Entropy production for diffusion processes across a semipermeable interface

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The emerging field of stochastic thermodynamics extends classical ideas of entropy, heat, and work to nonequilibrium systems. One notable finding is that the second law of thermodynamics typically only holds after taking appropriate averages with respect to an ensemble of stochastic trajectories. The resulting average rate of entropy production then quantifies the degree of departure from thermodynamic equilibrium. In this paper we investigate how the presence of a semipermeable interface increases the average entropy production of a single diffusing particle. Starting from the Gibbs-Shannon entropy for the particle probability density, we show that a semipermeable interface or membrane $\mathcal{S}$ increases the average rate of entropy production by an amount that is equal to the product of the flux through the interface and the logarithm of the ratio of the probability density on either side of the interface, integrated along $\mathcal{S}$. The entropy production rate thus vanishes at thermodynamic equilibrium, but can be nonzero during the relaxation to equilibrium, or if there exists a nonzero stationary equilibrium state (NESS). We then give a probabilistic interpretation of the interfacial entropy production rate using so-called snapping out Brownian motion. This also allows us to construct a stochastic version of entropy production. Finally, we illustrate the theory using the example of diffusion with stochastic resetting on a circle, and find that the average rate of interfacial entropy production is a nonmonotonic function of the resetting rate and the permeability.

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I. INTRODUCTION

In recent years there has been a rapid growth of interest in stochastic thermodynamics, which uses tools from the theory of stochastic processes to extend classical ideas of entropy, heat and work to nonequilibrium systems [1–4]. Examples include overdamped colloidal particles, biopolymers, enzymes, and molecular motors. One characteristic feature of such systems is that the second law of thermodynamics typically only holds after taking appropriate averages with respect to an ensemble of stochastic trajectories or over long time intervals. The resulting average rate of entropy production then quantifies the degree of departure from thermodynamic equilibrium. In addition, probabilistic methods such as Itô stochastic calculus, path integrals and Radon-Nikodym derivatives have been used to derive a variety of important fluctuation relations from the stochastic entropy evaluated along individual trajectories [5–8]. These fluctuation relations have subsequently been generalized using martingale theory [9–14].

In this paper we consider the following problem: How does the presence of a semipermeable interface contribute to the average entropy production rate of a single diffusing particle? Diffusion through semipermeable membranes has a wide range of applications, including molecular transport through biological membranes [15–17], diffusion magnetic resonance imaging (dMRI) [18–20], drug delivery [21,22], reverse osmosis [23], and animal dispersal in heterogeneous landscapes [24–26]. At the macroscopic level, the classical boundary condition for a semipermeable membrane takes the particle flux across the membrane to be continuous and to be proportional to the difference in concentrations on either side of the barrier. The constant of proportionality κ_0 is known as the permeability. The semipermeable boundary conditions are a particular version of the thermodynamically derived Kedem-Katchalsky (KK) equations [27–30]. At the single-particle level, the resulting diffusion equation can be reinterpreted as the Fokker-Planck (FP) equation for the particle probability density, which is supplemented by the interfacial boundary conditions. In particular, suppose that a semipermeable interface $\mathcal{S}$ partitions $\mathbb{R}^d$ into two complementary domains $\Omega_\pm$ with $\mathbb{R}^d = \Omega_+ \cup \Omega_- \cup \mathcal{S}$. If $\mathcal{J}(\mathbf{y}, t)$ denotes the continuous flux across a point $\mathbf{y} \in \mathcal{S}$ from Ω_- to Ω_+, then $\mathcal{J}(\mathbf{y}, t) = \kappa_0\ [p(\mathbf{y}^-, t) - p(\mathbf{y}^+, t)]/2$, where $p(\mathbf{y}^\pm, t)$ are the solutions on $\mathcal{S}_\pm = \overline{\Omega_\pm} \cap \mathcal{S}$, where $\overline{\Omega}$ denotes closure of a set Ω. We consider a natural generalization of the interfacial condition by allowing there to be a jump in the chemical potential across the interface. This results in a corresponding directional bias that can be implemented by taking $\mathcal{J}(\mathbf{y}, t) = \kappa_0\ [p(\mathbf{y}^-, t) - \sigma p(\mathbf{y}^+, t)]/2$ for some $\sigma \neq 1$.

Starting from the Gibbs-Shannon entropy for the particle probability density $p(\mathbf{x}, t)$, $\mathbf{x} \in \mathbb{R}^d$, we show in Sec. II that a semipermeable interface $\mathcal{S}$ increases the average rate of entropy production at a given time t by an amount $\mathcal{I}_{\rm int}(t) = \int_{\mathcal{S}} \mathcal{J}(\mathbf{y}, t) \ln[p(\mathbf{y}^-, t)/p(\mathbf{y}^+, t)] d\mathbf{y}$. In other words, $\mathcal{I}_{\rm int}(t)$ is equal to the product of the flux through the interface and the logarithm of the ratio of the probability density on either side of the interface, integrated along $\mathcal{S}$. It immediately follows that the entropy production rate vanishes at thermodynamic equilibrium, but can be nonzero during the relaxation to equilibrium. We illustrate the theory by calculating the average rate of entropy production for one-dimensional (1D) diffusion. In the 1D case, $\mathcal{S}$ reduces to a single point $x = 0$, say, so that $\Omega_- = (-\infty, 0^-]$ and $\Omega_+ = [0^+, \infty)$.

In Sec. III we present a probabilistic interpretation of $\mathcal{I}_{\rm int}$ based on so-called snapping out Brownian motion (BM) [31–34]. The latter generates individual stochastic trajectories of the dynamics by sewing together successive rounds of partially reflected BMs that are restricted to either the left or right of the barrier. Each round is killed (absorbed) at the barrier when its boundary local time exceeds an exponential random variable parameterized by the permeability κ_0. (The local time is a Brownian functional that specifies the contact time between a particle and a given boundary [35–39].) A new round is then immediately started in either direction with equal probability, assuming that there is no directional bias ($\sigma = 1$). It is the random switching after each killing event that is the source of the entropy production. We also use snapping out BM to construct a stochastic version of entropy production. Averaging the latter with respect to the distribution of sample paths recovers the results based on the Gibbs-Shannon entropy.

Finally, in Sec. IV we illustrate the theory using a well-studied mechanism for maintaining a diffusing particle out of thermodynamic equilibrium, namely, stochastic resetting. Resetting was originally introduced within the context of a Brownian particle whose position $\mathbf{X}(t)$ instantaneously resets to a fixed position $\mathbf{x}_0$ at a sequence of times generated from a Poisson process of constant rate r [40–42]. There have subsequently been a wide range of generalizations at the single particle level, see the review [43] and references therein. A signature feature of many diffusion processes with resetting is the existence of a nonequilibrium stationary state (NESS) that supports nonzero time-independent fluxes. A number of recent studies have considered the stochastic thermodynamics of diffusive systems with resetting [44–50]. One issue that emerges from these studies is that sharp resetting to a single point is a unidirectional process that has no time-reversed equivalent. This means that the average rate of entropy production calculated using the Gibbs-Shannon entropy cannot be related to the degree of time-reversal symmetry breaking. This connection can be established by considering resetting to a random position [51] or BM in an intermittent confining potential [52]. An additional subtle feature arises when considering the effects of resetting in the presence of a semipermeable interface [53–55]. In particular, it is natural to assume that the interface screens out resetting, in the sense that a resetting event cannot cross the interface. This means that a particle on one side of the interface $\partial\mathcal{M}$ cannot reset to a point on the other side. Hence, it is not possible to have a nonzero stationary flux across the interface, since there is no countervailing reset current in the opposite direction. We bypass the screening effect in Sec. IV by considering the example of single-particle diffusion on a ring with both stochastic resetting and a semipermeable interface. We derive an explicit expression for the resulting NESS and use this to calculate the various contributions to the average rate of entropy production in the stationary state, including those associated with resetting as well as those arising from the semipermeable interface.

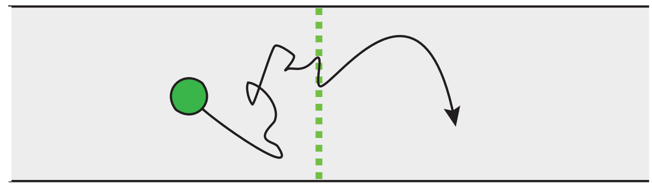

FIG. 1. BM in $\mathbb{R}$ with a semipermeable interface at $x = 0$. (The two-dimensional representation is for illustrative purposes.)

II. SINGLE-PARTICLE DIFFUSION ACROSS A SEMIPERMEABLE INTERFACE

A. Diffusion in $\mathbb{R}$

Consider an overdamped Brownian particle diffusing in a 1D domain with a semipermeable barrier or interface at $x = 0$; see Fig. 1. Suppose that the particle is also subject to a force $F(x, t)$. Let $p(x, t)$ denote the probability density of the particle at position x at time t. The corresponding FP equation takes the form

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}, \quad x \neq 0, \quad t > 0, \tag{2.1a}$$

with the probability flux

$$J(x,t) = -D\frac{\partial p(x,t)}{\partial x} + \frac{1}{\gamma}F(x,t)p(x,t), \tag{2.1b}$$

and the following pair of boundary conditions at the interface:

$$J(0^{\pm}, t) = \mathcal{J}(t) := \frac{\kappa_0}{2}[p(0^-, t) - \sigma p(0^+, t)], \tag{2.1c}$$

where κ_0 is a constant permeability and σ, $0 \leqslant \sigma < 1$, represents a directional asymmetry that can be interpreted as a step discontinuity in a chemical potential [27–29,56]. This asymmetry tends to enhance the concentration to the right of the interface. (If $\sigma > 1$, then we would have an interface with permeability $\kappa_0\sigma$ and bias $1/\sigma$ to the left. A symmetric interface corresponds to the case $\sigma = 1$.) The arbitrary factor of $1/2$ on the right-hand side of Eq. (2.1c) is motivated by the corresponding probabilistic interpretation of snapping out BM, see Sec. III. Finally, D is the diffusivity, γ is the friction coefficient, and the two quantities are related according to the Einstein relation $D\gamma = k_BT$. (In the following we set the Boltzmann constant $k_B = 1$.)

For simplicity, we take the diffusive medium to be spatially homogeneous. However, the domains $(-\infty, 0^-]$ and $[0^+, \infty)$ could have different diffusivities, for example. That is, $D = D_-$ for $x < 0$ and $D = D_+$ for $x > 0$ with $D_- \neq D_+$; the drag coefficients would also differ due to the Einstein relation. We also assume that the force $F(x, t)$ is continuous at the interface. In order to evaluate various thermodynamic quantities such as the average heat, work and entropy, we have to integrate with respect to $x \in \mathbb{R}$. Since the probability density has a discontinuity at $x = 0$, we partition each integral into the two domains $(-\infty, 0^-]$ and $[0^+, \infty)$, and introduce the notation

$$\fint dx = \int_{-\infty}^{0} dx + \int_{0}^{\infty} dx. \tag{2.2}$$

Continuity of the flux at $x = 0$ means that in most cases there is no contribution to the integral from the discontinuity. One notable exception occurs when we evaluate the average rate of entropy production.

In the 1D case we can always write the force as a gradient of a potential, $F(x,t) = -\partial_x V(x,t)$. This means that the average internal energy is

$$\mathcal{E}(t) = \fint dx\, p(x,t)V(x,t), \tag{2.3}$$

and

$$\frac{d\mathcal{E}}{dt} = \fint dx \left[\frac{\partial p(x,t)}{\partial t}V(x,t) + \frac{\partial V(x,t)}{\partial t}p(x,t)\right]. \tag{2.4}$$

Using Eqs. (2.1a), (2.1b) and integration by parts, we have

$$\begin{aligned}\int_{-\infty}^{0} dx\, \frac{\partial p(x,t)}{\partial t}V(x,t) \\ = \int_{-\infty}^{0} dx\, \frac{\partial V(x,t)}{\partial x}J(x,t) - J(0^-,t)V(0,t)\end{aligned} \tag{2.5}$$

and

$$\begin{aligned}\int_{0}^{\infty} dx\, \frac{\partial p(x,t)}{\partial t}V(x,t) \\ = \int_{0}^{\infty} dx\, \frac{\partial V(x,t)}{\partial x}J(x,t) + J(0^+,t)V(0,t).\end{aligned} \tag{2.6}$$

Imposing flux continuity at the interface leads to a nonequilibrium version of the first law of thermodynamics:

$$\frac{d\mathcal{E}}{dt} = \frac{d\mathcal{W}}{dt} - \frac{dQ}{dt}, \tag{2.7}$$

where $\mathcal{W}(t)$ is the average work done on the particle and $Q(t)$ is the average heat dissipated into the environment with

$$\frac{dQ}{dt} = -\fint dx\, \frac{\partial V(x,t)}{\partial x}J(x,t) \tag{2.8}$$

and

$$\frac{d\mathcal{W}}{dt} = \fint dx\, \frac{\partial V(x,t)}{\partial t}p(x,t). \tag{2.9}$$

If the potential is time-independent, then we have the further simplification that there exists a unique equilibrium stationary state given by the Boltzmann-Gibbs distribution,

$$\lim_{t\to\infty} p(x,t) = \frac{1}{Z}e^{-V(x)/T}, \quad \lim_{t\to\infty} J(x,t) = 0. \tag{2.10}$$

Since there are no fluxes at equilibrium, the semipermeable membrane becomes invisible, that is, it has no effect on the stationary state.

