \right)_T + T \left(\frac{\partial S}{\partial H} \right)_T \quad (76)$$

$$= - \left(\frac{\partial}{\partial H} \right)_T (\sum_i U_{k2}^i - TS) \quad (77)$$

since $(\delta M/\delta H)$ will be very small in a usual weak diamagnet. This is an important point which we shall discuss later for the Fermi gas. From Eq. (44), $\sum_i U_{k2}^i$ can include all the internal interactions of the diamagnetic entities and this is usually represented by the Hamiltonian of the entities. Then Eq. (77) tells us that a kind of Helmholtz free energy constructed from this Hamiltonian can in practice give accurate magnetization predictions, provided that the resultant diamagnetic moment is small.

C. Superconductor or An Idealized Fermi-Gas.

Now let us analyze the case of the superconductor. As we all know, this is a difficult problem and it will be not possible to construct a rigorous framework of thermodynamics without assumptions. We believe, however, that we have succeeded in constructing a fairly reasonable thermodynamical description. It is to be noted that, by the study of part I²⁾, we can regard the superconductor as merely a perfect conductor. Quantum effects are important in obtaining perfect conduction, but there is not so much mystery after that.

At first we should point out that the previous thermodynamical treatments^{15),16)} of the superconductor are inadequate in that they regard all the body as a single uniform subject. Since the major volume of a superconductor in an external magnetic field has no magnetic field, its thermodynamical energy must be identical to the energy which is present without the application of the magnetic field. Then, since the surface current layer is in intimate contact with the internal body, some thermodynamical func-

tion will be identical over the entire body of the superconductor, irrespectively of the presence of the magnetic field and the drift current.

Let us take a thin coaxial cylindrical shell unit volume in the superconductor and apply the second procedure of the diamagnet, with an additional condition that $\mathbf{M} = 0$ and $\mathbf{j} \neq 0$. We know²⁾ in this case that, since the magnetic field energy couples intrinsically with the other energies, this seems the only adequate procedure. Here, we assume that the shell is so thin* that it can be located inside of the surface current layer and the penetrated magnetic field \mathbf{H} is uniform over this volume. Then

$$U = U_L + \sum_i U_{k2}^i + \frac{H^2}{2} \quad (78)$$

will be obtained. Here $\sum_i U_{k2}^i$ will mean all the internal energies of the electron system, which are composed of the kinetic energy of the electrons and the electrons and the electric interaction energy with the lattice and the microscopic electric and magnetic mutual correlation energies of the electrons. The macroscopic magnetic interaction energy will be treated separately. Since we know that \mathbf{B} is identical to \mathbf{H} in the superconductor, we put $\mathbf{B} = \mathbf{H}$ from the first. Then the entropy

$$S = S(U, H) \quad (79)$$

and from Eqs. (70) and (30),

$$dU = TdS + HdH \quad (80)$$

can be obtained. In Eqs. (79) and (80), we have already assumed that thermodynamically, the current density $\mathbf{j}(\mathbf{r})$ is not independent of the magnetic field strength H . In deriving the last term of Eq. (80) from Eq. (40), the only one doubt concerns the effect of the $\mathbf{E} \cdot \mathbf{j} \delta t$ term. We, however, have concluded that this term, in contrast to $\mathbf{e} \cdot \mathbf{I}^\mu \delta t$ of the ideal diamagnet, cannot be distinguished from the heat input in our itinerant conduction electron system, and should be regarded as having been represented by TdS already. This will be an important assumption for which the relation to quantum effect should be discussed. One should remember, however, that the Joule heat in a normal conductor is regarded as nothing but the heat input and we keep the same physical interpretation in this case. Then

$$F = U - TS = U_L + \sum_i U_{k2}^i + \frac{H^2}{2} - TS \quad (81)$$

* Could be as thin as the width of a few Å.

$$dF = -SdT + HdH \quad (82)$$

and, as in Eq. (73),

$$G = F - H^2 = U_L + \sum_i U_{k2}^i - \frac{H^2}{2} - TS \quad (83)$$

$$dG = -SdT - HdH \quad (84)$$

Eqs. (83) and (84) tell us that the Gibbs free energy in this case is dependent on the magnitude of the penetrating magnetic field H with a negative sign as compared with the positive sign of the same term in the Helmholtz free energy F . Thermodynamically, the Gibbs function is important for phase equilibrium¹⁷⁾. Let us assume that the number of the interior conduction electrons which are commuting rapidly is a constant and that normal thermodynamics is still effective in this case. Then from Gibbs-Duhem's theorem, the Gibbs function G should be a constant over the whole volume of the superconductor¹⁷⁾. Then it is obvious that G must be independent of H , so that, in the surface current region,

$$\Delta \left(\sum_i U_{k2}^i \right) - T \Delta S = \frac{H^2}{2}$$

must be correct. Here, Δ means the increase from the value at $H = 0$. When we assume further that

$$\Delta S = 0 \quad (85)$$

because all the electrons may have only a constant shift of their velocity in the velocity space because of the action of the magnetic field²⁾, then we can expect

$$\Delta \left(\sum_i U_{k2}^i \right) = \frac{H^2}{2} \quad (86)$$

This equation has turned out to be identical to the London equation. If we can assume

$$\Delta \left(\sum_i U_{k2}^i \right) = n_s \frac{m}{2} v_D^2 \quad (87)$$

and

$$\mathbf{j} = -n_s e v_D \quad (88)$$

where n_s is the number of the superconducting electrons and v_D is their drift velocity, we can derive easily

$$H = H_0 \exp \left(-\sqrt{\frac{n_s}{m}} \cdot \frac{e}{c} \eta \right) \nabla \zeta \quad (89)$$

$$\mathbf{v}_D = \frac{H_0}{\sqrt{n_s m}} \exp\left(-\sqrt{\frac{n_s}{m}} \cdot \frac{e}{c} \boldsymbol{\eta}\right) \nabla \xi \quad (90)$$

Here; (ξ, η, ζ) are the cartesian coordinates, of which η is the normal to the surface boundary and ξ is parallel to the circumferential direction. Eq. (87) is the relation normally accepted. This relation can be derived in this paper from Eq. (109), or, from Eq. (87) of Ref. (2), thermodynamically, in which the magnetic energy has an identities of

$$\frac{-e \bar{\mathbf{v}} \cdot \mathbf{A}}{c} = -\frac{H^2}{2n_s} = -\frac{1}{n_s} \Delta \left(\sum_i U_{k2}^i \right) = -\frac{m}{2} \bar{\mathbf{v}}_D^2$$

Although here is an interface between quantum physics, the Maxwell-Lorentz classical physics, and the Maxwell physics, we believe that the relation (87) itself can still be understood classically. Since there must be strong electric Coulomb correlations, the movement of the electron system is essentially collective and thermodynamical, and n_s will be accurately constant. Then because of Eq. (109), the increase in the kinetic energy has to be cancelled by the corresponding decrease in the total magnetic energy which results in Eq. (86).

In §6, and paper III²⁸⁾, we shall give the fundamental electro-dynamical principle which leads to these proposed relations. A very important new magnetic electron-electron interaction term will be introduced there.

