Statistics of Entropy Production in Linearized Stochastic Systems

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We consider a wide class of linear stochastic problems driven off the equilibrium by a multiplicative asymmetric force. The force breaks detailed balance, maintained otherwise, thus producing entropy. The large deviation function of the entropy production in the system is calculated explicitly. The general result is illustrated using an example of a polymer immersed in a gradient flow and subject to thermal fluctuations.

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The Gibbs distribution, $\mathcal{P}_{\rm eq}(\boldsymbol{x}) \sim \exp[-U(\boldsymbol{x})/T]$, describes the probability for a system characterized by the microscopic potential $U(\boldsymbol{x})$ and maintained at equilibrium at temperature T to be observed in the state $\boldsymbol{x}$. In particular, in our model case of a polymer, the elastic potential $U(\boldsymbol{x})$ depends on the end-to-end position vector $\boldsymbol{x}$. The system at equilibrium maintains the detailed balance, which is the most fundamental principle of equilibrium statistical mechanics [1,2]. Formally, the detailed balance means that the probabilities $\mathcal{P}\{x\}$ and $\mathcal{P}\{x^*\}$ for a stochastic trajectory, $\{\boldsymbol{x}\} \equiv \{\boldsymbol{x}(t'); 0 < t' < t\}$ and its "conjugated twin" $\{\boldsymbol{x}\}^* \equiv \{\boldsymbol{x}^*(t') = \boldsymbol{x}(t - t'); 0 < t' < t\}$ are related by [3]

$$\underline{\text{in balance:}}\ \ln\frac{\mathcal{P}\{x\}}{\mathcal{P}\{x^*\}} = \frac{U[\boldsymbol{x}(t)] - U[\boldsymbol{x}(0)]}{T}. \qquad (1)$$

Asymmetric external force breaks down the detailed balance. For example, a shearing flow forces the polymer to tumble and results in steady entropy production [4]. In general, configurational entropy is naturally defined as a mismatch between the left-hand sides (lhs) and right-hand sides (rhs) of Eq. (1):

$$\underline{\text{off balance:}}\ \mathcal{S} = \ln\frac{\mathcal{P}\{\boldsymbol{x}^*\}}{\mathcal{P}\{\boldsymbol{x}\}} + \frac{U[\boldsymbol{x}(t)] - U[\boldsymbol{x}(0)]}{T} \neq 0. \qquad (2)$$

For a wide class of thermalized systems, driven out of equilibrium by external nonconservative forces the entropy has also a standard thermodynamic interpretation: It determines the total heat produced by the system over time t. In the off-detailed balance case entropy is a fluctuating function of the entire configurational trajectory $\{\boldsymbol{x}\}$. Therefore, in the statistically steady nonequilibrium case fluctuations occur on the top of a steady mean growth of the entropy and one can argue that at sufficiently large observation time the distribution function of the produced entropy $\mathcal{S}$ takes a large deviation form [5,6]:

$$\mathcal{P}(\mathcal{S}|t) \sim \exp[-t\mathcal{L}(\mathcal{S}\tau/t)/\tau], \qquad (3)$$

where τ is the typical correlation (turnover) time of the system and $\mathcal{L}(\omega)$ is referred to as the large deviation function. Description of the large deviation function for a truly nonequilibrium problem is a difficult task, and only a few successful results have been reported so far [7]. To clarify the difficulty let us also mention that a simpler problem of finding an off-detailed balance analog of the Gibbs distribution, posed in a classical work of Onsager [8], has been solved for a few examples only (see [9–11] for discussion of some difficulties, progress, and results achieved on this thorny path). It is also worth noting that the large deviation function for the entropy production has been computed and verified experimentally for a number of other physical situations, e.g., optically dragged Brownian particles, electrical circuits, and forced harmonic oscillators [12,13]. Although these works are ideologically similar, technically they study different nonequilibrium systems, which are either nonsteady or do not have the detailed balance broken.

