NON-MARKOVIAN EQUILIBRIUM DYNAMICS AND FLUCTUATION–DISSIPATION THEOREM ☆

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A macroscopic description for the thermal equilibrium dynamics of systems in terms of non-markovian processes is given and the classical fluctuation–dissipation theorem is derived.

In recent years the description of fluctuations in terms of stochastic processes has found wide application. In principle any macroscopic law should be derived from the microscopic equations for all degrees of freedom. In practice, however, one often sets up the macroscopic evolution laws in a phenomenological way. Usually the irreversible macroscopic behaviour which represents the global feature of the exact dynamics is described in terms of Markov processes [1–3]. But there may exist situations in which a clear-cut separation of the macroscopic time scale and the microscopic time scale, given for instance by the average time between collisions, is not possible. For example the motion of a particle in a fluid whose particle size lies between the macroscopic and atomic domains is subject to memory effects. Then a satisfactory description is possible in terms of non-markovian stochastic processes for the coarse-grained macrodynamics [4–6].

The fluctuations occurring in a system at equilibrium are related to the dissipation effects by the fluctuation–dissipation theorem of the first kind [7–11]. In special cases [7,8] this has been recognized on the basis of solely macroscopic concepts and thermodynamics a long time ago. The theorem has been derived generally by explicit use of microscopic dynamics [9, 10]. In terms of the linear response tensor $\chi(\tau)$ and the correlation matrix $C(\tau)$ of equilibrium fluctuations it can be written, for classical systems, in the form [10,11].

$$\chi(\tau) = -\theta(\tau)\beta(\mathrm{d}/\mathrm{d}\tau)C(\tau)\,. \tag{1}$$

Here β^{-1} denotes the temperature and $\theta(\tau)$ the unit step function. It is worthwhile to investigate if the same functional relationship can be derived on a *macroscopic level* if the system undergoes a non-Markov process [4–6]. Such an investigation is also desirable because of van Kampen's objection [12] to the microscopic derivation of linear response theory.

The macroscopic dynamics of non-markovian systems generally depends on the preparation of the initial state [4,5]. An important class of initial states contains those which are prepared by applying constant external fields F_j to a system of a given temperature β^{-1}.

In the linear approximation (denoted by $\doteq$) these initial states have the form

$$p(a_k) \doteq p_\beta(a_k)(1 + \beta F_j \delta a_j)\,, \tag{2}$$

if the fields F_j couple linearly to the macrovariables. Here $p_\beta(a_k)$ is the thermal equilibrium distribution at temperature β^{-1}, and $\delta a_j = a_j - \langle a_j\rangle_\beta$ denotes the deviation of the macrovariable a_j from its thermal equilibrium value $\langle a_j\rangle_\beta$.

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If the external fields are switched off at time t_0 the initial distribution relaxes towards thermal equilibrium. For all states in the class considered above this relaxation is governed by the same master equation [5]:

$$\dot{p}(t) = \mathbf{\Omega}_\beta p(t) + \int_{t_0}^{t} \mathbf{\Lambda}_\beta(t-s) p(s)\,\mathrm{d}s\,. \tag{3}$$

Note that the external fields F_j have only been used to construct, an appropriate class of initial states and that the stochastic operators $\mathbf{\Omega}_\beta$ and $\mathbf{\Lambda}_\beta$ are independent of these fields.

It is clear that the equilibrium distribution p_β has to be a stationary solution of eq. (3), hence

$$\mathbf{\Omega}_\beta p_\beta = 0\,, \tag{4}$$

$$\mathbf{\Lambda}_\beta(t) p_\beta = 0\,. \tag{5}$$

Further the kernel $G_\beta(a, a', \tau)$ of the Green's function $\mathrm{G}_\beta(\tau)$ of eq. (3) defined by

$$\dot{\mathrm{G}}_\beta(\tau) = \mathbf{\Omega}_\beta \mathrm{G}_\beta(\tau) + \int_0^\tau \mathbf{\Lambda}_\beta(\tau - s)\mathrm{G}_\beta(s)\,\mathrm{d}s\,,$$
$$\mathrm{G}_\beta(0) = 1\,, \tag{6}$$

coincides with the time-homogeneous conditional probability $p_\beta(a, \tau | a')$ of the stationary equilibrium process [5,6].

Let us now study the linear response of the equilibrium system to time-dependent external forces $F_j(t)$ at times $t > t_0$. The effect of this perturbation leads to additional terms in the master equation (3) which now takes the form

$$\dot{p}(t) = \mathbf{\Omega}_\beta p(t) + \int_{t_0}^{t} \mathbf{\Lambda}_\beta(t-s) p(s)\,\mathrm{d}s$$
$$+ \mathbf{\Omega}^{\mathrm{ext}}(t) p(t) + \int_{t_0}^{t} \mathbf{\Lambda}^{\mathrm{ext}}(t,s) p(s)\,\mathrm{d}s. \tag{7}$$

$\mathbf{\Omega}^{\mathrm{ext}}(t)$ describes an instantaneous effect, linear in the external forces, whereas $\mathbf{\Lambda}^{\mathrm{ext}}(t,s)$ generally is a complicated nonlinear functional of the history of the external forces $F_j(\tau)$ in the time interval $s < \tau < t$. These retardation effects are due to the non-markovian behaviour of the system.

