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Linear Response Theory for Systems Obeying the Master Equation

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Linear response theory is developed for systems whose time dependence is described by a master equation. The fluctuation dissipation theorem expressing the linear response of the system in terms of fluctuation properties of the system in equilibrium is derived. The time-dependent Ising spin system in interaction with a heat bath, the Glauber model, is discussed as a particular case of the formalism.

KEY WORDS: Linear response theory; master equation; fluctuation dissipation theorem; Ising spin system; Glauber model; magnetic susceptibility.

1. INTRODUCTION

The fluctuation dissipation theorem plays an important role in the studies of the time-dependent behavior of many-particle systems.[1] It provides relations between the response of a system to a small perturbation and equilibrium fluctuations of the system. Specifically, for magnetic systems, this theorem relates the frequency-dependent magnetic susceptibility to the Fourier transform of the correlation function of the magnetization in equilibrium. In general, relations of such a type can be derived starting from the Liouville–von Neumann equation for quantum mechanical systems and from the Liouville equation for classical systems.[1]

In recent years, the time-dependent behavior of an Ising spin system in interaction with a heat bath has been studied extensively.[2–16,18] This has been done assuming that the dynamics of the system are described by a master equation. Although the

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model of the system is stochastic, it has been argued that the fluctuation dissipation theorem could be derived for this system.[11] And, in fact, a few fluctuation dissipation relations have been obtained,[2,5,11] but since specific choices for the transition probabilities have been made, the question about general conditions for the validity of these relations remained unclarified.

In this paper, we develop linear response theory and derive fluctuation dissipation theorems for systems for which the dynamics may be correctly described by a master equation. In general, a physical system will fulfill detailed balance if it is in equilibrium. If, however, an outside, time-dependent force is applied, the Hamiltonian and the transition probabilities depend on time. Under certain not very restrictive conditions on the time dependence of the outside force, the system will still obey a time-dependent form of detailed balance. A more explicit formulation of this will be given in the text. A discussion of the validity of this assumption, especially with regards to the time dependence, is intimately related to the problem of deriving the master equation.[17] It is obvious that a derivation of this sort will somewhat limit the allowed variations in time of the Hamiltonian. A thorough discussion of this question is, however, outside the scope of our present investigation, which is primarily devoted to establishing under what conditions on the transition probabilities linear response theory and fluctuation dissipation relations can be developed. The derivation we will give is not dependent on the explicit form of detailed balance and will therefore be correct for systems obeying a slightly less restrictive relation. This relation will be formulated in the text.

In the last section, we consider the special case of the Ising spin system. It is shown that the form of the fluctuation dissipation theorem is independent of the specific choice for the transition probabilities.

A possible practical application of the ideas as developed in this paper is the study of transport coefficients by using Monte Carlo methods.

2. THE MASTER EQUATION

We consider a system which is in interaction with a heat bath or a heat and particle reservoir, which keep respectively the temperature or the temperature and the chemical potential constant. The states of the system are labeled by α, where α can be a continuous or a discrete variable or a combination of both. The time dependence is assumed to be described by the master equation

$$dP(\alpha; t)/dt = \int d\alpha' \, [W(\alpha \mid \alpha') \, P(\alpha'; t) - W(\alpha' \mid \alpha) \, P(\alpha; t)] \tag{1}$$

where $P(\alpha; t)$ is the probability that the system is in the state α at time t and $W(\alpha \mid \alpha')$ is the transition probability per unit time from the state α' to the state α. The integral is over all states of the system and indicates the sum in the discrete case. Although not explicitly indicated, the transition probabilities may depend on time. The problem of how to derive a master equation has been discussed in an extensive literature.[17] Here, we assume that we are dealing with systems for which the master equation is valid. The states α do not have to correspond to the classical or quantum mechanical states of the system but can be small sets of such states called phase cells. In that case, all quantities used are understood to be coarse-grained. The master equation can be written in a more compact way by introduction of the operator Γ, which is defined by

$$\Gamma_{\alpha,\alpha'} = W(\alpha \mid \alpha') - \delta(\alpha - \alpha') \int d\alpha'' \, W(\alpha'' \mid \alpha) \tag{2}$$

