Journal of Statistical Mechanics: Theory and Experiment (2007) P02006 (*15 pages*)

A fluctuation theorem for currents and nonlinear response coefficients

David Andrieux and Pierre Gaspard
Center for Nonlinear Phenomena and Complex Systems,
Université Libre de Bruxelles, Code Postal 231, Campus Plaine, B-1050 Brussels, Belgium

We use a recently proved fluctuation theorem for the currents to develop a response theory of nonequilibrium phenomena. In this framework, expressions for the response coefficients of the currents at arbitrary orders in the thermodynamic forces or affinities are obtained in terms of the fluctuations of the cumulative currents and remarkable relations are obtained which are the consequences of microreversibility beyond Onsager reciprocity relations.

Keywords: Exact results, stationary states (theory), current fluctuations.

I. INTRODUCTION

Onsager's classic work of 1931 [1] has shown that the linear response coefficients relating the currents to the thermodynamic forces or affinities [2] obey reciprocity relations as a consequence of the reversibility of the underlying microscopic dynamics. Another consequence of microreversibility is the so-called fluctuation theorems, which characterize the large fluctuations of physical quantities in nonequilibrium systems. They have been derived in deterministic [3–6] or Markovian stochastic systems [7–10] and concern different quantities such as the entropy production [5], the dissipated work [11, 12], or the currents crossing the system in a nonequilibrium situation [13–15]. Such relations are important because they are valid far from equilibrium. Close enough to equilibrium where the response of the system is linear in the affinities, the Onsager reciprocity relations can be deduced from the fluctuation theorem [6, 8, 13].

On the other hand, it is known that far-from-equilibrium systems may present nonlinear responses to nonequilibrium constraints. The response is said to be nonlinear if the currents crossing the nonequilibrium system depend nonlinearly on the affinities. The coefficients characterizing such nonlinear responses can be obtained by expanding the currents in the powers of the affinities. The terms linear in the affinities are the linear response coefficients obeying Onsager's reciprocity relations. The terms which are quadratic, cubic, quartic, etc... in the affinities are called the nonlinear response coefficients. We may wonder if the nonlinear response coefficients would obey relations beyond Onsager's ones as a consequence of the fundamental microreversibility.

The purpose of the present paper is to show that, indeed, the nonlinear response coefficients do obey remarkable relations which have their origin in microreversibility. For this purpose, we use a fluctuation theorem for the currents which was first proven for mechanically driven Markovian processes [8–10], then in the more general framework of Schnakenberg network theory [16] which includes reactive processes [13, 14], as well as in non-Markovian situations [17]. This fluctuation theorem directly concerns the generating function of the different fluctuating currents crossing a nonequilibrium system. Consequently, the nonlinear response coefficients can be directly obtained from the generating function by successive differentiations, so that the symmetry of the fluctuation theorem for the currents can be used in a straightforward way. The fluctuation theorem for the currents has been proved elsewhere [14] under the general conditions enunciated by Schnakenberg [16] and we start from this important result to obtain remarkable relations as the consequences of microreversibility.

The plan of the paper is the following. In Section II, we summarize the results about the fluctuation theorem for the currents. Section III is devoted to the derivation of the consequences of the fluctuation theorem on the response coefficients up to the cubic response coefficients with comparisons with known results. In Section IV, the nonlinear response coefficients are systematically calculated and the generalizations of Onsager relations are obtained at arbitrarily large orders. Conclusions are drawn in Section V.

II. FLUCTUATION THEOREM FOR THE CURRENTS

The fluctuation theorem for the currents relates the probability of observing given values for the cumulated currents to the probability of observing negative values via the following exponential relation valid in the long-time limit:

$$\frac{\mathrm{Prob}\left[\left\{\frac{1}{t}\int_0^t dt' j_\gamma(t') \in (\xi_\gamma, \xi_\gamma + d\xi_\gamma)\right\}\right]}{\mathrm{Prob}\left[\left\{\frac{1}{t}\int_0^t dt' j_\gamma(t') \in (-\xi_\gamma, -\xi_\gamma + d\xi_\gamma)\right\}\right]} \simeq \exp \sum_\gamma A_\gamma \xi_\gamma t \qquad (t \to \infty) \tag{1}$$

where $j_\gamma(t)$ denote the independent fluctuating currents and A_γ are the corresponding affinities (also called the thermodynamic forces) driving the system out of equilibrium [2, 16].

If we introduce the decay rate of the probability that the cumulated currents take given values

$$H(\{\xi_\gamma\}) \equiv \lim_{t\to\infty} -\frac{1}{t} \ln \mathrm{Prob}\left[\left\{\frac{1}{t}\int_0^t dt' j_\gamma(t') \in (\xi_\gamma, \xi_\gamma + d\xi_\gamma)\right\}\right] \tag{2}$$

the fluctuation theorem can be written as

$$H(\{-\xi_\gamma\}) - H(\{\xi_\gamma\}) = \sum_\gamma A_\gamma \xi_\gamma \tag{3}$$

The Legendre transform of the decay rate (2)

$$Q(\{\lambda_\gamma\}) = \mathrm{Min}_{\{\xi_\gamma\}}\left[H(\{\xi_\gamma\}) + \sum_\gamma \lambda_\gamma \xi_\gamma\right] \tag{4}$$

is the generating function of the currents defined by

$$Q(\{\lambda_\gamma\};\{A_\gamma\}) \equiv \lim_{t\to\infty} -\frac{1}{t} \ln \left\langle \mathrm{e}^{-\sum_\gamma \lambda_\gamma G_\gamma(t)} \right\rangle \tag{5}$$

in terms of the cumulative currents also called the Helfand moments [18]:

$$G_\gamma(t) \equiv \int_0^t j_\gamma(t')\, dt' \tag{6}$$

The fluctuation theorem for the currents (1) is now expressed as

$$Q(\{\lambda_\gamma\};\{A_\gamma\}) = Q(\{A_\gamma - \lambda_\gamma\};\{A_\gamma\}) \tag{7}$$

in terms of the generating function. This relation has been derived in the context of stochastic processes [14]. In this description the system is described by a probability distribution over the possible states and which is ruled by a master equation with several transition rates. The macroscopic affinities A_γ are then identified using Schnakenberg's network theory [16].

