Lower Bound for the Isothermal Magnetic Susceptibility

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It is shown that the zero-frequency magnetic susceptibility defined by Kubo is a lower bound for the zero-field isothermal magnetic susceptibility.

I. INTRODUCTION

With a system on equilibrium, one associates ensemble averages of operators. If the system is exposed to a time-varying field, the system may respond, and the initial ensemble averages may be replaced by averages evolving in time. Kubo[1] has discussed the evolution of the averages in terms of a perturbation-series solution to the Liouville equation. The perturbation parameter is the coupling between the unperturbed system and the applied field, and attention is usually focused only on the first-order term in the perturbation series—hence, "the theory of linear response." The linear term is characterized by a response function[1] or equivalently by a double-time Green's function.[2] A Fourier integral of the response function determines a quantity commonly called the frequency-dependent susceptibility.

Prior to the above statistical-mechanical theory, there existed a phenomenological theory[3] of linear response. The phenomenological theory also yields a frequency-dependent susceptibility which for zero frequency reduces to the familiar isothermal susceptibility. However, Kubo noted[1] that the statistical-mechanical theory gives a frequency-dependent susceptibility which at zero frequency does not necessarily equal the isothermal susceptibility.

It will be shown in this paper that at zero frequency Kubo's magnetic susceptibility is a lower bound for the familiar zero-field isothermal magnetic susceptibility.

II. RESPONSE FORMALISM

A concise derivation of the response formalism is found in a recently published translation of Tyablikov's book.[2] To establish the present notation and the essential equations, a summary of the derivation follows.

Let the unperturbed system be characterized by a Hamiltonian H_0 and let its equilibrium behavior be given in terms of the canonical ensemble density operator $\rho_0=\exp[-\beta(F_0-H_0)]$, where the unperturbed Helmholtz free energy is $F_0=-\beta^{-1}\ln\operatorname{Tr}\exp(-\beta H_0)$. Take the perturbing Hamiltonian

$$\bar{H}_1(t)=0, \qquad \text{for } t<t_0$$
$$=H_1(t), \qquad \text{for } t\geq t_0.$$

With the complete Hamiltonian,

$$H(t)=\bar{H}_1(t)+H_0$$

associate the density operator

$$\rho(t)=\rho_1(t)+\rho_0.$$

In the following, $\hbar$ will be replaced by 1; consequently, the Liouville equation is written

$$(id/dt)\rho(t)=[H(t),\rho(t)],$$

with the initial condition

$$\rho(t_0)=\rho_0.$$

For an operator $L(t)$, define

$$\tilde{L}(t)=\exp(iH_0t)\,L(t)\,\exp(-iH_0t),$$

so that the Liouville equation is transformed to

$$(id/dt)\tilde{\rho}_1(t)=[\tilde{\bar{H}}_1(t),\rho_0]+[\tilde{\bar{H}}_1(t),\tilde{\rho}_1(t)], \qquad (t\geq t_0)$$

with

$$\tilde{\rho}_1(t_0)=0.$$

The latter differential equation is iterated according to the scheme

$$(id/dt)\tilde{\rho}_{1,l}(t)=[\tilde{\bar{H}}_1(t),\rho_0]+[\tilde{\bar{H}}_1(t),\tilde{\rho}_{1,l-1}(t)],$$

with

$$\tilde{\rho}_{1,0}(t)=0, \qquad \text{for } t\geq t_0$$
$$\tilde{\rho}_{1,l}(t_0)=0, \qquad \text{for } l=1,2,\cdots.$$

The first iteration gives

$$\tilde{\rho}_{1,1}(t)=i^{-1}\int_{t_0}^{t}dt_1\,[\tilde{\bar{H}}_1(t_1),\rho_0]$$

and the second iteration gives

$$\tilde{\rho}_{1,2}(t)=i^{-1}\int_{t_0}^{t}dt_1\,[\tilde{\bar{H}}_1(t_1),\rho_0]+\left(\frac{1}{i}\right)^2\int_{t_0}^{t}dt_2\times\int_{t_0}^{t_2}dt_1\,[\tilde{\bar{H}}_1(t_2),[\tilde{\bar{H}}_1(t_1),\rho_0]];$$

thus an arbitrary contribution to the perturbation-series solution is easily generated.

