PHYSICAL REVIEW A VOLUME 8, NUMBER 4 OCTOBER 1973

Evolution of Nonequilibrium Fluctuations in Paramagnetic Systems

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(Received 29 December 1972)

The problem of the characterization of the fluctuations in statistical systems brought about by nonequilibrium states owing to external perturbations is considered. The time evolution of the second-order parameters of nonequilibrium fluctuations in paramagnetic systems is approached in detail. A connection is established between the temporal derivative of the dispersion of the magnetic-moment vector $\vec{M}$ and the expectation values of the components of this vector. This connection is regarded as a particular case of fluctuation-dissipation relations, which are functional relations between the different order parameters of the fluctuations. It is shown that, in the limit of the approximations in which the phenomenological equations of Bloch type are valid, the time evolution of the dispersion of the magnetic moment is directly conditioned only by the internal relaxation processes and not by the external magnetic fields.

Statistical systems (i.e., the systems formed by very large numbers of constituent particles) are characterized,[1,2] from the point of view of their observable properties, by macroscopic quantities. These are expected values of certain random quantities which depend on the characteristics of the constituent particles. Generally, the microscopic state of a statistical system changes in time, owing to its interactions with the surrounding medium and internal relaxation processes. In this case the random quantities are random functions, according to the probability theory.[3] That is, they are stochastic processes dependent on time. The statistical systems in equilibrium states have a remarkable property, that of remaining in this state for an indefinitely long period. The random functions of these systems are stationary random functions and, according to the ergodic theorems,[4] they are ergodic too.

One knows that in probability theory[3] the random functions are characterized by certain parameters—moment functions, correlation functions, cumulant functions, etc. In statistical physics[1,2] such parameters are generally used very infrequently, especially those of higher order. For statistical systems in equilibrium the expectation (or mean) values and centered moments of second order are usually used. The latter are almost exclusively used in order to characterize the deviations from the expectation values, i.e., the fluctuations. The higher-order-parameter approach of equilibrium fluctuations has been discussed recently.[5-7]

In order to describe systems not in equilibrium states, generally when irreversible processes occur, only the expectation values of the random functions that characterize them are used.[2] One only approaches the computation of the concrete expressions of these expected values in terms of external forces and structural details of the systems. The problem of random functions deviating from their expectation values in the case of nonequilibrium states has not, as far as we know, been approached either in a general form or in accord with the probability theory.

We would like to call attention here to some aspects of the problem of deviations from expectation values in nonequilibrium states—deviations which we shall call nonequilibrium fluctuations. These fluctuations should be treated by using the nonstationary random-functions theory.[3,8,9] In principle, such a systematic approach seems possible.[10] We have previously commented upon an interesting property of the nonequilibrium fluctuations,[6,7] pointing particularly to the generalization of the well-known fluctuation-dissipation theorem.[11] According to this generalization, there is a certain functional connection between the reaction functions of the s-order moment functions of nonequilibrium fluctuations and the $(s+1)$-order moment functions of equilibrium fluctuations.

Here we wish to focus attention on another problem regarding the nonequilibrium fluctuations—namely their time-evolution equations. It is known that in the nonequilibrium-process theory[2,12] the time evolution of the expectation values of the physical quantities is established. Bloch equations describe such an evolution[12] in a relatively simple form. We shall establish the evolution equations for the second-order moment functions of nonequilibrium fluctuations for a paramagnetic system, and shall operate within the domain of the same approximations in which the Bloch equations are deduced.

The nonequilibrium fluctuations of the quantities to which the operators A_i $(i=1,2,3,\ldots,n)$ correspond may be characterized[10]—in first-order approximations—by the one-time correlation functions $\langle\{A_i,A_j\}\rangle_t=\mathrm{Tr}[\{A_i,A_j\}\rho(t)]$, where $\{A_i,A_j\}=\frac{1}{2}(A_iA_j+A_jA_i)$ and $\rho(t)$ is the statistical (or density) operator of the system in the nonequilibrium state (generally dependent on time). In this approximation, the time evolution of nonequilibrium fluctuations of the quantities A_i will be given by the functions $d\langle\{A_i,A_j\}\rangle_t/dt$. The concrete expressions of these functions depend on the particular structure of the considered statistical system, as well as on the external perturbations which cause it to evolve through nonequilibrium states.

We shall direct our attention now upon a spin-$\frac{1}{2}$ paramagnetic system, and we shall take the Cartesian components of the spin operator $I_\alpha=\sum_j I_{j\alpha}$ ($I_{j\alpha}$ is the α component, $\alpha=x,y,z$ of the spin operator of the j constituent particle) for A_i operators. The components of the magnetic-moment operators M_α are connected[12] to the I_α operators by the relation $M_\alpha=\gamma\hbar I_\alpha$. In this case, in order to characterize the nonequilibrium-fluctuation evolution, the quantities $d\langle\{I_\alpha,I_\beta\}\rangle_t/dt$ must be calculated. In order to do this we may use the equation[12]

$$\frac{d\langle 0\rangle_t}{dt}=-i\gamma\sum_j\langle[\vec{\mathrm{H}}\cdot\vec{\mathrm{I}}_j,0]\rangle_t+\sum_{r,s}\sum_{i,j}\phi_{ij}^{rs}\langle I_j^s[0,I_i^r]+[I_i^s,0]I_j^r\rangle_t, \qquad (1)$$

