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Modified fluctuation-dissipation theorem for non-equilibrium steady states and applications to molecular motors

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Abstract – We present a theoretical framework to understand a modified fluctuation-dissipation theorem valid for systems close to non-equilibrium steady states and obeying Markovian dynamics. We discuss the interpretation of this result in terms of trajectory entropy excess. The framework is illustrated on a simple pedagogical example of a molecular motor. We also derive in this context generalized Green-Kubo relations similar to the ones obtained recently in Seifert U., *Phys. Rev. Lett.*, **104** (2010) 138101 for more general networks of biomolecular states.

Introduction. – The application of linear response theory to systems in thermodynamic equilibrium leads to the fluctuation-dissipation theorem (FDT) [1], which states that the response of an equilibrium system to small external perturbations is determined by correlations at equilibrium. Suppose that a system at thermal equilibrium and governed by the time-independent Hamiltonian H_0 is subject to a time-dependent perturbation $-\lambda(t)O$ from time t' on. Then the mean value of a dynamic observable $A(t)$ at time $t > t'$ over all path trajectories, $\langle A(t)\rangle_{\rm path}$, satisfies at first order in λ

$$R_{eq}(t,t') = \frac{\delta\langle A(t)\rangle_{\rm path}}{\delta\lambda(t')} = \beta\frac{\mathrm{d}}{\mathrm{d}t'}\langle O(t')A(t)\rangle_{eq}, \qquad (1)$$

where the correlation function on the r.h.s. is evaluated at equilibrium, $\beta = 1/k_BT$ being the inverse temperature. This relation is a fundamental tool in statistical mechanics since it allows to extract linear response transport coefficients from an equilibrium situation [2,3]. Beyond the equilibrium regime, the relation between response and correlations does not take a simple and universal form as shown by formal studies of such relations for stochastic processes [4] or for glassy systems [5]. Experimentally, departures away from FDT in non-equilibrium systems have been observed in a variety of systems such as granular matter, sheared fluids and biological systems [6].

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In the last decade, new directions of study on non-equilibrium systems have emerged. For instance, it has been realized that thermodynamic quantities like work [7,8] or entropy [9] acquire a well-defined meaning at the level of a single trajectory. Various exact relations among the statistical distributions of work or heat, called fluctuation relations, have been derived. They typically hold very generally for a large class of systems and arbitrarily far from equilibrium [7,10–13]. The entropy production has been related in Markovian systems to the difference between the forward and backward dynamical randomness [14] or as the relative entropy of the trajectory measures of the forward and backward dynamics [12,15]. For Hamiltonian dynamics, similarly, the entropy production has been understood in terms of the relative entropy between forward and backward probability distributions in phase space [16]. A classification of the various possible decompositions of the entropy production and of the corresponding fluctuation relations has been proposed [17]. Within the linear response regime and for slightly perturbed non-equilibrium steady states (NESS), the fluctuation relations lead to a modified fluctuation-dissipation theorem (MFDT) [15,18,19], which has been tested experimentally using colloidal particles in optical traps [20,21]. A thermodynamic interpretation of the MFDT using the concept of entropy flow has been proposed in [22]. Besides, beyond the linear regime, the

same fluctuation relations can be used to derive non-linear response relations of higher order [23].

Let us consider a system initially in a non-equilibrium steady state, characterized by a (set of) control parameters denoted by λ. For a given value of λ, we assume that there exists a steady state with stationary probability distribution $P_{st}(c,\lambda) = \exp(-\phi(c,\lambda))$. A time-dependent perturbation of the dynamics at time t' around the fixed value λ_0 will be described by $\lambda(t') = \lambda_0 + \delta\lambda(t')$. The response $R(t,t') = \delta\langle A(c(t),\lambda_0)\rangle_{\rm path}/\delta\lambda(t')$ of the dynamic observable A that depends on the microscopic configuration $c(t)$ at time $t > t'$ is given by the MFDT:

$$R(t,t') = -\frac{\rm d}{{\rm d}t'}\left\langle \left.\frac{\partial\phi(c(t'),\lambda)}{\partial\lambda}\right|_{\lambda=\lambda_0} A(c(t),\lambda_0)\right\rangle, \qquad (2)$$

where $\langle..\rangle$ denotes the average in the stationary state with the control parameter λ_0. The relation (2) has been derived in the recent ref. [24] for the particular observable $A(c,\lambda) = \partial\phi(c,\lambda)/\partial\lambda$, and before that in ref. [15] (relation 7.15) for the particular case of diffusion processes. We also note that in eq. (2), the function $\phi(c,\lambda)$ plays the role of the energy. For thermal equilibrium, we have $\phi(c,\lambda) = \beta(H(c) - \lambda O(c) - F(\lambda))$, where $F(\lambda)$ is the free energy and eq. (1) is retrieved (using the abbreviation $O(t') = O(c(t'))$).

