Fluctuation-dissipation theorem in nonequilibrium steady states

U. Seifert\textsuperscript{1} and T. Speck\textsuperscript{2,3}

\textsuperscript{1} II. Institut f"{u}r Theoretische Physik, Universit"{a}t Stuttgart - 70550 Stuttgart, Germany, EU
\textsuperscript{2} Department of Chemistry, University of California - Berkeley, CA 94720, USA
\textsuperscript{3} Chemical Sciences Division, Lawrence Berkeley National Laboratory - Berkeley, CA 94720, USA

received 31 July 2009; accepted in final form 9 December 2009
published online 21 January 2010

PACS 05.40.-a – Fluctuation phenomena, random processes, noise, and Brownian motion

Abstract – In equilibrium, the fluctuation-dissipation theorem (FDT) expresses the response of an observable to a small perturbation by a correlation function of this variable with another one that is conjugate to the perturbation with respect to energy. For a nonequilibrium steady state (NESS), the corresponding FDT is shown to involve in the correlation function a variable that is conjugate with respect to entropy. By splitting up entropy production into one of the system and one of the medium, it is shown that for systems with a genuine equilibrium state the FDT of the NESS differs from its equilibrium form by an additive term involving total entropy production. A related variant of the FDT not requiring explicit knowledge of the stationary state is particularly useful for coupled Langevin systems. The \textit{a priori} surprising freedom apparently involved in different forms of the FDT in a NESS is clarified.

Copyright © EPLA, 2010

Introduction. – Stochastic thermodynamics provides a framework for describing small driven systems embedded in a heat bath of still well-defined temperature [1]. Its crucial ingredients are a formulation of the first law [2] and the notion of a stochastic entropy [3] both valid along single fluctuating trajectories. Using these concepts several exact relations for distribution functions for quantities like work [4,5] and entropy production [3,6–9] have been derived. Experimental tests have been performed on a variety of different systems. Prominent examples include colloidal particles manipulated by laser traps [10–12], biomolecules pulled by AFM’s or optical tweezers [13,14], and single defects observed using fluorescence techniques [15]. Reviews of this very active field can be found in refs. [1,16,17].

A particularly interesting class of states are nonequilibrium steady states (NESS) characterized both by a time-independent distribution and, as a result of the external driving, nonvanishing currents. If such a NESS is perturbed by an additional small external force or field, one can ask whether the response of an observable of this system can be expressed by a correlation function involving this observable and a second one. For slightly perturbed equilibrium systems, such a connection between response and equilibrium fluctuation is given by the well-known fluctuation-dissipation theorem (FDT) [18,19]. The appropriate correlation function involves the observable whose response is sought for and another variable that is conjugate to the perturbation with respect to energy. The first purpose of this letter is to show that previously derived somewhat formal looking FDTs for general Markovian processes [20,21] acquire a particularly simple and transparent form using the concepts of stochastic thermodynamics: In a nonequilibrium steady state, the response of a system to an additional small perturbation is given by a correlation function of this observable and another one that is conjugate to the perturbation with respect to stochastic entropy. Moreover, by expressing entropy production in the system as the difference between total entropy production and that in the surrounding medium, we can show that for a large class of systems the FDT in a NESS can be obtained from the corresponding equilibrium form of the FDT by subtracting a term involving total entropy production. The latter result rationalizes and generalizes recent results for diffusive systems driven by an external force [22,23] or shear flow [24], see refs. [25,26] for first experimental tests of such extended FDTs. Adapting a recently introduced alternative strategy for deriving an FDT [27], we discuss a variant not requiring explicit knowledge of the typically unknown stationary distribution. This form will be particularly useful in simulations of coupled Langevin systems.

Finally, we clarify the \textit{a priori} surprising apparent freedom involved in different forms of the FDT in a NESS. For a broader overview of the FDT especially in systems with glassy dynamics, we refer to the review [28].

