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Fluctuation relations for systems in a constant magnetic field

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The validity of the fluctuation relations (FRs) for systems in a constant magnetic field is investigated. Recently introduced time-reversal symmetries that hold in the presence of static electric and magnetic fields and of deterministic thermostats are used to prove the transient FRs without invoking, as commonly done, inversion of the magnetic field. Steady-state FRs are also derived, under the t-mixing condition. These results extend the predictive power of important statistical mechanics relations. We illustrate this via the nonlinear response for the cumulants of the dissipation, showing how the alternative FRs enable one to determine analytically null cumulants also for systems in a single magnetic field.

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I. INTRODUCTION

Statistical mechanics has traditionally investigated macroscopic systems at or near thermodynamic equilibrium, where fluctuations of observables are negligible compared to their mean value. More recently, however, nano and biosciences have called attention to mesoscopic scales, in which fluctuations are considerably more relevant [1,2] and the notion of thermodynamic equilibrium problematic. Consequently, theories of fluctuations and of far-from-equilibrium response, have become a major chapter of contemporary statistical mechanics. In particular, a fruitful line of research on nonequilibrium fluctuations originated from Refs. [3–5], where a class of relations, now known as fluctuation relations (FRs), was introduced, relating the probabilities of opposite energy dissipations of a driven system. Close to equilibrium, FRs reproduce the Green-Kubo and Onsager relations [6,7]. Moreover, FRs are among the few exact results valid almost arbitrarily far from equilibrium and have therefore attracted considerable interest [8–11]. Related relations have, in fact, been determined, for observables such as work heat and energy dissipation, in diverse frameworks [10–22], including dynamical systems and stochastic processes, classical and quantum systems, transient, steady states, and aging systems, for both global and local quantities, and for steady and time-dependent states. FRs have also been experimentally verified in gravitational wave detectors [2].

The main ingredient to prove FRs is some kind of time reversibility. For deterministic dynamics this typically[1] means the standard reversibility defined by the momentum inversion operator $\mathcal{M}_s : \mathfrak{M} \to \mathfrak{M}$:

$$\mathcal{M}_s(\boldsymbol{r}, \boldsymbol{p}) = (\boldsymbol{r}, -\boldsymbol{p}), \quad \forall (\boldsymbol{r}, \boldsymbol{p}) \doteq \Gamma \in \mathfrak{M}, \tag{1}$$

where Γ is a point in the phase space $\mathfrak{M}$ of an N-particle system, with positions $\boldsymbol{r} = \{\boldsymbol{r}_i\}_{i=1}^N$ and momenta $\boldsymbol{p} = \{\boldsymbol{p}_i\}_{i=1}^N$. It is well known that the symmetry $\mathcal{M}_s$ is broken by an external magnetic field, $\boldsymbol{B}$. This has consolidated, also in the domain of FRs, the idea that statistical properties of charged systems in an external magnetic field necessitate special treatment. The usual approach extends the system to include the electric currents generating the magnetic field. Currents, and hence the magnetic field, are reversed under Eq. (1) so the symmetry is restored, in the nonextended problem, by considering two systems subject to opposite external magnetic fields. Following this argument, Casimir [25] modified the Onsager reciprocal relations to relate cross-transport coefficients of systems subject to $\boldsymbol{B}$ and $-\boldsymbol{B}$. Likewise, in his fundamental paper on linear response theory [26], Kubo established symmetry properties of time-correlation functions under the same conditions. In the context of FRs, results for currents and nonequilibrium response were derived that also relate systems under opposite fields [27–30]. Unfortunately, this approach significantly

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[1] Strict time-reversal invariance can be relaxed because the FRs are statistical relations [23,24].

limits the predictive power of the corresponding theories. For instance, identification of null values of transport coefficients in experiments concerning a single system in a given magnetic field based on symmetry is impossible. Similar considerations apply to systems rotating with constant angular velocity, where statistical relations involve two systems rotating with opposite angular velocities.