The average system entropy at time t is defined by

$$\mathcal{S}^{\rm sys}(t) := -\fint dx\, p(x,t)\ln p(x,t), \tag{2.11}$$

which takes the form of a Gibbs-Shannon entropy. To calculate the average rate of entropy production, we differentiate both sides of Eq. (2.11) with respect to time t:

$$\mathcal{R}^{\rm sys}(t) := \frac{d\mathcal{S}^{\rm sys}(t)}{dt} = -\fint dx\, \frac{\partial p(x,t)}{\partial t}[1 + \ln p(x,t)]. \tag{2.12}$$

Using the FP equation and performing an integration by parts, we have

$$\begin{aligned}\mathcal{R}^{\rm sys}(t) &= \fint dx\, \frac{\partial J(x,t)}{\partial x}[1 + \ln p(x,t)] \\ &= -\fint dx\, \frac{J(x,t)}{p(x,t)}\frac{\partial p(x,t)}{\partial x} + J(0^-,t)[1 + \ln p(0^-,t)] \\ &\quad - J(0^+,t)[1 + \ln p(0^+,t)].\end{aligned} \tag{2.13}$$

Using the definitions of the probability fluxes, the integrand can be rewritten as

$$-\frac{1}{p(x,t)}\frac{\partial p(x,t)}{\partial x}J(x,t) = \frac{J(x,t)^2}{Dp(x,t)} - \frac{F(x,t)J(x,t)}{T}. \tag{2.14}$$

In addition, imposing the flux continuity condition shows that

$$\begin{aligned}J(0^-,t)[1 + \ln p(0^-,t)] - J(0^+,t)[1 + \ln p(0^+,t)] \\ = \mathcal{J}(t)\ln[p(0^-,t)/p(0^+,t)].\end{aligned} \tag{2.15}$$

We thus obtain a generalization of the classical entropy production rate given by

$$\begin{aligned}\mathcal{R}^{\rm tot}(t) &:= \mathcal{R}^{\rm sys}(t) + \mathcal{R}^{\rm env}(t) \\ &= \fint dx\, \frac{J(x,t)^2}{Dp(x,t)} + \mathcal{I}_{\rm int}(t),\end{aligned} \tag{2.16}$$

where

$$\mathcal{I}_{\rm int}(t) = \frac{\kappa_0}{2}[p(0^-,t) - \sigma p(0^+,t)]\ln\left[\frac{p(0^-,t)}{p(0^+,t)}\right] \tag{2.17}$$

is the contribution to the entropy production from the semipermeable membrane, and

$$\mathcal{R}^{\rm env}(t) := \frac{1}{T}\frac{dQ}{dt} = \fint dx\, \frac{F(x,t)J(x,t)}{T} \tag{2.18}$$

is the average environmental entropy production rate due to heat dissipation, see Eq. (2.8). It is important to note that Eq. (2.16) is a general result for diffusion through an interface, while Eq. (2.17) is the particular form of the interfacial contribution for a semi-permeable membrane.

In the case of a symmetric interface ($\sigma = 1$), $[p(0^-,t) - p(0^+,t)]$ and $\ln[p(0^-,t)/\ln p(0^+,t)]$ have the same sign. It follows that $\mathcal{I}_{\rm int}(t) \geqslant 0$, and hence the average total entropy production rate satisfies the second law of thermodynamics in the sense that

$$\mathcal{R}^{\rm tot}(t) \geqslant 0, \quad t \geqslant 0. \tag{2.19}$$

However, if $0 < \sigma < 1$, then $\mathcal{I}_{\rm int}(t)$ is not necessarily positive. To obtain the correct second law of thermodynamics, we decompose $\mathcal{I}_{\rm int}(t)$ as

$$\mathcal{I}_{\rm int}(t) = \mathcal{I}_{\sigma}(t) + \frac{\kappa_0}{2}[p(0^-,t) - \sigma p(0^+,t)]\ln\sigma, \tag{2.20}$$

with

$$\mathcal{I}_\sigma(t) = \frac{\kappa_0}{2}[p(0^-,t) - \sigma p(0^+,t)] \ln\left[\frac{p(0^-,t)}{\sigma p(0^+,t)}\right] \geqslant 0. \tag{2.21}$$

Suppose that there is a discontinuity in the chemical potential across the interface, with $\mu = \mu_-$ for $x < 0$ and $\mu = \mu_+$ for $x > 0$. We then make the identification $\sigma = e^{(\mu_+ - \mu_-)/T}$ with $\mu_+ < \mu_-$ for $\sigma < 1$, such that

$$\mathcal{I}_{\rm int}(t) = \mathcal{I}_\sigma(t) + \mathcal{J}(t)\frac{\mu_+ - \mu_-}{T}. \tag{2.22}$$

The second term on the right-hand side represents the rate of reduction in the free energy due to the probability flux $\mathcal{J}(t)$ from a region with a high chemical potential μ_- to a region with a low chemical potential μ_+. This change in free energy contributes to the heat dissipated into the environment. Hence, redefining the environmental entropy according to

$$\mathcal{R}^{\rm env}(t) = \fint dx \frac{F(x,t)J(x,t)}{T} + \mathcal{J}(t)\frac{\mu_- - \mu_+}{T}, \tag{2.23}$$

we obtain the modified second law of thermodynamics

$$\mathcal{R}^{\rm tot}(t) = \fint dx \frac{J(x,t)^2}{Dp(x,t)} + \mathcal{I}_\sigma(t) \geqslant 0. \tag{2.24}$$

The existence of the contribution $\mathcal{I}_{\rm int}$ is one of the main results of our paper. We will give a physical interpretation of this result in Sec. III.

B. Interfacial entropy production for pure diffusion

In the particular case of a time-independent force $F(x) = -V'(x)$, the rate of entropy production vanishes in the limit $t \to \infty$ since there are no fluxes at equilibrium. However, $\mathcal{R}^{\rm tot}(t) > 0$ at finite times t. This result holds even for pure diffusion, where an explicit solution of Eqs. (2.1) can be obtained. For the sake of illustration, we will consider a symmetric interface. The simplest way to proceed is to Laplace transform Eqs. (2.1), under the initial condition $p(x,0) = \delta(x - x_0)$. For the sake of illustration we take $x_0 > 0$. It follows that

$$\widetilde{p}(x,s) := \int_0^\infty e^{-st} p(x,t)dt = G(x,x_0;s), \tag{2.25}$$

where $G(x_{,0};s)$ is the Green's function of the modified Helmholtz equation

$$\frac{d^2G}{dx^2} - sG(x,x_0;s) = -\delta(x - x_0), \tag{2.26a}$$

supplemented by the interfacial conditions

$$\begin{aligned} -D\frac{dG(x,x_0;s)}{dx}\bigg|_{x=0^-} &= -D\frac{dG(x,x_0;s)}{dx}\bigg|_{x=0^+} \\ &= \frac{\kappa_0}{2}[G(0^-,x_0;s) - G(0^+,x_0;s)], \end{aligned} \tag{2.26b}$$

and with $\lim_{x\to\pm\infty} G(x,x_0;s) = 0$.

Equation (2.26a) has the general solution

$$G(x,x_0;s) = \frac{e^{\sqrt{s/D}|x-x_0|}}{2\sqrt{sD}} + A(s)e^{\sqrt{s/D}x} + B(s)e^{-\sqrt{s/D}x}, \tag{2.27}$$

with the pair of coefficients $A(s)$ and $B(s)$ determined by the supplementary conditions (2.26b). Finally, inverting the resulting solution in Laplace space gives

$$\begin{aligned} p(x,t) &= \frac{1}{2\sqrt{\pi Dt}}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right) + \exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right] \\ &\quad - \frac{\kappa_0}{2D}\exp\left(\frac{\kappa_0}{D}(x + x_0 + \kappa_0 t)\right)\mathrm{erfc}\left(\frac{(x + x_0 + 2\kappa_0 t}{2\sqrt{Dt}}\right), \end{aligned} \tag{2.28a}$$

for $x > 0$ and

$$p(x,t) = \frac{\kappa_0}{2D}\exp\left(\frac{\kappa_0}{D}(x_0 - x + \kappa_0 t)\right)\mathrm{erfc}\left(\frac{x_0 - x + 2\kappa_0 t}{2\sqrt{Dt}}\right) \tag{2.28b}$$

for $x < 0$. The complementary error function is

$$\mathrm{erfc}(x) := \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-y^2}dy. \tag{2.29}$$

In the limit $\kappa_0 \to 0$, we see that $p(x,t) \to 0$ for $x < 0$ and $p(x,t) \to p_+(x,t)$ for $x > 0$, with

$$p_+(x,t) = \frac{1}{2\sqrt{\pi Dt}}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right) + \exp\left(-\frac{(x+x_0)^2}{4Dt}\right)\right]. \tag{2.30}$$

This is consistent with the fact that the interface becomes completely impermeable in the limit $\kappa_0 \to 0$ and the particle started to the right of the interface. We thus recover the solution of the diffusion equation on the half-line with a totally reflecting boundary at $x = 0$. To determine what happens in the limit $\kappa_0 \to \infty$, we use the asymptotic expansion

$$\mathrm{erfc}(x) \sim \frac{e^{-x^2}}{\sqrt{\pi}x}\left[1 - \frac{1}{2x^2} + \cdots\right]. \tag{2.31}$$

We find that the interface becomes completely transparent and $p(x,t)$ is given by the classical solution of free diffusion in $\mathbb{R}$. In Fig. 2 we show sample plots of the interfacial entropy production rate $\mathcal{I}_{\rm int}(t)$, see Eq. (2.17), as a function of time t for various initial positions x_0 and permeabilities κ_0. The unimodal dependence of $\mathcal{I}_{\rm int}(t)$ on the time t reflects the fact that the Green's function solution $p(0^\pm,t)$ on either side of the interface is also unimodal, with $p(0^\pm,t) \to 0$ as $t \to 0$ and $t \to \infty$. Since $x\log(x) \to 0$ as $x \to 0$, one also finds that $\mathcal{I}_{\rm int}(t) \to 0$ in the limits $t \to 0$ and $t \to \infty$. Moreover, $\mathcal{I}_{\rm int}(t) > 0$ for all finite t since $p(0^+,t) > p(0^-,t)$. Increasing the permeability κ_0 reduces the difference between the density on either side of the interface, so that $[p(0^-,t) - \sigma p(0^+,t)]\ln[\frac{p(0^-,t)}{p(0^+,t)}]$ is also reduced. However, this is counteracted by the multiplicative factor of κ_0 in Eq. (2.17) so that the initial rise of $\mathcal{I}_{\rm int}(t)$ actually increases with κ_0. As expected, the effects of the interface at $x = 0$ are greater when x_0 is closer to the origin.

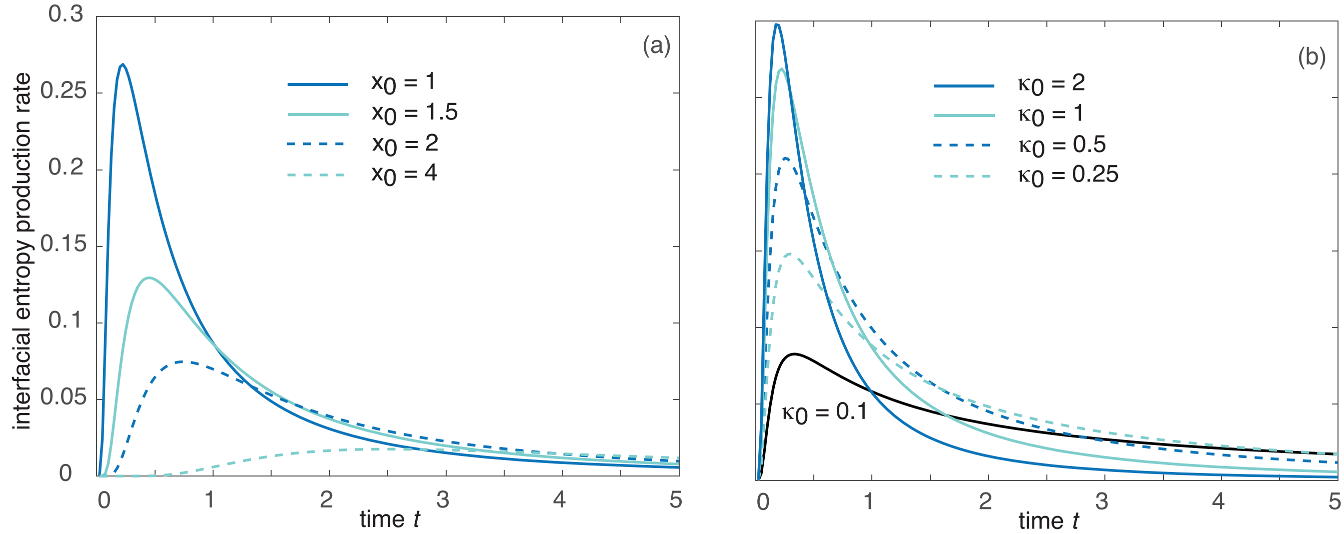

FIG. 2. Single-particle diffusion across a closed semipermeable interface in $\mathbb{R}$. Plots of the average interfacial entropy production rate as a function time for (a) various initial positions x_0 and fixed permeability $\kappa_0 = 1$ and (b) various κ_0 for fixed $x_0 = 1$.