Derivation of the FDT. – For a derivation of these results in a fairly general setting, we consider an arbitrary set of states \{n\}. These states could \textit{inter alia} signify...
discrete spatial variables for a set of driven interacting diffusive degrees of freedom obtained by spatially discretizing Langevin equations. Likewise, they could code the states of any (bio)chemical reaction network. A transition from state \( m \) to \( n \) happens with a rate \( w_{mn}(h) \), which depends on an external parameter \( h \). The probability \( \psi_m(t) \) for finding the system in state \( m \) at time \( t \) obeys the master equation

\[
\partial_t \psi_m(t) = \sum_n L_{mn} \psi_n(t)
\]

with generator

\[
L_{mn} \equiv w_{mn} - \delta_{mn} \sum_k w_{mk},
\]

where we suppress the \( h \)-dependence. The stochastic trajectory \( n(t) \) is a sequence of jumps at times \( \tau_j \) from \( n_j \) to \( n_j^+ \). An observable \( A \) acquires a time-dependence through \( A(t) = \sum_m A_m \delta_{mn}(t) \) along such a trajectory with mean \( \langle A(t) \rangle = \sum_m A_m \psi_m(t) \). A particularly relevant observable is the stochastic entropy \( B \) defined as \( s(t) = -\ln \psi_n(t) \), where we set the Boltzmann constant to one throughout the paper. For any fixed \( h \), we denote the stationary distribution by \( p_n \), which obeys \( \sum_n L_{mn} p_n = 0 \). In such a NESS, the stochastic entropy becomes the observable

\[
s(t) = -\ln p_n(t), \quad \text{i.e.,} \quad s_n = -\ln p_n. \tag{3}
\]

We are interested in the response of the system to a small perturbation \( h(t) \), where the system is initially prepared in the NESS corresponding to \( h = 0 \) with stationary distribution \( p_0 \). The resulting general FDT has been discussed first by Agarwal more than 30 years ago [20]. For completeness and later reference, we briefly repeat its derivation. The generator is expanded in powers of \( h \),

\[
L(t) = L^0 + h(t)L^1, \tag{4}
\]

where \( (L)_{mn} = L_{mn} \). Due to the perturbation the distribution becomes time-dependent and is obtained through formally solving the master equation (1),

\[
\psi_m(t) = \sum_n \left[ \exp \left\{ \int_{-\infty}^t d\tau L(\tau) \right\} \right] p_n^0.
\]

The exponential function is to be understood as time-ordered. The mean response of an observable \( A \) is given through

\[
R_A(t_2 - t_1) \equiv \left. \frac{\delta \langle A(t_2) \rangle}{\delta h(t_1)} \right|_{h=0} = \langle A(t_2) B(t_1) \rangle, \tag{6}
\]

where we have introduced the generic form of the FDT equating the response with a correlation function involving a second observable \( B \) for which we will find different forms \( B^{(i)} \) labeled by different superscripts.

Using the expansion of the generator eq. (4), one immediately finds

\[
R_A(t_2 - t_1) = \sum_{mn} A_m \left[ e^{L^0(t_2 - t_1)} L^1 \right]_{mn} p_n^0. \tag{7}
\]

Introducing the observable

\[
B_m^{(a)} \equiv \sum_n L_{nm} (p_n^0/p_m^0), \tag{8}
\]

we thus can relate the response function to the correlations of \( A \) with \( B \) in the unperturbed NESS,

\[
R_A(t_2 - t_1) = \langle A(t_2) B_m^{(a)}(t_1) \rangle. \tag{9}
\]

The observable eq. (8) can be cast in a more explicit form involving probabilities and rates by writing

\[
L_{mn} = w_{nm} \alpha_{nm} - \delta_{mn} \sum_k w_{mk} \alpha_{mk}, \tag{10}
\]

with the relative change of the rates

\[
\alpha_{nm} = \partial_t \ln w_{mn}. \tag{11}
\]

Hence, from eq. (8) we obtain the “Agarwal” form

\[
B_m^{(a)} = \sum_n (p_n^0/p_m^0) w_{nm} \alpha_{nm} = \sum_n w_{nm} \alpha_{mn} \tag{12}
\]

of the observable appearing at the earlier time in the FDT (9).