In the nonequilibrium steady state, the mean value of the current $j_\alpha(t)$ is given by

$$J_\alpha \equiv \frac{\partial Q}{\partial \lambda_\alpha}\Big|_{\{\lambda_\gamma=0\}} = \lim_{t\to\infty} \frac{1}{t}\int_0^t \langle j_\alpha(t')\rangle\, dt' = \lim_{t\to\infty} \frac{1}{t}\langle G_\alpha(t)\rangle \tag{8}$$

III. CONSEQUENCES FOR NONLINEAR RESPONSE

In this section, we prove that the fluctuation theorem (7) for the macroscopic currents (8) has important consequences not only on the linear response coefficients but also at the level of the nonlinear response. In general, the macroscopic currents can be expanded as power series of the macroscopic affinities:

$$J_\alpha = \sum_\beta L_{\alpha\beta} A_\beta + \frac{1}{2}\sum_{\beta,\gamma} M_{\alpha\beta\gamma} A_\beta A_\gamma + \frac{1}{6}\sum_{\beta,\gamma,\delta} N_{\alpha\beta\gamma\delta} A_\beta A_\gamma A_\delta + \cdots \tag{9}$$

The linear response of the currents J_α with respect to a small perturbation in the affinities A_β is characterized by the Onsager coefficients $L_{\alpha\beta}$, and the nonlinear response by the higher-order coefficients $M_{\alpha\beta\gamma}$, $N_{\alpha\beta\gamma\delta}$,...

A. Onsager reciprocity relations

The Onsager coefficients are defined close to the equilibrium in terms of the generating function (7) by

$$L_{\alpha\beta} \equiv \frac{\partial J_\alpha}{\partial A_\beta}\Big|_{\boldsymbol{A}=0} = \frac{\partial^2 Q}{\partial \lambda_\alpha \partial A_\beta}(0;0) \tag{10}$$

If we differentiate the expression (7) of the fluctuation theorem with respect to λ_α and A_β we find that

$$\frac{\partial^2 Q}{\partial\lambda_\alpha\partial A_\beta}(\boldsymbol{\lambda};\boldsymbol{A}) = -\frac{\partial^2 Q}{\partial\lambda_\alpha\partial\lambda_\beta}(\boldsymbol{A}-\boldsymbol{\lambda};\boldsymbol{A}) - \frac{\partial^2 Q}{\partial\lambda_\alpha\partial A_\beta}(\boldsymbol{A}-\boldsymbol{\lambda};\boldsymbol{A}) \tag{11}$$

Setting $\boldsymbol{\lambda}=0$ and $\boldsymbol{A}=0$, we obtain the relation

$$2\frac{\partial^2 Q}{\partial\lambda_\alpha\partial A_\beta}(0;0) = -\frac{\partial^2 Q}{\partial\lambda_\alpha\partial\lambda_\beta}(0;0) \tag{12}$$

or

$$L_{\alpha\beta} = -\frac{1}{2}\frac{\partial^2 Q}{\partial\lambda_\alpha\partial\lambda_\beta}(0;0) \tag{13}$$

as already shown in reference [6, 8]. Hence the Onsager reciprocity relations

$$L_{\alpha\beta} = L_{\beta\alpha} \tag{14}$$

We notice that no further relation is obtained by differentiating the fluctuation relation (7) twice with respect to either the parameters $\boldsymbol{\lambda}$ or the affinities $\boldsymbol{A}$.

B. Green-Kubo and Einstein-Helfand formulas

By using Eq. (13), we obtain the Onsager coefficients as

$$L_{\alpha\beta} = \frac{1}{2}\int_{-\infty}^{+\infty}\langle[j_\alpha(t)-\langle j_\alpha\rangle]\,[j_\beta(0)-\langle j_\beta\rangle]\rangle_{\rm eq}\,dt = \lim_{t\to\infty}\frac{1}{2t}\langle\Delta G_\alpha(t)\Delta G_\beta(t)\rangle_{\rm eq} \tag{15}$$

in terms of the time correlation functions of the instantaneous currents or the corresponding Helfand moments:

$$\Delta G_\alpha(t) \equiv G_\alpha(t) - \langle G_\alpha(t)\rangle \tag{16}$$

Here, the statistical average is carried out with respect to the state of thermodynamic equilibrium. In Eq. (15), the formulas giving the coefficients in terms of the time correlation functions are known as the Green-Kubo formulas [19, 20] (or the Yamamoto-Zwanzig formulas in the context of chemical reactions [21, 22]). The other formulas giving the coefficients in terms of the Helfand moments or cumulative currents are known as the Einstein-Helfand formulas [18, 23].

C. Relations for the second-order response coefficients

The second-order response coefficients are defined as

$$M_{\alpha\beta\gamma} \equiv \frac{\partial^3 Q}{\partial\lambda_\alpha\partial A_\beta\partial A_\gamma}(0;0) \tag{17}$$

in terms of one derivative with respect to the parameter λ_α generating the current J_α and two derivatives with respect to the affinities A_β and A_γ.

Our purpose is to relate these nonlinear response coefficients to quantities with a reduced number of derivatives with respect to the affinities, thus characterizing the fluctuations instead of the response.