Now the average of an operator Q is written $\langle Q\rangle$ and defined by

$$\langle Q\rangle=\operatorname{Tr}\rho(t)Q$$
$$=\operatorname{Tr}\rho_1(t)Q+\operatorname{Tr}\rho_0Q,$$

[1] R. Kubo, J. Phys. Soc. Japan, **12**, 570 (1957).
[2] S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum Press, Inc., New York, 1967), pp. 237–245.
[3] H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Dover Publications, Inc., New York, 1961), pp. 83–84.

where it is assumed that the traces exist and satisfy the usual invariance properties. Therefore, with $\langle Q\rangle_0$ denoting $\mathrm{Tr}\rho_0 Q$,

$$\langle Q\rangle-\langle Q\rangle_0=\mathrm{Tr}\rho_1(t)Q$$
$$=\mathrm{Tr}\exp(-iH_0t)\tilde{\rho}_1(t)\exp(iH_0t)Q.$$

If, as in the following discussion, only the linear response is considered, then $\tilde{\rho}_1(t)$ is replaced by $\tilde{\rho}_{11}(t)$, and

$$\langle Q\rangle-\langle Q\rangle_0=\mathrm{Tr}\tilde{\rho}_{11}(t)Q(t)+O(H_1^2)$$
$$=i^{-1}\int_{t_0}^{t}dt_1\,\mathrm{Tr}[\tilde{H}_1(t_1),\rho_0]Q(t)+O(H_1^2)$$
$$=i^{-1}\int_{t_0}^{t}dt_1\,\mathrm{Tr}[H_1(t_1),\rho_0]Q(t-t_1)+O(H_1^2),$$

with the understanding that dynamical quantities evolve according to

$$L(t)=\exp(iH_0t)L(O)\exp(-iH_0t).$$

For the present treatment select

$$H_1(t)=-Mh(t),$$

where $h(t)$ denotes a time-varying magnetic field and M denotes the component of the system's magnetization along $\mathbf{h}$. Now consider the response of the average value of M to the above Zeeman energy of perturbation.

$$\langle M\rangle-\langle M\rangle_0=i^{-1}\int_{t_0}^{t}dt_1\,h(t_1)$$
$$\times\mathrm{Tr}[M(t_1),\rho_0]M(t)+O(H_1^2)$$
$$=\int_{t_0}^{t}dt_1\,h(t_1)\phi(t-t_1)+O(H_1^2),$$

where $\phi(t-t_1)$ is the response function which is defined by

$$(1/i)\phi(t-t_1)=\mathrm{Tr}[M(t_1),\rho_0]M(t)$$
$$=-\mathrm{Tr}[\rho_0,M(t_1)]M(t).$$

At this point it is worthwhile to note the following identities[4]:

[4] Identity (3) is established easily by induction, whereas (1) is established by letting $g(\lambda)=\exp(\lambda A)B\exp(-\lambda A)-B$ and $f(\lambda)=\exp(-\lambda A)g(\lambda)$, then $g'(\lambda)=\exp(\lambda A)[A,B]\exp(-\lambda A)$ and

$$g(\lambda)=\int_0^{\lambda}d\lambda_1\exp(\lambda_1A)[A,B]\exp(-\lambda_1A),$$

which immediately gives the desired integral representation of the commutator $f(\beta)$. Identity (2) is established in a manner analogous to (1).

