Finite-time fluctuation theorem for diffusion-influenced surface reactions

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Received 10 June 2018
Accepted for publication 31 July 2018
Published 22 August 2018

Abstract. A finite-time fluctuation theorem is proved for the diffusion-influenced surface reaction $\text{A} \rightleftharpoons \text{B}$ in a domain with any geometry where the species A and B undergo diffusive transport between the reservoir and the catalytic surface. A corresponding finite-time thermodynamic force or affinity is associated with the symmetry of the fluctuation theorem. The time dependence of the affinity and the reaction rates characterizing the stochastic process can be expressed analytically in terms of the solution of deterministic diffusion equations with specific boundary conditions.

Keywords: chemical kinetics, fluctuation phenomena, large deviations in non-equilibrium systems, stochastic processes
1. Introduction

When driven out of equilibrium by thermodynamic forces or affinities, systems composed of atoms and molecules manifest macroscopic fluxes dissipating energy and producing thermodynamic entropy [1–5]. In particular, for diffusion-influenced surface reactions, reactant and product molecules diffuse between the reservoir where they enter or exit the system and the catalytic surface where they undergo interconversion...
On macroscopic scales, the standard description of such processes makes use of deterministic diffusion equations with suitable boundary conditions on the concentration fields of the reacting species. However, on mesoscopic scales, molecular motion is erratic and reactive events occur at random on the catalytic surface, which requires a description in terms of stochastic processes. Many approaches have been proposed to describe natural random phenomena, especially for molecular and colloidal systems [7–20]. In this context, time-reversal symmetry relations, known as fluctuation theorems [21–26], are satisfied by the fluctuations of the currents flowing across nonequilibrium systems. These theorems are formulated within the framework of large-deviation theory [27] since they concern the full counting statistics of the currents, including rare events that are exponentially suppressed in time. For systems in stationary states, fluctuation theorems are time-reversal symmetry relations holding in the long-time limit. This has been established, in particular, for systems sustaining reactions or transport by diffusion [28–36].

However, it has been shown in [37] that such time-reversal symmetry relations may also hold over finite time intervals for certain reactions taking place in systems without spatial extension. In these systems, a thermodynamic force or affinity can thus be defined at every time as a consequence of the finite-time symmetry.

Here, our purpose is to show that such a finite-time fluctuation theorem also holds in spatially extended systems where a surface reaction is influenced by the diffusion of reactants and products from and to the reservoir. The problem is formulated within the theory of stochastic partial differential equations in terms of stochastic diffusion equations coupled by stochastic boundary conditions for the reaction $A \rightleftharpoons B$ at the catalytic surface. In this framework, a finite-time fluctuation theorem is established for the probability distribution that a certain number of reactive events have occurred during some finite time interval. The theorem is proved by spatial discretization into small cells, leading to a Markov jump process ruling the time evolution of the numbers of molecules inside the cells. Using the linearity between the reaction rate and the molecular concentrations, the master equation of this Markov jump process can be exactly solved using the generating function method [18], which provides the analytical expression for the cumulant generating function at every time. Returning to the continuum description, the cumulant generating function is obtained in terms of finite-time rates given by solving deterministic diffusion equations with specific boundary conditions. The large-deviation properties of the spatially extended stochastic process can thus be found by solving deterministic partial differential equations.

The paper is organized as follows. The main result is presented in section 2 where the finite-time fluctuation theorem is stated for the probability distribution of the number of reactive events and the associated cumulant generating function. In this section, the finite-time rates and the corresponding affinity are expressed in terms of the solution of deterministic diffusion equations with the specific boundary conditions, and connection is made to the thermodynamic entropy production. The proof of the finite-time fluctuation theorem is carried out in section 3. Section 4 gives concluding remarks and perspectives.
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2. The main results

2.1. Stochastic partial differential equations for the diffusion-influenced surface reaction

Let us consider a diffusive medium of dimension $d$ and volume $V$, extending between three surfaces $\partial V = S_{\text{cat}} \cup S_{\text{inert}} \cup S_{\text{res}}$. $S_{\text{cat}}$ is a catalytic surface where the reaction $A \rightarrow B$ takes place. $S_{\text{inert}}$ is an inert surface where the species $A$ and $B$ are reflected. $S_{\text{res}}$ is a surface in contact with a reservoir for the species $A$ and $B$. These species undergo diffusion in the volume $V$ so that their concentrations, $c_A$ and $c_B$, obey the stochastic diffusion equations,

$$\partial_t c_A + \nabla \cdot j_A = 0, \quad j_A = -D_A \nabla c_A + \eta_A,$$

$$\partial_t c_B + \nabla \cdot j_B = 0, \quad j_B = -D_B \nabla c_B + \eta_B,$$

expressed in terms of Gaussian noise fields such that

$$\langle \eta_k(r, t) \rangle = 0, \quad \langle \eta_k(r, t) \otimes \eta_{k'}(r', t') \rangle = 2D_k c_k(r, t) \delta_{k,k'} \delta(r-r') \delta(t-t') \mathbf{1}$$

for $k, k' = A, B$, where $D_k$ are positive diffusion coefficients and $\mathbf{1}$ is the $d \times d$ identity matrix. The boundary conditions are given by

if $r \in S_{\text{cat}}$:

$$D_A \partial_{\perp} c_A(r, t) = -D_B \partial_{\perp} c_B(r, t) = \kappa_+ c_A(r, t) - \kappa_- c_B(r, t) + \xi(r, t),$$

if $r \in S_{\text{inert}}$:

$$\partial_{\perp} c_A(r, t) = 0, \quad \partial_{\perp} c_B(r, t) = 0,$$

if $r \in S_{\text{res}}$:

$$c_A(r, t) = \bar{c}_A, \quad c_B(r, t) = \bar{c}_B,$$

where $\partial_{\perp} = 1_\perp \cdot \nabla$ is the gradient in the direction of the unit vector $1_\perp$ normal to the surface and oriented towards the interior of the volume $V$, and $\kappa_{\pm}$ are the positive rate constants of the surface reactions. These rate constants have the SI units of meter per second. $\bar{c}_A$ and $\bar{c}_B$ denote the given concentrations at the reservoir. The Gaussian noise field due to the surface reaction is characterized by

$$\langle \xi(r, t) \rangle = 0, \quad \delta^r(\mathbf{r}) \langle \xi(r, t) \xi(r', t') \rangle \delta^r(\mathbf{r}') = (\kappa_+ c_A + \kappa_- c_B) \delta^r(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \delta(t-t'),$$

in terms of surface delta distributions $\delta^r(\mathbf{r})$, nonvanishing if $r \in S_{\text{cat}}$ [38].

2.2. The finite-time fluctuation theorem

Let the random variable $n$ denotes the number of reactive events $A \rightarrow B$ that have occurred during the time interval $[0, t]$, if the system is in a steady state with given concentrations $\bar{c}_A$ and $\bar{c}_B$ at the reservoir. The probability $P(n, t)$ that $n$ reactive events have occurred is equal to

$$P(n, t) = e^{-t(W_t^{(+)} + W_t^{(-)})} \left( \frac{W_t^{(+)}}{W_t^{(-)}} \right)^{n/2} I_n \left( 2t \sqrt{W_t^{(+)}/W_t^{(-)}} \right),$$

where $W_t^{(\pm)}$ are two finite-time rates explicitly given below and $I_n(u)$ is the modified regular Bessel function defined in section 9.6 of [39]. Since $I_n(u) = I_{-n}(u)$, this probability distribution obeys the finite-time fluctuation theorem.

https://doi.org/10.1088/1742-5468/aad7c2
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\[ \frac{P(n,t)}{P(-n,t)} = \exp(A_t n) \tag{9} \]

holding at every time with the finite-time affinity defined as

\[ A_t = \ln \frac{W_t^{(+)}}{W_t^{(-)}}. \tag{10} \]

The finite-time rates have the explicit forms

\[ W_t^{(+)} = \Sigma \kappa_+ \bar{c}_A + \frac{1}{\ell} \Psi(t), \tag{11} \]
\[ W_t^{(-)} = \Sigma \kappa_- \bar{c}_B + \frac{1}{\ell} \Psi(t), \tag{12} \]

with

\[ \Psi(t) = \ell^2 \kappa_+ \kappa_- \left[ \frac{\bar{c}_B}{D_A^2} \Upsilon_A(t) + \frac{\bar{c}_A}{D_B^2} \Upsilon_B(t) \right]. \tag{13} \]

The first terms on the right sides of equations (11) and (12) are proportional to the effective catalytic surface area

\[ \Sigma = \int_{\text{cat}} dS (1 - \phi), \tag{14} \]