C. Diffusion across a closed semipermeable membrane in $\mathbb{R}^d$

The expression (2.17) for the average rate of entropy production through a semipermeable interface generalizes to higher spatial dimensions. Suppose that $\mathcal{M}$ denotes a closed bounded domain $\mathcal{M} \subset \mathbb{R}^d$ with a smooth concave boundary $\partial\mathcal{M}$ separating the two open domains $\mathcal{M}$ and its complement $\mathcal{M}^c = \mathbb{R}^d \backslash \mathcal{M}$; see Fig. 3. The boundary acts as a semipermeable interface with $\partial\mathcal{M}_+$ ($\partial\mathcal{M}_-$) denoting the side approached from outside (inside) $\mathcal{M}$. Let $p(\mathbf{x}, t)$ denote the probability density function of an overdamped Brownian particle subject to a force field $\mathbf{F}(\mathbf{x})$. The multidimensional analog of the FP equation is

$$\frac{\partial p(\mathbf{x}, t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{x}, t), \quad \mathbf{x} \in \mathcal{M} \cup \mathcal{M}^c, \tag{2.32a}$$

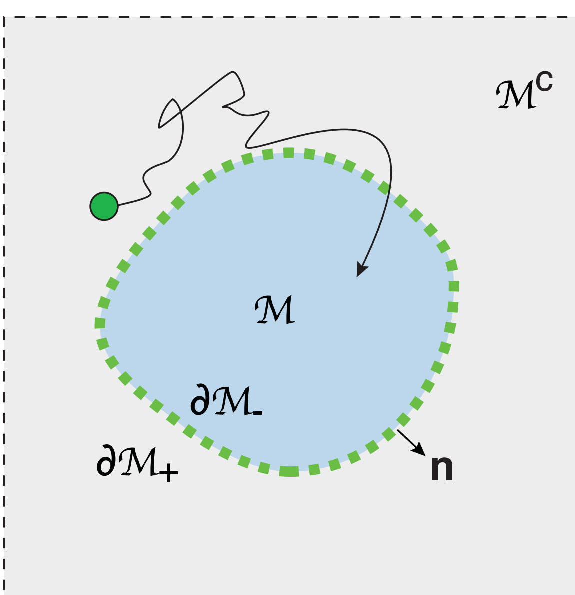

FIG. 3. Single-particle diffusion across a closed semipermeable membrane in $\mathbb{R}^d$.

$$\mathbf{J}(\mathbf{x}, t) = -D\nabla p(\mathbf{x}, t) + \frac{1}{\gamma}\mathbf{F}(\mathbf{x})p(\mathbf{x}, t), \tag{2.32b}$$

$$\mathbf{J}(\mathbf{y}^{\pm}, t) \cdot \mathbf{n} = \mathcal{J}(\mathbf{y}, t), \quad \mathbf{y} \in \partial\mathcal{M}, \tag{2.32c}$$

$$\mathcal{J}(\mathbf{y}, t) = \frac{\kappa_0}{2}[p(\mathbf{y}^-, t) - \sigma p(\mathbf{y}^+, t)], \quad \mathbf{y} \in \partial\mathcal{M}, \tag{2.32d}$$

where $\mathbf{n}$ is the unit normal directed out of $\mathcal{M}$.

The average system entropy at time t is defined by

$$\mathcal{S}^{\text{sys}}(t) := -\int_{\mathcal{M}} d\mathbf{x}\, p(\mathbf{x}, t) \ln p(\mathbf{x}, t) - \int_{\mathcal{M}^c} d\mathbf{x}\, p(\mathbf{x}, t) \ln p(\mathbf{x}, t). \tag{2.33}$$

Differentiating both sides of Eq. (2.33) with respect to time t gives

$$\mathcal{R}^{\text{sys}}(t) := \frac{d\mathcal{S}^{\text{sys}}(t)}{dt} = -\int_{\mathcal{M}} d\mathbf{x}\, \frac{\partial p(\mathbf{x}, t)}{\partial t}[1 + \ln p(\mathbf{x}, t)] - \int_{\mathcal{M}^c} d\mathbf{x}\, \frac{\partial p(\mathbf{x}, t)}{\partial t}[1 + \ln p(\mathbf{x}, t)]. \tag{2.34}$$

Using the FP Eq. (2.32) and performing an integration by parts according to the divergence theorem, we have

$$\begin{aligned}\mathcal{R}^{\text{sys}}(t) &= \int_{\mathcal{M}} d\mathbf{x}\, [1 + \ln p(\mathbf{x}, t)]\nabla \cdot \mathbf{J}(\mathbf{x}, t) + \int_{\mathcal{M}^c} d\mathbf{x}\, [1 + \ln p(\mathbf{x}, t)]\nabla \cdot \mathbf{J}(\mathbf{x}, t)\\ &= -\int_{\mathcal{M}} d\mathbf{x}\, \nabla p(\mathbf{x}, t) \cdot \frac{\mathbf{J}(\mathbf{x}, t)}{p(\mathbf{x}, t)} - \int_{\mathcal{M}^c} d\mathbf{x}\, \nabla p(\mathbf{x}, t) \cdot \frac{\mathbf{J}(\mathbf{x}, t)}{p(\mathbf{x}, t)}\\ &\quad + \int_{\partial\mathcal{M}_-} d\mathbf{y}\, [1 + \ln p(\mathbf{y}, t)]\mathbf{J}(\mathbf{y}, t) \cdot \mathbf{n} - \int_{\partial\mathcal{M}_+} d\mathbf{y}\, [1 + \ln p(\mathbf{y}, t)]\mathbf{J}(\mathbf{y}, t) \cdot \mathbf{n}.\end{aligned} \tag{2.35}$$

We now decompose the various contributions to $\mathcal{R}^{\rm sys}$ along analogous lines to the 1D case. This leads to the higher dimensional version of Eq. (2.16):

$$\begin{aligned}\mathcal{R}^{\rm tot}(t) &:= \mathcal{R}^{\rm sys}(t)+\mathcal{R}^{\rm env}(t)\\ &= \int_{\mathcal{M}} d\mathbf{x}\,\frac{\mathbf{J}(\mathbf{x},t)^2}{Dp(\mathbf{x},t)}+\int_{\mathcal{M}^c} d\mathbf{x}\,\frac{\mathbf{J}(\mathbf{x},t)^2}{Dp(\mathbf{x},t)}+\mathcal{I}_{\rm int}(t),\end{aligned} \tag{2.36}$$

where

$$\mathcal{I}_{\rm int}(t)=\int_{\partial\mathcal{M}} d\mathbf{y}\,\mathcal{J}(\mathbf{y},t)\ln\left[\frac{p(\mathbf{y}^-,t)}{p(\mathbf{y}^+,t)}\right] \tag{2.37}$$

is the contribution to the entropy production from the semipermeable membrane, and

$$\begin{aligned}\mathcal{R}^{\rm env}(t) &= \frac{1}{T}\frac{dQ}{dt}\\ &= \int_{\mathcal{M}} d\mathbf{x}\,\frac{\mathbf{F}(\mathbf{x},t)\cdot\mathbf{J}(\mathbf{x},t)}{T}+\int_{\mathcal{M}^c} d\mathbf{x}\,\frac{\mathbf{F}(\mathbf{x},t)\cdot\mathbf{J}(\mathbf{x},t)}{T}.\end{aligned} \tag{2.38}$$

III. PROBABILISTIC INTERPRETATION OF THE ENTROPY CONTRIBUTION $\mathcal{I}_{\rm int}$

In Sec. II we analyzed BM across a semipermeable interface using a Fokker-Planck description of the distribution of sample paths. To understand the origins of the interfacial entropy production term $\mathcal{I}_{\rm int}$, see Eq. (2.17) and its higher-dimensional analog (2.37), we turn to a probabilistic description of individual trajectories based on so-called snapping out BM [31–34]. Here we only cover the essential elements necessary for interpreting $\mathcal{I}_{\rm int}$ in 1D. The mathematical details of the 1D case are presented in the Appendix. Extensions of the probabilistic framework to higher-dimensional interfaces can be found in Ref. [34].

First suppose that the interface is impermeable ($\kappa_0=0$), so that the particle is restricted to the positive half-line $[0,\infty)$ and the boundary at $x=0$ is totally reflecting. Let $X(t)\in[0,\infty)$ denote the position of a Brownian particle at time t. To write down a stochastic differential equation (SDE) for the particle, it is necessary to introduce a Brownian functional known as the boundary local time [35–39]:

$$\begin{aligned}L(t) &= \lim_{\epsilon\to 0^+}\frac{\ell_\epsilon(t)}{\epsilon}=\lim_{\epsilon\to 0^+}\frac{D}{\epsilon}\int_0^t\Theta(\epsilon-X(\tau))d\tau\\ &= D\lim_{\epsilon\to 0^+}\int_0^t\delta(X(\tau)-\epsilon)d\tau,\end{aligned} \tag{3.1}$$

where Θ is the Heaviside function. The functional $\ell_\epsilon(t)$ measures the occupation time of the particle in a boundary layer of width ϵ. It can be shown that $L(t)$ exists and is a nondecreasing stochastic process. The position of the particle then evolves according to the so-called Skorokhod equation for reflected BM on the half-line:

$$dX(t)=F(X(t))dt+\sqrt{2D}dW(t)+dL(t), \tag{3.2}$$

where $dL(t)=D\lim_{\epsilon\to 0^+}\delta(X(t)-\epsilon)$ and $W(t)$ is a Wiener process satisfying

$$\langle W(t)\rangle=0,\quad \langle W(t)W(t')\rangle=\min\{t,t'\}. \tag{3.3}$$

Heuristically speaking, the differential of the local time generates a rightward impulsive kick whenever the particle hits the boundary. Now suppose that the diffusion process is killed when the local time $L(t)$ at $x=0$ exceeds a randomly generated threshold $\widehat{L}$ with

$$P[\widehat{L}>l]\equiv e^{-\kappa_0\ell/D}. \tag{3.4}$$

That is, the particle is absorbed at the stopping time

$$\mathcal{T}=\inf\{t>0:\ L(t)>\widehat{L}\}. \tag{3.5}$$

Since $L(t)$ is a nondecreasing process, the condition $t<\mathcal{T}$ is equivalent to the condition $L(t)<\widehat{L}$. It can be proven that the distribution of sample paths generated by the SDE (3.2) satisfies an FP equation with a Robin boundary condition at $x=0$ [39].

Let us now return to the case of a semipermeable interface ($\kappa_0>0$). First, suppose that the interface is symmetric ($\sigma=1$). The dynamics of snapping out BM consists of sewing together successive rounds of reflected BM, each of which evolves according to an SDE of the form (3.2) or its analog on the left-hand side of the interface, as illustrated in Fig. 4. [The local time when $X(t)\in(-\infty,0]$ is $L(t)=\lim_{\epsilon\to 0^+}(D/\epsilon)\int_0^t\Theta(\epsilon+X(\tau))d\tau$.] Each round is killed when the local time at the right-hand or left-hand side of the interface exceeds an exponentially distributed random threshold. (The threshold is independently generated each round.) Following each round of killing, an unbiased coin is thrown to determine which side of the interface the next round occurs. It can be proven that snapping out BM generates sample paths whose distribution is given by the solution of the corresponding FP Eq. (2.1), see Refs. [31–34] and the Appendix. It is the randomization following each killing event that accounts for the term $\mathcal{I}_{\rm int}$ appearing in Eq. (2.16). That is, $\mathcal{I}_{\rm int}$ is given by the product of the flux $\mathcal{J}(t)$ across the interface, which specifies the effective rate of randomization, and the corresponding entropy difference $\ln p(0^-,t)-\ln p(0^+,t)$. It is also possible to incorporate directional asymmetry into snapping out BM [34]. This is achieved by introducing a bias in the switching between the positive and negative directions of reflected BM following each round of killing.

