Variation of $\psi^\dagger$ and of ψ now yields

$$i\hbar\partial\psi/\partial t=\{mc^2\beta+c\boldsymbol{\alpha}\cdot\mathbf{p}_{\mathrm{op}}-e\mathfrak{A}\cdot\boldsymbol{\alpha}\}\psi+\tfrac{1}{2}e(V\psi+\psi V) \quad (28)$$

and hermitian conjugate equation. This is Dirac's equation, including self-interaction as V is given by (5a) and ψ is quantized according to the exclusion principle. Equations (17) and (18) are now replaced by the results of application of the generalized theorem of Ehrenfest, which gives the time-derivatives of $\int\psi^\dagger\mathbf{p}_{\mathrm{op}}\psi$ and of $\int\psi^\dagger\mathbf{x}\psi$, as calculated from (28) and conjugate equation.

From (27) and (28) and the commutativity of ρ and V one also easily finds again the continuity equation $\rho^t/c+\mathrm{div}\mathbf{j}=0$ (Eq. (22)), which we used in deriving Eq. (25) from Eq. (16). There are no other alterations in the derivation of the maxwell equations from (3) with (1) and (26) in quantum theory.

We remark that $\mathcal{L}$ is linear in time-derivatives. The pairs of canonical conjugates are $\mathbf{x}_i$ with $\mathbf{p}_i$ in the classical theory ($\mathbf{v}_i$ being derived variables, see footnote 3), or ψ with $i\hbar\psi^\dagger$ in wave mechanics; and $\mathfrak{E}(\mathbf{x})$ with $\mathfrak{A}(\mathbf{x})/4\pi c$ in both cases. The hamiltonian is obtained from $-\mathcal{L}$ by omission of the terms $-pq^t$ from it, and gives for the total energy the usual expression,

$$\mathcal{H}=\int\{\psi^\dagger(mc^2\beta-i\hbar c\boldsymbol{\alpha}\cdot\boldsymbol{\nabla})\psi+\tfrac{1}{2}\rho V \\ -\mathbf{j}\cdot\mathfrak{A}+(\mathfrak{E}^2+\mathfrak{B}^2)/8\pi\}. \quad (29)$$

Expanding the transverse fields $\mathfrak{E}$ and $\mathfrak{A}/4\pi c$ in fourier components, and quantizing these in the usual way as canonically conjugate variables, one finds, after recombination of the fourier components to transverse fields, that the commutator of $\mathfrak{E}$ and $\mathfrak{A}/4\pi c$ is $i\hbar\times$ the so-called *transverse delta-function*,[5] or

$$[\mathfrak{E}_k(\mathbf{x},t);\mathfrak{A}_l(\mathbf{x}',t)]=4\pi i\hbar c\delta_{kl}{}^{\mathrm{tr}}(\mathbf{x}-\mathbf{x}') \\ \equiv i\hbar c\{\nabla_k\nabla_l-\delta_{kl}\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\}(1/r). \quad (30)$$

The commutation relations of the coulomb field $\mathbf{E}_{\shortparallel}$, on the other hand, simply follow from those of the matter field, by (10a) with (5a). These are just the commutation relations of the gauge-independent quantum electrodynamics recently proposed by the author in collaboration with J. S. Lomont.[6]

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[5] F. J. Belinfante, Physica **12**, 1 (1946).

[6] F. J. Belinfante and J. S. Lomont, Phys. Rev. **83**, 225(A) (1951) and Phys. Rev. **84**, 541 (1951).

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Size and Thermal Conductivity Effects in Paramagnetic Relaxation*

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The Casimir-du Pré thermodynamic theory of paramagnetic relaxation is generalized by taking account of the thermal conductivity of the paramagnetic salt. The case of a spherical specimen in a constant temperature bath is considered. One finds that infinitely many times are required to characterize the relaxation when a magnetic field is suddenly applied. The alternating current susceptibility is calculated and is shown to contain terms depending on the size and thermal conductivity of the specimen. A limited comparison of the theory with experimental data is made.

IN 1938 Casimir and du Pré[1] developed a simple thermodynamic interpretation of the frequency dependence of the complex paramagnetic susceptibility. They considered the system of all ionic spins to be an entity separate from the crystalline lattice and assumed that the spin system was always in thermodynamic equilibrium with an oscillatory magnetic field. Energy is transferred from the field to the spin system which rises in temperature and transfers heat to the lattice. If isothermal conditions are maintained, there is a further transfer of heat from the lattice to the constant temperature bath. The mathematical development of these ideas leads to Debye-type curves for the susceptibility.

