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Theory of Adiabatic Susceptibility*

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A general proof of the equivalence between χ_S and χ_{iso} is presented in the framework of statistical thermodynamics. It is based on the observation that transitions do occur during adiabatic processes due to the neglected small interactions which can hardly be included in the acutal Hamiltonian. A new expression is found for χ_{iso} which is proved to coincide with χ_S and which is rederived straightforwardly from the ergodic theorem. As an example, a system of spins with a magnetic interaction under a strong magnetic field is considered by means of the perturbation method and shown to give consistent results.

I. INTRODUCTION

SINCE Casimir and Du Pré's classical work[1] the so-called adiabatic susceptibility, χ_S, has played an important role in investigations on paramagnetic relaxation processes. A considerable amount of knowledge has accumulated about this quantity from both the experimental and theoretical sides.[2] However, an interesting theoretical problem has been left unsolved for about ten years. Namely, Wright,[3] Broer,[4] and Caspers[5] calculated the susceptibility in the case of spin systems weakly coupled by a magnetic interaction under a strong magnetic field by means of the standard method of perturbation theory. They found that the "adiabatic" susceptibility

$$\chi_S=\chi_T-\left(\frac{\partial\langle M\rangle}{\partial T}\right)_H^2\left(\frac{\partial S}{\partial T}\right)_H^{-1}, \tag{1.1}$$

which is derived from thermodynamic considerations,[1] did not coincide with the "isolated" susceptibility

$$\chi_{\text{iso}}=\sum_n \frac{\partial M_n}{\partial H}e^{\beta(F-W_n)}, \tag{1.2}$$

which is a direct consequence of statistical mechanics. Here χ_T is the isothermal susceptibility, $\langle M\rangle$ the observed value of the magnetic moment, $\beta=1/kT$, F the Helmholtz free energy, M_n the diagonal element of the magnetic moment in the nth eigenstate with the energy W_n of the Hamiltonian and H the constant magnetic field applied to the spin system. Since then the two quantities, χ_S and χ_{iso}, have been distinguished from each other. In particular, Broer[4] presented a rather general discussion according to which χ_S and χ_{iso} agree with each other in the case of classical systems but *not* in the case of quantum-mechanical systems. Recently Caspers[6] gave a solution to this problem by an ingenious calculation. He supposed that the discrepancy between χ_S and χ_{iso} was due to the misuse of the perturbation method because in macroscopic systems it is associated with a divergence difficulty[7] which comes from the long-range magnetic interaction between spins. Avoiding use of the perturbation method, he succeeded in proving the equivalence of χ_S and χ_{iso}. Although he had to appeal to two hypotheses concerning the strucutre of the energy levels, his theory can be said to have given a correct answer to the present problem in the case of the particular spin systems considered, i.e., spins weakly coupled by magnetic interaction.

However, the following two points have still been left unsolved. First, the original problem, as proposed by Broer,[4] is not restricted to a particular type of spin system but is concerned with any kind of susceptibility, electric, compressional or magnetic. This means that the problem has to be solved on the same general basis as that on which the whole scheme of statistical thermodynamics stands. Second, there remains the question as to whether the perturbation method can really be applied to the evaluation of the adiabatic susceptibility. According to Broer's calculation,[4] a definite discrepancy between χ_S and χ_{iso} is expected even in the case of interactions such as an exchange interaction which has no divergence difficulty. Furthermore, the result for χ_S obtained through the perturbation method for magnetic interaction is not in contradiction with that given by Caspers.[6] Therefore the divergence difficulty associated with magnetic interaction should be considered another problem not directly connected with the present problem.

The purpose of the present paper is to discuss the two points stated in the preceding paragraph. We will provide a general proof of the equivalence between χ_S and χ_{iso} in Sec. II. Thereby a new expression for χ_{iso}, more practical than (1.2), will be found through statistical mechanical considerations. In Sec. III adiabatic changes will be discussed from the principles

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

[2] For example, C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1947); *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 266.