This point of view, adopted in classic textbooks [31,32], is correct. However, observing that invariance of the Hamiltonian under Eq. (1) is a sufficient but not necessary condition for the properties mentioned above, it was recently demonstrated [33] that a more general approach is possible. There exist, in fact, alternative time-reversal operators [34,35] that, together with the change $t \to -t$, leave the evolving equations invariant without changing the sign of the magnetic field. Exploiting them, standard statistical relations can be immediately reinstated. The generalized time-reversal symmetries defined in the following, and others previously introduced in the literature [33–36], lose the intuitive property of retracing the coordinates in the backward propagation in pairs of trajectories with opposite momenta. By identifying pairs of trajectories with opposite value of a relevant observable (in our case, the average current) upon time reversal, however, they play the same role as $\mathcal{M}_s$ in the derivation of statistical properties and have measurable physical effects. References [34,35] demonstrate this for time-correlation functions in the presence of a magnetic field, illustrating the result also with numerical simulations [34]. Such generalized symmetries might explain why no experimental evidence of the violation of the Onsager reciprocal relations is known [37].

Here, we extend this single-system description to transient and steady-state FRs and to their corollaries, such as relations linking cumulants of currents to driving dissipative forces.

II. THEORY

For convenience, we start by summarizing the derivation of transient and steady-state FRs for general systems, stressing the role of time-reversal symmetry, which is further detailed in the Supplemental Material [38]. Complete derivations of the FRs can be found, e.g., in Refs. [8,39,40].

A. General theory of FRs

Consider a point $\Gamma \in \mathfrak{M}$, evolving under the dynamical equation $\dot{\Gamma} = G(\Gamma)$, where $G : \mathfrak{M} \to \mathfrak{M}$ is a vector field. Once the initial state Γ_0 is specified, this equation admits the formal solution $\Gamma_t = \mathcal{U}_t\Gamma_0$ where $\mathcal{U}_t : \mathfrak{M} \to \mathfrak{M}$ is the propagator for a time $t \in \mathbb{R}$. For any observable $\Psi : \mathfrak{M} \to \mathbb{R}$ and time interval $[t, t+\tau]$ with $\tau > 0$ we define

$$\Psi_{t,t+\tau}(\Gamma) \doteq \int_t^{t+\tau} ds\, \Psi(\mathcal{U}_s\Gamma), \tag{2}$$

which is also an observable. The time average over a time τ of Ψ is given by $\overline{\Psi}_{t,t+\tau}(\Gamma) \doteq \tau^{-1}\Psi_{t,t+\tau}(\Gamma)$. For any interval $(a, b) \subset \mathbb{R}$ we denote by $\{\Psi\}_{(a,b)}$ the set of phase-space points such that Ψ takes values in (a, b):

$$\mathfrak{M} \supset \{\Psi\}_{(a,b)} \doteq \{\Gamma \in \mathfrak{M} : \Psi(\Gamma) \in (a, b)\}.$$

Let $\mathfrak{M}$ be endowed with a probability measure μ_0 of density f_0, at time $t = 0$, so that $d\mu_0(\Gamma) = f_0(\Gamma)d\Gamma$ is the probability of an infinitesimal volume element around Γ. The probability of finding the value of Ψ in a given interval (a, b) at time $t = 0$ is given by

$$\mu_0(\{\Psi\}_{(a,b)}) = \int_{\{\Psi\}_{(a,b)}} d\mu_0(\Gamma) = \int_{\{\Psi\}_{(a,b)}} f_0(\Gamma)d\Gamma$$

Assuming $f_0 \neq 0$ in $\mathfrak{M}$, the dissipation function $\Omega^{(0)}$ is

$$\Omega^{(0)}(\Gamma) \doteq -\nabla_\Gamma \ln f_0 \cdot G(\Gamma) - \Lambda(\Gamma), \tag{3}$$

where $\Lambda = \nabla_\Gamma \cdot \dot{\Gamma}$ is the phase-space expansion rate. An involution $\mathcal{M} : \mathfrak{M} \to \mathfrak{M}$ is a time-reversal symmetry if

$$\mathcal{U}_{-t}\Gamma = \mathcal{M}\mathcal{U}_t\mathcal{M}\Gamma \quad \forall t \in \mathbb{R},\ \forall\Gamma \in \mathfrak{M}. \tag{4}$$

Assuming f_0 even under the action of $\mathcal{M}$, $f_0(\mathcal{M}\Gamma) = f_0(\Gamma)$, it is easy to show that the dissipation function is odd: $\Omega^{(0)}(\mathcal{M}\Gamma) = -\Omega^{(0)}(\Gamma)$.