The delta function is understood to be the Kronecker delta in the case of discrete states. The master equation can now be written as

$$dP(\alpha; t)/dt = \Gamma P(\alpha; t) \tag{3}$$

The average value of a physical quantity A is defined as

$$\overline{A(t)} = \int d\alpha \, A(\alpha) \, P(\alpha; t) \tag{4}$$

The time derivative of this quantity is given by

$$\begin{aligned} d\overline{A(t)}/dt &= \int d\alpha \, A(\alpha) \, dP(\alpha; t)/dt \\ &= \int d\alpha \int d\alpha' \, A(\alpha)[W(\alpha \mid \alpha') \, P(\alpha'; t) - W(\alpha' \mid \alpha) \, P(\alpha; t)] \\ &= \int d\alpha \int d\alpha' \, W(\alpha' \mid \alpha)[A(\alpha') - A(\alpha)] \, P(\alpha; t) \end{aligned} \tag{5}$$

This can be written in a more compact way by defining a new operator, the negative left transpose L of Γ,

$$L_{,\alpha'} = -W(\alpha' \mid \alpha) + \delta(\alpha - \alpha') \int d\alpha'' \, W(\alpha'' \mid \alpha) \tag{6}$$

This gives

$$d\bar{A}/dt = -\overline{LA} \tag{7}$$

The relation between Γ and L is

$$\int d\alpha \, B(\alpha) \, \Gamma C(\alpha) = - \int d\alpha \, C(\alpha) \, LB(\alpha) \tag{8}$$

where B and C are arbitrary functions of α. This is the reason we call L the negative left transpose of Γ. For a function of L, this relation implies

$$\int d\alpha \, B(\alpha) f(\Gamma) \, C(\alpha) = \int d\alpha \, C(\alpha) f(-L) \, B(\alpha) \tag{9}$$

When the transition probabilities are independent of time, the equilibrium probability distribution $P^{(0)}(\alpha)$ is given by

$$P^{(0)}(\alpha) = [\exp -\beta\mathscr{H}(\alpha)] \Big/ \int d\alpha \exp -\beta\mathscr{H}(\alpha) \tag{10a}$$

or

$$P^{(0)}(\alpha) = \{\exp[\beta\mu N(\alpha) - \beta\mathscr{H}(\alpha)]\}\Big/\int d\alpha \exp[\beta\mu N(\alpha) - \beta\mathscr{H}(\alpha)] \tag{10b}$$

for the canonical and the grand canonical ensemble, respectively. Here, $\mathscr{H}(\alpha)$ is the energy and $N(\alpha)$ the number of particles of the system in the state α; β is equal to $1/kT$, where k is the Boltzmann constant and T is the temperature; and μ is the chemical potential.

The equilibrium distribution fulfills the relation

$$\Gamma P^{(0)} = 0 \tag{11}$$

Henceforth, it will be assumed that this relation holds even in the case when $\mathscr{H}$, and therefore Γ, depends on time and $P^{(0)}$ is formally given by equation (10). Equation (11) in the time-dependent form will be sufficient to develop linear response theory and to derive the fluctuation dissipation theorem. Equation (11) is a slightly more general form of the time-dependent version of detailed balance

$$W(\alpha \mid \alpha')\, P^{(0)}(\alpha') = W(\alpha' \mid \alpha)\, P^{(0)}(\alpha) \tag{12}$$

where both the transition probability and $P^{(0)}$ depend on the time.

3. LINEAR RESPONSE THEORY

We will now study the response of the system to an external force $K(t)$. The perturbed Hamiltonian is

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1 = \mathscr{H}_0 - AK(t) \tag{13}$$

A being the dynamical quantity coupled to the applied force $K(t)$. For quantum mechanical systems, $\mathscr{H}_1$ is only the secular part of the perturbing Hamiltonian; by secular, we mean that $\mathscr{H}_1$ has no off-diagonal matrix elements with respect to the states α. For a good discussion of the definition of phase cells, course-graining, and what the secular part of an operator is, the reader is referred to the derivation of the master equation as given by Van Kampen.[17]

Let us write the probability distribution in the form

$$P(\alpha; t) = P_0^{(0)}(\alpha) + P_1(\alpha; t) \tag{14}$$

where $P_0^{(0)}$ is the equilibrium distribution corresponding to $\mathscr{H}_0$ as defined by Eq. (10) in the case that the force is zero. P_1 is assumed to be small. Similarly, we write the operator Γ as

$$\Gamma = \Gamma_0 + \Gamma_1 \tag{15}$$

where Γ_0 is the operator if there is no external force. This gives the response equation

$$dP_1(\alpha; t)/dt = \Gamma_0 P_1(\alpha; t) + \Gamma_1 P_0^{(0)}(\alpha) \tag{16}$$

in the linear approximation, with the formal solution

$$P_1(\alpha; t) = \int_{-\infty}^{t} [\exp \Gamma_0(t - t')] \, \Gamma_1 P_0^{(0)} \, dt' \tag{17}$$

in which we use

$$P(\alpha; -\infty) = P_0^{(0)}(\alpha) \tag{18}$$

as the initial condition.