[3] A. Wright, Phys. Rev. **76**, 1826 (1949).

[4] L. J. F. Broer, Physica **17**, 155 (1951).

[5] W. J. Caspers, Physica **25**, 43 (1959).

[6] W. J. Caspers, Physica **25**, 645 (1959).

[7] N. Bloembergen, thesis, Leiden, 1948 (unpublished), p. 30.

of quantum statistical mechanics and the same expression for χ_{iso}, given in Sec. II, will be rederived. We will study in Sec. IV spin systems with magnetic interaction on the basis of the discussion given in Sec. II and show that the perturbation method yields a consistent result with respect to χ_S and χ_{iso}.

II. A GENERAL PROOF OF THE EQUIVALENCE BETWEEN χ_S AND χ_{iso}

The purpose of this section is to prove generally the equivalence between χ_S and χ_{iso} within the framework of statistical thermodynamics. We will use the language of magnetism but, of course, it can at once be applied to any other kind of susceptibility.

Suppose we have a spin system of macroscopic size. The interaction between spins need not be specified here. Let us assume that we know the true Hamiltonian of the system. Now we apply a weak magnetic field that is increased from zero quite slowly. According to quantum mechanics, the system which is assumed to exist originally in a certain eigenstate of the Hamiltonian does not make a quantum transition into another eigenstate provided that the change of the field is sufficiently slow. Thus we are at once led to the expression (1.2) for the susceptibility. However, the important point is the fact that (1.2) does refer to the true Hamiltonian of the system which is not generally tractable. That is, (1.2) is not convenient for practical applications.

Now suppose we know an approximate Hamiltonian of the system, many possible small disturbances being ignored. The system consists of a large number of identical spins, and thus the approximate Hamiltonian involves tremendous degeneracies. We then have to expect that the system makes continual transitions among degenerate eigenstates due to the neglected disturbances. This is also true when the magnetic field is changing slowly. We can now see that the expression (1.2), as it stands, ceases to be valid for such an approximate Hamiltonian. When we have a statistical ensemble which is subjected to an adiabatic change, it is not the weight of the individual eigenstate of the approximate Hamiltonian but the total weight of all the degenerate eigenstates belonging to a single energy value which is preserved during the adiabatic change. In the case of a canonical ensemble, the quantities which are kept constant are not the Boltzmann factors $e^{\beta(F-W_n)}$ of each of the approximate eigenstates but the sums of them over all the degenerate states corresponding to each of the allowed energy values.

The discussion given above leads us to the following expression for χ_{iso} for an approximate Hamiltonian:

$$\chi_{\text{iso}}=\sum_n \frac{\partial \bar{M}_n}{\partial H} e^{\beta(F-W_n)}, \tag{2.1}$$

where $\bar{M}_n$ is the average of M_n over all the degenerate states with energy W_n. It may be called the microcanonical average of M, after Gibbs. The only difference between (1.2) and (2.1) is, mathematically speaking, that the order of the differentiation with respect to H and the microcanonical averaging is reversed. Physically speaking, (1.2) excludes all mixing processes among the degenerate states, each of which does not always have the same magnetic moment, whereas (2.1) does not. Thus we will have different results from (1.2) and (2.1). (2.1) can also be derived straightforwardly from the ergodic theorem. This derivation will be given in the next section.

The proof of the equivalence between χ_S, given by (1.1), and χ_{iso}, given by (2.1), can readily be carried out if we proceed in the same way as Broer did in his classical proof.[4] Therefore we may merely outline the proof here. First the relation between χ_{iso} and χ_T is found as follows:

$$\chi_T-\chi_{\text{iso}}=\beta[\langle(\bar{M})^2\rangle-\langle M\rangle^2], \tag{2.2}$$

where $\langle\quad\rangle$ means the canonical average. The difference between χ_S and χ_T is given as

$$\chi_T-\chi_S=\beta(\langle MW\rangle-\langle M\rangle\langle W\rangle)^2/(\langle W^2\rangle-\langle W\rangle^2). \tag{2.3}$$