\( \phi \) being the solution of the following stationary problem,

\[ \nabla^2 \phi = 0, \tag{15} \]
\[ (\partial_{\perp} \phi)_{\text{cat}} = \ell^{-1} (\phi - 1)_{\text{cat}}, \tag{16} \]
\[ (\partial_{\perp} \phi)_{\text{inert}} = 0, \tag{17} \]
\[ (\phi)_{\text{res}} = 0, \tag{18} \]

where

\[ \ell \equiv \left( \frac{\kappa_+}{D_A} + \frac{\kappa_-}{D_B} \right)^{-1} \tag{19} \]

is the characteristic length of the diffusion-influenced surface reaction. In equation (13), \( \Psi(t) \) is given in terms of the time-dependent functions

\[ \Upsilon_k(t) = \int dV \phi(r) [\phi(r) - f_k(r, t)], \tag{20} \]

where \( f_k \) is the solution of the following time-dependent problem,

\[ \partial_t f_k = D_k \nabla^2 f_k, \tag{21} \]
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\[
(\partial_{\perp} f_k)_{\text{cat}} = \left( \frac{\kappa_+}{D_A} f_A + \frac{\kappa_-}{D_B} f_B \right)_{\text{cat}},
\]

(\ref{eq:finite-fluctuation-cat})

\[
(\partial_{\perp} f_k)_{\text{inert}} = 0,
\]

(\ref{eq:finite-fluctuation-inert})

\[
(f_k)_{\text{res}} = 0,
\]

(\ref{eq:finite-fluctuation-res})

\[
(f_k)_{t=0} = \phi,
\]

(\ref{eq:finite-fluctuation-t0})

for \( k = A, B \).

If the catalytic and inert surfaces \( S_{\text{inert}} \cup S_{\text{cat}} \), as well as the domain \( V \), are compact the constant \( \Sigma \) and the functions \( \Upsilon_k(t) \) are bounded, so that the rates (\ref{eq:long-time-limit-plus}) and (\ref{eq:long-time-limit-minus}) converge in the long-time limit \( t \to \infty \) to their asymptotic values

\[
W_\infty^+(\pm) = \Sigma \kappa_+ \bar{c}_A,
\]

(\ref{eq:asymptotic-plus})

\[
W_\infty^-(\pm) = \Sigma \kappa_- \bar{c}_B,
\]

(\ref{eq:asymptotic-minus})

whereupon the affinity (\ref{eq:finite-affinity}) converges to the finite value

\[
\mathcal{A}_\infty = \ln \frac{W_\infty^+(\pm)}{W_\infty^-(\pm)} = \ln \frac{\kappa_+ \bar{c}_A}{\kappa_- \bar{c}_B}.
\]

(\ref{eq:finite-affinity})

We expect the same behavior to hold if the catalytic and inert surfaces \( S_{\text{inert}} \cup S_{\text{cat}} \) are compact and delimit a finite volume, while the domain \( V \) is non-compact, but three-dimensional.

2.3. Formulation in terms of the cumulant generating function

Introducing the cumulant generating function

\[
Q_t(\lambda) \equiv -\frac{1}{t} \ln \sum_{n=-\infty}^{+\infty} e^{-\lambda n} P(n, t)
\]

(\ref{eq:cumulant-generating})

with the counting parameter \( \lambda \), we have the result that

\[
Q_t(\lambda) = W_t^{(+)}(1 - e^{-\lambda}) + W_t^{(-)}(1 - e^{\lambda}),
\]

(\ref{eq:cumulant-fluctuation})

where the finite-time rates \( W_t^{(\pm)} \) were defined in equations (\ref{eq:long-time-limit-plus}) and (\ref{eq:long-time-limit-minus}). As a consequence of the finite-time fluctuation theorem (\ref{eq:fluctuation-theorem}), the following symmetry relation is satisfied at every time,

\[
Q_t(\lambda) = Q_t(\mathcal{A}_t - \lambda),
\]

(\ref{eq:symmetry})

in terms of the finite-time affinity (\ref{eq:finite-affinity}). The mean current and the diffusivity at time \( t \) are thus given by

\[
J_t = \frac{\partial Q_t}{\partial \lambda}(0) = W_t^{(+)} - W_t^{(-)},
\]

(\ref{eq:mean-current})
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\[ D_t = -\frac{1}{2} \frac{\partial^2 Q_t}{\partial A^2} (0) = \frac{1}{2} \left( W_t^{(+)} + W_t^{(-)} \right). \]  

(33)

We notice that the mean current (32) does not depend on time because of the forms of the expressions (11) and (12) for the rates, implying

\[ J_t = J = W_t^{(+)} - W_t^{(-)} = \Sigma \left( \kappa_A c_A - \kappa_B c_B \right). \]

(34)

Moreover, the stationary solutions for the species concentrations are given by

\[ \langle c_k \rangle_{\text{st}} = \bar{c}_k + \frac{\nu_k \ell}{D_k} (\kappa_+ \bar{c}_A - \kappa_- \bar{c}_B) \phi \quad (k = A, B), \]

(35)

where \( \phi \) is the solution of the problem (15)-(18), while \( \nu_A = -1 \) and \( \nu_B = +1 \) are the stoichiometric coefficients of the reaction \( A \to B \). The equilibrium thermodynamic state occurs when the chemical equilibrium condition \( \kappa_+ \bar{c}_A = \kappa_- \bar{c}_B \) is satisfied, in which case the state is uniform. The stationary solution (35) determines the cumulant generating function at early time according to

\[ Q_t(\lambda) = \int_{\text{cat}} dS \left[ \kappa_+ \langle c_A \rangle_{\text{st}} (1 - e^{-\lambda}) + \kappa_- \langle c_B \rangle_{\text{st}} (1 - e^\lambda) \right] + O(t), \]

(36)

up to corrections that are linear in time.

The finite-time fluctuation theorem (9) and the associated results, which are stated above, are proved in section 3 by extending the result obtained in [37].

2.4. Thermodynamic entropy production

Here, we show the equivalence between the expressions for the entropy production given by macroscopic nonequilibrium thermodynamics and the fluctuation theorem under stationary conditions. On the one hand, according to nonequilibrium thermodynamics [2–3], the entropy production is equal to the sum of the contributions from diffusion in the domain \( V \) and reaction at the catalytic surface \( S_{\text{cat}} \),

\[ \frac{1}{k_B} \frac{dS}{dt} = \int_V dV \left[ D_a \frac{(\nabla a)^2}{a} + D_b \frac{b^2}{b} \right] + \int_{\text{cat}} dS (\kappa_+ a - \kappa_- b) \ln \frac{\kappa_+ a}{\kappa_- b} \geq 0 \]

(37)

with the notations \( a = \langle c_A \rangle_{\text{st}} \) and \( b = \langle c_B \rangle_{\text{st}} \). Now, we have that

\[ \int_V dV \frac{(\nabla a)^2}{a} = \int_V dV \nabla a \cdot \nabla (\ln \kappa_+ a) = \int_{\partial V} dS \cdot (\nabla a) \ln \kappa_+ a, \]

(38)

by using the divergence theorem and the fact that \( \nabla^2 a = 0 \) in a steady state. A similar expression is obtained for the other concentration field \( b \). The boundary \( \partial V \) of the domain \( V \) is composed of the catalytic, inert, and reservoir surface components, where \( dS = -1_\perp dS \) if \( 1_\perp \) is the unit vector normal to the surface and oriented towards the interior of the domain. Using the boundary conditions (4)–(6), we find that the contributions of the catalytic and inert components of the surface cancel and there remain the contributions of the surface component in contact with the reservoir,

\[ \frac{1}{k_B} \frac{dS}{dt} = \int_{\text{res}} dS (-D_A \partial_\perp a) \ln \kappa_+ a + \int_{\text{res}} dS (-D_B \partial_\perp b) \ln \kappa_- b. \]

(39)
Replacing the concentration fields at the reservoir by their expression \((35)\) in terms of the field \(\phi\) obeying equations \((15)\)–\((18)\), and using the fact that

\[
0 = \int_V d\mathbf{V} \nabla^2 \phi = \int_{\partial V} d\mathbf{S} \cdot \nabla \phi = \frac{1}{\ell} \Sigma - \int_{\text{res}} dS \partial_\perp \phi ,
\]

where \(\Sigma\) is defined in equation \((14)\), we find that the entropy production is given by

\[
\frac{1}{k_B} \frac{dS}{dt} = \Sigma (\kappa_+ \bar{c}_A - \kappa_- \bar{c}_B) \ln \frac{\kappa_+ \bar{c}_A}{\kappa_- \bar{c}_B} = \mathcal{J} \mathcal{A}_\infty \geq 0 ,
\]

which is determined by the reservoir values of the concentrations. Therefore, the entropy production is equal to the mean current \((34)\) multiplied by the asymptotic value \((28)\) of the affinity, as expected.