Modified fluctuation-dissipation theorems have appeared in various forms in the recent literature [3,15,19,22]. In the first section of this paper, we present an elementary and self-contained derivation of such a result, which holds for any single-time observable $A(t)$ and for systems close to non-equilibrium steady states and obeying Markovian dynamics. In the second section, we discuss the interpretation of this relation in terms of trajectory entropy excess, and finally we apply this framework to a simple model of molecular motor.

Derivation of a modified fluctuation-dissipation theorem. – We consider a system which evolves according to a continuous-time Markovian dynamics. The transition rate from a configuration c to a configuration c' is denoted by $W_\lambda(c',c)$ to emphasize its dependence on the control parameter $\lambda(t)$ which can vary with time. For each path trajectory, we introduce, as in [13], the functional $Y(t)$ given by

$$Y(t) = \int_0^t \dot\lambda(\tau)\frac{\partial\phi(c(\tau),\lambda(\tau))}{\partial\lambda}\,{\rm d}\tau. \qquad (3)$$

$Y(t)$ plays a role similar to the work in the Jarzynski relation [25]. The joint probability

$$P_t(c,Y) = \langle\delta(c-c(t))\delta(Y-Y(t))\rangle_{\rm path} \qquad (4)$$

for the system to be in configuration c at time t with $Y(t) = Y$ evolves according to

$$\frac{\partial P_t(c,Y)}{\partial t} = \sum_{c'} W_\lambda(c,c')P_t(c',Y) - \dot\lambda\frac{\partial\phi(c,\lambda)}{\partial\lambda}\frac{\partial P_t(c,Y)}{\partial Y}. \qquad (5)$$

The Laplace transform of $P_t(c,Y)$, given by $\hat P_t(c,\gamma) = \int {\rm d}Y\, P_t(c,Y)e^{-\gamma Y}$, obeys the modified master equation:

$$\frac{\partial\hat P_t}{\partial t} = \sum_{c'} W_\lambda^\gamma(c,c')\hat P_t(c') = W_\lambda^\gamma\cdot\hat P_t, \qquad (6)$$

where W_λ^γ is the matrix of elements

$$W_\lambda^\gamma(c,c') = W_\lambda(c,c') - \dot\lambda\gamma\frac{\partial\phi}{\partial\lambda}\delta_{c,c'}. \qquad (7)$$

For a fixed value of λ there exists a stationary state P_{st} such that $W_\lambda\cdot P_{st} = 0$. Then, it can be checked directly that the "accompanying" distribution (first defined in ref. [4]) $P_{st}(c,\lambda(t)) = e^{-\phi(c,\lambda(t))}$, solves eq. (6) for $\gamma = 1$. Note that this "accompanying" distribution $P_{st}(c,\lambda(t))$ is not stationary because it acquires a time dependence through $\lambda(t)$. Therefore, we have $\hat P_t(c,1) = e^{-\phi(c,\lambda(t))}$, or equivalently

$$\langle\delta(c-c(t))e^{-Y(t)}\rangle_{\rm path} = e^{-\phi(c,\lambda(t))}. \qquad (8)$$

