PHYSICAL REVIEW VOLUME 174, NUMBER 2 10 OCTOBER 1968

Bounds for the Isothermal, Adiabatic, and Isolated Static Susceptibility Tensors

R. M. Wilcox
National Bureau of Standards, Boulder, Colorado 80302

(Received 27 March 1968)

Quantum-statistical proofs are given that the isolated (or Kubo) susceptibility tensor is positive indefinite and is bounded from above by the adiabatic susceptibility tensor, while the isothermal susceptibility tensor is positive definite and is bounded from below by the adiabatic susceptibility tensor. The results apply to either the static dielectric or magnetic cases. Biasing fields and permanent dipole moments may be present if desired. Criteria for equality of the various susceptibilities are established. Contact is made with work of Falk, Caspers, Mountain, Klein, Rosenfeld, and Saitô.

1. INTRODUCTION

It has recently been shown by Falk[1] that the zero-frequency magnetic susceptibility defined by Kubo[2] (also called the isolated susceptibility) is bounded from above by the isothermal susceptibility. In this paper, our main result is to prove that the isolated susceptibility is also bounded from above by the adiabatic susceptibility. This is a stronger result than Falk's since it is already known from thermodynamics that the adiabatic susceptibility is bounded from above by the isothermal susceptibility. (In this paper, the word "susceptibility" will always mean "static dielectric or magnetic susceptibility" unless stated otherwise).

In order that our results may be applied to a variety of experimental situations regardless of symmetry considerations, we treat the tensor case. If desired, the system may have a permanent dipole moment (either electric or magnetic), and constant "biasing" fields may be present. Although the relationship between the isothermal and adiabatic susceptibilities is known from thermodynamics, we believe that it is obviously desirable to treat all three susceptibilities systematically from a quantum-statistical point of view.

In Secs. 2, 3, and 4, respectively, the isothermal, adiabatic, and isolated susceptibility tensors are defined and calculated in a manner which makes clear the differences between them. Although everyone understands the difference between an isothermal and adiabatic process, the distinction between an adiabatic and isolated process may not be widely appreciated.

In an isolated process, it is assumed that a perfectly isolated system undergoes a change due to some very slowly varying externally controlled parameter of its Hamiltonian. According to the quantum-mechanical adiabatic theorem,[3] the eigenstates and eigenvalues change continuously as the parameter (assumed here to be the applied field) changes with time, but the probability of being in a given eigenstate remains constant. Unless rather stringent restrictions are satisfied by the Hamiltonian, an initially canonical ensemble will not remain canonical,[4] i.e., describable by a Boltzmann distribution.

In an adiabatic process, on the other hand, it is assumed that the behavior of the system may at all times be described by a canonical ensemble. Such a system is no longer perfectly isolated but, in Tolman's terminology, is only essentially isolated[5]; i.e., although necessarily in contact with its immediate surroundings, no *net* interchange of energy takes place on the average. Tolman has argued persuasively that, for the long-time behavior of supposedly isolated systems commonly encountered in the laboratory, the concept of essential isolation is often the most appropriate.[5]

The susceptibility formulas obtained in Secs. 2–4 are expressed in a convenient "scalar product" notation defined by Eq. (A1) of the Appendix. In Sec. 5, these formulas are compared by means of the Schwarz inequality, Eq. (A4). In Sec. 6, conditions under which the adiabatic and isolated susceptibilities will be equal or unequal are discussed and are related to previous work on this subject.

2. ISOTHERMAL SUSCEPTIBILITY TENSOR

Consider a system described by a Hamiltonian $\mathcal{H}_0$ subject to a slowly varying applied field $\mathbf{F}$. Then in the presence of the field, the total Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H}=\mathcal{H}_0-\mathbf{M}\cdot\mathbf{F}, \tag{1}$$

where $\mathbf{M}$ is the dipole moment operator of the system. If the system is in thermal contact with a heat bath

[1] H. Falk, Phys. Rev. **165**, 602 (1968).
[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[3] This adiabatic theorem is the quantum analog of the classical Ehrenfest adiabatic principle. See, e.g., Richard C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), 1st ed., Chap. 11, Sec. 97, p. 414. A more mathematically sophisticated treatment is given in Albert Messiah, *Quantum Mechanics* (North-Holland Publishing Co., Amsterdam, 1962), Vol. 2, Chap. 17, Sec. 10, p. 744.
[4] It can be shown (see, e.g., Mountain, Ref. 16) that the condition for an initially canonical ensemble to remain canonical as the external parameter in the Hamiltonian is varied is that the ratio of the separations between any two different pairs of energy levels remain constant. In other words, the energy-level diagram can undergo at most a displacement plus a uniform expansion or contraction. This condition is satisfied by (1) a system of independent harmonic oscillators with linear dipole moments in the presence of an electric field, (2) a system of independent spins in a magnetic field, (3) an ideal gas enclosed in a box of adjustable volume. However, it is not difficult to find systems which do not satisfy this condition.
[5] Richard C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), 1st ed., pp. 498–501.