**Role of stochastic entropy.** To establish the connection between the generic FDT as expressed in eq. (6) and the stochastic entropy, we consider two NESS differing by an infinitesimal time-independent \( h \) with distributions \( p_0^h \) and \( p_0^h + hp_1^h \), respectively. Using eq. (4) and equating terms linear in \( h \), the relation

\[
\sum_n L_{mn} p_n^0 = - \sum_n L_{mn}^1 p_n^0 \tag{13}
\]

holds. With the identification

\[
\partial_h s_m(h)|_{h=0} = -p_m^1/p_m, \tag{14}
\]

following from eq. (3), we can express the response as

\[
R_A(t_2 - t_1) = - \sum_{mn} A_m \left[ e^{L^0(t_2 - t_1)} L_{km}^1 \right]_{mn} p_k^0, \tag{15}
\]

\[
\frac{\partial}{\partial t_1} \sum_{mn} A_m \left[ L^0(t_2 - t_1) \right]_{mn} (p_n^1/p_m^0) p_m^0, \tag{16}
\]

\[
= \frac{\partial}{\partial t_1} \langle A(t_2) [-\partial_h s(t_1)] \rangle = \langle A(t_2) B^{(e)}(t_1) \rangle \tag{17}
\]

with

\[
B^{(e)} = -\partial_h s, \tag{18}
\]

where \( s(t) \) is to be understood as observable in the sense of eq. (3). Thus, the response is given by a correlation.
Fluctuation-dissipation theorem in nonequilibrium steady states

function involving as second variable the one being conjugate to the perturbation with respect to stochastic entropy production. Formally similar relations have previously been derived for general stochastic processes [21] and also for the response of chaotic dynamics to changing initial conditions [29]. The FDT (17) contains as a special case an expression derived recently [30] following another route based on the Hatano-Sasa relation [31]. The advantage of the present discussion using the concepts of stochastic thermodynamics arises from the transparent physical identification of the conjugate variable as stochastic entropy, which constitutes our first main result.

As a consistency check, we consider the case where the steady state is a genuine equilibrium state for \( t = 0 \). In fact, two types of such systems should be distinguished. Class-I systems exhibit even for any small constant non-zero \( h \) a genuine equilibrium state like any magnetic system in the presence of a perturbing magnetic field. For such systems, the stationary distribution is given by the Boltzmann-Gibbs distribution

\[
p^{eq}_n(h) = \exp\{-E_n(h) - \mathcal{F}(h)/T\} / \sum_n \exp\{-E_n(h) - \mathcal{F}(h)/T\},
\]

where \( E_n(h) \) is the internal energy, \( T \) the temperature of the heat bath, and \( \mathcal{F}(h) \equiv -T \ln \sum_n \exp\{-E_n(h) - \mathcal{F}(h)/T\} \) the \( h \)-dependent free energy of the system. The stochastic entropy obeys \( s_n(h) = -\ln p^{eq}_n(h) = [E_n(h) - \mathcal{F}(h)]/T \). Along a single trajectory, \( \mathcal{F}(h) \) is constant and hence we have \( T \partial_h s(h)|_{h=0} = \partial_h E(h)|_{h=0} \). Inserted into (17), the FDT acquires its well-known equilibrium form

\[
TR_A(t_2 - t_1) = \frac{\partial}{\partial t_1} \langle A(t_2) \rangle_{h=0} - \langle A(t_2) \rangle_{h=0},
\]

involving the observable conjugate to \( h \) with respect to energy.

Class-II systems are in equilibrium at \( h = 0 \) but driven into a NESS even at constant small \( h \). The paradigmatic example is a perturbation through shear flow for which there is no corresponding \( E(h) \) for any \( h \neq 0 \). For such systems one still has the FDT in the form (17) but also in the Agarwal form with (9).

