Nonequilibrium statistical mechanics of shear flow: invariant quantities and current relations

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Abstract. In modeling nonequilibrium systems one usually starts with a definition of the microscopic dynamics, e.g., in terms of transition rates, and then derives the resulting macroscopic behavior. We address the inverse question for a class of steady state systems, namely complex fluids under continuous shear flow: how does an externally imposed shear current affect the microscopic dynamics of the fluid? The answer can be formulated in the form of invariant quantities, exact relations for the transition rates in the nonequilibrium steady state, as discussed in a recent letter (Baule and Evans, 2008 Phys. Rev. Lett. 101 240601). Here, we present a more pedagogical account of the invariant quantities and the theory underlying them, known as the nonequilibrium counterpart to detailed balance (NCDB). Furthermore, we investigate the relationship between the transition rates and the shear current in the steady state. We show that a fluctuation relation of the Gallavotti–Cohen type holds for systems satisfying NCDB.

Keywords: exact results, fluctuations (theory), stationary states, current fluctuations
1. Introduction

There is a certain class of highly nonequilibrium states of matter that possesses time-invariant statistics, and therefore might be approachable by exact statistical analysis without simplified modeling or near-equilibrium approximations. Such states arise when continuous shear flow is applied to complex fluids—materials composed of classical particles much larger than atoms. Under flow the structure of complex fluids can be radically re-ordered, even to the point of undergoing shear-induced phase transitions.

For instance, a solution of amphiphiles in the worm-like micelle phase can exhibit a negative gradient in the characteristic flow curve if driven at high shear rates. This means that for a range of shear rates the viscosity decreases under shear. If the fluid is continuously sheared in this regime, it becomes mechanically unstable and separates into ‘bands’ of high and low shear rate [1]. Also, at higher concentration the solution of amphiphiles can undergo a phase transition from a lamellar phase into complex densely packed onion-like structures [2]. Both phenomena are structural phase transitions that
are controlled by shear rate in addition to the usual parameters (temperature, pressure, concentration) and are examples in which the fluid undergoes drastic microscopic reconfiguration in response to the imposed (macroscopic) driving at the boundaries.

A fluid in a sheared steady state is described by the same Hamiltonian as at equilibrium, since no external field is applied to drive the system; only the boundary conditions are different. Nevertheless, since they contain non-zero fluxes, such states fall outside the jurisdiction of equilibrium statistical mechanics, despite exhibiting all the vast variety of reproducible behaviors, structures, and transitions seen in equilibrium thermodynamic systems.

A statistical description of complex fluids under continuous shear flow, starting from first principles, is provided by a theory of nonequilibrium transition rates, known as the nonequilibrium counterpart to detailed balance (NCDB) [3]–[5]. This theory addresses the following question: given an externally imposed macroscopic shear current at the boundaries of the fluid, what is the effect on the microscopic dynamics (the transition rates) in the bulk of the fluid? In the absence of any driving, that is, at thermal equilibrium, the microscopic transition rates are constrained to satisfy the principle of detailed balance, namely that the ratio of forward to reverse transition rates between any pair of microstates must equal the Boltzmann factor of their energy difference:

\[
\frac{\omega_{ij}}{\omega_{ji}} = e^{-\beta(E_j - E_i)},
\]

where \(\omega_{ij}\) denotes the rate of transition from microstate \(i\) to \(j\) and \(\beta\) the inverse temperature. Detailed balance is a consequence of the influence of the fluid’s thermal surroundings: it is immersed in a larger volume of fluid at a certain temperature which acts as an equilibrium heat reservoir. The stochastic influence of this heat reservoir puts constraints on the allowed microscopic transitions in the form of equation (1).

If shear is imposed at the boundaries of the heat reservoir, detailed balance no longer holds. However, a fluid region within the bulk continues to receive stochastic forces from the reservoir, which is now itself under flow. In the steady state this nonequilibrium heat reservoir imposes constraints on the transition rates according to NCDB, which can be expressed in the form of a one-to-one mapping between the transition rates at equilibrium and those in the sheared steady state.

Recently, it has been demonstrated that the constraints of NCDB can be cast into the form of invariant quantities that remain unchanged by the driving [6] and apply to any pair of microstates in the following way. (i) The product of forward and reverse transition rates remains invariant under the driving, i.e., is the same in the equilibrium and in the sheared steady state: \(\omega_{ij}\omega_{ji} = \Omega_{ij}\Omega_{ji}\) (where \(\Omega_{ij}\) denotes the transition rate in the sheared state). (ii) The difference of total exit rates remains invariant: \(\sum_k(\Omega_{ik} - \Omega_{jk}) = \sum_k(\omega_{ik} - \omega_{jk})\). These invariant quantities represent exact relations for the transition rates in the sheared steady state, arbitrarily far away from equilibrium.

In this paper we present a more pedagogical account of these recent results and the theory of NCDB underlying them. In particular, we provide a detailed derivation of the various representations of NCDB from a nonequilibrium sheared ensemble. Furthermore, we investigate the properties of the shear current in systems satisfying NCDB and show that a fluctuation relation of the Gallavotti–Cohen type holds.

The remainder of this paper is organized as follows. The nonequilibrium ensemble on which the derivation of NCDB relies is introduced in section 2. In section 3 we
present a detailed review of the different representations of NCDB as previously discussed in [3–5]. A graph representation is presented in section 4 providing an intuitive way to discuss master equation systems in discrete state spaces. The invariant quantities are derived in section 5, where we also formulate the method of systematic calculation for the transition rates in the sheared steady state. The relationship between the shear current and the transition rates is discussed in section 6. Our rather formal results are elucidated using two simple hopping models which allow for an explicit calculation of the driven transition rates and other relevant quantities of the NCDB formalism (sections 7 and 8). Even in these simple models it is evident that the predictive power of NCDB goes well beyond simple mean-field theories.

2. The nonequilibrium ensemble and path entropy

In order to describe nonequilibrium states of complex systems subject to noise, one usually relies on a probabilistic description in terms of transition rates. In such an approach the main quantity of interest is the set of probability distributions \{p_i(t)\} over states \(i = 1, \ldots, n\), which express the probability of finding the system in state \(i\) at time \(t\). The nature of these states depends on the level of description; for reasons that will become clear below, they are considered to be classical microstates in the following. The dynamical evolution of the system is then governed by the master equation, a balance equation for the probability:

\[
\frac{d}{dt} p_i(t) = \sum_{\{j\}} [\omega_{ji} p_j(t) - \omega_{ij} p_i(t)].
\]  

The sum is here taken over the set of states \(\{j\}\) connected with \(i\), where \(\omega_{ij}\) denotes the rate of transition from state \(i\) to state \(j\). The difference \(\omega_{ji} p_j(t) - \omega_{ij} p_i(t)\) is interpreted as the microscopic probability current between states \(i\) and \(j\), and therefore equation (2) states the conservation of probability. For a probabilistic interpretation of the \(p_i(t)\) we require the conditions \(0 \leq p_i(t) \leq 1\) and \(\sum_{i=1}^n p_i(t) = 1\).

A steady state is characterized by stationarity of the statistics, implying that all single-time distributions are time independent. If we set \(dp_i(t)/dt = 0\) in equation (2) we find that the condition for a steady state is given by the balance of total ingoing and outgoing flow for every state \(i\):

\[
\sum_{\{j\}} [\omega_{ji} p_j - \omega_{ij} p_i] = 0.
\]  

Nonequilibrium steady states are characterized by a non-zero net flow of particles, heat, etc, running through the system. By contrast, in equilibrium this flow vanishes, a fact which is manifest as the strong condition of detailed balance: the net probability current between any two configurations of the system is zero at equilibrium. This is expressed as

\[
\omega_{ji} p_j = \omega_{ij} p_i,
\]  

for all \(i, j\), so equation (3) is trivially satisfied.

For a canonical system the probability distribution of the system is known to satisfy Boltzmann’s law \(p_i^{eq} \propto e^{-\beta E_i}\) and the familiar form equation (1) arises. From a physical point of view, detailed balance can be interpreted as a statement of four fundamental
properties characterizing the system and heat reservoir [7]: (i) ergodicity, (ii) microscopic reversibility, (iii) time-translation invariance of statistical properties, and (iv) conservation of energy. As a result of these properties there are $m/2$ constraints acting on $m$ transition rates of the system, expressed by equation (1).

Having specified an equilibrium state in this way, we may consider a particular class of driven steady state systems, namely fluids under continuous shear. Let us consider a fluid region far from the boundaries as our ‘system’. The heat reservoir consists of the fluid volume surrounding this region. If we assume that any correlation lengths are negligibly small compared with the fluid volume (a condition that may be unenforceable for turbulent flows), then this reservoir is only characterized by its macroscopic observables, which are in this case mean energy and mean shear rate. The stochastic influence on the system is here not that of an equilibrium reservoir, but of a reservoir which is itself in a nonequilibrium condition, under shear. In this case the properties (i)–(iv) remain valid. Ergodicity is generally difficult to prove rigorously even for the simplest systems at equilibrium, but it is assumed on empirical grounds, since experimental observations are repeatable, irrespective of precise initial conditions. Since the shear acts only at the boundaries of the reservoir, the dynamics of individual molecules is still governed by the same equations of motion as in equilibrium and thus microscopic reversibility holds. Property (iii) remains true by definition, while (iv) continues to govern all interactions between the system and reservoir, or between different systems in an ensemble (figure 1). We therefore find that the four conditions for detailed balance apply to a sheared fluid, amended by an additional conserved quantity, the total shear. These amended conditions give rise to a nonequilibrium counterpart to detailed balance that can be derived from familiar statistical considerations in a straightforward way.

Before we proceed let us elucidate the types of fluid to which the above assumptions apply. In an experiment on an isolated system and reservoir, the fluid is in principle only in a quasi-steady state because energy is continually pumped into the system by

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the driving force, tending to heat the fluid. Nevertheless, the above assumptions can be experimentally realized to arbitrarily high accuracy. In many complex fluids a solvent acts as a thermostat for the system of interest, as it possesses many more degrees of freedom than the mesoscopic particles of interest, so the temperature remains relatively constant. In the limit of large ratio of solvent to complex degrees of freedom, the steady state condition becomes exactly realized. Since the relaxation time of the solvent is usually much smaller than that of the complex fluid, the solvent remains close to equilibrium even when the complex fluid is driven to a highly nonequilibrium state. In practice, experiments on complex fluids are able to obtain reproducible bulk steady state behavior, indicating that the system is insensitive to spatial or temporal temperature gradients. These form the class of systems for which NCDB is expected to hold, and that reproducible behavior is the subject of our exact theory.

With these prerequisites in place, we can begin the derivation of NCDB from a nonequilibrium ensemble. Imagine a very large volume of fluid divided into a large number $N$ of sub-volumes or ‘systems’. These sub-volumes are still large enough that correlated regions within them are negligibly small (see figure 1). The crucial idea in our derivation is to imagine this volume to be so large that it constitutes an ensemble in which the sub-volumes can be considered as representations of all possible realizations of our system under consideration. A certain constant shear rate $J$ is applied to the volume by moving top and bottom boundaries (while perpendicular dimensions are infinite or periodic). Each system $i$ then follows a particular trajectory in phase space over a time period $\tau$ accumulating a certain amount of shear. In order to ensure steady state properties we will eventually take $\tau \to \infty$, so that any initial transient behavior has decayed.

With the nonequilibrium ensemble constructed in this way, the probability distribution of trajectories can be found by Gibbs’ familiar method for deriving the probability distribution of a large collection of countable objects, which is exact when no correlations exist between those objects, as is the case here. The probability that a system follows phase space trajectory $\Gamma$ is $p(\Gamma) = n_\Gamma / N$, where $n_\Gamma$ is the number of times $\Gamma$ is realized in the ensemble. Here, we take phase space and time to be discretized to make trajectories countable. Eventually the discrete intervals will vanish in the continuum limit and probabilities $p(\Gamma)$ will be replaced by distributions $p[\Gamma] D\Gamma$.