One of the major advantages of the probabilistic formulation of snapping out BM is that it can be used to construct a stochastic version of entropy production. For the sake of illustration, we focus on the 1D unbiased case. Let $X(t)$ be the position of the Brownian particle at time t and consider the stochastic system entropy

$$S^{\rm sys}(t)=-\ln p(X(t),t), \tag{3.6}$$

where $p(x,t)$ is the solution of Eqs. (2.1). First suppose that the interface is impermeable ($\kappa_0=0$) and $X(0)>0$. Differentiating both sides of Eq. (3.6) with respect to t and using the chain rule in the Stratonovich version of stochastic calculus gives

$$\begin{aligned}dS^{\rm sys}(t) &= -\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial t}dt\\ &\quad -\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial x}\circ dX(t),\end{aligned} \tag{3.7}$$

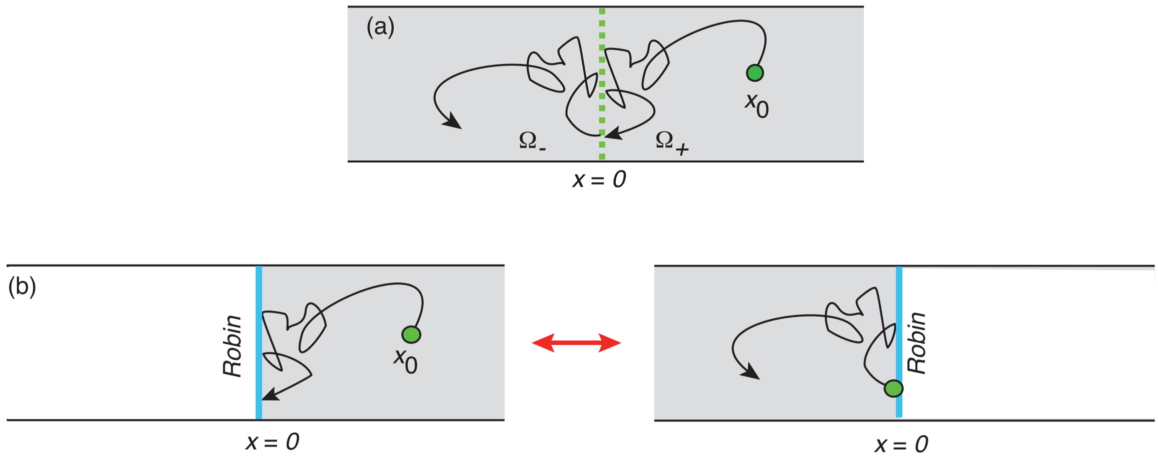

FIG. 4. Snapping out BM. (a) Single-particle diffusing across a semipermeable interface at $x = 0$. (b) Decomposition of snapping out BM into the random switching between two partially reflected BMs in the domains $\Omega_\pm$.

with $dX(t)$ satisfying Eq. (3.2) and $dL(t) = \lim_{\epsilon\to 0^+}\delta(X(t)-\epsilon)dt$. If $\kappa_0 > 0$, then in an infinitesimal time interval dt, there is a nonzero probability $\kappa_0 dt/2$ that the reflected BM is killed and the particle switches to the left-hand side of the interface. This results in a jump of the entropy given by $\Delta S^{\rm sys} = \ln[p(0^-,t)/p(0^+,t)]$. However, if the particle remains on the right-hand side after the killing event, which occurs with probability $1-\kappa_0 dt/2$, then there is no jump in the entropy. Equation (3.7) is thus modified as

$$dS^{\rm sys}(t) = -\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial t}dt - \frac{1}{p(X(t),t)} \times \frac{\partial p(X(t),t)}{\partial x}\circ dX(t) - \frac{\kappa_0}{2}\lim_{\epsilon\to 0^+}\delta(X(t)-\epsilon) \times \ln[p(0^-,t)/p(0^+,t)]dt, \tag{3.8}$$

with

$$dX(t) = -\frac{1}{\gamma}V'(X(t))dt + \sqrt{2D}dW + D[1-\kappa_0 dt/2]\lim_{\epsilon\to 0^+}\delta(X(t)-\epsilon)dt. \tag{3.9}$$

The last term on the right-hand side is the impulsive kick $dL(t)$ at $x = 0^+$ multiplied by the probability that the particle remains on the same side, that is, it is reflected rather than transmitted through the interface. A very similar result holds if the particle approaches the interface from the left-hand side, except that now the jump in entropy due to crossing the interface is $\Delta S^{\rm sys} = -\ln[p(0^-,t)/p(0^+,t)]$. Combining the two possibilities leads to the following general result:

$$dS^{\rm sys}(t) = -\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial t}dt - \frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial x}\circ dX(t) - \frac{\kappa_0}{2}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]\ln[p(0^-,t)/p(0^+,t)]dt, \tag{3.10}$$

with

$$dX(t) = -\frac{1}{\gamma}V'(X(t))dt + \sqrt{2D}dW + D[1-\kappa_0 dt/2]\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]dt. \tag{3.11}$$

In terms of the probability flux $J(x,t)$, we have

$$-\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial x}\circ dX(t) = \frac{J(X(t),t)}{Dp(X(t),t)}\circ dX(t) - dS^{\rm env}(X(t),t), \quad dS^{\rm env}(X(t),t) = -\frac{V'(X(t))}{T}\circ dX(t), \tag{3.12}$$

where $dS^{\rm env}(X(t),t)$ is the the infinitesimal change in the environmental entropy.

To determine the average entropy production rate we need to take expectations with respect to the white noise process. This is simplified by converting from Stratonovich to Itô calculus [1]. In particular, to leading order in dt,

$$\begin{aligned}\frac{J(X(t),t)}{Dp(X(t),t)}\circ dX &= -\frac{J(X(t),t)V'(X(t))}{T\,p(X(t),t)}dt + \sqrt{\frac{2}{D}}\frac{J(X(t),t)}{p(X(t),t)}\circ dW + \frac{J(X(t),t)}{Dp(X(t),t)}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]dt\\ &= -\frac{J(X(t),t)V'(X(t))}{T\,p(X(t),t)}dt + \sqrt{\frac{2}{D}}\frac{J(X(t),t)}{p(X(t),t)}\cdot dW + \frac{1}{p(X(t),t)}\frac{\partial J(X(t),t)}{\partial x}dt\\ &\quad - \frac{J(X(t),t)}{p^2(X(t),t)}\frac{\partial p(X(t),t)}{\partial x}dt + \frac{\mathcal{J}(t)}{Dp(X(t),t)}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]dt,\end{aligned}$$

since $J(0^-,t)=J(0^+,t)=\mathcal{J}(t)$. Hence, we can rewrite Eq. (3.12) as

$$dS^{\rm sys}(X(t),t)+dS^{\rm env}(X(t),t)=-\frac{1}{p(X(t),t)}\left[\frac{\partial p(X(t),t)}{\partial t}-\frac{\partial J(X(t),t)}{\partial x}\right]dt+\sqrt{\frac{2}{D}}\frac{J(X(t),t)}{p(X(t),t)}dW \tag{3.13}$$

$$+\frac{J^2(X(t),t)}{Dp^2(X(t),t)}dt-\frac{\kappa_0}{2}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]\ln[p(0^-,t)/p(0^+,t)]dt$$

$$+\frac{\mathcal{J}(t)}{Dp(X(t),t)}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]dt. \tag{3.14}$$

We now average each term in Eq. (3.13) with respect to the white noise process using the following identity for any integrable function $g(X(t))$:

$$\langle g(X(t))\rangle=\left\langle \fint dx\,\delta(x-X(t))g(x)\right\rangle = \fint dx\,g(x)\langle\delta(x-X(t))\rangle=\fint dx\,g(x)p(x,t). \tag{3.15}$$

First,

$$\left\langle\frac{1}{p(X(t),t)}\frac{\partial p(X(t),t)}{\partial t}\right\rangle=\fint dx\frac{\partial p(x,t)}{\partial t} =\frac{\partial}{\partial t}\fint dx\,p(x,t)=0, \tag{3.16}$$

by conservation of probability. Second,

$$\left\langle\frac{1}{p(X(t),t)}\frac{\partial J(X(t),t)}{\partial x}\right\rangle=\fint dx\frac{\partial J(x,t)}{\partial x} =J(0^-,t)-J(0^+,t)=0. \tag{3.17}$$

Third,

$$\left\langle\frac{1}{p(X(t),t)}\lim_{\epsilon\to 0^+}[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]\right\rangle =\lim_{\epsilon\to 0^+}\fint dx[\delta(x-\epsilon)-\delta(x+\epsilon)]=0. \tag{3.18}$$

Finally, taking expectation of the Wiener process in the Itô multiplicative noise terms also gives zero. Hence, averaging Eq. (3.13) gives

$$\begin{aligned}\langle dS^{\rm sys}(X(t),t)+dS^{\rm env}(X(t),t)\rangle &=\left\langle\frac{J^2(X(t),t)}{Dp^2(X(t),t)}\right\rangle dt-\frac{\kappa_0}{2}\ln[p(0^-,t)/p(0^+,t)]\\ &\quad\times\lim_{\epsilon\to 0^+}\langle[\delta(X(t)-\epsilon)-\delta(X(t)+\epsilon)]\rangle dt\\ &=\left[\fint dx\,\frac{J(x,t)^2}{Dp(x,t)}+\mathcal{I}_{\rm int}(t)\right]dt,\end{aligned} \tag{3.19}$$

with $\mathcal{I}_{\rm int}(t)$ satisfying Eq. (2.17). We thus recover Eq. (2.16), which indicates that we can reverse the order of integration and differentiation so that

$$\left\langle\frac{dS^{\rm tot}(X(t),t)}{dt}\right\rangle=\frac{d}{dt}\langle S^{\rm tot}(X(t),t)\rangle. \tag{3.20}$$

IV. STOCHASTIC RESETTING ON A CIRCLE WITH A SEMIPERMEABLE INTERFACE

To illustrate our results on interfacial entropy production, we consider an example that supports an NESS in the large time limit by combining diffusion across a semipermeable interface with stochastic resetting. In previous work we considered scenarios similar to the one shown in Fig. 5(a) [53,55]. We assumed that the semipermeable interface acts as a screen for resetting in the sense that a particle located in $\mathcal{M}$ cannot reset to a point $\mathbf{x}_0\in\mathcal{M}^c$ and vice versa. This means that although the NESS is characterized by nonzero stationary fluxes in both domains, the net flux across the interface is zero. The last result can be understood as follows. Suppose, for concreteness, that the stationary interfacial flux $\mathcal{J}^*$ is positive so that there is a net flow of probability from $\mathcal{M}$ to $\mathcal{M}^c$. The screening effect of the interface means that there is no reset flux in the opposite direction, which is impossible for a stationary state with $p^*(\mathbf{x})>0$ unless $\mathcal{J}^*=0$. The vanishing of the interfacial flux can also be confirmed by explicitly calculating the NESS [53,55].

Therefore, in contrast to our previous work, we consider a Brownian particle diffusing on a circle of circumference L. The circle is topologically equivalent to a finite interval $[0,L]$ with a semipermeable interface at $x=\{0^+,L^-\}$. The particle is taken to reset at a rate r to a random position $y\in(0,L)$ generated from the density $\sigma_0(y)$. In Fig. 5(b) we show the example of resetting to a single point x_0, which is obtained by taking $\sigma_0(y)=\delta(y-x_0)$. Since the particle cannot reset by crossing the semipermeable interface, it resets in the anticlockwise direction when $X(t)\in[0^+,x_0)$ and resets in the clockwise direction when $X(t)\in(x_0,L^-]$. For a random reset location, the probability density $p(x,t)$, $x\in[0,L]$, evolves according to the equation

$$\frac{\partial p}{\partial t}=D\frac{\partial^2 p(x,t)}{\partial x^2}-rp(x,t)+r\sigma_0(x), \tag{4.1a}$$

together with the interfacial conditions

$$-D\frac{\partial p(0^+,t)}{\partial x}=-D\frac{\partial p(L^-,t)}{\partial x}=\mathcal{J}(t), \tag{4.1b}$$

$$\mathcal{J}(t)=\kappa_0[p(L^-,t)-p(0^+,t)]. \tag{4.1c}$$

(A factor of 1/2 has been absorbed into κ_0, and we have set $\sigma=1$.)