In this Letter we present a *solution of this challenging task* for a wide class of linear problems driven by multiplicative asymmetric "force" and also connected to a Langevin reservoir. Such problems arise whenever a statistically steady nonequilibrium state is externally driven by space ($\boldsymbol{x}$-dependent) nonconservative external forces. Our main physical example is a Hookean polymer stretched and sheared by a mild constant external flow. For this linear nonequilibrium setting we report an explicit expression for the large deviation function of the entropy production in terms of elementary functions; see, e.g., Eq. (14). For the most general case our result is given as a solution of a well-defined system of algebraic equations or, alternatively, in terms of a one-dimensional integral Eq. (17). The most important features of the results derived in this Letter are: (a) The steady-state solutions are consistent with the fluctuation theorem [14]:

$$\mathcal{L}(\omega) - \mathcal{L}(-\omega) = -\omega. \qquad (4)$$

(b) The large deviation function is found to be very different from the Gaussian shape. Extreme tails of the entropy probability distribution function (PDF) are exponential, which are the steepest tails allowed by the large deviation form (3). (c) One observes reduction in the number of parameters that affect the shape of the large deviation function. For example, it is completely insensitive to the symmetric part of the velocity gradient in the case of the linear polymer immersed in a $2d$ flow.

The Letter is organized as follows. We first introduce the polymer-in-a-flow example and use it to illustrate the general methods for calculating $\mathcal{L}(\omega)$. Using the generating function formalism we reduce the problem to a set of algebraic equations and obtain the explicit expression for $\mathcal{L}(\omega)$ for general two-dimensional and some particular three-dimensional flows. Then, we switch to a general linear model with a constant multiplicative force (15), which is analyzed with a complementary approach by using a direct solution of the linear stochastic equations followed by averaging the resulting expression for the generating function over the Langevin noise.

The polymer's end-to-end vector, x_i satisfies a stochastic equation of motion [15]

$$\dot{x}_i - \sigma_{ij}x_j = -\partial_i U(\boldsymbol{x}) + \xi_i, \tag{5}$$

where the traceless matrix $\hat{\sigma}$ describes the local value of the velocity gradient in the generic incompressible flow ($i = 1, \ldots, d$). The smoothness of velocity on the scale of an even very extended polymer is justified by many experimental observations; see e.g. [15]. Equation (5) describes the balance of forces: the second term on the lhs represents the polymer deformation by the velocity field. The two terms on the rhs of Eq. (5) account for the polymer elasticity and for the Langevin thermal noise. In this Letter we consider a deterministic constant gradient flow, $\hat{\sigma} =$ const and focus on the case of a relatively weak $\hat{\sigma}$ and linear model of Hookean polymer, $U_H(\boldsymbol{x}) = \boldsymbol{x}^2/(2\tau)$. Yet, we will also discuss the other extreme of a stretched nonlinear polymer in a strong gradient flow. The Langevin term in Eq. (5) is modeled by the zero mean white Gaussian noise with $\langle \xi_i(t)\xi_j(t')\rangle = 2T\delta(t-t')\delta_{ij}$.

According to Eq. (5) the probability for a stochastic polymer trajectory in the configuration space is given by

$$\mathcal{P}\{\boldsymbol{x}\} \sim \exp\left[-\int_0^t dt'[\dot{\boldsymbol{x}} - \hat{\sigma}\boldsymbol{x} + \partial_{\boldsymbol{x}} U(\boldsymbol{x})]^2/(4T)\right]. \tag{6}$$

The expression for the configurational entropy follows from Eq. (6) with the conjugated trajectory defined according to $\dot{\boldsymbol{x}}^*(\tau) = -\dot{\boldsymbol{x}}(t-\tau)$ and the external matrix $\hat{\sigma}$ not affected by the conjugation [16]:

$$\mathcal{S} = \int_0^t dt' \dot{x}_i(t')(\sigma_{ij} - \sigma_{ji})x_j(t')/(2T) + \mathcal{O}(1). \tag{7}$$

Here the longest-time $t/\tau \gg 1$ statistics of $\mathcal{S}$ is naturally described within $\mathcal{O}(t/\tau)$.

