Generic Properties of Stochastic Entropy Production

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We derive an Itô stochastic differential equation for entropy production in nonequilibrium Langevin processes. Introducing a random-time transformation, entropy production obeys a one-dimensional drift-diffusion equation, independent of the underlying physical model. This transformation allows us to identify generic properties of entropy production. It also leads to an exact uncertainty equality relating the Fano factor of entropy production and the Fano factor of the random time, which we also generalize to non-steady-state conditions.

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The laws of thermodynamics can be extended to mesoscopic systems [1–5]. For such systems, energy changes on the order of the thermal energy k_BT are relevant. Here, k_B is the Boltzmann constant and T the temperature. Therefore, thermodynamic observables associated with mesoscopic degrees of freedom are stochastic. A key example of such thermodynamics observables is the stochastic entropy production in nonequilibrium processes. Recent experimental advances in micromanipulation techniques permit the measurement of stochastic entropy production in the laboratory [6–10].

Certain statistical properties of stochastic entropy production are generic; i.e., they are independent of the physical details of a system. Examples of such generic properties are the celebrated fluctuation theorems; for reviews, see [2,4,5]. Recently, it was shown that infima and passage probabilities of entropy production are also generic [11]. Other statistical properties of entropy production are system dependent, such as the mean value [12–15], the variance [16,17], the first-passage times of entropy production [18–20], and the large deviation function [21,22]. Nevertheless, these properties are sometimes constrained by universal bounds [11,14,16,17,23–27]. It remains unclear which statistical properties of stochastic entropy production are generic, and why.

In this Letter, we introduce a theoretical framework which addresses this question for nonequilibrium Langevin processes. We identify generic properties of entropy production by their independence of a stochastic variable τ which we call *entropic time*. We find that the evolution of steady-state entropy production as a function of τ is governed by a simple one-dimensional drift-diffusion process, independent of the underlying model. This allows us to identify a set of generic properties of entropy production and obtain exact results characterizing entropy production fluctuations.

We consider a mesoscopic system described by n slow degrees of freedom $\vec{X} = (X_1(t), X_2(t), \ldots, X_n(t))^\mathsf{T}$. The system is in contact with a thermostat at temperature T. The stochastic dynamics of the system can be described by the probability distribution $P(\vec{X}, t)$ to find the system in a configuration $\vec{X}$ at time t. This probability distribution satisfies the Smoluchowski equation

$$\partial_t P = -\vec{\nabla} \cdot \vec{J}, \tag{1}$$

where the probability current is given by

$$\vec{J} = \boldsymbol{\mu} \cdot \vec{F} P - \boldsymbol{D} \cdot \vec{\nabla} P. \tag{2}$$

Here, we have introduced the force at time t, $\vec{F} = -\vec{\nabla} U(\vec{X}(t), t) + \vec{f}(\vec{X}(t), t)$, where U is a potential and $\vec{f}$ is a nonconservative force. We always imply no flux or periodic boundary conditions. The state-dependent mobility and diffusion tensors, $\boldsymbol{\mu}(\vec{X}(t))$ and $\boldsymbol{D}(\vec{X}(t))$, respectively, are symmetric and obey the Einstein relation $\boldsymbol{D} = k_B T \boldsymbol{\mu}$. This system can also be represented by a Langevin equation with multiplicative noise as [21,28]

$$\frac{d\vec{X}}{dt} = \boldsymbol{\mu} \cdot \vec{F} + \vec{\nabla} \cdot \boldsymbol{D} + \sqrt{2}\boldsymbol{\sigma} \cdot \vec{\xi}. \tag{3}$$

Here, $\vec{\xi}(t) = (\xi_1(t), \xi_2(t), \ldots, \xi_n(t))^\mathsf{T}$ is a Gaussian white noise with mean $\langle \xi_i(t) \rangle = 0$ and autocorrelation $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t - t')$, where $\langle \ldots \rangle$ denotes an ensemble average. Here and throughout this Letter the noise terms are interpreted in the Itô sense. The tensor $\boldsymbol{\sigma}$ obeys $\boldsymbol{\sigma}\boldsymbol{\sigma}^\mathsf{T} = \boldsymbol{D}$ and can be chosen as $\boldsymbol{\sigma} = \boldsymbol{D}^{1/2}$. In the Itô interpretation, the term $\vec{\nabla} \cdot \boldsymbol{D}$ is required for consistency with Eqs. (1) and (2) as it compensates a noise-induced drift [29]. Examples of systems described by Eq. (3) that we consider in this Letter are represented in Fig. 1: a colloidal particle driven by a constant force along a one-dimensional periodic potential [Fig. 1(a)]; a colloidal particle in a two-dimensional

