Dissipation, lag, and drift in driven fluctuating systems

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This work deals with thermostated fluctuating systems subjected to driven transformations of the internal energetics. The main focus is on generally multidimensional systems with continuous configurational degrees of freedom over which overdamped Markovian fluctuations take place (diffusive regime of the motion). Mutual bounds are established between the average energy dissipation, the deviation between nonequilibrium probability density and underlying equilibrium distribution due to the system's lag, and the statistical properties of the components of the directed flow induced by the transformation itself. The directed flow is here expressed in terms of time-dependent "drift velocity" associated with the probability current in a advection-like formulation of the nonstationary Fokker-Planck equation. Consideration of the drift makes that the bounds achieved here extend the inequality derived by Vaikuntanathan and Jarzynski [Europhys. Lett. **87**, 60005 (2009)] involving only dissipation and lag. The key relations are then specified for the so-called stochastic pumps, i.e., systems that reach a periodic steady state in response of cyclic transformations and that are prototypes of nonautonomous dissipative converters of input energy into directed motion; a one-dimensional case model is adopted to illustrate the main features. Complementary results concerning bounds between the evolution rates of dissipation and lag, valid for both overdamped and underdamped dynamics, are also presented.

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I. INTRODUCTION

In recent years, especially thanks to the progress in mechanical manipulation at the nanoscale, there has been an ever-growing interest in the physics of fluctuating systems undergoing transformations driven by external means. This has led to development of the body of the so-called "stochastic thermodynamics" discipline [1], and devising the theoretical and computational machinery for making quantitative predictions about the dynamical response of a driven system. Three general and intuitive features characterize a fluctuating system when it is taken away from the thermal equilibrium state: (1) an out-of-equilibrium situation develops, (2) an amount of energy is dissipated, or "wasted," just because the operation is performed with a finite progression rate, and (3) a directed dynamical response (i.e., a "drift" in the system's configurational space) may be induced. The present work is aimed at establishing some interrelations between these three facets of the irreversible transformations at the nanoscale; namely, mutual bounds on quantitative descriptors of dissipation, lag, and drift will be derived.

Great attention is put nowadays on "thermodynamic uncertainty relations" linking the amount of dissipation to the statistical distribution of the currents induced in an out-of-equilibrium system (see, for example, Refs. [2–6] and references therein). While these studies focus mainly on discrete and autonomous systems taken to a nonequilibrium steady state by means of fixed or stochastic external causes, here we deal with continuous and nonautonomous systems subjected to a controlled finite-time transformation (transient case), or that eventually reach a *periodic* steady state if the transformation is cyclic and lasts indefinitely (e.g., the case of "stochastic pumps" discussed below).

Let us consider a fluctuating system in contact with a thermal bath of fixed temperature T. Let $\mathbf{x}$ be the set of continuous variables associated with the relevant degrees of freedom. The basic assumption is that the dynamics of $\mathbf{x}$ can be modeled as a Markov process, namely, a stationary process when the system is at equilibrium, and nonstationary during the transformation [7,8]. At this stage, $\mathbf{x}$ may comprise both configurational variables ($\mathbf{q}$ in the following) and the related momenta ($\mathbf{p}$) in a phase-space representation. In such a general situation, the regime of the motion is "underdamped" (i.e., "semi-inertial"). If the relevant variables $\mathbf{x}$ are only of pure configurational type, the regime of the motion is "overdamped" (or "diffusive").

Suppose that the system is initially at equilibrium and that an external means (some device in abstract sense) starts to modulate the internal energetics of the system according to a time-dependent *deterministic* protocol, for example, by acting on some internal coordinates or parameters of the system. Such driving causes the creation of an out-of-equilibrium situation associated with a nonequilibrium distribution $p(\mathbf{x},t)$. In all generality, henceforth $p(\mathbf{x},t)$ may be intended either as a distribution of states (in a statistical-ensemble view) or as a probability density (in a single-system view). The evolution of $p(\mathbf{x},t)$ from an initial distribution $p(\mathbf{x},0)$ is described by the nonstationary Fokker-Planck equation for the underdamped (Kramer-Klein form) or overdamped (Smoluchowski form) regimes of motion [7,8]. At any time t, let $p_{\mathrm{eq},t}(\mathbf{x})$ be the "underlying" equilibrium distribution that would be reached, in an indefinitely long relaxation phase after the time t, if the protocol were stopped at that time and the constraints imposed by the external means were kept fixed.

The out-of-equilibrium condition can be quantified in terms of deviation of $p(\mathbf{x},t)$ from $p_{\mathrm{eq},t}(\mathbf{x})$ by means of the scalar Kullback-Leibler divergence, or relative entropy, expressed by [9]

$$\mathcal{D}(t) \equiv \mathcal{D}(p||p_{\mathrm{eq},t}) = \int d\mathbf{x}\, p(\mathbf{x},t) \ln \frac{p(\mathbf{x},t)}{p_{\mathrm{eq},t}(\mathbf{x})}. \quad (1)$$

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Such a dimensionless quantity is non-negative and null only if the two distributions are identically equal. The presence of the inevitable "lag" due to the fact that the system cannot instantaneously equilibrate with respect to the changing constraints makes that $\mathcal{D}(t) \geqslant 0$.

Concerning the energy dissipation, an extra amount of energy (properly defined in the next section) has to be put into play just as a penalty for operating out-of-equilibrium since the transformation is conducted with a finite progression rate. Such a wasted quantity of energy, which constantly increases as the transformation proceeds, is here denoted as $\overline{w}_{\rm diss}(t)$ where the overbar can be intended in a twofold way: (1) an average taken over the statistical ensemble of realizations of the same transformation or (2) an expectation for the single transformation underway. A milestone in stochastic thermodynamics was the finding [10,11] that the Clausius-Duhem inequality, which is one of the facets of the Second Principle of Thermodynamics for systems transformed in contact with a thermal reservoir [12], can be recovered at the scale of fluctuating systems if the average dissipation is considered:

$$\overline{w}_{\rm diss}(t) \geqslant 0, \tag{2}$$

where the equality holds in the quasistatic limit. Notably, such an *inequality* follows mathematically as a corollary of the celebrated Jarzynski's *equality* [10,11,13]. Later in Ref. [14] the following inequality was derived:

$$\beta\, \overline{w}_{\rm diss}(t) \geqslant \mathcal{D}(t) \geqslant 0, \tag{3}$$

where $\beta = (k_B T)^{-1}$. Note that Eq. (3) is an inequality sharper than Eq. (2) since $\mathcal{D}(t)$ sets a lower bound to the average dissipation: one can state that if some transformation has produced a certain lag quantified by $\mathcal{D}(t)$ at the time t, then the average energy dissipation was *surely* not less than $k_B T\, \mathcal{D}(t)$. Remarkably, the relation Eq. (3) holds regardless of the dynamical regime of the fluctuations, underdamped or overdamped. Actually, it can be proved that Eq. (3) follows as a consequence of a more stringent inequality concerning the time derivatives:

$$\beta \frac{d\overline{w}_{\rm diss}}{dt} \geqslant \frac{d\mathcal{D}}{dt}. \tag{4}$$

The integration of Eq. (4) between time 0 [with $\overline{w}_{\rm diss}(0) = 0$ and $\mathcal{D}(0) = 0$] and time t yields Eq. (3). Although Eq. (4) is probably well known to researchers active in this field, to our knowledge is does not appear explicitly in past publications and it is worthwhile to frame it clearly. We mention that a special form of Eq. (4), however, can be found in Ref. [15] [see Eqs. (13)– (15) therein] for the case of one-dimensional underdamped motion in a parabolic potential. Here Eq. (4) will be derived in all generality, as a by-product of our main inspection, from the elaboration of the nonstationary Fokker-Planck equation for the evolution of $p(\mathbf{x},t)$ in both underdamped and overdamped regimes of motion.

Finally, the possible directed flow due to the external intervention on the system's energetics is quantified by the time-dependent probability current in the system's configurational space. Let us focus directly on the case of overdamped dynamics so that the ensemble $\mathbf{x}$ is constituted solely by configurational variables $\mathbf{q}$. The probability current, $\mathbf{J}(\mathbf{q},t)$, is such that, given an oriented hypersurface $\delta\Omega_+$, the flux $\int_{\delta\Omega_+} d\sigma(\mathbf{q})\, \hat{\mathbf{n}}(\mathbf{q})^T \mathbf{J}(\mathbf{q},t)$ gives the rate of probability transfer through that surface [in the integral, $d\sigma(\mathbf{q})$ stands for the area of a surface element centered in $\mathbf{q}$, and $\hat{\mathbf{n}}(\mathbf{q})$ is the unit vector normal to such oriented element]. At thermal equilibrium, the probability current is null at each configuration $\mathbf{q}$; in constrast, an evolving and non-identically null current is present in an out-of-equilibrium situation.

Instead of dealing with $\mathbf{J}(\mathbf{q},t)$, here we shall consider the associated *drift velocity* defined as

$$\mathbf{v}(\mathbf{q},t) := \mathbf{J}(\mathbf{q},t)/p(\mathbf{q},t). \tag{5}$$

In abstract terms, by analogy with the equations of fluid dynamics, $\mathbf{v}(\mathbf{q},t)$ would correspond to the velocity field of a virtual "medium" that transports the "extensive property" probability in the configurational space (just like the motion of a real fluid transports the matter dissolved in it across the three-dimensional space). It will be seen that $\mathbf{v}(\mathbf{q},t)$, rather than $\mathbf{J}(\mathbf{q},t)$, is the proper vector field directly related to lag and energy dissipation; namely, the time-dependent second moments of the evolving distribution on the drift velocity components, i.e., the averages $\langle v_i^2\rangle_t$ defined later in Eq. (22), will play a crucial role.

