Stochastic thermodynamics: Principles and perspectives

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Abstract. Stochastic thermodynamics provides a framework for describing small systems like colloids or biomolecules driven out of equilibrium but still in contact with a heat bath. Both, a first-law like energy balance involving exchanged heat and entropy production entering refinements of the second law can consistently be defined along single stochastic trajectories. Various exact relations involving the distribution of such quantities like integral and detailed fluctuation theorems for total entropy production and the Jarzynski relation follow from such an approach based on Langevin dynamics. Analogues of these relations can be proven for any system obeying a stochastic master equation like, in particular, (bio)chemically driven enzymes or whole reaction networks. The perspective of investigating such relations for stochastic field equations like the Kardar-Parisi-Zhang equation is sketched as well.

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1 Introduction

Stochastic thermodynamics as a conceptual framework combines the stochastic energetics approach introduced a decade ago by Sekimoto [1] with the idea that entropy can consistently be assigned to a single fluctuating trajectory [2]. Stochastic energetics has been developed for mesoscopic systems like colloidal particles or single (bio)molecules driven out of equilibrium by time-dependent forces but still embedded in a heat bath of well-defined temperature. The dynamics of the few degrees of freedom are modelled by a Langevin equation where the surrounding heat bath provides the thermal noise. A first-law-like energy balance relates applied or extracted work, exchanged heat and changes in internal energy along the single fluctuating trajectory. In the ensemble, these quantities acquire no longer sharp values but distributions. Since dissipated heat is typically associated with changes in entropy this program of using the classical thermodynamic notions to describe the trajectories of these small systems obviously requires also the concept of a fluctuating entropy with corresponding distribution in the ensemble.

Stochastic thermodynamics being based on stochastic equations of motion allows also to embed and categorize two recent developments orginally derived independently using different equations of motion. First, the (detailed) fluctuation theorem dealing with non-equilibrium steady states provides a symmetry between the probability to observe asymptotically a certain entropy production and the probability for the corresponding entropy annihilation [3–6]. Second, the Jarzynski relation expresses the free energy difference between two equilibrium states as a non-linear average over the non-equilibrium work required to drive the system from one state to the other in a finite time [7–10]. Within stochastic thermodynamics both of these relations can easily be derived and the latter shown to be a special case of a more general relation [2].

The purpose of this article is to describe the principles of stochastic thermodynamics in a systematic way and to sketch a few perspectives. By character mainly a concise review (with a few original results) from a personal unifying perspective, no attempt is made to achieve a comprehensive historical presentation. Several (mostly review) articles can provide complementary and occasionally broader perspectives [11–25]. Focussing on the theoretical concepts I will point to experimental work only where these experiments serve as an illustration of the theory. Reference to the growing number of experiments and numerical simulations where these concepts are used to learn details about particular systems can also be found in those articles.

2 Stochastic energetics

2.1 Stochastic Langevin dynamics

As basic model, we consider overdamped motion $x(\tau)$ of a “particle” or “system” governed by the Langevin equation

$$\dot{x} = \mu F(x, \lambda) + \zeta$$

where $F(x, \lambda)$ is a systematic force and $\zeta$ thermal noise with correlation $\langle \zeta(\tau) \zeta(\tau') \rangle = 2D\delta(\tau - \tau')$ where $D$ is the diffusion constant. In equilibrium, $D$ and the mobility $\mu$ are related by the Einstein relation $D = T \mu$ where $T$ is the
temperature of the surrounding medium with Boltzmann’s constant set to unity throughout the paper to make entropy dimensionless. In stochastic thermodynamics, one assumes that the strength of the noise is not affected by the presence of a time-dependent force. The range of validity of this crucial assumption can be tested experimentally or in simulations by comparing with theoretical result derived on the basis of this assumption.

The force

\[ F(x, \lambda) = -\partial_x V(x, \lambda) + f(x, \lambda) \quad (2) \]

can arise from a conservative potential \( V(x, \lambda) \) and/or be applied to the particle directly as \( f(x, \lambda) \). Both sources may be time-dependent through an external control parameter \( \lambda(\tau) \) varied according to some prescribed experimental protocol from \( \lambda(0) = \lambda_0 \) to \( \lambda(t) = \lambda_t \).