In order to check the critical field for the normal to superconducting phase transformation, the Gibbs function of the normal phase must be calculated. Then

$$U^n = U_L^n + \sum_i U_{k2}^i + \frac{B^2}{2}, \quad dU^n = TdS^n + HdB \quad (91)$$

$$F^n = U_L^n + \sum_i U_{k2}^i + \frac{B^2}{2} - TS^n \quad (92)$$

$$\begin{aligned} G^n &= U_L^n + \sum_i U_{k2}^i + \frac{B^2}{2} - HB - TS^n \\ &= U_L^n + \sum_i U_{k2}^i + \frac{B^2}{2} - TS^n \quad \left(\frac{M^2}{2} \ll \frac{H^2}{2} \right) \end{aligned} \quad (93)$$

Then the phase equilibrium at $H = H_c$ is

$$\begin{aligned} G^n &= G^s \\ U_L^n + \left(\sum_i U_{k2}^i \right)^n - \frac{H_c^2}{2} - TS^n &= U_L^s(H) + \left(\sum_i U_{k2}^i \right)_H^s - \frac{H^2}{2} - TS_H^s \quad (94) \\ &= U_L^s(0) + \left(\sum_i U_{k2}^i \right)_0^s - TS_0^s \end{aligned}$$

Therefore,

$$\mathcal{F}^n(H_c) = \mathcal{F}^s(0) + \frac{H_c^2}{2} \quad (95)$$

Here \mathcal{F} means the usually used Helmholtz free energy which neglects the magnetic energy. Although this way of thinking is quite different from the existing theory^{15),16),18)}, the final result is similar. What makes the superconductor different from the diamagnet is the difference between Eqs. (70) and (80). For the diamagnet, since there is \mathbf{M} , there is a microscopic persistent current reservoir the increase in the energy of which being represented by $-MdB$, but for the superconductor, there is no such explicit microscopic reservoir. As we see in Eq. (87), however, there is an implicit reservoir in the total kinetic energy of the electrons, when the magnetic field \mathbf{H} has penetrated.

Now, in the superconductor, what free energy should be minimized? This is a different problem, since the system is not homogeneous and one of the independent parameters, i. e., external field intensity, H^{ext} , is implicit in all the hitherto described equations.

§5. Thermodynamical Function of A Superconductor and Classical Derivation of the London Equation

In §4, we have already derived the London equation (90). Here, we shall derive the same equation from another point of view.

Now the total energy U^{total} of the system will be

$$U^{\text{total}} = \iiint [U_L(\mathbf{r}) + \sum_i U_{k^2}^i(\mathbf{r}) + \frac{\{H(\mathbf{r})\}^2}{2}] dV \quad (96)$$

and the total entropy S^{total} will be

$$S^{\text{total}} = \iiint S(U, H) dV \quad (97)$$

Then

$$\Delta S^{\text{total}} = \iiint [(\frac{\partial S}{\partial U})_H \Delta U + (\frac{\partial S}{\partial H})_U \Delta H] dV \quad (98)$$

$$\begin{aligned} \Delta U^{\text{total}} &= T \Delta S^{\text{total}} - \iiint T (\frac{\partial S}{\partial H})_U \Delta H dV \\ &= T \Delta S^{\text{total}} + \iiint H \Delta H dV \end{aligned} \quad (99)$$

Introduction of A New Principle in the Theory of Magnetism II

In deriving Eq. (99), Eq. (80) is employed. Now, from Eq. (99),

$$H = H^{\text{ext}} + H^{\text{int}} \quad (100)$$

$$\Delta H = \left[1 + \left(\frac{\partial H^{\text{int}}}{\partial H^{\text{ext}}} \right)_S \right] \Delta H^{\text{ext}} \quad (101)$$

Here, H^{int} means the magnetic field induced internally. Then, the total Helmholtz free energy

$$F^{\text{total}} = U^{\text{total}} - TS^{\text{total}} \quad (102)$$

$$\Delta F^{\text{total}} = -S^{\text{total}} \Delta T + \left[\iiint H \left(1 + \frac{\partial H^{\text{int}}}{\partial H^{\text{ext}}} \right) dV \right] \Delta H^{\text{ext}} \quad (103)$$

so that, at constant temperature and external magnetic field, $F^{\text{total}}(T, H^{\text{ext}})$,

$$F^{\text{total}} = \iiint \left[U_L + \sum_i U_{k2}^i + \frac{H^2}{2} - TS \right] dV \quad (104)$$

should be minimized. In this way, we get the thermodynamical function which contains magnetic energy term with its original sign. This is essentially different from the case of a diamagnet, as is seen from Eq. (73). This situation comes from the fact that H is not an independent quantity in this case, as is shown in Eq. (100).

Noticing that the boundary effect is essential, it is not so easy to minimize F^{total} at constant T and H^{ext} . However, as we mentioned already, the superconductor is an ideal material for magnetism and, the fact that the drift current exactly obeys Maxwell's equations encourages us to believe that there must be a general simple principle in the solution of Eq. (104).

Let us direct our attention to the kinematical motion of a single charge after the equilibrium has been attained. Then its Hamiltonian will be

$$\mathcal{H} = \frac{\left[\mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{r}) \right]^2}{2m} - e\phi(\mathbf{r}) \quad (105)$$

This charge could be a Cooper pair of the two electrons.

We shall assume for convenience, however, that this charge is that of an electron. Here $\mathbf{A}(\mathbf{r})$ and $\phi(\mathbf{r})$ are the final stationary self consistent vector and scalar potentials in the specimen. Eq. (105) represents the kinetic and electric interaction energies of $\sum_i U_{k2}^i$

in Eq. (104). Although we know that, if $\mathbf{A}(\mathbf{r})$ and $\phi(\mathbf{r})$ are stationary, Eq. (105) represents the correct Hamiltonian, by which the trajectory of this electron is accurately described, we believe that this description has no significant meaning in our problem, since we have high density electrons which are interacting mutually and $\phi(\mathbf{r})$ cannot be stationary even in the first approximation. Although we have developed the kinematical analysis of Eq. (105) in part I²⁾, it will be suitable only for dilute systems such as the plasma. Now one of the reliable quantities in the present thermostistical problem should be the energy of the total system. Let us calculate the electromagnetic interaction energy of the system in the framework of the Maxwell-Lorentz electromagnetism. The fundamental equations are^{1),7)}

$$\begin{aligned}
 u_e + u_m &= \iiint \left(\frac{\mathbf{e}^2}{2} + \frac{\mathbf{h}^2}{2} \right) dV \\
 &= \iiint \left[\frac{(\mathbf{E} + \mathbf{e}')^2}{2} + \frac{(\mathbf{H} + \mathbf{h}')^2}{2} \right] dV \\
 &= \iiint \left[\frac{\mathbf{E}^2 + \mathbf{H}^2}{2} + \frac{\mathbf{e}'^2 + \mathbf{h}'^2}{2} \right] dV \\
 &= \iiint \iiint \frac{\rho(\mathbf{r}_\alpha) \rho(\mathbf{r}_\beta)}{8 \pi r_{\alpha\beta}} dV_\alpha dV_\beta + \iiint \iiint \frac{\rho(\mathbf{r}_\alpha) \rho(\mathbf{r}_\beta) \mathbf{v}(\mathbf{r}_\alpha) \cdot \mathbf{v}(\mathbf{r}_\beta)}{8 \pi r_{\alpha\beta} c} \cdot dV_\alpha dV_\beta \\
 &\quad + \iiint \frac{\mathbf{e}'^2 + \mathbf{h}'^2}{2} dV \\
 &= \sum_{i \neq j} \frac{e_i e_j}{8 \pi r_{ij}} + \sum_{i \neq j} \frac{(\mathbf{e}_i \mathbf{v}_i) \cdot (\mathbf{e}_j \mathbf{v}_j)}{8 \pi r_{ij} c^2} + \iiint \frac{\mathbf{e}'^2 + \mathbf{h}'^2}{2} dV \quad (106)
 \end{aligned}$$