Returning to the general case of perturbing an arbitrary NESS, the main advantage of the present formulation using stochastic entropy becomes apparent when we split the entropy production in the NESS into two terms [3]:

\[
\dot{s}(t) = -\sum_j \delta(t - \tau_j) \ln \frac{P_{n_j}^+}{P_{n_j}^-} + \sum_j \delta(t - \tau_j) \ln \frac{w_{n_j}^+ n_j^+}{w_{n_j}^- n_j^-} + \sum_j \delta(t - \tau_j) \ln \frac{P_{n_j}^- w_{n_j}^- n_j^-}{P_{n_j}^+ w_{n_j}^+ n_j^+} \equiv -\dot{s}_{\text{med}}(t) + \dot{s}_{\text{tot}}(t).
\]

The first term on the right hand side, \( \dot{s}_{\text{med}} \), denotes the entropy production rate in the medium which can in many cases be identified with the heat flow (divided by \( T \)) into the surrounding aqueous solution. The second term is the total entropy production rate. On average, the latter is positive and integrated over a finite time obeys the detailed fluctuation theorem [3]. Pulling in the time-derivative in eq. (17) and using eq. (21), the correlation part of the FDT becomes a difference between two terms involving entropy production,

\[
R_A(t_2 - t_1) = \langle A(t_2) \partial_h s_{\text{med}}(t_1) \rangle - \langle A(t_2) \partial_h s_{\text{tot}}(t_1) \rangle.
\]

Note that, although the mean total entropy production is always non-negative, both terms can have either sign; see, e.g., fig. 3(a) in ref. [25].

We now show that for systems with a genuine equilibrium state the first term in eq. (22) corresponds to the equilibrium form of the FDT and hence the second term is an additive correction induced by the nonequilibrium conditions. Such an additive structure was found previously [28,32] without, however, giving the correction term a transparent physical meaning. In the special case of a driven Langevin particle [23], the correction term has been identified as a correlation function involving the local mean velocity and has later been rationalized by observing the process in the locally comoving frame [33,34]. Generally, the observable occurring in the first term in eq. (22) can be written

\[
\partial_h s_{\text{med}}(t) = \sum_j \delta(t - \tau_j) \partial_h \ln \frac{w_{n_j}^+ n_j^+}{w_{n_j}^- n_j^-} \equiv \sum_j \delta(t - \tau_j) \left[ \alpha_{n_j^+ n_j^-} - \alpha_{n_j^- n_j^+} \right].
\]

Since this observable appears in the correlation function at the earlier time \( t_1 \), we have to average over all trajectories reaching state \( n(\cdot) \), i.e.,

\[
\sum_j \delta(t - \tau_j) \alpha_{n_j^+ n_j^-} \rightarrow \sum_q p_q w_{kn}(t) \alpha_{n_q^+ n_q^-} \text{ and similarly for the } \alpha_{n_q^- n_q^+} \text{ term}. \]

Furthermore for an equilibrium system the detailed balance relation \( p_q w_{nm} = p_m w_{mn} \), this pre-averaged expression becomes eq. (12). Hence, for any system in equilibrium, the FDT (20) can also be written in the form

\[
R_A(t_2 - t_1) = \langle A(t_2) \partial_h s_{\text{med}}|_{h=0}(t_1) \rangle.
\]

If for the same system a NESS generated by a field \( h \) is additionally perturbed by the same field \( h \), one can thus keep the equilibrium two-point observable (but now evaluated under nonequilibrium conditions) and subtract the second term that involves the observable conjugate to total entropy production. This recipe for deriving the FDT in a NESS constitutes our second main result. It sharpens and proofs the hypothesis formulated in [24].

Path weight approach. – The main virtue of the insight provided by the identifications of the various terms entering the FDT as discussed above is of a conceptual nature. From a practical point of view, quite generally, the FDT allows to infer response functions from correlation functions, which are obtained more easily both in
experiments and in simulations. Necessary for a practical implementation, however, is an explicit knowledge of the variable entering the correlation function in the FDT. Any of the variants discussed above requires knowledge of the stationary distribution \( p_n \), which, in general, is not known explicitly. A form of the FDT not requiring such knowledge can indeed be derived following a recent suggestion \([27]\) exploited there with a different focus. In the following we derive the explicit form of such an FDT both for general master equations and for coupled Langevin equations.