We emphasize that the l.h.s. depends on the full path history between time 0 and t, because $c(t)$ and $Y(t)$ do so, whereas the r.h.s. is a function only of the steady-state probability corresponding to the value of λ at the final time t. This relation involves weighted averages with respect to the functional $e^{-Y(t)}$ and relates non-stationary expectation values to behavior in the stationary state. The use of appropriately weighted distribution functions lies at the core of the various nonequilibrium identities, as emphasized in the very first works of Jarzynski [7,25] (see also [12,26,27]). The relation (8) will also play a key role in deriving the modified FDT. Multiplying this equation by an arbitrary observable $A(c,\lambda)$ and summing over all microscopic configurations c, we obtain a detailed version of the Hatano-Sasa identity [13]:

$$\langle A(c(t),\lambda(t))e^{-Y(t)}\rangle_{\rm path} = \langle A(\lambda(t))\rangle_{\rm NESS}, \qquad (9)$$

where $\langle..\rangle_{\rm NESS}$ denotes the average in the stationary state at time t with control parameter $\lambda(t)$. We now take the functional derivative of this relation with respect to $\lambda(t')$ with $t' < t$ by considering a small variation in the vicinity of the stationary state $\lambda(t') = \lambda_0 + \delta\lambda(t')$ with $\delta\lambda(t') \ll 1$ and $\delta\dot\lambda(t') \ll 1$. Then, $Y(t)$ being small, we can write at first order $e^{-Y(t)} \simeq 1 - Y(t)$. Taking into account that the functional derivative of the r.h.s. of eq. (9) with respect to $\lambda(t')$ vanishes for $t' < t$, we obtain

$$\frac{\delta\langle A(c(t),\lambda(t))\rangle_{\rm path}}{\delta\lambda(t')} = \frac{\delta\langle Y(t)\,A(c(t),\lambda(t))\rangle_{\rm path}}{\delta\lambda(t')}. \qquad (10)$$

The functional derivative of the r.h.s. in the vicinity of λ_0 contains only one term instead of two because $Y(t)$ vanishes when $\lambda(t')$ takes the constant value λ_0. Using

$$\left.\frac{\delta Y(t)}{\delta\lambda(t')}\right|_{\lambda_0} = -\frac{\rm d}{{\rm d}t'}\frac{\partial\phi(c(t'),\lambda_0)}{\partial\lambda}, \qquad (11)$$

we obtain

$$R(t,t') = -\frac{\mathrm{d}}{\mathrm{d}t'}\left\langle \frac{\partial\phi(c(t'),\lambda_0)}{\partial\lambda} A(c(t),\lambda_0)\right\rangle. \tag{12}$$

In the expectation value the control parameter is now fixed at λ_0 and eq. (2) is proved. Introducing the observable $\mathcal{O}(c) = -\partial_\lambda P_{st}(c)/P_{st}(c)$, eq. (2) can be rewritten as

$$R(t,t') = -\frac{\mathrm{d}}{\mathrm{d}t'}\langle A(t)\mathcal{O}(t')\rangle. \tag{13}$$

Remark: more general versions of the FDT, valid for an arbitrary observable $F[c,\lambda]$, that depends on the whole path (and not on the final configuration only) can be derived [15] by comparing the weights of direct and reverse path trajectories and using a local detailed balance condition, in the spirit of [11]. The fundamental relation (8) has to be replaced by

$$\langle F[c,\lambda]e^{-Y(t)}\rangle_{\mathrm{path}} = \langle \tilde{F}[c,\lambda]\rangle^r_{\mathrm{path}}, \tag{14}$$

where the tilde and the index r denote an average with respect to reverse paths. We emphasize, however, that in the derivation given above of the relation (2) no symmetry property under time reversal has been used.

Connection between MFDT and entropy production. – An important step towards a unification of the various formulations of the FDT for non-equilibrium systems comes from the realization that the MFDT can be given by a thermodynamic interpretation in terms of trajectory entropy excess [19,22,28]. Recently, a new decomposition of the entropy production has been introduced in refs. [17,29] in a particularly clear way. This motivated us to revisit the derivation of the MFDT of refs. [19,28] with this formalism. As expected, the decomposition of the entropy production leads to an MFDT which is the sum of an equilibrium part and an additive correction.