On these bases, in the present work we shall derive quantitative interrelations between the lag $\mathcal{D}(t)$, the average dissipation $\overline{w}_{\rm diss}(t)$, and the features of the drift velocity $\mathbf{v}(\mathbf{q},t)$. The main result is constituted by the inequalities Eqs. (33) and (34) presented later in Sec. III B. These relations are an extension of Eq. (3) in a twofold sense: a positive lower bound is given for the quantity $\beta\overline{w}_{\rm diss}(t) - \mathcal{D}(t)$, and an upper bound is also provided. With reference to Eq. (34), it will be seen that these lower and upper bounds are determined by the extreme values taken by the averages $\langle v_i^2\rangle_t$ between time 0 and the actual time t, and by other quantities introduced as scaling factors to account for the possible inhomogeneity of the nature of the variables q_i.

After the presentation of such general results, in Sec. IV we shall specify the inequalities for systems transformed cyclically with some schedule of period τ. In this situation, a periodic steady state is asymptotically attained as the number of performed cycles increases; correspondingly, the probability distribution, the probability current, and the drift velocity settle respectively on some limits $p^\infty(\mathbf{q},t)$, $\mathbf{J}^\infty(\mathbf{q},t)$, and $\mathbf{v}^\infty(\mathbf{q},t)$, all featuring time periodicity τ. The inequalities take the form given later in Eq. (36) where all quantities are referred to one cycle at the periodic steady state. An illustration will be given for a one-dimensional toy model consisting of a hindered rotor-like diffusive system with an intrinsic configurational energy featuring two equivalent wells separated by two different barriers. The energy profile is cyclically modulated in the way that the symmetry is broken and both the depth of the wells and the height of the energy barriers change. Such a system is one of the model cases recently investigated in Ref. [16] (see "Case 2" in that work) where the target was to establish a quantitative connection between the average energy dissipation per cycle and the internal modes of fluctuation.

We remark that cyclically driven systems, conventionally termed "stochastic pumps," have been intensively studied since they are prototypes of converters of input energy (as work) into directed dynamical response with dissipation. In particular, a remarkable "no-pumping theorem" specifies the general conditions under which a net drift *cannot* be present at the periodic steady state [17–20] or, conversely, under which conditions a directed flow *may* be sustained. Concerning the dissipation at the periodic steady state, we mention the theoretical work of Harada and Sasa, who derived an equality, for overdamped systems, that relates the rate of energy dissipation to the extent of violation of the fluctuation-response relation [21]. Finally, we also mention recent efforts in the characterization of the periodic steady states within the framework of the linear nonequilibrium thermodynamics ("fluxes-affinities" relations) [22,23].

The remainder of the paper is structured as follows. In the next section, the average energy dissipation $\overline{w}_{\rm diss}(t)$ is defined and related to $\mathcal{D}(t)$ (some technical details are given in Appendix A). For the general situation of underdamped and overdamped dynamics, the key result will be the equality Eq. (15), which yields the inequality Eq. (4). Beginning in Sec. III, the focus will be on overdamped dynamics. The drift velocity $\mathbf{v}(\mathbf{q},t)$ is introduced and elaborated in Sec. III A (some insights are provided in Appendix B), while the lower and upper bounds for the quantity $\beta\overline{w}_{\rm diss}(t) - \mathcal{D}(t)$ are provided in Sec. III B. Section IV is devoted to the special case of stochastic pumps: the bounds of the average dissipation per cycle are given in Sec. IV A, and the explanatory case is illustrated in Sec. IV B. Section V summarizes the outcomes.

Remarks on the mathematical notation: Throughout the text, bold symbols will denote arrays (matrices and vectors); the vectors are meant to be arranged as column vectors; the symbol "T" denotes the transposed array; $\frac{\partial}{\partial \mathbf{x}}$ stands for the column-vector gradient operator on the set of variables $\mathbf{x}$.

II. DISSIPATION AND LAG FOR MARKOV DYNAMICS

Let us consider a fluctuating system subjected to a guided change of internal energetics while it fluctuates in contact with a thermal bath of temperature T. According to the notation given in the Introduction, $p_{{\rm eq},t}(\mathbf{x})$ is the underlying equilibrium distribution reached if the protocol is interrupted at time t and the system is left to relax under the constraints imposed by the external means, that is, $\lim_{t<\tau\to\infty} p(\mathbf{x},\tau) = p_{{\rm eq},t}(\mathbf{x})$. At thermal equilibrium, $p_{{\rm eq},t}(\mathbf{x})$ is the canonical distribution

$$p_{{\rm eq},t}(\mathbf{x}) = Z_t^{-1} e^{-\beta V_t(\mathbf{x})}, \quad Z_t = \int d\mathbf{x}\, e^{-\beta V_t(\mathbf{x})} \tag{6}$$

where the potential $V_t(\mathbf{x})$ has to be interpreted on the basis of the physical nature of the variables $\mathbf{x}$ (see below), and Z_t is the canonical partition function. With reference to the underlying equilibrium state at time t, the Helmholtz free energy is defined as

$$A_t = \mathrm{const}(T) - \beta^{-1} \ln Z_t, \tag{7}$$

where const(T) is an immaterial offset at the fixed temperature.

The amount of energy exchanged between the system and the external means during the guided transformation is identified as *work* [24,25]. Let us denote with $\overline{w}(t)$ the *average* amount of work. Such an average can be interpreted either as average over the statistical ensemble of realizations, or as a probabilistic expectation value in a single-system view. The time derivative of such an average can be expressed as

$$\frac{d\overline{w}(t)}{dt} = \int d\mathbf{x}\, p(\mathbf{x},t)\, \frac{\partial V_t(\mathbf{x})}{\partial t}, \tag{8}$$

where $p(\mathbf{x},t)$ is the nonequilibrium distribution developed at time t [the initial condition is $p(\mathbf{x},0) = p_{{\rm eq},0}(\mathbf{x})$]. The time integration of Eq. (8) from time 0 up to a generic time t, considering that $\overline{w}(0) = 0$, yields the value of $\overline{w}(t)$.

At any time, the difference between the average work and the variation of free energy gives the average dissipated work:

$$\overline{w}_{\rm diss}(t) := \overline{w}(t) - (A_t - A_0). \tag{9}$$

As stated in the Introduction, $\overline{w}_{\rm diss}(t) \geqslant 0$. By combining Eqs. (7)–(9), a few steps yield

$$\beta \frac{d\overline{w}_{\rm diss}(t)}{dt} = \int d\mathbf{x}\, \Phi_{\rm diss}(\mathbf{x},t)\, p(\mathbf{x},t), \tag{10}$$

where the function

$$\Phi_{\rm diss}(\mathbf{x},t) = -\frac{\partial \ln p_{{\rm eq},t}(\mathbf{x})}{\partial t} \tag{11}$$

specifies the transformation protocol in terms of rate of change of the underlying system's energetics. A few more elaborations allow one to get the identity

$$\Phi_{\rm diss}(\mathbf{x},t)\, p(\mathbf{x},t) = -\frac{\partial p(\mathbf{x},t)}{\partial t} - \left[\ln \frac{p(\mathbf{x},t)}{p_{{\rm eq},t}(\mathbf{x})}\right] \frac{\partial p(\mathbf{x},t)}{\partial t} + \frac{\partial}{\partial t}\left[p(\mathbf{x},t) \ln \frac{p(\mathbf{x},t)}{p_{{\rm eq},t}(\mathbf{x})}\right]. \tag{12}$$

By adopting $\mathcal{D}(t)$ in Eq. (1) to quantify the "lag" between nonequilibrium and underlying equilibrium distributions at time t, and considering that the normalization $\int d\mathbf{x}\, p(\mathbf{x},t) = 1$ holds at any time, the integration on $\mathbf{x}$ at both members of Eq. (12) yields

$$\beta \frac{d\overline{w}_{\rm diss}(t)}{dt} = \frac{d\mathcal{D}(t)}{dt} - \int d\mathbf{x} \left[\ln \frac{p(\mathbf{x},t)}{p_{{\rm eq},t}(\mathbf{x})}\right] \frac{\partial p(\mathbf{x},t)}{\partial t}. \tag{13}$$

To go further, the specification of the time derivative $\partial p(\mathbf{x},t)/\partial t$ on physical grounds is required.

Under the assumption that the fluctuations of $\mathbf{x}$ can be modeled as a Markov process, the evolution of the nonequilibrium distribution is governed by the nonstationary Fokker-Planck equation [7,8]

$$\frac{\partial p(\mathbf{x},t)}{\partial t} = -\hat{\Gamma}(t) p(\mathbf{x},t), \tag{14}$$

where $\hat{\Gamma}(t)$ is the evolution operator. The mathematical form $\hat{\Gamma}(t)$ depends, as will be indicated later, on the specific regime of the motion (diffusive or semi-inertial) and hence on the nature of the variables $\mathbf{x}$ themselves. The explicit time dependence borne by the operator arises from the deterministic control on some coordinate(s) of the system. A constraint on $\hat{\Gamma}(t)$ is that the relaxation of $p(\mathbf{x},t)$ towards $p_{{\rm eq},t}(\mathbf{x})$ must be ensured if the transformation protocol is stopped at a time t.

By inserting Eq. (14) in Eq. (13) it follows that

$$\beta \frac{d\overline{w}_{\rm diss}(t)}{dt} = \frac{d\mathcal{D}(t)}{dt} + \rho(t), \tag{15}$$

where $\rho(t)$ is the time-dependent rate

$$\rho(t) = \int d\mathbf{x} \left[\ln \frac{p(\mathbf{x},t)}{p_{{\rm eq},t}(\mathbf{x})} \right] \hat{\Gamma}(t)\, p(\mathbf{x},t). \tag{16}$$

In Appendix A we prove that

$$\rho(t) \geqslant 0 \tag{17}$$

regardless of the dynamical regime, diffusive or semi-inertial. This implies that the equality Eq. (15) turns into the inequality in the key relation Eq. (4). Then Eq. (3) readily follows as a corollary.