Identity (1):

$$[D,\exp(-\beta H_0)]=\exp(-\beta H_0)$$
$$\times\int_0^{\beta}d\lambda\,\exp(\lambda H_0)[H_0,D]\exp(-\lambda H_0).$$

Identity (2):

$$(\partial/\partial h)\exp[-\beta(H_0-hM)]=\exp[-\beta(H_0-hM)]$$
$$\times\int_0^{\beta}d\lambda\,\exp[\lambda(H_0-hM)]M\exp[-\lambda(H_0-hM)].$$

Identity (3): For a set of operators $\{C_0,C_1,\cdots,C_n\}$,

$$\mathrm{Tr}D[C_n,[C_{n-1},\cdots,[C_1,C_0]\cdots]]$$
$$=\mathrm{Tr}[\cdots[[D,C_n],C_{n-1}],\cdots,C_1]C_0.$$

From the definition of

$$\dot{L}(t)\equiv(d/dt)L(t)$$
$$=\exp(iH_0t)i[H_0,L(0)]\exp(-iH_0t)=i[H_0,L(t)]$$

and the definition of ρ_0, it follows from identities (1) and (3) that

$$-\mathrm{Tr}[\rho_0,A(t_1)]B(t)$$
$$=\mathrm{Tr}\rho_0[B(t),A(t_1)]$$
$$=\mathrm{Tr}[\rho_0,B(t)]A(t_1)$$
$$=\mathrm{Tr}[\rho_0,B(0)]A(t_1-t)$$
$$=-\mathrm{Tr}[\rho_0,A(0)]B(t-t_1)$$
$$=-i\int_0^{\beta}d\lambda\,\mathrm{Tr}\rho_0\exp(\lambda H_0)\dot{A}(t_1)\exp(-\lambda H_0)B(t)$$
$$=i\int_0^{\beta}d\lambda\,\mathrm{Tr}\rho_0\exp(\lambda H_0)\dot{B}(t)\exp(-\lambda H_0)A(t_1)$$
$$=i\int_0^{\beta}d\lambda\,\mathrm{Tr}\rho_0\exp(\lambda H_0)A(t_1)\exp(-\lambda H_0)\dot{B}(t),$$

where the last form was arrived at by changing the integration variable. The response function and the corresponding double-time Green's function[2] can thus take on a number of disguises. For this occasion, select the last one for which

$$\phi(t-t_1)=(d/d\tau)g(\tau),$$

where

$$g(\tau)=-\int_0^{\beta}d\lambda\,\mathrm{Tr}\rho_0\exp(\lambda H_0)M(0)\exp(-\lambda H_0)M(\tau)$$

and

$$\tau=t-t_1.$$

In accord with Kubo,[1] define the frequency-dependent susceptibility

$$\chi(\omega)=\lim_{\epsilon\to0+}\int_0^{\infty}d\tau\,\exp(-i\omega\tau-\epsilon\tau)(d/d\tau)g(\tau).$$

With $\omega=0$, integration by parts yields the following expression for the zero-frequency susceptibility:

$$\chi(0)=-g(0)+\lim_{\epsilon\to 0+}\epsilon\int_0^\infty d\tau\,\exp(-\epsilon\tau)g(\tau).$$

III. UPPER BOUND FOR $\chi(0)$

Consider the set of eigenstates $|\,l\rangle$ of H_0, where

$$H_0\,|\,l\rangle=E_l\,|\,l\rangle.$$

The trace appearing in $g(\tau)$ may be separated into three contributions, so that

$$g(\tau)=-s_1(0)-s_2(0)-s_3(\tau),$$

where

$$s_1(0)=\beta\sum_l[\exp(-\beta E_l)/\mathrm{Tr}\rho_0]\,|\,\langle l\,|\,M\,|\,l\rangle\,|^2,$$

$$s_2(0)=\beta\sum_{l,m}[\exp(-\beta E_l)/\mathrm{Tr}\rho_0]\,|\,\langle l\,|\,M\,|\,m\rangle\,|^2,\qquad (l\neq m,\ E_l=E_m),$$

$$s_3(\tau)=\int_0^\beta d\lambda\sum_{l,m}\frac{\exp(-\beta E_l)}{\mathrm{Tr}\rho_0}\exp[\lambda(E_l-E_m)]\times\exp[-i(E_l-E_m)\tau]\,|\,\langle l\,|\,M\,|\,m\rangle\,|^2,\qquad (E_l\neq E_m).$$