To derive the transient FR, consider the ratio of the initial probabilities to find the time average of $\Omega^{(0)}$ over τ in a neighborhood of size δ of A and of $-A$ [8,12]:

$$\frac{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta}} f_0(\Gamma)d\Gamma}{\int_{\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta}} f_0(\Gamma)d\Gamma}, \tag{5}$$

where we introduced the intervals $(\pm A)_\delta = (\pm A - \delta, \pm A + \delta) \subset \mathbb{R}$. Invoking the parity of f_0 under $\mathcal{M}$ and the relation between subsets of phase space

$$\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta} = \mathcal{M}\mathcal{U}_\tau\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta}, \tag{6}$$

Eq. (5) can be written as

$$\frac{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = \exp\{-\tau[A + \epsilon(\delta, A, \tau)]\}, \tag{7}$$

where ϵ is a correction term obeying $|\epsilon(\delta, A, \tau)| \leqslant \delta$. Equation (7) is the transient FR, where "transient" means that it expresses a property of an initial state that is not stationary under the dynamics determined by the vector field G. In [38], we show that Eq. (6) is a direct consequence of time-reversal invariance of the dynamical system under $\mathcal{M}$. Thus, time-reversal invariance of the dynamics and of f_0 are the only requirements for the proof: the specific form of $\mathcal{M}$ is irrelevant, as long as Eq. (4) is satisfied.

Introducing the evolved probability measure μ_t, defined by the conservation of probability $\mu_t(E) = \mu_0(\mathcal{U}_{-t}E)$, $E \subset \mathfrak{M}$, and taking the $t \to \infty$ limit followed by the $\tau \to \infty$ limit of Eq. (7), one may write [8,12]

$$\lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{\mu_\infty(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_\infty(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = -[A + \epsilon(A, \delta) - \mathcal{C}_0(A, \delta)], \tag{8}$$

where $\mu_\infty(E) = \lim_{t\to\infty} \mu_t(E)$, $|\epsilon(A, \delta)| \leqslant \delta$, and

$$\mathcal{C}_0(A, \delta) \doteq \lim_{\tau\to\infty} \frac{1}{\tau} \lim_{t\to\infty} \left\langle e^{-\Omega^{(0)}_{0,t} - \Omega^{(0)}_{t+\tau,2t+\tau}} \right\rangle^{(0)}_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)_\delta}} \tag{9}$$

with $\langle\cdot\rangle^{(0)}_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)_\delta}}$ denoting an average with respect to μ_0, under the condition $\overline{\Omega^{(0)}}_{t,t+\tau}(\Gamma) \in (A)_\delta$. Under the additional hypothesis that $\mathcal{C}_0(A,\delta)$ vanishes, Eq. (8) represents the steady-state (μ_∞) FR. That correlations behave in such a way that $\mathcal{C}_0(A,\delta)$ vanishes is a nontrivial requirement. There are indeed systems that remain indefinitely trapped and do not reach a steady state.

B. Fluctuation relations for $B \neq 0$

Let us now consider a three-dimensional system of N particles of charge q_i and mass m_i, subject to uniform and static electric and magnetic fields, in a volume $\mathcal{V}$. The Hamiltonian is

$$H(\Gamma) = H_0(\Gamma) - \sum_{i=1}^{N} q_i \boldsymbol{E}\cdot\boldsymbol{r}_i = \sum_{i=1}^{N} \frac{[\boldsymbol{p}_i - q_i\boldsymbol{A}(\boldsymbol{r}_i)]^2}{2m_i} + \sum_{i,j<i}^{N} V(r_{ij}) - \sum_{i=1}^{N} q_i\boldsymbol{E}\cdot\boldsymbol{r}_i, \tag{10}$$

where $\boldsymbol{A}(\boldsymbol{r})$ is the vector potential associated to the magnetic field $\boldsymbol{B} = \nabla_{\boldsymbol{r}} \times \boldsymbol{A}(\boldsymbol{r})$, $\boldsymbol{E}$ is the electric field, and $V(r_{ij})$ is a pairwise additive interaction potential, depending only on the modulus of the distance between particles: $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. We orient the fields as $\boldsymbol{E} = (E_x, 0, 0)$ and $\boldsymbol{B} = (0, 0, B_z)$. A compatible vector potential, enforcing the Coulomb gauge $\nabla_{\boldsymbol{r}}\cdot\boldsymbol{A}(\boldsymbol{r}) = 0$, is $\boldsymbol{A}(\boldsymbol{r}) = B_z/2(-y, x, 0)$. This setting, while not completely general, includes the majority of physically interesting cases and is usually adopted to discuss the time-reversal properties of systems in external magnetic fields [27,28,41,42]. Furthermore, the choice of the gauge, not altering the form of the evolution equations, does not affect our results (see also [43]).