Consider the mean

\[
\langle A(t) \rangle = \sum_{n(t)} A(t) P[n(t); h(t)]
\]

where \( P[n(t); h(t)] = \exp\{-S[n(t); h(t)]\} \) is the path weight in the perturbed system, \( S_0[n(t); h(t)] = \exp\{-S_0[n(t)]\} \) is the path weight in the unperturbed NESS, and the sum runs over all paths \( n(t) \). Taking the functional derivative of eq. (26) with respect to \( h(t_1) \) in order to calculate the response function (6), the result can again be cast into the generic form

\[
R_A(t_2 - t_1) = \langle A(t_2) B^{(p)}(t_1) \rangle.
\]

The correlation function is measured in the unperturbed NESS and the conjugate observable is now expressed through

\[
B^{(p)}(t_1) = -\frac{\delta S[n(t); h(t)]}{\delta h(t_1)} \bigg|_{h=0}.
\]

**Discrete state space.** For a dynamics with rates which become time-dependent through an external perturbation, \( \tau_{nm}(h(t)) \), the weight of a path starting at time \( t_0 < t_1 \) with some initial weight \( p_0 = p_0(n_0) \) and, after \( N_j \) jumps at \( \tau_j \), ending at time \( t > t_2 \) is given by

\[
P[n(t); h(t)] = p_0 \exp\left\{ -\int_0^t dt' \sum_{n \neq n_0} \sum_{j=1}^{N_j} \delta(t' - \tau_j) a_{n - n_j}^+ \right\}.
\]

where \( r_n = \sum_{n \neq n} \tau_{nm} \) is the exit rate out of state \( n \). Hence, eq. (28) becomes

\[
B^{(p)}(t) = -\sum_k \tau_{nk} a_{n_k} + \sum_j \delta(t - \tau_j) a_{n_j}^+.
\]

Due to its second term, this observable is observable to the jumps. As its main advantage, it does not require knowledge of the \( p_n \) in contrast to all forms discussed above. Since \( B^{(p)} \) appears in a correlation function at an earlier time, the average in eq. (27) over the jump times and the states before the jumps can be performed as explained for eq. (25) leading to the form (12), where the \( p_0 \) show up again explicitly. Whether in a simulation or an experiment one uses the conjugate variable in the form (12) or in the form (30) is a matter of convenience. The second form is particularly suitable if one knows the rates and their \( h \)-dependence but not the stationary distribution. If one knows (or can measure) the latter more easily without knowing the rates explicitly, the form (17) may even be more appropriate.

**Langevin dynamics.** The same approach can easily be followed for a set of \( N \) coupled degrees of freedom \( \mathbf{x} \equiv (x_1, \ldots, x_N) \) obeying a Langevin dynamics

\[
\dot{x}_\alpha = \mu_{\alpha\beta} \dot{F}_\beta + u_\alpha + \zeta_\alpha
\]

with correlations

\[
\langle \zeta_\alpha(t_1) \zeta_\beta(t_2) \rangle = 2T \mu_{\alpha\beta} \delta(t_2 - t_1).
\]

Here, \( F_\beta(x, h) \) is the force acting on the \( \beta \)-th particle and \( \mu_{\alpha\beta} \) are mobilities connecting these degrees of freedom. Advection by a fluid is included by a local velocity \( u_\alpha(x, h) \). Here, and in the following we sum implicitly from 1 to \( N \) over all greek indices occurring twice.

The path weight becomes

\[
P[\mathbf{x}(t); h(t)] = \mathcal{N} \exp\left\{ -\frac{1}{4T} \int_{t_1}^{t_2} dt \zeta_\alpha^2 \right\}
\]

with \( \zeta_\alpha \) replaced by the Langevin equation (31), where \( \mathcal{N} \) is an irrelevant normalization. Following the same steps as in the discrete case, one finds for the conjugate observable

\[
TB^{(w)} = \frac{1}{2} \langle \dot{x}_\alpha - \mu_{\alpha\beta} \dot{F}_\beta - u_\alpha \rangle (\partial_{h_\alpha} F_\alpha + \mu_{\alpha\gamma} \sum_{h_\gamma} \partial_{h_\gamma} u_\gamma).
\]

By using this variable in a simulation, one could thus predict the response function for any perturbation by just calculating the corresponding correlation function which constitutes our third main result.

