The geometric universality of currents

**V Y Chernyak**¹,², **M Chertkov**²,³ and **N A Sinitsyn**²,³

¹ Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202, USA
² Theoretical Division, Los Alamos National Laboratory, B258, Los Alamos, NM 87545, USA
³ New Mexico Consortium, Los Alamos, NM 87544, USA
E-mail: chernyak@chem.wayne.edu, chertkov@lanl.gov and nsinitsyn@lanl.gov

Received 19 April 2011
Accepted 11 August 2011
Published 14 September 2011

Online at stacks.iop.org/JSTAT/2011/P09006
doi:10.1088/1742-5468/2011/09/P09006

**Abstract.** We discuss a non-equilibrium statistical system on a graph or network. Particles are injected, interact with each other, and traverse and leave the graph in a stochastic manner. We show that under the assumption of constancy of a subset of parameters, the system demonstrates the universality of the statistics of the particle currents. In systems connected to a heat bath, this universality leads to fluctuation relations that forbid distinguishing stochastic currents in a strongly driven regime from the currents in thermodynamic equilibrium. We apply this universality to enabling examples from mesoscopic electronics and biochemistry.

**Keywords:** symmetries of integrable models, stochastic particle dynamics (theory), current fluctuations
1. Introduction

Understanding the statistics of currents generated in an open driven system that consists of multiple degrees of freedom is among the greatest goals of non-equilibrium statistical physics. The problem typically emerges in the context of multiple particles traversing a medium, subject to stochastic noise, and also interacting with each other. Studying an elementary current means counting the number of particles passing through a respective line element of the medium during a fixed observation time. Repeated a multiple number of times, measurements of the current show variable results due to the intrinsic stochastic nature of the underlying processes. To quantify these statistical variations one studies the probability distribution function (PDF) of the current.

Consider identical particles traversing the system, described by a connected open directed graph, $G = (G_0, G_1)$, for example that shown in figure 1, where $G_0$ and $G_1$ denote the sets of the graph vertices and edges, respectively. Particles enter the system from the exterior reservoir of infinite capacity, where $\lambda_0$ is a time dependent Poisson particle injection rate at node $i$. Upon arrival at an entry node the particle advances by jumping between the nodes along the directed edges, each characterized by the transition rate, $\Lambda_{ik} = n_i \lambda_{ik}(t; n(t))$, with $\lambda_{ik}$ being the rate per particle occupying node $i$. The internode per-particle rate, $\lambda_{ik}$, is finite and may depend on time explicitly, as well as implicitly via the dependence on the system state $n = (n_i | i \in G_0)$, with $n_i(t)$ being the number of particles at node $i$ at time $t$. We assume no intrinsic limitation on the number of particles residing at any node in the system, i.e. $n_i$ may be any nonnegative integer. A particle may leave the system along any of the outgoing links, with the corresponding departure rates $\Lambda_{i0} = n_i \lambda_{i0}$, the per-node rate $\lambda_{i0}$ being also generally dependent on both $n(t)$ and $t$. Models of the type shown in figure 1 are commonly known as Jackson networks in the theory of queuing. Introduced and studied in the work of Jackson [1] and Kelly [2], this subject became classical in operations research (OR); see e.g. the textbooks [3, 4].
The geometric universality of currents

Figure 1. Example of an open network of interacting particles represented by a directed graph. The sample graph consists of four vortices/stations, labeled 1, 2, 3, 4, with label 0 reserved for an external (reservoir) node. Transitions between the nodes are shown as directed edges. Loops (self-loops, as $1 \rightarrow 1$) are allowed. Each graph edge $(i, k)$ with $i \neq 0$ is equipped with a transition rate $\lambda_{ik}$, describing the rate of particle departure from site $i$ per current occupation number $n_i$ on the site. We consider the most general case of $\lambda_{ik}(n(t); t)$ being finite, and otherwise depending arbitrarily on time and the instantaneous global state $n(t)$ of the system. $\lambda_{0i}$ stands for the time independent rate of injection from the reservoir.

special properties of currents in Jackson networks with time independent parameters were considered previously [3, 5, 6].

Consider the statistics of currents in a generic Jackson network in the regime. Such a stochastic system of many identical interacting particles is described via the following master equation (ME) for the instantaneous distribution function of $n$:

$$\frac{\partial}{\partial t} P(n; t) = \sum_{(0,i) \in G_1} \lambda_{0i}(P(n_{-i}; t) - P(n; t))$$

$$+ \sum_{(i,j) \in G_1} \Lambda_{ij}(t; n_{+i}; t) P(n_{+i} - j; t) - \Lambda_{ij}(t; n) P(n; t),$$

(1)

where $n_{+i} = (\ldots, n_i + 1, \ldots)$, $n_{-i} = (\ldots, n_i - 1, \ldots)$ and $n_{+i} - j = (\ldots, n_i + 1, \ldots, n_j - 1, \ldots)$. In our models, we will additionally restrict kinetic rates to have the form $\Lambda_{ij}(t; n) = g_{ij}f_i(t; n)$. Such transition rates depend on the global state of the system, characterized by $n(t)$, and also depend on time explicitly, but any ratio of kinetic rates along the links that are outgoing from a common node remains constant in time.

