Contribution of the stochastic forces to the fluctuation theorem

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In some recent papers, the use of random forces has been related to a systematic breakdown of the fluctuation theorem. In the framework of nonequilibrium molecular dynamics, we provide a derivation of this theorem for systems driven by both deterministic and stochastic forces. It turns out that it is still valid and describes the total dissipation, explicitly the sum of two dimensionless works for which fluctuation relations may fail. We numerically study their range of validity, comment on experimental results, and point out in which limit a noise can be neglected.

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Since the early 1990s [1], new theorems have been proven that provide a much more accurate description of far from equilibrium systems than was previously possible and extend fluctuation-dissipation relations to this regime. They characterize the probability distribution of the dissipation (or generalized entropy production), extend some results of linear response theory to the nonlinear regime, and have been experimentally verified. For a system initially at equilibrium which is driven out of equilibrium, the transient fluctuation theorem (TFT) states that the so-called dissipation measured over a period of t, Ω_t, satisfies

$$\ln\left(\frac{\mathrm{p}(\Omega_t = A)}{\mathrm{p}(\Omega_t = -A)}\right) = A. \tag{1}$$

This relation is only asymptotically valid if the system is initially in a steady state, and is then referred to as the steady-state fluctuation theorem (SSFT).

There are three major derivations of the FTs: a physical one [2,3] and a more mathematical one [4] for deterministic dynamics, and another for Markov processes [5]. Their subject sometimes differs and we focus in this Brief Report on the ones that involve the dissipation function. The choice of a deterministic or stochastic framework essentially depends on how the thermostat or surroundings are seen. Markov processes, as Langevin dynamics are, describe the evolution of few particles (e.g., a harmonic oscillator [6], a colloidal particle [7]) and reduce the thermostat to a stochastic object. On the other hand, the thermostat is treated explicitly as part of the system in nonequilibrium molecular dynamics (NEMD), which lead to an exact description of the forces on the particles of interest. However, a fictitious force acts on the thermostat particles to constrain energy or temperature. From a practical point of view, Eq. (1) is valid in both descriptions [8]. Moreover, the approaches turn out to be complementary as some systems can only be described by stochastic dynamics (e.g., sets of spins) whereas the deterministic framework is the only one valid when the thermostat's history is involved, as for particles in a viscoelastic solvent [9]. A last distinction is the physical interest of the proofs: the origin of irreversibility is blurred by stochastic processes whereas it is related to phase-space properties in deterministic dynamics.

A topic of recent interest is the role of the nature of the external force (deterministic vs. stochastic). For example, in experiments carried out in an electronic RC circuit [10], vibrating metallic plates [11], wave turbulence [12], colloidal particles, and AFM cantilever [13], the FT has been reported to fail in presence of a stochastic force.

In the present Brief Report we consider a system driven by both stochastic and deterministic forces and derive the FT in the NEMD framework to complete the Markovian picture. The dissipation function, the equivalent in a continuous phase-space of the action functional $\bar{W}$ defined by Lebowitz and Spohn [5], turns out to be the sum of the dimensionless work done by all forces. Separately, these terms may or may not satisfy any fluctuation relation. We quantify this statement with the help of numerical simulations and explain the results of the previously cited experiments.

First, explicit dynamics must be set: a deterministic time-reversible thermostat is used [14] and, to be physically relevant, the random force ξ is chosen to be a Gaussian Ornstein-Uhlenbeck noise of mean $\langle\xi\rangle = 0$ and covariance $\langle\xi(t)\xi(t+s)\rangle = \sigma^2 e^{-s/\tau}$ (as in [10,13]). Therefore, the equations of motion are

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i(\mathbf{\Gamma})F_e, \tag{2a}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{q}) + \mathbf{D}_i(\mathbf{\Gamma})(F_e + \xi) - \alpha(\mathbf{p}_i - \boldsymbol{\zeta}_i), \tag{2b}$$

$$\dot{\xi} = -\frac{\xi}{\tau} + \eta, \tag{2c}$$

where $\mathbf{q}_i$ and $\mathbf{p}_i$ are the coordinates and momenta of the ith particle, $\mathbf{F}_i$ the interparticle force on this particle, $\mathbf{C}$ and $\mathbf{D}$ couple the external field F_e to the system, τ is the autocorrelation time of the stochastic force, α fixes the kinetic or total energy, $\boldsymbol{\zeta}_i$ is an instantaneous streaming velocity for particle i (which is system dependent and will be defined for a particular system later in this paper), and η is a Gaussian noise of zero mean and covariance $\langle\eta(t)\eta(t+s)\rangle = 2\sigma^2\delta(s)/\tau$.