which maintains its temperature constant at all times as the field is varied, then the thermally averaged dipole moment $\langle \mathbf{M} \rangle$ is given by

$$\langle \mathbf{M} \rangle = \mathrm{Tr}(\rho \mathbf{M}), \qquad (2)$$

where

$$\rho = \{\exp(-\beta \mathcal{H})/\mathrm{Tr}[\exp(-\beta \mathcal{H})]\}. \qquad (3)$$

The isothermal susceptibility tensor χ_{ij}^T is then defined by

$$\chi_{ij}^T = \partial \langle \mathbf{M}_j \rangle / \partial F_i |_\beta \qquad (i,j=x,y,z), \qquad (4)$$

where the differentiation is to be carried out at constant β $(=1/KT)$. Substituting Eqs. (1)–(3) in Eq. (4), the differentiation may be carried out by using the formula for the derivative of an exponential operator with respect to a parameter[6]:

$$\frac{\partial \exp(-\beta \mathcal{H})}{\partial F_i} = -\int_0^\beta du \exp[-(\beta-u)\mathcal{H}] \times \frac{\partial \mathcal{H}}{\partial F_i} \exp(-u\mathcal{H}). \qquad (5)$$

One obtains

$$\chi_{ij}^T = \beta \langle M_i \mid M_j \rangle - \beta \langle M_i \rangle \langle M_j \rangle, \qquad (6)$$

where the "scalar product" $\langle M_i \mid M_j \rangle$ is defined by Eq. (A1) of the Appendix.

Defining

$$\Delta \mathbf{M} \equiv \mathbf{M} - \langle \mathbf{M} \rangle, \qquad (7)$$

Eq. (6) may also be written

$$\chi_{ij}^T = \beta \langle \Delta M_i \mid \Delta M_j \rangle. \qquad (8)$$

3. ADIABATIC SUSCEPTIBILITY TENSOR

Now consider the system to be essentially isolated as explained in the Introduction. As the field is slowly varied, the temperature must change in such a way that no *net* energy transfer with the system's immediate surroundings takes place. In place of Eq. (4), the adiabatic susceptibility tensor χ_{ij}^s is thus defined by

$$\begin{aligned} \chi_{ij}^s &= \partial \langle M_j \rangle / \partial F_i |_s \\ &= \partial \langle M_j \rangle / \partial F_i |_\beta + (\partial \langle M_j \rangle / \partial \beta)(\partial \beta / \partial F_i)_s \\ &= \chi_{ij}^T - \langle \Delta \mathcal{H} \mid \Delta M_j \rangle (\partial \beta / \partial F_i)_s. \end{aligned} \qquad (9)$$

The quantity $(\partial \beta/\partial F_i)_s$ is calculated from the energy-conservation condition that the increase in the average internal energy of the system equals the average work done by the applied field,

$$d\langle \mathcal{H}_0 \rangle = \mathbf{F} \cdot d\langle \mathbf{M} \rangle. \qquad (10)$$

With the aid of Eq. (1), this may also be written

$$d\langle \mathcal{H} \rangle = -\langle \mathbf{M} \rangle \cdot d\mathbf{F}. \qquad (11)$$

Writing

$$d\langle \mathcal{H} \rangle = (\partial \langle \mathcal{H} \rangle / \partial \mathbf{F}) \cdot d\mathbf{F} + (\partial \langle \mathcal{H} \rangle / \partial \beta) d\beta \qquad (12)$$

and carrying out the indicated differentiations by means of Eq. (5), one obtains

$$(\partial \beta / \partial F_i)_s = \beta \langle \Delta \mathcal{H} \mid \Delta M_i \rangle / \langle \Delta \mathcal{H} \mid \Delta \mathcal{H} \rangle. \qquad (13)$$

Substituting Eqs. (8) and (13) into Eq. (9), one obtains

$$\chi_{ij}^s = \beta \langle \Delta M_i \mid \Delta M_j \rangle - \frac{\beta \langle \Delta \mathcal{H} \mid \Delta M_i \rangle \langle \Delta \mathcal{H} \mid \Delta M_j \rangle}{\langle \Delta \mathcal{H} \mid \Delta \mathcal{H} \rangle}. \qquad (14)$$

Although not essential to our arguments, it is nevertheless reassuring to note that Eq. (14) is equivalent to the thermodynamical identity

$$\chi_{ij}^s = \chi_{ij}^T - \frac{T}{C_F} \left(\frac{\partial M_i}{\partial T} \right)_F \left(\frac{\partial M_j}{\partial T} \right)_F, \qquad (15)$$

where C_F is the heat capacity at constant field.