A. Average entropy production

We begin by calculating the average rate of entropy production, and show that there are contributions from the interface

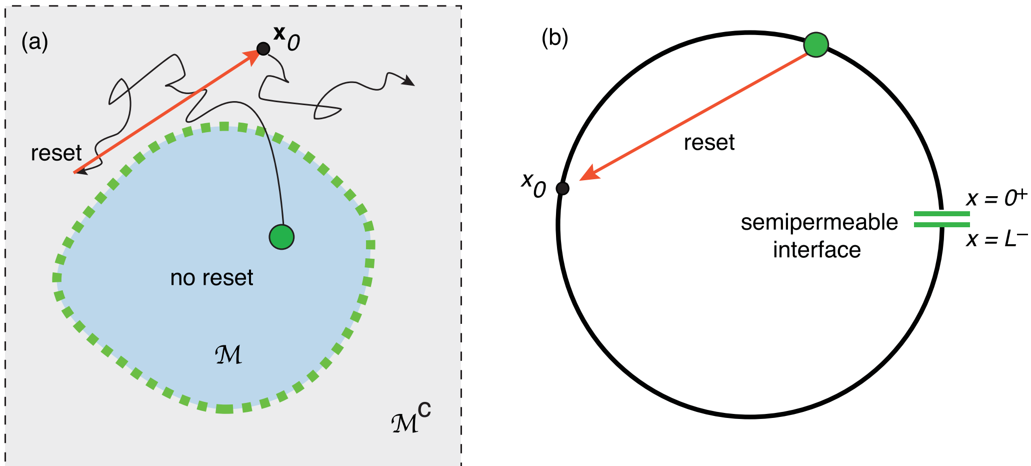

FIG. 5. Screening effect of a semipermeable membrane for a diffusing particle with resetting. (a) Closed semipermeable membrane $\partial\mathcal{M}$ in $\mathbb{R}^d$ with a resetting point $\mathbf{x}_0 \in \mathcal{M}^c$. Although the particle can diffuse across $\partial\mathcal{M}$ in either direction, it cannot reset to $\mathbf{x}_0$ whenever it is within $\mathcal{M}$. (b) Single particle diffusing on a circle with a semipermeable interface at $\{0, +, L^-\}$, and resetting to a point x_0. Let $X(t)$ denote the current particle position. If $X(t) \in [0^+, x_0)$, then it can only reset in the anticlockwise direction, otherwise it can only reset in the clockwise direction.

and the resetting protocol, We then calculate these contributions in the NESS. Substituting Eq. (4.1a) into the formula (2.12) for the average rate of entropy production gives

$$\mathcal{R}^{\text{sys}}(t) = \int_0^L dx\, \frac{\partial J(x,t)}{\partial x}[1 + \ln p(x,t)] + \mathcal{I}_r(t), \tag{4.2}$$

where $J(x,t) = -D\partial p(x,t)/\partial x$ and

$$\mathcal{I}_r(t) = r\int_0^L dx\ [p(x,t) - \sigma_0(x)] \ln p(x,t). \tag{4.3}$$

The integral on the right-hand side of Eq. (4.2) can be analyzed along identical lines to the case of no resetting. Since there are no forces, we find that

$$\mathcal{R}^{\text{sys}}(t) = \int_0^L dx\, \frac{J(x,t)^2}{Dp(x,t)} + \mathcal{I}_{\text{int}}(t) + \mathcal{I}_r(t), \tag{4.4}$$

with

$$\mathcal{I}_{\text{int}}(t) = \kappa_0[p(L^-,t) - p(0^+,t)] \ln\left[\frac{p(L^-,t)}{p(0^+,t)}\right]. \tag{4.5}$$

Hence, there are contributions from both the semipermeable interface and resetting.

In the special case $\sigma_0(x) = \delta(x - x_0)$ (resetting to a fixed location x_0), we have

$$\mathcal{I}_r(t) = r\int_0^L dx\, p(x,t) \ln p(x,t) - r\ln p(x_0,t). \tag{4.6}$$

Following along analogous lines to Ref. [3] we define $\mathcal{R}^{\text{reset}}(t) = -\mathcal{I}_r(t)$ and rewrite Eq. (4.4) as

$$\mathcal{R}^{\text{sys}}(t) + \mathcal{R}^{\text{reset}}(t) = \int_0^L dx\, \frac{J(x,t)^2}{Dp(x,t)} + \mathcal{I}_{\text{int}}(t) \geqslant 0. \tag{4.7}$$

Note that the left-hand side is the total rate of entropy production since, in this example, there is no external potential. As highlighted in the introduction, resetting to a single point is a unidirectional process that has no time-reversed equivalent. This means that the average rate of entropy production calculated using the Gibbs-Shannon entropy cannot be related to the degree of time-reversal symmetry breaking. However, as shown in Ref. [51], such a connection can be made in the case of a regular resetting density $\sigma_0(x) > 0$. The contribution $\mathcal{I}_r(t)$ is now decomposed as

$$\mathcal{I}_r(t) = K[p(\cdot,t)|\sigma_0] + K[\sigma_0|p(\cdot,t)] - \int_0^L dx\,[\sigma_0(x) - p(x,t)] \ln \sigma_0(x), \tag{4.8}$$

where $K[p|q]$ is the Kullback-Leibler divergence of any two measures p, q on $\mathbb{R}$:

$$K[p|q] = \int dx\, p(x) \ln[p(x)/q(x)]. \tag{4.9}$$

Using Jensen's inequality for convex functions it is straightforward to prove that $K[p|q] \geqslant 0$. Hence, we can rewrite the entropy production equation as

$$\mathcal{R}^{\text{sys}}(t) + \mathcal{R}^{\text{reset}}(t) = \int_0^L \frac{J(x,t)^2}{Dp(x,t)} + \mathcal{I}_{\text{int}}(t) + r(K[p(\cdot,t)|\sigma_0] + K[\sigma_0|p(\cdot,t)]) \geqslant 0, \tag{4.10}$$

where

$$\mathcal{R}^{\text{reset}}(t) = r\int_0^L dx\,[\sigma_0(x) - p(x,t)] \ln \sigma_0(x). \tag{4.11}$$

Equation (4.11) has a direct physical interpretation. Introducing the reset entropy, $S^{\text{reset}}(x)$ according to $\sigma_0(x) = \exp[S^{\text{reset}}(x)]$, we see that (up to the resetting rate r) $R^{\text{reset}}(t)$ can be expressed as the difference

$$R^{\text{reset}}(t) = r[\langle S^{\text{reset}}\rangle_{\text{insert}} - \langle S^{\text{reset}}(t)\rangle_{\text{remove}}], \tag{4.12}$$

between the average resetting entropy calculated with the probability density $\sigma_0(x)$ of the positions where the particles are inserted to the system, and the probability density of the positions from which those particles are removed, which is nothing but $p(x,t)$.

B. Nonequilibrium stationary state (NESS)

In contrast to the system without resetting, there exists a nonequilibrium stationary state (NESS) for which there are nonzero stationary fluxes $J^*(x)$ and $\mathcal{J}^*$, both of which contribute to the average rate of entropy production. Setting all time derivatives to zero in Eqs. (4.1) gives

$$D\frac{d^2p^*(x)}{dx^2} - rp^*(x) = -r\sigma_0(x), \tag{4.13a}$$

$$-D\frac{dp^*(0)}{dx} = -D\frac{dp^*(L)}{dx} = \mathcal{J}^* = \kappa_0[p^*(L)-p^*(0)]. \tag{4.13b}$$

For the moment, suppose that $\sigma_0(x)=\delta(x-x_0)$. The general solution of Eq. (4.13a) then takes the form

$$p^* = p_-^*(x,x_0) = A_1(x_0)\mathrm{e}^{\eta x} + B_1(x_0)\mathrm{e}^{-\eta x}, \quad 0<x<x_0, \tag{4.14a}$$

$$p^* = p_+^*(x,x_0) = A_2(x_0)\mathrm{e}^{\eta x} + B_2(x_0)\mathrm{e}^{-\eta x}, \quad x_0<x<L, \tag{4.14b}$$

with $\eta=\sqrt{r/D}$. There are four unknown coefficients and four supplementary conditions. The first pair arises from the conditions at x_0:

$$p_-^*(x_0,x_0) = p_+^*(x_0,x_0), \tag{4.15a}$$

$$D\frac{dp_+^*(x,x_0)}{dx}\bigg|_{x=x_0} - D\frac{dp_-^*(x,x_0)}{dx}\bigg|_{x=x_0} = -r, \tag{4.15b}$$

that is

$$A_2\mathrm{e}^{\eta x_0} + B_2\mathrm{e}^{-\eta x_0} = A_1\mathrm{e}^{\eta x_0} + B_1\mathrm{e}^{-\eta x_0}, \tag{4.16a}$$

$$A_2\mathrm{e}^{\eta x_0} - B_2\mathrm{e}^{-\eta x_0} = A_1\mathrm{e}^{\eta x_0} - B_1\mathrm{e}^{-\eta x_0} - \frac{r}{\eta D}. \tag{4.16b}$$

The second pair follow from the interfacial conditions (4.13b):

$$A_2\mathrm{e}^{\eta L} - B_2\mathrm{e}^{-\eta L} = A_1 - B_1, \tag{4.17a}$$

$$A_2\mathrm{e}^{\eta L} + B_2\mathrm{e}^{-\eta L} = \left(1-\frac{D\eta}{\kappa_0}\right)A_1 + \left(1+\frac{D\eta}{\kappa_0}\right)B_1. \tag{4.17b}$$

After some algebra we find that

$$A_1 = \frac{(a_-+b_-)\Gamma_-(x_0)\mathrm{e}^{\eta L} - (a_--b_-)\Gamma_+(x_0)\mathrm{e}^{-\eta L}}{b_-a_+ + b_+a_-}, \tag{4.18a}$$

$$B_1 = \frac{(a_+-b_+)\Gamma_-(x_0)\mathrm{e}^{\eta L} - (a_++b_+)\Gamma_+(x_0)\mathrm{e}^{-\eta L}}{b_-a_+ + b_+a_-}, \tag{4.18b}$$

and

$$A_2(x_0) = A_1(x_0) - \Gamma_-(x_0), \quad B_2(x_0) = B_1(x_0) + \Gamma_+(x_0), \tag{4.18c}$$

where

$$a_\pm = \mathrm{e}^{\pm\eta L} - 1, \quad b_\pm = a_\pm \pm \frac{D\eta}{\kappa_0}, \quad \Gamma_\pm(x_0) = \frac{r}{2\eta D}\mathrm{e}^{\pm\eta x_0}. \tag{4.19}$$

In Figs. 6(a) and 6(b) we plot the solutions $p_-^*(0,x_0)$ and $p_+^*(L,x_0)$ on either side of the semipermeable interface as a function of r and x_0, respectively. We fix the space and time units by setting $L=D=\kappa_0=1$. A number of observations can be made. First, if $x_0=0.5$ then $p_-^*(0,x_0)=p_+^*(L,x_0)$ for all resetting rates $r\geqslant 0$. This is a consequence of the symmetry of the configuration under the reflection $x\to 1-x$. This symmetry no longer holds when $x_0\neq 0.5$ and $r>0$. That is, $p_-^*(0,x_0) > p_+^*(L,x_0)$ for $x_0\in(0,0.5)$ and there is now an exchange symmetry $p_-^*(0,x_0)\leftrightarrow p_+^*(L,x_0)$ under reflection. Second, for fixed $x_0\in(0,L)$, the discontinuity across the interface is a nonmonotonic function of r, since the stationary state is at equilibrium when $r=0$ and the density at the interface vanishes in the limit $r\to\infty$. However, the discontinuity is a monotonically decreasing function of $x_0\in(0,0.5)$. These results are reflected in plots of the average entropy production rate at the interface,

$$\mathcal{I}_{\rm int}^* = \mathcal{J}^*(x_0)\ln[p_-^*(0,x_0)/p_+^*(L,x_0)], \tag{4.20}$$

with $\mathcal{J}^*(x_0)=\kappa_0[p_-^*(0,x_0)-p_+^*(L,x_0)]$; see Fig. 7. We also find that $\mathcal{I}_{\rm int}^*$ is a nonmonotonic function of the permeability κ_0, as illustrated in Fig. 8. This follows from the fact that $\mathcal{I}_{\rm int}^*$ vanishes in the limits $\kappa_0\to 0$ and $\kappa_0\to\infty$. In the first limit, the circle becomes topologically equivalent to a finite interval with totally reflecting boundaries at both end, whereas in the second limit the interface becomes totally transparent.