It is an interesting feature of the structure of electromagnetism that the macroscopic electric and magnetic energies are expressed by the first and second terms of the last expression of Eq. (106)^{1),7)}. Here, we have enumerated all the charges, including those of ion cores and of the external magnetic field source. By an elementary calculation, it is easy to show that the radiation energies which are traveling in space are extremely small in this kind of problem in which the highest velocity is less than $10c^{-2}$ and the motion of each electron is not correlated for the radiation⁷⁾. In this quasistatic situation, all the electron movements can be regarded as tightly coupled to the total electromagnetic energy with Eq. (106). The second term of the last expression of Eq. (106) is the magnetic orbit-orbit interaction, which is usually not only neglected but also disregarded in elementary Hamiltonians of atoms. In our problem, since the first term must be nearly constant and the third term is inseparable from the kinetic energy of

the electrons this is the most important term²⁸⁾. Now, the effective parts of the electromagnetic energies of Eq. (106), which are related to i -th electron, are

$$\Delta_i(u_e + u_m) = e_i \phi_i(\mathbf{r}_i, t) + e_i \frac{\mathbf{v}_i(t)}{c} \mathbf{A}_i(\mathbf{r}_i, t) \quad (107)$$

Here,

$$\begin{aligned} \phi_i(\mathbf{r}_i) &= \sum_{j \neq i} \frac{e_j}{4\pi r_{ij}} \approx \phi(\mathbf{r}_i) \\ \mathbf{A}_i(\mathbf{r}_i) &= \sum_{j \neq i} \frac{e_j \mathbf{v}_j}{4\pi r_{ij} c} \approx \mathbf{A}(\mathbf{r}_i) \end{aligned} \quad (108)$$

We know that, in the actual situation, in which all the electrons are distributed quite uniformly, $\phi_i(\mathbf{r}_i)$ and $\phi(\mathbf{r}_i)$ or $\mathbf{A}_i(\mathbf{r}_i)$ and $\mathbf{A}(\mathbf{r}_i)$ are not different. Eq. (105) does not contain the magnetic interaction energy of the second term of Eq. (107). A fundamental detailed explanation of this point will be given in paper III. In this way, we get the thermodynamical energy expression of a single electron as²⁾

$$\begin{aligned} U' &= \frac{[\mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{r})]^2}{2m} - e\phi(\mathbf{r}) - \frac{e\mathbf{v} \cdot \mathbf{A}(\mathbf{r})}{c} \\ &= \frac{\mathbf{p}^2}{2m} - e\phi(\mathbf{r}) - \frac{e^2}{2mc^2} \mathbf{A}^2 \end{aligned} \quad (109)$$

Accordingly we get an important conclusion that the thermodynamical energy expression of an electron is different from the Hamiltonian of the same electron in this case. Now let us change the viewpoint. Since we are dealing with a collective motion of an enormous number of electrons, let us regard Eq. (109) as a representative expression of a number of electrons which have cylindrically identical kinematical state at every symmetrical portion of a thin cylindrical shell in the specimen. Then we can regard Eq. (109) as the thermodynamical weight of the electrons at the location \mathbf{r} . Then when we have fixed the location \mathbf{r} and observe the momentum distribution of the electrons which pass through this location, we should expect from symmetry that

$$\overline{\mathbf{p}} = 0, \quad \overline{m\mathbf{v}} = \frac{e}{c} \mathbf{A}(\mathbf{r}) \quad (110)$$

provided that the derived solution can satisfy selfconsistency requirement. Here double bar means average over electrons. This is just the London equation²⁾. (In normal con-

ductors, because of the presence of the scattering by the lattice, the additional requirement would be $\bar{v} = 0$, which will lead to inconsistency with Eq. (110).)

Physically, Eq. (109) tells that the thermodynamical energy is considerably raised for the paramagnetic surface electrons which rotate clockwise in the boundary area making repeated collisions^{19),2)} and the number of these electrons diminishes by the thermal processes. It is easy to show that the increase can be as high as several tens of electron volts for a centimeter sized specimen²⁾. Therefore, it is easy to realize that the Meissner state can be generated, as a result of the thermal annihilation of these high energy paramagnetic electrons²⁾. It also should be mentioned that when the magnetic field is applied to a superconductor from outside, this change of state occurs dynamically and adiabatically as well by the action of the induced electric field E at the surface²⁾. Therefore, actually, the famous figure 5 of Ref. (5) will never be realized.

It is also to be noted that, if the specimen is not simply connected, then the well-known technical gauge change is necessary in Eq. (110), because otherwise self-consistency cannot be obtained.

§6. Environmental Situations and Discussions

In part²⁾, we have concluded that there was an insufficient understanding in the treatment of the magnetic energy of an externally applied magnetic field, and after introducing a correct way of processing this energy, it was stated that Miss Van Leeuwen's theorem must be wrong, that perfect conduction must lead to the Meissner effect, and that the usual treatment of Landau's diamagnetism will be incorrect in that it disregards the high magnetic energy of the orbitally paramagnetic electrons^{23)~27)}.

We believe that this paper has established these statements in terms of thermodynamical functions for the idealized paramagnet, diamagnet, and superconductor.

Here, we shall discuss several of the important points of our study. The first one is the physical meaning of the vector potential A . We insist that, as shown in Eq. (108), we should regard the vector potential A in the Lorentz gauge as a real physical entity and other than the mathematical technical gauge transformation, there is no physically significant freedom for the gauge transformation⁷⁾. Only one exception is the propagating wave, but, under given experimental conditions, they must also be uniquely determined. Detailed discussion on this most important problem will be made in paper III²⁸⁾, in which the presence of a fundamental orbit-orbit interaction of two moving

electrons will be established. In our situation, this interaction reduces to the form of

$$\frac{(-e\mathbf{v}_1) \cdot (-e\mathbf{v}_2)}{4\pi r_{12} c^2}$$

which represents the fundamental element for constructing the vector potential $\mathbf{A}(\mathbf{r})$ in free space. Therefore, under the given physical situation, there is no gauge freedom for the vector potential in the space. This situation is physically, identical to the case of the Coulomb electric potential

$$\frac{(-e)_1(-e)_2}{4\pi r_{12}}$$

for which no gauge freedom is considered usually. In Fig. 2, we show some examples. In (a) we have an infinitely long cylindrical coil, in which the vector potential \mathbf{A} extends outside of the coil where there is no magnetic field \mathbf{H} . The existence of this \mathbf{A} can be manifested when we change the current of the coil. Then we have a definite electric field of

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad (111)$$

which must be cylindrically symmetric. As is shown in (b), the shape of the line of force of \mathbf{A} must be different for the case of a coil with a circular cross section from that with a rectangular cross section. This must be reflected in Eq. (111), even if there is no magnetic field \mathbf{H} . In (c), we show another example, in which the case of a superconductor ring with surface current is presented. Now the vector potential \mathbf{A} must have an axial symmetry and it is present even inside of the ring. But, since

$$\nabla \times \mathbf{A} = 0 \quad (112)$$

inside of the superconductor, this \mathbf{A} does not have any action upon the electron in a stationary state, so that we must use a special technical gauge for obtaining the London equation in this case. But when we can change the surface current, for instance, this true \mathbf{A} should have an action to create an electric field according to Eq. (111). But, of course, the effect of the perfect conduction of the ring must be taken into account.