To keep the notation simple, we treat the coordinate \( x \) as if it were a single degree of freedom. In fact, all results discussed in the following hold for an arbitrary number of coupled degrees of freedom for which \( x \) and \( F \) become vectors and \( D \) and \( \mu \) (possibly \( x \)-dependent) matrices.

Equivalent to the Langevin equation is the corresponding Fokker-Planck equation for the probability \( p(x, \tau) \) to find the particle at \( x \) at time \( \tau \) as

\[ \partial_\tau p(x, \tau) = -\partial_x j(x, \tau) + \mu F(x, \lambda)p(x, \tau) - D \partial_x^2 p(x, \tau) \quad (3) \]

where \( j(x, \tau) \) is the current. This partial differential equation must be augmented by a normalized initial distribution \( p(x, 0) \equiv p_0(x) \). It will become crucial to distinguish the dynamical solution \( p(x, \tau) \) of this Fokker-Planck equation, which depends on this given initial condition, from the solution \( p^*(x, \lambda) \) for which the rhs of eq. (3) vanishes at any fixed \( \lambda \). The latter corresponds either to a steady state for a non-vanishing non-conservative force \( f \neq 0 \) or to equilibrium for \( f = 0 \), respectively.

A third equivalent description of the dynamics is given by assigning a weight

\[ p(x(\tau)|x_0) = \exp \left[ -\int_0^\tau d\tau \left( \dot{x} - \mu F \right)^2/4D + \mu F^2/2 \right] \quad (4) \]

to each path or trajectory. The last term in the exponent arises from the Jacobian \( |\partial \zeta/\partial x| \) in the Stratonovitch discretization required because the weight for a noise history \( p(\zeta(\tau)) \) is transformed into the weight of a trajectory \( p(x(\tau)) \). Path dependent observables can then be averaged using this weight in a path integral which requires a path-independent normalization such that summing the weight (4) over all paths is 1.

### 2.2 First law

As a major ingredient to stochastic thermodynamics, the first-law-like energy balance

\[ dw = dV + dq \quad (5) \]

identified for a Langevin equation by Sekimoto within his stochastic energetics approach [1] needs to be recalled.

The increment in work applied to the system

\[ dw = (\partial V/\partial \lambda) \dot{\lambda} d\tau + f d\tau \quad (6) \]

consists of two contributions. The first term arises from changing the potential (at fixed particle position) and the second from applying a non-conservative force to the particle directly. If one accepts these quite natural definitions, for the first law to hold along a trajectory the heat dissipated into the medium must be identified with

\[ dq = F dx. \quad (7) \]

This relation is quite physical since in an overdamped system the total force times the displacement corresponds to dissipation. Integrated along a trajectory of given length, one obtains the expression

\[ w[x(\tau)] = q[x(\tau)] + \Delta V = q[x(\tau)] + V(x_t, \lambda_t) - V(x_0, \lambda_0) \quad (8) \]

It is interesting and crucial to note that the heat dissipated along a trajectory can also be written using the path integral weight as

\[ q[x(\tau)] = \int_0^t F(x, \tau) \dot{x} d\tau = T \ln \frac{\tilde{p}[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} \quad (9) \]

where \( \tilde{p}[\tilde{x}(\tau)|\tilde{x}_0] \) is the weight of the backward path \( \tilde{x}(\tau) \equiv x(t - \tau) \) starting at \( \tilde{x}(0) = x(t) \) under the time-reversed protocol \( \lambda(\tau) \equiv \lambda(t - \tau) \).

In a recent experiment [26], the three quantities applied work, exchanged heat and internal energy were inferred from the trajectory of a colloidal particle pushed periodically by a laser trap against a repulsive substrate. The measured non-Gaussian distribution for the applied work shows that this system is driven beyond the linear response regime since it has been proven that within the linear response regime the work distribution is always Gaussian [27]. Moreover, the good agreement between the experimentally measured distribution and the theoretically calculated one indicates that the assumption of noise correlations being unaffected by the driving is still valid in this regime beyond linear response.