Such relations are obtained by continuing the procedure started to get the Onsager reciprocity relations by further differentiating the generating function. If we differentiate the identity (11) with respect to A_γ and set $\boldsymbol{\lambda}=0$ and $\boldsymbol{A}=0$, we obtain the second-order response coefficients as

$$M_{\alpha\beta\gamma} = -\frac{1}{2}\frac{\partial^3 Q}{\partial\lambda_\alpha\partial\lambda_\beta\partial\lambda_\gamma}(0;0) - \frac{1}{2}\frac{\partial^3 Q}{\partial\lambda_\alpha\partial\lambda_\beta\partial A_\gamma}(0;0) - \frac{1}{2}\frac{\partial^3 Q}{\partial\lambda_\alpha\partial\lambda_\gamma\partial A_\beta}(0;0) \tag{18}$$

Using the symmetry (7) of the current fluctuation theorem at equilibrium, we see that the generating function $Q(\boldsymbol{\lambda};0) = Q(-\boldsymbol{\lambda};0)$ is an even function of λ_γ at equilibrium. The first term of the right-hand side of equation (18) is a third derivative with respect to the parameters λ_γ calculated at equilibrium, hence it must vanish identically.

The other terms in Eq. (18) are related to the spectral function of the nonequilibrium current fluctuations defined by

$$\Sigma_{\alpha\beta}(\omega) \equiv \int_{-\infty}^{+\infty} \mathrm{e}^{i\omega t} \left\langle \left[j_\alpha(t) - \langle j_\alpha \rangle \right] \left[j_\beta(0) - \langle j_\beta \rangle \right] \right\rangle \, dt \tag{19}$$

where the statistical average is here taken with respect to the nonequilibrium steady state. Here, we introduce the quantities

$$\begin{aligned} R_{\alpha\beta,\gamma} &\equiv -\frac{\partial^3 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial A_\gamma}(0;0) \\ &= \frac{\partial}{\partial A_\gamma} \int_{-\infty}^{+\infty} \left\langle \left[j_\alpha(t) - \langle j_\alpha \rangle \right] \left[j_\beta(0) - \langle j_\beta \rangle \right] \right\rangle \, dt \Big|_{\boldsymbol{A}=0} \\ &= \frac{\partial}{\partial A_\gamma} \lim_{t\to\infty} \frac{1}{t} \langle \Delta G_\alpha(t) \Delta G_\beta(t) \rangle \Big|_{\boldsymbol{A}=0} \\ &= \frac{\partial}{\partial A_\gamma} \Sigma_{\alpha\beta}(\omega = 0) \Big|_{\boldsymbol{A}=0} \end{aligned} \tag{20}$$

which characterize the sensitivity of the current fluctuations out of equilibrium. Equation (20) shows that the sensitivity coefficients are given in terms of the derivative with respect to the affinities of the spectral function or, equivalently, of the diffusivities of the nonequilibrium currents defined by

$$D_{\alpha\beta} \equiv \lim_{t\to\infty} \frac{1}{2t} \langle \Delta G_\alpha(t) \Delta G_\beta(t) \rangle = -\frac{1}{2} \frac{\partial^2 Q}{\partial\lambda_\alpha \partial\lambda_\beta} \Big|_{\boldsymbol{\lambda}=0} \tag{21}$$

According to the fluctuation theorem and Eq. (18), we find that the second-order response coefficients are given in terms of the sensitivity coefficients by

$$M_{\alpha\beta\gamma} = \frac{1}{2} \left(R_{\alpha\beta,\gamma} + R_{\alpha\gamma,\beta} \right) \tag{22}$$

For the case $\beta = \gamma$ we find

$$M_{\alpha\beta\beta} = R_{\alpha\beta,\beta} \tag{23}$$

In particular the response coefficients $M_{\alpha\beta\gamma}$ present the expected symmetry $M_{\alpha\beta\gamma} = M_{\alpha\gamma\beta}$. The second-order coefficients are thus related to the diffusivities by

$$M_{\alpha\beta\gamma} = \left[\frac{\partial}{\partial A_\gamma} D_{\alpha\beta} + \frac{\partial}{\partial A_\beta} D_{\alpha\gamma} \right]_{\boldsymbol{A}=0} \tag{24}$$

Thanks to the fluctuation theorem for the currents, we can therefore relate the second-order nonlinear response coefficients to quantities characterizing the nonequilibrium fluctuations such as the spectral functions or the diffusivities of the currents in the nonequilibrium steady state. We notice that the number of derivatives with respect to the affinities has indeed been reduced.

Similar expressions can be found for even higher-order relations where the odd derivatives with respect to the λ's automatically vanish at equilibrium.

D. Relations for the third-order response coefficients

A similar reasoning can be carried out for the third-order response coefficients defined by

$$N_{\alpha\beta\gamma\delta} \equiv \frac{\partial^4 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma \partial A_\delta}(0;0) \tag{25}$$

Differentiating the identity (11) twice with respect to the affinities A_γ and A_δ shows that

$$N_{\alpha\beta\gamma\delta} = -\frac{1}{2} \frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(0;0) - \frac{1}{2} \left(S_{\alpha\beta\gamma,\delta} + S_{\alpha\beta\delta,\gamma} + S_{\alpha\gamma\delta,\beta} \right) + \frac{1}{2} \left(T_{\alpha\beta,\gamma\delta} + T_{\alpha\gamma,\beta\delta} + T_{\alpha\delta,\beta\gamma} \right) \tag{26}$$

with

$$S_{\alpha\beta\gamma,\delta} \equiv \frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial A_\delta}(0;0) \tag{27}$$

and

$$T_{\alpha\beta,\gamma\delta} \equiv -\frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial A_\gamma \partial A_\delta}(0;0) \tag{28}$$

Differentiating Eq. (11) twice with respect to the parameters λ_γ and λ_δ shows that

$$S_{\alpha\beta\gamma,\delta} = -\frac{1}{2}\frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(0;0) \tag{29}$$

which proves the total symmetry of this tensor. Accordingly, the third-order response coefficients are given by

$$N_{\alpha\beta\gamma\delta} = -\frac{1}{2}S_{\alpha\beta\gamma,\delta} + \frac{1}{2}\left(T_{\alpha\beta,\gamma\delta} + T_{\alpha\gamma,\beta\delta} + T_{\alpha\delta,\beta\gamma}\right) \tag{30}$$

We thus obtain the reciprocity relations that the fourth-order tensor

$$2N_{\alpha\beta\gamma\delta} - T_{\alpha\beta,\gamma\delta} - T_{\alpha\gamma,\beta\delta} - T_{\alpha\delta,\beta\gamma} \tag{31}$$

must be totally symmetric.