The next point of discussion is concerning the famous relation²⁹⁾ in magnetism of

$$\frac{\partial \mathcal{H}}{\partial \mathbf{H}_{\text{ext}}} = -\mu \quad (113)$$

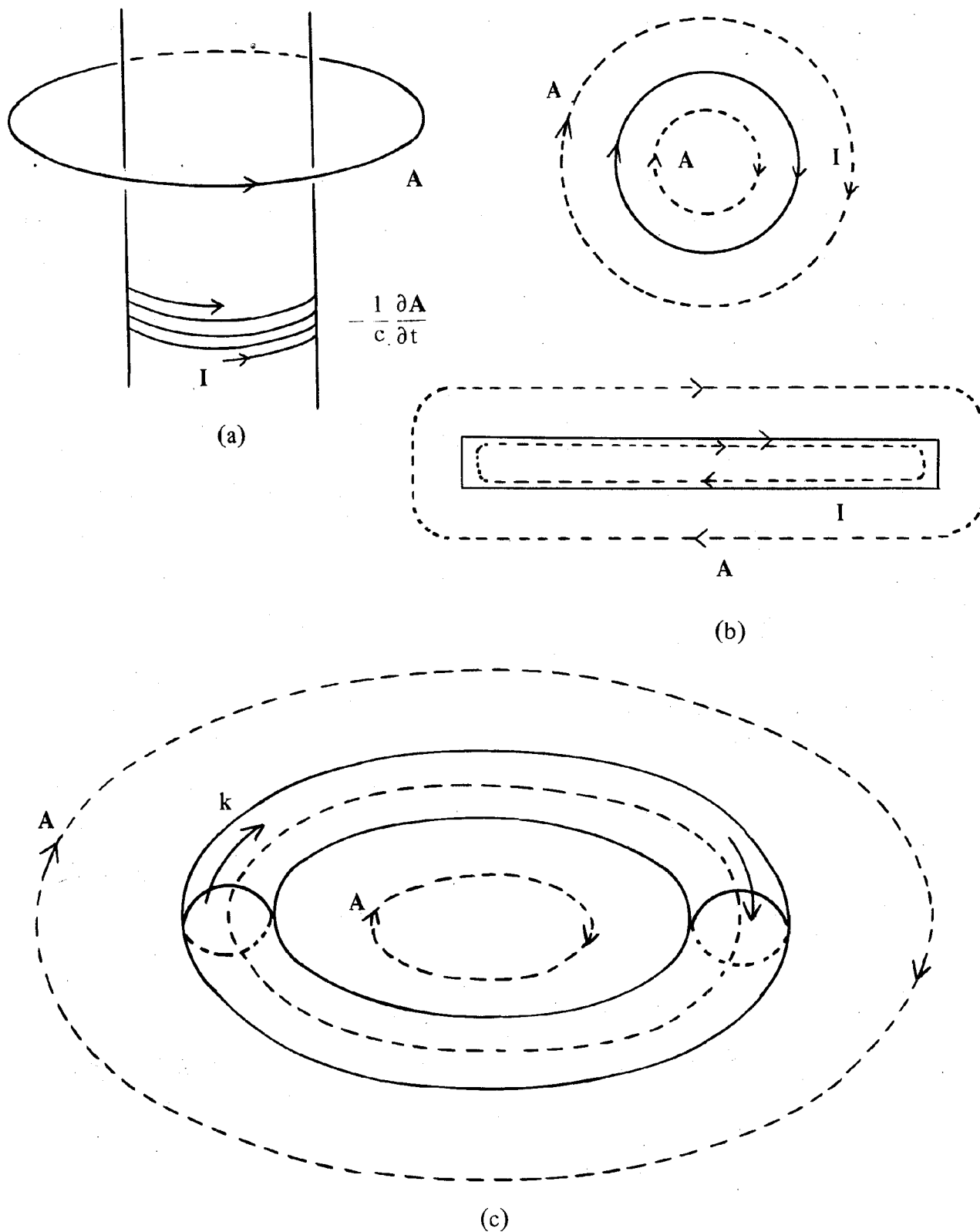


Fig. 2. Examples of the vector potential A , which is associated with a stationary magnetic field, and the electric field $-\frac{1}{c} \frac{\partial A}{\partial t}$, which is induced by the change in the electric current of the source of the magnetic field. (a), solenoid coil. (b), cross sections of a cylindrical coil and a rectangular coil. (c), superconducting toroid with a magnetic flux inside.

Introduction of A New Principle in the Theory of Magnetism II

in which μ is the total magnetic moment of the system. As has been analyzed in §6 of paper I²⁾, this equation is not generally correct. This equation, however, in some cases is misunderstood as the definition of the magnetic moment of the system. Therefore, we shall analyze this problem further from our thermodynamical point of view.

Now since Eq. (113) is a result of an adiabatic change, we can use our result and Eq. (30) as follows. In an ideal paramagnet, we have from Eq. (32)

$$\left[\frac{\partial (U_L - HM)}{\partial H} \right]_S = -M \quad (114)$$

Eq. (113) is correct, provided that we use

$$\mathcal{H} = U_L - H \cdot M \quad (115)$$

In an ideal diamagnet, we get from Eq. (66).

$$\left[\frac{\partial (U_L + \sum_i U_{k2}^i + \frac{M^2}{2})}{\partial H} \right]_S = -M \quad (116)$$

This means that Eq. (113) is not exactly correct, but if we assume

$$M \cdot \frac{dM}{dH} \ll M \quad (117)$$

then Eq. (113) is approximately correct if we take

$$\mathcal{H} = U_L + \sum_i U_{k2}^i \quad (118)$$

as the Hamiltonian. Note that we remarked on this situation when discussing Eq. (61). The same conclusion can be derived directly from Eq. (30).

$$\begin{aligned} -c \iint_S \mathbf{E} \times \mathbf{H} \cdot d\mathbf{S} &= \iiint_V \mathbf{H} \cdot \delta \mathbf{B} \, dV \\ &= \iiint_V \left[\delta \left(\frac{H^2}{2} + \mathbf{H} \cdot \mathbf{M} \right) - \mathbf{M} \cdot \delta \mathbf{H} \right] dV = \iiint_V \left[\delta \left(\frac{B^2}{2} - \frac{M^2}{2} \right) - \mathbf{M} \cdot \delta \mathbf{H} \right] dV \end{aligned} \quad (119)$$

Therefore, if we neglect $M^2/2$ and disregard the $B^2/2$ term as the magnetic energy of the space, we get Eq. (113).

We can also verify the incorrectness of Eq. (113) by using a microscopic current model. As shown in Fig. 3, let us assume a very small needle shaped persistent current system C_2 in the magnetic field of very large superconductor ring C_1 . C_2 is assumed to move on the symmetry axis of C_1 . Now the microscopically defined