On the other hand, the thermodynamic entropy production can be expressed as

\[
\frac{1}{k_B} \frac{dS}{dt} = \lim_{t \to \infty} \frac{1}{t} \sum_{n=-\infty}^{+\infty} P(n,t) \ln \frac{P(n,t)}{P(-n,t)} = \lim_{t \to \infty} \mathcal{J} \mathcal{A}_t = \mathcal{J} \mathcal{A}_\infty \geq 0
\]

in terms of the probability distribution \((8)\). Since this latter obeys the fluctuation theorem \((9)\), we recover the macroscopic value \((41)\) of the entropy production because the mean current in the steady state is given by \(\mathcal{J} = \langle n(t) \rangle_{\text{st}} / t\) according to equation \((34)\). The fluctuation theorem is thus consistent with macroscopic nonequilibrium thermodynamics for the diffusion-influenced surface reaction. In addition, the non-negative quantity \(\mathcal{J} \mathcal{A}_t \geq 0\) in equation \((42)\) can be interpreted as a finite-time entropy production in the measurement of the surface reaction using the full counting statistics of the reactive events.

### 3. Proof of the finite-time fluctuation theorem

The proof of the finite-time fluctuation theorem \((9)\) and the associated results stated in sections 2.2 and 2.3 is carried out by discretizing space into small cells and using the master equation of the stochastic process for the random numbers of molecules in the cells, which, in the continuum limit, is equivalent to the stochastic process ruled by equations \((1)\)–\((7)\). We solve this master equation using a method based on the moment generating function for the probability distribution of the molecular numbers and the number of reactive events occurring during some time interval [18, 37]. Since the kinetic equations for the mean values of the molecular numbers are linear, the steady state of the reaction-diffusion process is described by a Poisson distribution and the partial differential equation ruling the moment generating function admits an exact solution, yielding an expression for the cumulant generating function of the number of reactive events occurring during some time interval. Its dependence on the counting parameter is obtained by using projectors onto the subspaces corresponding to the molecules of species A and B, and we find that the cumulant generating function has the form \((30)\). As a consequence, the probability distribution of the random number of reactive events is given by equation \((8)\), implying the finite-time fluctuation theorem.
In this discrete-space formulation, matricial expressions are obtained for the time-dependent rates.

Returning to the continuum limit, we first show that we recover the macroscopic diffusion-reaction equations for the mean concentration fields. Next, we deduce the analytical expressions for the time-dependent rates by transforming the matricial equations obtained by space discretization into partial differential equations and their boundary conditions. This is performed by summing the matricial equations with arbitrary conjugate vectors in order to obtain expressions involving integrals in the continuum limit. This method allows us to obtain the partial differential equations and their boundary conditions by considering variations with respect to the space-dependent conjugate functions corresponding in the continuum limit to the aforementioned arbitrary conjugate vectors. In this way, the time-dependent rates are shown to be given by the solutions of the problems (15)–(18) and (21)–(25), finally yielding their analytical expressions (11 and 12) with the time-dependent function (13) and the constant (14). Also, expression (36) is obtained for the behavior of the cumulant generating function at early time.

3.1. Space discretization

3.1.1. Master equation. In order to prove the theorem, the $d$-dimensional volume $V$ is discretized into small cubic cells $\{C_r\}$ of side $\Delta r$, volume $\Delta r^d$, and centered on the nodes $r$ of a $d$-dimensional cubic lattice. Every cell contains a certain number of molecules of each species:

$$A_r = \int_{C_r} c_A(r') \, dr' \quad \text{and} \quad B_r = \int_{C_r} c_B(r') \, dr'.$$

Some of the cells are in contact with the catalytic surface, the inert surface, and the reservoir. Every cubic cell has 2$d$ faces, which correspond to the 2$d$ vectors

$$\Delta r \in \{ (\pm \Delta r, 0, \ldots, 0), (0, \pm \Delta r, \ldots, 0), \ldots, (0, 0, \ldots, \pm \Delta r) \},$$

joining the center of the cell to those of the next-neighboring cells. The cells in the bulk of the volume have all their faces in contact with next-neighboring cells. However, the other cells have some faces in contact with the catalytic surface, the inert surface, or the reservoir. Therefore, for every cell, the set of 2$d$ vectors is subdivided as

$$\{\Delta r\} = \{\Delta r\}_\text{diff} \cup \{\Delta r\}_\text{cat} \cup \{\Delta r\}_\text{inert} \cup \{\Delta r\}_\text{res},$$

into faces, through which particles can be exchanged by diffusion with next-neighboring cells or the reservoir, reflected on the inert surface, or transformed by reaction on the catalytic surface.

The molecular numbers change in time according to the following processes:

\begin{align*}
\text{diffusion} : \quad & A_r \xrightarrow{k_A} A_{r+\Delta r} \quad \text{if} \quad \Delta r \in \{\Delta r\}_\text{diff}, \\
& B_r \xrightarrow{k_B} B_{r+\Delta r} \quad \text{if} \quad \Delta r \in \{\Delta r\}_\text{diff}.
\end{align*}
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reaction : \( A_r \xrightleftharpoons[k_+]{k_-} B_r \) if \( \Delta r \in \{ \Delta r \}_{\text{cat}} \); \( (48) \)

exchanges with the reservoir : \( A_r \xrightarrow{k_A} \bar{A} \) if \( \Delta r \in \{ \Delta r \}_{\text{res}} \), \( (49) \)
\n\[ B_r \xrightarrow{k_B} \bar{B} \] if \( \Delta r \in \{ \Delta r \}_{\text{res}} \); \( (50) \)

and there is no change at the faces in contact with the inert surface. The rate constants are given by

\[ k_A = \frac{D_A}{\Delta r^2}, \quad k_B = \frac{D_B}{\Delta r^2}, \quad \text{and} \quad k_\pm = \frac{\kappa_\pm}{\Delta r} \] \( (51) \)

in terms of the diffusion coefficients and surface rate constants of the continuous-space formulation. These rate constants are positive and have the SI units of \((\text{second})^{-1}\).

We consider the time evolution of the probability \( P = P(n, \{ A_r \}, \{ B_r \}, t) \) \( (52) \) that the cells contain given molecular numbers and that \( n \) reactive events have occurred during the time interval \([0, t]\). This probability is ruled by the following master equation,

\[
\frac{dP}{dt} = \hat{L}P = \sum_r \left\{ \sum_{\{\Delta r\}_{\text{diff}}} k_A \left( e^{-\partial_{A_r} \Delta r} e^{\partial_{A_r} \Delta r} - 1 \right) A_r P \\
+ \sum_{\{\Delta r\}_{\text{diff}}} k_B \left( e^{-\partial_{B_r} \Delta r} e^{\partial_{B_r} \Delta r} - 1 \right) B_r P \\
+ \sum_{\{\Delta r\}_{\text{cat}}} k_+ \left( e^{-\partial_{A_r} \Delta r} e^{\partial_{A_r} \Delta r} - 1 \right) A_r P \\
+ \sum_{\{\Delta r\}_{\text{cat}}} k_- \left( e^{\partial_{A_r} \Delta r} e^{-\partial_{A_r} \Delta r} - 1 \right) B_r P \\
+ \sum_{\{\Delta r\}_{\text{res}}} \left[ k_A \bar{A} \left( e^{-\partial_{A_r} \Delta r} - 1 \right) P + k_A \left( e^{\partial_{A_r} \Delta r} - 1 \right) A_r P \right] \\
+ \sum_{\{\Delta r\}_{\text{res}}} \left[ k_B \bar{B} \left( e^{-\partial_{B_r} \Delta r} - 1 \right) P + k_B \left( e^{\partial_{B_r} \Delta r} - 1 \right) B_r P \right] \right\}, \tag{53}
\]

where \( \bar{A} = \bar{c}_A \Delta r^d \) and \( \bar{B} = \bar{c}_B \Delta r^d \).