where r and s signify $-,0,+$ and $I_j^{\pm}=I_{jx}\pm iI_{jy}$, $I_j^0=I_{jz}$. $\vec{\mathrm{H}}$ stands for the external magnetic field which acts upon the system. The ϕ_{ij}^{rs} quantities characterize[12] the effective magnetic field of the lattice where the spin system is operating. In the approximations in which the Bloch equations are obtained from Eq. (1) the following equations result:

$$\frac{d}{dt}\langle\{I_\alpha,I_\beta\}\rangle_t=\gamma\langle\{I_\alpha,(\vec{\mathrm{I}}\times\vec{\mathrm{H}})_\beta\}+\{(\vec{\mathrm{H}}\times\vec{\mathrm{I}})_\alpha,I_\beta\}\rangle_t+\sum_{r,s,\alpha}\sum_{i,j,k}\phi_{ij}^{rs}\langle I_i^s[\{I_{j\alpha},I_{k\alpha}\},I_i^r]+[I_i^s,\{I_{j\alpha},I_{k\alpha}\}]I_i^r\rangle_t, \qquad (2)$$

with $\phi_{ij}^{rs}=\delta_{ij}\phi_{ii}^{rs}$; $\phi_{ii}^{++}=\phi_{ii}^{--}=\phi_{ii}^{0+}=\phi_{ii}^{0-}=\phi_{ii}^{+0}=\phi_{ii}^{-0}=0$ and ϕ_{ii}^{+-}, ϕ_{ii}^{-+}, and ϕ_{ii}^{00} are different from zero (for the concrete expression of the last three functions see Ref. 12). The relations $\phi_{ij}^{rs}=\delta_{ij}\phi_{ii}^{rs}$ correspond to the fact that different spins relax independently of one another.

By some calculations which make use of the permutations relations $[I_{j\alpha},I_{k\beta}]=i\delta_{jk}\sum_\gamma\epsilon_{\alpha\beta\gamma}I_{k\gamma}$ ($\epsilon_{\alpha\beta\gamma}$ being the third-order Levi-Civita symbols) only, one obtains from Eq. (2):

$$\sum_\alpha\frac{d}{dt}\langle\{I_\alpha,I_\alpha\}\rangle_t=\frac{d}{dt}\langle\vec{\mathrm{I}}^2\rangle_t=0. \qquad (3)$$

Taking into account the relation (3) and the fact that in the aforementioned approximations the time evolution of $\langle\vec{\mathrm{I}}\rangle_t$ is given by the Bloch equation,[12]

$$\frac{d\langle\vec{\mathrm{I}}\rangle_t}{dt}=\gamma\langle\vec{\mathrm{I}}\rangle\times\vec{\mathrm{H}}-\hat{i}\,\frac{\langle I_x\rangle_t}{T_2}-\hat{j}\,\frac{\langle I_y\rangle_t}{T_2}-\hat{k}\,\frac{\langle I_z\rangle_t-\langle I_z\rangle_0}{T_1}$$

(T_1 and T_2 are the relaxation times and $\langle I_z\rangle_0$ represents the expectation value of I_z in the absence of the time-dependent magnetic field), one obtains the evolution equation for the mean-square deviation (i.e., for the dispersion) of the spin moment:

$$\frac{d}{dt}\langle(\vec{\mathrm{I}}-\langle\vec{\mathrm{I}}\rangle_t)^2\rangle_t=2\left(\frac{\langle I_x\rangle_t^2+\langle I_y\rangle_t^2}{T_2}+\frac{\langle I_z\rangle_t(\langle I_z\rangle_t-\langle I_z\rangle_0)}{T_1}\right). \qquad (4)$$

Equation (4) gives the evolution of a macroscopic quantity (mean-square deviation) which characterizes the nonequilibrium fluctuations of the magnetic moments (as we have already shown, the magnetic moment is given by $\langle\vec{\mathrm{M}}\rangle_t=\gamma\hbar\langle\vec{\mathrm{I}}\rangle_t$) for a paramagnetic system in the aforementioned approximations.

A remarkable property of Eq. (4) is the fact that no active term, containing the external magnetic field explicitly, appears in the right-hand side. This means that in the aforementioned approximations only the internal relaxation processes, and not the external perturbations (in this case external magnetic fields), are responsible for the evolution in time of the nonequilibrium fluctuations. This is a property which would be interesting to test experimentally. One must point particularly to the absence of direct influence of the external magnetic fields at the same time—a delayed influence of these fields upon the fluctuations being facilitated by the quantities $\langle I_\alpha\rangle_t$ (these depend on the external magnetic field via Bloch equations).

Another property of the evolution equation of the nonequilibrium fluctuations [Eq. (4)] is that its right-hand side is positive in enough large limits. Under these conditions the nonequilibrium-fluctuation dispersion is an increasing monotone function of time. It would be quite interesting to see whether such a property of the nonequilibrium-fluctuation dispersion is general, or whether it results from the general principles of the irreversible-process theory.

In connection with Eq. (4) the following fact is to be stressed. This equation gives a functional connection between second-order moments of nonequilibrium fluctuations and expectation values (i.e., first-order moments) of physical quantities. If the functional relationship between the various order moments of random functions which corresponds to physical quantities are called[6,7] fluctuation-dissipation relations (generalizations of the fluctuation-dissipation theorem[11]), then Eq. (4) is a fluctuation-dissipation relation.

Other problems in connection with nonequilibrium fluctuations (among these time-evolution equations of the higher-order parameters) will be discussed on another occasion.[10]

It is a pleasure to express our deep gratitude to Professor O. Gherman for helpful discussions and encouragements. We also wish to acknowledge some discussions with Dr. I. Inta.

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