We now consider deterministic thermostats coupled to this system. We first present time-reversal symmetries that make the proof of FRs applicable, then we obtain explicit expressions for $\Omega^{(0)}$ and for the FRs.

1. The isokinetic nonequilibrium ensemble

The isokinetic thermostat is often used in connection with FRs [8,44]. The isokinetic evolution associated to Eq. (10) is

$$\begin{aligned}
\frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i, & \frac{dp_i^x}{dt} &= F_i^x + \omega_i\big(p_i^y - m_i\omega_i x_i\big) + q_iE_x - \frac{\alpha_{\rm IK}}{2}\big(p_i^x + m_i\omega_i y_i\big),\\
\frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i, & \frac{dp_i^y}{dt} &= F_i^y - \omega_i\big(p_i^x + m_i\omega_i y_i\big) - \frac{\alpha_{\rm IK}}{2}\big(p_i^y - m_i\omega_i x_i\big),\\
\frac{dz_i}{dt} &= \frac{p_i^z}{m_i}, & \frac{dp_i^z}{dt} &= F_i^z - \frac{\alpha_{\rm IK}}{2}p_i^z,
\end{aligned} \tag{11}$$

where F_i^λ and $\omega_i = \frac{B_z q_i}{2m_i}$ are the λ Cartesian component of the interparticle force and the cyclotron frequency for particle i, respectively. Using Gauss' principle of least constraint (see [38]), the thermostat parameter $\alpha_{\rm IK}$ is obtained as

$$\alpha_{\rm IK} = \frac{\sum_{i=1}^N \boldsymbol{\Phi}_i\cdot\dot{\boldsymbol{r}}_i}{\frac{1}{2}\sum_{i=1}^N m_i|\dot{\boldsymbol{r}}_i|^2} = \frac{\sum_{i=1}^N \boldsymbol{\Phi}_i\cdot[\boldsymbol{p}_i - q_i\boldsymbol{A}(\boldsymbol{r}_i)]/m_i}{\sum_{i=1}^N |\boldsymbol{p}_i - q_i\boldsymbol{A}(\boldsymbol{r}_i)|^2/2m_i}, \tag{12}$$

where $\boldsymbol{\Phi}_i = -\nabla_{\boldsymbol{r}_i}H$ are the active forces. Similar to previous studies [44], we take f_0 as the equilibrium distribution

$$f_0(\Gamma) = \frac{\exp[-\beta H_0(\Gamma)]\delta[K(\Gamma) - K^*]}{\int_{\mathfrak{M}} d\Gamma \exp[-\beta H_0(\Gamma)]\delta[K(\Gamma) - K^*]}. \tag{13}$$

In the equation above, $H_0(\Gamma)$ is defined in Eq. (10), $K(\Gamma) = \sum_{i=1}^N m_i|\dot{\boldsymbol{r}}_i|^2/2$ is the microscopic estimator of the kinetic energy (K^* is the value fixed by the initial state), and $\beta = 1/k_BT$. As detailed in [38], Eq. (13) is the equilibrium distribution for the nondissipative isokinetic ensemble in the presence of a magnetic field. Note that, when $\boldsymbol{B} \neq 0$, the total momentum is conserved on average, not instantaneously, explaining the lack of the delta function on momentum usually present in the isokinetic density (see, e.g., Ref. [44]). Direct inspection of Eqs. (11) and (12) shows that the dynamical system is invariant under the time-reversal transformations:

$$\mathcal{M}^{(4)}\Gamma = (x, -y, z, -p^x, p^y, -p^z), \tag{14a}$$
$$\mathcal{M}^{(6)}\Gamma = (x, -y, -z, -p^x, p^y, p^z). \tag{14b}$$

(The superscripts reflect the nomenclature in Ref. [35] where both operators were introduced.) Inspection of Eq. (13) shows that the initial probability density is even. The hypotheses introduced in Sec. II A to derive Eqs. (7) and (8) are then satisfied and we can establish the explicit expression of the FRs for this system. Note that the validity of these time-reversal symmetries ($\mathcal{M}^{(4)}$ and $\mathcal{M}^{(6)}$) depends on the orientation of the magnetic and electric fields. In Ref. [35], however, it was shown that at least one time symmetry remains for arbitrary orientations of the fields, as long as the interparticle potential is isotropic.