III. OVERDAMPED DYNAMICS

A. Out-of-equilibrium drift

Let us focus on Markov dynamics in the overdamped regime of motion. In such a context, the variables $\mathbf{x}$ are identified with pure configurational variables $\mathbf{q}$. Let $p(\mathbf{q},t)$ be the nonequilibrium probability density (distribution) on such degrees of freedom. Given a generic function $f(\mathbf{q},t)$, the following compact notation will be adopted to indicate the ensemble average at a time t:

$$\langle f \rangle_t \equiv \int d\mathbf{q}\, p(\mathbf{q},t) f(\mathbf{q},t). \tag{18}$$

The evolution of the nonequilibrium distribution is governed by the nonstationary Fokker-Planck equation in the Smoluchowski form [7,8], with the evolution operator [see Eq. (A7) in Appendix A] ensuring that $\lim_{t<\tau\to\infty} p(\mathbf{q},\tau) = p_{{\rm eq},t}(\mathbf{q})$ if the transformation is stopped at time t. The Smoluchowski equation can be put in the form

$$\frac{\partial p(\mathbf{q},t)}{\partial t} = -\frac{\partial}{\partial \mathbf{q}}^T [p(\mathbf{q},t)\mathbf{v}(\mathbf{q},t)], \tag{19}$$

where $\mathbf{v}(\mathbf{q},t)$, defined in Eq. (5), is interpreted as the out-of-equilibrium *drift velocity* associated with the probability current $\mathbf{J}(\mathbf{q},t) \equiv p(\mathbf{q},t)\,\mathbf{v}(\mathbf{q},t)$. Explicitly,

$$\mathbf{v}(\mathbf{q},t) = -\mathbf{D}(\mathbf{q},t)\frac{\partial \Psi_t(\mathbf{q})}{\partial \mathbf{q}}, \tag{20}$$

where $\Psi_t(\mathbf{q})$ is the time-dependent scalar field

$$\Psi_t(\mathbf{q}) = \ln \frac{p(\mathbf{q},t)}{p_{{\rm eq},t}(\mathbf{q})} \tag{21}$$

and $\mathbf{D}(\mathbf{q},t)$ is the diffusion matrix generally dependent on the configuration and, possibly, also time-dependent in response to the transformation protocol [26]. Equation (19) has the same structure of an "advection-like equation" for the probability density field, where the velocity of the virtual "transporting medium" is the drift velocity determined by the probability density itself. We stress that $\mathbf{v}(\mathbf{q},t)$ must not be confused with the drift field that enters the Langevin equation associated with the Smoluchowski equation [27]. In fact, that drift field is present even for dynamics at equilibrium, whereas $\mathbf{v}(\mathbf{q},t)$ is a genuine out-of-equilibrium property.

Some general statements about $\mathbf{v}(\mathbf{q},t)$ can be made just on the basis of the structure of Eq. (20) (see Appendix B), while more insights require a case-by-case inspection of the specific system; for instance, Is the configurational space of the system open or bounded? Are there periodic coordinates?

The important fact here is that, at a given time, the drift velocity has a certain statistical distribution $\rho(\mathbf{v},t) \equiv \int d\mathbf{q}\, p(\mathbf{q},t)\,\delta[\mathbf{v}-\mathbf{v}(\mathbf{q},t)]$ where $\delta(\cdot)$ stands for the Dirac's delta function. In the next, the variances of such a distribution, i.e., ultimately, the averages

$$\langle v_i^2 \rangle_t = \int d\mathbf{q}\, p(\mathbf{q},t) v_i(\mathbf{q},t)^2 \tag{22}$$

will play a crucial role in the quantification of the lower and upper bounds for $\beta\overline{w}_{\rm diss}(t) - \mathcal{D}(t)$.

B. Dissipation, lag, and drift

By introducing the vector $\mathbf{u}(\mathbf{q},t) = \partial\Psi_t(\mathbf{q})/\partial\mathbf{q}$, the inversion of Eq. (20) yields $\mathbf{u}(\mathbf{q},t) = -\mathbf{D}(\mathbf{q},t)^{-1}\mathbf{v}(\mathbf{q},t)$. Then, from Eq. (A8) in Appendix A, the rate $\rho(t)$ results as

$$\rho(t) = \int d\mathbf{q}\, p(\mathbf{q},t)\, [\mathbf{v}(\mathbf{q},t)^T\, \mathbf{D}(\mathbf{q},t)^{-1}\mathbf{v}(\mathbf{q},t)]. \tag{23}$$

To get rid of the fact that the variables q_i may have a different physical nature, the strictly positive diagonal elements of the diffusion matrix are employed as scaling factors to build homogeneous quantities. For the sake of notation, let us introduce

$$D_{ii}^{\rm min}(t) = \min_{\mathbf{q}}\{D_{ii}(\mathbf{q},t)\},$$
$$D_{ii}^{\rm max}(t) = \max_{\mathbf{q}}\{D_{ii}(\mathbf{q},t)\}. \tag{24}$$

Then let $\tilde{\mathbf{D}}(\mathbf{q},t)$ be the positive-definite matrix with dimensionless elements

$$\tilde{D}_{ij}(\mathbf{q},t) = [\mathbf{D}(\mathbf{q},t)^{-1}]_{ij}\sqrt{D_{ii}(\mathbf{q},t)\, D_{jj}(\mathbf{q},t)}. \tag{25}$$

Finally, let us introduce the following time-dependent parameters:

$$\epsilon_{\rm min}(t) = \min_{\mathbf{q},\hat{\mathbf{w}}\,|\,\hat{\mathbf{w}}^T\hat{\mathbf{w}}=1}\{\hat{\mathbf{w}}^T\,\tilde{\mathbf{D}}(\mathbf{q},t)\hat{\mathbf{w}}\},$$
$$\epsilon_{\rm max}(t) = \max_{\mathbf{q},\hat{\mathbf{w}}\,|\,\hat{\mathbf{w}}^T\hat{\mathbf{w}}=1}\{\hat{\mathbf{w}}^T\,\tilde{\mathbf{D}}(\mathbf{q},t)\hat{\mathbf{w}}\}. \tag{26}$$

Note that $\epsilon_{\rm min}(t)$ and $\epsilon_{\rm max}(t)$ correspond, respectively, to the extreme values (over all the system's configurations) taken by the minimum and maximum eigenvalues of the matrix $\tilde{\mathbf{D}}(\mathbf{q},t)$, respectively. With these positions, a few steps reported in Ref. [28] lead us to establish that

$$\epsilon_{\rm min}(t)\sum_i \frac{\langle v_i^2\rangle_t}{D_{ii}^{\rm max}(t)} \leqslant^* \beta\frac{d[\overline{w}_{\rm diss}(t) - \mathcal{D}(t)]}{dt} \leqslant^* \epsilon_{\rm max}(t)\sum_i \frac{\langle v_i^2\rangle_t}{D_{ii}^{\rm min}(t)}, \tag{27}$$

where the averages $\langle v_i^2\rangle_t$ have been introduced in Eq. (22). We stress the important point that the inequalities in Eq. (27) are due only to the possible $\mathbf{q}$ dependence of the elements of the diffusion matrix, and to the possible spread of the eigenvalues of $\tilde{\mathbf{D}}(\mathbf{q},t)$; for "isotropic" and constant diffusion matrices, these inequalities are replaced by exact equalities. The informal notation "$\leqslant^*$," here and below, serves to recall such a kind of order relation.

The integration of both members of Eq. (27) between two times t_1 and t_2 gives

$$\beta[\overline{w}_{\rm diss}(t_2) - \overline{w}_{\rm diss}(t_1)] \leqslant^* \mathcal{D}(t_2) - \mathcal{D}(t_1) + \sum_i \frac{1}{d_{ii}^{\rm min}(t_1,t_2)} \int_{t_1}^{t_2} dt \left\langle v_i^2 \right\rangle_t \quad (28)$$

and

$$\beta[\overline{w}_{\rm diss}(t_2) - \overline{w}_{\rm diss}(t_1)] \geqslant^* \mathcal{D}(t_2) - \mathcal{D}(t_1) + \sum_i \frac{1}{d_{ii}^{\rm max}(t_1,t_2)} \int_{t_1}^{t_2} dt \left\langle v_i^2 \right\rangle_t, \quad (29)$$

where

$$d_{ii}^{\rm min}(t_1,t_2) = \min_{t_1 \leqslant t \leqslant t_2} \{D_{ii}(t)/\epsilon_{\rm max}(t)\},$$
$$d_{ii}^{\rm max}(t_1,t_2) = \max_{t_1 \leqslant t \leqslant t_2} \{D_{ii}(t)/\epsilon_{\rm min}(t)\}. \quad (30)$$

Weaker inequalities (in the sense of less tight) are then derived by considering the upper and lower bounds of the integral $\int_{t_1}^{t_2} dt \, \langle v_i^2 \rangle_t$ on the basis of the extreme values that $\langle v_i^2 \rangle_t$ can take in such a time interval, namely,

$$\beta[\overline{w}_{\rm diss}(t_2) - \overline{w}_{\rm diss}(t_1)] \leqslant \mathcal{D}(t_2) - \mathcal{D}(t_1) + (t_2 - t_1) \sum_i \frac{1}{d_{ii}^{\rm min}(t_1,t_2)} \max_{t_1 \leqslant t \leqslant t_2} \left\{ \left\langle v_i^2 \right\rangle_t \right\} \quad (31)$$

and

$$\beta[\overline{w}_{\rm diss}(t_2) - \overline{w}_{\rm diss}(t_1)] \geqslant \mathcal{D}(t_2) - \mathcal{D}(t_1) + (t_2 - t_1) \sum_i \frac{1}{d_{ii}^{\rm max}(t_1,t_2)} \min_{t_1 \leqslant t \leqslant t_2} \left\{ \left\langle v_i^2 \right\rangle_t \right\}. \quad (32)$$

The above relations hold regardless of the system's state at the initial time t_1 (equilibrium or nonequilibrium state). A relevant case, which also reflects the typical situation in the experimental practice, is that of transformations starting from an equilibrium state. In this case, Eqs. (28) and (29), taken together, reduce to

$$\mathcal{D}(t) + \sum_i \frac{1}{d_{ii}^{\rm max}(0,t)} \int_0^t dt' \left\langle v_i^2 \right\rangle_{t'} \leqslant^* \beta \overline{w}_{\rm diss}(t) \leqslant^* \mathcal{D}(t) + \sum_i \frac{1}{d_{ii}^{\rm min}(0,t)} \int_0^t dt' \left\langle v_i^2 \right\rangle_{t'}, \quad (33)$$

and the inequalities Eqs. (31) and (32) become

$$\mathcal{D}(t) + t \sum_i \frac{\min_{0 \leqslant t' \leqslant t} \left\{ \left\langle v_i^2 \right\rangle_{t'} \right\}}{d_{ii}^{\rm max}(0,t)} \leqslant \beta \overline{w}_{\rm diss}(t) \leqslant \mathcal{D}(t) + t \sum_i \frac{\max_{0 \leqslant t' \leqslant t} \left\{ \left\langle v_i^2 \right\rangle_{t'} \right\}}{d_{ii}^{\rm min}(0,t)}. \quad (34)$$

Note that the relation $\mathcal{D}(t) \leqslant \beta \overline{w}_{\rm diss}(t)$ [14] is implicit in Eqs. (33) and (34), since the terms added to $\mathcal{D}(t)$ at the left member are strictly positive.