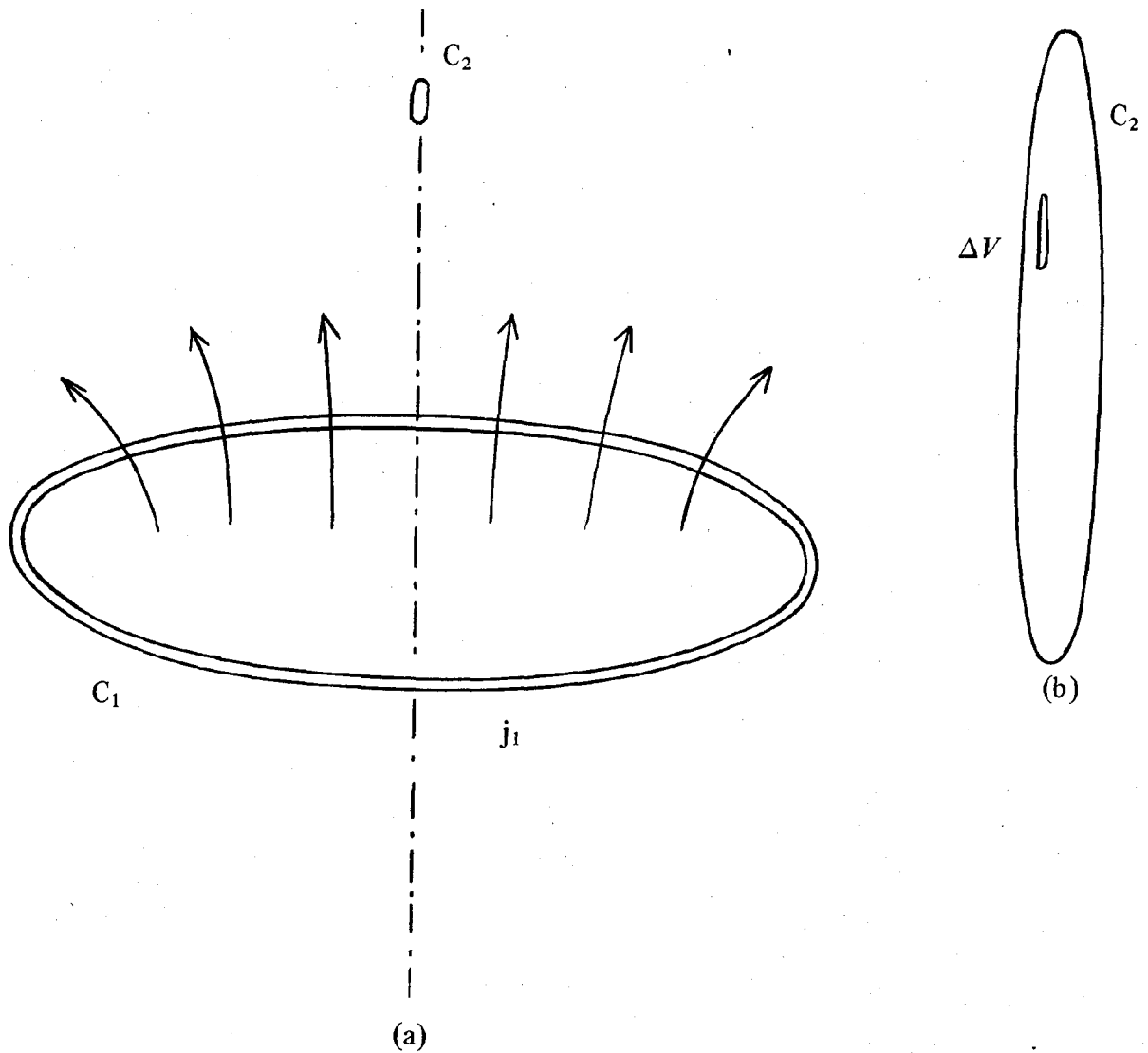


Fig. 3. (a), Small needle specimen C_2 placed in a magnetic field of large superconductor ring C_1 . (b), a small needle volume ΔV taken inside of C_2 .

total magnetic energy of the system, U_m , is (see Eq. (1))

$$U_m = \sum_{\lambda \neq \mu} \frac{1}{2} L_{\lambda\mu} \Delta I_\lambda \Delta I_\mu + \sum_{j \neq i} \frac{1}{2} L_{ij} \Delta I_i \Delta I_j + \sum_{\lambda, 1} L_{\lambda i} \Delta I_\lambda \Delta I_i \quad (120)$$

in which ΔI_λ and ΔI_i are the differential current intensities of the closed current loops λ and i , in C_1 and C_2 respectively. Current loop λ is very large, but current loop i could be microscopic or could be macroscopic.

Then, if we displaced C_2 by δr and change \mathbf{H}_{21} the magnetic field produced by C_1 , by $\delta \mathbf{H}_{21}$, the variation of U_m is

$$\begin{aligned}
 \delta_{\mathbf{r}} U_m &= \sum_{\lambda} \Delta I_{\lambda} \frac{\delta \Phi_{\lambda}}{c} + \sum_i \Delta I_i \frac{\delta \Phi_i}{c} - \sum_{\lambda, i} \delta L_{\lambda i} \Delta I_{\lambda} \Delta I_i \\
 &\quad - \sum_{\lambda, \mu} \frac{1}{2} \delta L_{\lambda \mu} \Delta I_{\lambda} \Delta I_{\mu} - \sum_{i, j} \frac{1}{2} \delta L_{ij} \Delta I_i \Delta I_j \\
 &= -\delta_{\mathbf{r}} G_1 - \delta_{\mathbf{r}} G_2 - \delta_{\mathbf{r}} \mathbf{H}_{21} \cdot \boldsymbol{\mu}_2
 \end{aligned} \tag{121}$$

In obtaining the last equality of Eq. (121), we have assumed that, in the process of the differential displacement of the location of C_2 , or $\delta_{\mathbf{r}} \mathbf{H}_{21}$,

$$\delta_{\mathbf{r}} L_{\lambda \mu} = 0, \quad \delta_{\mathbf{r}} L_{ij} = 0 \tag{122}$$

because the route of the current is already determined by the other conditions and the introduction of $\delta_{\mathbf{r}} \mathbf{H}_{21}$, or $\delta_{\mathbf{r}} \mathbf{e}$, only introduce an acceleration of current along the route, or a change in the velocity of current flow at each location, and not a change of the relative location of the paths of C_1 or C_2 . G_1 and G_2 are the non-magnetic self-energies of C_1 and C_2 . Now

$$\delta_{\mathbf{r}} (U_m + G_1 + G_2) = -\delta_{\mathbf{r}} \mathbf{H}_{21} \cdot \boldsymbol{\mu}_2 \tag{123}$$

gives the work given to the total system from outside. Eq. (123) is consistent with the well-known expression of the mechanical force which is operationg upon C_2 , i. e.

$$\mathbf{F}_2 = (\boldsymbol{\mu}_2 \cdot \nabla_2) \mathbf{H}_{21}(\mathbf{r}_2) = \nabla_2 [\boldsymbol{\mu}_2 \cdot \mathbf{H}_{21}(\mathbf{r}_2)] \tag{124}$$

because

$$\delta_{\mathbf{r}} \mathbf{H}_{21} = (\delta \mathbf{r} \cdot \nabla_2) \mathbf{H}_{21}(\mathbf{r}_2) \tag{125}$$

and

$$-\delta_{\mathbf{r}} \mathbf{H}_{21} \cdot \boldsymbol{\mu}_2 = (\delta \mathbf{r} \cdot \nabla_2) [\boldsymbol{\mu}_2 \cdot \mathbf{H}_{21}(\mathbf{r}_2)] \tag{126}$$

For the purpose of simplification, when we assume further that C_1 is an ideal superconductor, then

$$\delta_{\mathbf{r}} G_1 = 0 \tag{127}$$

and

$$G_2 = \mathcal{H}_2 \tag{128}$$

could be the Hamiltonians of the system C_2 . Therefore we get

$$\delta_{\mathbf{r}} \mathcal{H}_2 + \delta_{\mathbf{r}} U_m = -\boldsymbol{\mu}_2 \cdot \delta \mathbf{H}_{21} \tag{129}$$