We also assume that the graph and the rates are chosen such that the solution of equation (1) converges to a non-singular distribution of $n$ in some finite time, $\tau$, which can be also viewed as the typical time that a particle spends in the system. To characterize the non-equilibrium features of this steady state one may also want to know the statistics of the vector $J = (J_{ik} | (i, k) \in G_1)$ of currents, with the edge-
labeled components, $J_{ik}$, defined as the number of particles that traverse through the edge $(i, k)$ during time $T$. For an observation time, $T$, that is long compared to the correlation time, $\tau$, the PDF of the currents obeys the following large deviation (LD) form: $-\ln(P(J|T))/T = S(J/T) + o(\tau/T)$, where $S(J/T)$, often referred to as the LD function, is a convex function of its multi-variant argument.

Our consideration applies to systems widespread in biology, zero-range processes [8], and operations research. Yet another application domain which requires very precise evaluation of the statistics of currents belongs to the field of mesoscopic electronics, e.g. electric circuits in systems made of quantum dots and tunnel junctions [9]–[16]. Better understanding of the electron transport/current in such devices is of benefit in designing fast and reliable information processing systems. This application will help us to illustrate the power of our main result.

2. The geometric universality of currents (GUC)

The GUC is the main statement of this paper, and suggests that for $T \gg \tau$ and under the condition that the tested currents are not very large (imposed so that the average $n$ conditioned on the value of the currents is non-singular and finite), the LD function is invariant with respect to any (e.g. time and $n(t)$ dependent) transformations that keep the graph intact and the branching ratios, $\forall (i, k) \in G_1 | i \neq 0: \frac{\lambda_{ik}(t; n(t))}{\sum_{l \in G_1} \lambda_{il}(t; n(t))} = \theta_{ik}$, constant, i.e. the relative transition probabilities $\theta_{ik}$ are independent of the time $t$ and the state $n(t)$ of the network. In particular, the statement means that $S(J/t)$ can be calculated by considering an auxiliary problem with $\lambda_{ik}(t; n) \rightarrow \theta_{ik}$, thus replacing the interacting system with its much simpler non-interacting surrogate. This reduction makes the evaluation of the LD function computationally easy. We label the universality geometric, to emphasize its interpretation in terms of the statistics of open single-particle trajectories, and specifically of their geometries. If injection rates depend on time arbitrarily, for example in a quasi-periodic fashion, with the result that the time averaged rates $\bar{\lambda}_{0i} \equiv T^{-1} \int_0^T dt \lambda_{0i}(t)$ are finite, then, under the same conditions (universality and independence of time for all $\theta$ in equation (2), and finiteness of the queues) as for the above statement of the GUC, we find that the statistics of currents is universal, with the LD function calculated as if the injection rates were constant and equal to $\bar{\lambda}_{0i}$.

Although the condition (2) may seem artificial at first sight, it is, in fact, realized quite often. For example, it describes any local (on-site) interactions and time independent $\lambda_{ij}$. In addition, we will show that parameters $\theta_{ik}$ have a separate physical meaning from other parameters when the model corresponds to a mesoscopic system that is strongly coupled to a heat bath. In such a case, parameters $\theta_{ik}$ can be controlled separately from other parameters. We will show a realistic example of a driven electric circuit in which we can naturally make all parameters except $\theta_{ik}$ time dependent. We will also show that, in fact, under conditions of the validity of the GUC, the full statistics of particle currents can be found explicitly and exactly (which also provides an alternative proof of the GUC).

Here we should clearly state that the goal of this article is not to provide a rigorous mathematical proof of the GUC, which would require the explicit identification of the
limits of its validity in strongly interacting and explicitly time dependent systems. Instead, in the present section, we will provide intuitive arguments in support of the applicability of the GUC to a large class of realistic mesoscopic stochastic systems such as electric circuits and biochemical enzymatic reactions. A specific property of such systems is their restricted capacity, namely, the probabilities of observing very large populations should be strongly suppressed so that particle escape rates grow sufficiently fast with state populations starting from certain values, and condensation-like phenomena, e.g. those discussed in [6, 7], do not happen.

To explain why the GUC should be valid in such systems, let us focus on a single-particle trajectory, $x = (s, t)$, fully characterized by the following finite sequences: $s = (s_1, \ldots, s_k)$ and $t = (t_0, t_1, \ldots, t_k)$, where $s_l$ and $t_l$, with $1 \leq l \leq k$, stand for the position (node $s_l \in G_0$) and time stamp of the particle leaving the station $s_l$ for the next station $s_{l+1}$ along the path. We assume that $t_0$ and $t_k$ are the times when the particle enters and leaves the system, respectively; the temporal stamps are time ordered: $0 \leq t_0 \leq \cdots \leq t_k \leq T$, where $T \gg \tau$ is a sufficiently long time and $\tau$ is the correlation time (estimated as the typical time that a particle spends inside the system); a particle can visit the same station a number of times; and the total number, $k$, of jumps can be an arbitrary integer. It will be important for the forthcoming discussion to separate the geometrical, $s = (s_1, \ldots, s_k)$, and temporal, $t = (t_0, \ldots, t_k)$, characteristics of the trajectory. In particular, the total current generated by a single-particle trajectory, whose individual (per-edge) component measures the number of times that the trajectory passes through any given edge, depends on its geometrical component, $s$, only, and the current generated by a stochastic realization of our system is the sum of the single-trajectory currents. Thus, to describe a single-particle trajectory, for example one of the two shown in figure 2, we naturally pose the following question: what is the probability for a particle observed entering and leaving the network over a sufficiently long time horizon $[0; T]$ to choose this particular path, $s$? This probability should depend on the factors $\theta_{s_l s_{l+1}}$ only and, therefore, it shows no correlations with other trajectories. The information contained in this probability distribution, $P(s)$, is geometric and independent of the temporal details $t$ of the trajectory. The assumed invariance (2) of our general model, with respect to any changes in the system keeping the transition (branching) probabilities $\theta_{il}$ constant, guarantees that the probability of a path, $P(s) = \prod_{l=1}^{k} \theta_{s_l s_{l+1}}$ (with $s_{l+1} = 0$), is universal/invariant as well. The probability of a temporal realization of a many-particle trajectory shows strong correlations between single-particle trajectories and can be explicitly expressed in terms of $\kappa_{il}(t; n(t)) = \sum_{s \in G_0} \lambda_{si}$; however, the currents generated are not sensitive to this complex temporal structure.