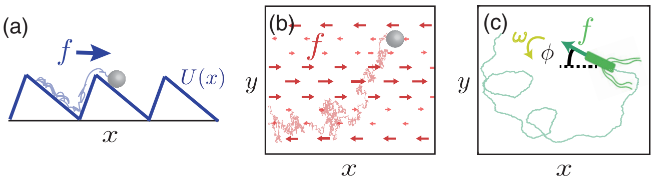

FIG. 1. Examples of nonequilibrium steady states. (a) Brownian particle driven by a constant nonconservative force in a periodic 1D sawtooth potential, $dX/dt = \mu[f - \partial_x U(X)] + \sqrt{2D}\xi$, with the potential $U(x) = (U_0 x)/x^*$ for $x \in [0, x^*]$ and $U(x) = U_0(1-x)/(1-x^*)$ for $x \in [x^*, 1]$. (b) 2D transport in a force field: $dX/dt = \mu f \cos(2\pi Y) + \sqrt{2D}\xi_x$ and $dY/dt = \sqrt{2D}\xi_y$. (c) Chiral active Brownian motion described by 3 degrees of freedom: position coordinates $dX/dt = \mu f \cos(\phi) + \sqrt{2D}\xi_x$, $dY/dt = \mu f \sin(\phi) + \sqrt{2D}\xi_y$, and orientation angle $d\phi/dt = \mu_\phi \omega + \sqrt{2D_\omega}\xi_\omega$. In (b) and (c) $U = 0$ and f is an external nonconservative force.

nonconservative force field pointing in the x direction [Fig. 1(b)]; and a chiral active Brownian motion in two dimensions [30] [Fig. 1(c)].

We now discuss the stochastic thermodynamics of the process described by Eq. (3). In Itô's calculus, the rate of change of the potential $U(\vec{X}(t), t)$ is given by Itô's lemma [31]:

$$\frac{dU}{dt} = \partial_t U + \vec{\nabla} U(\vec{X}(t), t) \cdot \frac{d\vec{X}}{dt} + \mathrm{Tr}[\boldsymbol{D} \cdot \vec{\nabla}\vec{\nabla} U]. \quad (4)$$

where Tr denotes the trace and the dots denote tensor contractions. In stochastic thermodynamics, the first law can be expressed as $dU = dW + dQ$, where dW is the work performed on the system and dQ is the mesoscopic heat exchanged with the thermostat during a time interval dt [1]. In Itô's calculus, the rates of change of work and heat are given by [21]

$$\frac{dW}{dt} = \partial_t U + \vec{f} \cdot \frac{d\vec{X}}{dt} + \mathrm{Tr}[\boldsymbol{D} \cdot \vec{\nabla} \vec{f}], \quad (5)$$

$$\frac{dQ}{dt} = -\vec{F} \cdot \frac{d\vec{X}}{dt} - \mathrm{Tr}[\boldsymbol{D} \cdot \vec{\nabla} \vec{F}]. \quad (6)$$

The expressions (5) and (6) are the Itô versions of the stochastic work and mesoscopic heat originally defined by Sekimoto using the Stratonovich interpretation [1,32].

We define the stochastic entropy production S_{tot}/k_B as the logarithm of the ratio of probabilities of forward and time-reversed stochastic trajectories [3,21,33]. This definition is equivalent to $dS_{\mathrm{tot}}/dt = -(1/T)dQ/dt - k_B d\ln P(\vec{X}(t), t)/dt$, where the first term can be interpreted as an exchange of entropy with the reservoir and the second term as a change of system entropy. Using Eq. (6) and Itô's lemma, as in Eq. (4) (see [34]), we obtain the following Itô stochastic differential equation for the entropy production rate:

$$\frac{dS_{\mathrm{tot}}}{dt} = -2k_B \partial_t \ln P + v_S + \sqrt{2k_B v_S}\xi_S. \quad (7)$$