**Classification.** Different approaches allowed us to derive apparently different forms of the FDT in a NESS. However, as the response function depends only on the observable \( A \), all these different correlation functions must be the same. Hence, there is a class of equivalent observables \( \{B\} \) leading to the same value of the correlation function. In particular,

\[
B^{(a)} \cong B^{(p)} \cong B^{(c)},
\]

where \( \cong \) denotes the equivalence of these observables if they appear as observable at the earlier time in a two-time correlation function taken in the NESS. Moreover, in principle there are infinitely many variants of the FDT since with \( B^{(1)} \cong B^{(2)} \) any normalized linear combination \( \{c_1 B^{(1)} + c_2 B^{(2)}\}/(c_1 + c_2) \), with \( c_{1,2} \) real, will be admissible.

The three main variants for the second variable \( B \) appearing in the FDT can more formally be classified as follows: i) The Agarwal form \( B^{(a)} \) (12) is distinguished by the fact that it involves only state variables and no time-derivative, i.e., no observables evaluated at jumps for the discrete case or no velocity observables for Langevin systems. ii) The form \( B^{(p)} \) (14) is the unique one where

---

\[1\]This result is independent of the chosen stochastic calculus (Itô or Stratonovich) as long as the mobility coefficients are independent of \( h \) and \( h \) is a spatially homogeneous perturbation.
the $B$ observable is written as a time-derivative of such a state variable, which turns out to be the $h$-derivative of the stochastic entropy. iii) The observable $B^{(p)}$ is the unique one not requiring explicit knowledge of the stationary distribution.

Examples. – We now illustrate both the general recipe for deriving an FDT for a NESS and the equivalence of the main three forms of such an FDT for two previously studied cases of driven Langevin dynamics sketched in fig. 1.

Driven colloidal particle. An overdamped colloidal particle with mobility $\mu_0$ is driven by a force $f$ along a periodic potential $V(x)$ and hence subject to the total force $F(x) = -V'(x) + f$ [23]. The Langevin equation reads

$$\dot{x}(t) = \mu_0 F(x) + \zeta(t),$$

(36)

where the noise has zero mean and correlations $\langle \zeta(t_1) \zeta(t_2) \rangle = 2T \mu_0 \delta(t_2 - t_1)$. In the stationary state, the constant probability current can be written as

$$j = \mu_0 \langle F(x)p(x) - T \delta_x p(x) \rangle = \nu(x) p(x)$$

(37)

with the local mean velocity $\nu(x)$. The three variants of the FDT can be derived as follows:

i) A perturbation of the driving force $f$ corresponds to the operator $L^2 = -\mu_0 \delta_x$, which implies with the continuum version of eq. (8) and using eq. (37) the Agarwal form

$$TB^{(a)} = \nu(x) - \mu_0 F(x)$$

(38)

distinguished by the fact that it does not involve any fluctuating velocity variable.

ii) The stochastic entropy production rate in the medium is given by [3,35]

$$\dot{s}_{med} = (1/T) [-V'(x) + f] \dot{x}.$$  

(39)

Then $T \partial_x \dot{s}_{med} = \dot{x}$, which corresponds to the equilibrium form of the FDT since $x$ is the conjugate variable of the force with respect to energy. In a former study [23], we found that the excess correlates $A$ with the local mean velocity $\nu(x)$ and hence

$$TB^{(c)} = \dot{x} - \nu(x).$$

(40)

Since the total entropy production rate obeys $\dot{s}_{tot} = \dot{x} \nu(x)/(\mu_0 T)$, we get the by no means obvious equivalence

$$T \partial_x \dot{s}_{tot} = (\dot{x}/\mu_0) \partial_x \nu(x) \equiv \nu(x)$$

(41)

when appearing in a correlation function at earlier times. iii) Finally, specializing the observable (34) to this case, we get as conjugate observable

$$TB^{(p)} = \frac{1}{2} (\dot{x} - \mu_0 F).$$

(42)

This third form, which does not require knowledge of the stationary distribution, can easily be expressed as a linear combination of the first two variants.