We now focus on individual stochastic trajectories taken by the system. Between the time $t=0$ and $t=T$, these trajectories can be represented by the set of discrete values $\mathcal{C} = \{c_0, c_1 \ldots c_N\}$ and jumping times τ_i. The system stochastic entropy is defined as $s(t) = -\ln P_t(c(t))$, as a trajectory-dependent quantity with $c(t)$ taking values in $\mathcal{C}$ [9]. Following [29], we define the rate of change of the excess entropy

$$\dot{s}_{ex}(t) = \sum_{i=1}^{N} \delta(t-\tau_i) \ln \frac{P_{st}(c_i,\lambda_{\tau_i})}{P_{st}(c_{i-1},\lambda_{\tau_i})}, \tag{15}$$

where τ_i represents the time where the system jumps from state c_{i-1} to state c_i. It follows that the integral of $\dot{s}_{ex}(t')$ from $t'=0$ to t, $\Delta s_{ex}(t)$ corresponds to the excess heat defined in [13], which satisfies $\Delta s_{ex}(t) = Y(t) - \Delta\phi(t)$, where $\Delta\phi(t) = \phi(c(t),\lambda(t)) - \phi(c(0),\lambda(0))$.

On a trajectory where λ is fixed at λ_0,

$$\begin{aligned}\left.\frac{\partial\dot{s}_{ex}(t)}{\partial\lambda}\right|_{\lambda=\lambda_0} &= \sum_{i=1}^{N}\delta(t-\tau_i)\frac{\partial}{\partial\lambda}\ln\frac{P_{st}(c_i,\lambda_0)}{P_{st}(c_{i-1},\lambda_0)},\\ &= \frac{\mathrm{d}}{\mathrm{d}t}\sum_n \delta_{c(t)n}\frac{\partial}{\partial\lambda}\ln P_{st}(n,\lambda_0),\\ &= -\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\phi(c(t),\lambda_0)}{\partial\lambda}.\end{aligned} \tag{16}$$

After moving the time derivative on the r.h.s. of eq. (2) into the correlation function, we can then use eq. (16) to obtain another formulation of the MFDT:

$$R(t,t') = \left\langle \frac{\partial\dot{s}_{ex}(t')}{\partial\lambda} A(t)\right\rangle. \tag{17}$$

As shown in refs. [17,29], the excess entropy can be decomposed as $\dot{s}_{ex} = \dot{s}_r - \dot{s}_a$, where s_r is the reservoir entropy and s_a the adiabatic entropy (also called housekeeping heat [13]). These quantities satisfy

$$\begin{aligned}\dot{s}_r(t) &= \sum_{i=1}^{N}\delta(t-\tau_i)\ln\frac{W_{\lambda_{\tau_i}}(c_i,c_{i-1})}{W_{\lambda_{\tau_i}}(c_{i-1},c_i)},\\ \dot{s}_a(t) &= \sum_{i=1}^{N}\delta(t-\tau_i)\ln\frac{W_{\lambda_{\tau_i}}(c_i,c_{i-1})P_{st}(c_{i-1},\lambda_{\tau_i})}{W_{\lambda_{\tau_i}}(c_{i-1},c_i)P_{st}(c_i,\lambda_{\tau_i})}.\end{aligned}$$

In the stationary state (NESS) at $\lambda=\lambda_0$, it follows from eq. (15) that $\dot{s}_{ex} = -\dot{s}$, and thus eq. (17) agrees with eq. (17) of ref. [19]. This also implies $\dot{s}_{na} = 0$, and $\dot{s}_a = \dot{s}_{tot}$, and since $\dot{s}_r = s_{med}$, the splitting of the entropy excess which is used here is the same as that of ref. [19].

We now proceed in deriving another form of MFDT with this framework. We assume that the system satisfies a generalized detailed balance condition

$$\frac{W_\lambda(c,c')}{W_\lambda(c',c)} = \frac{W_{\lambda_0}(c,c')}{W_{\lambda_0}(c',c)}\exp(\delta\lambda d(c,c')), \tag{18}$$

where $d(c,c')$ describes the variation of a dimensionless physical quantity during a transition from state c' to state c such that $d(c,c') = -d(c',c)$ [28]. Using eq. (18) and the definition of $\dot{s}_r$ one obtains

$$\partial_\lambda\dot{s}_r(t') = \sum_{i=1}^{N}\delta(t'-\tau_i)d(c_i,c_{i-1}) = j(t'), \tag{19}$$

where $j(t')$ corresponds to a physical current. Similarly, one can define $\nu(t') = \partial_\lambda\dot{s}_a(t')$, in such a way that the response function takes the form

$$R(t-t') = \langle A(t)(j(t') - \nu(t'))\rangle. \tag{20}$$

This form is analogous to the one first obtained for a particle obeying Langevin dynamics [18], which has the property that an equilibrium form of the FDT can be restored in a locally moving frame [15]. However,

it is important to realize that the ν introduced above is different from the mean local velocity used in these references, although both quantities lead to the same correlation function [19].