Here, we define the entropic drift $v_S(\vec{X}(t), t) \geq 0$ as

$$v_S = k_B \frac{\vec{J} \cdot \boldsymbol{D}^{-1} \cdot \vec{J}}{P^2}, \quad (8)$$

which on average equals the average rate of entropy production, $\langle v_S \rangle = \langle dS_{\mathrm{tot}}/dt \rangle$ [5,28]. Entropy fluctuations are governed by the noise term $\xi_S = \vec{\xi} \cdot \boldsymbol{\sigma}^{-1} \cdot \vec{J}/\sqrt{\vec{J} \cdot \boldsymbol{D}^{-1} \cdot \vec{J}}$ which is a one-dimensional Gaussian white noise with $\langle \xi_S(t) \rangle = 0$ and $\langle \xi_S(t)\xi_S(t') \rangle = \delta(t - t')$. The Itô Eq. (7) is equivalent to the Langevin equation for entropy production in the Stratonovich interpretation given in Ref. [33]. For each trajectory generated by Eq. (3), Eq. (7) generates the corresponding entropy production. From Eq. (7) we can derive several generic properties of stochastic entropy production in nonequilibrium processes.

We first discuss properties of nonequilibrium steady states for which $\partial_t P = 0$. We now calculate the time derivative of $e^{-S_{\mathrm{tot}}/k_B}$ in steady state. Using Itô's lemma, we obtain from Eq. (7)

$$\frac{de^{-S_{\mathrm{tot}}/k_B}}{dt} = -\sqrt{2\frac{v_S}{k_B}} e^{-S_{\mathrm{tot}}/k_B}\xi_S, \quad (9)$$

which reveals that $e^{-S_{\mathrm{tot}}/k_B}$ is a geometric Brownian motion with zero drift and time-dependent diffusion coefficient. The fact that $e^{-S_{\mathrm{tot}}/k_B}$ has no drift implies that $e^{-S_{\mathrm{tot}}/k_B}$ is a martingale process [11,31,38]. Using $S_{\mathrm{tot}}(0) = 0$ the integral fluctuation theorem $\langle e^{-S_{\mathrm{tot}}(t)/k_B} \rangle = 1$ follows immediately from Eq. (9).

In steady state, Eq. (7) can be simplified by introducing the dimensionless entropic time

$$\tau = \frac{1}{k_B}\int_0^t v_S(\vec{X}(t'))dt', \quad (10)$$

which is an example of a random time [31]. Note that, in steady state, $v_S(\vec{X}(t), t) = v_S(\vec{X}(t))$ represents the expected rate of entropy production at a given point in phase space $\vec{X}(t)$ and τ thus represents the accumulated expected entropy production. In nonequilibrium situations with $v_S > 0$, the entropic time $\tau(t)$ is monotonically increasing with t. Integrating Eq. (7) we obtain

$$S_{\mathrm{tot}}(t)/k_B = \tau(t) + M(t). \quad (11)$$

Equation (11) represents the decomposition of entropy production into a monotonically increasing process $\tau(t)$ and a martingale $M(t) = \sqrt{2/k_B}\int_0^t \sqrt{v_S(\vec{X}(t'))}\xi_S(t')dt'$ that has zero mean, $\langle M(t) \rangle = 0$, as illustrated in Fig. 2. This decomposition is unique and is known as the Doob-Meyer decomposition [39].

We now discuss an important implication of Eqs. (7) and (10). Performing the random-time transformation

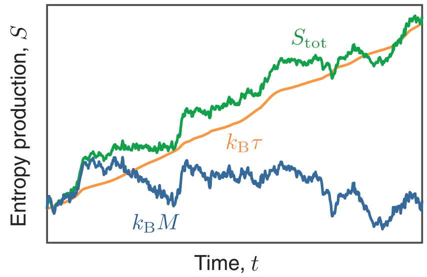

FIG. 2. Illustration of the decomposition of stochastic entropy production. In nonequilibrium steady states, the stochastic entropy production $S_{\rm tot}(t)$ (green) is given by the Boltzmann constant k_B times the sum of the monotonically increasing entropic time $\tau(t)$ (orange), and the martingale process $M(t)$ (blue), see Eq. (11).