For the derivation to be rigorous, all the computations are done with a discrete version of Eq. (2c) where the stochastic force is constant over $\delta t = t/N_T$ time intervals, with N_T a number that can be taken as large as desired.

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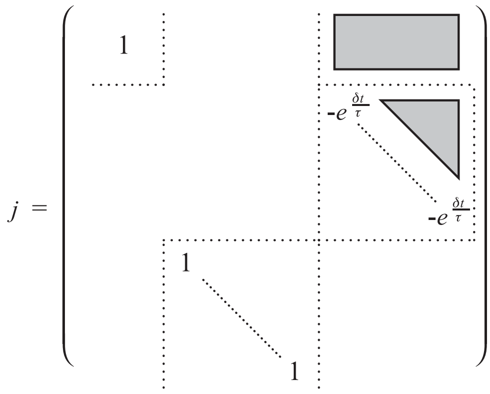

FIG. 1. Fundamental block of the Jacobian matrix for M^{T}.

The usual derivation of the FT relies on the existence of a time-reversal mapping M^{T} [3]: for any function of interest $\Phi(\mathbf{\Gamma})$ (a flux, a work, etc.), $\Phi_t(\mathbf{\Gamma}) = \int_0^t \Phi(\mathbf{\Gamma}(s))ds$ and $\Phi_t(\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}(t))$ take exact opposite values. For simplicity, we assume that the properties of $\mathbf{C}$ and $\mathbf{D}$ mean that without noise M^{T} is a simple velocity reversal. To preserve time reversibility, we consider an extended phase-space $E_{\mathrm{ex}} = \{\mathbf{\Gamma}_{\mathrm{ex}} = (\mathbf{q},\mathbf{p},\xi,\{\eta(s)\}_{s=-t..t})\}$. In a way, we deal with the stochastic behavior by adding information about the random force. Given Eq. (2c), an analytic expression of this mapping, which is no longer volume preserving, can be derived:

$$\begin{matrix} \mathbf{q} & & \mathbf{q} \\ \mathbf{p} & & -\mathbf{p} \\ \xi & \overrightarrow{\mathrm{M}^{\mathrm{T}}} & \xi \\ \{\eta(-s)\}_{s=0..t} & & \{\eta(s)\}_{s=0..t} \\ \{\eta(s)\}_{s=0..t} & & \{\eta^*(s)\}_{s=0..t} \end{matrix} \tag{3}$$

with

$$\eta^*(s) = \frac{2}{\tau}e^{s/\tau}\left(\xi - \int_0^s \eta(-k)e^{-k/\tau}dk\right) - \eta(-s). \tag{4}$$

As expected, the future of $\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}$ depends on the past history of $\mathbf{\Gamma}$. In the discrete case, the Jacobian matrix for one particle and one Cartesian dimension, restricted to $\{\xi,\{\eta(s)\}_{s=-t..t}\}$ is shown Fig. 1. The determinant of this matrix is $|j| = e^{t/\tau}$ and the one of the whole Jacobian matrix is therefore $|J| = e^{Nd_c t/\tau}$, where N is the number of particles to which the stochastic force is applied and d_c the Cartesian dimension of the physical space. As in [3], we define the usual phase-space expansion rate Λ and dissipation function Ω_t via

$$\Lambda(\mathbf{\Gamma}) = \frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}, \quad \Omega_t(\mathbf{\Gamma}) = \ln\left(\frac{f_{\Gamma}(\mathbf{\Gamma}(0),0)}{f_{\Gamma}(\mathbf{\Gamma}(t),0)}\right) - \Lambda_t(\mathbf{\Gamma}), \tag{5}$$