4. ISOLATED SUSCEPTIBILITY TENSOR

Now consider the system to have been initially (long ago at $t=-\infty$) in thermal contact with a heat reservoir so that initially the system has a density matrix described by Eq. (1). (All constant electric or magnetic "biasing" fields or other constant externally controllable parameters are assumed to be contained in $\mathcal{H}$.) The system is then perfectly isolated and the field turned on very slowly so that the density matrix evolves according to the standard equation

$$i\hbar[\partial \rho(t)/\partial t] = [\mathcal{H}(t), \rho(t)]. \qquad (16)$$

In Eq. (16), $\mathcal{H}(t)$ is assumed to have the form

$$\mathcal{H}(t) = \mathcal{H} - e^{\epsilon t} \mathbf{f} \cdot \mathbf{M}, \qquad (17)$$

where ϵ is a small positive number which is to go to zero at the end of the calculation, and $\mathbf{f}$ represents an incremental deviation of the applied field from its biasing value $\mathbf{F}$. The isolated static susceptibility tensor is then defined by

$$\chi_{ij}^I = \lim_{f \to 0} \frac{[\mathrm{Tr}\rho(0) M_j - \mathrm{Tr}(\rho M_j)]}{f_i}, \qquad (18)$$

where $\rho(0)$ is the solution of Eq. (16) at $t=0$ subject to the initial condition $\rho(-\infty)=\rho$.

It is well known and easy to verify that the solution of Eq. (16) to terms linear in $\mathbf{f}$ is given by

$$\rho(t) = \rho + \rho_1(t), \qquad (19)$$

where

$$\rho_1(t) = -(i\hbar)^{-1} \int_{-\infty}^t d\tau\, e^{\epsilon \tau} \exp[\mathcal{H}(t-\tau)/i\hbar][\mathbf{f}\cdot\mathbf{M}, \rho] \times \exp[-\mathcal{H}(t-\tau)/i\hbar]. \qquad (20)$$

[6] See, e.g., R. M. Wilcox, J. Math. Phys. 8, 962 (1967).

Setting $t=0$, using the well-known identities

$$[M,\rho]=-\rho\int_0^\beta du\,\exp(u\mathcal{H})[M,\mathcal{H}]\exp(-u\mathcal{H}) \quad (21)$$

and

$$[\exp(-\mathcal{H}\tau/i\hbar)M\exp(\mathcal{H}\tau/i\hbar),\mathcal{H}]$$
$$=i\hbar\frac{\partial}{\partial\tau}[\exp(-\mathcal{H}\tau/i\hbar)M\exp(\mathcal{H}\tau/i\hbar)], \quad (22)$$

and substituting into Eq. (18), one obtains

$$\chi_{ij}{}^I=\beta\int_{-\infty}^0 d\tau\, e^{\epsilon\tau}\left\langle\frac{\partial}{\partial\tau}[\exp(-\mathcal{H}\tau/i\hbar)M_i \times\exp(\mathcal{H}\tau/i\hbar)]\mid M_j\right\rangle. \quad (23)$$

After an integration by parts, Eq. (23) becomes

$$\chi_{ij}{}^I=\beta\langle M_i\mid M_j\rangle-\beta\epsilon\int_{-\infty}^0 d\tau\, e^{\epsilon\tau}$$
$$\times\langle\exp(-\mathcal{H}\tau/i\hbar)M_i\exp(\mathcal{H}\tau/i\hbar)\mid M_j\rangle. \quad (24)$$

In the second term of Eq. (24) we set

$$\mathbf{M}=\mathbf{M}'+\mathbf{M}'', \quad (25)$$

where $\mathbf{M}'$ connects eigenstates of $\mathcal{H}$ having the same energy, while $\mathbf{M}''$ connects states having different energies. Then after performing the time integration and letting ϵ approach zero, one finds that the terms involving $\mathbf{M}''$ vanish,[7] so that Eq. (24) becomes finally

$$\chi_{ij}{}^I=\beta\langle M_i\mid M_j\rangle-\beta\langle M_i'\mid M_j'\rangle \quad (26a)$$
$$=\beta\langle M_i''\mid M_j''\rangle. \quad (26b)$$