2. The dissipation function and the fluctuation relations

The explicit dissipation function is obtained by inserting the specific form of f_0, Eq. (13), and of the equations of motion, Eq. (11), into Eq. (3). As shown in [38], one obtains

$$\Omega^{(0)}(\Gamma) = \beta\sum_{i=1}^N q_i\boldsymbol{E}\cdot\dot{\boldsymbol{r}}_i = \beta\mathcal{V}\boldsymbol{J}(\Gamma)\cdot\boldsymbol{E},$$

where the last equality defines the microscopic estimator for the electric current $\boldsymbol{J} = \mathcal{V}^{-1}\sum_{i=1}^N q_i\dot{\boldsymbol{r}}_i$. The time-averaged dissipation function is obtained from Eq. (2) as $\overline{\Omega^{(0)}}_{0,\tau} = \beta\mathcal{V}\overline{\boldsymbol{J}}_{0,\tau}(\Gamma)\cdot\boldsymbol{E}$. The dissipation function is proportional to the dissipative flux, hence to the dissipated energy. Moreover, as expected, $\Omega^{(0)}$ is odd under $\mathcal{M}^{(4)}$ and $\mathcal{M}^{(6)}$. The transient FR is obtained substituting in Eq. (7):

$$\frac{\mu_0(\{\beta\mathcal{V}\overline{\boldsymbol{J}}_{0,\tau}\cdot\boldsymbol{E}\}_{(-A)_\delta})}{\mu_0(\{\beta\mathcal{V}\overline{\boldsymbol{J}}_{0,\tau}\cdot\boldsymbol{E}\}_{(A)_\delta})} = \exp\{-\tau[A+\epsilon(\delta,A,\tau)]\} \qquad (15)$$

For the steady-state FR to hold, $\mathcal{C}_0(A,\delta)$ of Eq. (9) must vanish. Numerical findings show that the steady-state FR typically holds in chaotic particle systems, characterized by fast decay of correlations [12,13]. In Ref. [44], the test is explicitly performed for color diffusion, but it has never been done for systems in a magnetic field. While interparticle interactions promote disorder, hence decay of correlations, the Lorentz force tends to induce ordered circular motions that may hinder the decay of $\mathcal{C}_0(A,\delta)$. However, such an ordering effect may not be critical, as illustrated by the following example of noninteracting charged particles in constant external magnetic and electric fields oriented as in Eq. (10). In the absence of a thermostat, this model is analytically solvable and yields

$$\mathcal{C}_0(A,\delta) = \lim_{\tau\to\infty}\frac{1}{\tau}\lim_{t\to\infty}\left\langle \exp\left[-\beta\sum_i^N \frac{E_x q_i v_i^\perp}{\omega_i}\left\{\Upsilon_i(t) + 2\sin\left(\frac{\omega_i t}{2}\right)[\Theta_i(t)\cos(\omega_i\tau) + \Xi_i(t)\sin(\omega_i\tau)]\right\}\right]\right\rangle^{(0)}_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)_\delta}},$$

where

$$\Upsilon_i(t) = \cos(\phi_i)[1-\cos(\omega_i t)] + \sin(\phi_i)\sin(\omega_i t),$$

$$\Theta_i(t) = \cos(\phi_i)\sin\left(\frac{3\omega_i t}{2}\right) - \sin(\phi_i)\cos\left(\frac{3\omega_i t}{2}\right),$$

$$\Xi_i(t) = \cos(\phi_i)\cos\left(\frac{3\omega_i t}{2}\right) - \sin(\phi_i)\sin\left(\frac{3\omega_i t}{2}\right),$$

and $v_i^\perp$ and ϕ_i are constants fixed by the initial conditions and by the relative intensities of the fields (see [38] for details). Notably, the expression in angular brackets is bounded for all values of t and τ implying that $\mathcal{C}_0(A,\delta)$ for this model is indeed zero. The thermostatted solution can be obtained numerically. As shown in [38], for appropriate relative intensities of the fields, the motion remains bounded in the direction parallel to the electric field, canceling the correlation term also for a noninteracting isokinetic model. This analysis holds in general for the components of the electric field orthogonal to the magnetic field. If the fields have a parallel component, the magnetic field, which only influences the orthogonal motion, does not directly affect dissipation in the parallel direction. Since interactions should further reduce correlation times, this argument suggests that the steady-state condition can be verified. Future studies will investigate more general situations.