where $\mathbf{\Gamma} = (\mathbf{q},\mathbf{p})$ and f_{Γ} is the related physical distribution function. Because of the use of a deterministic thermostat, Λ does not vanish but characterizes heat exchanges between the particles of interest and the thermostat [14]. In the extended phase-space E_{ex}, it contributes to the volume change of an element $d\Gamma_{\mathrm{ex}}$ which evolves in time according to the equations of motion. Its contraction or expansion is quantified by the Liouville's theorem, notably leading to the relation $\mathrm{M}^{\mathrm{T}}d\Gamma_{\mathrm{ex}}(t) = d\Gamma_{\mathrm{ex}}|J|e^{\Lambda_t(\mathbf{\Gamma})-Nd_c t/\tau} = d\Gamma_{\mathrm{ex}}e^{\Lambda_t(\mathbf{\Gamma})}$. Moreover, we assume that the noise $\mathbf{\Gamma}_s = (\xi,\{\eta(s)\}_{s=-t..t})$ is initially selected from a steady distribution $f_{\mathbf{\Gamma}_s}$, which therefore fulfils $f_{\mathbf{\Gamma}_s}(\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}_s(t)) = f_{\mathbf{\Gamma}_s}(\mathbf{\Gamma}_s)$. Thus, the fluctuation theorem is straightforward:

$$\begin{aligned} \mathrm{p}(\Omega_t = A) &= \int_{\mathbf{\Gamma}_{\mathrm{ex}},\Omega_t(\mathbf{\Gamma}_{\mathrm{ex}})=A} d\Gamma_{\mathrm{ex}} f(\mathbf{\Gamma}_{\mathrm{ex}},0) \\ &= \int_{\mathbf{\Gamma}_{\mathrm{ex}},\Omega_t(\mathbf{\Gamma}_{\mathrm{ex}})=-A} \mathrm{M}^{\mathrm{T}}d\Gamma_{\mathrm{ex}}(t) f(\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}_{\mathrm{ex}}(t),0) \\ &= \int_{\mathbf{\Gamma}_{\mathrm{ex}},\Omega_t(\mathbf{\Gamma}_{\mathrm{ex}})=-A} d\Gamma_{\mathrm{ex}}e^{\Lambda_t(\mathbf{\Gamma})} f(\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}_{\mathrm{ex}}(t),0) \\ &= e^A \int_{\mathbf{\Gamma}_{\mathrm{ex}},\Omega_t(\mathbf{\Gamma}_{\mathrm{ex}})=-A} d\Gamma_{\mathrm{ex}} f_{\mathbf{\Gamma}}(\mathbf{\Gamma},0) f_{\mathbf{\Gamma}_s}(\mathrm{M}^{\mathrm{T}}\mathbf{\Gamma}_s(t)) \\ &= e^A \int_{\mathbf{\Gamma}_{\mathrm{ex}},\Omega_t(\mathbf{\Gamma}_{\mathrm{ex}})=-A} d\Gamma_{\mathrm{ex}} f_{\mathbf{\Gamma}}(\mathbf{\Gamma},0) f_{\mathbf{\Gamma}_s}(\mathbf{\Gamma}_s) \\ &= e^A \mathrm{p}(\Omega_t = -A). \end{aligned} \tag{6}$$

We use the fact that Ω_t is odd under time-reversal mapping and that at time zero, i.e., when the stochastic force is turned on, distributions of $\mathbf{\Gamma}$ and $\mathbf{\Gamma}_s$ are independent. This result is a direct and more formal extension of the one derived in [15]. We note that both the Gaussian deterministic thermostat, the stochastic and the deterministic forces can be chosen to act on only few particles.

It is interesting to sum up the assumptions used. As in the previous derivation, the accessible phase-space at any time must be included in the initial one (that is *ergodic consistency* [3]) and the initial distribution function for the positions and momenta must be invariant via time reversal, as every equilibrium distribution is. Moreover, the stochastic force has to adopt a constant distribution from $t = 0$. The question of time reversibility is more sensitive: deterministic dynamics has to be time reversible, otherwise although the FT would still be valid by considering the system a Markov process, Ω_t might take a physically useless form.

Recent experiments using random forces [10–13] are not in contradiction with this result. We simply note that the FT describes a particular function, the dissipation function, that is not the one studied is these articles and is not always the dimensionless mechanic work done on the system (for instance, see [7]). Generally speaking, as soon as thermal fluctuations are neglected and recorded work values are very much larger than $k_B T$, it is not possible to apply the FT derived above. Indeed, because of macroscopic irreversibility, negative values of the dissipation will not be observed.