$t \to \tau$ in Eq. (7) we obtain a Langevin equation for steady-state entropy production at entropic times [31]

$$\frac{1}{k_B}\frac{dS_{\rm tot}}{d\tau} = 1 + \sqrt{2}\eta(\tau), \tag{12}$$

where $\eta(\tau(t)) = \sqrt{k_B/v_S(\vec{X}(t))}\xi_S(t)$ such that $\eta(\tau)$ is Gaussian white noise with $\langle\eta(\tau)\rangle = 0$ and $\langle\eta(\tau)\eta(\tau')\rangle = \delta(\tau - \tau')$. Equation (12) states that a temporal trajectory of entropy production of any nonequilibrium steady state can be mapped to a trajectory of a drift-diffusion process with constant drift k_B and diffusion coefficient k_B^2, where the mapping consists in a time-dependent, stochastic contraction or dilation of time. This implies that all properties of $S_{\rm tot}$ that are invariant under such transformation are generic.

One such property is the distribution of entropy production at fixed values of τ, which must be a Gaussian with average $k_B\tau$ and variance $2k_B^2\tau$ because of Eq. (12). This is indeed the case for all three model examples, see Fig. 3(a). Note that the distribution of entropy production at fixed time t is very different for the three models, as shown in the inset of Fig. 3(a). Another generic property is the distribution of the global infimum of entropy production $S_{\rm inf}$, previously derived using martingale theory [11] and given by an exponential distribution $P(S_{\rm inf}) = e^{S_{\rm inf}/k_B}/k_B$ with mean $-k_B$ and $S_{\rm inf} \leq 0$ [Fig. 3(b)]. Also the supremum of entropy production before the infimum is generic and distributed according to

$$P(S_{\rm sup}) = 2e^{S_{\rm sup}/k_B}{\rm acoth}(2e^{S_{\rm sup}/k_B} - 1) - 1, \tag{13}$$

with $S_{\rm sup} \geq 0$. Its average value is $\langle S_{\rm sup}\rangle = (\pi^2/6 - 1)k_B \approx 0.645k_B$. The number of times that entropy production crosses a given threshold value is also generic. An example is the number of times $N_\times$ that entropy production crosses from $-\Delta$ to Δ with $\Delta > 0$. The distribution of $N_\times$ is

$$P(N_\times;\Delta) = \begin{cases} 1 - e^{-\Delta/k_B} & N_\times = 0 \\ 2\sinh(\Delta/k_B)e^{-2N_\times\Delta/k_B} & N_\times \geq 1. \end{cases} \tag{14}$$

Equations (13) and (14) are in excellent agreement with numerical simulations, as shown in Figs. 3(c) and 3(d).

With Eq. (11), we can also compute the moments of $S_{\rm tot}(t)$. The first moment reads simply $\langle S_{\rm tot}\rangle = k_B\langle\tau\rangle$. The second moment is $\langle S_{\rm tot}^2\rangle = 2k_B^2\langle\tau\rangle + k_B^2\langle\tau^2\rangle$, see [34]. Combining these two results, the Fano factor of the entropy production can be expressed as

$$\frac{1}{k_B}\frac{\sigma^2_{S_{\rm tot}}}{\langle S_{\rm tot}\rangle} = 2 + \frac{\sigma^2_\tau}{\langle\tau\rangle}, \tag{15}$$

where $\sigma_y^2 = \langle y^2\rangle - \langle y\rangle^2$ denotes the variance. The thermodynamic Fano factor equality given by Eq. (15) is an exact relation, valid for finite times, between the fluctuations of entropy production and the fluctuations of the entropic time τ. This equation provides further physical insight into the