The Casimir-du Pré theory is in fairly good agreement with experiment.[2] However recent measurements by Kramers, Bijl, and Gorter[3] and by Benzie and Cooke[4] have revealed discrepancies. These authors have suggested that a suitable distribution of spin-lattice relaxation times could account for the experimental results. An alternative suggestion—that the thermal conductivity of the specimen alters the theoretical susceptibility curves—is considered here.

We shall consider a spherical specimen of a paramagnetic salt immersed in a constant temperature bath since no new results are obtained for an adiabatically isolated specimen. The differential equation for the

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[1] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).

[2] For an extensive survey of experimental results see C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., Amsterdam, 1947).

[3] Kramers, Bijl, and Gorter, Physica **16**, 65 (1950).

[4] R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **A63**, 20 (1950).

conduction of heat in an isotropic solid is

$$\rho c\partial T/\partial t = K\nabla^2 T + Q(x, y, z, t). \tag{1}$$

In this equation ρ is the density, c the specific heat, T the temperature, K the thermal conductivity, and $Q(x, y, z, t)$ the heat input per unit time per unit volume. In the present application ρ is the density of the salt; c is taken to be c_L, the specific heat of the lattice; and T is taken to be T_L, the lattice temperature. We shall assume Q to be proportional to the local temperature difference of the lattice and spin systems,

$$Q(x, y, z, t) = \alpha(T_S - T_L) = \alpha\theta. \tag{2}$$

By virtue of the first law of thermodynamics the amount of heat transferred per unit volume from the spin system to the lattice in time dt can be written as

$$\delta Q = dU - HdM = -\alpha\theta dt, \tag{3}$$

which can easily be transformed into

$$\left[\left(\frac{\partial U}{\partial T_S}\right)_H - H\left(\frac{\partial M}{\partial T_S}\right)_H\right]dT_S + \left[\left(\frac{\partial U}{\partial H}\right)_{T_S} - H\left(\frac{\partial M}{\partial H}\right)_{T_S}\right]dH = -\alpha\theta dt. \tag{4}$$

The variation of the bracketed quantities with t will be neglected. This approximation also occurs in the work of Casimir and du Pré.

We shall set

$$\begin{aligned} H &= H_0 && (t<0), \\ H &= H_0 + h_0 e^{i\omega t} && (t\geq 0). \end{aligned} \tag{5}$$

By combining (1), (2), (4), and (5) one obtains

$$\rho c_L \partial T_L/\partial t = K\nabla^2 T_L + \alpha\theta \tag{6}$$

$$\begin{aligned} A\partial\theta/\partial t + A\partial T_L/\partial t + \alpha\theta &= 0 && (t<0) \\ &= -Ci\omega h_0 e^{i\omega t} && (t\geq 0), \end{aligned} \tag{7}$$

where

$$A = (\partial U/\partial T_S)_H - H(\partial M/\partial T_S)_H, \tag{8}$$

$$\begin{aligned} C &= (\partial U/\partial H)_{T_S} - H(\partial M/\partial H)_{T_S} \\ &= \rho(c_H - c_M)(\partial M/\partial H)_{T_S}/(\partial M/\partial T_S)_H. \end{aligned} \tag{9}$$

It follows immediately from (4) that A is equal to ρc_H, c_H being the specific heat of the spin system at constant H. The second expression for C in (9) can be derived fairly easily. c_M is the specific heat of the spin system at constant magnetization.