Next, we approximate all the canonical averages in (2.2) and (2.3) using the following expansion formula due to Gibbs:

$$\langle G\rangle=\bar{G}_{\langle W\rangle}+\tfrac{1}{2}(\langle W^2\rangle-\langle W\rangle^2)\partial^2\langle G\rangle/\partial W^2, \tag{2.4}$$

where G is the operator corresponding to an arbitrary extensive quantity. Since (2.4) is quite satisfactory for any macroscopic system which obeys the laws of statistical thermodynamics, its application does not cause any appreciable errors. From (2.2), (2.3) and (2.4) we finally reach the required result

$$\chi_S=\chi_{\text{iso}}. \tag{2.5}$$

We see now that there is no reason to distinguish χ_{iso} from χ_S so long as we remain within the framework of statistical thermodynamics. Henceforth we will not distinguish (2.1) from (1.1), the common notation, χ_S, being used for both expressions. Of course this does not exclude the possibility that χ_{iso}, given by (1.2), might correspond to a real quantity experimentally observable in some situations, as was suggested by Caspers.[6] However, such a possibility clearly falls outside of the range of applicability of statistical thermodynamics and it should be discussed on the basis of a dynamical theory such as that given by Kubo and Tomita.[8]

III. FORMAL DERIVATION OF THE EXPRESSION (2.1) FOR χ_S

The expression (2.1) for χ_S will be derived here in a straightforward way from the principles of quantum

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[8] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

mechanics and statistical mechanics to make the discussion given in the preceding section more definite.

We will consider the same system as in Sec. II. It is assumed to exist at $t=0$ in the state which is described by a canonical ensemble ρ_0 with temperature k/β. The system is also assumed to be isolated from its surroundings. In order to measure the adiabatic susceptibility, a weak magnetic field $\Delta H(t)$ is applied which increases linearly from zero at $t=0$ to ΔH at $t=t$. The rate of change of magnetic field is assumed to be infinitesimally small so that even after a sufficiently long time ΔH is still a small quantity. We may take into consideration only first order effects in ΔH. The equation of motion is now

$$\partial\rho/\partial t=(i/\hbar)[\rho,\mathcal{H}-\Delta H(t)M], \tag{3.1}$$

where $\mathcal{H}$ is the true Hamiltonian of the isolated system. Equation (3.1) is integrated in the approximation referred to above with the result

$$\rho(t)=\rho_0+\frac{i}{\hbar}\Delta H\int_0^t dt'\left(1-\frac{t'}{t}\right)[M(-t'),\rho_0]. \tag{3.2}$$

$M(-t')$ is the magnetic moment at $t=-t'$ in the Heisenberg picture. The increment in the average value of the magnetic moment at t becomes

$$\langle\Delta M\rangle(t)=\frac{i}{\hbar}\Delta H\int_0^t dt'\left(1-\frac{t'}{t}\right)\langle[M(t'),M]\rangle. \tag{3.3}$$

$\langle\ \rangle$ on the right-hand side of (3.3) refers to the initial canonical ensemble, ρ_0. After rewriting (3.3) in the representation diagonalizing $\mathcal{H}$, and making some elementary calculations, we obtain the following expression for the susceptibility:

$$\chi=\int_0^\beta d\lambda\,\langle MM(i\hbar\lambda)\rangle-\lim_{t\to\infty}\frac{1}{t}\int_0^t dt'\int_0^\beta d\lambda \times\langle M(t')M(i\hbar\lambda)\rangle. \tag{3.4}$$