The statistical weight of the ensemble $W_N$ is the number of distinct ways in which we can arrange the systems in the ensemble, which is given by the usual combinatorial formula

$$W_N = \frac{N!}{\sum \Gamma n_\Gamma!}, \quad (5)$$

since systems following the same trajectory are indistinguishable. The most likely distribution of trajectories (the one adopted by the overwhelming majority of such ensembles) is the one with maximal statistical weight and can be found by maximizing the corresponding ensemble entropy $S_E = \ln W_N$. Applying Stirling’s formula $\ln N! \approx N \ln N - N$ for large $N$ yields

$$S_E = -N \sum \Gamma p(\Gamma) \ln p(\Gamma). \quad (6)$$
Thus, the ensemble entropy per system is the path entropy

$$S_\Gamma = - \sum_\Gamma p(\Gamma) \ln p(\Gamma). \tag{7}$$

This path entropy is familiar from approaches to nonequilibrium statistical mechanics in the spirit of Jaynes’ method of maximum entropy inference [8,9], in which, e.g., the fluctuation theorem for entropy production has been derived [10]. However, the derivation of equation (7) above (and in [5]) is distinctive in that it makes explicit use of the ensemble’s geometry for the special case of shear flow (figure 1) to demonstrate that the only nonequilibrium conditioning on the ensemble is specified by the ensemble average of the shear flux. Hence, uniquely in our derivation, the nonequilibrium constraint is not chosen arbitrarily. As a counter-example, for instance, in the context of living systems, the choice of constraining only a set of macroscopic observables [11] is not at all justified.

The distribution $p(\Gamma)$ is found by maximizing $S_\Gamma$ subject to the constraint

$$\sum_\Gamma p(\Gamma) \gamma(\Gamma) = J\tau \tag{8}$$

due to conservation of shear. Here, $\gamma(\Gamma)$ is the total shear acquired by an individual system following path $\Gamma$. With $J = 0$, the maximization just returns $p^{eq}(\Gamma)$, the equilibrium distribution of trajectories defined as the prior for the calculation. In the driven steady state we obtain instead the result

$$p^{dr}(\Gamma) \propto p^{eq}(\Gamma) e^{\nu\gamma(\Gamma)}, \tag{9}$$

where $\nu$ is the Lagrange multiplier associated with the shear constraint, equation (8). This form of the nonequilibrium distribution is a direct consequence of the way in which the system is driven, namely by fluid at the boundaries such that the equations of motion of the driven system are the same as in equilibrium. In fact, the measure defined on trajectory space for the driven ensemble is the same as in equilibrium; the trajectories are only reweighted under the additional shear constraint giving rise to the factor $e^{\nu\gamma(\Gamma)}$.

Now that we are in possession of the statistical weight of nonequilibrium trajectories, we can consider the implications of equation (9) for the individual transition rates, which give rise to all the complexity of the system’s evolution. It is with this change of perspective that a useful and testable result can be obtained.

### 3. Rules for transition rates

From now on we denote a rate of transition between states $i$ and $j$ in the driven steady state as $\Omega_{ij}$ in order to distinguish it from the corresponding equilibrium transition rate $\omega_{ij}$ that satisfies equilibrium detailed balance. The transition rate is defined as the probability of making the transition $i \rightarrow j$ per unit time $\Delta t$, where it is understood that $\Delta t$ is so small that only one transition can occur. This means that transitions from $i$ to $j$ via a third state are neglected. In probability theory the definition of the transition probability $P(j|i)$ is usually in terms of a joint probability $P(j,i)$, i.e. $P(j|i) = P(j,i)/P(i)$. If the distribution of trajectories $p(\Gamma)$ is known, these probabilities of individual microstates are determined by counting those trajectories containing state $i$ at time $t$ and state $j$ at time $t + \Delta t$. A transition rate is then defined as $\Omega_{ij} = P(j|i)/\Delta t$ in the limit of vanishing $\Delta t$. 

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where

$$P(j|i) = \frac{\sum_{\Gamma|i,j) \in \Gamma} p(\Gamma)}{\sum_{\Gamma|i} p(\Gamma)}.$$  \hfill (10)

The sum $\sum_{\Gamma|i,j}$ denotes a summation over all trajectories $\Gamma$ containing the transition $i \to j$. Using equation (9) a transition rate in the driven steady state can be written as

$$\Omega_{ij} = \frac{P(j|i)}{\Delta t} = \frac{\sum_{\Gamma|i,j) \in \Gamma} p^{eq}(\Gamma) e^{\nu \gamma(\Gamma)}}{\sum_{\Gamma|i} p^{eq}(\Gamma) e^{\nu \gamma(\Gamma)}}.$$  \hfill (11)

Inserting unity as the delta function $\int \delta(\gamma - \gamma(\Gamma)) \, d\gamma$ in equation (11) and factoring out the equilibrium transition rate $\omega_{ij}$, one obtains then for the driven transition rate (see appendix A)

$$\Omega_{ij} = \omega_{ij} \lim_{\tau \to \infty} \frac{\int_{-\infty}^{\infty} p^{eq}_{\tau}(\gamma|i,j) \, e^{\nu \gamma} \, d\gamma}{\int_{-\infty}^{\infty} p^{eq}_{\tau}(\gamma|i) \, e^{\nu \gamma} \, d\gamma}.$$  \hfill (12)

Here, the distribution $p^{eq}_{\tau}(\gamma|i,j)$ contains the probability that the system at equilibrium accumulates a total amount of shear $\gamma$ over a time period $\tau$ due to equilibrium fluctuations, given that it made a transition from $i$ to $j$. Similarly, the denominator in equation (11) leads to an expression containing $p^{eq}_{\tau}(\gamma|i)$. The subscript $\tau$ denotes the implicit dependence of these distributions on the duration of the trajectory $\Gamma$.

We refer to this result as the canonical-flux representation of NCDB for a transition rate $i \to j$ in the driven ensemble [4]. Note that the driven rate is a function of the Lagrange multiplier $\nu$, the flux conjugate parameter. This parameter is the analog of the inverse temperature $\beta$ which characterizes the heat transfer in canonical equilibrium systems. One notices that the driven transition rate is proportional to the equilibrium rate, enhanced or attenuated by a factor which is determined by the equilibrium statistics. If an equilibrium transition from $i$ to $j$ is likely to lead on to a certain amount of shear in the future, then this transition is enhanced in the driven steady state. As in the equilibrium case, $m/2$ constraints act on $m$ driven transition rates; therefore equation (12) can be considered as a nonequilibrium counterpart to detailed balance. The important conclusion is that for the class of driven steady states obeying the principles (i)–(iv) we obtain the microscopic dynamics of the nonequilibrium steady state from the corresponding equilibrium ensemble.

The result equation (12) is different from other nonequilibrium generalizations of detailed balance in that it is based on a fundamental description of the physical system in the form of the shear ensemble. Other generalizations are often postulated without derivation (e.g., the local detailed balance conditions in [12]) or derived for a particular model system only [13]. Local detailed balance may be applicable to a wider variety of different systems than the present theory, but all of them near equilibrium. Our approach should also not be confused with Kramers’ theory of reaction rates, which applies to rates of transition between coarse-grained metastable states for a given microscopic dynamics [14]. We address the question of how to obtain this microscopic dynamics for a given imposed constraint in the case of shear flows. Subsequently, the coarse-grained dynamics resulting from NCDB could be determined using Kramers’ theory.
Depending on the physical system, many sets of equilibrium (prior) rates $\omega_{ij}$ are possible, from exact and deterministic ones obtained from a Hamiltonian formulation to stochastic ones. Transitions which have zero probability in equilibrium (i.e., unphysical ones) are forbidden in the driven system as well.

In the above derivation of NCDB the nonequilibrium ensemble was constrained by a fixed shear $J\tau$ (equation (8)). By the analogy to equilibrium ensembles we can therefore consider equation (12) as a canonical representation of the driven ensemble: shear is a quantity which can be exchanged between the system and the nonequilibrium reservoir with a fixed average. Indeed both the numerator and the denominator in the enhancement factor take the form of an average over all possible shears $\gamma$, where the conditional probabilities, $p_{eq}^\tau(\gamma|i,j)$ and $p_{eq}^\tau(\gamma|i)$, respectively, are weighted with $e^{\nu\gamma}$.

A microcanonical-flux ensemble allows only for a fixed total shear $\gamma_0$. One can intuitively argue that in this ensemble the flux distribution has to be substituted by a Dirac delta function: $e^{\nu\gamma} \rightarrow \delta(\gamma - \gamma_0)$ (for an alternative derivation see [4]). With this substitution, equation (12) reads

$$\Omega_{ij} = \omega_{ij} \lim_{\tau \to \infty} \frac{p_{eq}^\tau(\gamma_0|i,j)}{p_{eq}^\tau(\gamma_0|i)}.$$  (13)

This representation proves favorable when the conditional probability distributions of $\gamma_0$ are explicitly known. Similarly to the ensembles in equilibrium statistical mechanics, microcanonical- and canonical-flux ensembles yield the same result in the thermodynamic limit, which is here the limit of large $N$ and $\tau$.

From equation (12) it is also possible [4] to derive a representation of the driven transition rates that is independent of the arbitrarily long duration $\tau$ of the steady state trajectories. For completeness we reproduce the derivation in appendix B. The result is

$$\Omega_{ij}(\nu) = \omega_{ij} e^{\nu \Delta x_{ji}} e^{\Delta_q_{ji}(\nu)+Q(\nu)\Delta t}.$$  (14)

If we compare equation (24) with equation (12) we realize that the ratio of equilibrium Green’s functions is here translated into three distinct factors. The factor $e^{\nu \Delta x_{ji}}$ measures the direct flux contribution of a transition and is large if either the flux carried by the transition $i \to j$ is large ($\Delta x_{ji} \gg 1$) or the system is strongly driven ($\nu \gg 1$). By itself this factor would simply boost every transition in the flux direction irrespective of the state space structure. The important extension to such mean-field ideas is expressed in the factor $e^{\Delta q_{ji}(\nu)}$, where $\Delta q_{ji}$ is defined as

$$\Delta q_{ji}(\nu) \equiv \lim_{\tau \to \infty} \left[ \ln \int_{-\infty}^{\infty} \frac{p_{eq}^\tau(\gamma|i,j) e^{\nu\gamma} d\gamma}{\int_{-\infty}^{\infty} p_{eq}^\tau(\gamma|i) e^{\nu\gamma} d\gamma} \right].$$  (15)

This quantity measures the increase (or decrease) in probability that the system will go on to exhibit the imposed shear $\gamma$ if it performs the transition $i \to j$. Thus the rate of a transition depends not only on the immediate flux contribution, but also on the prospect for future flux. The function $Q(\nu)$ in equation (14) is defined as

$$Q(\nu) \equiv \lim_{\tau \to \infty} \frac{\partial}{\partial \tau} \ln \int_{-\infty}^{\infty} p_{eq}^\tau(\gamma|i) e^{\nu\gamma} d\gamma,$$  (16)

which is a function independent of the initial state $i$. One can show that, in terms of the intensive shear current $J = \gamma/\tau$ (i.e. the shear rate), $Q(\nu)$ is the Legendre transform of the

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rate function of $J$ or scaled cumulant generating function in the sense of large deviation theory [15] (see appendix C). This implies that $\nu$ and $J$ are conjugate quantities and $Q(\nu)$ and $J$ are related via
\[ \frac{d}{d\nu} Q(\nu) = J. \] (17)
In the following we refer to the function $Q(\nu)$ as the ‘flux potential’ due to the analogy with the usual thermodynamic potentials.

In order to fully determine the transition rates of a system in the driven steady state according to equation (14) one therefore has to know the set of equilibrium transition rates and their individual shear contribution $\Delta x_{ji}$ as well as the flux potential $Q$ and the functions $\Delta q_{ji}$. At equilibrium the $\omega_{ij}$ are usually strongly constrained by detailed balance and symmetry considerations. The $\Delta x_{ji}$ are local and constant properties of the states. The crucial and non-trivial task is to find the potential $Q$ and the set of $\Delta q_{ji}$, which depend on the global structure of the state space.