The Fokker-Planck technique is applied via relating the large deviation function to its generating function defined by

$$Z_q \equiv \langle \exp(-q\mathcal{S})\rangle_\xi. \tag{8}$$

Utilizing the large deviation asymptotic (3) we can reformulate averaging over the Langevin noise in Eq. (8) in terms of integration over $\mathcal{S}$ and further evaluate the integral using the saddle-point approximation (justified for the asymptotically long time). This establishes the following Legendre transform relation between the generating and the large deviation functions:

$$Z_q \sim \exp(-[\mathcal{L}(\omega_q) - \omega_q\mathcal{L}'(\omega_q)]t/\tau), \quad -q = \mathcal{L}'(\omega_q). \tag{9}$$

Substituting Eqs. (7) into the definition (8) followed by averaging over the stochastic dynamics (5) we arrive at the Fokker-Planck equation:

$$\partial_t Z_q = \hat{L}_q Z_q, \tag{10}$$

$$\begin{aligned} \hat{L}_q &= -\nabla_i[\sigma_{ij}x_j - \partial_i U(\mathbf{x})] + T\nabla_i\nabla_i, \\ \nabla_i &= \partial_i + q(\hat{\sigma} - \hat{\sigma}^+)_{ij}x_j/(2T), \end{aligned} \tag{11}$$

Assuming that the operator $\hat{L}_q$ has a discrete spectrum, the large time asymptotics of Z_q is completely dominated by the ground state of $\hat{L}_q$. Therefore, the large deviation function is fully described by its ground-state eigenvalue and, specifically, its dependence on q.

Here we consider the case when velocity gradient is relatively weak compared to the elastic force (or when stretching components in $\hat{\sigma}$ are zero) so that the steady state is achieved in the regime when elasticity in Eq. (11) is linear, $U(\mathbf{x}) = \boldsymbol{x}^2/(2\tau)$ (the so-called coiled, rather then stretched, state). The spectral problem (10) in the case of Hookean elasticity is of an "integrable" type and is similar to a single-particle quantum mechanics in a constant magnetic field, when the ground-state eigenfunction is Gaussian. Therefore, one looks for the solution of Eq. (10) in a form $Z_q = \exp(-\lambda_q t)\exp[-x_i B_q^{ij} x_j/(2T)]$, with $\hat{B}$ being a $d \times d$ symmetric matrix. Substituting the Gaussian ansatz into Eq. (10) we derive the following eigenvalue relations for $\hat{B}_q$ and λ_q:

$$\begin{aligned} &\lambda_q = \mathrm{Tr}(\hat{B}_q + \hat{\sigma} - \hat{1}/\tau), \qquad \hat{M} + \hat{M}^+ = 0, \\ &\hat{M} \equiv [\hat{B}_q + q(\hat{\sigma} - \hat{\sigma}^+)/2] \\ &\qquad \times [\hat{\sigma} - \hat{1}/\tau + \hat{B}_q - q(\hat{\sigma} - \hat{\sigma}^+)/2], \end{aligned} \tag{12}$$

that correspond to $x^2\exp(\ldots)$ and $\exp(\ldots)$ terms, respectively. Equations (12) are generic, i.e., valid for the full formulation given by Eqs. (10) and (11); the $\lambda_0 = 0$ and the $q = 0$ version of Eqs. (12) defines the steady distribution function for the end-to-end polymer length $\boldsymbol{x}$ (see, e.g. [11]).

For the 2×2 velocity gradient matrix $\sigma_{11} = -\sigma_{22} = a$ and $\sigma_{12} = b + c$, $\sigma_{21} = b - c$ one derives from Eq. (12)

$$\lambda_q = (\sqrt{1 + 4q(1-q)c^2\tau^2} - 1)\tau^{-1}, \tag{13}$$

where the generating function and the eigenvalue of the ground state are well defined only within a finite interval, $q \in [q_-; q_+]$, where $q_\pm \equiv 1/2 \pm \sqrt{1/4 - 1/(c^2\tau^2)}$. Note that the eigenvalue λ_q given by Eq. (13) does not depend on the symmetric part of $\hat{\sigma}$, even though the resulting $\hat{B}_q$ function does depend explicitly on both symmetric and antisymmetric components. Formally this reflects the invariance of the Fokker-Planck operator with respect to a family of isospectral transformations that keep the spectra (or at least its ground state) invariant. We do not know, however, a physically intuitive explanation for this remarkable symmetry in the model. A similar and equally surprising reduction in the degrees-of-freedom number that control the large deviation function of a current has been recently reported for a different nonequilibrium system [7]. Combining Eqs. (9) and (13) yields