In passing from Eq. (33) to Eq. (34), one deals only with the extreme values taken by the variances $\langle v_i^2 \rangle_{t'}$ in the course of the transformation, but at the price of accepting weaker bounds. We emphasize that Eq. (34) can be viewed from different angles. In particular, providing that everything is known about the diffusion matrix and its possible time dependence, the quantity $[\beta \overline{w}_{\rm diss}(t) - \mathcal{D}(t)]/t$ ultimately sets a global constraint between the maximum values of the variances; namely, they must be such that $\sum_i \max_{0 \leqslant t' \leqslant t} \{\langle v_i^2 \rangle_{t'}\}/d_{ii}^{\rm min}(0,t)$ is not less than that quantity. In one dimension the picture is clear: during the transformation of duration t, it happens *for sure* that $\langle v^2 \rangle_{t'}$ [as a measure of the broadening of the distribution $\rho(v,t')$ for $0 \leqslant t' \leqslant t$] goes beyond the value $d^{\rm min}(0,t) \times [\beta \overline{w}_{\rm diss}(t) - \mathcal{D}(t)]/t$.

IV. PERIODIC STEADY STATES IN CYCLIC STOCHASTIC PUMPING

A. General relations

Let us consider a system subjected to a cyclic energy transformation of period τ. From now on, we shall use also the term "energy perturbation" to stress that the external means intervenes on the energetics of the unperturbed system.

According to Floquet's theory applied to periodically driven stochastic systems [29], in the long-time limit the system reaches a unique "periodic steady state" in the presence of the external driving. Throughout in the following, the superscript "∞" will serve to denote such a condition. The periodic steady state is such that, for all configurations $\mathbf{q}$, the invariance condition $p^\infty(\mathbf{q},t_0 + \tau) = p^\infty(\mathbf{q},t_0)$ holds for any t_0. Thus, all out-of-equilibrium properties also own such a τ periodicity. The features of the periodic steady state clearly depend on the *kind* of energy perturbation. In addition, there is also a subtle dependence on the initial distribution $p(\mathbf{q},0)$ when the perturbation is turned on [in the present context, $p(\mathbf{q},0) = p_{\rm eq,0}(\mathbf{q})$] and on the *phase* of the cyclic perturbation [29].

With reference to the periodic steady state conditions, let us introduce the average dissipated energy per cycle given by [30]

$$\overline{w}_{\rm diss}^\infty := \lim_{t_0 \to \infty} [\overline{w}_{\rm diss}(t_0 + \tau) - \overline{w}_{\rm diss}(t_0)]. \quad (35)$$

Clearly $\overline{w}_{\rm diss}^\infty$ depends on τ. We mention that an analytic expression for such a dependence on τ has been recently derived [16] in the limit of weak enough perturbations and for the initial condition $V_{t=0}(\mathbf{q}) = V_0(\mathbf{q})$ where $V_0(\mathbf{q})$ is the mean-field potential of the unperturbed system up to time 0^- (this fixes the initial phase mentioned above).

Due to the periodicity of the probability density, it follows that $\mathcal{D}(t_0) = \mathcal{D}(t_0 + \tau)$ as $t_0 \to \infty$. By using this condition and considering Eq. (35), Eqs. (34) reduce to

$$\tau \sum_i \frac{\left\langle v_i^2 \right\rangle_{\rm min}^\infty}{d_{ii}^{\infty,\rm max}} \leqslant \beta \overline{w}_{\rm diss}^\infty \leqslant \tau \sum_i \frac{\left\langle v_i^2 \right\rangle_{\rm max}^\infty}{d_{ii}^{\infty,\rm min}} \quad (36)$$

with

$$\left\langle v_i^2 \right\rangle_{\rm min}^\infty = \lim_{t_0 \to \infty} \min_{t_0 \leqslant t \leqslant t_0+\tau} \left\{ \left\langle v_i^2 \right\rangle_t \right\},$$
$$\left\langle v_i^2 \right\rangle_{\rm max}^\infty = \lim_{t_0 \to \infty} \max_{t_0 \leqslant t \leqslant t_0+\tau} \left\{ \left\langle v_i^2 \right\rangle_t \right\} \quad (37)$$

and

$$d_{ii}^{\infty,\rm min} = \lim_{t_0 \to \infty} d_{ii}^{\rm min}(t_0,t_0 + \tau),$$
$$d_{ii}^{\infty,\rm max} = \lim_{t_0 \to \infty} d_{ii}^{\rm max}(t_0,t_0 + \tau). \quad (38)$$

From Eq. (22), one can also write

$$\langle v_i^2\rangle_{\min}^{\infty} = \min_{t_0\leqslant t\leqslant t_0+\tau}\int d\mathbf{q}\, p^{\infty}(\mathbf{q},t)\, v_i^{\infty}(\mathbf{q},t)^2,$$
$$\langle v_i^2\rangle_{\max}^{\infty} = \max_{t_0\leqslant t\leqslant t_0+\tau}\int d\mathbf{q}\, p^{\infty}(\mathbf{q},t)\, v_i^{\infty}(\mathbf{q},t)^2 \qquad (39)$$

for t_0 sufficiently long, where $v_i^{\infty}(\mathbf{q},t)$ stands for the ith component of the drift velocity at the periodic steady state.

Finally, the division of $\beta\overline{w}_{\text{diss}}^{\infty}$ by the period τ gives the time-averaged (over one cycle) rate of entropy production, σ_S^{∞}, in k_B units. Thus, Eq. (36) yields also lower and upper bounds for σ_S^{∞}.

Let us focus now on some features of the probability current, namely, on the $\mathbf{q}$-dependent probability current time-averaged over one period of perturbation starting from a generic time t_0:

$$\overline{\mathbf{J}}(\mathbf{q},t_0) := \frac{1}{\tau}\int_{t_0}^{t_0+\tau} dt\, \mathbf{J}(\mathbf{q},t). \qquad (40)$$

As t_0 is taken ever longer so that the periodic steady state is asymptotically reached, the integral over an interval of duration τ becomes independent of t_0. Thus, the limit $t_0 \to \infty$ does exist:

$$\lim_{t_0\to\infty} \overline{\mathbf{J}}(\mathbf{q},t_0) = \overline{\mathbf{J}}^{\infty}(\mathbf{q}). \qquad (41)$$

By integrating both members of Eq. (19) on t between t_0 and $t_0+\tau$, then using the definition Eq. (40) and taking the limit $t_0 \to \infty$, one gets

$$\lim_{t_0\to\infty}[p(\mathbf{q},t_0+\tau) - p(\mathbf{q},t_0)] = -\tau\, \frac{\partial}{\partial \mathbf{q}}^{T}\overline{\mathbf{J}}^{\infty}(\mathbf{q}). \qquad (42)$$

Since the left-hand side of Eq. (42) vanishes due to the periodic steady state condition, it follows

$$\frac{\partial}{\partial \mathbf{q}}^{T}\overline{\mathbf{J}}^{\infty}(\mathbf{q}) = 0 \quad \text{for all } \mathbf{q}, \qquad (43)$$

that is, $\overline{\mathbf{J}}^{\infty}(\mathbf{q})$ is a divergence-free vector field. Clearly Eq. (43) is equivalent to state that the flux of $\overline{\mathbf{J}}^{\infty}(\mathbf{q})$ through any closed and oriented surface $\delta\Omega^{+}$ embedded in the configurational space is null: $\int_{\delta\Omega^{+}} d\sigma(\mathbf{q})\,\hat{\mathbf{n}}(\mathbf{q})^{T}\overline{\mathbf{J}}^{\infty}(\mathbf{q}) = 0$ with the notation already specified in the Introduction.

Equation (43), together with the proper boundary conditions at the border of the configurational space for the specific system, imposes some constraints on the vector field $\overline{\mathbf{J}}^{\infty}(\mathbf{q})$. The conditions at the border may be the "natural" ones in the case of energy boundedness, or they may be the reflecting or periodic boundary conditions on the probability current [7]. The analysis of the multidimensional case is not trivial since, in all generality, $\overline{\mathbf{J}}^{\infty}(\mathbf{q})$ is not a conservative field [31] and a case-by-case inspection is required to make fully explicit the constraints imposed by Eq. (43) with the proper boundary conditions. On the contrary, as reported in the next section, the one-dimensional case has a simple and unequivocal solution.