Sheared suspension. For a second illustration, consider $N$ colloidal particles with potential energy $U(\{r_k\})$ composed of pairwise interactions immersed into a fluid which is sheared [24]. We neglect hydrodynamic interactions through $\mu_{kl} = \mu_0 \delta_{kl}$. The velocity profile of the fluid is assumed to be $u(r) = \gamma(y,0,0)^T$, where $\gamma$ is the strain rate and $r = (x,y,z)^T$. Response relations in sheared suspensions have recently been studied also in the framework of mode-coupling theory [36]. In our formalism, the three main variants of the FDT specialize to the following expressions:

i) The “Agarwal” form when perturbing the system through a small variation of the strain rate reads

$$TB^{(a)} = -T \sum_k y_k \frac{\partial}{\partial x_k} \ln p = \sigma_{xy} - \sigma_{xy},$$

(43)

where we have introduced the microscopic stress due to particle interactions

$$\sigma_{xy} = \sum_k y_k \frac{\partial U}{\partial x_k}.$$ (44)

The position of the $k$-th particle is $r_k$ and the sum runs over all particles. The second term is

$$\sigma_{xy} = \sum_k y_k \frac{\partial}{\partial x_k} [U + T \ln p] = -\frac{1}{\mu_0} \sum_k y_k (\nu_{k,x} - \gamma y_k),$$

(45)

where $\nu_{k,x}$ is the local mean velocity of the $k$-th particle.

ii) The medium entropy production rate is [35]

$$\dot{s}_{med} = (1/T) \sum_k [\dot{r}_k - u(r_k)] \cdot [-\nabla U]$$

(46)

and hence

$$T \partial_x \dot{s}_{med} = \sum_k y_k \frac{\partial U}{\partial x_k} = \sigma_{xy}$$

(47)

becomes the microscopic stress. Comparing with the form (22) we can therefore deduce that $T \partial_x \dot{s}_{tot} \equiv \sigma_{xy}$. Here, the Agarwal form and the one based on entropy production become identical because $\sigma_{xy}$ depends only on $\{r_k\}$ and not on velocities. As noted earlier, $\sigma_{xy}$ cannot be written as a conjugate observable with respect to
energy since for any $\gamma \neq 0$ the system reaches a genuine NESS instead of another equilibrium state.

iii) Following the path weight approach, we obtain by specializing eq. (34)

$$TB^{(p)} = \sum_k \frac{1}{2\mu_0} \left( \dot{x}_k + \mu_0 \frac{\partial U}{\partial x_k} - \gamma y_k \right) y_k$$

$$= \frac{1}{2} \sigma_{xy} + \frac{1}{\mu_0} \sum_k y_k (\dot{x}_k - \gamma y_k),$$

which can easily be used in simulations.

A straightforward combination of the forms (43) and (48) leads to

$$T[2B^{(p)} - B^{(a)}] = \frac{1}{\mu_0} \sum_k y_k (\dot{x}_k - \nu_{k,x})$$

as another admissible observable appearing in the FDT for a perturbation of the strain rate $\gamma$. This form stresses the relevance of deviations from the local mean velocity in analogy to the form (40) for the driven colloidal particle.

**Summary.** – We have discussed the FDT for Markov processes driven into a NESS. The response of any observable to a perturbation can be expressed by a correlation function involving the observable conjugate to the perturbation with respect to stochastic entropy production. By expressing the latter through entropy production in the medium and the total one, the nonequilibrium form of the FDT can be written as the equilibrium one and an additive correction. Alternatively, we have derived a variant of the FDT not requiring explicit knowledge of the stationary distribution. A classification based on the concept of equivalent observables shows that, quite generally, there exist two linearly independent forms of the FDT from which one can derive three main variants distinguished by the nature of the conjugate observable. Our general framework not only rationalizes previous results obtained for case studies but should also be helpful in studying the FDT in specific future applications like, e.g., driven biochemical networks or active biophysical systems.

***

US acknowledges funding through DFG project SE1119/3-1 and ESF network EPSD. TS acknowledges funding through Alexander von Humboldt foundation and the Helios Solar Energy Research Center which is supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We are grateful to J. MEHL for providing us with fig. 1a).