3.1.2. Kinetic equations for the mean numbers. As a consequence, the time evolution of the mean numbers,

\[
\langle A_r \rangle = \sum_{n, \{ A_r \}, \{ B_r \}} A_r P, \tag{54}
\]
\[
\langle B_r \rangle = \sum_{n, \{ A_r \}, \{ B_r \}} B_r P, \tag{55}
\]
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\[ \langle n \rangle = \sum_{n_0 \{ A_r \}; \{ B_r \}} n P, \quad (56) \]

is ruled by the following equations,

\[
\frac{d}{dt} \langle A_r \rangle = \sum_{(\Delta r)_{\text{diff}}} k_A \left( \langle A_{r+\Delta r} \rangle - \langle A_r \rangle \right) - \sum_{(\Delta r)_{\text{cat}}} \left( k_+ \langle A_r \rangle - k_- \langle B_r \rangle \right) + \sum_{(\Delta r)_{\text{res}}} k_A \left( A - \langle A_r \rangle \right), \quad (57)
\]

\[
\frac{d}{dt} \langle B_r \rangle = \sum_{(\Delta r)_{\text{diff}}} k_B \left( \langle B_{r+\Delta r} \rangle - \langle B_r \rangle \right) + \sum_{(\Delta r)_{\text{cat}}} \left( k_+ \langle A_r \rangle - k_- \langle B_r \rangle \right) + \sum_{(\Delta r)_{\text{res}}} k_B \left( B - \langle B_r \rangle \right), \quad (58)
\]

\[
\frac{d}{dt} \langle n \rangle = \sum_{r} \sum_{(\Delta r)_{\text{cat}}} \left( k_+ \langle A_r \rangle - k_- \langle B_r \rangle \right). \quad (59)
\]

In equations (57) and (58), the sums over \( (\Delta r)_{\text{cat}} \) and \( (\Delta r)_{\text{res}} \) are possibly vanishing if the cell located at \( r \) is not in contact with the catalytic surface or the reservoir.

If the mean numbers are larger than unity, the fluctuations around the mean values become Gaussian. In this limit, the Markov jump process described by the master equation can be transformed into a diffusive process described by a Fokker–Planck equation by expanding the raising and lowering operators up to second order in the partial derivatives [40]. In this way, we can obtain the stochastic partial differential equations (1) and (2) with the boundary conditions (4)–(6) and the Gaussian white noises (3) and (7).

3.1.3. Equation for the moment generating function. In order to solve the master equation, we introduce with Gardiner [18] the moment generating function,

\[ G(z, \{ x_r \}, \{ y_r \}, t) \equiv \sum_{n_0 \{ A_r \}; \{ B_r \}} z^n \prod_{r} x_r^{A_r} \prod_{r} y_r^{B_r} P(n, \{ A_r \}, \{ B_r \}, t), \quad (60) \]

where

\[ z = e^{-\lambda} \quad (61) \]

and \( \lambda \) is the counting parameter. This generating function obeys the following first-order partial differential equation,

\[
\partial_t G + \sum_r \left\{ \sum_{(\Delta r)_{\text{diff}}} \left[ k_A (x_r - x_{r+\Delta r}) \partial_{x_r} G + k_B (y_r - y_{r+\Delta r}) \partial_{y_r} G \right] \\
+ \sum_{(\Delta r)_{\text{cat}}} \left[ k_+ (x_r - y_r) \partial_{x_r} G + k_- (y_r - z^{-1} x_r) \partial_{y_r} G \right] \\
+ \sum_{(\Delta r)_{\text{res}}} \left[ k_A (x_r - 1) \partial_{x_r} G + k_B (y_r - 1) \partial_{y_r} G \right] \right\} \\
= \sum_{r} \sum_{(\Delta r)_{\text{res}}} \left[ k_A \bar{A} (x_r - 1) + k_B \bar{B} (y_r - 1) \right] G. \quad (62)
\]
Setting
\[ s \equiv (\{x_r\}, \{y_r\}). \] (63)
equation (62) can be written as
\[ \partial_t G + (\mathbf{L} \cdot s + \mathbf{f}) \cdot \partial_s G = (\mathbf{g} \cdot s + h) G, \] (64)
where
\[
(\mathbf{L} \cdot s) \cdot \chi \equiv \sum_r \left\{ \sum_{\{\Delta r\}_{\text{diff}}} [k_A (x_r - x_{r+\Delta r}) \alpha_r + k_B (y_r - y_{r+\Delta r}) \beta_r] 
+ \sum_{\{\Delta r\}_{\text{cat}}} [k_+ (x_r - z y_r) \alpha_r + k_- (y_r - z^{-1} x_r) \beta_r] 
+ \sum_{\{\Delta r\}_{\text{res}}} (k_A x_r \alpha_r + k_B y_r \beta_r) \right\},
\] (65)
\[
\mathbf{f} \cdot \chi \equiv -\sum_r \sum_{\{\Delta r\}_{\text{res}}} (k_A \alpha_r + k_B \beta_r),
\] (66)
\[
\mathbf{g} \cdot s \equiv \sum_r \sum_{\{\Delta r\}_{\text{res}}} (k_A \bar{A} x_r + k_B \bar{B} y_r),
\] (67)
and
\[
h \equiv -\sum_r \sum_{\{\Delta r\}_{\text{res}}} (k_A \bar{A} + k_B \bar{B}),
\] (68)
with the arbitrary vector
\[ \chi \equiv (\{\alpha_r\}, \{\beta_r\}). \] (69)

3.1.4. Solving the equation for the moment generating function. As a first-order partial differential equation, equation (64) can be solved by the method of characteristics [18]. The equations for the characteristics are given by
\[
\frac{ds}{dt} = \mathbf{L} \cdot s + \mathbf{f},
\] (70)
\[
\frac{dG}{dt} = (\mathbf{g} \cdot s + h) G,
\] (71)
where the matrix \( \mathbf{L} \) defined by equation (65) contains the rate constants and depends on \( z \). Setting \( \lambda = 0 \) and thus \( z = 1 \) in this matrix defines the matrix \( \mathbf{L}_0 \) such that the kinetic equations (57) and (58) together read
\[
\frac{d\mathbf{\Gamma}}{dt} = \mathbf{L}_0^T \cdot (\mathbf{\Gamma}_0 - \mathbf{\Gamma}),
\] (72)
where
\[ \Gamma = (\{A_r\}, \{B_r\}) \] (73)
are the mean molecular numbers. The stationary values of these molecular numbers are given by
\[ \Gamma_0 = L_0^{-1T} \cdot g \] (74)
in terms of the vector \( g \) defined by equation (67) and containing the elements with the boundary values \( A \) and \( B \). Moreover, the vector \( f \) can be written as
\[ f = -L_0 \cdot 1, \] (75)
which follows by comparing its definition (66) with equation (65) after setting \( s = 1 \) and \( z = 1 \). Similarly, the coefficient (68) is given by
\[ h = -g \cdot 1. \] (76)

The solution of equation (70) gives the characteristics
\[ s = e^{Lt} \cdot \left[ s_0 + L^{-1} \cdot (1 - e^{-Lt}) \cdot f \right], \] (77)
while the solution of equation (71) is given by
\[ G = G_0 \exp \left[ g \cdot L^{-1} \cdot (1 - e^{-Lt}) \cdot (s + L^{-1} \cdot f) + (h - g \cdot L^{-1} \cdot f) \cdot t \right]. \] (78)
The initial condition is the Poisson distribution describing the steady state of equation (72) and the counter reset to zero \( n = 0, \) so that
\[ G_0(z, s_0) = e^{\Gamma_0 \cdot (s_0 - 1)} \] (79)
with the vector (74) of the stationary mean values of the molecular numbers. The solution of the partial differential equation (62) is thus equal to
\[ G(z, s, t) = \exp \left[ g \cdot L^{-1} \cdot (1 - e^{-Lt}) \cdot (s + L^{-1} \cdot f) + (h - g \cdot L^{-1} \cdot f) \cdot t \right] \times \exp \left\{ \Gamma_0 \cdot \left[ e^{-Lt} \cdot s - L^{-1} \cdot (1 - e^{-Lt}) \cdot f \cdot 1 \right] \right\}. \] (80)

3.1.5. Obtaining the cumulant generating function. We notice that the moment generating function of the number \( n \) of reactive events is given by
\[ G(z, 1, t) = \langle e^{-\lambda n} \rangle_t \] (81)
because of equation (61). The cumulant generating function at time \( t \) is thus defined as
\[ Q_t(\lambda) \equiv -\frac{1}{t} \ln G(z = e^{-\lambda}, 1, t), \] (82)
so that we find
\[ Q_t(\lambda) = g \cdot \left( 1 + L^{-1} \cdot f \right) - \frac{1}{t} g \cdot \left( L^{-1} - L_0^{-1} \right) \cdot (1 - e^{-Lt}) \cdot (1 + L^{-1} \cdot f), \] (83)
which can be written in the form
Finite-time fluctuation theorem for diffusion-influenced surface reactions

\[ Q_t(\lambda) = Q_\infty(\lambda) - \frac{1}{t} \Xi_t(\lambda), \]  

where

\[ Q_\infty(\lambda) = g \cdot (1 + L^{-1} \cdot f) \]  

and

\[ \Xi_t(\lambda) = g \cdot \left( L^{-1} - L_0^{-1} \right) \cdot \left( 1 - e^{-L_0 t} \right) \cdot \left( 1 + L^{-1} \cdot f \right). \]  

We notice that equation (86) converges exponentially towards a constant in the limit \( t \to \infty \) if the matrix \( L \) is supposed to be positive, which can be satisfied for some values of \( z \) (or \( \lambda \)) since the rate constants (51) are positive.