The tensor (27) can be expressed as

$$S_{\alpha\beta\gamma,\delta} = \frac{\partial}{\partial A_\delta}\lim_{t\to\infty}\frac{1}{t}\langle \Delta G_\alpha(t)\Delta G_\beta(t)\Delta G_\gamma(t)\rangle\Big|_{\boldsymbol{A}=0} \tag{32}$$

which do not vanish in general as for the even-order cases. Equation (32) shows that the tensor (27) characterizes the sensitivity of the third-order moments of the cumulative currents with respect to the nonequilibrium constraints. Moreover, the expression (29) shows that this tensor can also be calculated at equilibrium as

$$\begin{aligned} S_{\alpha\beta\gamma,\delta} = \lim_{t\to\infty} \quad \frac{1}{2t}\Big[&\langle \Delta G_\alpha(t)\Delta G_\beta(t)\Delta G_\gamma(t)\Delta G_\delta(t)\rangle \\ &-\langle \Delta G_\alpha(t)\Delta G_\beta(t)\rangle\langle \Delta G_\gamma(t)\Delta G_\delta(t)\rangle \\ &-\langle \Delta G_\alpha(t)\Delta G_\gamma(t)\rangle\langle \Delta G_\beta(t)\Delta G_\delta(t)\rangle \\ &-\langle \Delta G_\alpha(t)\Delta G_\delta(t)\rangle\langle \Delta G_\beta(t)\Delta G_\gamma(t)\rangle\Big]_{\rm eq} \end{aligned} \tag{33}$$

where it characterizes the fluctuations. The equality between Eqs. (32) and (33) is another remarkable consequence of the fluctuation theorem.

On the other hand, the tensor (28) is given by

$$\begin{aligned} T_{\alpha\beta,\gamma\delta} &= \frac{\partial}{\partial A_\gamma}\frac{\partial}{\partial A_\delta}\int_{-\infty}^{+\infty}\langle [j_\alpha(t) - \langle j_\alpha\rangle]\,[j_\beta(0) - \langle j_\beta\rangle]\rangle\, dt\Big|_{\boldsymbol{A}=0} \\ &= \frac{\partial}{\partial A_\gamma}\frac{\partial}{\partial A_\delta}\lim_{t\to\infty}\frac{1}{t}\langle \Delta G_\alpha(t)\Delta G_\beta(t)\rangle\Big|_{\boldsymbol{A}=0} \\ &= \frac{\partial}{\partial A_\gamma}\frac{\partial}{\partial A_\delta}\Sigma_{\alpha\beta}(\omega=0)\Big|_{\boldsymbol{A}=0} \end{aligned} \tag{34}$$

Accordingly, the tensor (28) also characterizes the sensitivity of the nonequilibrium fluctuations but now in terms of the second derivatives of the power spectrum with respect to the affinities. We notice the similarity with Eq. (20). Again, the number of derivatives with respect to the affinities has been reduced compared to the definition (25) of the third-order response coefficients and this thanks to the fluctuation theorem for the currents.

The expansion can be carried out to higher orders as done in the next section.

IV. RELATIONS AT ARBITRARY ORDERS

In a macroscopic description, we consider general affinities A_α conjugated to currents J_α. The mean value of the currents can be developed as

$$J_\alpha = \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\beta,\cdots,\mu} C^{(n)}_{\alpha\beta\cdots\mu} \underbrace{A_\beta \dots A_\mu}_{n} \tag{35}$$

with the coefficients

$$C^{(n)}_{\alpha\beta\cdots\mu} \equiv \frac{\partial^n J_\alpha}{\partial A_\beta \cdots \partial A_\mu}\Big|_{\boldsymbol{A}=0} = \frac{\partial^{n+1} Q}{\partial \lambda_\alpha \partial A_\beta \cdots \partial A_\mu}\Big|_{\boldsymbol{\lambda}=0,\boldsymbol{A}=0} \tag{36}$$

contain $n+1$ indices. The expansion in powers of the affinities gives Onsager's linear response coefficients $C^{(1)}_{\alpha\beta}$ as well as higher-order coefficients $C^{(n)}$ characterizing the nonlinear response of the system with respect to the nonequilibrium constraints $\{A_\epsilon\}$.

We now want to use the fluctuation theorem for the currents (7) to obtain expressions for the response coefficients. To do so we will consider expressions for the derivatives of Q at arbitrary orders. This will provide us with several non trivial relationships and we will have to combine them to obtain a simple form for the response coefficients.

Using the fluctuation theorem (7), the derivatives of Q are given by

$$Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma} = (-1)^k \sum_{p=0}^{n-k} Q^{(k+p,n)}_{\alpha\cdots\eta\{\rho\cdots\sigma\}_p} \tag{37}$$

where the derivatives are calculated at $\boldsymbol{\lambda} = \boldsymbol{A} = 0$. The notation $Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma}$ means that we have taken n derivatives with k of them corresponding to λ_α,...,λ_η and $n-k$ corresponding to A_ρ,...,A_σ:

$$Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma} \equiv \frac{\partial^n Q}{\underbrace{\partial\lambda_\alpha \cdots \partial\lambda_\eta}_{k} \underbrace{\partial A_\rho \cdots \partial A_\sigma}_{n-k}}(0;0) \tag{38}$$