Let us now turn to a resetting protocol in which the particle resets to a random point according to the density

$$\sigma_0(y,x_0) = \Lambda_0(x_0)\mathrm{e}^{-|y-x_0|\xi_0}, \tag{4.21a}$$

$$\Lambda_0(x_0) = \frac{\xi_0}{2-\mathrm{e}^{-x_0\xi_0}-\mathrm{e}^{-(L-x_0)\xi_0}}. \tag{4.21b}$$

Note that $\sigma_0(y,x_0)\to\delta(x-x_0)$ in the limit $\xi_0\to\infty$ and $\sigma_0(y,x_0)\to 1/L$ in the limit $\xi_0\to 0$. The corresponding NESS is

$$p^*(x) = \int_0^x dy\, p_+(x,y)\sigma_0(y,x_0) + \int_x^L dy\, p_-(x,y)\sigma_0(y,x_0) = \mathcal{A}(x,x_0)\mathrm{e}^{\eta x} + \mathcal{B}(x,x_0)\mathrm{e}^{-\eta x}, \tag{4.22}$$

where

$$\mathcal{A}(x,x_0) = \int_0^L dy\, A_1(y)\sigma_0(y,x_0) - \int_0^x dy\, \Gamma_-(y)\sigma_0(y,x_0), \tag{4.23a}$$

$$\mathcal{B}(x,x_0) = \int_0^L dy\, B_1(y)\sigma_0(y,x_0) + \int_0^x dy\, \Gamma_+(y)\sigma_0(y,x_0). \tag{4.23b}$$

Moreover,

$$\int_0^x dy\, \Gamma_\pm(y)\sigma_0(y,x_0) = f_\pm(x), \tag{4.24}$$

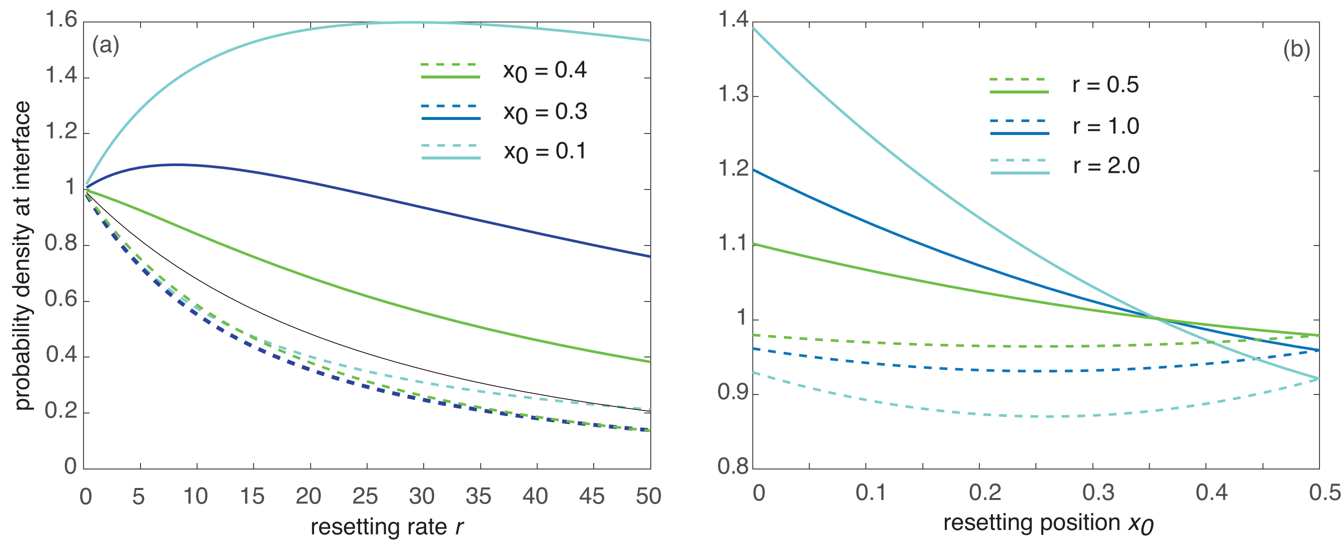

FIG. 6. Single-particle diffusion on a ring with resetting to the same location x_0. The ring is mapped to the interval $[0, L]$ with a semipermeable interface at $x = \{0^+, L^-\}$. Plots of the stationary densities $p^*(0^+)$ (solid curves) and $p^*(L^-)$ (dashed curves) on either side of the interface as a function of (a) the resetting rate r for fixed x_0 and (b) the resetting position x_0 for fixed r. Other parameter values are $D = \kappa_0 = L = 1$. The thin solid line in (a) is the stationary density when $x_0 = 0.5$. Note that by symmetry the density is continuous across the interface when $x_0 = 0.5$, as can be seen in panel (b).

for $x < x_0$ and

$$\int_0^x dy\, \Gamma_\pm(y)\sigma_0(y, x_0) = f_\pm(x_0) + \frac{\sqrt{r/D}\Lambda_0 e^{x_0\xi_0}}{2} \frac{(e^{x[\pm\eta-\xi_0]} - e^{x_0[\pm\eta-\xi_0]})}{\pm\eta - \xi_0} \tag{4.25}$$

for $x > x_0$, where

$$f_\pm(x) := \frac{\sqrt{r/D}\Lambda_0 e^{-x_0\xi_0}}{2} \frac{(e^{x[\pm\eta+\xi_0]} - 1)}{\pm\eta + \xi_0}. \tag{4.26}$$

In Fig. 9 we plot the corresponding interfacial entropy production rate $\mathcal{I}^*_{\rm int}$ as a function of r for different values of the decay parameter ξ_0 in the definition of the resetting position density given by Eq. (4.21). Since $\sigma_0(x)$ becomes a uniform distribution in the limit $\xi_0 \to 0$, it follows that $\mathcal{I}^*_{\rm int} \to 0$ by symmetry. However, in the limit $\xi_0 \to \infty$, we recover the curve obtained for resetting to x_0. Finally, Eq. (4.10) implies that for $0 < \xi_0 < \infty$, there is also a positive contribution to the average entropy production rate from resetting. The stationary version takes the form

$$\mathcal{I}^*_r = r \int_0^L dx\, [p^*(x) - \sigma_0(x, x_0)] \ln(p^*(x)) - \ln \sigma_0(x, x_0)]. \tag{4.27}$$

Example numerical plots of $\mathcal{I}^*_r$ as a function of r and ξ_0 are shown in Fig. 10. As expected, $\mathcal{I}^*_r$ blows up in the limit

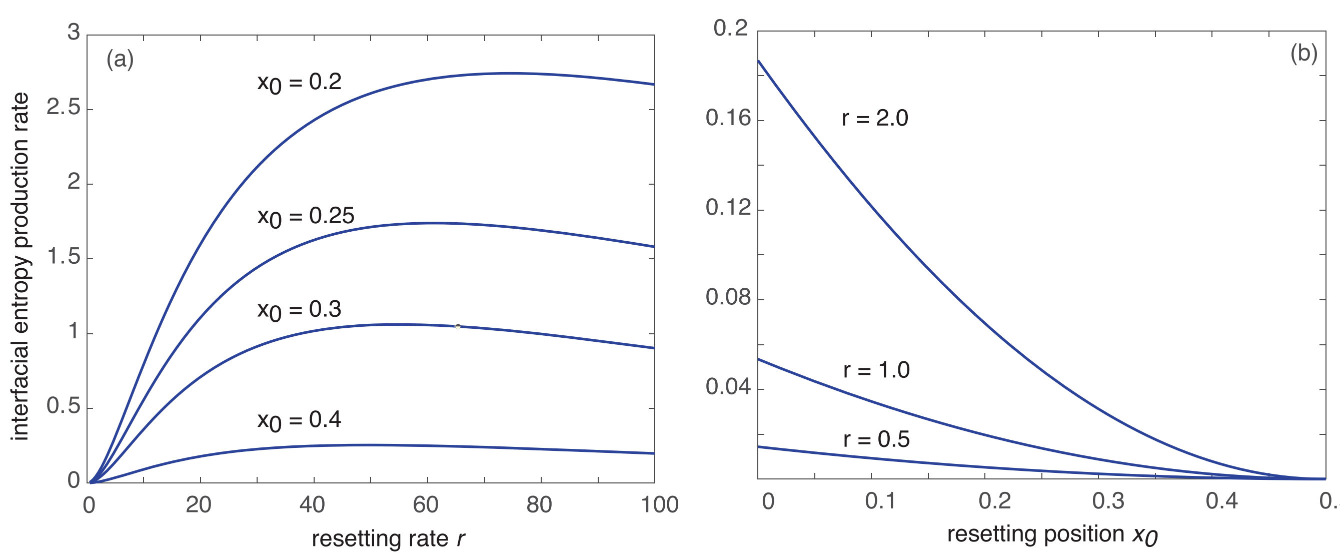

FIG. 7. Single-particle diffusion on a ring with resetting to the same location x_0. Plots of the average rate of interfacial entropy production $\mathcal{I}^*_{\rm int}$ as a function of (a) the resetting rate r and (b) the resetting location x_0. Other parameter values are the same as Fig. 6.

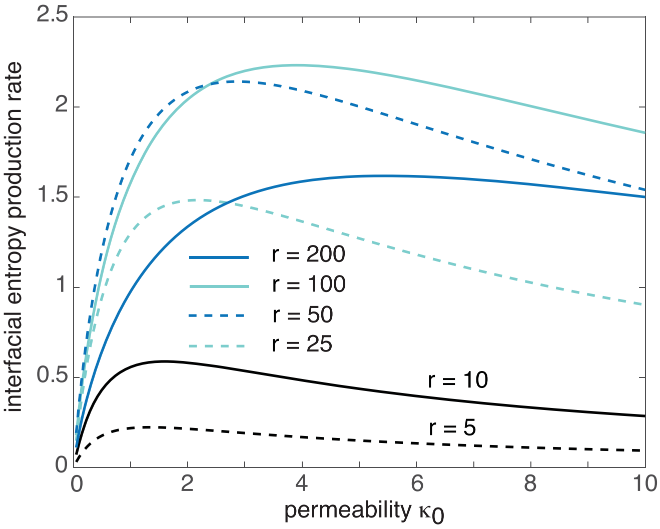

FIG. 8. Single-particle diffusion on a ring with resetting to the same location $x_0 = 0.25$. Plots of the average rate of interfacial entropy production $\mathcal{I}^*_{\rm int}$ as a function of the permeability κ_0 and different values of r. Other parameter values are the same as Fig. 6.

$\xi_0 \to \infty$ since the corresponding Kullback-Leibler divergences become singular.

V. DISCUSSION

In this paper we showed how the presence of a semipermeable interface $\mathcal{S}$ increases the average rate of entropy production of a single diffusing particle by an amount that is equal to the product of the flux through the interface and the logarithm of the ratio of the probability density on either side of the interface, integrated along $\mathcal{S}$. We also presented a probabilistic interpretation of the interfacial entropy production rate that is based on snapping out BM. The latter represents individual stochastic trajectories as sequences of partially reflected BMs that are restricted to one side of the interface or the other. When a given round of partially reflected BM is terminated, a Bernoulli random variable is used to determine which side of the interface the next round takes place. We identified this switching process as the source of interfacial entropy production. Moreover, we showed how a biased switching process is equivalent to a directionally biased interface arising from a jump discontinuity in the chemical potential. The latter contributes to the dissipation of heat into the environment. Snapping out BM also allowed us to construct a stochastic version of entropy production defined along individual trajectories. Averaging with respect to the distribution of trajectories recovered the expression for the average rate of entropy production obtained from the Gibbs-Shannon entropy. Finally, we illustrated our formula for the interfacial entropy production rate using the example of diffusion with stochastic resetting on a circle, and found that the average rate of

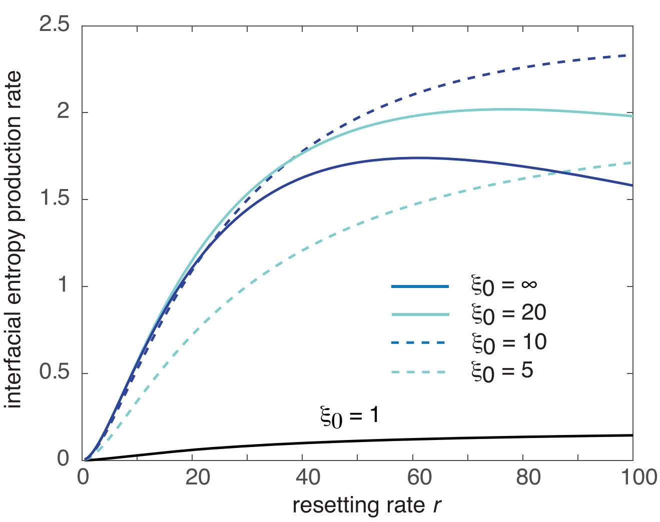

FIG. 9. Single-particle diffusion on a ring with resetting to a random location that is distributed according to the probability density (4.21) parameterized by ξ_0. Plots of the average rate of interfacial entropy production $\mathcal{I}^*_{\rm int}$ as a function of r for different values of ξ_0. Other parameters are $D = L = 1$, $\kappa_0 = 1$, and $x_0 = 0.25$.