3.1.6. The dependence of the cumulant generating function on the counting parameter.

A further observation is that

\[ L = M \cdot L_0 \cdot M^{-1} \]  

with

\[ M \equiv z P_A + P_B \]  

expressed in terms of the projection matrices

\[ P_A = \begin{pmatrix}
1 & \cdots & 0 & \cdots & 0 \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
0 & \cdots & 1 & 0 & \cdots \\
0 & \cdots & 0 & 0 & \cdots \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
0 & \cdots & 0 & 0 & \cdots
\end{pmatrix}, \quad \text{and} \quad P_B = \begin{pmatrix}
0 & \cdots & 0 & \cdots & 0 \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
0 & \cdots & 0 & 1 & \cdots \\
0 & \cdots & 0 & 0 & \cdots \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
0 & \cdots & 0 & 0 & 1
\end{pmatrix}, \]  

respectively onto the variables of species A and those of species B. These projection matrices satisfy the condition \( P_A + P_B = I \). We thus have

\[ M = I + (z - 1) P_A = I + \left( e^{\lambda} - 1 \right) P_A, \]  

\[ M^{-1} = I + (z^{-1} - 1) P_A = I + \left( e^{-\lambda} - 1 \right) P_A. \]  

Therefore, the cumulant generating function can be written as

\[ Q_t(\lambda) = g \cdot \left[ I - M \cdot L_0^{-1} \cdot M^{-1} \cdot L_0 \\
- \frac{1}{t} \left( M \cdot L_0^{-1} - L_0^{-1} \cdot M \right) \cdot \left( 1 - e^{-L_0 t} \right) \cdot \left( M^{-1} - L_0^{-1} \cdot M^{-1} \cdot L_0 \right) \right] \cdot 1. \]  

As a consequence of equations (90) and (91), the previous expression becomes

https://doi.org/10.1088/1742-5468/aad7c2
\[ Q_t(\lambda) = g \cdot \left[ (1-z) P_A + (1-z^{-1}) L_0^{-1} \cdot P_A \cdot L_0 - (2-z-z^{-1}) P_A \cdot L_0^{-1} \cdot P_A \cdot L_0 \right. \\
\left. + \frac{1}{t} (2-z-z^{-1}) (L_0^{-1} \cdot P_A - P_A \cdot L_0^{-1}) \cdot (1 - e^{-L_0 t}) \cdot (P_A - L_0^{-1} \cdot P_A \cdot L_0) \right] \cdot 1. \] (93)

Because of equation (74) and since \( P_B = I - P_A \), the cumulant generating function has the form (30) with the rates

\[ W_0^+(t) = \Gamma_0 \cdot L_0 \cdot P_A \cdot L_0^{-1} \cdot P_B \cdot L_0 \cdot 1 + \frac{1}{t} \Psi(t), \] (94)

\[ W_0^-(t) = \Gamma_0 \cdot L_0 \cdot P_B \cdot L_0^{-1} \cdot P_A \cdot L_0 \cdot 1 + \frac{1}{t} \Psi(t), \] (95)

where

\[ \Psi(t) \equiv \Gamma_0 \cdot (P_A - L_0 \cdot P_A \cdot L_0^{-1}) \cdot (1 - e^{-L_0 t}) \cdot (P_A - L_0^{-1} \cdot P_A \cdot L_0) \cdot 1. \] (96)

We have thus proved that the cumulant generating function has the form (30) and we have obtained explicit expressions for the rates (11) and (12) and the function (13) for a discretized space.

3.1.7. Deducing the probability distribution and its finite-time symmetry. According to equation (82) and the previous results, the moment generating function has the following expression,

\[ G(z, 1, t) = \sum_{n=-\infty}^{+\infty} z^n P(n, t) = e^{tW_0^+(z-1)+tW_0^-(z^{-1}-1)}, \] (97)

with the probability distribution

\[ P(n, t) \equiv \sum_{\{A_r\}; \{B_r\}} P(n, \{A_r\}, \{B_r\}, t) \] (98)

for the number \( n \) of reactive events during the time interval \([0, t]\). As shown in [37], we can use the generating series of Bessel functions given by equation (9.6.33) of [39],

\[ e^{u(q+q^{-1})/2} = \sum_{n=-\infty}^{+\infty} q^n I_n(u) \quad \text{for} \quad q \neq 0. \] (99)

Taking

\[ u = 2t \sqrt{W_0^{(+)} W_0^{(-)}}, \] (100)

\[ q = z \sqrt{\frac{W_0^{(+)} W_0^{(-)}}{W_0^{(+)} W_0^{(-)}}}, \] (101)

we get equation (8) in section 2, hence the finite-time fluctuation theorem (9). Q.E.D.
3.2. The continuum limit

3.2.1. The mean concentrations. In the continuum limit, we should recover the noiseless diffusion equations (1) and (2) with the noiseless boundary conditions (4)–(6) for the mean concentrations \( \langle c_A \rangle \) and \( \langle c_B \rangle \). To obtain this result, we introduce the notations

\[
a_r \equiv \langle A_r \rangle / \Delta r^d, \quad b_r \equiv \langle B_r \rangle / \Delta r^d,
\]

where \( \Delta V = \Delta r^d \) is the volume element, and we consider equation (57) for a cell in the bulk of the domain \( V \), in which case there is diffusion with all the 2d next-neighboring cells and \( \{ \Delta r \} = \{ \Delta r \}_\text{diff} \). Consequently, equation (57) gives

\[
\frac{da_r}{dt} = \frac{D_A}{\Delta r^2} \sum_{\{ r_{+\Delta r} \}} (a_{r+\Delta r} - a_r),
\]

which is the discrete version of the diffusion equation

\[
\partial_t \langle c_A \rangle = D_A \nabla^2 \langle c_A \rangle
\]

for the mean concentration of species A, \( \langle c_A(r, t) \rangle = \lim_{\Delta r \to 0} a_r(t) = \lim_{\Delta r \to 0} \langle A_r(t) \rangle / \Delta r^d \). Similarly, we get

\[
\partial_t \langle c_B \rangle = D_B \nabla^2 \langle c_B \rangle.
\]

Next, we consider equation (57) for a cell in contact with the catalyst by the facets \( \{ \Delta r \}_\text{cat} \). Therefore, \( \{ \Delta r \}_\text{diff} = \{ \Delta r \} \setminus \{ \Delta r \}_\text{cat} \) and we find

\[
\frac{da_r}{dt} = \frac{D_A}{\Delta r^2} \sum_{\{ r_{+\Delta r} \}} (a_{r+\Delta r} - a_r) - \frac{D_A}{\Delta r^2} \sum_{\{ r_{+\Delta r} \}_\text{cat}} (a_{r+\Delta r} - a_r) - \frac{1}{\Delta r} \sum_{\{ r_{+\Delta r} \}_\text{cat}} (\kappa_+ a_r - \kappa_- b_r).
\]

As before, the first term gives the discrete version of the Laplacian, while the second can be approximated using

\[
a_{r+\Delta r} \simeq a_r + \Delta r \cdot \nabla a_r = a_r - \Delta r 1_\perp \cdot \nabla a_r,
\]

where, as noted earlier, \( 1_\perp \) is the unit vector normal to the surface and oriented towards the interior of the volume \( V \). For this cell, we thus have

\[
\partial_t a_r \simeq D_A \nabla^2 a_r + \frac{1}{\Delta r} \sum_{\{ r_{+\Delta r} \}_\text{cat}} [D_A 1_\perp \cdot \nabla a - (\kappa_+ a - \kappa_- b)]_r,
\]

where the derivative \( da_r/dt \) becomes the partial derivative \( \partial_t a_r \). In the limit \( \Delta r \to 0 \), consistency is established if every diverging term in the right side is vanishing, which yields the boundary condition

\[
D_A \partial_\perp \langle c_A \rangle = \kappa_+ \langle c_A \rangle - \kappa_- \langle c_B \rangle \quad \text{if} \quad r \in S_\text{cat},
\]

for the mean concentrations, thus recovering equation (4). Similarly, equation (58) gives

\[
-D_B \partial_\perp \langle c_B \rangle = \kappa_+ \langle c_A \rangle - \kappa_- \langle c_B \rangle \quad \text{if} \quad r \in S_\text{cat}.
\]

The boundary conditions on an inert surface are recovered by setting the rate constants equal to zero, \( \kappa_\pm = 0 \).