Let us present an application of this theorem by considering a system driven out of equilibrium by a noisy external field. We set the following dynamics:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m}, \tag{7a}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i(\mathbf{q}) + c_i(F_e + \xi(t))\mathbf{e}_x - \alpha\left(\mathbf{p}_i - c_i\frac{J_x}{N}\mathbf{e}_x\right), \tag{7b}$$

$$\dot{\xi}(t) = -\frac{\xi(t)}{\tau} + \eta(t), \tag{7c}$$

where $c_i = (-1)^i$ is a physical quantity (e.g., electric charge) and $\mathbf{e}_x$ is the unity vector in the x direction. An external field is applied with mean value F_e and with exponentially time-correlated noise $\xi(t)$, which induces a flux $J_x = \sum c_i \dot{\mathbf{q}}_i \cdot \mathbf{e}_x$. The thermostat α fixes the kinetic energy $[\frac{1}{2m}\sum \mathbf{p}_i \cdot (\mathbf{p}_i - c_i \frac{J_x}{N}\mathbf{e}_x)]$, and is given by $\alpha = \sum \mathbf{F}_i \cdot (\mathbf{p}_i - c_i \frac{J_x}{N}\mathbf{e}_x)/\sum \mathbf{p}_i \cdot (\mathbf{p}_i - c_i \frac{J_x}{N}\mathbf{e}_x)$. If $H(\mathbf{\Gamma})$ is the Hamiltonian characterizing the initial canonical distribution, the dissipation function is [3]

$$\Omega_t(\mathbf{\Gamma}) = \int_0^t \{\beta \dot{H}(\mathbf{\Gamma}(s)) + d_c N \alpha(\mathbf{\Gamma}(s))\} ds \quad (8a)$$

$$= \beta F_e \int_0^t J_x(s) ds + \beta \int_0^t \xi(s) J_x(s) ds. \quad (8b)$$

Therefore, Ω_t is found to be the sum of a mean field term $\Omega_{F_e,t}$ and a noise-related one $\Omega_{\xi,t}$. The experimental use of the FT is to measure a mean external force via the recording of a flux. In such a situation, one focused only on one part of the dissipation function, Ω_{F_e}, whose behavior is so far unknown. We address this question numerically, considering a set of particles under a color field (an electric field without any electrostatic interparticle forces). The simulation used 32 particles of color $c_i = (-1)^i$ interacting via the Weeks-Chandler-Anderson short-ranged repulsive pair potential [16] in a two-dimensional space with periodic boundary conditions. The temperature was set at 1, the density at 0.4 and the integration time at 1.6. All trajectories started from an isokinetic equilibrium distribution. We define the asymmetry functions ρ_{tot}, ρ_{F_e} and ρ_ξ as the left-hand side of Eq. (1) and equivalents. First, we fix $\tau = 0.1$ and $\sigma = 2F_e$ in which case we find $\langle \Omega_{F_e,t}\rangle \simeq \langle \Omega_{\xi,t}\rangle$.

If $\langle \Omega_t \rangle \ll 1$, the PDF of $\Omega_{F_e,t}$ appears Gaussian whereas those of $\Omega_{\xi,t}$ and Ω_t have exponential tails (Fig. 2) [17]. The FT is found to be valid for these two functions, indicating there is little correlation.