4. The graph representation for NCDB

Master equation systems can be discussed intuitively with the help of a graph representation, in which vertices are assigned to the different states $i$ of the system and edges to the possible transitions [16]. If a transition is physically allowed to take place, i.e., $\omega_{ij} > 0$, then equilibrium detailed balance demands that the reverse transition $\omega_{ji}$ is also non-zero. Only connected graphs are considered in order to satisfy the requirement of ergodicity. For the following discussion of driven steady states further assumptions are necessary. In order to guarantee that the system can exhibit a constant macroscopic steady state shear current $J$, it is assumed that the state space has a periodic structure along a direction $x$, which is associated with the amount of shear accumulated. This assumption is made without loss of generality since one period may be arbitrarily large.

A transition $i \rightarrow j$ contributes the shear increment $\Delta x_{ji} \equiv x_j - x_i$. The periodic structure implies that, for a given period $n$, the $j + n$th vertex is of the same type as the $j$th with the $x$-position shifted by a fixed amount. Likewise, if vertices $i$ and $j$ with $1 \leq i, j \leq n$ are connected by an edge, so are vertices $n + i$ and $n + j$.

We define the basic graph as the graph corresponding to the non-periodic connected set of $n$ vertices. Its set of edges will be called interior edges in order to distinguish them from exterior edges connecting vertices of the basic graph with vertices of the next or preceding period. More precisely, an edge is exterior if it connects a vertex $i$ of the basic graph with a vertex $l$ where $l \geq n + 1$ or $l \leq 0$. Obviously, exterior edges always occur in pairs connecting the same states in different periods. Using this convention one has to bear in mind that two states of the same type can be connected by more than one edge, namely by one interior edge and multiple exterior edges (connecting, e.g., to the previous or next period, or both). See figure 2 for a depiction of such a basic graph. The total number of transition rates in the system is $\sum_{i=1}^{n} d_i$, where $d_i$ is the degree (or connectivity) of the $i$th vertex of the simple graph including exterior edges. The minimal number of transition rates in an $n$-state driven system is $2n$ which corresponds to a graph in the form of a simple connected path. For this class of state spaces the problem of finding the driven transition rates has a particularly straightforward solution (see section 5.2 below).
Figure 2. Example diagram of a basic graph for a five-state system. The dotted line denotes an exterior edge connecting the same kinds of states in different periods. Here states 0 and 5 as well as states 1 and 6 are of the same type.

Figure 3. Example diagram of a three-state system mapping onto a periodic graph structure.

This notion of a periodic graph structure is basically a convenient way to visualize the current in the state space. Systems with a limited number of states would usually be depicted as a basic graph alone, without any exterior edges. Yet, if the system exhibits a nonequilibrium steady state with some kind of current, the periodicity automatically arises as a consequence of the flux carrying transitions. Consider for example the three-state system in figure 3. The only way the system can be in a driven steady state is by featuring a rotational current which is measured by the windings performed in time $\tau$. This then naturally maps onto a periodic network with a simple connected path as the basic graph. The loop $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ in the original depiction then becomes an external loop $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$, where state 4 is of the same type as 1 yet distinct due to the accumulated integrated current of one period.

At this point it is appropriate to briefly discuss the distinction between external and internal loops, which is connected to Kolmogorov’s criterion, an equivalent statement of equilibrium detailed balance [17,18]. In order to elucidate this we focus on transition rates in continuous time with $\Delta t \rightarrow 0$ such that equation (14) assumes the simpler form of equation (24).

If we consider a closed internal loop in the basic graph, i.e., a closed path leading back to the identical state such as the loop $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$ in figure 2, we see that the product of transition rates following this loop in a given direction of rotation is the same as in equilibrium:

$$\Omega_{23} \Omega_{34} \Omega_{42} = \omega_{23} \omega_{34} \omega_{42}. \quad (18)$$
This is a simple consequence of the fact that both $\Delta x_{ji}$ and $\Delta q_{ji}$ are given as differences of state properties, implying that along a closed internal loop the product of exponential factors vanishes. Therefore, for any internal closed loop in the basic graph we have

$$\Omega_{12} \cdots \Omega_{n-1,n} \Omega_{n1} = \omega_{12} \cdots \omega_{n-1,n} \omega_{n1}. \tag{19}$$

Since the equilibrium rates satisfy detailed balance, the ratio of forward and backward transitions is given as $\omega_{12}/\omega_{21} = e^{-\beta(E_2-E_1)}$. It is then easy to see that the following equality holds:

$$\frac{\omega_{12} \cdots \omega_{n-1,n} \omega_{n1}}{\omega_{21} \cdots \omega_{n,n-1} \omega_{1n}} = 1. \tag{20}$$

Due to equation (19) the same relation is true for the product of driven transition rates

$$\Omega_{12} \cdots \Omega_{n-1,n} \Omega_{n1} = \Omega_{21} \cdots \Omega_{n,n-1} \Omega_{1n}. \tag{21}$$

Kolmogorov’s criterion now states that equilibrium detailed balance holds if and only if equation (21) is satisfied for every closed path in state space. NCDB according to equation (24) satisfies this criterion for every internal loop. However, this does not lead to a contradiction, since Kolmogorov’s criterion is violated for external loops in state space. For an external loop we have instead of equation (21)

$$\frac{\Omega_{12} \cdots \Omega_{n-1,n} \Omega_{n1'}}{\Omega_{21} \cdots \Omega_{n,n-1} \Omega_{1'n}} = e^{2\nu\Delta x_{1'}} \tag{22},$$

where $1'$ denotes the state of type 1 in the next period and $\Delta x_{1'}$ is the accumulated shear or ‘length’ of a period. The conclusion of this discussion is that the graph representation for NCDB in terms of a periodic graph structure is consistent if the system does exhibit a steady state current. In this case NCDB leads to a violation of Kolmogorov’s criterion as expected.

At equilibrium the validity of detailed balance, or Kolmogorov’s criterion, implies that for every two states $k$ and $l$ the ratio

$$S_{kl} \equiv \frac{\omega_{k1} \omega_{12} \cdots \omega_{n-1,n} \omega_{nl}}{\omega_{1k} \omega_{21} \cdots \omega_{n,n-1} \omega_{ln}} \tag{23}$$

is independent of the path between $k$ and $l$. Out of equilibrium this path independence is not generally expected. Instead one can consider $\ln S_{kl}$ as an ‘action functional’ associated with a particular path and derive a fluctuation relation for the entropy production [20].

5. The total exit rate relation

In the remainder of this paper we focus on NCDB in the context of continuous time Markov chains, where the time step $\Delta t \to 0$. The $\tau$ independent representation of NCDB then assumes the form

$$\Omega_{ij}(\nu) = \omega_{ij} e^{\nu \Delta x_{ji} + \Delta q_{ji}^i(\nu)}. \tag{24}$$

In this case it is possible to derive a fundamental relationship between the flux potential $Q(\nu)$ and the driven transition rates which is a central result of this paper and leads to a variety of important conclusions for NCDB.
Consider an individual state $i$ connected to $d_i$ other states. The system in state $i$ spends a random time before making a transition to one of the connected states. For a continuous time Markov chain this waiting time has the exponential distribution [18]

$$h_i(t) = \sigma_i e^{-\sigma_i t},$$ \hspace{1cm} (25)

where the total exit rate is defined as $\sigma_i \equiv \sum_{\langle j \rangle} \omega_{ij}$. The probability that the particle jumps to site $j$ is then $P_{ij} = \omega_{ij}/\sigma_i$. Our quantities of interest are the conditional probabilities or Green’s functions $p_{\nu}^{eq}(\gamma|i)$ which, if known, would fully specify the driven transition rates via equations (15) and (24). The Green’s function for state $i$ can be determined by the following considerations. From state $i$ the system can only perform a transition to a connected state $j$ within the network, from where its further displacement is determined by the Green’s function of that state $j$. Taking into account the waiting time in state $i$ and the probability $P_{ij}$ of performing the jump to state $j$, $p_{\nu}^{eq}(\gamma|i)$ is therefore related to the $d_i$ Green’s functions of the neighboring sites according to

$$p_{\nu}^{eq}(\gamma|i) = \int_0^\tau dt h_i(\tau - t) \sum_{\langle j \rangle} P_{ij} p_{\nu}^{eq}(\gamma - \Delta x_{ji}|j) + \psi_i(\tau)\delta(\gamma),$$ \hspace{1cm} (26)

where $\psi_i(\tau)\, d\tau$ denotes the probability that no jump has occurred out of state $i$ up to time $\tau$: $\psi_i(\tau) = 1 - \int_0^\tau h_i(t)\, dt = e^{-\sigma_i \tau}$. In the next step we introduce the quantities $m_i(\nu, \tau)$ defined as

$$m_i(\nu, \tau) \equiv \ln \int_{-\infty}^{\infty} p_{\nu}^{eq}(\gamma|i) e^{\nu \gamma} \, d\gamma,$$ \hspace{1cm} (27)

which are ultimately related to the functions $g_i(\nu)$ in the long time limit via (see below). Multiplying equation (26) by $e^{\nu \gamma}$ and summing over all possible shear $\gamma$ from state $i$ yields, after a shift in the summation variable $\gamma$,

$$e^{m_i(\nu, \tau)} = \int_0^\tau dt h_i(\tau - t) \sum_{\langle j \rangle} P_{ij} e^{m_j(\nu, \tau) + \nu \Delta x_{ji}} + e^{-\sigma_i \tau},$$ \hspace{1cm} (28)

In the next step we can substitute $P_{ij}$, and $h_i(t)$ (equation (25)). Rearranging terms then yields

$$e^{m_i(\nu, \tau) + \sigma_i \tau} = \int_0^\tau dt e^{\sigma_i t} \sum_{\langle j \rangle} \omega_{ij} e^{m_j(\nu, \tau) + \nu \Delta x_{ji}} + 1.$$ \hspace{1cm} (29)

The integral can be removed by taking a derivative with respect to $\tau$ on both sides. This leads to

$$\left( \frac{\partial}{\partial \tau} m_i(\nu, \tau) + \sigma_i \right) e^{m_i(\nu, \tau) + \sigma_i \tau} = \sigma_i \sum_{\langle j \rangle} \omega_{ij} e^{m_j(\nu, \tau) + \nu \Delta x_{ji}}.$$ \hspace{1cm} (30)

Or, after further rearrangement,

$$\frac{\partial}{\partial \tau} m_i(\nu, \tau) + \sigma_i = \sum_{\langle j \rangle} \omega_{ij} e^{m_j(\nu, \tau) - m_i(\nu, \tau) + \nu \Delta x_{ji}}.$$ \hspace{1cm} (31)

\footnote{The contribution of $\psi_i(\tau)\delta(\gamma)$ to the Green’s function $p_{\nu}^{eq}(\gamma|i)$ was erroneously neglected in the derivation presented in [6]. Nevertheless, the final result, equation (35), remains unchanged.}

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In the long time limit we have
\[
\lim_{\tau \to \infty} [m_j(\nu, \tau) - m_i(\nu, \tau)] = \Delta q_{ji}(\nu),
\]
(32)
due to equation (15) and
\[
\lim_{\tau \to \infty} \frac{\partial}{\partial \tau} m_i(\nu, \tau) = Q(\nu),
\]
(33)
due to equation (16), using the definition of the functions \( m_i(\nu, \tau) \), equation (27). The result of taking the \( \tau \to \infty \) limit in equation (31) is thus
\[
Q(\nu) + \sigma_i = \sum_j \omega_{ij} e^{\Delta q_{ji}(\nu) + \nu \Delta x_{ji}}.
\]
(34)
We can identify on the right-hand side the transition rates in the driven steady state according to equation (24). We therefore obtain a fundamental relationship between the equilibrium transition rates, the corresponding rates in the driven steady state, and the flux potential \( Q(\nu) \):
\[
Q(\nu) = \Sigma_i(\nu) - \sigma_i,
\]
(35)
where \( \Sigma_i(\nu) \equiv \sum_{\langle j \rangle} \Omega_{ij}(\nu) \). Equation (35) states that, for every state \( i \), the total exit rate in the driven steady state differs from its equilibrium counterpart only by a flux dependent (but state independent) constant. On the basis of this central result a number of important implications of NCDB can be derived. It turns out that it is not necessary to know the Green’s functions of the equilibrium system in order to determine the \( \Delta q's \) and the driven transition rates. Rather, as we will see more explicitly below, the quantities of the NCDB formalism are intrinsically related to the graph structure via equation (35).