Figure 2. Geometrically distinct single-particle trajectories.
We now consider the probability of observing a given vector of the current for the observation time, \( T \) (the component of the vector associated with an edge counts the number of particles that have crossed the edge in time \( T \)):

\[
P(J|T) = \sum_{n=1}^{\infty} \sum_{s_1 \cdots s_n} \mathcal{P}(s) \prod_{(i,k) \in \mathcal{G}_1} \delta(J_{ik} - \chi_{ik}(s)) \mathcal{P}_0(s_0^1, \ldots, s_0^n),
\]

where \( \mathcal{P}_0(s_0^1, \ldots, s_0^n) \) is the probability of \( n \) particles being injected into the network at the corresponding nodes and \( \chi_{ik}(s) \) simply counts the number of times that the particles traversing the path \( s \) went through the edge \((i,k)\). Obviously, equation (3) is evaluated as an expectation over all possible single-particle paths. (Equation (3) is an asymptotic expression, valid for \( T \gg \tau \) only, because it completely ignores the trajectories trapped in the system for periods longer than \( T \).) Therefore, one concludes that asymptotically \( \mathcal{P}(J|T) \) is a single-particle object which is also universal/invariant with respect to equation (2) in view of its linear relation to \( \mathcal{P}(s) \) and the previously discussed universality of the latter.

3. The generating function of currents in networks with constant branching ratios of kinetic rates

Here we will show that under the conditions of equal branching ratios of rates and in the large observation time limit, all cumulants of the current distribution can be obtained explicitly even when all remaining parameters are quasi-periodically time dependent and when possible interactions are allowed. We will find that, as expected from the GUC, the result depends only on the branching ratios \( \theta_{ik} \) and on ingoing kinetic rates averaged over time. However, the derivation in this section cannot be considered an alternative derivation of the GUC. We will obtain the full counting statistics by ‘guessing’ an ansatz solution for the evolution equation of the generating function of the current distribution. Such an approach to a complex interacting system driven by time dependent fields generally would not guarantee that the solution obtained describes currents in the regime under consideration. However, we will argue that the GUC, if applicable, guarantees the general applicability of this solution.

Consider the generating function

\[
Z(q;T) = \sum_{J} \mathcal{P}(J|T) \prod_{(i,k) \in \mathcal{G}_1} q_{ik}^{J_{ik}},
\]

depending on the multi-variant argument \( q = (q_{ik}|(i,k) \in \mathcal{G}_1) \). We will focus on the analysis of the \( T \gg \tau \) asymptote, where \( Z(q;T) \sim e^{T \Delta(q)} \). Since \( S(j) \), with \( j = J/T \), is related to \( \Delta(q) \) by the standard Legendre transform

\[
S(j) = \sum_{(i,k) \in \mathcal{G}_1} j_{ik} \ln q_{ik}^* - \Delta(q^*), \quad \forall (i,k) \in \mathcal{G}_1 : \quad j_{ik} = q_{ik}^* \partial_{q_{ik}} \Delta(q^*),
\]

the universality of the LD function, \( S(j) \), under the transformations considered is equivalent to the universality of \( \Delta(q) \).

Within the respective operator, so-called Doi–Peliti, formalism [17, 18] (see also [6, 19]) the Master equation becomes \( \partial P(n;t)/\partial t = \hat{H}(t)P(n;t) \), where the time dependent
operator $\hat{H}(t)$ is
\[
\hat{H}(t) = \sum_{(i,j) \in G_1} \lambda_{ij}(\hat{a}_i^\dagger - 1) + \sum_{(i,j) \in G_1} \theta_{ij}\hat{a}_j^\dagger \hat{b}_i(t) + \sum_{(i,0) \in G_1} \theta_{i0} \hat{b}_i(t) - \sum_{k \in G_0} \hat{a}_k^\dagger \hat{b}_k(t),
\]
with $\hat{a}_i^\dagger P(n) \equiv P(n_i)$ and
\[
\hat{b}_k(t) P(n) \equiv (n_j + 1) \kappa_k(t, n_{+k}) P(n_{+k}).
\]
In deriving the last term in equation (6) we used $\sum_{k} \theta_{ik} = 1$. Note that $\hat{H}(t)$ has a very simple form, being expressed via the standard ‘creation’ operators $\hat{a}_k^\dagger$, which are local and time independent, and the non-standard ‘annihilation’ operators $\hat{b}_k(t)$, which are nonlocal and depend on time explicitly. The complexity of the system stochastic dynamics is hidden in the time dependent, nonlocal, and nonlinear nature of the ‘annihilation’ operators, $\hat{b}_k(t)$. As we will see, the function $\Delta(q)$ is not sensitive to the specific form of $\hat{b}_k(t)$.