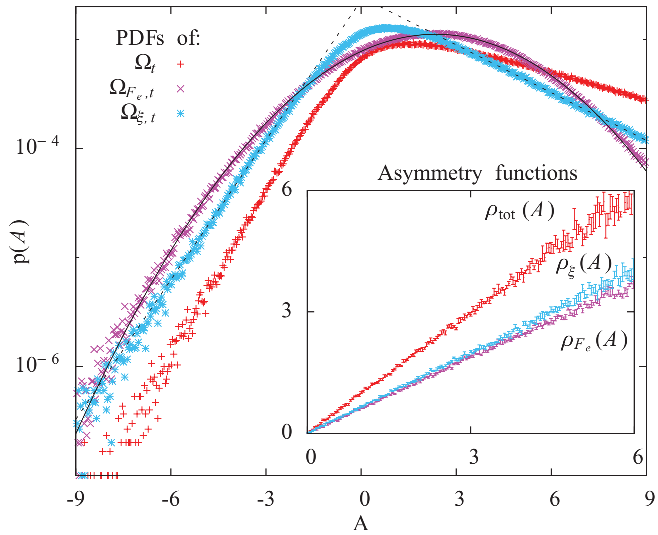

FIG. 3. (Color online) PDFs and asymmetry functions for $\sigma = 2F_e = 0.4$, that is $\langle \Omega_t \rangle \simeq 5$. Gaussian and exponential fits are solid and dashed lines. The slopes of linear fits are 0.996 ± 0.002 for ρ_{tot}, 0.617 ± 0.001 for ρ_{F_e} and 0.660 ± 0.001 for ρ_ξ.

For most important fields ($\langle \Omega_t \rangle \sim 1$), the shapes of the PDFs remain the same, but ρ_{F_e} and ρ_ξ are straight lines of slope less than one, cf. Fig. 3. The correlations between $\Omega_{F_e,t}$ and $\Omega_{\xi,t}$ become sizable and even if some responses remain linear (e.g., $\langle J_{x,t}\rangle \propto F_e$), the system no longer acts as if it is at equilibrium.

For high fields ($\langle \Omega_t \rangle \gg 1$) ρ_ξ ceases to be a straight line. Once again, the total dissipation function has to be considered for the FT to be valid, cf. Fig. 4. Another point of interest is the condition for the noise to be neglected. If we assume that the flux is normally distributed, ρ_{F_e} is a straight line whose

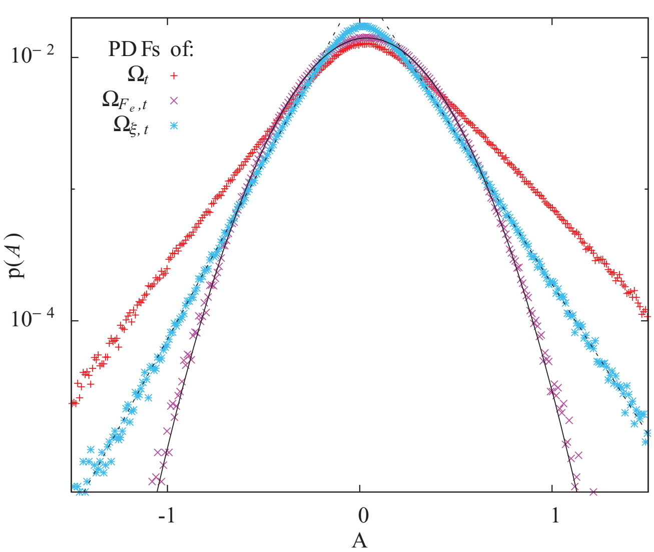

FIG. 2. (Color online) PDFs for $\sigma = 2F_e = 0.1$, that is $\langle \Omega_t \rangle \simeq 0.1$. Gaussian and exponential fits are solid and dashed lines. The slopes of linear fits are 0.995 ± 0.004 for ρ_{tot}, 0.993 ± 0.005 for ρ_{F_e} and 0.992 ± 0.005 for ρ_ξ.

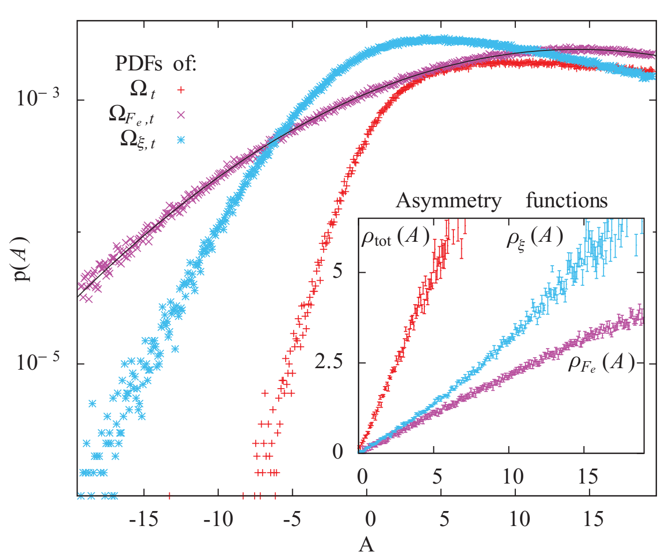

FIG. 4. (Color online) PDFs and asymmetry functions for $\sigma = 2F_e = 2$, that is $\langle \Omega_t \rangle \simeq 30$. The solid line is the Gaussian fit. The slopes of linear fits are 0.995 ± 0.004 for ρ_{tot} and 0.211 ± 0.001 for ρ_{F_e}. ρ_ξ is not linear.