**REFERENCES**

[1] Seifert U., *Eur. Phys. J. B*, 64 (2008) 423.
[2] Sekimoto K., *J. Phys. Soc. Jpn.*, 66 (1997) 1234.
[3] Seifert U., *Phys. Rev. Lett.*, 95 (2005) 040602.
[4] Jarzynski C., *Phys. Rev. Lett.*, 78 (1997) 2690.
[5] Crooks G. E., *Phys. Rev. E*, 61 (2000) 2361.
[6] Evans D. J., Cohen E. G. D. and Morriss G. P., *Phys. Rev. Lett.*, 71 (1993) 2401.
[7] Gallavotti G. and Cohen E. G. D., *Phys. Rev. Lett.*, 74 (1995) 2694.
[8] Kurchan J., *J. Phys. A: Math. Gen.*, 31 (1998) 3719.
[9] Lebowitz J. L. and Spohn H., *J. Stat. Phys.*, 95 (1999) 333.
[10] Wang G. M., Sevick E. M., Mittag E., Searles D. J. and Evans D. J., *Phys. Rev. Lett.*, 89 (2002) 050601.
[11] Blickle V., Speck T., Helden L., Seifert U. and Bechinger C., *Phys. Rev. Lett.*, 96 (2006) 070603.
[12] Andreaux D., Gaspard P., Ciliberto S., Garnier N., Joubaud S. and Petrosyan A., *Phys. Rev. Lett.*, 98 (2007) 150601.
[13] Liphardt J., Dumont S., Smith S. B., Tinoco Jr I. and Bustamante C., *Science*, 296 (2002) 1832.
[14] Collin D., Ritort F., Jarzynski C., Smith S., Tinoco I. and Bustamante C., *Nature*, 437 (2005) 231.
[15] Tietz C., Schuler S., Speck T., Seifert U. and Wраchtrup J., *Phys. Rev. Lett.*, 97 (2006) 050602.
[16] Bustamante C., Liphardt J. and Ritort F., *Phys. Today*, 58, issue No. 7 (2005) 43.
[17] Ritort F., *Adv. Chem. Phys.*, 137 (2007) 31.
[18] Kubo R., Toda M. and Hashitsume N., *Statistical Physics II*, 2nd edition (Springer-Verlag, Berlin) 1991.
[19] Marconi U. M. B., Puglisi A., Rondoni L. and Vulpiani A., *Phys. Rep.*, 461 (2008) 111.
[20] Agarwal G. S., *Z. Phys.*, 252 (1972) 25.
[21] Hänggi P. and Thomas H., *Phys. Rep.*, 88 (1982) 207.
[22] Harada T. and Sasa S., *Phys. Rev. Lett.*, 95 (2005) 130602.
[23] Speck T. and Seifert U., *Europhys. Lett.*, 74 (2006) 391.
[24] Speck T. and Seifert U., *Phys. Rev. E*, 79 (2009) 040102.
[25] Blickle V., Speck T., Lutz C., Seifert U. and Bechinger C., *Phys. Rev. Lett.*, 98 (2007) 210601.
[26] Gomez-Solano J. R., Petrosyan A., Ciliberto S., Chetrite R. and Gawedzki K., *Phys. Rev. Lett.*, 103 (2009) 040601.
[27] Baiesi M., Maes C. and Wynants B., *Phys. Rev. Lett.*, 103 (2009) 010602.
[28] Crisanti A. and Ritort F., *J. Phys. A: Math. Gen.*, 36 (2003) R181.
[29] Falcioni M. and Vulpiani A., *Physica A*, 215 (481) 1995.
[30] Prost J., Joanny J.-F. and Parrondo J. M. R., *Phys. Rev. Lett.*, 103 (2009) 090601.
[31] Hatano N. and Sasa S., *Phys. Rev. Lett.*, 86 (2001) 3463.
[32] Diezemann G., *Phys. Rev. E*, 72 (2005) 011104.
[33] Chetrite R., Falkovich G. and Gawedzki K., *J. Stat. Mech.: Theory Exp.*, (2008) P08005.
[34] Chetrite R. and Gawedzki K., arXiv:0905.4667v1 [cond-mat.stat-mech] (2009).
[35] Speck T., Mehl J. and Seifert U., *Phys. Rev. Lett.*, 100 (2008) 178302.
[36] Krüger M. and Fuchs M., *Phys. Rev. Lett.*, 102 (2009) 135701.