Each term is easily integrated, i.e.,

$$\lim_{\epsilon\to 0+}\epsilon\int_0^\infty d\tau\,\exp(-\epsilon\tau)s_1(0)=s_1(0)$$

and similarly for $s_2(0)$. Furthermore with $x=(E_l-E_m)\neq 0$,

$$\lim_{\epsilon\to 0+}\epsilon\int_0^\infty d\tau\,\exp(-\epsilon\tau)\exp(ix\tau)=0;$$

thus $s_3(\tau)$ contributes nothing to $\chi(0)$, and

$$\chi(0)=-g(0)-s_1(0)-s_2(0).$$

Notice that for non-negative temperature

$$-s_2(0)\leqq 0.$$

Next consider $s_1(0)$ in terms of

$$\gamma_l\equiv\exp(-\beta E_l)/\mathrm{Tr}\rho_0$$

and

$$\mu_l\equiv\langle l\,|\,M\,|\,l\rangle;$$

then

$$\gamma_l\geqq 0$$

and

$$\sum_l\gamma_l=1.$$

From the Schwarz inequality,

$$\beta(\sum_l\gamma_l\mu_l)^2=\beta(\sum_l\gamma_l^{1/2}\gamma_l^{1/2}\mu_l)^2\leqq\beta\sum_{l'}\gamma_{l'}\sum_l\gamma_l\mu_l^2=s_1(0),$$

and we have

$$\chi(0)\leqq-g(0)-s_1(0)\leqq-g(0)-\beta(\sum_l\gamma_l\mu_l)^2,$$

thus

$$\chi(0)\leqq\int_0^\beta d\lambda\,[\langle M(-i\lambda)M(0)\rangle_0-\langle M\rangle_0^2].$$

But the right side of the inequality is just the zero-field isothermal susceptibility χ_T^0, since

$$\chi_T^0\equiv\{-(\partial/\partial h)^2[-\beta^{-1}\ln\mathrm{Tr}\exp(-\beta(H_0-hM))]\}_{h=0}$$

$$=-\beta^{-1}\left[\left(\frac{(\partial/\partial h)\,\mathrm{Tr}\exp[-\beta(H_0-hM)]}{\mathrm{Tr}\exp[-\beta(H_0-hM)]}\right)^2-\left(\frac{(\partial/\partial h)^2\,\mathrm{Tr}\exp[-\beta(H_0-hM)]}{\mathrm{Tr}\exp[-\beta(H_0-hM)]}\right)\right]_{h=0}.$$

Apply identity (2) and the cyclic-invariance property of the trace to see that

$$(\partial/\partial h)\,\mathrm{Tr}\exp[-\beta(H_0-hM)]=\beta\,\mathrm{Tr}M\exp[-\beta(H_0-hM)]$$

and

$$\{(\partial/\partial h)^2\,\mathrm{Tr}\exp[-\beta(H_0-hM)]\}_{h=0}=\beta\int_0^\beta d\lambda\,\mathrm{Tr}\exp[-\beta H_0]M(-i\lambda)M(0).$$

This demonstrates that

$$\chi(0)\leqq\chi_T^0.$$

IV. REMARKS

Kubo has discussed[1] conditions for which $\chi(0)=\chi_T^0$, and a very interesting calculation[5] of $\chi^\perp(0)$ for the two-dimensional Ising model indicates that $\chi^\perp(0)=\chi_T^{0\perp}$ for the hexagonal lattice and $\chi^\perp(0)\leq\chi_T^{0\perp}$ for the square lattice. A physical explanation of this sensitivity to lattice structure is given by the authors.