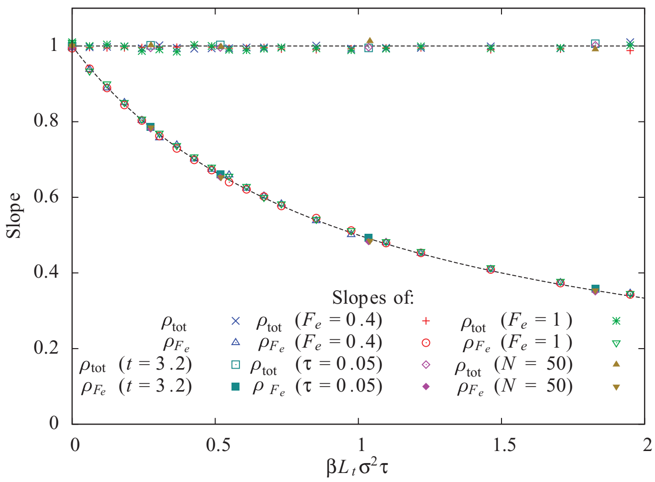

FIG. 5. (Color online) Slopes of linear fits versus σ for parameters differing from $F_e = 0.1$, $t = 1.6$, $\tau = 0.1$, and $N = 32$. All the $\rho_{\rm tot}$ data have a slope ~ 1. When plotted versus $\beta L_t \sigma^2 \tau$, all the ρ_{Fe} data lie on a master curve with equation $f(x) = (1 + x)^{-1}$ (dashed line).

slope s is

$$s = \frac{2\langle J_{x,t}(\sigma, F_e)\rangle}{\beta F_e \sigma^2_{J_{x,t}}(\sigma, F_e)}, \tag{9}$$

where $\langle J_{x,t}\rangle$ and $\sigma^2_{J_{x,t}}$ are the mean value and the variance of the integrated flux and (σ, F_e) denotes that the dynamics involve a stochastic and a mean field. Given that the noise does not change the mean value of the flux,

$$2\langle J_{x,t}(\sigma, F_e)\rangle = 2\langle J_{x,t}(0, F_e)\rangle = \beta F_e \sigma^2_{J_{x,t}}(0, F_e). \tag{10}$$

The last equality is the FT for a system driven by a constant field. Introducing the linear response coefficient L_t defined by $\langle J_{x,t}(F_e)\rangle = t F_e L_t$, we can see that $\sigma_{J_{x,t}}$ does not depend on F_e in this regime. It is then natural to assume $\sigma_{J_{x,t}}(\sigma, F_e) = \sigma_{J_{x,t}}(\sigma, 0)$ and finally

$$s = \frac{\sigma^2_{J_{x,t}}(0,0)}{\sigma^2_{J_{x,t}}(\sigma,0)}. \tag{11}$$

Therefore, in the linear regime and for Gaussian fluxes, the behavior of ρ_{F_e} does not depend on the dimensionless number σ/F_e but on that describing the response to noise, i.e., $\beta L_t \sigma^2 \tau$. According to the numerical results, for this system the values of the slopes are given by the function $(1 + \beta L_t \sigma^2 \tau)^{-1}$, cf. Fig. 5.

We have shown that the FT is valid for systems driven out of equilibrium by both stochastic and deterministic forces, provided the full dissipation function is considered. The assumption of time reversibility is then weaker than it initially seemed. A main result is that the unavoidable noise of an external field can be neglected in the limit $\beta L_t \sigma^2 \tau \ll 1$ (and not in the limit $\sigma \ll F_e$).

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[17] For small noise, Ω_ξ is approximately the product of two uncorrelated and normally distributed random numbers, whose PDF has an exponential asymptotic decrease.