5.1. Invariant quantities

It is now straightforward to formulate two sets of **invariant quantities** for the sheared steady state. The first was found in [4] and is a consequence of the asymmetric property of \( \Delta q_{ji} \) and \( \Delta x_{ji} \). From equation (24), the ‘product constraint’ follows directly,
\[
\Omega_{ij} \Omega_{ji} = \omega_{ij} \omega_{ji}.
\]
(36)
Secondly, equation (35) directly implies the ‘total exit rate constraint’,
\[
\Sigma_i - \Sigma_j = \sigma_i - \sigma_j.
\]
(37)
We therefore find that in the driven steady state both the product of forward and reverse transition rates and the difference of total exit rates for every pair of microstates are the same as in equilibrium and therefore invariant with respect to the driving. No near-equilibrium assumptions have been made in the derivation, so the above relations are both exact and valid arbitrarily far from equilibrium.

With the formalism devised here, the task of finding the microscopic nonequilibrium dynamics given an imposed macroscopic current is greatly simplified and follows straightforward rules. The above relations are furthermore accessible to verification in an experiment or simulation [19].

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5.2. Network rules

With these results we are able to devise a systematic method for determining the driven transition rates for arbitrary graph configurations. Considering the whole basic graph with \( n \) states, there are \( n \) equations in the form of equation (35). This set of equations is sufficient for determining all the unknown quantities, i.e., the flux potential \( Q \) and the \( \Delta q_s \), as we now show. Due to the relationship \( \Delta q_{ij} = -\Delta q_{ji} \), every edge of the basic graph is associated with two transition rates (forward and backward transitions) depending on one \( \Delta q \). The number of independent \( \Delta q_s \) is further constrained by closed paths (loops) in the graph, i.e., paths that begin and end at the same type of vertex, because the sum of \( \Delta q_s \) along such a path is obviously zero (the loop constraint). One can then easily see that the total number of independent \( \Delta q_s \) in the basic graph is always \( n - 1 \), as follows.

Consider first the simplest basic graph configuration, namely all \( n \) states connected as a simple path without any loops. In this case the number of edges is trivially \( n \). Since one loop constraint is generated by the periodicity, there are \( n - 1 \) independent \( \Delta q_s \). From this simple connected graph all graphs of higher degrees can be generated by adding new edges. But adding an edge generates a new \( \Delta q \) and at the same time a new loop constraint, so the number of independent \( \Delta q_s \) always remains \( n - 1 \).

We formulate the following network rules for the calculation of the driven transition rates in networks of arbitrary connectivity:

- **The edge rule.** Every interior edge and every pair of exterior edges in the basic graph corresponds to two rates containing the dependence on one \( \Delta q \). The driven transition rates are given by equation (24).
- **The vertex rule.** For every vertex in the basic graph the difference between the driven and equilibrium total exit rates equals the flux potential \( Q \) (equation (35)).
- **The loop rule.** For every closed path of edges the sum of the \( \Delta q_s \) along this path is zero.

In this formulation there are in total \( n \) equations and \( n \) unknowns, namely one \( Q \) and \( n - 1 \) \( \Delta q_s \). The number of independent equations can always be further reduced by eliminating \( Q \), such that one is essentially left with \( n - 1 \) equations for \( n - 1 \) unknown \( \Delta q_s \). The solution of this system of equations fully specifies all the driven rates in the system as well as the flux \( J \) which is related to the flux potential via \( dQ(\nu)/d\nu = J \), equation (17). In the given framework the driven transition rates and the flux are determined as functions of the flux conjugated parameter \( \nu \).

An alternative, \( \nu \) independent representation is based on equations (36) and (37). However, the number of constraints is here not sufficient for determining all the driven rates for general network structures. On the one hand there are \( \sum_{i=1}^{n} d_i/2 \) product constraints and \( n - 1 \) exit rate constraints. On the other hand, for an arbitrary graph configuration, there are \( \sum_{i=1}^{n} d_i \) transition rates. Therefore only for graphs with the topology of a simple connected path (where \( d_i = 2 \)) can we determine the rates completely from the invariant quantities without using the network rules. In this case we have \( 2n \) transition rates and \( 2n - 1 \) constraints stemming from the exact relations. The transition rates are fully determined if additionally the relationship between the transition rates and the current is provided. In this formulation the driven rates depend on \( J \) directly instead of being parametrized in terms of the parameter \( \nu \). The relationship between current and rates is further elucidated in the next section.
6. Current relations

In master equation systems the stationary current $J$ is generally defined as the average of the flux contributions of every state $i$ over the steady state distributions $p_i$:

$$ J = \sum_i p_i \sum_{\{j\}} \Delta x_{ji} \Omega_{ij}. \quad (38) $$

At equilibrium $J$ is identically zero due to detailed balance, equation (4), and the property $\Delta x_{ji} = -\Delta x_{ij}$. In general, at steady state, the distribution $p_i$ is the solution of the master equation (2) under the condition of stationarity $d p_i(t)/dt = 0$ and normalization $\sum_i p_i = 1$. The solution can be formally obtained by matrix inversion as follows [17]. In matrix notation equation (2) is given as (writing the transition rates now capitalized)

$$
\begin{pmatrix}
-\Sigma_1 & \bar{\Omega}_{21} & \bar{\Omega}_{31} & \ldots & \bar{\Omega}_{n1} \\
\bar{\Omega}_{12} & -\Sigma_2 & \bar{\Omega}_{32} & \ldots & \bar{\Omega}_{n2} \\
\bar{\Omega}_{13} & \bar{\Omega}_{23} & -\Sigma_3 & \ldots & \bar{\Omega}_{n3} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\bar{\Omega}_{1n} & \bar{\Omega}_{2n} & \bar{\Omega}_{3n} & \ldots & -\Sigma_n
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2 \\
p_3 \\
\vdots \\
p_n
\end{pmatrix} = 0,
$$

i.e., as $\sum_j M_{ij} p_j = 0$, where $M$ is a $n \times n$ matrix with entries

$$ M_{ij} = \bar{\Omega}_{ij} - \delta_{ij} \Sigma_i. \quad (40) $$

It has been noted earlier that, due to the periodic graph structure, in addition to the internal edge, there can be multiple exterior edges connecting the same kinds of states in different periods. These additional rates are contained in $\bar{\Omega}_{ij}$ which denotes the sum of all transition rates from a state of type $i$ into a state of type $j$. In the master equation this is considered in the summation $\{j\}$ over the set of adjacent sites which includes the exterior edges. Denoting the transition rate matrix including the normalization (e.g., in the first row) by $\tilde{M}$, that is

$$
\tilde{M} =
\begin{pmatrix}
1 & 1 & 1 & \ldots & 1 \\
\bar{\Omega}_{12} & -\Sigma_2 & \bar{\Omega}_{32} & \ldots & \bar{\Omega}_{n2} \\
\bar{\Omega}_{13} & \bar{\Omega}_{23} & -\Sigma_3 & \ldots & \bar{\Omega}_{n3} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\bar{\Omega}_{1n} & \bar{\Omega}_{2n} & \bar{\Omega}_{3n} & \ldots & -\Sigma_n
\end{pmatrix},
$$

the master equation including normalization reads

$$
\begin{pmatrix}
1 & 1 & 1 & \ldots & 1 \\
\bar{\Omega}_{12} & -\Sigma_2 & \bar{\Omega}_{32} & \ldots & \bar{\Omega}_{n2} \\
\bar{\Omega}_{13} & \bar{\Omega}_{23} & -\Sigma_3 & \ldots & \bar{\Omega}_{n3} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\bar{\Omega}_{1n} & \bar{\Omega}_{2n} & \bar{\Omega}_{3n} & \ldots & -\Sigma_n
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2 \\
p_3 \\
\vdots \\
p_n
\end{pmatrix} =
\begin{pmatrix}
1 \\
0 \\
0 \\
\vdots \\
0
\end{pmatrix}.
$$

We therefore find the occupancies $p_i$ by matrix inversion as $\tilde{M}^{-1} e_1$, i.e. in the first column of the inverse matrix $\tilde{M}^{-1}$. 

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A new relationship between the current \( J \) and the transition rates is obtained when we take the derivative (denoted by a prime) of equation (35) with respect to \( \nu \):

\[
Q' = \sum_{\{j\}} (\Delta q'_{ji} + \Delta x_{ji}) \Omega_{ij},
\]

for every state \( i \). Here and in the following the \( \nu \) dependence is dropped. Using \( \Delta q'_{ji} = q'_j - q'_i \) we can rewrite these equations as

\[
Q' + q'_i \Sigma_i - \sum_{\{j\}} q'_j \Omega_{ij} = \sum_{\{j\}} \Delta x_{ji} \Omega_{ij}.
\]

(43)

Since all relevant physical information is contained in the differences rather than the individual \( q_i \)s, we have the freedom to fix one boundary value. If we choose \( q'_1 = \text{const.} \), obviously \( q'_i = -\Delta q'_1 \). Defining the two column vectors

\[
\mathbf{q}' \equiv (Q', \Delta q'_{12}, \ldots, \Delta q'_{1n})^T \quad \text{and} \quad \mathbf{a} = (a_1, \ldots, a_n)^T \quad \text{with} \quad a_i \equiv \sum_{\{j\}} \Delta x_{ji} \Omega_{ij},
\]

we can cast the system of equations (44) into the following matrix form:

\[
\begin{pmatrix}
1 & \bar{\Omega}_{12} & \cdots & \bar{\Omega}_{1n} \\
1 & -\Sigma_2 & \cdots & \bar{\Omega}_{2n} \\
1 & \bar{\Omega}_{32} & -\Sigma_3 & \cdots & \bar{\Omega}_{3n} \\
\vdots & \vdots & \ddots & \vdots \\
1 & \bar{\Omega}_{n2} & \cdots & -\Sigma_n & \cdots & \bar{\Omega}_{nn}
\end{pmatrix}
\begin{pmatrix}
Q' \\
\Delta q'_{12} \\
\Delta q'_{13} \\
\vdots \\
\Delta q'_{1n}
\end{pmatrix}
= 
\begin{pmatrix}
a_1 \\
a_2 \\
a_3 \\
\vdots \\
a_n
\end{pmatrix}.
\]

(45)

We realize that the left-hand side reveals the transpose matrix of \( \bar{M} \). Equation (45) is therefore equally expressed as

\[
\bar{M}^T \mathbf{q}' = \mathbf{a}.
\]

(46)

With this result we can rederive the fundamental relationship equation (17) between the flux potential \( Q \) and the flux \( J \). Equation (46) is formally solved via matrix inversion:

\[
\mathbf{q}' = \left( \bar{M}^T \right)^{-1} \mathbf{a}.
\]

(47)

For any matrix the transpose of the inverse matrix is the inverse of the transpose matrix:

\( (\bar{M}^T)^{-1} = (\bar{M}^{-1})^T \). Since \( \bar{M}^{-1} \mathbf{e}_1 \) is the formal solution of the master equation, we can deduce that the first row of \( (\bar{M}^T)^{-1} \) contains the steady state occupancies \( p_i \). Solving equation (47) for \( Q' \) with the given expressions \( a_i \) therefore leads to

\[
Q' = \sum_i p_i \sum_{\{j\}} \Delta x_{ji} \Omega_{ij},
\]

(48)

so, by comparison with equation (38), we can conclude that \( Q' = J \), i.e., equation (17) holds. We have therefore shown that

\[
J = \sum_{\{j\}} (\Delta q'_{ji} + \Delta x_{ji}) \Omega_{ij},
\]

(49)

for every state \( i \), which is a new representation of the steady state current \( J \) in terms of \( \Delta q'_{ji} \) instead of the microstate distributions \( p_i \),

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At this point it is instructive to associate a physical interpretation with the \( \nu \) derivative of the \( \Delta q_{ji} \). Taking the derivative of equation (15) with respect to \( \nu \) leads to the following expression:

\[
\Delta q'_{ji} = \lim_{\tau \to \infty} \left[ \frac{\int_{-\infty}^{\infty} \gamma p_{\tau}^q(\gamma|j) e^{\nu \gamma} \, d\gamma}{\int_{-\infty}^{\infty} p_{\tau}^q(\gamma|j) e^{\nu \gamma} \, d\gamma} - \frac{\int_{-\infty}^{\infty} \gamma p_{\tau}^q(\gamma|i) e^{\nu \gamma} \, d\gamma}{\int_{-\infty}^{\infty} p_{\tau}^q(\gamma|i) e^{\nu \gamma} \, d\gamma} \right].
\]  