B. One-dimensional systems and a case model

Let us consider underdamped one-dimensional systems with a single variable q defined in a domain $[q_{\min},q_{\max}]$. First, the inequalities Eq. (36) apply directly for the single contribution in place of the summations. Then, if the system is bounded by either "natural" or reflecting boundaries, one can state that $\overline{J}^{\infty}(q) = 0$ for all q, whereas for a periodic system (i.e., if q is a periodic coordinate with $q_{\min} = 0$ and $q_{\max} = 2\pi$) one has that $\overline{J}^{\infty}(q) \equiv \overline{J}^{\infty}$ for all q. In the latter situation, the constant $\overline{J}^{\infty}$ may be null or non-null depending on the kind of energy transformation. In a series of papers, a remarkable "no-pumping theorem" has been formulated to state under which operative conditions the one-period-averaged probability current (i.e., the constant $\overline{J}^{\infty}$ in our notation) would be null *for sure*. That theorem, initially formulated for Markov jumps among discrete sites whose energy levels are externally modulated [17–19], has been later extended to the continuous case [20]. In essence, the one-period-averaged probability current *may be* non-null only if the perturbation modulates the background energy profile $V_0(q)$ in a way that both the energy level of the wells

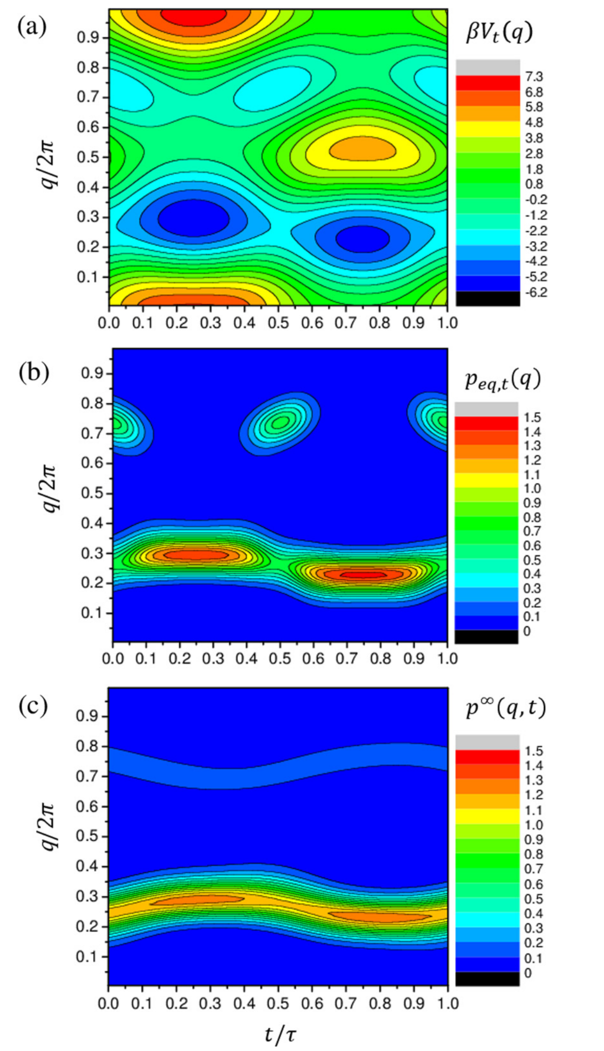

FIG. 1. Energetics of the one-dimensional case model subjected to cyclic energy perturbation. (a) Contour plot of the system's energy $V_t(q)$ as function of coordinate q and time t over one period of the perturbation (the quantities are scaled as indicated); (b) contour plot of the underlying equilibrium distribution $p_{\text{eq},t}(q)$; (c) contour plot of the nonequilibrium distribution at the periodic steady state for $\tau = 1$.

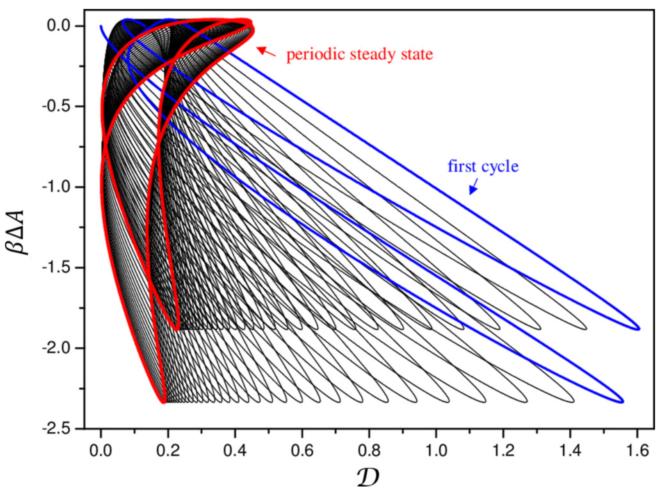

FIG. 2. Trajectories in the plane of the variables $\beta\Delta A(t)$ and $\mathcal{D}(t)$ for the one-dimensional case model under the cyclic energy perturbation with $\tau = 1$ starting from thermal equilibrium (thin black line). The medium-thickness blue line corresponds to the first cycle. The thicker red line corresponds to a cycle when the periodic steady state is considered to be reached (see the text for details).

and the heights of the well-to-well barriers are affected; the one-dimensional toy model treated in the following satisfies such a requisite. Finally, $\overline{J}^{\infty}$ and the time-dependent average of the drift velocity, $\langle v\rangle_t^{\infty} = \int_{q_{\rm min}}^{q_{\rm max}} dq\, p^{\infty}(q,t)v^{\infty}(q,t)$, are related by the integral expression

$$\int_{t_0}^{t_0+\tau} dt\, \langle v\rangle_t^{\infty} = 2\pi\tau\,\overline{J}^{\infty} \tag{44}$$

for $t_0 \to \infty$ (in practice, for any sufficiently long t_0). Unfortunately, this relation does not provide useful information about the values of $\langle v^2\rangle_{\rm min}^{\infty}$ and $\langle v^2\rangle_{\rm max}^{\infty}$ that enter the one-dimensional version of Eq. (36).

For illustrative purposes, let us adopt the simple one-dimensional system already studied in Ref. [16] (see the situation termed there as "Case 2"). The system features a single angular variable q. The unperturbed energetics is described by a double-well symmetric potential $\beta V_0(q) = \alpha_1\cos(q) + \alpha_2\cos(2q)$ with $\alpha_1 = 1$ and $\alpha_2 = 3$ in the calculations. The energy perturbation is such that the time-dependent potential is $\beta V_t(q) = \beta V_0(q) + \Delta\,\epsilon(t)\cos[q + \phi\,\epsilon(t)]$ where $\epsilon(t) = \sin(2\pi t/\tau)$. For the calculations we set $\phi = 0.7$ and $\Delta = 4$ as in Ref. [16]. The motion is diffusive with constant diffusion coefficient D. The time variable is meant to be expressed in some physical units, and $D = 1$ is employed. The Smoluchowski equation for the evolution of $p(q,t)$ from $p(q,0) = p_{\rm eq,0}(q)$ has been solved numerically by means of forward-Euler propagation steps and a finite-differences scheme on the q variable under application of periodic boundary conditions at $q = 0$ and $q = 2\pi$. Technical details are given in Ref. [16].

Figure 1(a) shows the contour plot of $\beta V_t(q)$ over one period of the perturbation, and Fig. 1(b) shows the corresponding underlying equilibrium probability density. In Fig. 1(c) is shown, again over one period, the nonequilibrium probability density attained at the periodic steady state; such a contour plot refers to the case $\tau = 1$, a value for which the amount of average energy dissipation per cycle was found to be close to a maximum [16].

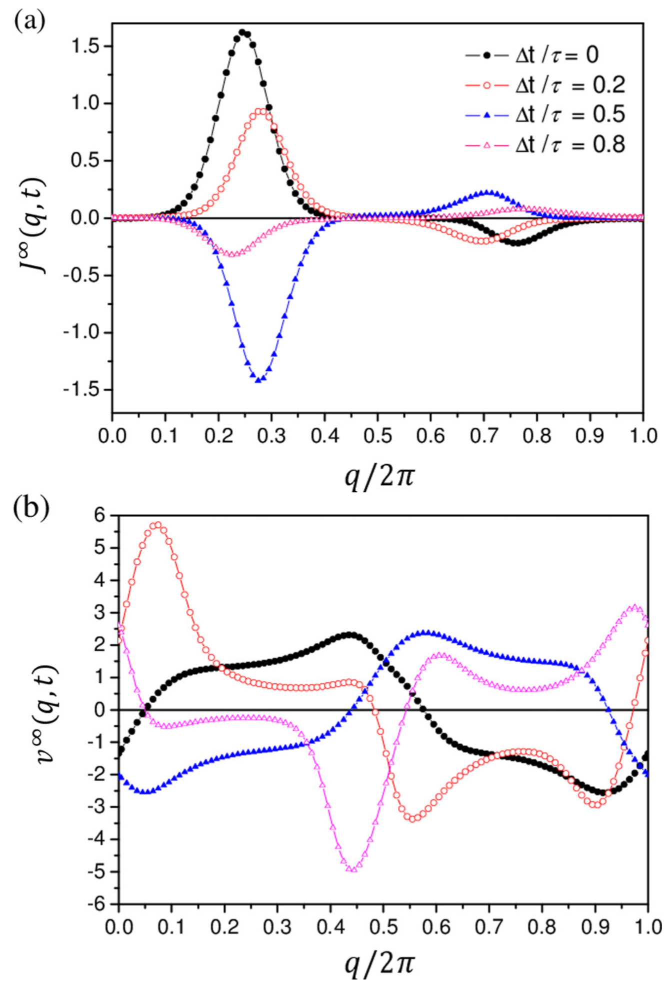

FIG. 3. Profiles of the probability current (a) and of the related drift velocity (b), versus the coordinate q, for the one-dimensional case model at the periodic steady state under cyclic energy perturbation with $\tau = 1$. The panels show profiles at various advancements over one cycle.