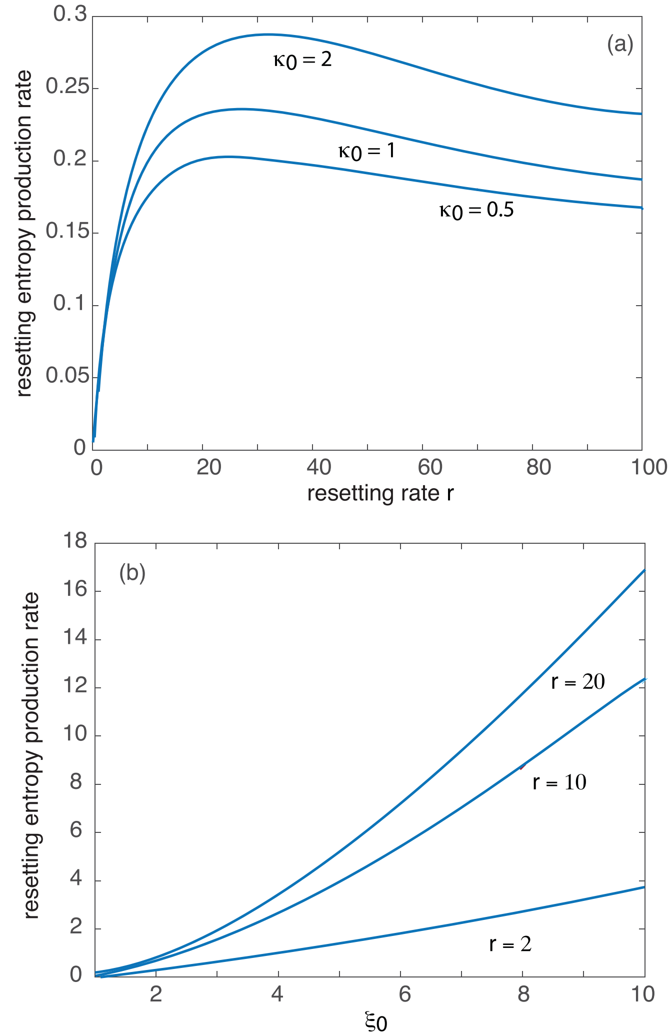

FIG. 10. Single-particle diffusion on a ring with resetting to a random location that is distributed according to the probability density (4.21) parameterized by ξ_0. Plots of the average rate of resetting entropy production $\mathcal{I}^*_r$ as a function of (a) r for different values of ξ_0 and (b) ξ_0 for different values of r. Other parameters are $D = L = 1$, $\kappa_0 = 1$, and $x_0 = 0.25$.

interfacial entropy production in the NESS is a nonmonotonic function of the resetting rate and the permeability.

One direction for future work would be to relate the stochastic entropy for diffusion through a semipermeable interface to the ratio of forward and backward path probabilities [1,3]. More specifically, a fundamental result of stochastic thermodynamics is that for many continuous stochastic processes, the total stochastic or instantaneous entropy production can be expressed as

$$S^{\rm tot}(t) = \ln\left[\frac{\mathcal{P}[X(\tau), 0 \leqslant \tau \leqslant t]}{\mathcal{P}[X(t-\tau), 0 \leqslant \tau \leqslant t]}\right]. \tag{5.1}$$

Such a relationship provides a basis for deriving a variety of fluctuation relations [1,3]. The corresponding average production rate in steady state is then

$$\mathcal{R}^{\rm tot} = \lim_{t\to\infty} \frac{1}{t}\left\langle \ln\left[\frac{\mathcal{P}[X(\tau), 0 \leqslant \tau \leqslant t]}{\mathcal{P}[X(t-\tau), 0 \leqslant \tau \leqslant t]}\right]\right\rangle. \tag{5.2}$$

One way to establish a result of the form (5.1) is to use path integrals. Within a path integral framework, one could treat diffusion as a random walk on a lattice in which a semipermeable barrier is represented in terms of local defects [57–60].

Another possible extension of the paper is to apply the theory to a more general class of stochastic processes that result in an NESS at the interface. We considered the particular example of instantaneous resetting, under the assumption that the particle cannot reset by crossing the interface. However, instantaneous resetting is not physically realizable. One physical implementation of noninstantaneous resetting is BM in an intermittent confining potential, where the potential is randomly switched on and off [61–65]. During the ON phases, a diffusing particle tends to move toward the minimum of the potential, which thus plays an analogous role to the resetting position in instantaneous resetting. This return phase is clearly of finite duration. Moreover, once the particle reaches a neighborhood of the minimum, it tends to remain there until switching to an OFF state, which is analogous to a refractory phase. One issue that would need to be addressed is whether or not a semipermeable membrane screens the potential when it is ON. It would also be interesting to derive general conditions under which resetting results in an interfacial entropy production rate that is a unimodal function of the effective resetting rate, analogous to Figs. 6–10.

Finally, note that in this paper we considered a mesoscopic model of diffusion through a semipermeable interface, which involved phenomenological parameters such as the permeability κ_0 and the directional bias σ. These also appeared as parameters in snapping out BM, with κ_0 determining the rate at which each round of partially reflected BM is killed and σ specifying the bias of the switching Bernoulli process. Another direction of future work would be to develop a microscopic model of a semipermeable interface that identifies the biophysical mechanisms underlying κ_0, σ, and interfacial entropy production. Along these lines, we have recently proposed a more general model of snapping out BM, in which each round of partially reflected BM is killed according to a more general threshold distribution than the exponential (A6) [33,34]. The corresponding effective permeability becomes a time-dependent function that can have heavy tails. A more realistic biophysical model would also need to consider an interface with finite width. Indeed, one can derive the standard interfacial equations (2.1c) by considering the zero width limit of a thin sheet of membrane.

APPENDIX: MATHEMATICAL FORMULATION OF SNAPPING OUT BM

The dynamics of snapping out BM is formulated in terms of a sequence of killed reflected BMs in either $\Omega_- = (-\infty, 0^-]$ or $\Omega_+ = [0^+, \infty)$ [31–34]. Let $\mathcal{T}_n$ denote the time of the $n^{\rm th}$ killing (with $\mathcal{T}_0 = 0$). Immediately after the killing event, the position of the particle is taken to be

$$X(\mathcal{T}_n^+) = \lim_{\epsilon\to 0^+} [-Y_n\epsilon + (1-Y_n)\epsilon], \tag{A1}$$

where Y_n is an independent Bernoulli random variable with $\mathbb{P}[Y_n = 1] = \mathbb{P}[Y_n = 0] = 1/2$. (We are assuming the interface is symmetric, that is, $\sigma = 1$.) Suppose that $X(t) \in \Omega_+$ for $t \in (\mathcal{T}_n, \mathcal{T}_{n+1})$, that is, $X(\mathcal{T}_n^+) = 0^+$, and introduce the boundary local time [35–39]

$$L_n^+(t) = \lim_{\epsilon\to 0^+} \frac{D}{\epsilon}\int_0^t \Theta(\epsilon - X(\tau+\mathcal{T}_n))d\tau. \tag{A2}$$

The boundary local time $L_n^+(t)$ tracks the amount of the time the particle is in contact with the right-hand side of the interface over the time interval $[\mathcal{T}_n, t]$. The SDE for $X(t)$, $t \in (\mathcal{T}_n, \mathcal{T}_{n+1})$, is given by the Skorokhod equation for reflected BM in the half-line Ω_+:

$$dX(t) = \frac{1}{\gamma}F(X(t))dt + \sqrt{2D}dW(t) + dL_n(t) \tag{A3}$$

for $t \in (\mathcal{T}_n, \mathcal{T}_{n+1})$, where $W(t)$ is a Wiener process with $W(0) = 0$. Formally speaking,

$$dL_n^+(t) = \lim_{\epsilon\to 0^+} \delta(X(t+\mathcal{T}_n) - \epsilon)dt, \tag{A4}$$

so that each time the particle hits the interface it is given a positive impulsive kick back into the domain. The time of the next killing is then determined by the condition

$$\mathcal{T}_{n+1} = \mathcal{T}_n + \inf\{t > 0,\ L_n^+(t) \geqslant \widehat{\ell}\}, \tag{A5}$$

where $\widehat{\ell}$ is an independent randomly generated local time threshold with

$$\mathbb{P}[\widehat{\ell} > \ell] = {\rm e}^{-\kappa_0\ell/D}, \quad \ell \geqslant 0. \tag{A6}$$

However, if $X(\mathcal{T}_n^+) = 0^-$, then the next round of reflected BM takes place in the domain Ω_-. The corresponding SDE is

$$dX(t) = \frac{1}{\gamma}F(X(t))dt + \sqrt{2D}dW(t) - dL_n^-(t), \tag{A7}$$

with $t \in (\mathcal{T}_n, \mathcal{T}_{n+1})$, $X(t) \in \Omega_-$,

$$L_n^-(t) = \lim_{\epsilon\to 0^+} \frac{D}{\epsilon}\int_0^t \Theta(\epsilon + X(\tau+\mathcal{T}_n))d\tau, \tag{A8}$$

and

$$\mathcal{T}_{n+1} = \mathcal{T}_n + \inf\{t > \mathcal{T}_n: L_n^-(t) \geqslant \widehat{\ell}\}. \tag{A9}$$

We now use renewal theory to sketch a proof that the distribution of sample paths in 1D snapping out BM is given by the solution of the corresponding FP Eq. (2.1). For an alternative proof in 1D see Ref. [31] and for the generalization to higher spatial dimensions see Ref. [34]. Let $p(z,t)$ denote the probability density of snapping out BM for $p(x,0)=\delta(x-x_0)$ and $x_0>0$. Let $q(z,t|x_0)$ be the corresponding solution for partially reflected BM in Ω_+. (It is straightforward to generalize the analysis to the case of a general distribution of initial conditions $g(x_0)$ that spans both sides of the interface.) The densities p are related to q according to the last renewal equation [33,34]

$$p(x,t)=q(x,t|x_0)+\frac{\kappa_0}{2}\int_0^t q(x,\tau|0)[p(0^+,t-\tau) + p(0^-,t-\tau)]d\tau,\quad x>0, \tag{A10a}$$

$$p(x,t)=\frac{\kappa_0}{2}\int_0^t q(|x|,\tau|0)[p(0^+,t-\tau) + p(0^-,t-\tau)]d\tau,\quad x<0. \tag{A10b}$$

The first term on the right-hand side of Eq. (A.10a) represents all sample trajectories that have never been absorbed by the barrier at $x=0^\pm$ up to time t. The corresponding integrand represents all trajectories that were last absorbed (stopped) at time $t-\tau$ in either the positively or negatively reflected BM state and then switched to the appropriate sign to reach x with probability 1/2. Since the particle is not absorbed over the interval $(t-\tau,t]$, the probability of reaching $x\in\Omega_+$ starting at $x=0^\pm$ is $q(x,\tau|0)$. The probability that the last stopping event occurred in the interval $(t-\tau,t-\tau+d\tau)$ irrespective of previous events is $\kappa_0 d\tau$. A similar argument holds for Eq. (A.10b).

The renewal Eqs. (A10) can be used to express p in terms of q using Laplace transforms. First,

$$\widetilde{p}(x,s)=\widetilde{q}(x,s|x_0)+\frac{\kappa_0}{2}\widetilde{q}(x,s|0)[\widetilde{p}(0^+,s)+\widetilde{p}(0^-,s)],\quad x>0, \tag{A11a}$$

$$\widetilde{p}(x,s)=\frac{\kappa_0}{2}\widetilde{q}(|x|,s|0)[\widetilde{p}(0^+,s)+\widetilde{p}(0^-,s)],\quad x<0. \tag{A11b}$$

Setting $x=0^\pm$ in Eq. (A11), summing the results and rearranging shows that

$$\widetilde{p}(0^+,s)+\widetilde{p}(0^-,s)=\frac{\widetilde{q}(0,s|x_0)}{1-\kappa_0\widetilde{q}(0,s|0)}. \tag{A12}$$

Substituting back into Eqs. (A11) yields the explicit solution

$$\widetilde{p}(x,s)=\widetilde{q}(x,s|x_0)+\frac{\kappa_0\widetilde{q}(0,s|x_0)/2}{1-\kappa_0\widetilde{q}(0,s|0)}\widetilde{q}(x,s|0),\quad x>0, \tag{A13a}$$

$$\widetilde{p}(x,s)=\frac{\kappa_0\widetilde{q}(0,s|x_0)/2}{1-\kappa_0\widetilde{q}(0,s|0)}\widetilde{q}(|x|,s|0),\quad x<0. \tag{A13b}$$

Calculating the full solution $p(x,t)$ thus reduces to the problem of finding the corresponding solution $q(x,t|x_0)$ of partially reflected BM in Ω_+. As we have shown elsewhere, this then establishes that $p(x,t)$ satisfies the interfacial conditions (2.1c).