(50)

In the discussion of the path entropy maximization in section 3 we obtained the fundamental result (equation (9)) that in the driven ensemble the trajectories are reweighted with the exponential factor \( e^{\nu \gamma} \). This implies that in the present context \( p_{\tau}^q(\gamma|j) e^{\nu \gamma} \) can be related to the unnormalized conditional probability that the system exhibits shear \( \gamma \) from state \( i \) under the driven dynamics, i.e.,

\[
p_{\tau}^{dr}(\gamma|i) \propto p_{\tau}^q(\gamma|i) e^{\nu \gamma},
\]  

(51)

in the limit of large \( \tau \). Introducing

\[
\langle \gamma_i(\tau, \nu) \rangle \equiv \frac{\int_{-\infty}^{\infty} \gamma p_{\tau}^q(\gamma|i) e^{\nu \gamma} \, d\gamma}{\int_{-\infty}^{\infty} p_{\tau}^q(\gamma|i) e^{\nu \gamma} \, d\gamma},
\]  

(52)

which denotes the mean shear that the system accumulates over time \( \tau \) in the steady state from state \( i \), one can then express equation (50) as

\[
\Delta q'_{ji} = \lim_{\tau \to \infty} \left[ \langle \gamma_j(\tau, \nu) \rangle - \langle \gamma_i(\tau, \nu) \rangle \right],
\]  

(53)

i.e., as the difference in mean shear between states \( i \) and \( j \) over infinite time. Furthermore, from equation (47) we find that the quantities \( \Delta q'_{ji} \) can be determined using Cramer’s rule [17]:

\[
\Delta q'_{ji} = \frac{\det \left[ (\tilde{M}^T)^{(i)} \right]}{\det \left[ \tilde{M}^T \right]},
\]  

(54)

where \((\tilde{M}^T)^{(i)}\) means that the \( i \)th column of \( \tilde{M}^T \) has to be replaced by \( a \). From the set of \( \Delta q'_{ii} \) all other quantities \( \Delta q'_{ji} \) follow by subtraction: \( \Delta q'_{ji} = \Delta q'_{jj} - \Delta q'_{ij} \).

Relationship (49) is remarkable because the stationary shear current is determined from the properties of a single state and its neighbors only, instead of the average equation (38) over the whole basic graph. It does not involve energetics, since the knowledge of two constant ‘shear values’ in addition to the transition rates is sufficient for determining the current. One constant, \( \Delta x_{ji} \), measures the immediate difference in shear between states \( i \) and \( j \) and the other, \( \Delta q'_{ji} \), the difference in mean shear that the system accumulates in the steady state over infinite time from states \( i \) and \( j \). The set of \( \Delta q'_{ji} \) is directly related to the transition rate matrix \( \tilde{M} \) via equation (54).

From a computational point of view, no advantage is gained by determining the flux via equation (49) if the quantities \( \Delta q'_{ji} \) are determined by the same formal matrix inversion method as the probability distributions. However, equation (49) provides us with a new interpretation of the steady state current and of the elements of the inverse transition rate matrix \( \tilde{M}^{-1} \). The quantities \( \Delta q'_{ji} \) have a precise physical meaning independent of the NCDB formalism. It might be possible to identify related current expressions for other steady state systems that are not contained in the class of systems for which NCDB is valid.

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6.1. The fluctuation relation for the shear current

**Fluctuation theorems** are mathematical relations for the fluctuations of thermodynamic quantities like heat (entropy production) or work in nonequilibrium systems (see [21] and references therein). In a nonequilibrium steady state the so called asymptotic or steady state fluctuation theorem (SSFT) states that the probability distribution \( p_\tau(\rho) \) for finding a particular value of the thermodynamic quantity \( \rho \) over time \( \tau \) satisfies a certain symmetry relation of the form (cf [20], [22]–[24])

\[
\frac{p_\tau(\rho)}{p_\tau(-\rho)} \approx e^{c\rho \tau},
\]

(55)

where \( \approx \) indicates the asymptotic behavior for large \( \tau \) and \( c \) is a constant. The SSFT equation (55) (also referred to as the Gallavotti–Cohen fluctuation theorem) represents a refinement of the second law of thermodynamics in that it quantifies the probability of observing temporary violations of the second law (negative \( \rho \)) in the nonequilibrium steady state. Relations similar to equation (55) have been derived for a variety of systems with different thermostating mechanisms. For deterministic systems in a compact phase space the SSFT for the entropy production is expected to hold universally under the chaotic hypothesis [23]. However, stochastic systems do not exhibit the same generality in their fluctuation behavior. Here, the validity of equation (55) relies, e.g., on the characteristics of the noise, or on the thermodynamic quantity considered. In a particular paradigmatic nonequilibrium particle model the SSFT has been shown to hold for the heat fluctuations, when the system is thermostatted by an equilibrium heat bath with Gaussian white noise characteristics [25]. However, when one considers the heat fluctuations, or the work fluctuations under the influence of non-Gaussian noise, the SSFT is violated [26]–[30].

In a shear flow, a fluid region in the bulk of the volume receives noise from the sheared fluid surrounding it, which represents a nonequilibrium heat bath. NCDB quantifies the stochastic influence of such a nonequilibrium heat bath on the dynamics of the fluid. In systems satisfying NCDB a relation in the form of the SSFT holds for the fluctuations of the shear current and can be derived in a straightforward way. Our starting point is the nonequilibrium path distribution \( p^{\text{dr}}(\Gamma) \) of equation (9). Using this path distribution, the distribution of the shear current \( J = \gamma/\tau \) can be formally expressed as

\[
p_\tau(J) = \frac{\sum_{\Gamma} \delta(J - \gamma(\Gamma)/\tau)p^{\text{dr}}(\Gamma)}{\sum_{\Gamma} p^{\text{dr}}(\Gamma)},
\]

(56)

where the total shear of a phase space trajectory \( \Gamma \) is denoted by \( \gamma(\Gamma) \). Substituting equation (9) yields

\[
p_\tau(J) \approx e^{\nu J \tau} \frac{\sum_{\Gamma} \delta(J - \gamma(\Gamma)/\tau)p^{\text{eq}}(\Gamma)}{\sum_{\Gamma} e^{\nu \gamma(\Gamma)} p^{\text{eq}}(\Gamma)}.
\]

(57)

Here, the numerator is just the unnormalized probability distribution for observing the shear current \( J \) at equilibrium. Clearly, this distribution has to be symmetric under a change of sign of \( J \), i.e., at equilibrium the probability of observing a shear current \( J \) over time \( \tau \) is the same as that of observing \(-J\) over the same time period. Taking the ratio
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\[ \frac{p_\tau(J)}{p_\tau(-J)} \] then immediately implies

\[ \frac{p_\tau(J)}{p_\tau(-J)} \approx e^{2\nu J \tau}, \tag{58} \]

for large \( \tau \). The distribution \( p_\tau(J) \) depends implicitly on the parameter \( \nu \).

The current fluctuation relation, equation (58), characterizes the fluctuations of \( J \) in the steady state and implies that the system’s trajectory is overwhelmingly likely to follow the direction prescribed by the imposed driving, which is specified by the sign of the flux conjugated parameter \( \nu \). Similar fluctuation relations for currents have previously been derived in the context of the Schnakenberg network theory [31] and lattice gas models [32] (see also [21] and references therein). In the present case equation (58) follows very naturally due to the Gibbs property of the path distribution \( p^{dr}(\Gamma) \), without evoking the transition rates. The general relationship between the SSFT and Gibbs distributions has been discussed in [33].

In the remainder of this paper we apply the formal results of the previous sections to two simple Markovian jump models.

7. The analytic solution for the two-state graph

As our first example we discuss a basic graph with two different kinds of states, 1 and 2. For generality, an asymmetric separation between the states is assumed. Two distinct arrangements are then possible: (i) a simple connected path leading to a zigzag shaped graph, and (ii) a graph in the form of connected triangles. (Other connectivities are also possible, one of which was considered in [4].) For both kinds of graphs the driven transition rates can be calculated exactly using the results of the previous sections. Obviously, (i) is a special case of (ii) where the horizontal transition rates are set to zero. For clarity we first discuss the simpler zigzag graph in some detail in sections 7.1 and 7.2 and then present results for case (ii) in section 7.3.

Let us first consider a zigzag arrangement of the two states leading to a ratchet shaped state space. Although the solution of this two-state model follows quite intuitively, we apply the network rules of section 5.2 in a systematic way.

7.1. Network rules

The edge rule. The basic graph in figure 4 reveals one interior edge and one pair of exterior edges. In the following we use an intuitive notation for (u)pward and (d)ownward rates in the positive (+) and negative directions (−). Driven rates are capitalized while their equilibrium counterparts are lower case. With the interior edge the transition rates \( U^+ \equiv \Omega_{12} \) and \( D^- \equiv \Omega_{21} \) are associated, depending on \( \Delta q_{21} \) and carrying the shear \( \pm \Delta x_{21} \). With the pair of exterior edges we associate the rates \( U^- \equiv \Omega_{10} \) and \( D^+ \equiv \Omega_{23} \), which depend on \( \Delta q_{32} \) and \( \pm \Delta x_{32} \) (note that \( \Delta q_{32} = \Delta q_{10} \) and \( \Delta x_{32} = \Delta x_{10} \)). At equilibrium the number of different transition rates remains 4 due to the asymmetry of the state space, but equilibrium detailed balance requires that \( u^-/d^+ = u^+/d^- = e^{-\beta \Delta E} \), with \( \Delta E \) being the energy difference between states of types 1 and 2. Throughout the following calculations the inverse temperature \( \beta \) is set to unity. According to equation (24) the
The driven transition rates are then given by
\[ U^+ = u^+ e^{\nu \Delta x_21 + \Delta q_{21}}, \quad D^- = d^- e^{-\nu \Delta x_21 - \Delta q_{21}}, \]
\[ U^- = u^- e^{-\nu \Delta x_32 - \Delta q_{32}}, \quad D^+ = d^+ e^{\nu \Delta x_32 + \Delta q_{32}}. \] (59)

The vertex rule. There are two distinct vertices in the basic graph. To each corresponds an equation in the form of equation (35):
\[ Q = U^+ + U^- - (u^+ + u^-), \]
\[ Q = D^+ + D^- - (d^+ + d^-). \] (60)

The loop rule. There is one external closed loop \( 1 \rightarrow 2 \rightarrow 3 \) corresponding to subsequent transitions \( U^+ \) and \( D^+ \). The loop constraint for the \( \Delta q \)s then reads
\[ \Delta q_{21} + \Delta q_{32} = 0. \] (61)

In total we have the system of equations
\[ u^+ e^{\nu \Delta x_21 + \Delta q_{21}} + u^- e^{-\nu \Delta x_32 - \Delta q_{32}} - (u^+ + u^-) = Q, \]
\[ d^- e^{-\nu \Delta x_21 - \Delta q_{21}} + d^+ e^{\nu \Delta x_32 + \Delta q_{32}} - (d^+ + d^-) = Q, \]
\[ \Delta q_{21} + \Delta q_{32} = 0. \] (62)(63)(64)

for the three unknowns \( Q, \Delta q_{21}, \) and \( \Delta q_{32} \). The solution can be found in a straightforward way. We simplify notation by setting \( \Delta q \equiv \Delta q_{21} = -\Delta q_{32}, \) as well as \( \Delta x_1 \equiv \Delta x_{21} \) and \( \Delta x_2 \equiv \Delta x_{32}. \) Furthermore, we use the notation for the total exit rates \( \sigma_1 = u^+ + u^- \) and \( \sigma_2 = d^+ + d^- \). Substitution of the loop constraint yields
\[ (u^+ e^{\nu \Delta x_1} + u^- e^{-\nu \Delta x_2})e^{\Delta q} - \sigma_1 = Q, \]
\[ (d^- e^{-\nu \Delta x_1} + d^+ e^{\nu \Delta x_2})e^{-\Delta q} - \sigma_2 = Q. \] (65)(66)