Extending the standard operator approach developed for generating functions in [6] to the most general case, where the rates depend on the occupation numbers and time arbitrarily, we derive
\[
\begin{align*}
Z(q; T) &= \sum_n \hat{U}_q P_0(n), \\
\hat{U}_q(T) &= \text{Texp} \left( \int_0^T dt \hat{H}_q(t) \right).
\end{align*}
\]

Here, $P_0(n)$ is the initial distribution, Texp stands for the time-ordered exponential, and the twisted master operator $\hat{H}_q(t)$ is
\[
\begin{align*}
\hat{H}_q(t) &= \sum_{(i,j) \in G_1} \lambda_{ij}(q_{ij}\hat{a}_i^\dagger - 1) + \sum_{i \in G_0} \hat{c}_i^\dagger(q) \hat{b}_i(t) \\
\hat{c}_i^\dagger(q) &\equiv \sum_{k \neq 0} q_{ik}\theta_{ik}\hat{a}_k^\dagger - \hat{a}_i^\dagger + q_{i0}\theta_{i0}.
\end{align*}
\]
Solving the eigenvalue problem $\hat{U}_q|\Psi_q\rangle = z_q|\Psi_q\rangle$ in the most general case does not appear feasible, thus reflecting the complexity of the stochastic dynamics of interacting particles. However, the simplicity in the system shows itself when we study the eigenvalue problem for the bra-eigenstate, rather than the ket-eigenstate: $\langle \Psi_q|\hat{U}_q = \langle \Psi_q|z_q$. The bra-eigenvalue problem for the highest absolute value can be treated explicitly by observing that for given $q$ the family of operators $\hat{H}_q(t)$, parameterized by time, all share the same bra-eigenstate with the same eigenvalue, i.e., $\langle \Psi_q|\hat{H}_q(t) = \langle \Psi_q|\omega_q$, so $z_q = e^{\omega_q T}$, which yields $\Delta(q) = \omega_q$.

We will search for the bra-eigenstate in the form of a coherent state $\langle \Psi_q| = \langle \zeta| \equiv \langle \rho|\prod_{j \in G_0} e^{\zeta_j a_j^\dagger}$, with $\langle \rho|$ denoting the state with no particles. The coherent states are parameterized by $\zeta = \langle \zeta_j| j \in G_0 \rangle$ and satisfy the following important property: $\langle \zeta|\hat{a}_j^\dagger = \langle \zeta|\zeta_j$. Due to the latter property, to ensure that $\langle \zeta|$ is an eigenstate of $\hat{H}_q(t)$, it

doi:10.1088/1742-5468/2011/09/P09006
The geometric universality of currents

is sufficient to verify that \( \langle \zeta | c_i^\dagger = 0 \) for all \( i \). This condition results in a system of linear equations

\[
\sum_{k \neq 0} \theta_{ik}(q_{ik}\zeta_k - \zeta_i) + \theta_{i0}(q_{i0} - \zeta_i) = 0, \quad \omega_q = \sum_i \bar{\lambda}_{0i}(q_{0i}\zeta_i - 1),
\]

where \( \bar{\lambda}_{0i} = T^{-1} \int^T_0 dt \lambda_{0i}(t) \). Solution (11) fully identifies \( \Delta(q) = \omega_q \), and hence the generating function in the \( T \to \infty \) limit, \( Z(q; T) \sim e^{\Delta(q)T} \), and the LD function given by (5).

To show that (11) is the solution that corresponds to the regime of GUC validity, we note that in agreement with GUC, (11) depends only on the time independent parameters, \( \theta_{ik} \) and \( \bar{\lambda}_{0i} \), i.e. it is the same as it would be in the case of a non-interacting problem without driven parameters. To show that it is the true steady state distribution in the non-interacting and nondriven version of our model, we also note that at unit values of all parameters, \( q \), the operator \( \hat{H}_q \) becomes just a master operator for the given model, and the left eigenvector, \( |\Psi_q\rangle \), becomes a bra-vector with all unit values. This vector corresponds to the unique steady bra-eigenstate of the master operator. Consequently, for non-unit values of \( q \), \( |\Psi_q\rangle \) corresponds to the eigenstate of the nondriven and non-interacting version of \( \hat{H}_q \) that describes currents in the steady state, and via GUC it describes currents in the full version of \( \hat{H}_q \) in the regime of the validity of the GUC.

A sufficient condition for the validity of the solution (11) in the limit of large observation time should be the existence of a family of models with a non-degenerate largest eigenvalue of \( \hat{U}_q \). Such a family includes both the original model and the corresponding steady state non-interacting model. Models in the family differ from each other by a continuous change of parameters responsible for interactions and the time dependence of kinetic rates. This guarantees that the solution (11) obtained corresponds to the observed statistics of currents in the long observation time limit.

4. Applications of GUC to biochemical networks and single-molecule experiments

In the main text, we discussed an enabling application of the GUC: to electric currents in mesoscopic systems of quantum dots. Here we show that, similarly to the electric currents case, the GUC can be viewed as a no-go restriction on the ability to interpret experimental data on the statistics of reaction events (biochemical networks). These restrictions follow from the fact that the statistics of currents actually depends only on the time independent relative probabilities, \( \theta_{ij} \), as ratios of transition rates, rather than the complete transition rates themselves.