These derivatives correspond to the response of the kth cumulant with respect to the macroscopic affinities:

$$Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma} \equiv (-1)^{k+1} \frac{\partial^{n-k}}{\partial A_\rho \cdots \partial A_\sigma} \lim_{t\to\infty} \frac{1}{t} \langle\langle G_\alpha \cdots G_\eta \rangle\rangle\Big|_{\boldsymbol{A}=0} \tag{39}$$

where $\langle\langle\cdot\rangle\rangle$ denotes the cumulant. The notation $\{\cdot\}_p$ means the symmetrized ensemble with the derivatives taken after the term p. For example, $\{\alpha\beta\gamma\delta\}_1 \equiv \alpha, \beta\gamma\delta + \beta, \alpha\gamma\delta + \gamma, \alpha\beta\delta + \delta, \alpha\beta\gamma$. In the same way, $\{\alpha\beta\gamma\delta\}_2 \equiv \alpha\beta, \gamma\delta + \alpha\gamma, \beta\delta + \alpha\delta, \gamma\beta + \beta\gamma, \alpha\delta + \beta\delta, \alpha\gamma + \gamma\delta, \alpha\beta$. There are $m!/[p!(m-p)!]$ terms if there are m terms in the ensemble. The derivative (37) is thus expressed as the sum of 2^{n-k} terms. The sign $(-1)^k$ comes from the derivatives with respect to λ while the structure of the sum comes from the derivatives with respect to A. Indeed, each such derivative generates two terms, one with a derivative with respect to A and the other with respect to λ as can be seen from Eq. (7). Noting that the term $p = 0$ in Eq. (37) is the same as the left-hand side of the equation, we have

$$\left[1 + (-1)^{k+1}\right] \; Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma} = (-1)^k \sum_{p=1}^{n-k} Q^{(k+p,n)}_{\alpha\cdots\eta\{\rho\cdots\sigma\}_p} \tag{40}$$

so that

$$0 \;=\; \sum_{p=1}^{n-k} Q^{(k+p,n)}_{\alpha\cdots\eta\{\rho\cdots\sigma\}_p} \quad k \text{ even} \tag{41}$$

$$2\, Q^{(k,n)}_{\alpha\cdots\eta,\rho\cdots\sigma} \;=\; -\sum_{p=1}^{n-k} Q^{(k+p,n)}_{\alpha\cdots\eta\{\rho\cdots\sigma\}_p} \quad k \text{ odd} \tag{42}$$

As explained above each derivative $Q^{(k,n)}$ can be expressed as derivatives with respect to $n-k$ affinities of a cumulant of order k at equilibrium. We thus have a number of non trivial relations between different moments and their derivatives with respect to the affinities calculated at equilibrium.

In particular, the response coefficients (36) of order $n-1$ are given by

$$C^{(n-1)}_{\alpha\beta\cdots\sigma} = Q^{(1,n)}_{\alpha,\beta\cdots\sigma} = -\frac{1}{2}\sum_{p=1}^{n-1} Q^{(1+p,n)}_{\alpha\{\beta\cdots\sigma\}_p} \tag{43}$$

where we used Eq. (42) with $k=1$ which is odd. The response coefficients are thus expressed as a sum of $2^{n-1}-1$ terms with $n-1$ different tensors.

The relations (37) can be used to simplify the expressions of the response coefficients. For example, the relations (41)-(42) with $k=n-1$ give

$$Q^{(n,n)}_{\alpha\cdots\sigma,} = 0 \quad n \text{ odd} \tag{44}$$

$$2\, Q^{(n-1,n)}_{\alpha\cdots\eta,\sigma} = -\, Q^{(n,n)}_{\alpha\cdots\sigma,} \quad n \text{ even} \tag{45}$$

so that the derivatives with respect to λ vanish if n is odd and we obtain the total symmetry of the tensor $Q^{(n-1,1)}_{\alpha\cdots\eta,\sigma}$ if n is even:

$$\frac{\partial}{\partial A_\sigma}\lim_{t\to\infty}\frac{1}{t}\langle\langle G_\alpha\cdots G_\eta\rangle\rangle\Big|_{\boldsymbol{A}=0} = \frac{1}{2}\lim_{t\to\infty}\frac{1}{t}\langle\langle G_\alpha\cdots G_\eta G_\sigma\rangle\rangle_{\rm eq} \tag{46}$$

which is totally symmetric. These are non-trivial consequences derived from the fluctuation theorem. If $k=n$ we do not get any new informations. If $k=0$ we find a constraint on the sum of the response coefficients but it can be recovered from their expressions (43). In fact all relations (41) with k even can be recovered from relations (42) for k odd. We now have to use them to simplify the expression of the response coefficients.

To do this, we will thus choose to use relations (42) to eliminate all terms of the form $Q^{(k,n)}$ where k is odd. However, the terms in the right hand side of Eq. (43) are all totally symmetrized with respect to the $n-1$ indices $\{\beta\cdots\sigma\}$ while relations (42) are not. The first step is thus to symmetrize relations (42) to get

$$Q^{(k,n)}_{\alpha\{\beta\cdots\sigma\}_{k-1}} = -\frac{1}{2}\sum_{l=k}^{n-1}\begin{pmatrix} l \\ k-1\end{pmatrix} Q^{(l+1,n)}_{\alpha\{\beta\cdots\sigma\}_l} \quad \text{for } k \text{ odd} \tag{47}$$

where

$$\begin{pmatrix} l \\ k-1\end{pmatrix} \equiv \frac{l!}{(k-1)!(l-k+1)!} \tag{48}$$

These coefficients are obtained by symmetrizing the relations (42). As all relations become thus totally symmetric, there are $\begin{pmatrix} l \\ k-1\end{pmatrix}$ identically terms $Q^{(l+1,n)}_{\alpha\{\beta\cdots\sigma\}_l}$ arising by this procedure. These coefficients are given by the numbers of terms in $Q^{(k,n)}_{\alpha\{\beta\cdots\sigma\}_{k-1}}$ times the number of terms in $Q^{(l+1,n)}_{\alpha\cdots\eta\{\rho\cdots\sigma\}_{l-k+1}}$ divided by the number of terms in $Q^{(l+k,n)}_{\alpha\{\beta\cdots\sigma\}_l}$. Unfortunately expression (47) is expressed in terms of $Q^{(k,n)}$ with k odd and even. We will thus have to use this relation recursively to eliminate all terms with k odd within itself.