Now we have reached the stage where we can introduce the ergodic theorem due to von Neumann.[9] Namely the time average of M over a long time is replaced by its microcanonical average $\bar{M}$. The operator $\bar{M}$ is defined as follows: The true Hamiltonian $\mathcal{H}$ is approximated by a suitable operator $\mathcal{H}^0$ with tremendous degeneracies. The diagonal elements of M in the representation diagonalizing $\mathcal{H}^0$ are averaged within each degenerate subspace of $\mathcal{H}^0$. With these values as its eigenvalues, the operator $\bar{M}$ is defined so that it commutes with $\mathcal{H}^0$.[10] The adiabatic susceptibility thus turns out to be

$$\chi_S=\int_0^\beta d\lambda\,\langle MM(i\hbar\lambda)\rangle-\beta\langle(\bar{M})^2\rangle. \tag{3.5}$$

Incidentally the isothermal susceptibility, χ_T, can also be obtained from (3.4) if we replace the time average of M by its canonical average. Thus we have

$$\chi_T=\int_0^\beta d\lambda\,\langle MM(i\hbar\lambda)\rangle-\beta\langle M\rangle^2. \tag{3.6}$$

This result was first found by Kubo and Tomita[8] through consideration of the response of the system to an oscillating field. (3.6) can easily be verified to agree with the original definition of $\chi_T=(\partial\langle M\rangle/\partial H)_T$, which may be approximated by using $\mathcal{H}^0$ in it instead of $\mathcal{H}$. From the resulting expression for χ_T, together with (3.5) and (3.6), we finally arrive at the required expression (2.1) for χ_S, if we identify the energy values W_n in (2.1) with those of the approximate Hamiltonian $\mathcal{H}^0$.

Before closing the discussion in this section, two comments may be added. First, it should be emphasized that mixing processes among the degenerate states have been taken into account through the ergodic theorem. It is this theorem which allows us to ignore many kinds of small hidden disturbances within the system which are extremely hard to know anything about. Without this theorem, as is easily confirmed, we would be led to the expression (1.2), χ_{iso}, which obviously is much more inconvenient for practical applications than (2.1). Second, the mixing processes, referred to above, do not lead to any change in the value of the entropy, insofar as first order effects in ΔH are concerned. This is simply because the entropy already has its maximum value at $t=0$ so that any first order redistribution in the ensemble can not affect it. From this fact we can obtain a most vivid impression of the physical significance of the principle of maximum entropy.

IV. SYSTEM OF SPINS WEAKLY COUPLED BY MAGNETIC INTERACTION UNDER A STRONG MAGNETIC FIELD

The general discussion given in the preceding sections will be applied to simple spin systems. The purpose is to show that the standard perturbation method is really applicable for the calculation of (2.1) to get the same result as that obtained from (1.1). To this end, we may confine ourselves to as simple systems as possible. Namely the Hamiltonian consists only of a Zeeman term and a magnetic dipole-dipole interaction. The latter will be treated as a small perturbation, the magnetic field being assumed sufficiently strong.

Our principal task is to find the expression for $\bar{M}_n$. As is well known, the evaluation of a microcanonical average is generally far more difficult than finding the corresponding canonical average. In fact the microcanonical averaging requires detailed information about the structure of the energy levels. Caspers' calculation[6] can indeed be supposed to have been done in this way.

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[9] J. von Neumann, Z. Physik **57**, 30 (1929).

[10] An example of $\mathcal{H}^0$ and of $\bar{M}$ will be shown in the next section.

Here we will take another approach to get an approximate result by a perturbation calculation. We will make use of the expansion formula (2.4) in its reversed form:

$$\bar{M}_{W=\langle W\rangle'}=\langle M\rangle'-\tfrac{1}{2}(\langle W^2\rangle-\langle W\rangle^2)\partial^2\langle M\rangle'/\partial W^2. \qquad (4.1)$$

$\langle\ \rangle'$ means to take the average over the canonical distribution whose temperature β' is determined so that the average energy $\langle W\rangle'$ is equal to W. Now we have to re-express the right-hand side of (4.1) as a function of H and W.