When the number of molecules involved in a biochemical reaction is not too large, e.g. when it is of the order of or less than 100, the effects of noise on the reaction kinetics of a moderate-size system (often called a mesoscopic system) are significant. For example in vivo reactions inside living bacteria [20]–[23] constitute an exemplary mesoscopic system of this type. Effects of fluctuations in such systems are often analyzed in vitro using single-molecule experiments and methods of fluorescence correlation spectroscopy [24]–[30]. These and other related techniques try to reconstruct the complex stochastic mechanisms of biochemical networks. In particular, the techniques are capable of uncovering new microscopic information on reaction kinetics, inaccessible via standard macroscopic (bulk)
experiments. This is achieved by measuring variances and autocorrelation functions of the reaction events. Examples of observations, which became available with the invention of single-molecule techniques, include the discovery of new (not known before) internal states of enzymes [27]. The opportunities provided by these techniques are exciting; however they are also accompanied by significant challenges in interpreting the statistical measurements. Direct numerical simulations of even simple biochemical processes are prohibitively expensive and inconclusive for reconstructing the full statistics of reaction events [31], thus emphasizing the importance of alternative analytical methods. This paper contributes to the task of developing analytical methods to describe delicate and important fluctuation effects in mesoscopic biochemical reactions.

Consider the conversion of molecules of one type, called the substrate, into ones of another type, called the product, via an enzymatic mechanism. In this section, we specifically work out the exemplary Michaelis–Menten (MM) enzymatic reaction [32]; however, our arguments are easy to generalize to more complex models that include multiple substeps that mediate the substrate to product conversion.

The MM process involves interactions of a substrate molecule with another molecule, called the enzyme, that results in the creation of an enzyme–substrate complex. Let $S$, $P$, $E$, and $C$ denote the substrate, the product, the enzyme, and the enzyme–substrate complex molecules, respectively. The complex, $C$, is created from $E$ and $S$, followed by splitting into either $E + S$ or $E + P$. Assume that the latter reaction is observable. This is possible, e.g. via attaching the so-called green fluorescent protein (GFP) tag that fluoresces each time a product molecule is created. The light intensity is proportional to the number of product molecules. Measurements of the average intensity, its variance, and higher cumulants provide valuable information on the statistics of the number of transitions in the $C \to E + P$ sub-chain. The enzyme molecules are also permanently generated and undergo degradation. To summarize, the full set of elementary reactions that characterize the model is shown in figure 3(a). It represents:

(i) creation of enzyme molecules, $0 \to E$, with rate $k_+$;
(ii) degradation of the enzyme–substrate complex $C \to 0$ with rate $k_C[C]$;

Figure 3. (a) Set of reactions that include a complex Michaelis–Menten process, as well as enzyme creation and degradation. (b) Equivalent Jackson network with kinetic rates which are proportional to the number of molecules, represented by the nodes. The first and second nodes represent free enzymes and enzyme–substrate complexes, respectively.
(iii) degradation of enzyme molecules, \( E \rightarrow 0 \), with rate \( k_E[E] \);

(iv) conversion of \( S \) into \( P \) via a Michaelis–Menten reaction, which involves three sub-processes:

(a) creation of an enzyme–substrate complex \( E + S \rightarrow C \) with rate \( k_1[E][S] \);

(b) reverse reaction of a complex, splitting into free enzyme and substrate molecules, \( C \rightarrow E + S \), with rate \( k_{-1}[C] \);

(c) irreversible splitting of a complex into free enzyme and product molecules, \( C \rightarrow E + P \), with rate \( k_2[C] \).

Here \([\cdot \cdot \cdot]\) is standard biochemical notation for abundance \([31]\), i.e. the number of molecules of the given type in the system. We assume that the substrate molecules are supplied in macroscopic quantities, thus keeping the corresponding concentration \([S] = \text{const.} \). Note that the stochastic model of biochemical kinetics described can be viewed in terms of stochastic transitions in the reaction graph shown in figure 3(b), where the number of transitions through a given link represents the number of reaction events during the observation time. Assuming all transitions to be Poisson, we observe that the set of biochemical reactions in figure 3(a) can be viewed as an instance of a general stochastic network model with the GUC. Specifically, the relations between the parameters of the biochemical models with fluctuating numbers of enzymes and the notation for the rates in our general network model are as follows: \( \Lambda_{01} = k_+, \Lambda_{10} = k_E[E] \), \( \Lambda_{02} = 0 \), \( \Lambda_{20} = k_C[C] \), \( \Lambda_{12} = k_1[E][S] \), \( \Lambda_{21} = k_{-1}[C] \), \( \Lambda_{212} = k_2[C] \).

Suppose that one performs measurements of the number of product molecules converted from the substrate by enzyme molecules via a set of enzymatic reactions. Assume that this experiment can be performed in a single-molecule setting and repeated not only to determine the average rate of the product creation, but also to measure and quantify mesoscopic fluctuations of the currents. One can attempt to use the measured data to extract information on the reaction mechanisms, e.g. to determine the kinetic rates for elementary reactions, involved in the enzymatic reaction. A consequence of the GUC, which is relevant for this model, as well as for its generalizations to more complicated models of enzymatic reactions, is as follows.

The counting statistics of the enzymatic reaction events (that is the set of cumulants of the distribution of the number of created product molecules) does not provide full quantitative information on all kinetic rates of elementary reactions involved in the process.

The number of independent parameters that cannot be determined is, at least, equal to the number of different states of the enzyme and the enzyme–substrate complex. This restriction follows from the observation that if we multiply all outgoing rates from any node of the graph of transformations by a constant factor, the full counting statistics of transitions through any link in the network will not change. Therefore, for each network node there is a set of parameters that cannot be extracted from the counting statistics.