For $t<0$ (6) and (7) have the trivial solutions $T_L = T_0$, the temperature of the bath, and $\theta = 0$. Consequently only the case $t\geq 0$ will be considered henceforth. (6) and (7) can be solved by a laplace transform method. To determine T_L uniquely it is necessary to impose the physical requirement that it remain finite as $r\rightarrow 0$. The following abbreviations are introduced to facilitate writing the solution:

$$\begin{aligned} B &= \alpha + \alpha A/\rho c_L = \alpha(1 + c_H/c_L), \\ \kappa &= K/\rho c_L, \\ \lambda &= (i\omega/\kappa)^{\frac{1}{2}}(Ai\omega + B)^{\frac{1}{2}}(Ai\omega + \alpha)^{-\frac{1}{2}}. \end{aligned}$$

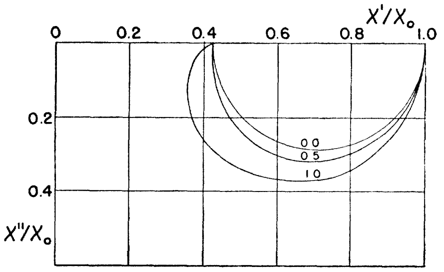

FIG. 1. Theoretical susceptibility curves for $(c_H - c_M)/c_H = 0.571$ and various values of T/τ.

We shall also denote by $p_n^{\pm}$ the two roots of

$$p^2 + [(B/A) + (n^2\pi^2\kappa/r_0^2)]p + n^2\pi^2\kappa\alpha/r_0^2 A = 0, \qquad (n = 1, 2, 3, \cdots) \tag{10}$$

r_0 is the radius of the specimen. One then has

$$\begin{aligned} T_L = T_0 &+ \alpha C h_0 e^{i\omega t}[\rho c_L(B + Ai\omega)]^{-1} \\ &\times\{(r_0 \sinh\lambda r)(r \sinh\lambda r_0)^{-1} - 1\} \\ &+ (2\alpha Ci\omega h_0\kappa/\rho c_L r r_0)\sum_{\substack{n=1 \\ \pm}}^{\infty} \exp(p_n^{\pm} t) \\ &\times(B + Ap_n^{\pm})^{-1}(p_n^{\pm} - i\omega)^{-1}(p_n^{\pm})^{-1} \\ &\times(Ap_n^{\pm} + \alpha)^2(A^2 p_n^{\pm 2} + 2Ap_n^{\pm}\alpha + \alpha B)^{-1} \\ &\times(-1)^n \sin(n\pi r/r_0)(in\pi). \end{aligned} \tag{11}$$

θ can readily be calculated from (6) by substituting (11). An inspection of the roots of (10) reveals that $p_n^{\pm}$ always contains a real part which is less than zero. The establishment of equilibrium when a magnetic field is suddenly applied therefore proceeds with the infinitely many relaxation times $\mathrm{Re}(1/p_n^{\pm})$.

In calculating the susceptibility it is not necessary to retain the exponentially decreasing terms since they will be negligible a certain time after turning on the oscillatory field. They will therefore be omitted from future consideration.

It follows from

$$dM/dH = (\partial M/\partial H)_{T_S} + (\partial M/\partial T_S)_H dT_S/dH,$$

the expression given for C in (9), and the definition of θ that

$$\begin{aligned} dM/dH = (\partial M/\partial H)_{T_S}\{&1 + \rho C^{-1}(c_H - c_M) \\ &\times(d\theta/dH + dT_L/dH)\}. \end{aligned} \tag{12}$$

$\chi_0 = (\partial M/\partial H)_{T_S}$ is the static or isothermal value of the susceptibility while dM/dH is the quantity determined experimentally. From (12), (11), and the solution of (6) for θ, one finds

$$\begin{aligned} dM/dH = \chi_0\{&1 + \rho(c_H - c_M)[-(B + Ai\omega)^{-1} \\ &\times(\alpha/\rho c_L + i\omega) + (\alpha^2/\rho c_L)(B + Ai\omega)^{-1} \\ &\times(\alpha + Ai\omega)^{-1}(r_0 \sinh\lambda r) \\ &\times(r \sinh\lambda r_0)^{-1}]\}. \end{aligned} \tag{13}$$

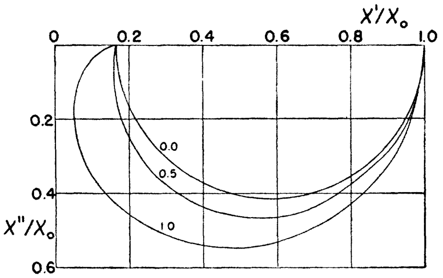

FIG. 2. Theoretical susceptibility curves for $(c_H-c_M)/c_H=0.842$ and various values of T/τ.