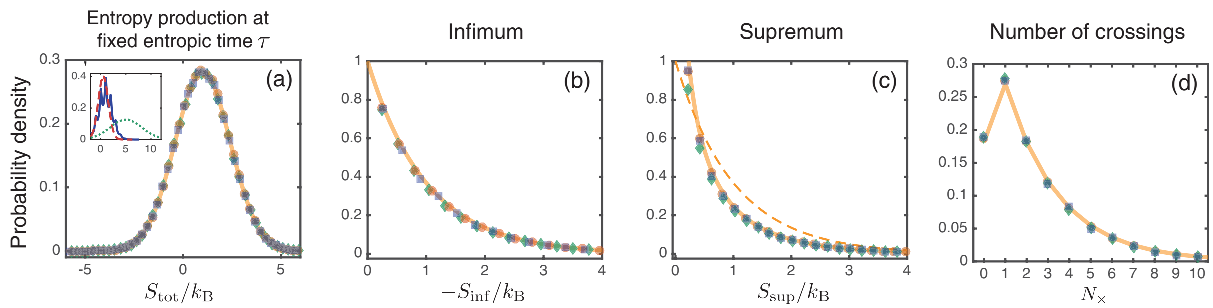

FIG. 3. Generic properties of stochastic entropy production. Distributions of (a) entropy production at fixed $\tau = 1$, (b) infimum of entropy production, (c) supremum of entropy production before the infimum, (d) number of crossings of entropy production, with $\Delta = 0.2k_B$. The symbols are obtained from numerical simulations of the three models sketched in Fig. 1 (blue squares, model A; red circles, model B; green diamonds, model C). The inset of (a) shows numerically estimated distributions of $S_{\rm tot}$ for the three models at fixed $t = 1$ for comparison. The solid orange curves are the theoretical expressions (a) a Gaussian distribution with average $k_B\tau$ and variance $2k_B^2\tau$ (b) an exponential distribution with average $-k_B$ (c) Eq. (13); (d) Eq. (14). The dashed line in (c) is the theoretical distribution of minus the infimum for comparison. In all simulations, parameters are $\boldsymbol{\mu} = \mathbb{I}, \boldsymbol{D} = k_BT\mathbb{I}$, where $\mathbb{I}$ is the identity matrix, and $f = 1$. In model A we chose $U_0 = k_BT$ and $x^* = 0.3$. In model C we chose $\omega = 2$. Here, and in the following figures, each point represents an average over 10^6 simulations.

previously introduced finite-time uncertainty relation $\sigma^2_{S_{\rm tot}}/\langle S_{\rm tot}\rangle \geq 2k_B$ [26,27]. The variance obeys the equality $\sigma^2_{S_{\rm tot}}/\langle S_{\rm tot}\rangle = 2k_B$ only if the entropic time satisfies $\sigma^2_\tau/\langle\tau\rangle = 0$, which holds, e.g., near equilibrium. In this case, the distribution of entropy production is Gaussian. Another example for which $\sigma^2_\tau/\langle\tau\rangle = 0$ is the chiral active Brownian motion shown in Fig. 1(c).

For long times, the variance of the entropic time can be estimated by a Green-Kubo formula as an integral over a correlation function [34]

$$\frac{\sigma^2_\tau}{\langle\tau\rangle} = \frac{2}{k_B\langle v_S\rangle}\int_0^\infty dt'[\langle v_S(\vec{X}(t'))v_S(\vec{X}(0))\rangle - \langle v_S\rangle^2]. \tag{16}$$

Using Eqs. (15) and (16) we obtain explicit expressions for the Fano factor as a function of the driving force for our three models; see Fig. 4 for a comparison with numerical simulations.

Our theory can also be applied to nonequilibrium processes out of steady state. From Eq. (7) we derive the general Fano factor equality

$$\frac{1}{k_B}\frac{\sigma^2_{S_{\rm tot}}}{\langle S_{\rm tot}\rangle} = 2 + \frac{\sigma^2_\tau}{\langle\tau\rangle} + \frac{2\Omega}{\langle\tau\rangle}, \tag{17}$$

where

$$\Omega = \frac{1}{k_B}\int_0^t dt'\int_0^{t'} dt''\langle -2\partial_{t''}\ln P(X(t''),t'')v_S(\vec{X}(t'),t')\rangle, \tag{18}$$

and $\tau = (1/k_B)\int_0^t v_S(\vec{X}(t'),t')dt'$ is the entropic time for non-steady-state processes. At steady state, $\Omega = 0$, and Eq. (17) reduces to Eq. (15). Note that the argument of the integral in Eq. (18) is the correlation of the two drift terms in Eq. (7) at different times. In Fig. 5, we illustrate Eq. (17) for a particle confined in a harmonic trap, where the stiffness of the trap is instantaneously quenched from a value κ_i to a value κ_f. When $\kappa_f > \kappa_i$, one has $\Omega > 0$, so that the Fano factor of entropy production is larger than two according to Eq. (17). When instead $\kappa_f < \kappa_i$, one has $\Omega < 0$, and the Fano factor of entropy production is lower than two.