For practical applications of this result, more explicit expressions of the currents $j(t')$ and $\nu(t')$ are needed. For the part of the response function coming from the reservoir entropy (the equilibrium part), we can write

$$\langle A(t)j(t')\rangle = \left\langle A(t)\sum_{i=1}^{N}\delta(t'-\tau_i)d(c_i,c_{i-1})\right\rangle,$$
$$=\sum_{c,c',n} A_n P(n,t|c,t'^{+})P(c,t'^{+}|c',t'^{-})P_{st}(c',\lambda_0)d(c,c'),$$

which corresponds to a sum over trajectories which jump at time t'. We have denoted $P(n,t|c,t'^{+})$ the conditional probability to be in state n at time t provided that the state c was visited immediately after the jump at time t'^{+}. This quantity needs to be evaluated at $\lambda(t')=\lambda_0$. Then, it follows that $\langle A(t)j(t')\rangle$ is equal to

$$\sum_{c,c',n} A_n \langle \delta_{c(t)n}\delta_{c(t')c}\rangle \frac{W_{\lambda_0}(c,c')}{P_{st}(c,\lambda_0)}P_{st}(c',\lambda_0)d(c,c') = \left\langle A(t)\sum_{c}\delta_{c(t')c}j(c,\lambda_0)\right\rangle, \quad (21)$$

where $j(c,\lambda_0)$ are components of the current $j(t')$ defined by

$$j(c,\lambda_0)=\sum_{c'}\frac{P_{st}(c',\lambda_0)}{P_{st}(c,\lambda_0)}W_{\lambda_0}(c,c')d(c,c'). \quad (22)$$

A similar calculation can be carried out for the part of the response function associated with the adiabatic entropy:

$$\langle A(t)\nu(t')\rangle = \left\langle A(t)\sum_{c}\delta_{c(t')c}\nu(c,\lambda_0)\right\rangle, \quad (23)$$

where the components of the local current $\nu(t')$ are given by

$$\nu(c,\lambda_0)=\sum_{c'}\frac{J_{st}(c',c)}{P_{st}(c,\lambda_0)}\partial_\lambda \ln W_{\lambda_0}(c',c), \quad (24)$$

and $J_{st}(c',c)$ denotes the probability current $P_{st}(c,\lambda_0)W_{\lambda_0}(c',c)-P_{st}(c',\lambda_0)W_{\lambda_0}(c,c')$. Note that eq. (24) agrees with the results given in ref. [28].

A discrete ratchet model. – We now apply the framework developed above to a discrete ratchet model of a molecular motor. Single molecular motors have been traditionally modeled either by continuous models such as the flashing ratchet model [30] or by discrete models based on the master equation formalism [31]. In previous works, we have shown that the Gallavotti-Cohen symmetry is present both in discrete models [32,33] and in continuous ones [34] when all the relevant variables are taken into account.

In the discrete ratchet model, a single motor evolves on a linear discrete lattice by hopping from one site to neighboring sites, either consuming or producing ATP molecules as shown in fig. 1. The position of the motor is denoted by $x=nd_0$, where $2d_0$ is the step size of the motor, and y denotes the number of ATP molecules consumed. Because of the periodicity of the filament, all the even (a) sites and all the odd (b) sites are equivalent. Denoted by $\overleftarrow{\omega}_a$ (and $\overrightarrow{\omega}_a$) are the transition rates for the motor to jump from site a to the neighboring site b to the left (to the right), respectively. A similar definition holds for the site b and we use the abbreviations $\omega_i=\overleftarrow{\omega}_i+\overrightarrow{\omega}_i$ for $i=a,\ b$, and $\Omega=\omega_a+\omega_b$.

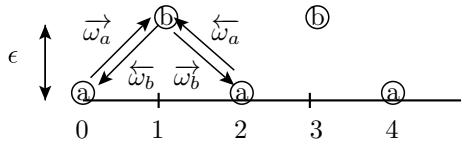

Fig. 1: A schematic representation of the motor on a linear lattice of sites a (even) and b (odd). All possible transitions are displayed with their corresponding rates.