This is a very important general equation which is definitely different from Eq. (113). We can get Eq. (113) only when

$$\frac{\partial U_m}{\partial \mathbf{r}} = 0$$

The correctness of our procedure will be rechecked as follows. Let us take a small needle volume ΔV in C_2 , as shown in (b) of Fig. 3. Then the change of the magnetic energy of ΔV is

$$u_m^{\Delta V} = \iiint_{\Delta V} \frac{\mathbf{h}^2}{2} dV \quad (131)$$

$$\begin{aligned} \delta u_m^{\Delta V} &= \iiint_{\Delta V} \mathbf{h} \cdot \delta \mathbf{h} dV = \iiint (\mathbf{H} + \mathbf{h}^\mu)(\delta \mathbf{H} + \delta \mathbf{h}^\mu) dV \\ &= \iiint_{\Delta V} (\mathbf{H} \cdot \delta \mathbf{B} + \mathbf{M} \cdot \delta \mathbf{H} + \mathbf{h}^\mu \cdot \delta \mathbf{h}^\mu) dV \end{aligned} \quad (132)$$

in which \mathbf{h}^μ is the magnetic field produced by the magnetic moment μ_i inside of the volume ΔV . On the other hand, in general

$$\begin{aligned} \iiint_{\Delta V} \mathbf{h}^\mu \cdot \delta \mathbf{h}^\mu dV &= \delta u_\mu^{\Delta V} = \sum_{i,j} L_{ij} \Delta I_i \delta(\Delta I_j) + \sum_{i>j} \delta L_{ij} \Delta I_i \Delta I_j \\ &= \frac{1}{c} \sum_i \Delta I_i \delta \Phi_i^\mu = \frac{1}{c} \sum_i \Delta I_i (\delta \Phi_i - \mathbf{S}_i \cdot \delta \mathbf{H}_{21}) \\ &= \sum_i (-\delta g_i^\mu) - \sum_i \mu_i \cdot \delta \mathbf{H}_{21} \\ &= -\sum_i \delta g_i^\mu - \iiint_{\Delta V} \mathbf{M} \cdot \delta \mathbf{H} dV \end{aligned} \quad (133)$$

$$\delta u_m^{\Delta V} + \sum_i \delta g_i^\mu = \iiint_{\Delta V} (\mathbf{H} \cdot \delta \mathbf{B}) dV \quad (134)$$

Therefore, we get the exact agreement with Eq. (30). Now let us check the meaning of Eq. (129).

In the case of a single electron, although u_m can be well defined, because of a certain complicated structure, Eq. (113) is still applicable, which will be explained in paper III²⁸⁾.

In the case of a paramagnet, Eqs. (114) and (129) tell us that

$$\left[\frac{\partial (U_L - HM)}{\partial H} \right]_S = \left[\frac{\partial (\mathcal{X}_2 + u_m)}{\partial H} \right]_S \quad (135)$$

Introduction of A New Principle in the Theory of Magnetism II

Here, we have assumed a unit volume for convenience. This is justified by the meaning of the Zeeman energy $-(\mathbf{H} \cdot \mathbf{M})$, as analyzed in Eq. (14). But we should be careful that, when we have used $-(\mathbf{H} \cdot \mathbf{M})$ as the Hamiltonian, this means that we have replaced the microscopic expression $\mathcal{X}_2 + u_m$ in Eq. (135) with the macroscopic expression $-(\mathbf{H} \cdot \mathbf{M})$.

In the case of a diamagnet, we have

$$\left[\frac{\partial (U_L + \sum_i U_{k2}^i + \frac{M^2}{2})}{\partial H} \right]_S = \left[\frac{\partial (\mathcal{X}_2 + u_m)}{\partial H} \right]_S \quad (136)$$

and, in the argument of Eq. (61), we have assumed that

$$U_L + \sum_i U_{k2}^i = \mathcal{X}_2 + \iiint \frac{\mathbf{h}'^2}{2} dV = \mathcal{X}'_2 \quad (137)$$

Now, in Eqs. (120) and (121), we can rewrite

$$\begin{aligned} \delta_r u_m &= \iiint_{\infty} \delta \left[\frac{(\mathbf{h}_1 + \mathbf{h}_2)^2}{2} \right] dV \\ &= \iiint_{\infty} (\mathbf{h}_1 \cdot \delta \mathbf{h}_1 + \mathbf{h}_1 \cdot \delta \mathbf{h}_2 + \mathbf{h}_2 \cdot \delta \mathbf{h}_1 + \mathbf{h}_2 \cdot \delta \mathbf{h}_2) dV \\ &= \sum_{\lambda, \mu} \Delta I_{\lambda} [L_{\lambda \mu} \delta(\Delta I_{\mu}) + L_{\lambda i} \delta(\Delta I_i) + \delta L_{\lambda i} \Delta I_i] \\ &\quad + \sum_{\lambda, i} L_{\lambda i} \delta(\Delta I_{\mu}) \Delta I_i + \sum_{i, j} L_{ij} \Delta I_i \delta(\Delta I_i) \\ &= -\delta_r G_1 + \iiint_{\infty} \mathbf{h}_2 \cdot \delta_r \mathbf{h}_1 dV + \iiint_{\infty} \mathbf{h}_2 \cdot \delta_r \mathbf{h}_2 dV \\ &= \iiint_{\infty} (\mathbf{M} \cdot \delta_r \mathbf{M} + \mathbf{h}' \cdot \delta_r \mathbf{h}') dV = \iiint_{\infty} \left[\delta_r \left(\frac{M^2}{2} \right) + \delta_r \left(\frac{\mathbf{h}'^2}{2} \right) \right] dV \quad (138) \end{aligned}$$

Here, \mathbf{h}_1 and \mathbf{h}_2 are the magnetic fields produced by C_1 and C_2 respectively and

$$\mathbf{h}_2 = \bar{\bar{\mathbf{h}}}_2 + (\mathbf{h}_2 - \bar{\bar{\mathbf{h}}}_2) = \mathbf{M} + \mathbf{h}' \quad (139)$$

Further we have assumed that

$$\delta_r G_1 = 0 \quad (140)$$

and

$$\sum_{\lambda, \mu} L_{\lambda i} \delta_r (\Delta I_{\lambda}) \Delta I_i = \iiint_{\infty} \mathbf{h}_2 \cdot \delta_r \mathbf{h}_1 dV \quad (141)$$

is the interaction of the small induced variation $\delta_r \mathbf{h}_1$ with \mathbf{h}_2 which is localized and can be set equal to zero. Physically

$$\delta_{\mathbf{r}} \mathbf{h}_1 \ll \delta_{\mathbf{r}} \mathbf{h}_2 \quad (142)$$

or,

$$\begin{aligned} \sum_{\lambda, i} L_{\lambda i} \delta_{\mathbf{r}} (\Delta I_{\lambda}) \Delta I_i &= \sum_{\lambda, i} \left\{ -\frac{L_{\lambda i}}{L_{\lambda \mu}} [L_{\lambda i} \delta_{\mathbf{r}} (\Delta I_i) + \delta_{\mathbf{r}} L_{\lambda i} \Delta I_i] \Delta I_i \right\} \\ &\ll \sum_{i, j} L_{ij} \delta_{\mathbf{r}} (\Delta I_i) \Delta I_i \end{aligned} \quad (143)$$

Therefore from Eq. (138)

$$\delta_{\mathbf{r}} \left(u_m - \iiint_{\infty} \frac{\mathbf{h}'^2}{2} dV \right) = \iiint \delta_{\mathbf{r}} \left(\frac{M^2}{2} \right) dV \quad (144)$$

This means that we have microscopically derived and confirmed Eqs. (136) and (137) from our persistent current model.