The relation for P_1 can be transformed to a relation containing $\mathscr{H}_1$ rather than Γ_1 using Eqs. (10) and (11).

Equation (10) yields

$$P_1^{(0)} = -\beta[\mathscr{H}_1 - \langle \mathscr{H}_1 \rangle] \, P_0^{(0)} \tag{19}$$

again in the linear approximation, where $\langle \cdots \rangle$ stands for the average in the zero-force equilibrium distribution $P_0^{(0)}$. Equation (11) yields

$$\Gamma_0 P_1^{(0)} + \Gamma_1 P_1^{(0)} = 0 \tag{20}$$

Combination of these two equations gives

$$\Gamma_1 P_0^{(0)} = \beta \Gamma_0 \mathscr{H}_1 P_0^{(0)} \tag{21}$$

Substituting this result in Eq. (17) gives for P_1

$$\begin{aligned} P_1(\alpha; t) &= \beta \int_{-\infty}^{t} [\exp \Gamma_0(t - t')] \, \Gamma_0 \mathscr{H}_1 P_0^{(0)} \, dt' \\ &= -\beta \int_{-\infty}^{t} K(t')[\exp \Gamma_0(t - t')] \, \Gamma_0 A P_0^{(0)} \, dt' \end{aligned} \tag{22}$$

The response of the system to the force is now observed in the change of a physical quantity B. This change is given by

$$\overline{\Delta B(t)} = \overline{B(t)} - \langle B \rangle = \int d\alpha \, B(\alpha) \, P_1(\alpha; t) \tag{23}$$

Using Eq. (22) for P_1, this can be written as

$$\overline{\Delta B(t)} = \int_{-\infty}^{t} K(t') \, \phi_{BA}(t - t') \, dt' \tag{24}$$

in which ϕ_{BA} is the response function and is equal to

$$\phi_{BA}(t) = -\beta \int d\alpha \, B(\alpha) \, e^{\Gamma_0 t} \Gamma_0 A(\alpha) \, P_0^{(0)}(\alpha) \tag{25a}$$

$$= \beta \langle A e^{-Lt} L B \rangle \tag{25b}$$

where Eq. (9) is used and A was the dynamical quantity coupled to the force K.

For a periodic force

$$K = K_0 e^{i\omega t} \tag{26}$$

the response is expressed as

$$\overline{\Delta B(t)} = \chi_{BA}(\omega)\, K_0 e^{i\omega t} \tag{27}$$

where the admittance χ_{BA} is given by

$$\chi_{BA}(\omega) = \int_0^\infty e^{-i\omega t} \phi_{BA}(t)\, dt \tag{28a}$$

$$= \beta \int_0^\infty e^{-i\omega t} \langle A e^{-Lt} L B \rangle\, dt \tag{28b}$$

$$= -\beta \int_0^\infty e^{-i\omega t} (d/dt) \langle A e^{-Lt} B \rangle\, dt \tag{28c}$$

$$= \chi_{BA}(0) - i\omega\beta \int_0^\infty e^{-i\omega t} \langle A e^{-Lt} B \rangle\, dt \tag{28d}$$

These are all different forms of the fluctuation dissipation theorem. They are equivalent to the more familiar form

$$\begin{aligned} \chi_{BA}(\omega) &= -\beta \int_0^\infty e^{-i\omega t} (d/dt) \langle A(0)\, B(t) \rangle\, dt \\ &= \chi_{BA}(0) - i\omega\beta \int_0^\infty e^{-i\omega t} \langle A(0)\, B(t) \rangle\, dt \end{aligned} \tag{29}$$