The last line follows from Eq. (25) and the "orthogonality" of $\mathbf{M}'$ and $\mathbf{M}''$,

$$\langle\mathbf{M}'\mid\mathbf{M}''\rangle=0. \quad (27)$$

It may be verified that the diagonal elements $\chi_{ij}{}^I$ as given by Eqs. (26) are equivalent to Falk's result for the zero-frequency limit of the Kubo susceptibility.[1] If one also makes the "high-temperature approximation," as in Eq. (A8), then Eqs. (26) may also be shown to be equivalent to expressions obtained by Caspers for the paramagnetic isolated susceptibility, provided that the latter are properly interpreted.[8]

5. "SIZES" OF THE TENSORS

We first note that all of the susceptibility tensors are real and symmetric, as follows from Eqs. (A6). A real symmetric tensor χ_{ij} is said to be *positive definite* if for all real nonzero vectors $\mathbf{V}$ the quantity

$$\sum_{ij}V_i\chi_{ij}V_j \quad (28)$$

is always positive.[9] If instead this quantity is always non-negative, it is said to be *positive indefinite*. It is easily shown that the diagonal elements and eigenvalues of a positive-definite tensor are all positive, while those of a positive-indefinite tensor are all non-negative.

In comparing two tensors, we will say that the tensor $\chi_{ij}{}^2$ is "no larger than" the tensor $\chi_{ij}{}^1$ if the difference tensor

$$\chi_{ij}=\chi_{ij}{}^1-\chi_{ij}{}^2 \quad (29)$$

is positive indefinite. (We use quotes to indicate that although the statement is always literally true for the diagonal elements of the two tensors, this need not be the case for the off-diagonal elements.) Note that if $\chi_{ij}{}^2$ "$\leq$" $\chi_{ij}{}^1$ and $\chi_{ij}{}^3$ "$\leq$" $\chi_{ij}{}^2$, then $\chi_{ij}{}^3$ "$\leq$" $\chi_{ij}{}^1$.

Now consider the isothermal susceptibility tensor $\chi_{ij}{}^T$. Equations (8), (28), and (A2) show that it will always be positive definite since

$$\langle(\mathbf{V}\cdot\Delta\mathbf{M})\mid(\mathbf{V}\cdot\Delta\mathbf{M})\rangle>0. \quad (30)$$

This is true since $\mathbf{M}$ is an *omnidirectional* operator; **i.e.,** it is impossible to find a nonzero vector $\mathbf{V}$ such that $(\mathbf{V}\cdot\mathbf{M})=0$.

Next consider the adiabatic susceptibility tensor $\chi_{ij}{}^s$. From Eq. (14) and the Schwarz inequality, Eq. (A4), it is apparent that (assuming finite heat capacity) $\chi_{ij}{}^s$ is "no larger than" $\chi_{ij}{}^T$. The two tensors will be equal iff[10] $\langle\Delta\mathcal{H}\mid\Delta\mathbf{M}\rangle$ vanishes. This occurs for unpolarized materials in the absence of biasing fields, since the same symmetry conditions which cause $\langle\mathbf{M}\rangle$ to vanish also cause $\langle\Delta\mathcal{H}\mid\Delta\mathbf{M}\rangle$ $(=-\partial\langle\mathbf{M}\rangle/\partial\beta)$ to vanish. It is also easily seen from the Schwarz inequality that $\chi_{ij}{}^s$ is positive indefinite. For a given direction $\hat{n}$, iff $(\Delta\mathbf{M}\cdot\hat{n})$ is proportional to $\Delta\mathcal{H}$, then the diagonal component in that direction, $\chi_{nn}{}^s$, vanishes.[11]

Finally, consider the isolated susceptibility tensor $\chi_{ij}{}^I$. Equation (26b) implies that $\chi_{ij}{}^I$ is positive indefinite since

$$\langle(\hat{n}\cdot\mathbf{M}'')\mid(\hat{n}\cdot\mathbf{M}'')\rangle\geq0. \quad (31)$$

Although $\mathbf{M}$ is always omnidirectional, this may not be true for $\mathbf{M}'$ and $\mathbf{M}''$ separately. Even if $\mathbf{M}''$ is nonzero, there may be a direction $\hat{n}$ for which $(\hat{n}\cdot\mathbf{M}'')$ vanishes. For a particular direction $\hat{n}$, $\chi_{nn}{}^I$ will be positive iff $(\hat{n}\cdot\mathbf{M}'')$ is nonzero. Note that iff $(\hat{n}\cdot\mathbf{M})$ commutes with $\mathcal{H}$, then $(\hat{n}\cdot\mathbf{M}'')$ (and hence also $\chi_{nn}{}^I$) vanishes.

To compare $\chi_{ij}{}^s$ with $\chi_{ij}{}^I$, we first convert Eq. (26a)

[7] This may be seen by taking matrix elements in a representation in which $\mathcal{H}$ is diagonal.