One has then to eliminate successively the terms $Q^{(3,n)}_{\alpha\{\beta\cdots\sigma\}_2}$, $Q^{(5,n)}_{\alpha\{\beta\cdots\sigma\}_4}$,...,$Q^{(p,n)}_{\alpha\{\beta\cdots\sigma\}_{p-1}}$. When this is done, one can express the response coefficients in the form

$$C^{(n-1)}_{\alpha\beta\cdots\sigma} = \gamma_1\, Q^{(2,n)}_{\alpha\{\beta\cdots\sigma\}_1} + \gamma_3\, Q^{(4,n)}_{\alpha\{\beta\cdots\sigma\}_3} + \cdots + \gamma_{n-2}\, Q^{(n-1,n)}_{\alpha\{\beta\cdots\sigma\}_{n-2}} \qquad (n \text{ odd}) \tag{49}$$

and

$$C^{(n-1)}_{\alpha\beta\cdots\sigma} = \gamma_1\, Q^{(2,n)}_{\alpha\{\beta\cdots\sigma\}_1} + \gamma_3\, Q^{(4,n)}_{\alpha\{\beta\cdots\sigma\}_3} + \cdots + \gamma_{n-1}\, Q^{(n,n)}_{\alpha\beta\cdots\sigma} \qquad (n \text{ even}) \tag{50}$$

where we used that $Q^{(n,n)}=0$ for n odd. We find here the important property that the coefficients $\begin{pmatrix} l \\ k-1\end{pmatrix}$ are independent of n which implies that the coefficients γ_i do not depend on n. The odd response coefficients are thus expressed in terms of $(n-1)/2$ different tensors which is far better than the $n-1$ tensors needed in expression (43). The even response coefficients are thus expressed in terms of $n/2$ different tensors. By construction, they are symmetric for the permutations of the $n-1$ indices $\{\beta\cdots\sigma\}$ as it should be.

In particular, the tensor

$$C^{(n-1)}_{\alpha\beta\cdots\sigma} - \left[\gamma_1\, Q^{(2,n)}_{\alpha\{\beta\cdots\sigma\}_1} + \gamma_3\, Q^{(4,n)}_{\alpha\{\beta\cdots\sigma\}_3} + \cdots + \gamma_{n-3}\, Q^{(n-2,n)}_{\alpha\{\beta\cdots\sigma\}_{n-3}}\right] = \gamma_{n-1}\, Q^{(n,n)}_{\alpha\beta\cdots\sigma} \tag{51}$$

with n even is totally symmetric.

We now want to calculate the coefficients γ_i, with i odd, associated with the terms $Q^{(i+1,n)}_{\alpha\{\beta\cdots\sigma\}_i}$. The first term γ_1 takes the value $-1/2$. The next ones are given by the successive elimination of the terms $Q^{(3,n)}_{\alpha\{\beta\cdots\sigma\}_2}$, $Q^{(5,n)}_{\alpha\{\beta\cdots\sigma\}_4}$,..., $Q^{(p,n)}_{\alpha\{\beta\cdots\sigma\}_{p-1}}$. Each successive elimination will change the coefficients in front of the $Q^{(l+1,n)}_{\alpha\{\beta\cdots\sigma\}_l}$. We thus introduce numbers χ^l_k which denote the coefficients weighting the terms $Q^{(l+1,n)}_{\alpha\{\beta\cdots\sigma\}_l}$ at the kth successive elimination. From Eq. (43) we set $\chi^l_0 = -1/2\ \forall l$. The first step is thus to eliminate the term $Q^{(3,n)}_{\alpha\{\beta\cdots\sigma\}_2}$ so that

$$\chi^l_1 = \begin{cases} \chi^l_0 - \frac{1}{2}\begin{pmatrix} l \\ 2 \end{pmatrix}\chi^2_0 & \text{if } l \geq 3 \\ 0 & l = 2 \\ \chi^l_0 & \text{if } l = 1 \end{cases} \tag{52}$$

according to Eq. (47). We can continue and eliminate the term $Q^{(5,n)}_{\alpha\{\beta\cdots\sigma\}_4}$ to get

$$\chi^l_2 = \begin{cases} \chi^l_1 - \frac{1}{2}\begin{pmatrix} l \\ 4 \end{pmatrix}\chi^4_1 & \text{if } l \geq 5 \\ 0 & \text{if } l = 4 \\ \chi^l_1 & \text{otherwise} \end{cases} \tag{53}$$

and after k steps we have

$$\chi^l_k = \begin{cases} \chi^l_{k-1} - \frac{1}{2}\begin{pmatrix} l \\ 2k \end{pmatrix}\chi^{2k}_{k-1} & \text{if } l \geq 2k+1 \\ 0 & l = 2k \\ \chi^l_{k-1} & \text{otherwise} \end{cases} \tag{54}$$

These numbers are independent of n as they should be. The coefficients γ_i in Eq. (49)-(50) are then given by χ^i_k once they remain invariant that is when $k \geq (i-1)/2$. This construction can be summarized in the form :

$$\gamma_i = \frac{1}{4}\sum_{p=3}^{i,2} \xi_p \begin{pmatrix} i \\ p-1 \end{pmatrix} - \frac{1}{2} \tag{55}$$

where the notation $\sum_{p=a}^{b,2}$ means that we sum from $p = a$ to b by steps of 2. We also absorbed in the expression of γ_i the factor $-\frac{1}{2}$ in front of expression (43). The constant $-\frac{1}{2}$ is the contribution from the original terms $Q^{(i+1,n)}$ in Eq. (43). The coefficients ξ_p give the number of terms $Q^{(p,n)}_{\alpha\{\beta\cdots\sigma\}_{p-1}}$ coming from the elimination of the previous odd terms. They are given by

$$\xi_p = 1 - \frac{1}{2}\sum_{l=3}^{p-2,2} \begin{pmatrix} p-1 \\ l-1 \end{pmatrix} \xi_l \tag{56}$$

We then find

$$\xi_3 = 1,\ \xi_5 = -2,\ \xi_7 = \frac{17}{2},\ \xi_9 = -62,\ \ldots \tag{57}$$