The probability to find the motor in a given state, say $i=a,b$ is $P_i(t)=\langle\delta_{ic(t)}\rangle_{\rm path}$, where $c(t)$ is the configuration of the system at time t in the space of configuration a,b. Similarly, the joint probability to be in state i at time t and in state j at time t' is $P(i,t;j,t')=\langle\delta_{ic(t)}\delta_{jc(t')}\rangle_{\rm path}$. Both quantities can be calculated analytically for this model *even for time-dependent rates*. We now assume that the rates depend on time only via an arbitrary controlled parameter $\lambda(t)$, and we note that this dependence can be non-linear. As a result, the time dependance of an arbitrary observable $A(c(t),\lambda)$ has the form

$$A(c(t),\lambda)=A_a(\lambda)\delta_{ac(t)}+A_b(\lambda)\delta_{bc(t)}. \quad (25)$$

In particular, the function $\phi(c(t),\lambda)$ has this form with $\phi_a(\lambda)=-\log P_{st}(a,\lambda)=-\log[\omega_b(\lambda)/\Omega(\lambda)]$ and $\phi_b(\lambda)=-\log P_{st}(b,\lambda)=-\log[\omega_a(\lambda)/\Omega(\lambda)]$.

With the above equations, we can characterize the response of the system to a perturbation of the rates of the form $\omega_i(\lambda(t))=\omega_i(\lambda_0)+\delta\lambda(t)\partial_\lambda\omega_i(\lambda_0)$ for $i=a,b$. We have separately calculated both sides of eq. (2), and we found in agreement with this equation the same quantity, which is the response function associated with the observable $A(c,\lambda)$:

$$R(t,t') = \frac{\omega_a(\lambda_0)\partial_\lambda\omega_b(\lambda_0)-\omega_b(\lambda_0)\partial_\lambda\omega_a(\lambda_0)}{\Omega(\lambda_0)} \times\left[A_a(\lambda_0)-A_b(\lambda_0)\right]\exp[-\Omega(\lambda_0)(t-t')], \quad (26)$$

for $t>t'$.

Decomposition of the response function. We now proceed in decomposing the above response function into a sum of two terms, which correspond to the two parts of the entropy production discussed in the previous section. In the following, we chose for the control parameter either the normalized force applied on the motor, f, or the

normalized chemical-potential difference associated with the ATP hydrolysis reaction, $\Delta\mu$. These quantities are defined as $f = Fd_0/k_BT$ and $\Delta\mu = \Delta\tilde{\mu}/k_BT$, in terms of the applied force F, and the chemical-potential difference $\Delta\tilde{\mu}$. The sign convention for the force is such that it is positive when it is in the motor motion direction.

In the case of a pure mechanical perturbation, $\lambda(t) = f(t) = f_0 + \delta f(t)$. The generalized detailed balance relations of eq. (18) now takes the following form:

$$\frac{\overrightarrow{\omega_b}(f)}{\overleftarrow{\omega_a}(f)} = \frac{\overrightarrow{\omega_b}(0)}{\overleftarrow{\omega_a}(0)} e^{f}, \quad \frac{\overleftarrow{\omega_b}(f)}{\overrightarrow{\omega_a}(f)} = \frac{\overleftarrow{\omega_b}(0)}{\overrightarrow{\omega_a}(0)} e^{-f}, \tag{27}$$

with the correspondance $d(n \pm 1, n) = \pm 1$, valid for any position n. These relations are obeyed by the following parametrization of the rates

$$\begin{aligned} \overrightarrow{\omega_a}(f) &= \omega e^{-\epsilon + \theta^+ f}, & \overrightarrow{\omega_b}(f) &= \omega' e^{+(1-\theta^-)f}, \\ \overleftarrow{\omega_a}(f) &= \omega' e^{-\epsilon - \theta^- f}, & \overleftarrow{\omega_b}(f) &= \omega e^{-(1-\theta^+)f}, \end{aligned} \tag{28}$$

where θ^+ and θ^- are load distribution factors [31].