[8] W. J. Caspers, *Theory of Spin Relaxation* (Interscience Publishers, Inc., New York, 1964), Chap. 1, pp. 29–30, Eqs. (I. 4. 21) and (I. 4. 23). In Eq. (I. 4. 23) it must be assumed that degenerate eigenstates are so chosen that the matrix elements of M_z vanish between different states of the same energy. This can always be done.

[9] Richard Bellman, *Introduction to Matrix Analysis* (McGraw-Hill Book Co., New York, 1960), Chap. 3, Sec. 7, p. 40.

[10] The word "iff" means "if and only if."

[11] The treatment given to this point on the isothermal and adiabatic tensors is essentially the same as that given in an unpublished manuscript by the author on the quantum theory of the static dielectric susceptibility tensor.

to the form

$$\chi_{ij}{}^{I}=\beta\langle\Delta M_i \mid \Delta M_j\rangle-\beta\langle\Delta M_i' \mid \Delta M_j'\rangle. \qquad (32)$$

This follows since

$$\langle \mathbf{M}'\rangle=\langle \mathbf{M}\rangle. \qquad (33)$$

Also, in Eq. (14) we may replace $\langle\Delta\mathcal{H} \mid \Delta\mathbf{M}\rangle$ by $\langle\Delta\mathcal{H} \mid \Delta\mathbf{M}'\rangle$ (since $\langle\mathcal{H} \mid \mathbf{M}''\rangle$ vanishes) and then subtract Eq. (32) to obtain

$$\chi_{ij}{}^{s}-\chi_{ij}{}^{I}=\beta\langle\Delta M_i' \mid \Delta M_j'\rangle - (\beta\langle\Delta\mathcal{H} \mid \Delta M_i'\rangle\langle\Delta\mathcal{H} \mid \Delta M_j'\rangle/\langle\Delta\mathcal{H} \mid \Delta\mathcal{H}\rangle). \qquad (34)$$

From Eq. (34) and the Schwarz inequality it is apparent that $\chi_{ij}{}^{I}$ is "no larger than" $\chi_{ij}{}^{s}$. For a given direction $\hat{n}$, the diagonal elements will be equal,

$$\chi_{nn}{}^{s}=\chi_{nn}{}^{I}, \qquad (35)$$

iff

$$(\hat{n}\cdot\Delta\mathbf{M}')=\alpha\Delta\mathcal{H} \qquad (36)$$

for some scalar α. By taking matrix elements, Eq. (36) may be shown to be equivalent to the Klein criterion for equality of adiabatic and isolated susceptibilities.[12]

The Klein criterion is, in a sense, equivalent to the criterion mentioned in Ref. 4 for the density matrix in an isolated process to remain canonical. If (during an isolated process caused by a changing field) an initially canonical ensemble remains canonical, then from their definitions it is apparent that the adiabatic and isolated susceptibilities are equal; hence the Klein criterion must be satisfied. Conversely, if the Klein criterion is satisfied during an isolated process, it may be shown that the criterion mentioned in Ref. 4 is satisfied.

It has been pointed out by a number of authors[8,13–16] that even when the Klein criterion is not satisfied exactly, it is still possible that the isolated and adiabatic susceptibilities regarded as intensive quantities (χ/V) will be the same in the thermodynamic limit in which the volume V becomes arbitrarily large:

$$\lim_{V\to\infty}(\chi_{nn}{}^{s}/V)=\lim_{V\to\infty}(\chi_{nn}{}^{I}/V). \qquad (37)$$

From Eq. (34), this condition may also be written

$$\langle R^2\rangle<(\text{const})\,V^P, \qquad (38)$$

where R is defined by

$$R\equiv(\hat{n}\cdot\Delta\mathbf{M}')-\frac{\langle(\hat{n}\cdot\Delta\mathbf{M}') \mid \Delta\mathcal{H}\rangle\Delta\mathcal{H}}{\langle\Delta\mathcal{H} \mid \Delta\mathcal{H}\rangle} \qquad (39)$$

and P is some number less than unity. A sufficient condition for Eq. (38) to be satisfied is that

$$\langle(\hat{n}\cdot\Delta\mathbf{M}')^2\rangle<(\text{const})\,V^P. \qquad (40)$$

In concluding this section, we point out that the treatment given in the Appendix for the "Van Vleck" and "high-temperature approximations" implies that if these approximations are made consistently, all of our criteria and conclusions regarding "sizes" of the various tensors will remain valid.