In the case of the idealized conduction electron system, the situation is not simple. We believe, however, that the logical sequence from Eq. (120) to Eq. (130) is still effective, but that the configurations of the closed current loops may be strongly time dependent. This means that δU_m is also involved in this case and there must be Eddy current or diamagnetically induced electric current phenomena, which will cause Eq. (113) to be incorrect. Eq. (131) through (134) may not be valid, since there is no clear magnetization \mathbf{M} inside. We have found that there is a very clever way to analyze the problem utilizing the results already obtained for the diamagnet. In Fig. 4, we show a very large solenoid coil C_1 , and also very large number of fine cylindrical specimens $S_1, S_2, \dots, S_i, \dots, S_N$, which are distributed uniformly inside of the Coil C_1 as shown in (b). Then, we can regard the total set of specimens as a single insulating material with the magnetization

$$\mathbf{M}V = \sum_V \boldsymbol{\mu}_i \quad (145)$$

in which V is the volume where $\sum_V \boldsymbol{\mu}_i$ is located. Then, when we change \mathbf{H}_{ext} , the magnetic field from C_1 , Eq. (30) can be used to show that the total energy entered in V is

$$\begin{aligned} \iiint_V \mathbf{H}_{\text{ext}} \cdot \delta \mathbf{B} dV &= \iiint_V \mathbf{H}_{\text{ext}} \cdot \delta (\mathbf{H}_{\text{ext}} + \mathbf{M}) dV \\ &= \iiint_{V-\nu_{\mu}} \mathbf{H}_{\text{ext}} \cdot \delta \mathbf{H}_{\text{ext}} dV + \iiint_{\nu_{\mu}} \mathbf{H}_{\text{ext}} \cdot \delta \mathbf{H}_{\text{ext}} dV + \mathbf{H}_{\text{ext}} \cdot \delta \left(\sum_V \boldsymbol{\mu}_i \right) \end{aligned}$$

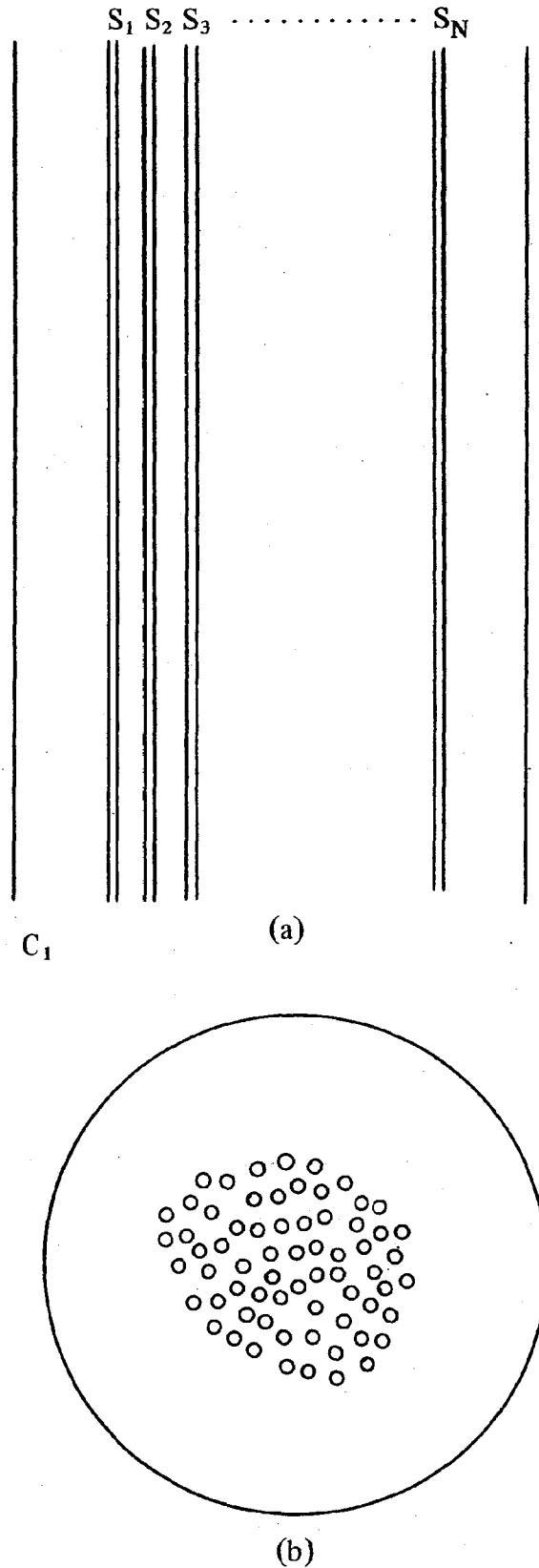


Fig. 4. Millions of fine cylindrical specimens S_1, S_2, \dots, S_N located inside of a large solenoidal coil C_1 . (a), side view, (b), cross section.

$$= \iiint_{V-V} \delta \left(\frac{\mathbf{H}_{\text{ext}}^2}{2} \right) dV + \iiint_V \delta \left(\frac{\mathbf{H}_{\text{ext}}}{2} \right) dV + \delta \left[\mathbf{H}_{\text{ext}} \cdot \sum_V \boldsymbol{\mu}_i \right] - \sum_V \boldsymbol{\mu}_i \cdot \delta \mathbf{H}_{\text{ext}} \quad (146)$$

Here, V_μ is the volume of the specimens in V , and $\tilde{\mathbf{B}}$ and $\tilde{\mathbf{M}}$ are the artificially defined \mathbf{B} and \mathbf{M} of the system. On the other hand, the usual interpretation of Eq. (30) gives that the total electromagnetic energy entered in the specimen volume as

$$\iiint_{V_\mu} \left[\delta \left(\frac{\mathbf{H}^2}{2} \right) + \delta \left(\frac{\mathbf{E}^2}{2} \right) + (\mathbf{E} \cdot \mathbf{j}) \delta t \right] dV \quad (147)$$

Here, by assumption, there is no \mathbf{M} nor \mathbf{P} . We know that Eq. (147) is identical to

$$\iiint_{V_\mu} \delta \left(\frac{\mathbf{H}^2}{2} \right) dV + \delta \mathcal{H} \quad (148)$$

since the electric energy can always be directly included in the Hamiltonian, but, the long range nonoscillating magnetic energy is not²²⁾. \mathcal{H}' means the Hamiltonian including the electromagnetic short range interaction energies of \mathbf{e}' and \mathbf{h}' . (e. g., see Eq. (60)).

Now

$$\mathbf{H} = \mathbf{H}_{\text{ext}} + \mathbf{H}_{\text{int}} \quad (149)$$

and from Eqs. (146) and (148),

$$\delta \mathcal{H}'_i = - \boldsymbol{\mu}_i \cdot \delta \mathbf{H}_{\text{ext}} + \delta \left[\mathbf{H}_{\text{ext}} \cdot \boldsymbol{\mu}_i \right] - \iiint_{V_i} \left[\delta (\mathbf{H}_{\text{ext}} \cdot \mathbf{H}_{\text{int}}) + \delta \left(\frac{\mathbf{H}_{\text{int}}^2}{2} \right) \right] dV \quad (150)$$

Here, we have taken only one specimen for simplification. When we can assume cylindrical symmetry, then the $\boldsymbol{\mu}_i$ can be transformed into an integration of the effective magnetization, $\mathbf{M}^{*7)$, as defined by

$$\mathbf{M}^* = \mathbf{H}_{\text{int}} \quad , \quad \boldsymbol{\mu}_i = \iiint_{V_i} \mathbf{H}_{\text{int}} dV \quad (151)$$

Then, we get

$$\begin{aligned} \delta \mathcal{H}'_i &= - \boldsymbol{\mu}_i \cdot \delta \mathbf{H}_{\text{ext}} dV - \iiint_V \delta \left(\frac{\mathbf{H}_{\text{int}}^2}{2} \right) dV \\ &= - \iiint_{V_i} \mathbf{H}_{\text{int}} \cdot \delta \mathbf{H}_{\text{ext}} dV - \iiint_{V_i} \mathbf{H}_{\text{int}} \cdot \delta \mathbf{H}_{\text{int}} dV \end{aligned} \quad (152)$$

Therefore, if we could assume that

$$\delta_{\mathbf{r}} \mathbf{H}_{\text{ext}} \gg \delta \mathbf{H}_{\text{int}} \quad (153)$$

we can get Eq. (113), but, as we know already, this is not always true. Typical case is the superconductor and, in this case,

$$\delta \mathbf{H}_{\text{int}} = - \delta \mathbf{H}_{\text{ext}} \quad (154)$$

in almost all the volume V_i . We have the similar situation in a classical Fermi gas²⁾, and high temperature plasma. The transient phenomena of Eddy currents in highly conductive materials correspond essentially to the same situation.