Equation (13) is an expression for what we might call the local value of the susceptibility. The susceptibility of the specimen as a whole can be obtained by averaging (13) over its volume. The result is

$$\begin{aligned}(dM/dH)_{total}=\chi_0\{1+\rho(c_H-c_M)[-(B+Ai\omega)^{-1}\\ \times(\alpha/\rho c_L+i\omega)+(3\alpha^2\kappa/r_0{}^2\rho c_L i\omega)(Ai\omega+B)^{-2}\\ \times[\lambda r_0\coth\lambda r_0-1]]\}.\quad(14)\end{aligned}$$

Equation (14) can be evaluated readily in the limiting cases of 0 and ∞ frequency. For $\omega=0$ one finds

$$dM/dH=\chi_0.$$

As the frequency goes to zero, the measured value of the susceptibility approaches the isothermal value and the temperature of the specimen remains constant. For $\omega=\infty$ one obtains

$$dM/dH=\chi_0 c_M/c_H,$$

which is the well-known formula of Debye for the adiabatic susceptibility.

If only the first few terms in the series expansion of the hyperbolic cotangent are retained the following expressions for the real and imaginary parts of the susceptibility are obtained:

$$\begin{aligned}\chi'/\chi_0=1-c_H{}^{-1}(c_H-c_M)[\omega^2\tau^2(1+\omega^2\tau^2)^{-1}\\ +(T/\tau)(2\omega^2\tau^2)(1+\omega^2\tau^2)^{-2}+\cdots],\quad(15)\end{aligned}$$

$$\begin{aligned}\chi''/\chi_0=c_H{}^{-1}(c_H-c_M)[\omega\tau(1+\omega^2\tau^2)^{-1}\\ +(T/\tau)(\omega\tau-\omega^3\tau^3)(1+\omega^2\tau^2)^{-2}+\cdots].\quad(16)\end{aligned}$$

In these expressions,

$$\tau=(A/B)(1+c_H/c_L),\quad T=\rho c_H r_0{}^2/15K.$$

Theoretical curves for the susceptibility calculated by using (15) and (16) are given in Figs. 1 and 2 for two values of $(c_H-c_M)/c_H$ and for three values of the ratio T/τ. It is clear from the curves that size and thermal conductivity effects alter their shape. Because of the scarcity of experimental data in the low temperature region it is difficult to say whether or not the terms involving T/τ in the foregoing expansions are actually important. The substance on which the most work has been done is probably potassium chrome alum. Bijl[5] has measured the specific heat resistance, which is the reciprocal of the thermal conductivity, in the liquid helium temperature region. He found that this quantity depended on the way the salt was cooled. At 2°K, K has a value somewhere between 0.03 and 0.12 watt $\text{cm}^{-1}\,\text{deg}^{-1}$. We shall take K to be 0.08 watt $\text{cm}^{-1}\,\text{deg}^{-1}$ as an average value. c_H-c_M is equal to CH^2T^{-2} and c_H is equal to $(b+CH^2)T^{-2}$. Here C is the constant in the curie law and according to data cited by Burton, Grayson Smith, and Wilhelm[6] has a value of 0.0033 deg g^{-1} at 2°K. Kramers, Bijl, and Gorter[3] assign the value 0.75×10^6 oersted^2 to b/C. The density of potassium chrome alum is 1.83 g cm^{-3}. Casimir, Bijl, and du Pré[7] in measurements on a powder specimen immersed in liquid helium at 2.04°K found that the relaxation time τ was about 3.1×10^{-3} sec in a field of 1000 oersted and about 5.2×10^{-3} sec in a field of 2000 oersted. The values of T/τ computed from these data for a specimen of 1-cm radius are 0.07 at 1000 oersted and 0.12 at 2000 oersted. It therefore appears that at 2.04°K the size and thermal conductivity do not affect the relaxation in potassium chrome alum in an important way. At lower temperatures the decrease of the thermal conductivity may necessitate consideration of the additional terms in (15) and (16). The increase of c_H at lower temperatures should be nearly compensated by the increase of τ.

I am indebted to Dr. F. Rodgers for suggesting to me that the thermal conductivity might influence the theoretical curves for the susceptibility. I should also like to thank Dr. Rodgers for several discussions of the problem.

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[5] D. Bijl, Physica 14, 684 (1948–49).

[6] Burton, Grayson Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940).

[7] Casimir, Bijl, and du Pré, Physica 8, 449 (1941).