Here we illustrate the general principle, using the model shown in figure 3. We are interested in the counting statistics of transitions through the link \((2,1)^2\) only, thus setting all the generating factors in equation (11), except \( q_{212} \), to 1. To simplify the notation, in this paragraph we will be using \( q \) instead of \( q_{212} \). Our focus is on the analysis of...
\[ \Delta(q) = k_+(\zeta_1 - 1), \]  
where \( \zeta_1 \) satisfies the following equation, which is a version of (11):

\[ k_1[S](\zeta_2 - \zeta_1) - k_E \zeta_1 = -k_E, \quad k_{-1}(\zeta_1 - \zeta_2) + k_2(q\zeta_1 - \zeta_2) - k_C \zeta_2 = -k_C. \]  

This results in the following explicit expression for the leading exponent in the generating function:

\[ \Delta(q) = \frac{(q - 1)k_1[S]k_2k_+}{k_1[S](k_2(1 - q) - k_C) + k_E(k_2 + k_C + k_{-1})}. \]  

This expression shows the dependence on the relative probabilities \( k_C/k_2, k_{-1}/k_2 \) and \( k_E/k_1[S] \) only, and it does not depend on the rates explicitly. Obviously, a similar statement can be made regarding the LD function of the current, defined according to the Legendre transform (5). To avoid bulky expressions we are not showing LD function explicitly, but rather present the corresponding expressions for the average current and its variance (these are the two major characteristics currently available experimentally, while measuring the higher cumulants still represents a significant experimental challenge as it requires higher accuracy):

\[ \langle j \rangle = q \partial_q \Delta(q)|_{q=1} \approx \frac{k_2[S](k_+/k_-)}{[S] + K_{MM}}, \quad K_{MM} = \frac{k_2 + k_{-1}}{k_1}, \]  

\[ \frac{1}{T} \langle (j - \langle j \rangle)^2 \rangle = \langle \partial_q q \partial_q \Delta(q) - (q \partial_q \Delta(q))^2 \rangle |_{q=1} \approx \frac{2[S]^2k_2^2k_+}{k^2([S] + K_{MM})^2}. \]  

In deriving equation (14) we assumed that the enzyme and its complex degrade with the same rate \( k_E = k_C \equiv k_- \) and considered the limit of slow degradation, \( k_- \ll k_{-1}, k_2, k_1[S] \). The combination of parameters, denoted in equations (14) and (15) by \( K_{MM} \), is called the Michaelis–Menten constant. Since the average number of enzymes is given by the ratio \( k_+/k_- \), the average current \( \langle j \rangle \) in equation (13) is given by the famous Michaelis–Menten law for the average enzyme concentration. The effect of the enzyme number fluctuations on the variance of the product creation rate is, however, dramatic. It has been shown previously [31] that the noise in an MM reaction with a fixed number of enzymes is suppressed, so the so-called Fano factor \( f \equiv T\langle (j - \langle j \rangle)^2 \rangle/\langle j \rangle \) is smaller than unity, thus showing sub-Poisson statistics. In our case the Fano factor is given by

\[ f = 1 + \frac{2k_2[S]}{k_-([S] + K_{MM})}, \]  

i.e. the underlying statistics is super-Poissonian, with the Fano factor being much larger than 1, as \( k_2/k_- \ll 1 \). From the Michaelis–Menten curve for the average current, presented as a function of \( [S] \), one can measure only two independent quantities, namely \( k_2k_+/k_- \) and the MM constant \( K_{MM} \). Measurements of the Fano factor provide additional information on the ratio \( k_2/k_- \), thus allowing the value of \( k_+ \) to be extracted from a combination of the two measurements. However, the other rates, \( k_1 \) and \( k_{-1} \), cannot be determined, even if \( k_- \) is known independently from some complementary experiment. It is instructive to compare these no-go results with the calculations of the Fano factor for the class of enzymatic mechanisms with a fixed number of enzyme molecules, considered in [30], where it was shown that if the number of enzyme molecules is fixed, measurements of the Fano factor are sufficient for distinguishing among different enzymatic mechanisms, even if on
average they produce identical MM curves. Moreover, according to [30], it was possible to
determine the values of all the kinetic rates for the transitions among the metastable states
within these complex reactions. Our result shows that for a wider class of reactions, such
measurements of the reaction event statistics can be insufficient for fixing the complete
set of kinetic rates. Hence other statistical characteristics that are also sensitive to the
temporal, rather than only geometric properties of stochastic trajectories (e.g. representing
statistics of the time intervals between successive events) would be required.

5. Application of GUC to transport in mesoscopic systems with time dependent
parameters at detailed balance

Many mesoscopic systems in physics and chemistry can be modeled in terms of stochastic
transitions that satisfy the detailed balance (DB) constraints. DB guarantees that for
time independent kinetic rates the system attains the equilibrium Boltzmann–Gibbs
distribution. In a system with DB, an allowed transition from state \( i \) to state \( j \) is always
accompanied by the reversed transition. A transition between two states \( i \) and \( j \) can be
viewed in terms of a barrier, with the transition strength characterized by a symmetric
characteristic \( g_{ij} = g_{ji} \), independent of the system state \( n(t) \) (number of particles at a
given node at a given time) and that can be directly identified with parameters \( \theta_{ij} \). Nodes
are represented by the local trap potentials with energies \( E_i \) and \( E_j \), that control the
asymmetry between the forward and backward transitions. Energies may generally depend
on the state (which represents multi-particle interactions) and time. It is convenient to
adopt the Arrhenius parameterization of the DB per-particle kinetic rates transitions
\( \lambda_{ij} = \varepsilon_i g_{ij} \) and \( \lambda_{ji} = \varepsilon_j g_{ij} \) for the \((i, j)\) and \((j, i)\) transitions, respectively, with \( \varepsilon_i = e^{\beta E_i} \),
and \( \beta \) being the inverse temperature in energy units. We also assume that all nodes of
the open system are exchanging particles with the (external) reservoir. In fact, it may
be convenient to introduce individual reservoirs for the nodes of the ‘state’ graph, and
characterize them in terms of their chemical potentials, \( \mu_i \), and the barrier strengths, \( g_i \).
We assume \( g_i \) to be independent of the time and state, while the chemical potentials, \( \mu_i \),
may depend on time. Kinetic rates for transitions from node \( i \) to its reservoir and vice
versa are \( \lambda_{0i} = \varepsilon_i g_i \) and \( \Lambda_{0i} = \varepsilon_i g_i \), respectively, with \( \varepsilon_i \equiv e^{\beta \mu_i} \).