Here, we should notice one interesting correspondence to the diamagnet. From Eqs. (137), (136) and (144), we have

$$\delta_{\mathbf{r}} (u_m - u'_m) = \delta \left(\frac{M^2}{2} \right) \quad (155)$$

$$u'_m = \iiint_{\infty} \frac{\mathbf{h}'^2}{2} dV \quad (156)$$

and from Eqs. (129) and (152) we have

$$\delta_{\mathbf{r}} (u_m - u'_m) = \delta \left(\frac{\mathbf{H}_{\text{int}}^2}{2} \right) = \delta \left(\frac{M^{*2}}{2} \right) \quad (157)$$

Therefore, the two expressions are essentially identical, if we regard \mathbf{H}_{int} as the magnetization \mathbf{M}^* . This means that the idealized conduction electron system and the diamagnet are similar in the structure of their macroscopic magnetic energies. Since u'_m can be assumed constant or can be included in the Hamiltonian²²⁾, from Eq. (129), the applicability of Eq. (113) depends on whether or not

$$\mathbf{M} \cdot \delta \mathbf{M} \quad \text{or} \quad \mathbf{M}^* \cdot \delta \mathbf{M}^* \quad (158)$$

can be assumed to be negligible as compared with

$$\mathbf{M} \cdot \delta \mathbf{H}_{\text{ext}} \quad \text{or} \quad \mathbf{M}^* \cdot \delta \mathbf{H}_{\text{ext}} \quad (159)$$

This means that, in a weak magnet, we can in practice usually still use Eq. (113) and the famous Boltzmann factor

$$\exp [-\beta \mathcal{H}] \quad (160)$$

On the other hand we cannot use Eq. (113) or (160) for the strongly magnetizable materials or the phenomena, appearing in superconductors and plasmas or for situations

where Eddy currents are important.

We must be careful to understand the relation (155) and (157), because these equations show only that the total magnetic energy will increase when the magnetic field is supplied from an idealized superconductor (Fig. 3) and the specimen has been displaced into the location where the magnetic field is more intense, and do not indicate that the electromagnetic energy needed to magnetize the diamagnet is proportional to $M^2/2$. As has been shown in Eq. (30), this energy is definitely lower for the diamagnet than for the paramagnet and, for an idealized perfect diamagnet, no energy at all is necessary to magnetize the specimen up to its highest magnetization $M^* = -H_{\text{ext}}$. We should recall the tricky dynamical structure of the magnetic energy as has been discussed in §3.

In conclusion, we have established an entirely new way of understanding magnetism of magnetizable materials. The meaning of the magnetic energy of the orbital motion of electrons becomes quite different from what it was in the conventional theory. The difference from the old way of treating magnetic are most distinct for the case of the superconductor and, the new treatment brings an essentially new way of understanding the Meissner effect of the superconductor.

In terms of mathematical strictness the famous representation

$$\exp [-\beta \mathcal{U}] \quad (161)$$

is usually incorrect, because there will be another factor such as

$$\iiint \frac{M^2}{2} dV \quad (162)$$

of Eq. (67),

$$\iiint \frac{H^2}{2} dV \quad (163)$$

of Eq. (14), or,

$$\sum_i \frac{e v_i \cdot \mathbf{A}(\mathbf{r}_i)}{c} \quad (164)$$

of Eq. (107), to be added to \mathcal{U} .

In a weak magnet, however, Eqs. (113) and (161) are still practically correct, because the necessary correction is small.

We can however, definitely say that Miss. Van Leeuwen's theorem is wrong and the treatment of Landau's diamagnetism must be carefully done because the expression

Introduction of A New Principle in the Theory of Magnetism II

of the magnetic energy of the orbital motion of electrons becomes entirely different from what is predicted by conventional electromagnetism.

Acknowledgment

The English of this paper has been checked by Professor R. L. White of the Stanford University, while he was staying in the Department of Physics, the University of Tokyo, as a visiting professor. The author is very much indebted to him for this very kind effort.

References

- 1) S. Iida : "New Electromagnetism", Maruzen Co., Ltd, Tokyo (1975), (in Japanese), Vol. 1 & 2.
- 2) S. Iida : "Bussei Kenkyu" (in English), 24 (1975) 1.
- 3) S. Iida : J. Phys. Soc. Japan 37 (1974) 1183.
- 4) P. G. de Gennes : "Superconductivity of Metals and Alloys" Translated in English, W. A. Benjamin Inc., New York et al., (1966), p. 6.
- 5) J. H. Van Vleck : "The Theory of Electric and Magnetic Susceptibilities", Oxford (1932), p. 90.
- 6) G. H. Wannier : "Statistical Physics", John & Wiley & Sons, Inc., New York (1966) p. 317.
- 7) Ref. (1), Vol. 2.
- 8) C. Kittel : "Elementary Statistical Physics", John & Wiley & Sons, Inc., New York (1958) p. 77.
- 9) R. Becker and W. Döring : "Ferromagnetism, J. Springer, Berlin (1937), p. 53.
- 10) A. B. Pippard : "Classical Thermodynamics", Cambridge Univ. Press (1957) p. 24.
- 11) H. E. Stanley : "Introduction to Phase Transitions and Critical Phenomena", Clarendon Press (1971) §2. 6.
- 12) Ref. 6), p. 316.
- 13) L. D. Landau and E. M. Lifshitz : "Electrodynamics of Continuous Media", Translated in English, Pergamon Press (1960), p. 126.
- 14) S. Iida : "Bussei Kenkyu", 21, No. 1 (1973) 1, (in Japanese).
- 15) D. Shoenberg : "Superconductivity", Cambridge at the Univ. Press : (1952), §III.
- 16) R. D. Parks : "Superconductivity" I, Marcel Dekker Inc., New York (1969), p. 158.

- 17) Ref. 6), §7, 2.
- 18) Ref. 4), p. 50.
- 19) Ref. 5), p. 102; J. H. Van Vleck : Nuovo Cimento (Supplement) 6 (1957), 865.
- 20) J. H. Van Leeuwen : J. de Phys. (6) 2, (1921) 361.
- 21) Ref. 5), p. 102.
- 22) W. Heitler : "The Quantum Theory of Radiation", 3rd Ed. Oxford, At the Clarendon Press (1954) p. 47.
- 23) L. Landau : Z. f Phys. 64 (1930) 629.
- 24) R. E. Peierls : "Quantum Theory of Solids". Clarendon Press (1955) p. 144.
- 25) J. H. Van Vleck : Nuovo Cimento (Supplement) 6 (1957) 857.
- 26) F. S. Ham : Phys. Rev. 92 (1953) 1113
- 27) H. Welker : Z. Physik 114 (1939) 525.
- 28) S. Iida : to be published in J. Phys. Soc. Japan.
- 29) R. Kubo : "Magnetism", Iwanami Gendai Butsurigaku, II, I, Iwanami Book Co., (1955) p. 5 (in Japanese).