We may refer to the original paper by Broer[4] concerning the expressions for the energy levels and the free energy of our system due to the second order perturbational calculation: the energy levels are given as

$$W_n=-HM_n{}^0+V_n+B_n/H, \qquad (4.2)$$

or more conveniently in the operator form

$$\mathbf{W}=-H\mathbf{M}^0+\mathbf{V}+\mathbf{B}/H; \qquad (4.3)$$

the free energy is then

$$F(\beta,H)=-\tfrac{1}{2}\beta\{H^2\langle(\mathbf{M}^0)^2\rangle_{\rm Av}+\langle\mathbf{V}^2\rangle_{\rm Av}-2\langle\mathbf{M}^0\mathbf{B}\rangle_{\rm Av}\} \qquad (4.4)$$

in the high-temperature approximation. The first term on the right-hand side of each of (4.2), (4.3), and (4.4) corresponds to the Zeeman energy, the second term to the first order perturbation energy due to the diagonal interaction and the third term to the second order perturbation energy due to the non-diagonal interaction. All the operators $\mathbf{W}$, $\mathbf{M}^0$, $\mathbf{V}$, and $\mathbf{B}$ are diagonal and their eigenfunctions need not be specified here. The angular brackets in (4.4) mean taking the average over all the eigenstates of $\mathbf{W}$ with equal weight.

We can calculate from (4.4) the average energy $\langle W\rangle'=W$ corresponding to the temperature β'. The resulting equation is solved for β':

$$\beta'=-\frac{W}{H^2\langle(\mathbf{M}^0)^2\rangle_{\rm Av}+\langle\mathbf{V}^2\rangle_{\rm Av}-2\langle\mathbf{M}^0\mathbf{B}\rangle_{\rm Av}}. \qquad (4.5)$$

Again from (4.4) we can obtain

$$\langle M\rangle'=-(\partial F(\beta',H)/\partial H)_{\beta'},$$

which can be rewritten by use of (4.5) as follows:

$$\langle M\rangle'=-\frac{W}{H^3\langle(\mathbf{M}^0)^2\rangle_{\rm Av}}[H^2\langle(\mathbf{M}^0)^2\rangle_{\rm Av}-\langle\mathbf{V}^2\rangle_{\rm Av}+2\langle\mathbf{M}^0\mathbf{B}\rangle_{\rm Av}]. \qquad (4.6)$$

Inserting (4.6) into (4.1) we get the required expression for $\bar{M}_W$:[11]

$$\bar{\mathbf{M}}=\mathbf{M}^0-\frac{\mathbf{V}}{H}-\frac{\mathbf{B}}{H^2}-\frac{\mathbf{M}^0}{H^2\langle(\mathbf{M}^0)^2\rangle_{\rm Av}}\times(\langle\mathbf{V}^2\rangle_{\rm Av}-2\langle\mathbf{M}^0\mathbf{B}\rangle_{\rm Av}). \qquad (4.7)$$

After differentiating (4.7) with respect to H and putting the result into (2.1), we finally obtain in the present approximation

$$\chi_S=(\beta/H^2)(\langle\mathbf{V}^2\rangle_{\rm Av}-2\langle\mathbf{M}^0\mathbf{B}\rangle_{\rm Av}). \qquad (4.8)$$

This is just the result which Broer derived from (1.1) in the same approximation.[4] We recall that, when Broer calculated (1.2), on the other hand, he got a result which lacked the first term on the right-hand side of (4.8), the contribution from the diagonal interaction. His result is not hard to understand, because (1.2) does not imply mixing processes among the degenerate states. Hence, the only processes which can change the value of the magnetic moment during adiabatic processes are due to the nondiagonal interaction explicitly involved in the Hamiltonian $\mathbf{W}$.

The calculation presented in this section can be said to show the applicability of the perturbation method even to spin systems with magnetic interaction as well as to provide an illustrative example of the general proof given in Sec. II.

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[11] $\mathbf{W}$, given by (4.3), and $\bar{\mathbf{M}}$, given above, correspond to $\mathcal{H}^0$ and $\bar{M}$ in the preceding section, respectively.