The motor velocity can be defined generally by $\langle v(t)\rangle = \sum_n n \partial P_n(t)/\partial t$, with $P_n(t)$ the probability to find the motor on an integer position n at time t. Since this velocity is the current of the position variable, eq. (22) can be used to define the components of this current:

$$v(a, f_0) = d_0 \frac{P_{st}(b, f_0)}{P_{st}(a, f_0)} [\overrightarrow{\omega_b}(f_0) - \overleftarrow{\omega_b}(f_0)],$$

and similarly for $v(b, f_0)$ by exchanging a and b. In a similar way, the components of the local current can be obtained from eq. (24):

$$\nu(a, f_0) = \frac{(\theta^+ + \theta^-)\bar{v}}{2P_{st}(a, f_0)}, \qquad \nu(b, f_0) = \frac{(2 - \theta^+ - \theta^-)\bar{v}}{2P_{st}(b, f_0)},$$

with $\bar{v} = \langle v(t)\rangle = \langle \nu(t)\rangle$. Now, as in eq. (20), we obtain the response function associated with an observable A:

$$\frac{\delta\langle A(t)\rangle_{\rm path}}{\delta f(t')} = \frac{1}{d_0}\langle A(t)(v(t') - \nu(t'))\rangle. \tag{29}$$

For the case of a chemical perturbation in the concentrations of ATP, or of ADP and P, the control parameter is $\lambda(t) = \Delta\mu(t) = \Delta\mu_0 + \delta\Delta\mu(t)$. The transition rates for the motor to jump from a site i to a neighboring site on the left or on the right with l $(= -1, 0, 1)$ ATP molecules consumed are $\omega_i^l = \overrightarrow{\omega_i}^l + \overleftarrow{\omega_i}^l$, with $i = a, b$. Local detailed balance conditions similar to eq. (27) imply the following parametrization of the rates:

$$\begin{aligned} \omega_a^1 &= (\alpha + \alpha')e^{-\epsilon + \sigma\Delta\mu}, & \omega_b^{-1} &= (\alpha + \alpha')e^{(\sigma-1)\Delta\mu}, \\ \omega_a^0 &= (\omega' + \omega)e^{-\epsilon}, & \omega_b^0 &= \omega + \omega', \end{aligned} \tag{30}$$

where σ plays the same role as the θ^+ and θ^- before. Then, by a similar calculation, the response function can be written as

$$\frac{\delta\langle A(t)\rangle_{\rm path}}{\delta(\Delta\mu(t'))} = \langle A(t)(r(t') - \mathcal{R}(t'))\rangle, \tag{31}$$

where $r(t')$ is the instantaneous ATP consumption rate and $\mathcal{R}(t')$ the local ATP consumption rate, defined by their components

$$\begin{aligned} r(a, \Delta\mu_0) &= -\omega_b^{-1}(\Delta\mu_0) P_{st}(b, \Delta\mu_0)/P_{st}(a, \Delta\mu_0), \\ r(b, \Delta\mu_0) &= \omega_a^1(\Delta\mu_0) P_{st}(a, \Delta\mu_0)/P_{st}(b, \Delta\mu_0), \\ \mathcal{R}(a, \Delta\mu_0) &= \sigma\bar{r}/P_{st}(a, \Delta\mu_0), \\ \mathcal{R}(b, \Delta\mu_0) &= (1 - \sigma)\bar{r}/P_{st}(b, \Delta\mu_0). \end{aligned}$$

Now, we can also introduce more general rates, which depend on both control parameters f and $\Delta\mu$ [32]. The method presented above in the particular cases where only a mechanical degree of freedom or only a chemical degree of freedom is taken into account, can be extended to more general situations where the state of motor is described by both variables. In this case, the same function $\phi(c, \lambda)$ can be used, with the understanding that c contains some dummy variables (the position variable $x(t)$ or the chemical variable $y(t)$) in addition to the variables used to describe the non-equilibrium steady state (namely $i = a, b$). By proceeding just as above, one obtains the response functions in eq. (32), which take the form of modified Green-Kubo relations [28,35]

$$\begin{aligned} \langle v(t)\rangle_{\rm path} - \langle v\rangle &= \int_0^t {\rm d}t' \, \frac{\delta f(t')}{d_0} \langle v(t)(v(t') - \nu(t'))\rangle \\ &\quad + \int_0^t {\rm d}t' \, \delta\Delta\mu(t') \langle v(t)(r(t') - \mathcal{R}(t'))\rangle, \\ \langle r(t)\rangle_{\rm path} - \langle r\rangle &= \int_0^t {\rm d}t' \, \frac{\delta f(t')}{d_0} \langle r(t)(v(t') - \nu(t'))\rangle \\ &\quad + \int_0^t {\rm d}t' \, \delta\Delta\mu(t') \langle r(t)(r(t') - \mathcal{R}(t'))\rangle. \end{aligned} \tag{32}$$