This can easily be seen by using the conditional probability $P_0(\alpha; t \mid \alpha'; t')$ that the system is in the state α at time t after being in the state α' at time t', all in the zero-force case. This probability satisfies the obvious condition

$$P_0(\alpha; t \mid \alpha'; t) = \delta(\alpha - \alpha') \tag{30}$$

This leads to

$$\begin{aligned} \langle A e^{-Lt} B \rangle &= \int d\alpha\, B(\alpha)\, e^{\Gamma_0 t} A(\alpha)\, P_0^{(0)}(\alpha) \\ &= \int d\alpha \int d\alpha'\, B(\alpha)\, e^{\Gamma_0 t} A(\alpha')\, P_0^{(0)}(\alpha')\, P_0(\alpha; 0 \mid \alpha'; 0) \\ &= \int d\alpha \int d\alpha'\, B(\alpha)\, A(\alpha')\, P_0^{(0)}(\alpha')\, P_0(\alpha; t \mid \alpha'; 0) \\ &= \langle A(0)\, B(t) \rangle \end{aligned} \tag{31}$$

4. THE TIME-DEPENDENT ISING SPIN SYSTEM, THE GLAUBER MODEL

Consider a system of N interacting Ising spins. The state of the system $\{\sigma\}$ is given by specifying the values of σ_j of all the spins in the system. In addition to the mutual interaction among spins, the system interacts with a heat bath at the constant temperature T. The time dependence is supposed to be described by the master equation, Eq. (1) with $\alpha = \{\sigma\}$ and $\int d\alpha = \sum_{\{\sigma\}}$. The Ising spin system has the Hamiltonian

$$\mathscr{H} = -\sum_{i \neq j} J_{ij}\sigma_i\sigma_j - mH\sum_j \sigma_j = \mathscr{H}_0 - HM \tag{32}$$

where J_{ij}, m, and H are respectively the interaction parameter between the pair (ij), the magnetic moment associated with a spin, and the magnetic field. $M = m\sum_j \sigma_j$ is the magnetization of the system.

The results of the third section can now be applied to give relations for the response of the spin system to a time-dependent magnetic field. The average magnetization of the system is given by

$$\overline{M(t)} = \overline{\Delta M(t)} = \int_{-\infty}^{t} H(t')\, \phi(t-t')\, dt' \tag{33}$$

where the response function is given by

$$\phi(t) = -\beta \sum_{\{\sigma\}} M e^{\Gamma_0 t}\Gamma_0 M P_0^{(0)}(\{\sigma\}) \tag{34a}$$

$$= \beta\langle M e^{-Lt} L M\rangle \tag{34b}$$

$$= \beta\, d\langle M(0)\, M(t)\rangle/dt \tag{34c}$$

These relations are direct consequence of Eqs. (24), (25a, b), and (31). The fluctuation dissipation theorem gives for the frequency-dependent magnetic susceptibility[5]

$$\chi(\omega) = -\beta \int_0^\infty e^{-i\omega t} \sum_{\{\sigma\}} M e^{\Gamma_0 t}\Gamma_0 M P_0^{(0)}(\{\sigma\})\, dt \tag{35a}$$

$$= \beta \int_0^\infty e^{-i\omega t}\langle M e^{-Lt} L M\rangle\, dt \tag{35b}$$

$$= \chi(0) - i\omega\beta \int_0^\infty e^{-i\omega t}\langle M e^{-Lt} M\rangle\, dt \tag{35c}$$

$$= \chi(0) - i\omega\beta \int_0^\infty e^{-i\omega t}\langle M(0)\, M(t)\rangle\, dt \tag{35d}$$

These relations follow from Eqs. (28a–d) and (29). Two of these relations for the susceptibility, Eqs. (35b) and (35d) have been frequently used in recent years.[2,5,6,11,15] The imaginary part of the susceptibility is given by

$$\operatorname{Im}\chi(\omega) = -\tfrac{1}{2}\beta\omega \int_{-\infty}^{\infty} \langle M(0)\, M(t)\rangle\, e^{-i\omega t}\, dt \tag{36}$$

[5] The apparent difference in sign in Glauber's paper is due to a difference in the definition of $\chi(\omega)$. His definition of $\chi(\omega)$ corresponds to $\chi(-\omega)$ in this and in Suzuki and Kubo's paper. For the special transition probabilities he used $LM = \alpha(1-\gamma)M$ which gives his equation (106) for the fluctuation dissipation theorem.

In the previous publications on the Glauber model, the transition probability $W(\alpha \mid \alpha')$ has a particular form that is chosen to satisfy detailed balance. Here, we have not chosen any special form for the transition probability since we deal with the quite general operator Γ which satisfied the condition (11). Hence, all previous results are special cases of our results.

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