Injecting those numbers in relations (55) we find

$$\gamma_1 = -\frac{1}{2},\ \gamma_3 = \frac{1}{4},\ \gamma_5 = -\frac{1}{2},\ \gamma_7 = \frac{17}{8},\ \gamma_9 = -\frac{31}{2}, \ldots \tag{58}$$

A shorter relation in order to obtain the γ_i , $i > 1$, is given by

$$\gamma_i = \frac{1}{4} - \frac{1}{2} \sum_{l=3}^{i-2,2} \left(\begin{array}{c} i-1 \\ l-1 \end{array} \right) \gamma_l \tag{59}$$

We have thus obtained expressions for the response coefficients of order n in terms of microscopic correlation functions and their response to the affinity. Using the symmetry of the current fluctuation theorem we were able to simplify the original expressions (43). We found a simple structure in terms of $(n-1)/2$ or $(n/2)$ different tensors if n is respectively odd or even. These tensors characterize the fluctuations of the currents and their response to affinities up to an order inferior to the response coefficient. The numerical coefficients weighting the different tensors turned out to be independent of n, so that the same expressions arise independently of n and of its parity. Nevertheless, a difference arises between odd and even response coefficients: for n even there exists a totally symmetric part arising in the expression of $C^{(n)}$ that does not appear for n odd.

For example, using (50) Onsager's coefficients are given by

$$C^{(1)}_{\alpha\beta} = \gamma_1 \; Q^{(2,2)}_{\alpha\beta,} = -\frac{1}{2} \; Q^{(2,2)}_{\alpha\beta,} = L_{\alpha\beta} \tag{60}$$

according to Eq. (15) in terms of the time correlation functions of the instantaneous currents [19, 20] or the corresponding Helfand moments [18]. Onsager's symmetry [1] is therefore verified. Here, the statistical average is carried out with respect to the state of thermodynamic equilibrium.

The second-order response is expressed as

$$C^{(2)}_{\alpha\beta\gamma} \;=\; \gamma_1 \; Q^{(2,3)}_{\alpha\{\beta\gamma\}_1} = -\frac{1}{2} \; Q^{(2,3)}_{\alpha\{\beta\gamma\}_1} = -\frac{1}{2} \left[Q^{(2,3)}_{\alpha\beta,\gamma} + Q^{(2,3)}_{\alpha\gamma,\beta} \right] \tag{61}$$

which gives the response coefficients $C^{(2)}_{\alpha\beta\gamma}$ in terms of the expressions (20):

$$Q^{(2,3)}_{\alpha\beta,\gamma} = -R_{\alpha\beta,\gamma} \tag{62}$$

The third-order response coefficients are given by

$$\begin{aligned} C^{(3)}_{\alpha\beta\gamma\delta} \;&=\; \gamma_1 \; Q^{(2,4)}_{\alpha\{\beta\gamma\delta\}_1} + \gamma_3 \; Q^{(4,4)}_{\alpha\beta\gamma\delta} \\ &=\; -\frac{1}{2} \left[Q^{(2,4)}_{\alpha\{\beta\gamma\delta\}_1} - \frac{1}{2} \; Q^{(4,4)}_{\alpha\beta\gamma\delta} \right] \end{aligned} \tag{63}$$

where $Q^{(4,4)}$ is the cumulant of order 4 calculated at equilibrium by Eqs. (33) and $Q^{(2,4)}$ are the second derivatives of the power spectra with respect to the affinities at equilibrium by Eq. (34):

$$Q^{(4,4)}_{\alpha\beta\gamma\delta} \;=\; -2S_{\alpha\beta\gamma\delta} \tag{64}$$

$$Q^{(2,4)}_{\alpha\{\beta\gamma\delta\}_1} \;=\; -T_{\alpha\beta,\gamma\delta} - T_{\alpha\gamma,\beta\delta} - T_{\alpha\delta,\beta\gamma} \tag{65}$$

To illustrate the elimination of the $Q^{(k,n)}$ with k even in a non trivial case, let us consider the fourth-order response coefficients. They are given by

$$\begin{aligned} C^{(4)}_{\alpha\beta\gamma\delta\epsilon} \;&=\; -\frac{1}{2} \sum_{p=1}^{4} Q^{(1+p,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_p} \\ &=\; -\frac{1}{2} \left[Q^{(2,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_1} + Q^{(3,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_2} + Q^{(4,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_3} \right] \\ &=\; -\frac{1}{2} \left[Q^{(2,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_1} - \frac{1}{2} \; Q^{(4,5)}_{\alpha\{\beta\gamma\delta\epsilon\}_3} \right] \end{aligned} \tag{66}$$

where we used that $Q_{\alpha\beta\gamma\delta\epsilon} = 0$ to go from the first line to the second and the relations (42) to go from the second to the third line.

The fourth-order response coefficients can thus be expressed in terms of the third derivatives of the spectrum with respect to the affinities and in terms of the first derivative of the fourth-order correlation functions with respect to the affinities. In particular, it presents the expected symmetry $C^{(4)}_{\alpha\beta\gamma\delta\epsilon} = C^{(4)}_{\alpha\gamma\beta\delta\epsilon} = C^{(4)}_{\alpha\epsilon\gamma\delta\beta} = \cdots = C^{(4)}_{\alpha\beta\gamma\epsilon\delta}$. The

expression (66) could have been obtained immediately using the general form (49) with coefficients γ_i given by (58). One can also note that the coefficients γ_i are the same as in expression (61) as it should.

In the same way, the fifth-order response coefficients is immediately given by Eq. (50) which reads

$$C^{(5)}_{\alpha\beta\gamma\delta\epsilon\mu} = -\frac{1}{2}\left[Q^{(2,6)}_{\alpha\{\beta\gamma\delta\epsilon\mu\}_1} - \frac{1}{2}\,Q^{(4,6)}_{\alpha\{\beta\gamma\delta\epsilon\mu\}_3} + \,Q^{(6,6)}_{\alpha\beta\gamma\delta\epsilon\mu}\right]$$

as can be verified using using relations (45) and (42) on the expression (43) of the tensor.