6. DISCUSSION

From the preceding section, we see that it is quite easy to find models such that $\chi_{zz}{}^{I}$ vanishes while $\chi_{zz}{}^{s}$ does not. All that is necessary is to find a Hamiltonian which commutes with M_z without being a linear function of M_z. One such case is the exactly soluble X-Y isotropic linear Heisenberg model treated by Katsura.[17] Falk[18] has previously explicitly calculated that for this model $\chi_{zz}{}^{I}$ vanishes while $\chi_{zz}{}^{s}$ does not. Other cases are systems of spins having isotropic exchange interactions, and the Ising model in one, two, and three dimensions.

Explicit calculations readily show that $(\chi_{zz}{}^{s}/V)$ is also nonzero *in the thermodynamic limit* for the following cases: (1) the model treated by Katsura; (2) the one-dimensional Ising lattice; (3) a Bravais lattice of spins in the approximation in which the Hamiltonian may be represented by a collection of noninteracting magnons. We believe that the same is likely to be true for other more complicated models described by a Hamiltonian which commutes with M_z without being a linear function of M_z. In particular, if the model has no permanent dipole moment in the absence of a biasing field, then $(\chi_{zz}{}^{s}/V)$ must equal $(\chi_{zz}{}^{T}/V)$, a quantity which is positive in the thermodynamic limit, while $\chi_{zz}{}^{I}$ vanishes.

On the other hand, one can easily conceive of systems for which the Klein criterion is satisfied, so that $\chi_{nn}{}^{I}=\chi_{nn}{}^{s}$. For example, if the Hamiltonian has a nondegenerate energy spectrum and is invariant to reflections in a plane perpendicular to $\hat{n}$, then $(\hat{n}\cdot\mathbf{M}')$ must vanish. In this case, Eq. (36) will be satisfied by setting $\alpha=0$. It is possible that this situation may be satisfied by some real many-body systems, since it is expected that the effect of interactions between dipoles is to remove degeneracy.

As mentioned previously, even if the Klein criterion is not satified exactly, it is still conceivable that isolated and adiabatic susceptibilities becomes equal in the thermodynamic limit. In his treatment of paramagnetic spin systems, Caspers[8] has argued that this should be the case for real systems. He has formulated two plausible but unprovable hypotheses such that the Klein criterion is satisfied in the thermodynamic limit.

Rosenfeld[13] and Saitô,[14] independently improving upon earlier work of Broer,[15] have given quite general "proofs" that adiabatic and isolated susceptibilities become equal in the thermodynamic limit. (A similar proof has been given by Mountain[16] for the case of the compressional susceptibility.) Since, as we have seen,

[12] M. J. Klein, Phys. Rev. **86**, 807 (1952). [See Eq. (13).]
[13] L. Rosenfeld, Physica **27**, 67 (1961).
[14] N. Saitô, J. Phys. Soc. Japan **16**, 621 (1961).
[15] L. J. Broer, Physica **17**, 531 (1951).
[16] R. D. Mountain, Physica **30**, 808 (1964).
[17] S. Katsura, Phys. Rev. **127**, 1508 (1962).
[18] Reference 1, Sec. IV.

there exist model systems for which $\chi^I \neq \chi^s$ in the thermodynamic limit, we believe that it is desirable to reexamine the assumptions (explicit or implicit) made in these works. We will do this by giving a similar "proof" which we believe contains the essential features, even though it admittedly oversimplifies or bypasses many arguments and detailed considerations of these authors.

We assume that for a large many-body system the energy levels become sufficiently close together so that we may replace the sum over states implicit in the definition of our thermal averages by an integration over energy E with a density function f which is highly peaked near the average energy ($\bar{E} \equiv \langle \mathcal{H} \rangle$) of the system. We assume that this density function has the functional form

$$f = f[(\Delta E) V^{-1/2}], \tag{41}$$

where $\Delta E \equiv E - \bar{E}$. The function f is non-negative and is assumed to approach zero rapidly for large positive and negative values of its argument so that the ensemble average of any diagonal operator Q may be represented as

$$\langle Q \rangle = \int_{-\infty}^{\infty} Q(\bar{E} + \Delta E) f[(\Delta E) V^{-1/2}] d(\Delta E) V^{-1/2}. \tag{42}$$

Of course, it is required that f be normalized such that $\langle 1 \rangle = 1$. Then the assumed functional form of Eq. (41) ensures that the heat capacity $\propto \langle (\Delta E)^2 \rangle$ is an extensive quantity.