For systems with DB, described above, the symmetry property (2) is naturally built
in, provided the barrier parameters \( g_{ij} \) and \( g_i \) are kept independent of the time and
state. Stated differently, the barrier parameters are single-particle, i.e. non-interacting,
characteristics. Many-body interactions are represented by a (possibly complex and
generally arbitrary) dependence of the node activation rates \( \varepsilon = (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N) \), on
the system state \( n(t) \). Moreover, the non-equilibrium/driver nature of the system
state originates from additional explicit time dependence of the activation rates \( \varepsilon = (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N) \) and \( \varepsilon = (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N) \) for the nodes and reservoirs, respectively.
Reformulating the GUC in terms of sizes of barriers, state energies and chemical potentials
of reservoirs, we arrive at the following general (as applied to any open DB system driven
externally in a periodic or quasi-periodic fashion) no-pumping fluctuation relation (NPFR)
that states that if the barrier characteristics \( g_{ij} \) of the transitions and \( g_i \) of the reservoirs
remain time independent, while the vectors \( \varepsilon \) and \( \varepsilon \) of the activation rates are changing
arbitrarily in time (periodically or quasi-periodically) and \( \varepsilon \) generally depends on the local
node populations, then, provided the observation time is long compared to all correlation
The geometric universality of currents

**Figure 4.** Electric circuit made of three quantum dots (QD), controlled by gate voltages, $V_i$ ($i = 1, 2, 3$). Quantum dots are coupled to each other and to the leads via tunnel junctions with barriers, characterized by the parameters $g_{ij} = g_{ji}$ and $g_i$, respectively. Leads (green) are characterized by their chemical potentials, $\mu_i$. Inset: experimental realization of a double quantum dot from figure 7(a) in [37]. Electron transport between source (S) and drain (D) proceeds through tunneling via two dots with potentials, tunable via gate voltages, $G_l$ and $G_r$. The barrier strengths at the tunnel junctions between two dots and between the dots and the leads S and D are controlled by additional gate voltages $G_L$, $G_R$ and $G_C$.

In particular, NPFR guarantees that if the vector $\bar{\epsilon}$ of the reservoir activation rates has all the same entries, then all odd current cumulants remain zero, i.e. the current statistics are indistinguishable from their counterparts for the currents in thermodynamic equilibrium, even if the driving protocol explicitly breaks time-reversal symmetry. The NPFR is related to but is different from the results stated for the average currents [33]–[36] in closed networks. The latter, however, cannot be generalized to current fluctuations.

Transport in a network with DB can be implemented in an electric circuit, such as in figure 4, which includes a number of semiconductor quantum dots populated by electrons. Electrons are allowed to hop through the tunnel junctions. Electric circuits made up of several quantum dots with tunable parameters have been implemented experimentally [11]–[13]. Such systems are used to create new devices capable of few-electron information processing [11], as well as showing useful features of quantum dot ratchets [12]. Measurements of the full counting statistics of currents in driven nanoscale devices, with otherwise DB conditions on kinetic rates, represent a feasible state of the art in mesoscopic experiments in electronics [15, 16, 38] and soft matter [39]. We consider electric circuits at sufficiently high temperatures, so the number of available states inside
a quantum dot is large compared to a typical number of electrons in a dot. In this regime, quantum coherence effects and exclusion interactions due to the Pauli principle can be disregarded, so electronic transitions through tunnel junctions are thermally activated and the corresponding rates can be described using the Arrhenius parameterization. Kinetic rates are controlled by application of gate voltages to quantum dots, as shown in figure 4. Many-body electron interactions inside the same quantum dots, e.g. corresponding to the Coulomb electrostatic interaction, are allowed.

NPFR helps to determine better strategies for controlling currents using the so-called pump effect that refers to the generation of currents by external periodic changes of parameters, such as gate voltages that control the charging energies in the quantum dots [13,40]. When the gate voltages are fixed, the electric current is not generated; however, under proper conditions, periodic driving generates currents whose magnitudes can be controlled with high precision, thanks to the experimental ability to control the number of electrons pumped per cycle of the driving protocol [41]. NPFR predicts that, in the thermally dominated regime, one cannot induce a directed current among the leads or tunnel junctions connecting quantum dots, no matter how gate voltages are modulated. Moreover, currents integrated over the driving protocol period will show counting statistics that are indistinguishable from that observed in the thermodynamic equilibrium.