Interfacial asymmetry ($\sigma<1$) can be incorporated into snapping out BM by taking the independent Bernoulli random variable Y_n in Eq. (A1) to have the biased probability distribution $\mathbb{P}[Y_n=0]=\alpha$ and $\mathbb{P}[Y_n=1]=1-\alpha$ for $0<\alpha<1$ [34]. The 1D renewal Eq. (A11) becomes

$$\widetilde{p}(x,s)=\widetilde{q}(x,s|x_0)+\frac{\kappa_0\alpha}{2}\widetilde{q}(x,s|0)[\widetilde{p}(0^+,s)+\widetilde{p}(0^-,s)],\quad x>0 \tag{A14a}$$

$$\widetilde{p}(x,s)=\frac{\kappa_0[1-\alpha]}{2}\widetilde{q}(|x|,s|0)[\widetilde{p}(0^+,s)+\widetilde{p}(0^-,s)],\quad x<0. \tag{A14b}$$

Setting $x=0^\pm$ in Eqs. (A14), summing the results and rearranging recovers Eq. (A12). It can then be shown that snapping out BM with biased switching and $\alpha>1/2$ is equivalent to single-particle diffusion through a directed semipermeable barrier with an effective permeability $\kappa_0\alpha/2$ and bias $\sigma=(1-\alpha)/\alpha$.

[1] L. Peliti and S. Pigolotti, *Stochastic Thermodynamics* (Princeton University Press, Princeton, NJ, 2021).
[2] K. Sekimoto, *Stochastic Energetics*, Lecture Notes in Physics Vol. 799 (Springer, Berlin, 2010).
[3] U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, Rep. Prog. Phys. **75**, 126001 (2012).
[4] L. Cocconi, R. Garcia-Millan, Z. Zhen, B. Buturca, and G. Pruessner, Entropy production in exactly solvable systems, Entropy **22**, 1252 (2020).
[5] U. Seifert, Entropy production along a stochastic trajectory and an integral fluctuation theorem, Phys. Rev. Lett. **95**, 040602 (2005).
[6] C. Jarzynski, Equalities and inequalities: Irreversibility and the second law of thermodynamics at the nanoscale, Annu. Rev. Condens. Matter Phys. **2**, 329 (2011).
[7] E. M. Sevick, R. Prabhakar, S. R. Williams, and D. J. Searles, Fluctuation theorems, Annu. Rev. Phys. Chem. **59**, 603 (2008).
[8] R. Chetrite and K. Gawedzki, Fluctuation relations for diffusion processes, Commun. Math. Phys. **282**, 469 (2008).
[9] R. Chetrite and S. Gupta, Two refreshing views of fluctuation theorems through kinematics elements and exponential martingale, J. Stat. Phys. **143**, 543 (2011).
[10] S. Pigolotti, I. Neri, É. Roldán, F. Jülicher, Generic properties of stochastic entropy production, Phys. Rev. Lett. **119**, 140604 (2017).
[11] I. Neri, E. Roldan, S. Pigolotti, and F. Jülicher, Statistics of infima and stopping times of entropy production and applications to active molecular processes, Phys. Rev. X **7**, 011019 (2017).
[12] I. Neri, E. Roldán, S. Pigolotti, and F. Jülicher, Integral fluctuation relations for entropy production at stopping times, J. Stat. Mech. (2019) 104006.
[13] H. Ge, C. Jia, and X. Jin, Martingale structure for general thermodynamic functionals of diffusion processes under second-order averaging, J. Stat. Phys. **184**, 17 (2021).
[14] E. Roldán, I. Neri, R. Chetrite, S. Gupta, S. Pigolotti, F. Jülicher, and K. Sekimoto, Martingales for physicists: A treatise on stochastic thermodynamics and beyond, Adv. Phys. 1 (2024).

[15] R. Phillips, J. Kondev, J. Theriot, H. G. Garcia, and N. Orme, *Physical Biology of the Cell* (Garland, New York, NY, 2012).

[16] V. Nikonenko and N. Pismenskaya (Eds.), Ion and molecule transport in membrane systems (special issue), Int. J. Mol. Sci. **22**, 3556 (2021).

[17] P. C. Bressloff, *Stochastic Processes in Cell Biology* (Springer, Cham, Switzerland, 2021).

[18] J. E. Tanner, Transient diffusion in a system partitioned by permeable barriers. Application to NMR measurements with a pulsed field gradient, J. Chem. Phys. **69**, 1748 (1978).

[19] A. Coy and P. T. Callaghan, Pulsed gradient spin echo nuclear magnetic resonance for molecules diffusing between partially reflecting rectangular barriers, J. Chem. Phys. **101**, 4599 (1994).

[20] D. S. Grebenkov, Pulsed-gradient spin-echo monitoring of restricted diffusion in multilayered structures, J. Magn. Reson. **205**, 181 (2010).

[21] G. Pontrelli, and F. de Monte, Mass diffusion through two-layer porous media: An application to the drug-eluting stent, Int. J. Heat Mass Transf. **50**, 3658 (2007).

[22] H. Todo, T. Oshizaka, W. R. Kadhum, and K. Sugibayashi, Mathematical model to predict skin concentration after topical application of drugs, Pharmaceutics **5**, 634 (2013).

[23] D. Li and H. Wang, Recent developments in reverse osmosis desalination membranes, J. Mater. Chem. **20**, 4551 (2010).

[24] J. Assis, H. C. Giacomini, and M. C. Ribeiro, Road permeability index: Evaluating the heterogeneous permeability of roads for wildlife crossing, Ecol. Indic. **99**, 365 (2019).

[25] H. L. Beyer, E. Gurarie, L. Børger, M. Panzacchi, M. Basille, I. Herfindal, B. Van Moorter, S. R. Lele, and J. Matthiopoulos, "You shall not pass!": Quantifying barrier permeability and proximity avoidance by animals, J. Anim. Ecol. **85**, 43 (2016).

[26] V. M. Kenkre and L. Giuggioli, *Theory of the Spread of Epidemics and Movement Ecology of Animals: An Interdisciplinary Approach Using Methodologies of Physics and Mathematics* (Cambridge University Press, Cambridge, UK, 2021).

[27] O. Kedem and A. Katchalsky, Thermodynamic analysis of the permeability of biological membrane to non-electrolytes, Biochim. Biophys. Acta **27**, 229 (1958).

[28] A. Katchalsky and O. Kedem, Thermodynamics of flow processes in biological systems, Biophys. J. **2**, 53 (1962).

[29] A. Kargol, M. Kargol, and S. Przestalski, The Kedem-Katchalsky equations as applied for describing substance transport across biological membranes, Cell. Mol. Biol. Lett. **2**, 117 (1996).

[30] V. Aho, K. Mattila, T. Kühn, P. Kekäläinen, O. Pulkkine, R. B. Minussi, M. Vihinen-Ranta, and J. Timonen, Diffusion through thin membranes: Modeling across scales, Phys. Rev. E **93**, 043309 (2016).

[31] A. Lejay, The snapping out Brownian motion, Ann. Appl. Probab. **26**, 1727 (2016).

[32] A. Lejay, Monte Carlo estimation of the mean residence time in cells surrounded by thin layers, Math. Comput. Simul. **143**, 65 (2018).

[33] P. C. Bressloff, A probabilistic model of diffusion through a semi-permeable barrier, Proc. R. Soc. A **478**, 20220615 (2022).

[34] P. C. Bressloff, Renewal equations for single-particle diffusion through a semi-permeable interface, Phys. Rev. E **107**, 014110 (2023).

[35] P. Lèvy, Sur certains processus stochastiques homogènes, Compos. Math. **7**, 283 (1940).

[36] K. Itô and H. P. McKean, Brownian motions on a half line, Illinois J. Math. **7**, 181 (1963).

[37] E. B. Dynkin, *Markov Processes I and II* (Springer-Verlag, Berlin, 1965).

[38] H. P. McKean, Brownian local time, Adv. Math. **16**, 91 (1975).

[39] D. S. Grebenkov, Partially reflected Brownian motion: A stochastic approach to transport phenomena, in *Focus on Probability Theory*, edited by L. R. Velle (Nova Science Publishers, Hauppauge, 2006), pp. 135–169.

[40] M. R. Evans and S. N. Majumdar, Diffusion with stochastic resetting, Phys. Rev. Lett. **106**, 160601 (2011).

[41] M. R. Evans and S. N. Majumdar, Diffusion with optimal resetting, J. Phys. A: Math. Theor. **44**, 435001 (2011).

[42] M. R. Evans and S. N. Majumdar, Diffusion with resetting in arbitrary spatial dimension, J. Phys. A **47**, 285001 (2014).

[43] M. R. Evans, S. N. Majumdar, and G. Schehr, Stochastic resetting and applications, J. Phys. A **53**, 193001 (2020).

[44] J. Fuchs, S. Goldt, and U. Seifert, Stochastic thermodynamics of resetting, Europhys. Lett. **113**, 60009 (2016).

[45] A. Pal and S. Rahav, Integral fluctuation theorems for stochastic resetting systems, Phys. Rev. E **96**, 062135 (2017).

[46] D. M. Busiello, D. Gupta, and A. Maritan, Entropy production in systems with unidirectional transitions, Phys. Rev. Res. **2**, 023011 (2020).

[47] D. Gupta, C. A. Plata, and A. Pal, Work fluctuations and Jarzynski equality in stochastic resetting, Phys. Rev. Lett. **124**, 110608 (2020).

[48] A. Pal, S. Reuveni, and S. Rahav, Thermodynamic uncertainty relation for systems with unidirectional transitions, Phys. Rev. Res. **3**, 013273 (2021).

[49] F. H. Gonzalez, A. P. Riascos, and D. Boyer, Diffusive transport on networks with stochastic resetting to multiple nodes, Phys. Rev. E **103**, 062126 (2021).

[50] J. Q. Toledo-Marin and D. Boyer, First passage time and information of a one-dimensional Brownian particle with stochastic resetting to random positions, Physica A **625**, 129027 (2023).

[51] F. Mori, K. S. Olsen, and S. Krishnamurthy, Entropy production of resetting processes, Phys. Rev. Res. **5**, 023103 (2023).

[52] H. Alston, L. Cocconi, and T. Bertrand, Non-equilibrium thermodynamics of diffusion in fluctuating potentials, J. Phys. A: Math. Theor. **55**, 274004 (2022).

[53] P. C. Bressloff, Diffusion-mediated surface reactions and stochastic resetting, J. Phys. A **55**, 275002 (2022).

[54] Z. Benkhadaj and D. S. Grebenkov, Encounter-based approach to diffusion with resetting, Phys. Rev. E **106**, 044121 (2022).

[55] P. C. Bressloff, Diffusion with stochastic resetting screened by a semi-permeable interface, J. Phys. A **56**, 105001 (2023).

[56] O. Farago, Algorithms for Brownian dynamics across discontinuities, J. Comput. Phys. **423**, 109802 (2020).

[57] J. G. Powles, M. Mallett, G. Rickayzen, and W. Evans, Exact analytic solutions for diffusion impeded by an infinite array of partially permeable barriers, Proc. R. Soc. London A **436**, 391 (1992).

[58] V. M. Kenkre, L. Giuggiol, and Z. Kalay, Molecular motion in cell membranes: Analytic study of fence-hindered random walks, Phys. Rev. E **77**, 051907 (2008).

[59] D. Novikov, E. Fieremans, J. Jensen, and J. A. Helpern, Random walks with barriers, Nat. Phys. **7**, 508 (2011).

[60] T. Kay and L. Giuggioli, Diffusion through permeable interfaces: Fundamental equations and their application to first-passage and local time statistics, Phys. Rev. Res. **4**, L032039 (2022).

[61] O. Tal-Friedman, A. Pal, A. Sekhon, S. Reuveni, and Y. Roichman, Experimental realization of diffusion with stochastic resetting, J. Phys. Chem. Lett. **11**, 7350 (2020).

[62] D. Gupta, C. A. Plata, A. Kundu, and A. Pal, Stochastic resetting with stochastic returns using an external trap, J. Phys. A **54**, 025003 (2021).

[63] G. Mercado-Vasquez, D. Boyer, S. N. Majumdar, and G. Schehr, Intermittent resetting potentials, J. Stat. Mech. (2020) 113203.

[64] I. Santra, S. Das, and S. K. Nath, Brownian motion under intermittent harmonic potentials, J. Phys. A: Math. Theor. **54**, 334001 (2021).

[65] P. Xu, T. Zhou, R. Metzler, and W. Deng, Stochastic harmonic trapping of a Lévy walk: Transport and first-passage dynamics under soft resetting strategies, New J. Phys. **24**, 033003 (2022).