If equation (57) is considered for a cell in contact with the reservoir by the facets \( \{ \Delta r \}_\text{res} \), we have that \( \{ \Delta r \}_\text{diff} = \{ \Delta r \} \setminus \{ \Delta r \}_\text{res} \) and
\[
\frac{d a_r}{dt} = \frac{D_A}{\Delta r^2} \sum_{\{\Delta r\}} (a_{r+\Delta r} - a_r) \frac{D_A}{\Delta r^2} \sum_{\{\Delta r\}_\text{res}} (a_{r+\Delta r} - a_r) + \frac{D_A}{\Delta r^2} \sum_{\{\Delta r\}_\text{res}} (\bar{c}_A - a_r),
\]

because \( \bar{c}_A = \bar{A}/\Delta r^d \). Since the first term of equation (111) can also be approximated in terms of the Laplacian and the next terms can be grouped together, we obtain

\[
\partial_t a_r \simeq \frac{D_A}{\Delta r^2} \nabla^2 a_r + \frac{D_A}{\Delta r^2} \sum_{\{\Delta r\}_\text{res}} (\bar{c}_A - a_r). \tag{112}
\]

Again, the consistency is established in the limit \( \Delta r \to 0 \) if every diverging term in the right side is vanishing, whereupon we find the boundary conditions \( a_{r+\Delta r} = \bar{c}_A \), if \( r \) is the center of a cell next to the reservoir and \( \Delta r \in \{\Delta r\}_\text{res}. \) Consequently, we recover the boundary conditions

\[
\langle c_A \rangle = \bar{c}_A \quad \text{and} \quad \langle c_B \rangle = \bar{c}_B \quad \text{if} \quad r \in S_\text{res},
\]

which are given by equation (6) for the mean concentrations.

In addition, equation (59) becomes

\[
\frac{d}{dt} \langle n \rangle = \int \text{cat} dS (\kappa_+ \langle c_A \rangle - \kappa_- \langle c_B \rangle) \tag{114}
\]

in the limit \( \Delta r \to 0 \), because the rates are given by equation (51), the surface element is \( \Delta S = \Delta r^{d-1} \), and the sum over the cells having some facets \( \{\Delta r\}_\text{cat} \) in common with the catalytic surface converges to a surface integral over the catalyst.

The continuum description is thus recovered for the mean concentrations from the stochastic process introduced by spatial discretization.

### 3.2.2. The matrix \( L_0 \) in the continuum limit.

In order to interpret more precisely the matrix \( L_0 \) in the continuum limit, we take the scalar product of the kinetic equation (72) with the vector (63) and use equation (74) to get

\[
\mathbf{s} \cdot \frac{d \mathbf{r}}{dt} = -\mathbf{r} \cdot \mathbf{L}_0 \cdot \mathbf{s} + \mathbf{g} \cdot \mathbf{s}. \tag{115}
\]

With the notation \( \mathbf{r} = (\{a_x \Delta r^d\}, \{b_y \Delta r^d\}) \), equation (65) for \( z = 1 \), and equation (67), we obtain

\[
\mathbf{s} \cdot \frac{d \mathbf{r}}{dt} = \sum_r \Delta r^d \left( x_r \frac{da_r}{dt} + y_r \frac{db_r}{dt} \right)
\]

\[
= - \sum_r \Delta r^d \left\{ \sum_{\{\Delta r\}_\text{diff}} [k_A (x_r - x_{r+\Delta r}) a_r + k_B (y_r - y_{r+\Delta r}) b_r]
\]

\[
+ \sum_{\{\Delta r\}_\text{cat}} (x_r - y_r) (k_+ a_r - k_- b_r)
\]

\[
+ \sum_{\{\Delta r\}_\text{res}} [k_A x_r (a_r - \bar{c}_A) + k_B y_r (b_r - \bar{c}_B)] \right\}, \tag{116}
\]

https://doi.org/10.1088/1742-5468/aad7c2
Using the identity
\[
\sum_r \sum_{\{\Delta r\}_{\text{diff}}} x_{r+\Delta r} a_r = \sum_r \sum_{\{\Delta r\}_{\text{diff}}} x_r a_{r+\Delta r},
\]
(117)
a similar relation for \( y_{r+\Delta r} \) and \( b_r \), as well as \( \{\Delta r\}_{\text{diff}} = \{\Delta r\} \setminus \{\Delta r\}_{\text{cat}} \setminus \{\Delta r\}_{\text{res}} \), equation (116) becomes
\[
s \cdot \frac{d\Gamma}{dt} = \sum_r \Delta r^d \left( x_r \frac{da_r}{dt} + y_r \frac{db_r}{dt} \right)
\]
\[
= \sum_r \Delta r^d \sum_{\{\Delta r\}} [k_A x_r (a_r + \Delta r - a_r) + k_B y_r (b_r + \Delta r - b_r)]
\]
\[
- \sum_r \Delta r^d \sum_{\{\Delta r\}_{\text{cat}}} [k_A x_r (a_r + \Delta r - a_r) + k_B y_r (b_r + \Delta r - b_r) + (x_r - y_r) (k_+ a_r - k_- b_r)]
\]
\[
- \sum_r \Delta r^d \sum_{\{\Delta r\}_{\text{res}}} [k_A x_r (a_r + \Delta r - c_A) + k_B y_r (b_r + \Delta r - c_B)].
\]
(118)
Substituting the expressions (51) for the rates, and using the approximations (107), we have that
\[
\sum_r \Delta r^d \left( x_r \frac{da_r}{dt} + y_r \frac{db_r}{dt} \right)
\]
\[
\approx \sum_r \Delta r^d \left( D_A x_r \nabla^2 a_r + D_B y_r \nabla^2 b_r \right)
\]
\[
+ \sum_r \Delta r^{d-1} \sum_{\{\Delta r\}_{\text{cat}}} \left[ D_A x_r \mathbf{1}_\perp \cdot \nabla a_r + D_B y_r \mathbf{1}_\perp \cdot \nabla b_r - (x_r - y_r) (\kappa_+ a_r - \kappa_- b_r) \right]
\]
\[
- \sum_r \Delta r^{d-2} \sum_{\{\Delta r\}_{\text{res}}} \left[ D_A x_r (a_r + \Delta r - c_A) + D_B y_r (b_r + \Delta r - c_B) \right].
\]
(119)
In the limit \( \Delta r \to 0 \), the last terms at the boundary with the reservoir are vanishing because of the boundary conditions \( a_{r+\Delta r} = c_A \) and \( b_{r+\Delta r} = c_B \) and we find
\[
\int \mathcal{D}V \left( x \partial_r a + y \partial_r b \right) = \int \mathcal{D}V \left( x D_A \nabla^2 a + y D_B \nabla^2 b \right)
\]
\[
+ \int_{\text{cat}} \mathcal{D}S \left[ x (D_A \partial_\perp a - \kappa_+ a + \kappa_- b) + y (D_B \partial_\perp b + \kappa_+ a - \kappa_- b) \right].
\]
(120)
We notice that the diffusion equations and the reactive boundary conditions are recovered by considering variations of this equation with respect to \( x \) and \( y \). Therefore, the matrix \( L_0 \) can be interpreted as the evolution operator of the diffusion equations combined with the boundary conditions of the problem. The result is consistent with the fact that equation (72) corresponds to the macroscopic diffusion equations.