Elimination of \( e^{\Delta q} \) in this set of equations leads to a quadratic equation for \( Q \), namely
\[ Q^2 + (\sigma_1 + \sigma_2)Q + (\sigma_1 \sigma_2 - (u^+ e^{\nu \Delta x_1} + u^- e^{-\nu \Delta x_2})(d^- e^{-\nu \Delta x_1} + d^+ e^{\nu \Delta x_2})) = 0. \] (67)

Due to equilibrium detailed balance we furthermore have
\[ \sigma_1 \sigma_2 - (u^+ e^{\nu \Delta x_1} + u^- e^{-\nu \Delta x_2})(d^- e^{-\nu \Delta x_1} + d^+ e^{\nu \Delta x_2}) = 2u^+ d^+(1 - \cosh(\nu (\Delta x_1 + \Delta x_2))). \] (68)

\( \text{doi:10.1088/1742-5468/2010/03/P03030} \)
The positive root then reads
\[ Q(\nu) = \frac{1}{2} \sqrt{(\sigma_1 + \sigma_2)^2 + 8u^+d^+(\cosh(\nu(\Delta x_1 + \Delta x_2)) - 1) - \frac{1}{2}(\sigma_1 + \sigma_2)}. \] (69)

In turn, \( \Delta q \) is determined from equation (65) as
\[ \Delta q = \ln \left[ \frac{Q + \sigma_1}{u^+e^\nu + u^-e^{-\nu}\Delta x_2} \right]. \] (70)

For a given set of equilibrium rates, the driven transition rates are now completely determined as functions of the flux conjugated parameter \( \nu \). With \( Q \) and \( \Delta q \) we can furthermore calculate the shear current \( J(\nu) = dQ(\nu)/d\nu \) and the mean shear difference \( \Delta q' = d\Delta q(\nu)/d\nu \) (see also below). Equilibrium is characterized by \( \nu = 0 \). As expected the flux then vanishes: \( J(\nu = 0) = 0 \). One can also easily see that for \( \nu = 0 \) both \( Q(0) = 0 \) and \( \Delta q(0) = 0 \), and the driven rate equations (59) reduce to the equilibrium rates.

7.2. Invariant quantities

Since the asymmetric two-state zigzag graph is obviously a simple connected path, we can alternatively determine the driven transition rates using the \( \nu \) independent representation. To this end we have to set up the invariant quantities and found the relation between the rates and the particle flux. The invariant quantities follow immediately from equations (36) and (37):
\[ U^+D^- = u^+d^-, \] (71)
\[ D^+U^- = d^+u^-, \] (72)
\[ D^+D^- - (U^+U^-) = d^+d^- - (u^+u^-). \] (73)

Finally, to find the flux, we calculate the probability distributions of states 1 and 2. The master equation for the two-state graph has the following matrix form:
\[
\begin{pmatrix}
-(U^+ + U^-) & D^+ + D^- \\
U^+ + U^- & -(D^+ + D^-)
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2
\end{pmatrix}
= 0.
\] (74)

Including the normalization in the transition matrix leads to
\[ \tilde{M} \begin{pmatrix} p_1 \\ p_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \] (75)
where
\[ \tilde{M} = \begin{pmatrix} 1 & U^+ \\ U^+ & - (D^+ + D^-) \end{pmatrix}. \] (76)

Matrix inversion then yields the probability distributions (or occupancies) \( p_1, p_2 \), which, in turn, allow for the calculation of the current \( J \) via equation (38). The results for the probability distributions as functions of the driven transition rates are
\[ p_1 = \frac{D^+ + D^-}{U^+ + U^- + D^+ + D^-}, \] (77)
\[ p_2 = \frac{U^+ + U^-}{U^+ + U^- + D^+ + D^-}. \] (78)

\[ \text{doi:10.1088/1742-5468/2010/03/P03030} \]
According to the results of section 6 we can alternatively determine the current and the mean shear differences $\Delta q'$ from equation (47). This equation is given by
\[
\begin{pmatrix}
J \\
-\Delta q'
\end{pmatrix} = (\tilde{M}^{-1})^T \begin{pmatrix}
U^+ \Delta x_1 - U^- \Delta x_2 \\
D^+ \Delta x_2 - D^- \Delta x_1
\end{pmatrix}.
\] (79)

The matrix algebra is straightforward and yields
\[
J = (\Delta x_1 + \Delta x_2) \left( \frac{U^+ D^+ - U^- D^-}{U^+ + U^- + D^+ + D^-} \right),
\] (80)
\[
\Delta q' = \frac{(D^+ + U^-) \Delta x_2 - (U^+ + D^-) \Delta x_1}{U^+ + U^- + D^+ + D^-}.
\] (81)

The last two expressions agree with the ones obtained in the $\nu$-representation, if the driven rates are substituted according to equation (59) with the known expressions for $Q$ and $\Delta q$, equations (69) and (70).

For a given set of equilibrium rates and a prescribed particle flux, the transition rates in the driven steady state are determined as solutions of the set of equations (71)–(73) and (80). In this case the driven rates are parametrized by $J$.

### 7.3. The two-state graph with a loop

If we add two additional external edges $2 \to 0$ and $2 \to 4$ to the two-state zigzag graph of figure 4, we obtain a state space with the structure of figure 5. The system in state 2 can now choose to reach state 4 directly or by going first ‘downhill’ to a state of type 1 and then ‘uphill’. The choice will depend on which path is more favorable for achieving the imposed flux $J$ for given parameter values. As before, NCDB precisely quantifies the change in the transition rates under driving.

We denote the transition rates associated with the additional exterior edges with $H^+ \equiv \Omega_{24}$ and $H^- \equiv \Omega_{20}$. Both rates are independent of $\Delta q$ since they connect states of the same type and symmetry requires that the corresponding equilibrium rates are equal. The rates are therefore fully specified as
\[
H^+ = h e^{\nu(\Delta x_1 + \Delta x_2)}, \quad H^- = h e^{-\nu(\Delta x_1 + \Delta x_2)}.
\] (82)
The effect of the additional edges on the other rates can be calculated analogously to the zigzag graph. The total exit rate relation for state 2 (used in the vertex rule) has to be extended with the new rates, whereas the relation for state 1 remains unchanged. This leads to

\[ Q = U^+ + U^- - (u^+ + u^-), \]
\[ Q = D^+ + D^- + H^+ + H^- - (d^+ + d^- + 2h). \]

Introducing the total exit rate \( \sigma_2 = d^+ + d^- + 2h \) and substituting the expressions for the driven rates, we can write the system of equations as

\[ (d^- e^{-\nu \Delta x_1} + d^+ e^{\nu \Delta x_2})e^{-\Delta q} + 2h \cosh(\nu(\Delta x_1 + \Delta x_2)) - \sigma_2 = Q, \]
\[ (u^+ e^{\nu \Delta x_1} + u^- e^{-\nu \Delta x_2})e^{\Delta q} - \sigma_1 = Q. \]

The quadratic equation for the flux potential then reads

\[ 0 = Q^2 + (\sigma_1 + \sigma_2 - 2h \cosh(\nu(\Delta x_1 + \Delta x_2)))Q + \sigma_1 \sigma_2 - \sigma_1 2h \cosh(\nu(\Delta x_1 + \Delta x_2)) \]
\[ - (u^+ e^{\nu \Delta x_1} + u^- e^{-\nu \Delta x_2})(d^- e^{-\nu \Delta x_1} + d^+ e^{\nu \Delta x_2}), \]

with the positive root

\[ Q(\nu) = \frac{1}{2} \sqrt{\sigma_1 + \sigma_2 - 2h \cosh(\nu(\Delta x_1 + \Delta x_2))}^2 + 8(\sigma_1 h + u^+ d^+) \cosh(\nu(\Delta x_1 + \Delta x_2)) - 1 \]
\[ - \frac{1}{2}(\sigma_1 + \sigma_2 - 2h \cosh(\nu(\Delta x_1 + \Delta x_2))). \]

As above, \( \Delta q \) is determined from equation (70).

Having thus specified all the driven rates, we can determine the remaining quantities in the matrix formalism. Since the rates \( H^+ \) and \( H^- \) connect two states of the same type, their effect on the occupancies balances to zero. The transition rate matrix \( \tilde{M} \) is therefore identical to equation (76) and the probability distributions are given by equations (77) and (78) as in the zigzag case. The shear current \( J \) and the mean shear difference \( \Delta q' \) are determined by equation (47), which reads here

\[ \begin{pmatrix} J \\ -\Delta q' \end{pmatrix} = (\tilde{M}^{-1})^T \begin{pmatrix} U^+ \Delta x_1 - U^- \Delta x_2 \\ (D^+ + H^+ - H^-) \Delta x_2 - (D^- + H^- - H^+) \Delta x_1 \end{pmatrix}. \]

We thus obtain

\[ J = (\Delta x_1 + \Delta x_2) \frac{U^+ D^+ - U^- D^- + (U^+ + U^-)(H^+ - H^-)}{D^+ + D^- + U^+ + U^-}, \]
\[ \Delta q' = \frac{(D^+ + U^-) \Delta x_2 - (U^+ + D^-) \Delta x_1 + (H^+ - H^-)(\Delta x_1 + \Delta x_2)}{D^+ + D^- + U^+ + U^-}. \]

In the limit \( h \to 0 \) the two-state loop model obviously reduces to the zigzag model discussed in the previous section. The four transition rates \( U^+, U^-, D^+, D^- \) in this case are plotted in figure 6(a) parametrically as functions of the current \( J \) for given values of the parameters \( \Delta E, d^+, d^-, \Delta x_1, \) and \( \Delta x_2 \). Clearly, the rates of transition in the direction of \( J \) are enhanced for larger \( J \), while the transition rates in the opposite direction are attenuated. For large \( J \) the rates of transition in the direction of the driving become proportional to \( J \), as implied by the current relation, equation (90). The occupancies \( p_1, \)
Figure 6. (a) The four transition rates of the two-state zigzag model \((h = 0.0)\) plotted as functions of the current \(J\). (b) The function \(\Delta q(\nu)\) of equation (70) (with \(Q(\nu)\) given by equation (88)) for two values of the equilibrium rate \(h\). Parameter values: \(\Delta E = 2.0\), \(d^+ = 1.0\), \(d^- = 0.8\), \(\Delta x_1 = 1.0\), \(\Delta x_2 = 0.5\).

Figure 7. The occupancies \(p_1\) and \(p_2\) of equations (77) and (78) plotted as functions of the current \(J\) for parameter values \(\Delta E = 2.0\), \(d^+ = 1.0\), \(d^- = 0.8\), \(\Delta x_1 = 1.0\), \(\Delta x_2 = 0.5\). (a) In the two-state zigzag model both distributions converge to 1/2 for large \(J\). (b) In the two-state loop model, with \(h = 0.5\). The occupancy of type 2 states, \(p_2\), converges to 1 for large \(J\), while \(p_1\) decays to zero.

\(p_2\), which at equilibrium \((J = 0)\) are determined by Boltzmann’s law, converge to the value 1/2 in the limit of \(J \to \infty\), indicating that the energy difference between states 1 and 2 becomes irrelevant for strong driving (see figure 7(a)).

When \(h \neq 0\) the system is able to gain a shear increment \(\Delta x_1 + \Delta x_2\) by going directly from state 2 to state 4, i.e., another state of type 2, without first going to state 3, a state of type 1. This implies that, under (strong) forward driving, it is advantageous for the system in state 2 to make the transition 2 \(\to\) 4 instead of the transition 2 \(\to\) 3, because it is then able to gain an increment \(\Delta x_1 + \Delta x_2\) in one step instead of two. This intuitively expected behavior of the two-state loop model is evident in figure 8, where we plot the three forward transition rates under forward driving. While in the zigzag case the rate \(D^+\) is enhanced under increased forward driving, it is attenuated in the loop case due to the presence of the additional edge. The system finds that being in state 1 is less favorable for achieving shear than being in state 2.