In Fig. 2 the reaching of the periodic steady state is displayed in a geometric representation where the (time-dependent) free energy difference ΔA is plotted against the (time-dependent) lag $\mathcal{D}$. The profile refers to the case $\tau = 1$. It can be noted that the curve settles down on a limit closed path that corresponds to a cycle at the periodic steady state. On computational grounds, we adopt here the criterion that, for a given value of τ, the n_c-th cycle is considered to occur under periodic steady state conditions if the relative variation $[\mathcal{D}(n\tau) - \mathcal{D}((n-1)\tau)]/\mathcal{D}[(n-1)\tau]$ is less than 0.01%, in modulus, for both $n = n_c$ and $n = n_c - 1$. In the figure, the thicker red line corresponds to the first performed cycle ($n_c = 34$ in this case) for which such a condition is fulfilled.

Figures 3 and 4 characterize the out-of-equilibrium drift under periodic steady state conditions. Figure 3 refers to $\tau = 1$; both $J^{\infty}(q,t)$ and $v^{\infty}(q,t)$ are plotted versus q for several advancements $\Delta t/\tau$ over one cycle. Then it has been verified

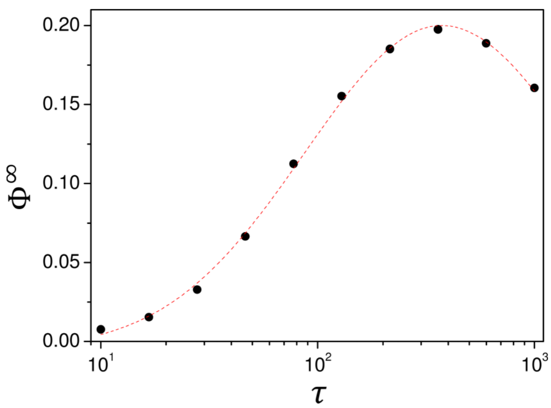

FIG. 4. τ dependence, on the logarithmic scale, of the steady state probability current integrated over one cycle of perturbation for the one-dimensional case model (filled circles). The dashed line is the fit with a Gaussian function.

that $\overline{J}^\infty(q)$ is practically independent of q, in agreement with the fact that such a quantity should be constant. For example, the variations with respect to the average value, which are likely due to a residual displacement from the periodic steady state, are at most of $\sim 6\%$ for $\tau = 10$ and of $\sim 0.5\%$ for $\tau = 100$. In Fig. 4 the probability current integrated over one period, $\Phi^\infty = \int_{t_0}^{t_0+\tau} dt\, J^\infty(q,t) \equiv \tau \overline{J}^\infty$, is plotted versus τ in a logarithmic abscissa scale. Note that values $\Phi^\infty \neq 0$ are in accord with the no-pumping theorem [17–20] since the perturbation of $V_0(q)$ modulates both the energy of the wells and the well-to-well barriers. Interestingly, the values of Φ^∞ versus τ in the logarithmic scale can be well fitted by a Gaussian profile. This means that $\ln|\Phi^\infty(\tau)| \simeq a - b(\ln \tau/\tau_c)^2$ with a, b, and τ_c system-dependent parameters. Such a feature is here reported only as empiric observation, while its formal rationale is left to future inspections [32].

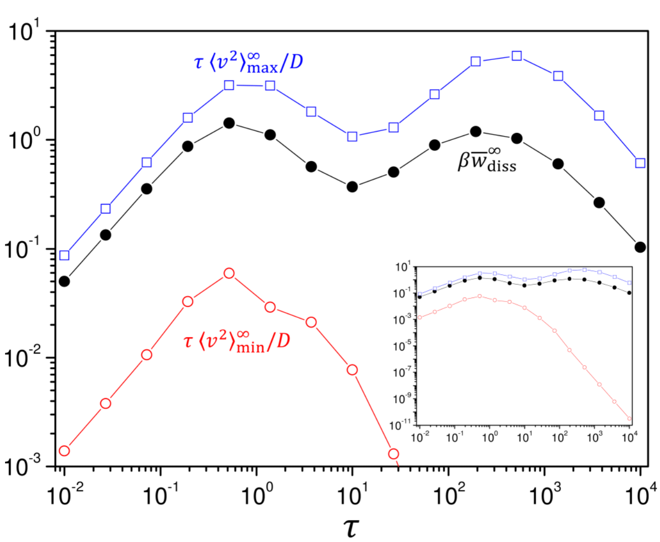

FIG. 5. τ dependence of the average energy dissipation per cycle, $\beta\overline{w}^\infty_{\rm diss}$, and of the provided upper and lower bounds, for the one-dimensional case model at the periodic steady state under cyclic perturbation. The inset shows the same profiles on a wider range.

Figure 5 contains the main outcome. In the double-logarithmic scale, the filled black circles show the profile of $\beta\overline{w}^\infty_{\rm diss}$ versus τ, and the empty blue squares and the empty red circles refer to the upper and lower bounds, respectively; these bounds follow directly from Eq. (36) taking into account that the summations reduce to a single contribution and that the diffusion coefficient is constant: $\tau\,\langle v^2\rangle^\infty_{\rm min}/D \leqslant \beta\overline{w}^\infty_{\rm diss} \leqslant \tau\,\langle v^2\rangle^\infty_{\rm max}/D$. The inset shows the same profiles on a wider range. The dependence of $\beta\overline{w}^\infty_{\rm diss}$ on τ has been investigated in Ref. [16] in the limit of weak energy perturbations. In particular, the two local maxima, which correspond to maxima of the average rate of energy dissipation (or, equivalently, of entropy production), fall at frequencies $2\pi/\tau$ that match the intrinsic rates of some internal modes of fluctuation of the system at the unperturbed equilibrium. Note that the upper bound also displays a similar profile, at least for the present case model.

V. REMARKS AND CONCLUSIONS

In this work we have established a connection, in terms of mutual bounds, between average energy dissipation, system's lag, and out-of-equilibrium drift for a thermostated fluctuating system subjected to a driven energy transformation. Although many of the introductory statements hold regardless of the regime of the motion, the key relations in Eqs. (33) and (34) are valid for overdamped dynamics on configurational degrees of freedom. Those relations express that the difference $\beta\overline{w}_{\rm diss}(t) - \mathcal{D}(t)$, which was previously established being greater than zero [14], is bounded by quantities related to the time-dependent distribution of the drift velocity $\mathbf{v}(\mathbf{q},t)$, Eq. (5), associated with the probability current in the configurational space.

The inequalities Eq. (34) have been then specified for the widely studied "stochastic pumps" in which a cyclic transformation can be exploited to induce out-of-equilibrium currents [17–20]. The main results are represented by the inequalities in Eq. (36), which have been illustrated and tested for the one-dimensional system already studied in Ref. [16].

In essence, this work establishes some connection between two aspects of the physics of driven fluctuating systems that, at least in our opinion, are still scarcely interfaced for continuous and nonautonomus systems: the energy dissipation (stochastic thermodynamics context) and the induction of directed flow (stochastic dynamics context). The development here was to turn from the probability current to the drift velocity field $\mathbf{v}(\mathbf{q},t)$, which was revealed to be the crucial quantity to work out quantitative relations. Future efforts will be devoted to better characterizing such a drift velocity field and, hopefully, to confer on it a "physical guise" beyond the definition in Eq. (5) and mere mathematical properties like those presented in Appendix B.

APPENDIX A: PROOF OF Eq. (17)

Here we prove the validity of Eq. (17), and hence of Eq. (4), for two classes of nonstationary Markov dynamics under the requisite that the relaxation towards $p_{{\rm eq},t}(\mathbf{x})$ occurs once the driving protocol is stopped. First, we shall consider the situation of semi-inertial (underdamped) dynamics. In this case, $\mathbf{x}$ contains both configurational variables $\mathbf{q}$ and the conjugate momenta $\mathbf{p}$. Then we shall turn to diffusive (overdamped) motions in which the relevant variables are only of a configurational type. The latter situation might appear redundant if it is meant to derive by reduction of the semi-inertial situation in the case of high friction and when the dynamics is observed at time intervals long enough so that the momenta lose the time correlation with the preceding state. However, it is worthwhile to treat explicitly also the diffusive situation since, in all generality, the variables $\mathbf{q}$, or at least some of them, may be generalized variables without an associated momentum. In such a case, the diffusive context is self-standing, and it cannot be obtained by reduction from an "upper" semi-inertial level.

1. Semi-inertial regime of motion

In the semi-inertial regime, the potential $V_t(\mathbf{q},\mathbf{p})$ corresponds to the mechanical energy of the system's microstate, that is, to the Hamiltonian function $H(\mathbf{q},\mathbf{p},t) = U(\mathbf{q},t) + E_{\rm kin}(\mathbf{p})$ with $U(\mathbf{q},t)$ the time-dependent potential energy and $E_{\rm kin}(\mathbf{p}) = \mathbf{p}^T\mathbf{M}^{-1}\mathbf{p}/2$ the kinetic energy ($\mathbf{M}$ is the mass matrix of the multibody system). At the given temperature, the underlying Maxwell-Boltzmann equilibrium distribution at time t is $p_{{\rm eq},t}(\mathbf{q},\mathbf{p}) \propto \exp\{-\beta H(\mathbf{q},\mathbf{p},t)\}$. Then let $\xi(\mathbf{q},t)$ be the friction matrix. Such a matrix, which is required to be positive-definite on physical grounds, is generally configuration-dependent and, possibly, also time-dependent as a consequence of the deterministic control on some system's coordinate(s). For $\mathbf{x} \equiv (\mathbf{q},\mathbf{p})$, the Fokker-Planck operator takes the Kramers-Klein form (subscript "KK") [7,8]:

$$\hat{\Gamma}_{\rm KK}(t) = \hat{\mathcal{L}}(t) - \frac{\partial}{\partial \mathbf{p}}^T \xi(\mathbf{q},t)\mathbf{M}^{-1}\mathbf{p} - \beta^{-1}\frac{\partial}{\partial \mathbf{p}}^T \xi(\mathbf{q},t)\frac{\partial}{\partial \mathbf{p}}. \tag{A1}$$