3.2.3. The asymptotic cumulant generating function. Here, we calculate the asymptotic value (85) of the cumulant generating function (83). Denoting \( \gamma \) the solution of the problem
\[
L^T \cdot \gamma = \mathbf{g},
\]
(121)
and using equation (75), the asymptotic cumulant generating function can be expressed as

$$Q_\infty(\lambda) = \gamma \cdot (L - L_0) \cdot 1.$$  \hfill (122)

With the same method as before and replacing in equation (65) the vector $\chi$ by

$$\gamma = (\{\tilde{a}_r \Delta r^d\}, \{\tilde{b}_r \Delta r^d\}),$$  \hfill (123)

we get

$$\gamma \cdot L \cdot s \simeq - \int dV \left( x D_A \nabla^2 \tilde{a} + y D_B \nabla^2 \tilde{b} \right)$$

$$- \int_{\text{cat}} dS \left[ x \left( D_A \partial_\perp \tilde{a} - \kappa_+ \tilde{a} + z^{-1} \kappa_- \tilde{b} \right) + y \left( D_B \partial_\perp \tilde{b} + z \kappa_+ \tilde{a} - \kappa_- \tilde{b} \right) \right]$$

$$+ \frac{1}{\Delta r} \int_{\text{res}} dS \left( x D_A \tilde{a} + y D_B \tilde{b} \right),$$  \hfill (124)

while equation (67) becomes

$$g \cdot s \simeq \frac{1}{\Delta r} \int_{\text{res}} dS \left( x D_A \tilde{c}_A + y D_B \tilde{c}_B \right).$$  \hfill (125)

Since equation (121) implies the equality $\gamma \cdot L \cdot s = g \cdot s$ for any vector $s$, its solution can be expressed in terms of the fields $\tilde{a}(r) \equiv \lim_{\Delta r \to 0} \tilde{a}_r$ and $\tilde{b}(r) \equiv \lim_{\Delta r \to 0} \tilde{b}_r$ that are given by solving

$$\nabla^2 \tilde{a} = 0,$$  \hfill (126)

$$\nabla^2 \tilde{b} = 0,$$  \hfill (127)

$$D_A \left( \partial_\perp \tilde{a} \right)_{\text{cat}} = \left( \kappa_+ \tilde{a} - z^{-1} \kappa_- \tilde{b} \right)_{\text{cat}},$$  \hfill (128)

$$D_B \left( \partial_\perp \tilde{b} \right)_{\text{cat}} = - \left( z \kappa_+ \tilde{a} - \kappa_- \tilde{b} \right)_{\text{cat}},$$  \hfill (129)

$$(\tilde{a})_{\text{res}} = \tilde{c}_A,$$  \hfill (130)

$$(\tilde{b})_{\text{res}} = \tilde{c}_B.$$  \hfill (131)

Setting

$$\tilde{a}(r) = \tilde{c}_A - \frac{\ell}{D_A} \left( \kappa_+ \tilde{c}_A - z^{-1} \kappa_- \tilde{c}_B \right) \phi(r),$$  \hfill (132)

$$\tilde{b}(r) = \tilde{c}_B + \frac{\ell}{D_B} \left( z \kappa_+ \tilde{c}_A - \kappa_- \tilde{c}_B \right) \phi(r),$$  \hfill (133)

we find that the field $\phi(r)$ is the solution of equations (15)–(18).
In order to calculate (122), we set \( s = 1 \) in equation (124) and subtract the same expression with \( z = 1 \). Since \( z = e^{-\lambda} \), we obtain

\[
Q_\infty(\lambda) = \int_{\text{cat}} dS \left[ \kappa_+ \tilde{a} (1 - e^{-\lambda}) + \kappa_- \tilde{b} (1 - e^{\lambda}) \right]
\]

(134)

in terms of the solution of equations (126)–(131). Substituting equations (132) and (133) therein yields

\[
Q_\infty(\lambda) = \int_{\text{cat}} dS (1 - \phi) \left[ \kappa_+ \tilde{c}_A (1 - e^{-\lambda}) + \kappa_- \tilde{c}_B (1 - e^{\lambda}) \right].
\]

(135)

According to equation (14), we thus find

\[
Q_\infty(\lambda) = W^{(+)}_{\infty} (1 - e^{-\lambda}) + W^{(-)}_{\infty} (1 - e^{\lambda}),
\]

(136)

proving that the asymptotic values of the rates (11) and (12) are indeed given by equations (26) and (27).

3.2.4. The time-dependent contribution to the cumulant generating function. Here, we calculate the time-dependent function (86), which appears in the last term of the cumulant generating function (83). Using equation (87), the function (86) becomes

\[
\Xi_t(\lambda) = g \cdot (L^{-1} - L^{-1}_0) \cdot M \cdot (I - e^{-L_0 t}) \cdot M^{-1} \cdot (1 + L^{-1} \cdot f).
\]

(137)

On the one hand, the vector \( g \) can be expressed in terms of the stationary state \( \Gamma_0 \) according to equation (74), as well as in terms of the vector \( \gamma \) given above by equation (121),

\[
g = L^T_0 \cdot \Gamma_0 = L^T \cdot \gamma.
\]

(138)

On the other hand, the vector \( f \) can be written as in equation (75). Consequently, the function (137) is of the form

\[
\Xi_t(\lambda) = \eta \cdot (I - e^{-L_0 t}) \cdot \xi
\]

(139)

with

\[
\eta \equiv (\gamma - \Gamma_0) \cdot M
\]

(140)

and

\[
\xi \equiv L^{-1}_0 \cdot M^{-1} \cdot (L - L_0) \cdot 1.
\]

(141)

Using equations (90) and (91), we notice that

\[
\eta = (1 - z) \Gamma_0 \cdot (P_A - L_0 \cdot P_A \cdot L_0^{-1}),
\]

(142)

\[
\xi = (z^{-1} - 1) (P_A - L_0^{-1} \cdot P_A \cdot L_0) \cdot 1,
\]

(143)

showing that we should expect the factorizations of \( 1 - z \) and \( z^{-1} - 1 \), respectively. In order to establish this factorization and obtain the analytical expressions for (140) and (141) in the continuum limit, we proceed as follows.
Multiplying equation (140) by an arbitrary vector \( \mathbf{s} = (\{x_r\}, \{y_r\}) \) and using the notations (123),
\[
\eta = \{(u_r \Delta r^d), \{v_r \Delta r^d\}\}, \quad \Gamma_0 = \{\{\langle A_r \rangle_{st}\}, \{\langle B_r \rangle_{st}\}\},
\]
as well as the definition (88), we have that
\[
\eta \cdot \mathbf{s} = \sum_r \Delta r^d (u_r x_r + v_r y_r) = \sum_r \left[ z (\tilde{a}_r \Delta r^d - \langle A_r \rangle_{st}) x_r + (\tilde{b}_r \Delta r^d - \langle B_r \rangle_{st}) y_r \right].
\]
Since
\[
\langle A_r \rangle_{st} = \langle c_A(r) \rangle_{st} \Delta r^d \quad \text{and} \quad \langle B_r \rangle_{st} = \langle c_B(r) \rangle_{st} \Delta r^d.
\]
Equations (35), (132) and (133) yield
\[
u_r = (1 - z) \ell \kappa_+ \tilde{c}_B \frac{D_A}{D_B} \phi(r),
\]
and expressing \( \phi(r) \) in terms of the solution \( \phi(r) \) of the stationary problem (15)–(18).

Multiplying equation (141) by \( \mathbf{L}_0 \) and an arbitrary vector (69), we obtain the equation
\[
\chi \cdot \mathbf{L}_0 \cdot \xi = \chi \cdot \mathbf{M}^{-1} \cdot (\mathbf{L} - \mathbf{L}_0) \cdot 1
\]
that the vector \( \xi = (\{\tilde{x}_r\}, \{\tilde{y}_r\}) \) should satisfy. With the same method as before, we get
\[
\chi \cdot \mathbf{L}_0 \cdot \xi \simeq -\frac{1}{\Delta r^d} \int dV (\tilde{x} D_A \nabla^2 \alpha + \tilde{y} D_B \nabla^2 \beta) - \frac{1}{\Delta r^d} \int_{\text{cat}} dS (\tilde{x} (D_A \partial_\perp \alpha - \kappa_+ \alpha + \kappa_- \beta) + \tilde{y} (D_B \partial_\perp \beta + \kappa_+ \alpha - \kappa_- \beta)) + \frac{1}{\Delta r^{d+1}} \int_{\text{res}} dS (\tilde{x} D_A \alpha + \tilde{y} D_B \beta),
\]
and
\[
\chi \cdot \mathbf{M}^{-1} \cdot (\mathbf{L} - \mathbf{L}_0) \cdot 1 \simeq \frac{1}{\Delta r^d} \int_{\text{cat}} dS (z^{-1} - 1) (\kappa_+ \alpha - \kappa_- \beta).
\]
At the leading order \( 1/\Delta r^{d+1} \), the equality (149) between (150) and (151) shows that the boundary conditions \( (\tilde{x})_{\text{res}} = (\tilde{y})_{\text{res}} = 0 \) should be satisfied on the reservoir. Now, integrating by parts leads to
\[
\int dV \tilde{x} \nabla^2 \alpha = \int dV \alpha \nabla^2 \tilde{x} + \int dS (\alpha \partial_\perp \tilde{x} - \tilde{x} \partial_\perp \alpha)
\]
and a similar relation between \( \tilde{y} \) and \( \beta \). Accordingly, at the subleading order \( 1/\Delta r^d \), equation (149) becomes