The quantity \(\Delta q = \Delta q_{21}\), equation (70) (with \(Q\) of equation (88)), is plotted in figure 6(b) for the two cases \(h = 0\) and \(h \neq 0\). In the zigzag case \((h = 0)\) one notices that, for the given choice of the parameters \(\Delta x_1 > \Delta x_2\), \(\Delta q\) becomes negative for large
Figure 8. The three forward transition rates in the two-state loop model. Parameter values: $\Delta E = 2.0$, $d^+ = 1.0$, $d^- = 0.8$, $\Delta x_1 = 1.0$, $\Delta x_2 = 0.5$, $h = 0.5$.

Figure 9. Basic graph of a three-state model with an interior loop. The dotted lines denote exterior edges.

forward driving (large $\nu$), indicating that state 1 has a larger propensity for future shear than state 2. This is because the system can gain a larger (forward) shear increment from state 1 ($\Delta x_1$) than from state 2 ($\Delta x_2$). For weak driving (small $\nu$) a crossover behavior is observed, where $\Delta q$ exhibits local maxima and minima. In the loop case ($h \neq 0$) state 2 is favored due to the additional edge and thus $\Delta q$ increases for both larger forward and backward driving. In fact, from the analytical expression equation (70), one finds that $\Delta q(\nu) \propto |\nu|$ for large $\pm \nu$ in the case $h \neq 0$, while $\Delta q(\nu) \propto \nu(\Delta x_2 - \Delta x_1)$ in the case $h = 0$.

8. The three-state graph

A basic graph with three distinct states allows for a variety of periodic graph structures with different connectivities. In the following we consider a basic graph that contains an internal closed loop (see figure 9). For this arrangement the driven transition rates can only be found using the network rules, since the number of independent rates exceeds the number of invariant quantities plus the current relation.

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The edge rule. There are three internal edges and one pair of external edges in the basic graph. The three internal edges correspond to six distinct rates: $\Omega_{12}$, $\Omega_{13}$, $\Omega_{23}$, and the associated reverse rates. The pair of external edges is associated with $\Omega_{10}$ and $\Omega_{34}$, where state 0 is of the same type as state 3 and state 4 of the same type as state 1. The set of driven transition rates is specified as in equation (24):

$$\Omega_{ij} = \omega_{ij} e^{\nu \Delta x_{ji} + \Delta q_{ij}}.$$  

The vertex rule. Equation (35) gives one relation for each vertex. These three equations read

$$Q = \Omega_{12} + \Omega_{13} + \Omega_{10} - (\omega_{12} + \omega_{13} + \omega_{10}),$$  

$$Q = \Omega_{23} + \Omega_{21} - (\omega_{23} + \omega_{21}),$$  

$$Q = \Omega_{31} + \Omega_{32} + \Omega_{34} - (\omega_{31} + \omega_{32} + \omega_{34}).$$  

The loop rule. There is one external loop 0 $\to$ 1 $\to$ 3 and one internal loop 1 $\to$ 2 $\to$ 3 $\to$ 1 so the constraints on the four $\Delta q$s read

$$\Delta q_{10} + \Delta q_{31} = 0,$$  

$$\Delta q_{21} + \Delta q_{32} + \Delta q_{13} = 0.$$  

Furthermore the internal loop requires that $\Delta x_{31} = \Delta x_{21} + \Delta x_{32}$. We use the following simplifying notation:

$$\ln z \equiv \Delta q_{21},$$  

$$\ln y \equiv \Delta q_{32},$$  

$$W_{ij} \equiv \omega_{ij} e^{\nu \Delta x_{ji}}.$$  

The loop constraints then imply that $\Delta q_{01} = \Delta q_{31} = \ln(yz)$. In this notation the vertex rules read

$$W_{12} z + (W_{10} + W_{13})yz - \sigma_1 = Q,$$  

$$W_{23} y + W_{21} z^{-1} - \sigma_2 = Q,$$  

$$(W_{31} + W_{34})(yz)^{-1} + W_{32} y^{-1} - \sigma_3 = Q.$$  

where the total exit rates are as before $\sigma_i = \sum_j \omega_{ij}$. Elimination of $Q$ then leads to two quadratic equations

$$(W_{10} + W_{13})z^2 y + W_{12} z^2 - W_{23} yz + (\sigma_2 - \sigma_1)z - W_{21} = 0,$$  

$$W_{23} y^2 z + (\sigma_3 - \sigma_2)yz + W_{21} y - W_{32} z - (W_{31} + W_{34}) = 0.$$  

One realizes that for the three-state model an analytical solution is already exceedingly difficult to obtain. Solving for example equation (103) for $y$ and substituting into equation (104) yields an equation for $z$ which is of fifth order and therefore not exactly solvable. Alternatively one can determine the driven transition rates in a straightforward way by solving equations (103) and (104) numerically for $y$ and $z$. 

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The current and probability distributions are most easily obtained from the matrix methods outlined in section 6. For the three-state graph of figure 9 the master equation reads in matrix form

\[
\begin{pmatrix}
- (\Omega_{13} + \Omega_{12} + \Omega_{10}) & \Omega_{21} & \Omega_{31} + \Omega_{34} \\
\Omega_{12} & - (\Omega_{23} + \Omega_{21}) & \Omega_{32} \\
\Omega_{13} + \Omega_{10} & \Omega_{23} & - (\Omega_{31} + \Omega_{32} + \Omega_{34})
\end{pmatrix}
\begin{pmatrix}
p_1 \\
p_2 \\
p_3
\end{pmatrix}
= 0.
\] (105)

The probability distributions are then obtained as

\[
\begin{pmatrix}
p_1 \\
p_2 \\
p_3
\end{pmatrix} = \tilde{M}^{-1}
\begin{pmatrix}
1 \\
0 \\
0
\end{pmatrix},
\] (106)

where

\[
\tilde{M} = \begin{pmatrix}
\Omega_{12} & - (\Omega_{23} + \Omega_{21}) & 1 \\
1 & \Omega_{23} & - (\Omega_{31} + \Omega_{32} + \Omega_{34}) \\
\Omega_{13} + \Omega_{10} & \Omega_{23} & - (\Omega_{31} + \Omega_{32} + \Omega_{34})
\end{pmatrix}.
\] (107)

Using equation (47) we can then determine the shear current and the mean shear differences:

\[
\begin{pmatrix}
J \\
\Delta q_{12} \\
\Delta q_{13}
\end{pmatrix} = (\tilde{M}^{-1})^T
\begin{pmatrix}
\Omega_{13}(\Delta x_{32} + \Delta x_{21}) + \Omega_{12}\Delta x_{21} - \Omega_{10}\Delta x_{32} \\
\Omega_{23}\Delta x_{32} - \Omega_{21}\Delta x_{21} \\
\Omega_{34}\Delta x_{32} - \Omega_{32}\Delta x_{32} - \Omega_{31}\Delta x_{31}
\end{pmatrix}.
\] (108)

By solving equations (103) and (104) numerically for \(\Delta q_{21}\) and \(\Delta q_{32}\) given a set of equilibrium rates \(\omega_{ij}\) and distances \(\Delta x_{ji}\), one can determine the driven transition rates as well as the flux potential for the three-state graph of figure 9. Equations (106) and (108) can then be used to obtain the probability distributions, the current and the mean shear differences.

The results for the driven transition rates in the forward direction are shown in figure 10. For forward shear three of the transition rates are strongly enhanced. However, we observe that the transition \(1 \rightarrow 2\) is attenuated at high shear rate, even though it contributes a positive shear increment \(\Delta x_{21}\). This indicates that the system disfavors the path via state 2 that requires two transitions to acquire the shear increment \(\Delta x_{32}\). For large shear rates the system will thus predominantly choose the high-mobility ‘channel’ \(1 \rightarrow 3\). A similar observation is made for the transition \(2 \rightarrow 3\), which, for backward driving, remains significant because it connects to the favorable direct channel.

Accordingly, the steady state occupancies \(p_1\) and \(p_3\) converge to the value \(1/2\) for strong driving in both forward and backward directions (cf figure 11). On the other hand, the occupancy of state 2, energetically favored over states 1 and 3 at equilibrium, decays to zero for larger shear.

9. Conclusion and remarks

The search for fundamental principles governing the behavior of systems in out of equilibrium situations has long been an area of intensive research. We have discussed a statistical theory (NCDB) that starts from first principles and governs the steady state motion of any flowing system on which work is done by a weakly coupled nonequilibrium
reservoir that is ergodic and microscopically reversible, such as a complex fluid under continuous shear. NCDB provides a description of the microscopic dynamics of these systems in the form of exact constraints on the transition rates in the driven steady state, arbitrarily far away from equilibrium, akin to the principle of detailed balance for equilibrium systems. In this paper we have investigated this theory for systems evolving in discrete state spaces. We derived a simple relationship between the flux potential and the total exit rates, which leads to a number of important further results.

Two simple sets of invariant quantities have been formulated: (i) the product of forward and reverse transition rates and (ii) the differences in total exit rates, for every pair of microstates, equal the corresponding equilibrium values and are thus unchanged by the driving. These invariant quantities are non-trivial and experimentally accessible predictions of NCDB. We have devised a systematic method for determining the driven transition rates by setting up a system of equations from simple network rules. Furthermore, we have investigated properties of the shear current in systems satisfying NCDB. We have shown that the stationary shear current can be determined independently.

Figure 10. The four forward transition rates of the three-state loop model of figure 9. Parameter values: \( \Delta E_{12} = 3.0 \), \( \Delta E_{32} = 2.0 \), \( \omega_{10} = 1.0 \), \( \omega_{13} = 1.0 \), \( \omega_{32} = 1.5 \), \( \Delta x_{21} = 1.8 \), \( \Delta x_{32} = 1.0 \), \( \Delta x_{43} = 0.5 \).

Figure 11. The steady state distributions \( p_1 \), \( p_2 \), \( p_3 \) of equation (106) plotted parametrically as functions of the current \( J \). Parameter values: \( \Delta E_{12} = 3.0 \), \( \Delta E_{32} = 2.0 \), \( \omega_{10} = 1.0 \), \( \omega_{13} = 1.0 \), \( \omega_{32} = 1.5 \), \( \Delta x_{21} = 1.8 \), \( \Delta x_{32} = 1.0 \), \( \Delta x_{43} = 0.5 \).
Nonequilibrium statistical mechanics of shear flow of the steady state distribution of microstates, and that the fluctuations of this shear current satisfy a fluctuation relation of the Gallavotti–Cohen type.

In a system with two kinds of states all quantities of the NCDB formalism can be expressed analytically. However, even for just three states, results are only obtainable numerically. Both kinds of systems show consistent behavior. In state spaces containing a loop, the particular path favored at highest driving is the one most accommodating for carrying flux. Even in these simple models the non-local nature of NCDB becomes evident. Whereas mean-field theories without the quantity $\Delta q$ would simply boost any transition in the forward flux direction, NCDB takes into account the future propensity for achieving flux. That propensity depends on the global structure of the state space, and is communicated in the noise from the reservoir of other systems exploring the possibilities of the steady state dynamics. A particular transition will thus be attenuated if it connects to a state which is blocked or from where subsequent transitions carry low flux. This striking property indicates that NCDB might ultimately be able to describe the counter-intuitive phase behavior exhibited for example by real complex fluids under shear.

It is an open question how our theory of the detailed transition rates in sheared fluids relates to more general theories of macroscopic quantities such as the distribution of fluctuations in nonequilibrium steady states [34,35] and steady state thermodynamics [36,37]. It is unclear to us whether those theories, in using concepts such as heat and noise, implicitly require the existence of an equilibrium heat bath, or whether they also cover the case of a system receiving noise from a nonequilibrium heat bath of sheared fluid that we have studied.

Future work will predominantly focus on further applications of NCDB to more realistic models as well as independent experimental tests. In particular the invariant quantities provide a straightforward criterion for checking the validity of the theory (cf [19]). Even though these new exact relations are based on a rigorous statistical mechanical derivation, only comparison with experimental data can shed light on their significance for our understanding of nonequilibrium phenomena.