The first addend in Eq. (A1) is the classical Liouville operator, $\hat{\mathcal{L}}(t) = (\frac{\partial H(\mathbf{q},\mathbf{p},t)}{\partial \mathbf{p}})^T \frac{\partial}{\partial \mathbf{q}} - (\frac{\partial H(\mathbf{q},\mathbf{p},t)}{\partial \mathbf{q}})^T \frac{\partial}{\partial \mathbf{p}}$ (we follow Zwanzig's proposal, see section 2.1 of Ref. [8], about absorbing the imaginary factor into the operator's definition); the second and third addends provide the dissipation-fluctuation contribution. With a few algebraic steps, Eq. (A1) can be put in the form

$$\hat{\Gamma}_{\rm KK}(t) = \hat{\mathcal{L}}(t) - \beta^{-1}\frac{\partial}{\partial \mathbf{p}}^T \xi(\mathbf{q},t)p_{{\rm eq},t}(\mathbf{q},\mathbf{p})\frac{\partial}{\partial \mathbf{p}}p_{{\rm eq},t}(\mathbf{q},\mathbf{p})^{-1}. \tag{A2}$$

The Liouville operator gives a vanishing contribution to $\rho(t)$ in Eq. (16). To prove this, let us adopt the following form of the Liouville operator (arguments of the functions are omitted for brevity) [33]:

$$\hat{\mathcal{L}}(t) = \beta^{-1}\frac{\partial}{\partial \mathbf{q}}^T p_{{\rm eq},t}\frac{\partial}{\partial \mathbf{p}}p_{{\rm eq},t}^{-1} - \beta^{-1}\frac{\partial}{\partial \mathbf{p}}^T p_{{\rm eq},t}\frac{\partial}{\partial \mathbf{q}}p_{{\rm eq},t}^{-1}. \tag{A3}$$

For the sake of notation, let us introduce $\Psi_t(\mathbf{q},\mathbf{p}) = \ln[p(\mathbf{q},\mathbf{p},t)/p_{{\rm eq},t}(\mathbf{q},\mathbf{p})]$. The identities $p_{{\rm eq},t}[\partial(p/p_{{\rm eq},t})/\partial \mathbf{q}] \equiv p\partial\Psi_t/\partial\mathbf{q}$ and $p_{{\rm eq},t}[\partial(p/p_{{\rm eq},t})/\partial \mathbf{p}] \equiv p\partial\Psi_t/\partial\mathbf{p}$ allow us to express the contribution of $\hat{\mathcal{L}}(t)$ to Eq. (16) as

$$\begin{aligned}\int d\mathbf{q}\int d\mathbf{p}\,\Psi_t(\mathbf{q},\mathbf{p},t)\hat{\mathcal{L}}(t)p(\mathbf{q},\mathbf{p},t) &= \beta^{-1}\int d\mathbf{p}\int d\mathbf{q}\,\Psi_t\frac{\partial}{\partial \mathbf{q}}^T\left(p\frac{\partial\Psi_t}{\partial\mathbf{p}}\right)\\ &\quad - \beta^{-1}\int d\mathbf{q}\int d\mathbf{p}\,\Psi_t\frac{\partial}{\partial \mathbf{p}}^T\left(p\frac{\partial\Psi_t}{\partial\mathbf{q}}\right).\end{aligned} \tag{A4}$$

The integrals in the addends at the right-hand side are solved by doing a first integration by parts. In the integration by parts on $\mathbf{q}$ (for the first addend) consider that $p\partial\Psi_t/\partial\mathbf{q}$ vanishes at the boundaries of the configurational space in the case of energetically bounded systems [$p(\mathbf{q},\mathbf{p},t) \to 0$ at the boundaries of the $\mathbf{q}$-space], or it takes equal values in the case of periodic coordinates (periodic boundary conditions); in the integration by parts on $\mathbf{p}$ (for the second addend) consider that $p\partial\Psi_t/\partial\mathbf{p}$ vanishes at the boundaries of the momenta space as $|p_i| \to \infty$. As a whole, the net contribution to Eq. (16) for the KK operator results in being $\rho_{\rm KK}(t) = -\beta^{-1}\int d\mathbf{q}\int d\mathbf{p}\,\Psi_t\frac{\partial}{\partial \mathbf{p}}^T\xi(\mathbf{q},t)p_{{\rm eq},t}\frac{\partial(p/p_{{\rm eq},t})}{\partial\mathbf{p}}$. Integration by parts on $\mathbf{p}$, with the consideration that $p_{{\rm eq},t}(\mathbf{q},\mathbf{p})$ vanishes at the boundaries of the momenta space, yields the final result:

$$\begin{aligned}\rho_{\rm KK}(t) = \beta^{-1}\int d\mathbf{q}\int d\mathbf{p}\,p(\mathbf{q},\mathbf{p},t)\\ \times[\mathbf{u}(\mathbf{q},\mathbf{p},t)^T\,\xi(\mathbf{q},t)\mathbf{u}(\mathbf{q},\mathbf{p},t)],\end{aligned} \tag{A5}$$

where $\mathbf{u}(\mathbf{q},\mathbf{p},t)$ is the column vector:

$$\mathbf{u}(\mathbf{q},\mathbf{p},t) = \frac{\partial\ln[p(\mathbf{q},\mathbf{p},t)/p_{{\rm eq},t}(\mathbf{q},\mathbf{p})]}{\partial\mathbf{p}}. \tag{A6}$$

Since the friction matrix is positive-definite, the scalar quantity within square brackets in Eq. (A5) is non-negative, hence also the integral itself non-negative; actually, $\rho_{\rm KK}(t) = 0$ only in the case the vector $\mathbf{u}(\mathbf{q},\mathbf{p},t)$ is identically null in the whole phase space, that is, only if $p(\mathbf{q},\mathbf{p},t)$ coincides with $p_{{\rm eq},t}(\mathbf{q},\mathbf{p})$ (no system's lag).

2. Diffusive regime of motion

In the diffusive regime (variables $\mathbf{x} \equiv \mathbf{q}$), $V_t(\mathbf{q})$ is interpreted as mean-field potential [34], and the evolution operator takes the Smoluchowski form (subscript "S") [7,8]:

$$\hat{\Gamma}_{\rm S}(t) = -\frac{\partial}{\partial \mathbf{q}}^T \mathbf{D}(\mathbf{q},t)p_{{\rm eq},t}(\mathbf{q})\frac{\partial}{\partial \mathbf{q}}p_{{\rm eq},t}(\mathbf{q})^{-1}, \tag{A7}$$

where $\mathbf{D}(\mathbf{q},t)$ is the diffusion matrix generally dependent on the configuration and, possibly, also time-dependent in response to the deterministic control exerted by the external means [26]. The diffusion matrix must be positive-definite to ensure the relaxation to the underlying equilibrium distribution. In adopting Eq. (A7) it is implicit that the "drift" and the "diffusion" contributions in the Fokker-Planck equation [7] (and in the corresponding overdamped Langevin-type equation as well [27]) are detailed linked in the way that $\lim_{t<\tau\to\infty} p(\mathbf{q},\tau) = p_{{\rm eq},t}(\mathbf{q})$ if the transformation is stopped at a time t.

By inserting Eq. (A7) in Eq. (16), and integrating by parts on the $\mathbf{q}$ variables by considering (as above) that $p_{\mathrm{eq},t}\partial(p/p_{\mathrm{eq},t})/\partial\mathbf{q}$ vanishes at the boundaries, or it gives identical contributions that cancel, it is readily shown that

$$\rho_S(t) = \int d\mathbf{q}\, p(\mathbf{q},t)\, [\mathbf{u}(\mathbf{q},t)^T\, \mathbf{D}(\mathbf{q},t)\mathbf{u}(\mathbf{q},t)], \tag{A8}$$

where

$$\mathbf{u}(\mathbf{q},t) = \frac{\partial \ln[p(\mathbf{q},t)/p_{\mathrm{eq},t}(\mathbf{q})]}{\partial \mathbf{q}}. \tag{A9}$$

Again, the quantity within square brackets in Eq. (A8) is non-negative since the diffusion matrix is positive-definite. This implies that the integral is also non-negative, and equal to zero only if $p(\mathbf{q},t)$ coincides with $p_{\mathrm{eq},t}(\mathbf{q})$, that is, in the absence of a system's lag.

As a whole, the rate $\rho(t)$ in Eq. (16) is always non-negative regardless of the kind of motion, diffusive or semi-inertial.

APPENDIX B: SOME GENERAL PROPERTIES OF THE VELOCITY FIELD $\mathbf{v}(\mathbf{q},t)$

The following general properties of the drift velocity field $\mathbf{v}(\mathbf{q},t)$ can be deduced from the structure of Eq. (20):

(1) The stationary points (local maxima and minima in the configurational space) of $\Psi_t(\mathbf{q}) = \ln[p(\mathbf{q},t)/p_{\mathrm{eq},t}(\mathbf{q})]$ are points of zero drift at the time t.

(2) The value of $\Psi_t(\mathbf{q})$ decreases monotonically moving along the "streamlines" of the drift velocity field $\mathbf{v}(\mathbf{q},t)$ at a fixed t; as a consequence, these streamlines must originate from points of local maximum of $\Psi_t(\mathbf{q})$ and end at points of local minimum.