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\[ \int dV \left( \alpha D_A \nabla^2 \tilde{x} + \beta D_B \nabla^2 \tilde{y} \right) + \int_{\text{cat}} dS \left\{ \alpha \left[ D_A \partial_\perp \tilde{x} - \kappa_+ \left( \tilde{x} - \tilde{y} + 1 - z^{-1} \right) \right] + \beta \left[ D_B \partial_\perp \tilde{y} + \kappa_- \left( \tilde{x} - \tilde{y} + 1 - z^{-1} \right) \right] \right\} = 0. \] (153)

Taking variations with respect to $\alpha$ and $\beta$, we find that the fields $\tilde{x}$ and $\tilde{y}$ are the solutions of the following problem:

\[ \nabla^2 \tilde{x} = 0, \] (154)

\[ \nabla^2 \tilde{y} = 0, \] (155)

\[ D_A (\partial_\perp \tilde{x})_{\text{cat}} = \kappa_+ \left( \tilde{x} - \tilde{y} + 1 - z^{-1} \right)_{\text{cat}} ; \] (156)

\[ D_B (\partial_\perp \tilde{y})_{\text{cat}} = -\kappa_- \left( \tilde{x} - \tilde{y} + 1 - z^{-1} \right)_{\text{cat}} ; \] (157)

\[ (\tilde{x})_{\text{res}} = 0, \] (158)

\[ (\tilde{y})_{\text{res}} = 0. \] (159)

With the substitution

\[ \tilde{x}(r) = (z^{-1} - 1) \ell \frac{\kappa_+}{D_A} \phi(r), \] (160)

\[ \tilde{y}(r) = - (z^{-1} - 1) \ell \frac{\kappa_-}{D_B} \phi(r), \] (161)

the problem is reduced to finding the solution $\phi(r)$ of equations (15)–(18).

Now, equation (139) can be rewritten as

\[ \Xi_t(\lambda) = \eta \cdot (\xi - \xi_t) \] (162)

in terms of the time-dependent vector

\[ \xi_t = e^{-\mathbf{L}_0 t} \cdot \xi, \] (163)

which is the solution of

\[ \frac{d\xi_t}{dt} = -\mathbf{L}_0 \cdot \xi_t \] (164)

and denoted $\xi_t = (\{\tilde{x}_{t,r}\}, \{\tilde{y}_{t,r}\})$. Multiplying equation (164) by an arbitrary vector (69) and using the same method as above, we find that

\[ \int dV \left( \alpha \partial_t \tilde{x}_t + \beta \partial_t \tilde{y}_t \right) = \int dV \left( \alpha D_A \nabla^2 \tilde{x}_t + \beta D_B \nabla^2 \tilde{y}_t \right) \]

\[ + \int_{\text{cat}} dS \left\{ \alpha \left[ D_A \partial_\perp \tilde{x}_t - \kappa_+ \left( \tilde{x}_t - \tilde{y}_t \right) \right] + \beta \left[ D_B \partial_\perp \tilde{y}_t + \kappa_- \left( \tilde{x}_t - \tilde{y}_t \right) \right] \} \] (165)

with the boundary conditions $(\tilde{x}_t)_{\text{res}} = (\tilde{y}_t)_{\text{res}} = 0$. The fields $\tilde{x}_t$ and $\tilde{y}_t$ are thus the solutions of the following problem:

https://doi.org/10.1088/1742-5468/aad7c2
\[ \partial_t \tilde{x}_t = D_A \nabla^2 \tilde{x}_t, \] (166)
\[ \partial_t \tilde{y}_t = D_B \nabla^2 \tilde{y}_t, \] (167)
\[ D_A (\partial_{\perp} \tilde{x}_t)_{\text{cat}} = \kappa_+ (\tilde{x}_t - \tilde{y}_t)_{\text{cat}}, \] (168)
\[ D_B (\partial_{\perp} \tilde{y}_t)_{\text{cat}} = -\kappa_- (\tilde{x}_t - \tilde{y}_t)_{\text{cat}}, \] (169)
\[ (\tilde{x}_t)_{\text{res}} = 0, \] (170)
\[ (\tilde{y}_t)_{\text{res}} = 0, \] (171)
\[ \tilde{x}_t=0 = \tilde{x}, \] (172)
\[ \tilde{y}_t=0 = \tilde{y}, \] (173)

where the initial conditions are given in terms of the previously obtained stationary functions \( \tilde{x} \) and \( \tilde{y} \). Setting
\[ \tilde{x}_t(r) = (z^{-1} - 1) \ell \frac{\kappa_+}{D_A} f_A(r, t), \] (174)
\[ \tilde{y}_t(r) = - (z^{-1} - 1) \ell \frac{\kappa_-}{D_B} f_B(r, t), \] (175)

we conclude that the functions \( f_k(r, t) \) obey the time-dependent problem of equations (21)–(25) for \( k = \text{A, B} \). We note that the factorization expected by equation (143) is confirmed by equations (160), (161), (174) and (175).

Substituting the results (147), (148), (160), (161), (174) and (175) into equation (162), we find
\[ \Xi_t(\lambda) = \sum_r \Delta r^d [u_r (\tilde{x}_r - \tilde{x}_{t,r}) + v_r (\tilde{y}_r - \tilde{y}_{t,r})] \]
\[ \approx (1 - z) (z^{-1} - 1) \ell^2 \kappa_+ \kappa_- \sum_r \Delta r^d \phi(r) \left\{ \frac{\epsilon_B}{D_A} [\phi(r) - f_A(r, t)] + \frac{\epsilon_A}{D_B} [\phi(r) - f_B(r, t)] \right\}. \] (176)

Since \( z = e^{-\lambda} \), we finally obtain
\[ \Xi_t(\lambda) = (e^\lambda + e^{-\lambda} - 2) \Psi(t) \] (177)
expressed in terms of the function (13) in the continuum limit \( \Delta r \to 0 \).

The analytic expressions (11) and (12) for the rates are thus proved.

3.2.5. The cumulant generating function at early time. Expanding the function (139) in powers of time, keeping the term of first order in the time \( t \), and replacing \( Q_\infty(\lambda) \) with its expression (122) in equation (84), we get the following expression,
\[ Q_t(\lambda) = \Gamma_0 \cdot (L - L_0) \cdot 1 + O(t), \] (178)

showing that the early-time behavior of the cumulant generating function is given by an expression similar to equation (122), but with the vector \( \gamma \) corresponding to the fields
(\tilde{a}, \tilde{b}) substituted by the stationary state (74) corresponding to the fields \((\langle c_A \rangle_{st}, \langle c_B \rangle_{st})\). Carrying out this substitution in equation (134), which is the continuum limit of equation (122), we obtain equation (36).

4. Conclusion and perspectives

In this paper, a finite-time fluctuation theorem was established for the diffusion-influenced surface reaction \(A \rightleftharpoons B\) ruled by stochastic partial differential equations. The theorem was deduced by solving the evolution equation for the moment generating function of a corresponding spatially discretized system, thereafter taking the continuum limit. The analytical expression of the cumulant generating function is thus given in terms of the finite-time rates of the diffusion-influenced reaction process. In this way, the large-deviation properties of the spatially extended stochastic process are obtained by solving deterministic diffusion equations with specific boundary conditions.

The results show that, in stationary states, the full counting statistics of the reactive events satisfies a time-reversal symmetry over every finite time interval. The affinity of the fluctuation theorem also depends on time with a known analytical dependence. In this diffusion-influenced system, one of the prominent features of this affinity is that it may take different values at finite time than its asymptotic value predicted by the standard infinite-time fluctuation theorem.

The finite-time fluctuation theorem holds because the macroscopic rate of the reaction \(A \rightleftharpoons B\) is linear in the concentrations (although nonlinear in the affinity). Therefore, the generating function (80) of the joint conditional probability distribution for the numbers of molecules and reactive events remains exponential in the generating variables, \(s\), associated with the numbers of molecules, if the counting starts from the Poissonian stationary state. In this regard, we may conjecture that the result can be extended to networks of diffusion-influenced surface reactions having macroscopic rates that are linearly dependent on the concentrations. In such systems, several currents may be coupled together, leading to Onsager reciprocal relations and their generalizations to the nonlinear response regimes [29].

Acknowledgments

The Authors thank Patrick Grosfils and Mu-Jie Huang for fruitful discussions. Financial support from the International Solvay Institutes for Physics and Chemistry, the Université libre de Bruxelles (ULB), the Fonds de la Recherche Scientifique—FNRS under the Grant PDR T.0094.16 for the project ‘SYMSTATPHYS’, and the Natural Sciences and Engineering Research Council of Canada is acknowledged.

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