$$\mathcal{L}(\omega) = \sqrt{(1 + c^2\tau^2)(4c^2\tau^2 + \omega^2)} - 1 - \omega/2. \tag{14}$$

Note that, first, $\mathcal{L}(\omega)$ satisfies the fluctuation theorem (4), and, second, the asymptotics of $\mathcal{L}(\omega)$ at $|\omega| \gg c\tau$ are both linear in ω, making the extreme deviation asymptotics of the entire distribution function of $\mathcal{S}$ exponential and time independent. Tracking the origin of the exponential tails back to a special form of the generating function (13), one finds that these extreme asymptotics correspond to the square root singularity of λ_q at $q_\pm$. Emergence of the exponential tails is a special feature of linear modeling, that was also reported and analyzed in [13,17]. Time independence of the $\mathcal{P}(\mathcal{S}|t)$ asymptotics means that typical trajectories contributing the PDF tail are correlated at some finite times, so that the observational time t increase does not change the corresponding probabilities. Figure 1 shows the large deviation function given by Eq. (14) verified versus Brownian dynamics simulations. In the case of a $d = 3$ gradient flow the algebraic system of Eqs. (12) is too complicated to allow a solution in terms of elementary functions for an arbitrary form of the velocity gradient matrix $\hat{\sigma}$. Thus we mention only a special example of a $3d$ flow with the following nonzero elements of $\hat{\sigma}$: $\sigma_{11} = -a_1$, $\sigma_{22} = a_1 + a_2$, $\sigma_{33} = -a_2$, $\sigma_{13} = c$, $\sigma_{31} = -c$. In this case the generating function and the large deviation function is given by Eqs. (14) modified according to the following simple renormalization of $\tau \to \tau/|1 + (a_1 + a_2)\tau|$ (and ω, respectively).

An alternative derivation of the large deviation function starts with considering a general linear problem

$$\dot{x}_i = \Phi_{ij}x_j + \Upsilon_{ij}\xi_j, \tag{15}$$

where $\hat{\Phi}$ and $\hat{\Upsilon}$ are arbitrary constant matrices. Equation (15) describes linear stochastic dynamics around a fixed point, that can be stable or unstable. We discuss here a truly nonequilibrium (off-detailed balance) steady state maintained if the fluctuations do not exceed a threshold so that nonlinear effects can be ignored (see [11] and references therein). A flux state observed in a diffusive system [18] is a popular example that involves an infinite-dimensional configurational variable $\boldsymbol{x}$. Many examples of the off-detailed balance steady systems, e.g., vesicles or red-blood cells in external flows [19] and macromolecular biological devices, such as enzyme motors [20], come from biology and soft-matter physics. Obviously, the $\hat{\Upsilon} = \hat{1}$ version of Eq. (15) describes the aforemention two-beads Hookean polymer model as well; however, it is worth mentioning that the full version of Eq. (15) also appears naturally in a more general polymer context, where the $\hat{\Upsilon} \neq \hat{1}$ case models hydrodynamic interactions between the different parts of the polymer chain [15]. Equation (15) also describes fluctuations around a stretched state above the coil-stretch transition [21–23] in a strong flow [24].