For nonequilibrium processes starting at thermal equilibrium and undergoing a defined protocol to a final state, one has $TS_{\rm tot} = W - \Delta F$, where W is the work performed during the protocol and ΔF is the change of equilibrium free-energy $F = \langle U\rangle_{\rm eq} + k_BT\langle\ln P\rangle_{\rm eq}$ associated with the final and initial states [40–42]. Here, $\langle\cdot\rangle_{\rm eq}$ denotes an equilibrium average over the Boltzmann distribution. For such protocols, Eq. (17) implies

$$\Delta F = \langle W\rangle - \frac{\sigma^2_W}{2k_BT} + \frac{k_BT}{2}(\sigma^2_\tau + 2\Omega). \tag{19}$$

Note that ΔF also obeys Jarzynski's equality $\Delta F = -k_BT\ln\langle e^{-W/k_BT}\rangle$ [40], which has the form of a cumulant generating function. Comparing it with Eq. (19), one can relate the term in parenthesis in (19) to a sum of cumulants of W/k_BT of order 3 and higher. This sum vanishes if the work distribution is Gaussian [40].

We have shown that, in steady-state Langevin processes, entropy production is governed by a Langevin equation

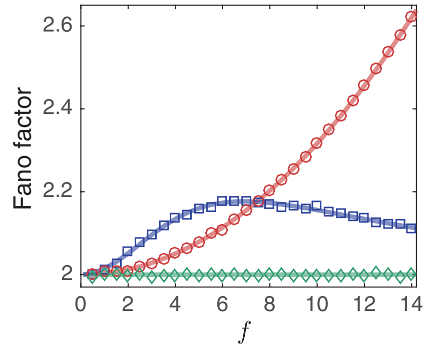

FIG. 4. Thermodynamic Fano factor equality. Long-time Fano factor of entropy production $\sigma^2_{S_{\rm tot}}/(k_B\langle S_{\rm tot}\rangle)$ as a function of the external force f. The symbols are obtained from numerical simulations of the models shown in Fig. 1(a) (blue), Fig. 1(b) (red), and Fig. 1(c) (green). The solid lines are the prediction of Eq. (15) and have been calculated by means of Eq. (16) (see [34]). All the parameters of the numerical simulations except of the external force f are the same as in Fig. 3.

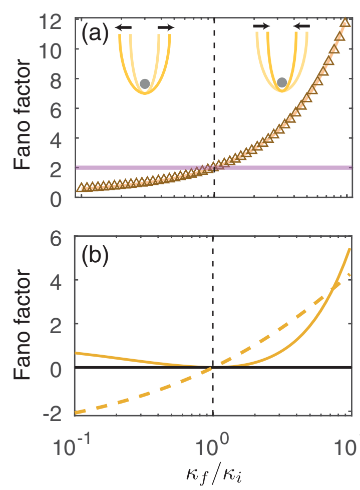

FIG. 5. Fano factor of stochastic entropy production out of steady state. The position of a Brownian particle is governed by the equation $dX/dt = -\mu\kappa_f X + \sqrt{2D}\xi$ with $\mu = 1$ and $D = \mu k_BT$. The particle is initially at equilibrium with stiffness $\kappa_i = 1$ (see inset). (a) Comparison between the exact value (orange line) of the long-time Fano factor of entropy production and the value obtained from numerical simulations (brown triangles) as a function of κ_f. The exact value is given by $\sigma^2_{S_{\rm tot}}/k_B\langle S_{\rm tot}\rangle = (\kappa_f/\kappa_i - 1)^2/[(\kappa_f/\kappa_i - 1) - \log(\kappa_f/\kappa_i)]$; see Supplemental Material for details [34]. In simulations we measure $\langle\tau\rangle$, σ^2_τ, and Ω and use Eq. (17). The horizontal purple line is set to 2 for comparison. (b) Behavior of $\sigma^2_\tau/\langle\tau\rangle$ (solid line) and $2\Omega/\langle\tau\rangle$ (dashed line) as a function of κ_f.

which only depends on the system's details via the entropic drift v_S. As a consequence, all system-specific features of stochastic entropy production can be absorbed into a single stochastic quantity, the entropic time τ. Entropy productions of different systems at equal entropic time have the same statistics, and all properties independent of the entropic time are generic. Fluctuations of the entropic time uniquely determine the Fano factor of entropy production, providing physical insight for previously obtained bounds [16,17,23–27].

We have demonstrated our results for coupled overdamped Langevin equations but expect our results to hold more generally for continuous processes, as is the case for the infimum of entropy production [11]. Using the Doob-Meyer decomposition of entropy production, our definition of entropic time can also be generalized to underdamped systems [43,44] and jump processes [45]. Our results can be experimentally tested, for example, with optical tweezers [6–8,46,47], feedback traps [9], single-electron transistors [10], and light-activated phototactic microparticles [48].

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