Splitting $p(t)$ into

$$p(t) = p_\beta + \delta p(t)\,, \tag{8}$$

we find from eq. (7) with eqs. (4), (5):

$$\delta p(t) = \int_{t_0}^{t} \mathrm{G}_\beta(t-s) \left\{ \mathbf{\Omega}^{\mathrm{ext}}(s) p(s) + \int_{t_0}^{s} \mathbf{\Lambda}^{\mathrm{ext}}(s,\tau) p(\tau)\,\mathrm{d}\tau \right\} \mathrm{d}s\,, \tag{9}$$

where we have used the Green's function (6) and

$$p(t_0) = p_\beta\,. \tag{10}$$

In the linear approximation we put

$$\mathbf{\Omega}^{\mathrm{ext}}(t) p(t) + \int_{t_0}^{t} \mathbf{\Lambda}^{\mathrm{ext}}(t,s) p(s)\,\mathrm{d}s$$
$$\doteq \mathbf{\Omega}^{\mathrm{ext}}(t) p_\beta + \int_{t_0}^{t} \mathbf{\Lambda}_{\mathrm{L}}^{\mathrm{ext}}(t,s) p_\beta\,\mathrm{d}s\,, \tag{11}$$

where $\mathbf{\Lambda}_{\mathrm{L}}^{\mathrm{ext}}$ means the linearization of $\mathbf{\Lambda}^{\mathrm{ext}}$ with respect to the forces $F_j(t)$. The right hand side of eq. (11) is a linear functional of the past history of $F_j(t)$ and may be written as

$$\mathbf{\Omega}^{\mathrm{ext}}(t) p_\beta + \int_{t_0}^{t} \mathbf{\Lambda}_{\mathrm{L}}^{\mathrm{ext}}(t,s) p_\beta\,\mathrm{d}s$$
$$= A_j F_j(t) + \int_{t_0}^{t} B_j(t-s) F_j(s)\,. \tag{12}$$

To determine A_j and B_j we consider the master equation (7) in the case of constant external forces $F_j(t) \equiv F_j$. Then, in the linear approximation (11), the distribution (2) has to be a stationary solution of eq. (7). This requirement leads to

$$A_j = -\beta \mathbf{\Omega}_\beta p_\beta \delta a_j\,, \quad B_j(t) = -\beta \mathbf{\Lambda}_\beta(t) p_\beta \delta a_j\,. \tag{13}$$

Inserting eq. (13) into eq. (12), we find from eq. (9) in the linear approximation (11):

$$\delta p(t) \doteq -\beta \int_{t_0}^{t} F_j(s) \left\{ \mathrm{G}_\beta(t-s)\boldsymbol{\Omega}_\beta + \int_0^{t-s} \mathrm{d}\tau\, \mathrm{G}_\beta(t-s-\tau)\boldsymbol{\Lambda}_\beta(\tau) \right\} (\delta a_j p_\beta)\,\mathrm{d}s\,. \tag{14}$$

From eq. (6) we obtain, for instance by Laplace transform,

$$\dot{\mathrm{G}}_\beta(\tau) = \mathrm{G}_\beta(\tau)\boldsymbol{\Omega}_\beta + \int_0^{\tau} \mathrm{G}_\beta(\tau - s)\boldsymbol{\Lambda}_\beta(s)\,\mathrm{d}s\,, \tag{15}$$

which combines with eq. (14) to

$$\delta p(t) \doteq -\beta \int_{t_0}^{t} F_j(s) \frac{\partial}{\partial t} \mathrm{G}_\beta(t-s)(\delta a_j p_\beta)\,\mathrm{d}s\,. \tag{16}$$

Hence, the linear deviation $\delta\langle a_k(t)\rangle = \int \mathrm{d}a\, a_k \delta p(t)$ from the thermal equilibrium value $\langle a_k\rangle_\beta$ due to the external forces $F_j(t)$ reads:

$$\delta\langle a_k(t)\rangle \doteq -\beta \int_{t_0}^{t} F_j(s) \frac{\partial}{\partial t} \int \mathrm{d}a\, \delta a_k \mathrm{G}_\beta(t-s)(\delta a_j p_\beta)\,\mathrm{d}s\,, \tag{17}$$

so that the response tensor emerges as

$$\chi_{kj}(\tau) = -\theta(\tau)\beta \frac{\partial}{\partial \tau} \int \mathrm{d}a\, \delta a_k \mathrm{G}_\beta(\tau)(\delta a_j p_\beta)\,. \tag{18}$$

Since the kernel of G_β coincides with the stationary conditional probability, we immediately find eq. (1). In frequency space eq. (1) takes the more familiar form

$$\chi''_{kj}(\omega) = \tfrac{1}{2}\omega\beta C_{kj}(\omega)\,, \tag{19}$$

where $\chi''_{kj}(\omega) = (1/2\mathrm{i})(\chi_{kj}(\omega) - \chi_{jk}(-\omega))$ is the dissipative part of the response tensor.

We would like to emphasize that eq. (19) has been derived without use of a detailed balance condition or special choices of the transition probabilities, and independently of the magnitude of the fluctuations. There is only one essential point. By applying constant external fields F_j to the equilibrium system we prepare a certain class of nonequilibrium states. The relaxation of these nonequilibrium states towards equilibrium is governed by the same master equation (3). This can be viewed as a version of Onsager's regression theorem [13] in the non-markovian case since eq. (3) governs also the time evolution of equilibrium correlation functions. However, in contrast to the regression theorem for markovian systems, its non-markovian version applies – even in the linear regime – only to the above-mentioned class of initial states.

Now consider a steady nonequilibrium state. There is always a certain class of initial states relaxing towards this steady state according to the same master equation that governs the time-evolution of the stationary correlation functions. If the linear effect of the external forces disturbs the steady state in such a way that the new state belongs to this class, we obtain a fluctuation–dissipation theorem even for nonequilibrium states. The importance of the appropriate coupling of the external forces in this context has recently been pointed out by Graham [14] for markovian systems. However, while the appropriate forces are known for an equilibrium system (they couple linearly to the macrovariables), they are not generally known for non-equilibrium systems, and further investigation is needed.

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