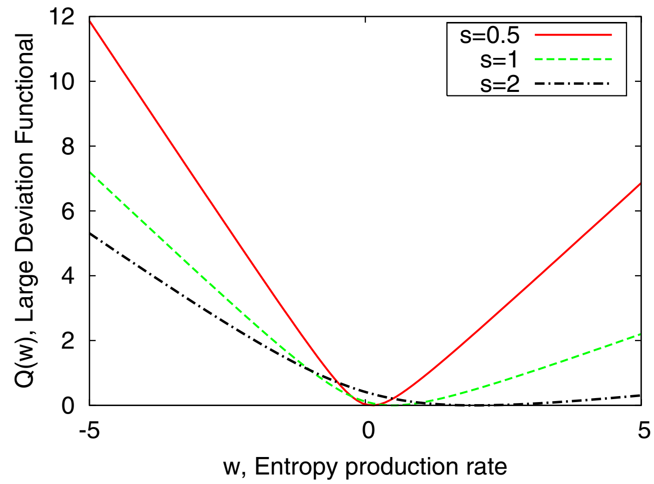

FIG. 1 (color online). Large deviation function in $d = 2$ for three values of the governing parameter $c\tau = 1.0$; 2.0; 4.0.

According to Eq. (2) the entropy production in the system described by Eq. (15) is given by $\mathcal{S} = \int_0^t dt' \dot{\boldsymbol{x}}^+(t')(\hat{K}\hat{\Phi} - \hat{\Phi}^+\hat{K})\boldsymbol{x}(t')/(2T)$, where $\hat{K} \equiv (\hat{\Upsilon}\hat{\Upsilon}^+)^{-1}$. To discuss dynamics at large, yet finite time t, it is convenient to invoke a discrete (in the manner of Matsubara) frequency representation

$$\boldsymbol{x}(t') = \sum_k [\boldsymbol{c}_k \exp(i\omega_k t') + \boldsymbol{c}_k^* \exp(-i\omega_k t')]/\sqrt{t},$$

$$Z_q = \int \prod_k \mathcal{D}c_k \mathcal{D}c_k^* \exp\Big[-\sum_k c_k^\dagger A_q(\omega_k) c_k/(2T)\Big],$$

$$A_q(\omega) \equiv \omega^2\hat{K} + \hat{\Phi}^+\hat{K}\hat{\Phi} + i\omega(1-2q)(\hat{K}\hat{\Phi} - \hat{\Phi}^+\hat{K}), \tag{16}$$

where $\omega_k \equiv 2\pi k/t$, $k = 1, 2, \ldots$. Straightforward Gaussian integration in Eq. (16) yields: $\lambda_q t = \sum_k \log[\det A_q(\omega_k)/\det A_0(\omega_k)]$. In the $t \to \infty$ limit one replaces summation over k by integration and arrives at

$$\lambda_q = \int_0^\infty \frac{d\omega}{2\pi} \log\left(\frac{\det A_q(\omega)}{\det A_0(\omega)}\right), \tag{17}$$

which is the most general long-time asymptotic result reported in this Letter. It is straightforward to verify that in the special case of a linear polymer advected by a $d = 2$ gradient flow, $\hat{\Phi} = \hat{\sigma} - \hat{1}/\tau$, and Langevin driving, $\hat{\Upsilon} = \hat{1}$, the integral representation (17) for λ_q turns into Eq. (13) derived earlier using the spectral method.

Note that Eq. (17) also suggests a convenient way to determine the values of $q_\pm$ for a general linear system (15). One finds that q_+ is a minimal positive value of q for which a solution of the equation $\det A_q(\omega) = 0$ does exist. The value of ω which solves this equation is related to the characteristic time scale of an optimal fluctuation which controls the exponential tail of the entropy PDF.

We conclude by compiling an incomplete list of future challenges related to the approach and results reported in this Letter. First, our analysis of the entropy production in a polymer system extends to the case of chaotic flows, e.g., realized in the recently discovered elastic turbulence [25]. Of a particular interest here is to check the sensitivity of the large deviation function to the coil-stretch transition observed in the chaotic problem [21–23]. Second, introducing a finite time protocol for a controlled parameter (e.g., shear in the polymer solution experiments) one may be interested to go beyond the analysis of the stationary problem, in particular, discussing an off-detailed balance version of the Jarzynski relation [2,26–28]. This may also help to reconstruct (experimentally or numerically) the nonequilibrium steady-state landscape that would be akin to experiments developed for the systems that do not violate the detailed balance, see, e.g. [29].

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