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Appendix A. The canonical-flux representation

Inserting unity as the delta function $\int \delta(\gamma - \gamma(\Gamma)) \, d\gamma$ in equation (11) yields

$$\Omega_{ij} = \frac{\int_{-\infty}^{\infty} e^{\nu\gamma} \sum_{\Gamma(i,j) \in \Gamma} \delta(\gamma - \gamma(\Gamma)) \, p_{\text{eq}}^{\gamma}(\Gamma) \, d\gamma}{\Delta t \int_{-\infty}^{\infty} e^{\nu\gamma} \sum_{\Gamma(i) \in \Gamma} \delta(\gamma - \gamma(\Gamma)) \, p_{\text{eq}}^{\gamma}(\Gamma) \, d\gamma}. \quad (A.1)$$

We notice that the average over the delta function $\delta(\gamma - \gamma(\Gamma))$ is related to the conditional probability distribution $p_{\gamma i}^{\text{eq}}(\gamma | i, j)$:

$$p_{\gamma i}^{\text{eq}}(\gamma | i, j) = \frac{\sum_{\Gamma(i,j) \in \Gamma} \delta(\gamma - \gamma(\Gamma)) p_{\text{eq}}^{\gamma}(\Gamma)}{\sum_{\Gamma(i,j) \in \Gamma} p_{\text{eq}}^{\gamma}(\Gamma)}. \quad (A.2)$$
The distribution \( p_{\text{eq}}^{\tau}(\gamma|i,j) \) contains the probability that the system at equilibrium accumulates a total amount of shear \( \gamma \) over a time period \( \tau \) due to equilibrium fluctuations, given that it made a transition from \( i \) to \( j \). Similarly, the denominator in equation (11) leads to an expression containing \( p_{\text{eq}}^{\tau}(\gamma|i) \). The subscript \( \tau \) denotes the implicit dependence of these distributions on the duration of the trajectory \( \Gamma \). The driven rate now reads

\[
\Omega_{ij} = \lim_{\tau \to \infty} \frac{\sum_{\Gamma|(i,j) \in \Gamma} p_{\text{eq}}(\Gamma) \int_{-\infty}^{\infty} p_{\text{eq}}^{\tau}(\gamma|i,j) e^{\nu \gamma} \, d\gamma}{\Delta t \sum_{\Gamma|i \in \Gamma} p_{\text{eq}}(\Gamma) \int_{-\infty}^{\infty} p_{\text{eq}}^{\tau}(\gamma|i) e^{\nu \gamma} \, d\gamma}.
\]

Here, the \( \tau \to \infty \) limit guarantees that the system has attained its stationary state. After factoring out the equilibrium rate \( \omega_{ij} = \sum_{\Gamma|(i,j) \in \Gamma} p_{\text{eq}}(\Gamma) \Delta t \sum_{\Gamma|i \in \Gamma} p_{\text{eq}}(\Gamma) \int_{-\infty}^{\infty} p_{\text{eq}}^{\tau}(\gamma|i) e^{\nu \gamma} \, d\gamma \),

in equation (A.3) one obtains the canonical-flux representation of NCDB, equation (12).

**Appendix B. The \( \tau \) independent representation**

We reproduce the derivation here in full as it is used in the investigation of NCDB in the context of discrete state spaces. Let us define the quantity \( \Delta x_{ji} \) which denotes the shear contribution of the transition \( i \to j \) in time \( \Delta t \). Using \( \Delta x_{ji} \) we can write the conditional probability distribution \( p_{\text{eq}}^{\tau}(\gamma|i,j) \) as

\[
p_{\text{eq}}^{\tau}(\gamma|i,j) = p_{\text{eq}}^{\tau-\Delta t}(\gamma - \Delta x_{ji}|j),
\]

i.e., \( p_{\text{eq}}^{\tau}(\gamma|i,j) \) is given by the probability distribution of accumulating the remaining shear \( \gamma - \Delta x_{ji} \) in the remaining time \( \tau - \Delta t \), starting from state \( j \). Defining the function \( m_{i}(\nu, \tau) \) as

\[
m_{i}(\nu, \tau) \equiv \ln \int_{-\infty}^{\infty} p_{\text{eq}}^{\tau}(\gamma|i) e^{\nu \gamma} \, d\gamma,
\]

allows us to rewrite equation (12) in the form

\[
\ln \frac{\Omega_{ij}}{\omega_{ij}} = \lim_{\tau \to \infty} \left( \ln \int_{-\infty}^{\infty} p_{\text{eq}}^{\tau-\Delta t}(\gamma - \Delta x_{ji}|i) e^{\nu \gamma} \, d\gamma - m_{i}(\nu, \tau) \right).
\]

A change of the integration variable then leads to

\[
\ln \frac{\Omega_{ij}}{\omega_{ij}} = \nu \Delta x_{ji} + \lim_{\tau \to \infty} [m_{j}(\nu, \tau - \Delta t) - m_{i}(\nu, \tau)]
\]

\[
= \nu \Delta x_{ji} + \lim_{\tau \to \infty} [m_{j}(\nu, \tau) - m_{i}(\nu, \tau)] - \zeta(\nu, \Delta t),
\]

where

\[
\zeta(\nu, \Delta t) \equiv \lim_{\tau \to \infty} [m_{j}(\nu, \tau) - m_{j}(\nu, \tau - \Delta t)].
\]

An important property of the function \( \zeta \) is its state independence, which follows from equation (B.5) upon changing \( \tau \to \tau + \Delta t \). To first order in \( \Delta t \) we then have

\[
\zeta(\nu, \Delta t) = \lim_{\tau \to \infty} \frac{\partial}{\partial \tau} m_{j}(\nu, \tau) \Delta t.
\]
We now introduce two important \( \tau \) independent quantities \[4\]. Firstly, we identify
\[ \Delta q_{ji} = q_j(\nu) - q_i(\nu) \equiv \lim_{\tau \to \infty} [m_j(\nu, \tau) - m_i(\nu, \tau)], \]
and secondly, the state independent rate of change of \( m_i(\nu, \tau) \) in the long time limit is denoted as
\[ Q(\nu) \equiv \lim_{\tau \to \infty} \frac{\partial}{\partial \tau} m_i(\nu, \tau). \]
We therefore see that equation (B.5) gives rise to
\[ \Omega_{ij}(\nu) = \omega_{ij} e^{\nu \Delta x_{ji}} + \Delta q_{ji}(\nu) - Q(\nu) \Delta t, \]
which is just equation (14).

Appendix C. The large deviation formalism

The functions \( m_i(\nu, \tau) \), defined by equation (B.2), are the cumulant generating functions of the shear \( \gamma \) over time \( \tau \), conditional on the initial state \( i \). Instead of the extensive shear \( \gamma \), i.e., \( \gamma \) increases with increasing \( \tau \), one can consider the shear current \( J = \gamma / \tau \), which is an intensive quantity. The \( m_i(\nu, \tau) \) transform as follows:
\[
m_i(\nu, \tau) \equiv \ln \int_{-\infty}^{\infty} p^\text{eq}_\tau(\gamma | i) e^{\nu \gamma} d\gamma \tag{C.1}
\]
\[
= \ln \int_{-\infty}^{\infty} p^\text{eq}_\tau(J \tau | i) e^{\nu J \tau} dJ \tag{C.2}
\]
\[
= \ln \int_{-\infty}^{\infty} p^\text{eq}_\tau(J | i) e^{\nu J} dJ. \tag{C.3}
\]
In turn, the equilibrium distribution of the shear current \( p^\text{eq}_\tau(J | i) \) satisfies a large deviation principle
\[
p^\text{eq}_\tau(J | i) \approx e^{-\tau H(J)}, \tag{C.4}
\]
where \( \approx \) indicates the behavior for large \( \tau \), so the dependence on \( i \) can be neglected on the right-hand side. The convex function \( H(J) \) is the rate function of the shear current. The large deviation principle holds with convex rate function, because the shear is generated by the equilibrium dynamics described by the equilibrium set of transition rates \( \{ \omega_{ij} \} \), which represents an ergodic Markov process [15]. Using equation (C.4) in (C.3) leads to
\[
m_i(\nu, \tau) \approx \ln \int_{-\infty}^{\infty} e^{\tau [\nu J - H(J)]} dJ \tag{C.5}
\]
\[
\approx \ln \left( e^{\tau \sup_J [\nu J - H(J)] + O(\ln \tau^{-1/2})} \right). \tag{C.6}
\]
In the last step the integral has been replaced by the saddle point of the exponent, which is the limiting form for large \( \tau \) due to the convexity of \( H(J) \). The corrections to the saddle point are then of the order of \( \ln \tau^{-1/2} \). The flux potential \( Q(\nu) \), defined by equation (16), is thus given by
\[
Q(\nu) \equiv \lim_{\tau \to \infty} \frac{\partial}{\partial \tau} m_i(\nu, \tau) = \sup_J [\nu J - H(J)], \tag{C.7}
\]
which is just the Legendre transform of the rate function \( H(J) \). This implies that \( \nu \) and \( J \) are conjugate quantities and \( dQ/d\nu = J \).
References

[1] Spenley N A, Cates M E and McLeish T C B, 1993 Phys. Rev. Lett. 71 939
[2] Roux D, Nallet F and Diat O, 1993 Europhys. Lett. 24 53
[3] Evans R M L, 2004 Phys. Rev. Lett. 92 150601
[4] Evans R M L, 2005 J. Phys. A: Math. Gen. 38 293
[5] Simha R A, Evans R M L and Baule A, 2008 Phys. Rev. E 77 031117
[6] Baule A and Evans R M L, 2008 Phys. Rev. Lett. 101 240601
[7] Van Kampen N G, 1992 Stochastic Processes in Physics and Chemistry (Amsterdam: North-Holland)
[8] Jaynes E T, 1957 Phys. Rev. 106 620
[9] Jaynes E T, 1957 Phys. Rev. 108 171
[10] Dewar R, 2005 J. Phys. A: Math. Gen. 38 L371
[11] Niven R K, 2009 Phys. Rev. E 80 021113
[12] Katz S, Lebowitz J L and Spohn H, 1983 Phys. Rev. B 28 1655
[13] Taniguchi T and Cohen E G D, 2007 J. Stat. Phys. 126 1
[14] Haenggi P, Talkner P and Borkovec M, 1990 Rev. Mod. Phys. 62 251
[15] Touchette H, 2009 Phys. Rep. 478 1
[16] Schnakenberg J, 1976 Rev. Mod. Phys. 48 571
[17] Evans R M and Blythe R A, 2002 Physica A 313 110
[18] Kelly F P, 1979 Reversibility and Stochastic Networks (New York: Wiley)
[19] Evans R M L, Simha R A, Baule A and Olmsted P D, 2009 arXiv:0911.0830
[20] Lebowitz J L and Spohn H, 1999 J. Stat. Phys. 95 333
[21] Harris R J and Schutz G M, 2007 J. Stat. Mech.: Theor. Exp. P07020
[22] Evans D J, Cohen E G D and Morriss G P, 1993 Phys. Rev. Lett. 71 2401
[23] Gallavotti G and Cohen E G D, 1995 Phys. Rev. Lett. 74 2694
[24] Kurchan J, 1998 J. Phys. A: Math. Gen. 31 3719
[25] van Zon R and Cohen E G D, 2003 Phys. Rev. E 67 046102
[26] van Zon R and Cohen E G D, 2003 Phys. Rev. Lett. 91 110601
[27] Touchette H and Cohen E G D, 2007 Phys. Rev. E 76 020101(R)
[28] Touchette H and Cohen E G D, 2009 Phys. Rev. E 80 011114
[29] Baule A and Cohen E G D, 2009 Phys. Rev. E 79 030103(R)
[30] Baule A and Cohen E G D, 2009 Phys. Rev. E 80 011110
[31] Andrieux D and Gaspard P, 2006 J. Stat. Phys. 127 107
[32] Derrida B, 2007 J. Stat. Mech.: Theor. Exp. P07023
[33] Maes C, 1999 J. Stat. Phys. 95 367
[34] Bertini L, De Sole A, Gabrielli D, Jona-Lasinio G and Landim C, 2001 Phys. Rev. Lett. 87 040601
[35] Bertini L, De Sole A, Gabrielli D, Jona-Lasinio G and Landim C, 2006 J. Stat. Phys. 123 237
[36] Oono Y and Paniconi M, 1998 Prog. Theor. Phys. Suppl. 130 29
[37] Sasa S and Tasaki H, 2006 J. Stat. Phys. 125 125