Eventually, we can construct in the same way the higher-order relations for the fluctuations. Indeed the reasoning remain unchanged when considering the fluctuations and their responses. Using relations (42) recursively yields, for odd m,

$$Q^{(m,n)}_{\alpha_1\cdots\alpha_m,\beta\cdots\sigma} = \gamma_1\,Q^{(m+1,n)}_{\alpha_1\cdots\alpha_m\{\beta\cdots\sigma\}_1} + \gamma_3\,Q^{(m+3,n)}_{\alpha_1\cdots\alpha_m\{\beta\cdots\sigma\}_3} + \cdots + \gamma_{n-2}\,Q^{(n-1,n)}_{\alpha_1\cdots\alpha_m\{\beta\cdots\sigma\}_{n-m-2}} \qquad (n \text{ odd}) \tag{67}$$

and

$$Q^{(m,n)}_{\alpha_1\cdots\alpha_m,\beta\cdots\sigma} = \gamma_1\,Q^{(m+1,n)}_{\alpha_1\cdots\alpha_m\{\beta\cdots\sigma\}_1} + \gamma_3\,Q^{(m+3,n)}_{\alpha_1\cdots\alpha_m\{\beta\cdots\sigma\}_3} + \cdots + \gamma_{n-1}\,Q^{(n,n)}_{\alpha_1\cdots\alpha_m\beta\cdots\sigma} \qquad (n \text{ even}) \tag{68}$$

The fluctuations are thus expressed in terms of the independent tensors with the same weights as for the response coefficients.

V. CONCLUSIONS

In this paper, we have shown that the fluctuation theorem for the currents (1) or (7) implies not only Onsager's reciprocity relations [1] along with the Green-Kubo and Einstein-Helfand formulas [18–20, 23] for the linear response coefficients, but also further remarkable relations for the nonlinear response coefficients at arbitrarily high orders. These results find their origin in the validity of the fluctuation theorem for the currents far from equilibrium in stochastic rate processes. The obtained relations are thus the consequences of the microreversibility.

The response coefficients are defined by expanding the currents crossing the nonequilibrium system in powers of the affinities (or thermodynamic forces). Therefore, the response coefficients are defined with respect to the equilibrium state where the affinities vanish. Nevertheless, we can estimate the currents further away from equilibrium if we use an expansion up to high powers of the affinities. This explains that we need a general property valid far from equilibrium, such as the fluctuation theorem for the currents, in order to obtain relations on the nonlinear response coefficients at arbitrary orders.

Typically, the relations described in the present paper connect quantities measuring the statistical correlations among m fluctuating cumulative currents to corresponding quantities among $m-1$ of them with an extra derivative with respect to an affinity. The former characterizes the fluctuations at m^{th} order and the latter the sensitivity of the fluctuations at the lower $(m-1)^{\text{th}}$ order with respect to the nonequilibrium constraints. This is the case for instance for the equality between Eq. (32) which measures the sensitivity of the nonequilibrium correlations among three cumulative currents under changes of an affinity and Eq. (33) which characterizes the fluctuations between four cumulative currents in the equilibrium thermodynamic state. This is the feature which is found in the relations here described.

In conclusion, the theory developed in the present paper provides a general framework to formulate the nonlinear response theory in nonequilibrium processes. The results here reported have important applications for the nonlinear response properties of many nonequilibrium systems such as the chemical and biochemical reactions [13], the full counting statistics in mesoscopic conductors [15], the effusion of ideal gases [24], and Van den Broeck's demons [25]. The present results could be especially important in nonequilibrium systems at the micro- and nano-scales, where the nonlinear response properties turn out to be dominant [26].

Acknowledgments. D. Andrieux is Research Fellow at the F.N.R.S. Belgium. This research is financially supported by the "Communauté française de Belgique" (contract "Actions de Recherche Concertées" No. 04/09-312) and the National Fund for Scientific Research (F. N. R. S. Belgium, contract F. R. F. C. No. 2.4577.04).

[1] L. Onsager, Phys. Rev. **37**, 405 (1931).
[2] T. De Donder and P. Van Rysselberghe, *Affinity* (Stanford University Press, Menlo Park CA, 1936).

[3] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[4] D. J. Evans and D. J. Searles, Phys. Rev. E **50**, 1645 (1994).
[5] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[6] G. Gallavotti, Phys. Rev. Lett. **77**, 4334 (1996).
[7] J. Kurchan, J. Phys. A: Math. Gen. **31**, 3719 (1998).
[8] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[9] C. Maes, J. Stat. Phys. **95**, 367 (1999).
[10] C. Maes and K. Netočný, J. Stat. Phys. **110**, 269 (2003).
[11] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
[12] R. van Zon and E. G. D. Cohen, Phys. Rev. Lett. **91**, 110601 (2003).
[13] D. Andrieux and P. Gaspard, J. Chem. Phys. **121**, 6167 (2004).
[14] D. Andrieux and P. Gaspard, cond-mat/0512254 (2005).
[15] D. Andrieux and P. Gaspard, J. Stat. Mech.: Th. Exp. P01011 (2006).
[16] J. Schnakenberg, Rev. Mod. Phys. **48**, 571 (1976).
[17] D. Andrieux and P. Gaspard, in preparation
[18] E. Helfand, Phys. Rev. **119**, 1 (1960).
[19] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).
[20] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[21] T. Yamamoto, J. Chem. Phys. **33**, 281 (1960).
[22] R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).
[23] A. Einstein, *Investigations on the theory of the Brownian movement* (Dover, New York, 1956).
[24] B. Cleuren, C. Van den Broeck, and R. Kawai, Phys. Rev. E **74**, 021117 (2006).
[25] C. Van den Broeck, P. Meurs, and R. Kawai, New J. Phys. **7**, 10 (2005).
[26] D. Andrieux and P. Gaspard, Phys. Rev. E **74**, 011906 (2006).