Assertion (1) follows immediately from Eq. (20). To prove assertion (2), let us focus on the "static picture" at a fixed time t. By considering $\mathbf{u}(\mathbf{q},t) = \partial\Psi_t(\mathbf{q})/\partial\mathbf{q}$, it follows that the vector field $-\mathbf{D}(\mathbf{q},t)^{-1}\mathbf{v}(\mathbf{q},t)$ [which corresponds to $\mathbf{u}(\mathbf{q},t)$] is a conservative field associated with the "potential" $\Psi_t(\mathbf{q})$. Then let γ_t be a "streamline" of the velocity field $\mathbf{v}(\mathbf{q},t)$ at fixed t, that is, the curve generated by integration of $d\mathbf{q}^{\gamma_t}(\tilde{t})/d\tilde{t} = \mathbf{v}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)$ from a given initial point with $\tilde{t}$ a progression variable having physical dimension of time. First, moving along γ_t, the quantity $p(\mathbf{q}^{\gamma_t}(\tilde{t}),t)/p_{\mathrm{eq},t}(\mathbf{q}^{\gamma_t}(\tilde{t}))$ decreases. In other terms, for any two points on such a curve it holds

$$\tilde{t}_2 \geqslant \tilde{t}_1: \quad p(\mathbf{q}^{\gamma_t}(\tilde{t}_2),t) \leqslant p(\mathbf{q}^{\gamma_t}(\tilde{t}_1),t)\, \frac{p_{\mathrm{eq},t}(\mathbf{q}^{\gamma_t}(\tilde{t}_2))}{p_{\mathrm{eq},t}(\mathbf{q}^{\gamma_t}(\tilde{t}_1))}.$$

This property can be proved by considering that the line integral of the vector $\mathbf{u}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)$ along the streamline gives $\int_{\tilde{t}_1}^{\tilde{t}_2} d\tilde{t}\, \mathbf{u}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)^T \frac{d\mathbf{q}^{\gamma_t}(\tilde{t})}{d\tilde{t}} = \Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_2)) - \Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_1))$. By inserting the expressions for $\mathbf{u}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)$ and $d\mathbf{q}^{\gamma_t}(\tilde{t})/d\tilde{t}$ it follows $\Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_2)) - \Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_1)) = -\int_{\tilde{t}_1}^{\tilde{t}_2} d\tilde{t}\, \mathbf{v}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)^T\mathbf{D}(\mathbf{q}^{\gamma_t}(\tilde{t}),t)^{-1}\mathbf{v}(\mathbf{q}^{\gamma_t}(s),t)$. Since the diffusion matrix is positive-definite, the integral at the right-hand side of such equation is non-negative, hence $\Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_2)) \leqslant \Psi_t(\mathbf{q}^{\gamma_t}(\tilde{t}_1))$. This corresponds to assertion (2).

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[26] In abstract terms, suppose that the transformation is exerted on a set of some "backbone parameters" Λ_i of the system. For a given set of values $\mathbf{\Lambda}$, the internal friction, which affects the diffusion matrix through general Stokes-Einstein-like relations, depends on $\mathbf{\Lambda}$. Thus, $\mathbf{D}(\mathbf{q},t)$ is the diffusion matrix corresponding to $\mathbf{\Lambda}(t)$ during the transformation. As an example, think of the stretching of a polypeptide in which the single controlled parameter λ is the end-to-end distance between two residues. As the stretching proceeds, the $\mathbf{q}$-dependent viscous friction (here $\mathbf{q}$ are some relevant conformational variables of the polypeptide) may depend on the value $\lambda(t)$ at time t because of the change of hydrodynamic interactions between elements of secondary structure.

[27] The Langevin equation for overdamped dynamics on the $\mathbf{q}$ variables reads $\dot{\mathbf{q}} = \mathbf{v}_0(\mathbf{q},t) + [2\mathbf{D}(\mathbf{q},t)]^{1/2}\eta(t)$, where $\mathbf{v}_0(\mathbf{q},t) = \mathbf{D}(\mathbf{q},t)\frac{\partial \ln p_{\mathrm{eq},t}(\mathbf{q})}{\partial \mathbf{q}} + \mathbf{d}(\mathbf{q},t)$ with $d_i(\mathbf{q},t) = \sum_j \partial D_{i,j}(\mathbf{q},t)/\partial q_j$, and $\eta(t)$ is an array of uncorrelated white-noise sources each of zero-mean and unit variance [i.e., $\overline{\eta_i}(t) = 0$ and $\overline{\eta_i(t)\eta_j(t')} = \delta_{i,j}\delta_D(t-t')$ with the overlines standing for ensemble averages, $\delta_{i,j}$ is the Kronecker's delta, and $\delta_D(\cdot)$ is the Dirac's delta function]. Note that the contribution $\mathbf{d}(\mathbf{q},t)$ is non-null only if the diffusion matrix depends on the configurational variables. By recalling Eq. (20), some algebraic steps lead to $\mathbf{v}(\mathbf{q},t) = \mathbf{v}_0(\mathbf{q},t) - \mathbf{D}(\mathbf{q},t)\frac{\partial \ln p(\mathbf{q},t)}{\partial \mathbf{q}} + \mathbf{d}(\mathbf{q},t)$. Clearly $\mathbf{v}(\mathbf{q},t) \neq \mathbf{v}_0(\mathbf{q},t)$.

[28] Let us introduce the array $\tilde{\mathbf{v}}$ with components $\tilde{v}_j(\mathbf{q},t) = v_j(\mathbf{q},t)/\sqrt{D_{ii}(\mathbf{q},t)}$ whose physical dimension is the inverse of the square root of time. Equation (23) becomes $\rho(t) = \int d\mathbf{q}\, p(\mathbf{q},t)[\tilde{\mathbf{v}}(\mathbf{q},t)^T\tilde{\mathbf{D}}(\mathbf{q},t)\tilde{\mathbf{v}}(\mathbf{q},t)]$ with the matrix $\tilde{\mathbf{D}}(\mathbf{q},t)$ defined in Eq. (25). Let us rewrite this expression as $\rho(t) = \int d\mathbf{q}[\hat{\mathbf{v}}(\mathbf{q},t)^T\tilde{\mathbf{D}}(\mathbf{q},t)\hat{\mathbf{v}}(\mathbf{q},t)] \times p(\mathbf{q},t)\tilde{\mathbf{v}}(\mathbf{q},t)^T\tilde{\mathbf{v}}(\mathbf{q},t)$ where $\hat{\mathbf{v}} = \tilde{\mathbf{v}}/\sqrt{\tilde{\mathbf{v}}^T\tilde{\mathbf{v}}}$ is the unit vector collinear with $\tilde{\mathbf{v}}$. Now consider that the quantity within square brackets is positive-valued [since $\tilde{\mathbf{D}}(\mathbf{q},t)$ is positive-definite] and takes a value between the extremes $\epsilon_{\min}(t)$ and $\epsilon_{\min}(t)$ defined in Eq. (26). Thus, $\rho(t) \leqslant \epsilon_{\max}(t)\sum_i \int d\mathbf{q}\, p(\mathbf{q},t)v_i(\mathbf{q},t)^2/D_{ii}(\mathbf{q},t) \leqslant \epsilon_{\max}(t)\sum_i \langle v_i^2\rangle_t D_{ii}^{\min}(t)^{-1}$ where the notation in Eq. (22) has been adopted for the average, and the definition of $D_{ii}^{\min}(t)$ given in Eq. (24) has been recalled for the latter majorization. The analogous relation for the lower bound is readily derived with the operations max and min switched.

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[30] One might take $t_0 = t_{n_c-1} = (n_c - 1)\tau$, that is, the initial time of the n_c-th cycle. In that case, the difference computed in Eq. (35) corresponds to the average dissipated work in such a cycle of transformation (from time 0 on) and the limit becomes $n_c \to \infty$. However, at the periodic steady state, the value $\overline{w}_{\mathrm{diss}}^{\infty}$ is invariant under any shift of the initial time t_0.

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[32] From preliminary calculations it appears the same kind of τ dependence for $\Phi^{\infty}(\tau)$ is found also for different forms of $V_0(q)$, at least under the same kind of energy perturbation applied here; a systematic inspection is however required to make sound statements.

[33] The starting point to derive Eq. (A3) is adopting the following equivalent expression for the classical Liouville operator: $\hat{\mathcal{L}}(t) = \frac{\partial}{\partial \mathbf{q}}^T(\frac{\partial H(\mathbf{q},\mathbf{p},t)}{\partial \mathbf{p}}) - \frac{\partial}{\partial \mathbf{p}}^T(\frac{\partial H(\mathbf{q},\mathbf{p},t)}{\partial \mathbf{q}})$. Such a form is obtained by applying $\hat{\mathcal{L}}(t)$ (in its original form given in the main text) to a generic function of $\mathbf{q}$ and $\mathbf{p}$, expanding the derivatives of products of functions, and deleting the terms with cross derivatives of the Hamiltonian since such derivatives are identically null (and, in any case, the cross terms would cancel by virtue of the Schwarz identity). Equation (A3) then follows by (1) considering that $\frac{\partial \mathcal{H}}{\partial \mathbf{q}} \equiv -\beta^{-1}p_{\mathrm{eq},t}^{-1}\frac{\partial p_{\mathrm{eq},t}}{\partial \mathbf{q}}$ and $\frac{\partial \mathcal{H}}{\partial \mathbf{p}} \equiv -\beta^{-1}p_{\mathrm{eq},t}^{-1}\frac{\partial p_{\mathrm{eq},t}}{\partial \mathbf{p}}$, (2) employing the identities $p_{\mathrm{eq},t}^{-1}\frac{\partial p_{\mathrm{eq},t}}{\partial \mathbf{q}} \equiv \frac{\partial}{\partial \mathbf{q}} - p_{\mathrm{eq},t}\frac{\partial}{\partial \mathbf{q}}p_{\mathrm{eq},t}^{-1}$ and $p_{\mathrm{eq},t}^{-1}\frac{\partial p_{\mathrm{eq},t}}{\partial \mathbf{p}} \equiv \frac{\partial}{\partial \mathbf{p}} - p_{\mathrm{eq},t}\frac{\partial}{\partial \mathbf{p}}p_{\mathrm{eq},t}^{-1}$, and (3) substituting the previous relations in the form of $\hat{\mathcal{L}}(t)$ given above and applying the Schwarz identity to eliminate the contributions with cross derivatives $\frac{\partial}{\partial \mathbf{q}}^T\frac{\partial}{\partial \mathbf{p}}$ and $\frac{\partial}{\partial \mathbf{p}}^T\frac{\partial}{\partial \mathbf{q}}$.

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