For $[M,\ H_0]=0$, $\chi(0)=0$; whereas the zero-field isothermal susceptibility χ_T^0 and the corresponding adiabatic susceptibility χ_s^0 may both be nonzero. An example of just such a situation is provided by the exactly soluable X-Y model for which χ_T and χ_s are readily calculated from formulas given by Katsura[6]

[5] G. A. T. Allen and D. D. Betts, Can. J. Phys. (to be published).

[6] S. Katsura, Phys. Rev. **127**, 1508 (1962).

and by using the thermodynamic relation[7]

$$\chi_T=\chi_s+\frac{T(\partial M/\partial T)_h^2}{C_h},$$

where C_h is the specific heat at fixed field.

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[7] J. H. Van Vleck, Z. Physik. Chem. (Frankfurt) 16, 358 (1958).

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Transport Properties of the "Excitonic Insulator": Electrical Conductivity*

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The dc conductivity of the "excitonic insulator" recently discussed in the literature is calculated in the semimetallic region. The calculations are based on recent work on the description of the excitonic phase in the presence of impurities. It is shown that the conductivity decreases below the transition temperature to the excitonic state. For low impurity concentrations the system acquires insulating properties. For higher impurity concentrations the conductivity is still nonzero at $T=0$. Thus, metallic properties prevail in the excitonic phase. It is pointed out that this behavior depends essentially on the form of the excitation spectrum of the system, i.e., the presence or absence of a gap. At the transition temperature the conductivity-versus-temperature curve has a finite slope.

I. INTRODUCTION

RECENTLY, several papers have discussed the properties of an excitonic phase which is expected to occur in solids with small energy band gap.[1,2] The phase can be described as a condensate of bound pairs of electrons and holes due to an effective attractive interaction between conduction-band and valence-band states. In the normal state one considers both a positive band gap (semiconductor) and a negative band gap (semimetals). The most extensive study of the properties of this phase has been given by Jerome, Rice, and Kohn.[1] Besides the question of experimental observability, they have discussed in detail the ordering phenomenon which takes place in the new state.

While the thermodynamic properties of the excitonic phase are similar to those of a superconductor, the electromagnetic properties are perhaps more interesting from an experimental point of view. According to the work of Jerome, Rice, and Kohn[1] the excitonic phase turns out to be an insulator. This is especially interesting in the case where the underlying two-band model has a negative band gap (semimetallic region) and therefore would conventionally have metallic properties.

This paper deals with the electrical conductivity of the excitonic phase at low temperatures where the main scattering mechanism is due to impurities and imperfections. Jerome, Rice, and Kohn[1] have calculated the frequency-dependent complex conductivity for the pure system and have derived the dc conductivity by using Kramers-Kronig relations and a simple ansatz for taking scattering into account. The more rigorous calculation in this paper does not confirm their results. The reason for this is that the impurities play a rather intricate role. In a former paper[3] we have considered the influence of randomly distributed impurities on the excitonic phase. We found that the situation is very similar to the case of magnetic impurities in superconductors, i.e., the impurities have a pair-breaking

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[1] D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. 158, 462 (1967).

[2] L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela 6, 2791 (1964) [English transl.: Soviet Phys.—Solid State 6, 2219 (1965)]; Yu. V. Kopaev, Fiz. Tverd. Tela 8, 223 (1966) [English transl.: Soviet Phys.—Solid State 8, 175 (1966)]; A. N. Kozlov and L. A. Maksimov, Zh. Eksperim. i Teor. Fiz. 48, 1184 (1965); 49, 1284 (1965) [English transls.: Soviet Phys.—JETP 21, 790 (1965); 22, 889 (1966)]; J. Zittartz, Phys. Rev. 162, 752 (1967). Other references can be found in Ref. 1.

[3] J. Zittartz, Phys. Rev. 164, 575 (1967). This paper will be referred to as I.