Assuming convergence of Eq. (9), and apart from an error $O(\tau^0)$ in the exponential, the steady-state FR can be written as

$$\frac{\mu_\infty\left(\{\beta\mathcal{V}\overline{\boldsymbol{J}}_{0,\tau}\cdot\boldsymbol{E}\}_{(-A)_\delta}\right)}{\mu_\infty\left(\{\beta\mathcal{V}\overline{\boldsymbol{J}}_{0,\tau}\cdot\boldsymbol{E}\}_{(A)_\delta}\right)} = \exp\{-\tau[A+\epsilon(\delta,A,\tau)]\}, \qquad (16)$$

where $|\epsilon(\delta,A,\tau)| \leqslant \delta$.

It is worth stressing that, although Eqs. (15) and (16) are misleadingly similar, they refer to very different situations. Transient FRs are associated to the statistics of the ensemble describing the initial (typically equilibrium) state. They describe a statistical property of many experiments of (short or long) duration τ. Differently, steady-state FRs refer to the steady-state statistics of the currents of a single object or realization of the system. They require a kind of decorrelation between initial and final macrostates, which is why t has to become large before τ does. This is not the mixing condition of ergodic theory, which corresponds to decay of correlations of microscopic events *within* a steady state [12,13,45]. If correlations do not decay, some kind of FR may still hold, but they (and derived relations) would take a different form (see, e.g., Refs. [39,46–48]).

3. The generalized Nosé-Hoover thermostat

While it is widely used in theoretical and simulation problems, the isokinetic thermostat does not sample the canonical ensemble in equilibrium situations and therefore its interest is somewhat limited. Recently, a generalization of the Nosé-Hoover thermostat has been proposed for systems in external magnetic field [49]. As for the case $\boldsymbol{B}=0$, this generalization is based on the extension of the phase space through conjugate variables s and ξ, mimicking the effect of a thermal bath. This thermostat can be easily modified to include an (static) external electric field (see also discussion in [49]), which allows us to extend the applicability of FRs. The resulting generalized Nosé-Hoover dynamical system is

$$\frac{dx_i}{dt} = \frac{p_i^x}{m_i} + \omega_i y_i, \qquad \frac{dp_i^x}{dt} = F_i^x + \omega_i\left(p_i^y - m_i\omega_i x_i\right) + q_i E_x - \xi\left(p_i^x + m_i\omega_i y_i\right),$$

$$\frac{dy_i}{dt} = \frac{p_i^y}{m_i} - \omega_i x_i, \qquad \frac{dp_i^y}{dt} = F_i^y - \omega_i\left(p_i^x + m_i\omega_i y_i\right) - \xi\left(p_i^y - m_i\omega_i x_i\right),$$

$$\frac{dz_i}{dt} = \frac{p_i^z}{m_i}, \qquad \frac{dp_i^z}{dt} = F_i^z - \xi p_i^z,$$
$$\frac{d\ln s}{dt} = \xi, \qquad \frac{d\xi}{dt} = \frac{1}{\tau_{NH}^2}\left[\frac{K(\Gamma) - K^*}{K^*}\right] = \frac{\delta K(\Gamma)}{\tau_{NH}^2}, \tag{17}$$

where τ_{NH} is the characteristic time of the thermostat. It is important to note that the kinetic energy of this system now fluctuates around the target value K^*, related to the temperature of the system via $\beta = 3N/(2K^*)$. As proved in [49], the dynamical system (17) with $E_x = 0$ conserves the quantity $H_{NH}(\Gamma, \xi, s) = H_0(\Gamma) + K^*[\tau_{NH}^2\xi^2 + 2\ln s]$ and samples the equilibrium distribution

$$f_0(X) = \mathcal{Z}^{-1}\exp[-\beta H_0(\Gamma)]\exp\left[-\beta K^*\tau_{NH}^2\xi^2\right], \tag{18}$$

where $\mathcal{Z}$ is the partition function and X denotes the extended phase space $X = (\Gamma, \xi)$. As in standard Nosé-Hoover dynamics, the marginal probability obtained integrating Eq. (18) with respect to ξ is the canonical density for the physical variables.