For a system with DB, the GUC allows us to derive the full counting statistics of currents. To express this, it is convenient to consider undirected links that can be traversed in both directions, so that the current associated with an original (undirected) link is the difference between particles moving in the main (positive) and reverse (negative) directions. These currents will be referred to as bi-directional currents. Obviously, the statistics of bi-directional currents are obtained from $\Delta(\mathbf{q})$ by setting $q_{ij} = 1/q_{ji}$ in the argument of the generating function. Then, according to GUC for dynamic pumping, the statistics for the vector of bi-directional currents, built up from the components associated with undirected edges (we will still use $\mathbf{q}$ for the argument of the generating function, so as not to complicate the notation), is characterized by

$$\Delta(\mathbf{q}) = \sum_i q_i \bar{\epsilon}_i (\zeta_j/q_{0i} - 1),$$

where $\bar{\epsilon} = (\bar{\epsilon}_i = T^{-1} \int_0^T dt \epsilon_i(t) | i \in G_0)$, and the set of $\zeta = (\zeta_i | i \in G_0)$ (defined at all graph vertices) satisfies

$$\forall k : \sum_i g_{ik}(q_{ik}\zeta_i - \zeta_k) = g_k(-q_{0k} + \zeta_k).$$

Equations (17) and (18) confirm that in spite of the many-body interaction and explicit time dependence of the parameters $\epsilon$ and $\epsilon$, the statistics of currents appears to be the same as in the auxiliary time independent and non-interacting system with $\bar{\epsilon}$ expressing the effective constant chemical potentials of the reservoirs.

6. Conclusions

We have formulated and demonstrated a principle, referred to as the geometric universality of currents. The GUC imposes restrictions on stochastic currents generated over long times in the systems of interacting particles in open networks. We have shown that
The geometric universality of currents

The geometric universality of currents. We have observed that the GUC extends only to the LD function (the leading, exponential term in the PDF) while the pre-exponential factor is not universal, but is insignificant in the limit $T \to \infty$. The GUC imposes strong restrictions on control of stochastic currents and on the amount of information that one can extract by measuring the statistics of currents. From this viewpoint, studying the conditions under which the GUC can be violated and extending the GUC to more general settings can be expected to have an increasingly important role in the future. This may take place via finding the dead ends and opening new venues for interpretations of experimental measurements in terms of the underlying stochastic mechanisms and microscopic parameters, as well as identifying efficient strategies for design and optimization of nanoscale electronic and biochemical devices.

We would like to conclude with a brief discussion of possible future generalizations of the GUC. The most general setting considered in this paper still has three basic restrictions: the observed currents are not too large, the particles occupying a node are unrestricted in number, and particles are identical, of only one kind. It has been recently shown [6,7] in the context of Jackson networks that even when the network is stable (i.e. when particles do not accumulate in the steady state), generation of atypically large currents is accompanied by accumulation of particles in the system. However, even in this regime of extreme currents, the LD form of the current distribution holds, $P(J|T) \sim \exp(-TS(J/T))$, and the LD function $S(j)$ remains well defined. The most probable way to reach these atypically large values of $j$ is associated with the accumulation of particles at some, so-called saturated, nodes. In this regime of extreme currents a finite fraction of particles will not leave the system during the observation time (in spite of the fact that the latter is much larger than the correlation time $\tau$), thus violating one of the key assumptions used to derive GUC. However, and as shown in [6], the saturated nodes start acting as additional Poisson sources (reservoirs), thus leading to survival of GUC in a partial form—with respect to variations in rates at the non-saturated nodes. Studying this effect of the partial breakdown/survival of GUC under extreme currents is an interesting task for the future.

Introducing limitations on the number of particles that can occupy the same node, as well as analyzing several kinds of particles that interact with each other differently at different nodes (the two regimes are known in the queuing literature as that of the finite waiting room, and that characterized by graph-inhomogeneous priorities, respectively), makes the analysis of currents much more complicated. Addressing these issues in the context of GUC should become yet another challenge for the future. Finally, let us mention that the GUC analysis may also be extended by evaluating LD functions of currents in various interesting non-equilibrium cases quantitatively, e.g. in the spirit of [6,42,43].

Acknowledgments

The work at LANL was carried out under the auspices of the National Nuclear Security Administration of the US Department of Energy at Los Alamos National Laboratory under Contract No. DE-AC52-06NA25396. This material is also based upon work supported in part by the NSF under CHE-0808910 at Wayne State U, and under EMT-0829945 and ECCS-0925618 at NMC.

doi:10.1088/1742-5468/2011/09/P09006
The geometric universality of currents

[34] Chernyak V Y and Sinitsyn N A, *Pumping restriction theorem for stochastic networks*, 2008 Phys. Rev. Lett. 101 160601

[35] Maes C, Netočný K and Thomas S R, 2010 J. Chem. Phys. 132 234116

[36] Horowitz J E and Jarzynski C, 2009 J. Stat. Phys. 136 917

[37] Fujisawa T, Hayashi T and Sasaki S, *Time-dependent single-electron transport through quantum dots*, 2006 Rep. Prog. Phys. 69 759

[38] Esposito M, Harbola U and Mukamel S, *Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems*, 2009 Rev. Mod. Phys. 81 1665

[39] Gomez-Solano J R, Petrosyan A, Ciliberto S, Chetrite R and Gawedzki K, *Experimental verification of a modified fluctuation-dissipation relation for a micron-sized particle in a nonequilibrium steady state*, 2009 Phys. Rev. Lett. 103 040601

[40] Ajdari A, Mukamel D, Peliti L and Prost J, *Rectified motion induced by ac fences in periodic structures*, 1994 J. Physique I 4 1551

[41] Astumian R D and Dernyi I, *Towards a chemically driven molecular electron pump*, 2001 Phys. Rev. Lett. 86 3859

[42] Turitsyn K, Chertkov M, Chernyak V Y and Puliafito A, *Statistics of entropy production in linearized stochastic systems*, 2007 Phys. Rev. Lett. 98 180603

[43] Chernyak V Y, Chertkov M, Malinin S V and Teodorescu R, *Non-equilibrium thermodynamics and topology of currents*, 2009 J. Stat. Phys. 137 109