The quantity R defined by Eq. (39) may now be rewritten

$$R = \Delta M_n' - [\langle (\Delta M_n')(\Delta E) \rangle \Delta E / \langle (\Delta E)^2 \rangle]. \tag{43}$$

We assume also that the diagonal operator M_n' can be represented as an extensive quantity of the form

$$M_n' = V \mu(\epsilon), \tag{44}$$

where μ is an intensive differentiable function of the energy density $\epsilon = E/V$:

$$\mu(\epsilon) = \mu(\bar{\epsilon}) + \mu'(\bar{\epsilon}) \Delta\epsilon + \tfrac{1}{2}\mu''(\bar{\epsilon})(\Delta\epsilon)^2 + \cdots, \tag{45}$$

where $\bar{\epsilon} \equiv \bar{E}/V$ and $\Delta\epsilon = \Delta E/V$. Then $\langle(\epsilon)\rangle = \mu(\bar{\epsilon}) + O(V^{-1})$ and

$$\Delta M_n' = \mu'(\bar{\epsilon}) \Delta E + \tfrac{1}{2}\mu''(\bar{\epsilon})(\Delta\epsilon)^2 V + O(V^0). \tag{46}$$

Substituting Eq. (46) into Eq. (43), one finds that the terms in $\mu'(\bar{\epsilon})$ cancel and

$$\begin{aligned} R &= \tfrac{1}{2}\mu''(\bar{\epsilon}) \left[\frac{(\Delta E)^2}{V} - \frac{\langle (\Delta E)^3 \rangle \Delta E}{V \langle (\Delta E)^2 \rangle} \right] + O(V^0) \\ &= O(V^{-1})(\Delta E)^2 + O(V^{-1/2}) \Delta E + O(V^0). \end{aligned} \tag{47}$$

Hence $\langle R^2 \rangle = O(V^0)$, so that the criterion of Eq. (38) is satisfied with $P = 0$. Therefore, adiabatic and isolated susceptibilities should be equal in the thermodynamic limit.

Where does our "proof" break down in the case of the models cited previously? One possible place may be the form assumed for Eq. (44), since really all one has a right to require is that the average dipole moment $\langle M_n \rangle = \langle M_n' \rangle$ be an extensive quantity. Although Eq. (44) assures that this will be the case, it is not obvious that Eq. (44) is the only possible form which will accomplish this. We note that if, instead of Eq. (44), one makes the slightly weaker assumption that M_n' $V\mu(\epsilon) + V^{1/2}\nu(\epsilon)$ (in order to account for fluctuations from the mean), the conclusion of our "proof" remains the same.

Even if Eq. (44) is valid, it is still possible that $\mu(\epsilon)$ is not differentiable as assumed in Eq. (45). Rosenfeld has previously pointed out that such an assumption may not be justified for cases where the energy levels are degenerate.[19] The fact that much degeneracy occurs in the models for which we have found $\chi^I \neq \chi^s$ appears to confirm Rosenfeld's warning. The paper by Saitô,[14] on the other hand, does not note this possible difficulty and concludes that adiabatic and isolated susceptibilites will always be the same in the thermodynamic limit. While it is possible that this may be the case for all real systems, it is certainly not the case for all model systems.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Robert L. Peterson for many stimulating conversations, both recently and over the past few years, which have contributed to this paper. In particular, Dr. Peterson directed me to the work concerning the equality of isolated and adiabatic susceptibilities. I also wish to thank Dr. Raymond D. Mountain for commenting on an earlier draft of this paper, and for referring me to the paper by Saitô. I also thank Dr. H. Falk for criticisms which have improved this paper.

APPENDIX

Let A and B be any two operators, and define[20]

$$\langle A \mid B \rangle \equiv \beta^{-1} \int_0^\beta du\, \langle \exp(u\mathcal{H}) A^\dagger \exp(-u\mathcal{H}) B \rangle. \tag{A1}$$

Then it is easily verified that $\langle A \mid B \rangle$ satisfies all the basic properties of a complex scalar product for a space whose "vectors" are operators in the usual sense. In particular, for nonzero A and B, $\langle A \mid B \rangle$ satisfies

$$\langle A \mid A \rangle > 0, \tag{A2}$$

$$\langle A \mid B \rangle^* = \langle B \mid A \rangle, \tag{A3}$$

as well as the usual linearity properties. Hence it im-

[19] Reference 13, Sec. 6.

[20] A similar scalar product has been used previously by H. Nakano, Progr. Theoret. Phys. (Kyoto) **23**, 526 (1960); Proc. Phys. Soc. **B2**, 757 (1963); H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965); H. Primas and J. Riess, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by Per-Olov Löwdin (Academic Press Inc., New York, 1966), p. 332.

mediately follows that the Schwarz inequality is satisfied:

$$|\langle A \mid B\rangle|^2 \leq \langle A \mid A\rangle\langle B \mid B\rangle. \qquad \text{(A4)}$$

The equality holds iff the operators A and B are proportional to each other.