Direct inspection shows that (17) is invariant under

$$\mathcal{M}_{ext}^{(4)}(\Gamma, s, \xi) = (x, -y, z, -p^x, p^y, -p^z, s, -\xi), \tag{19a}$$
$$\mathcal{M}_{ext}^{(6)}(\Gamma, s, \xi) = (x, -y, -z, -p^x, p^y, p^z, s, -\xi) \tag{19b}$$

together with time inversion. The equilibrium density Eq. (18) is even under these transformations. The conditions for the transient FR are then verified and we can calculate the dissipation function, Eq. (3). In the same fashion as the isokinetic case (see [38]), it is possible to show that $\nabla_X \ln f_0 \cdot \dot{X} = \beta 2K^*\xi - \beta\sum_{i=1}^N q_i\dot{\boldsymbol{r}}_i \cdot \boldsymbol{E} - \beta\xi\delta K(\Gamma)$ while the compressibility of the (extended) phase space is given by $\Lambda = -\beta 2K^*\xi$. Substituting in Eq. (3) we obtain

$$\Omega^{(0)}(X) = \beta V\boldsymbol{J}(\Gamma)\cdot\boldsymbol{E} + \beta\xi\delta K(\Gamma) \tag{20}$$

for the *instantaneous* dissipation function of the system (17), odd under the valid time-reversal symmetries. There are now two sources of dissipation: the electric field and the temperature gradient between system and reservoir. In the expression for the average dissipation function $\overline{\Omega^{(0)}}_{0,\tau}$, the contribution due to the temperature gradient is negligible compared to the other, for $\tau \gg \tau_{NH}$. In this limit the FR takes the same form as for the isokinetic case.

In Fig. 1 we illustrate the effect of the generalized time-reversal symmetry on the instantaneous dissipation function, Eq. (20), computed for a system of 125 molecules of liquid NaCl at $T = 1550$ K along a "forward" (red curve, open squares) and a "backward" (blue curve, open triangles) trajectory under $\mathcal{M}_{ext}^{(4)}$. The plot clearly shows the odd signature of the observable. The result was obtained simulating the dynamical system (17) with the algorithm and the basic setup described in Ref. [49]. First, the system is equilibrated for 25 ps at zero electric and magnetic fields. The two fields are then switched on and the system is evolved until a steady state is reached. The values used for the fields are compatible with other simulations of the same (nondissipative) system and have been set to $B_z = 50$ and $E_x = 10$ in code units (c.u.) (see Ref. [49] for details). A production run is then started, evolving the system for 25 ps ("forward" trajectory). The final phase-space point is then transformed through $\mathcal{M}_{ext}^{(4)}$ and the system evolved again for 25 ps ("backward" trajectory). During the two production runs, $\Omega^{(0)}$ is computed every 5 fs, with the results shown in the figure.

III. CONCLUDING REMARKS

We have shown that transient and steady-state FRs can be derived in the presence of a static and uniform magnetic field, without inversion of $\boldsymbol{B}$. This is possible because the dynamical system admits time-reversal symmetries that, at variance with the standard momentum reversal, are not violated by the field. Steady-state FRs require, as always, the decay of appropriate correlations. For $\boldsymbol{B} = 0$, this condition may be violated under strong drivings inducing ordered phases, in which back currents are suppressed [47,48,50]. The effect of magnetic fields on these correlations needs further investigation, but in the case discussed above they do not alter the validity of the FRs.

Use of a single magnetic field immediately improves the predictive power of the theory. For instance, consider a vector of n affinities $\mathscr{F}$, the corresponding n amounts of energy and matter exchanged between the reservoirs and a reference reservoir in a time interval $[0, t]$, Δx, and an n-dimensional vector of parameters λ. Let the cumulant generating function of $\mathscr{F}$ be defined by

$$G_t(\lambda, \mathscr{F}; \boldsymbol{B}) = \int p_t(\Delta x, \mathscr{F}; \boldsymbol{B})\exp(-\lambda\Delta x)d^n\Delta x,$$