A few remarks about these equations are in order: First, in the particular case of an equilibrium steady state (when $\nu = \mathcal{R} = 0$), the Einstein and Onsager relations are clearly recovered from these equations. Secondly, near a non-equilibrium steady state, these equations characterize the response of the motor in the linear response regime, thus extending the results of ref. [32] to the case of time-dependent perturbations. As expected from the linearity of the problem, the response can be decomposed as the sum of contributions corresponding to the cases of pure mechanical and pure chemical perturbations.

Furthermore, we note that the Einstein relation for the mechanical variable is recovered only near stalling, just as in the case of time-independent perturbations [33]. However, as pointed out in ref. [28], in more general networks of chemical reactions, there are additional conditions besides the stalling condition for the Einstein relation to hold. In this model a mechanical perturbation applied to the motor at stalling is thus unable to detect that the system is in a NESS. But, if a perturbation in

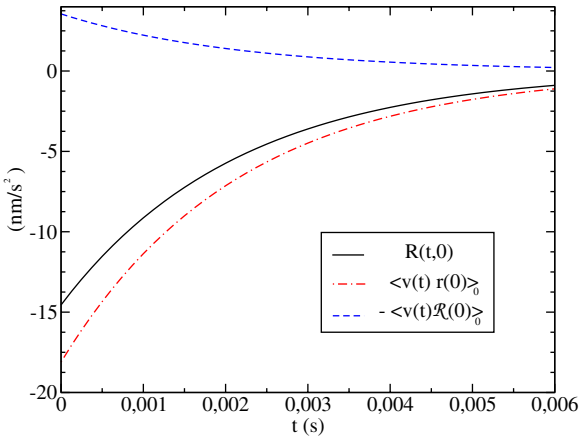

Fig. 2: (Colour on-line) Response function of the motor velocity $R(t,0)$, as a function of time t for a perturbation of the chemical potential $\Delta\mu$ applied at time 0 (solid line), correlation function of the velocity with the ATP consumption rate, $\langle v(t)r(0)\rangle$ (dash-dotted curve), and correlation function of the velocity with the local ATP consumption rate $\langle v(t)\mathcal{R}(0)\rangle$ (dashed line). The initial condition corresponds to stalling for which $\bar{v}=0$. For these curves, we have used the following parameters: $\epsilon=10.81$, $d_0=4\,\mathrm{nm}$, $\omega=3.5\,\mathrm{s}^{-1}$, $\omega'=108.15\,\mathrm{s}^{-1}$, $\alpha=0.57\,\mathrm{s}^{-1}$, $\alpha'=1.3\times10^{-6}\,\mathrm{s}^{-1}$, $\theta^+=0.705$, $\theta^-=1.375$, $\sigma=0.8$, $\Delta\mu=11.8$ and $f=-3.82$ (stalling force). The sum of the two dashed lines gives the solid curve as imposed by eq. (32).

the more relevant chemical variable is considered, then the NESS can be detected. This point is illustrated in fig. 2, which shows the deviation from the standard FDT (at equilibrium), deviation which can be predicted from eq. (32).

Conclusion. – We have presented a general self-contained derivation of the modified FDT for systems close to non-equilibrium steady states and obeying Markovian dynamics. We believe that this derivation, which is related to many recent works on fluctuation relations, is sufficiently general to lead to further developments. We have also shown that the MFDT can be expressed as the correlation function of a general observable with the trajectory entropy excess, which leads to the decomposition of the MFDT into two terms.

We have applied this framework to a simple model of molecular motor for which the steady-state probability distribution is known analytically. Finally, we have observed that the modified FDT relation requires a knowledge of the relevant degrees of freedom in order to be able to distinguish an equilibrium state from a non-equilibrium steady state. In this choice of the relevant degrees of freedom, the markovianity of the dynamics plays a central role, as it does for the existence of a Gallavotti-Cohen symmetry.

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