[To prove Eq. (A2), evaluate the trace in a representation in which $\mathcal{H}$ is diagonal and note that the integrand is positive for all values of the integration variable u. To prove Eq. (A3), use the fact that the complex conjugate of a trace equals the trace of the Hermitian conjugate, and make use of the cyclic property of the trace.]

In addition to these properties, one can prove the relation

$$\langle A \mid B\rangle = \langle B^\dagger \mid A^\dagger\rangle. \qquad \text{(A5)}$$

[To do this, change the integration variable in Eq. (A1) to $u' = \beta - u$ and make use of the cyclic property of the trace.] If A and B are both Hermitian, it follows from Eqs. (A3) and (A5) that the scalar product will then be real and symmetric,

$$\langle A \mid B\rangle = \langle A \mid B\rangle^* = \langle B \mid A\rangle. \qquad \text{(A6)}$$

In the Van Vleck approximation, it is assumed that A and B have matrix elements different from zero only for states whose energy difference is small compared with $1/\beta$. The scalar product defined in Eq. (A1) may then be approximated by

$$\langle A \mid B\rangle \equiv \tfrac{1}{2}\langle (A^\dagger B + BA^\dagger)\rangle. \qquad \text{(A7)}$$

It is easy to verify that this scalar product has all of the properties mentioned above.

In the high-temperature approximation, it is further assumed that β may be set equal to zero in the definition of ρ, Eq. (3), so that Eq. (A7) may be approximated by

$$\langle A \mid B\rangle = [\mathrm{Tr}(A^\dagger B)/\mathrm{Tr}(1)]. \qquad \text{(A8)}$$

This scalar product also has all of the properties mentioned above.

PHYSICAL REVIEW VOLUME 174, NUMBER 2 10 OCTOBER 1968

Diffuse and Propagating Modes in the Heisenberg Paramagnet

HERBERT S. BENNETT
National Bureau of Standards, Washington, D. C. 20234

(Received 22 January 1968)

The spectral weight function of the frequency ω and wave number q for the spin pair correlation function in a Heisenberg system is studied in the paramagnetic region. It is suggested that this function will exhibit propagating modes at short wavelengths and at temperatures T not much greater than the transition temperature T_c. This suggestion follows from the approximation used to evaluate the moments of the spectral weight function and from the assumption that the generalized diffusivity, of which the pair correlation function is a functional, contains no δ-function terms $\delta(\omega)$ and is a smooth monotonic function. The region for which the dispersion equation has real solutions (propagating modes) $\omega = \omega_B(\mathbf{q})$ is obtained by estimating the moment-fluctuation ratio $R(\mathbf{q}) = \langle\omega^2\rangle_\mathbf{q}^2/\langle(\omega^2 - \langle\omega^2\rangle_\mathbf{q})^2\rangle_\mathbf{q}$ for the pair correlation function. When $T > T_c$ and when q is greater than a critical wave number q_c, the estimate gives $R(\mathbf{q}) > 1$ and thereby predicts propagating modes. An approximate nonlinear integral equation for the susceptibility is used to estimate $R(\mathbf{q})$. It is shown that the critical wave number q_c is proportional to the inverse square root of the static susceptibility, $q_c \sim \chi^{-1/2}(T)$. This approximation yields an expression for $R(\mathbf{q})$ at high temperature which is in substantial agreement with the exact high-temperature evaluation of $R(\mathbf{q})$. The exact and approximate evaluations of $R(\mathbf{q})$ for high temperature predict that $R(\mathbf{q}) < 1$ for all values of wave vector $\mathbf{q}$ in the first Brillouin zone, and consequently suggest that there are no high-frequency propagating modes at high temperatures.

I. INTRODUCTION

THE Heisenberg model of magnetism may be a suitable model with which to study some of the magnetic insulators such as the ferromagnets EuO and EuS and the antiferromagnets $RbMnF_3$ and MnF_2. Among these four magnetic insulators, the perovskite $RbMnF_3$ comes closest to the idealized isotropic Heisenberg magnet with only nearest-neighbor exchange interactions. The magnetic Mn^{++} ions form a simple cubic lattice. When we discuss such magnetic insulators within the framework of the Heisenberg Hamiltonian with no external fields and above their critical temperatures T_c, we call them Heisenberg paramagnets.

We shall propose that the generalized diffusivity $\Gamma(\mathbf{q}, \omega)$ for the paramagnetic state contains no δ function of frequency terms $\delta(\omega)$ and is a smooth monotonic function. We shall also present a nonlinear approximation for the spectral weight function. The spectral weight function of the spin pair correlations is directly proportional to the absorptive response of the Heisenberg paramagnet to weak external magnetic fields. This nonlinear approximation arises within the context of a microscopic theory and is exact at zero temperature