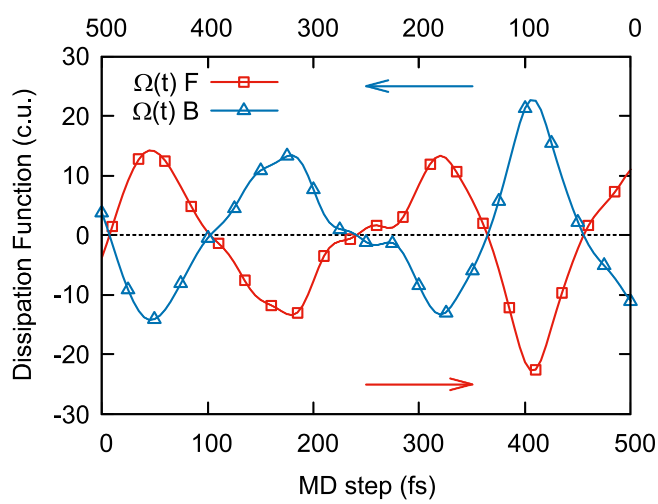

FIG. 1. Instantaneous dissipation function from Eq. (20) for the last 500 fs of the "forward" trajectory (red curve, open squares) and for the first 500 fs of the "backward" trajectory (blue curve, open triangles) obtained via $\mathcal{M}_{ext}^{(4)}$. The opposite values of the dissipation demonstrate the odd signature under the generalized time reversal. This does not require trajectories to be traced backward in configuration space. Results are for liquid NaCl.

where p_t is the probability density of Δx derived from the grand-canonical ensemble, at fixed affinities and constant $\boldsymbol{B}$. Then, following the procedure for the asymptotic (not necessarily steady-state) FR [8], Ref. [28] defines the asymptotic generating function as $Q(\lambda, \mathscr{F}; \boldsymbol{B}) = -\lim_{t\to\infty}(1/t)\ln G_t(\lambda, \mathscr{F}; \boldsymbol{B})$. The corresponding cumulants, i.e., the derivatives of Q with respect to the components of λ evaluated at $\lambda = 0$, are then expanded as a power series of $\mathscr{F}$, around $\mathscr{F} = 0$:

$$Q(\lambda, \mathscr{F}; \boldsymbol{B}) = \sum_{m,n=0}^{\infty} \frac{Q_{\alpha_1\cdots\beta_n}(\boldsymbol{B})}{m!n!}\lambda_{\alpha_1}\cdots\lambda_{\alpha_m}\mathscr{F}_{\beta_1}\cdots\mathscr{F}_{\beta_n}$$

with λ_i the ith element of λ, $\mathscr{F}_j$ the jth affinity, and

$$Q_{\alpha_1\cdots\beta_n}(\boldsymbol{B}) = \left.\frac{\partial^{m+n}Q}{\partial\lambda_{\alpha_1}\cdots\partial\lambda_{\alpha_m}\partial\mathscr{F}_{\beta_1}\cdots\partial\mathscr{F}_{\beta_n}}\right|_{\lambda=0;\mathscr{F}=0}.$$

In terms of Q and of the reversibility based on the inversion of $\boldsymbol{B}$, the asymptotic FR is then written as $Q(\lambda, \mathscr{F}; \boldsymbol{B}) = Q(\mathscr{F} - \lambda, \mathscr{F}; -\boldsymbol{B})$ which imposes certain constraints on $Q_{\alpha_1\cdots\beta_n}$. For instance, Eq. (43) of Ref. [28] states that $Q_{\alpha_1\cdots\alpha_m}(0; \boldsymbol{B}) = (-1)^m Q_{\alpha_1\cdots\alpha_m}(0; -\boldsymbol{B})$. Using instead $\mathcal{M}^{(4)}$ or $\mathcal{M}^{(6)}$ of Eqs. (14), one also obtains $Q_{\alpha_1\cdots\alpha_m}(0; \boldsymbol{B}) = (-1)^m Q_{\alpha_1\cdots\alpha_m}(0; \boldsymbol{B})$ which entails the stronger result $Q_{\alpha_1\cdots\alpha_m}(0; \boldsymbol{B}) = 0$ for odd m and any $\boldsymbol{B}$.

The work presented in this Rapid Communication thus enables a reformulation of general results, based in particular on FRs, e.g., Refs. [8,28], relaxing the prescription of opposite magnetic fields (or angular velocities) and restores the full predictive power of a number of statistical results for systems long considered as exceptions. The two deterministic thermostats considered in this Rapid Communication are commonly used to discuss FRs (isokinetic) and to run constant temperature molecular dynamics simulations (Nosé-Hoover). Future work will investigate the issue of time reversibility and the FRs in the presence of magnetic fields also for stochastic thermostats [15].

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