### 3 Entropy production

#### 3.1 Entropy production in the medium

The heat dissipated into the environment should be identified with an increase in entropy of the medium

\[ \Delta s_m[x(\tau)] \equiv q[x(\tau)]/T. \quad (10) \]

From a purely classical perspective, it might be disturbing to define an entropy change which depends on the trajectory and thus becomes a stochastic quantity. Usually, entropy is considered to be an ensemble quantity. In fact, it turns out that one can and should go even one step further and assign a second contribution to entropy as follows.
3.2 System entropy

Having solved the Fokker-Planck equation (3), one defines as a trajectory-dependent entropy of the system the quantity [2]

\[ s(\tau) \equiv -\ln p(x(\tau), \tau) \]  

(11)

where the probability \( p(x, \tau) \) obtained by solving the Fokker-Planck equation is evaluated along the stochastic trajectory \( x(\tau) \). Obviously, for any given trajectory \( x(\tau) \), the entropy \( s(\tau) \) depends on the given initial data \( p_0(x) \) and thus contains information on the whole ensemble. What at first sight might look just as a definition becomes useful thus contains information on the whole ensemble. What at first sight might look just as a definition becomes useful and interesting through the following observations:

(i) Upon averaging with the given ensemble \( p(x, \tau) \), the trajectory-dependent entropy becomes the usual ensemble entropy

\[ S(\tau) \equiv -\int dx \, p(x, \tau) \ln p(x, \tau) = \langle s(\tau) \rangle. \]  

(12)

(ii) In equilibrium, i.e. for \( f \equiv 0 \) and constant \( \lambda \), this definition assigns a stochastic entropy

\[ s(x(\tau)) = \langle V(x(\tau), \lambda) - F(\lambda) \rangle / T, \]  

(13)

with the free energy

\[ F(\lambda) \equiv -T \ln \int dx \, \exp[-V(x, \lambda)/T]. \]  

(14)

Thus, in equilibrium the well-known thermodynamic relation now holds along the trajectory at any time.

(iii) Most significantly, the total entropy change along a trajectory

\[ \Delta s_{\text{tot}} \equiv \Delta s_m + \Delta s \]  

(15)

with

\[ \Delta s = -\ln p(x_t, \lambda_t) + \ln p(x_0, \lambda_0) \]  

(16)

now obeys an integral fluctuation theorem (IFT) [2]

\[ \langle e^{-\Delta s_{\text{tot}}} \rangle = 1 \]  

(17)

which can be interpreted as a refinement of the second law \( \langle \Delta s_{\text{tot}} \rangle \geq 0 \). The latter follows from (17) by Jensen’s inequality. Here and throughout the paper the brackets \( \langle \ldots \rangle \) denote the non-equilibrium average generated by the Langevin dynamics from some given initial distribution \( p(x, 0) = p_0(x) \).

This integral fluctuation theorem for \( \Delta s_{\text{tot}} \) is quite universal since it holds for any kind of initial condition (not only for \( p_0(x_0) = p^0(x_0, \lambda_0) \)), any time-dependence of force and potential, with (for \( f = 0 \)) and without (for \( f \neq 0 \)) detailed balance at fixed \( \lambda \), and any length of trajectory \( t \).

3.3 Invariance under coordinate transformations

The entropy as defined in (11) has the formal deficiency that strictly speaking \( \ln p(x(\tau), \tau) \) is not defined since \( p(x, \tau) \) is a density. Apparently more disturbingly, this expression is not invariant under non-linear transformations of the coordinates. In fact, both deficiencies which also hold for the ensemble entropy (12) are related and can be cured easily as follows by implicitly invoking the notion of relative entropy.

A formally proper definition of the stochastic entropy starts by describing the trajectory using canonical variables. After integrating out the momenta, for a system with \( N \) particles with Cartesian positions \( \{x_i\} \), one should define the entropy as

\[ s(\{x_i(\tau)\}) \equiv -\ln[p(\{x_i(\tau)\})] \]  

(18)

where \( \lambda_T \) is the thermal de Broglie length. If one now considers this dynamics in other coordinates \( \{y_i\} \), one should use

\[ s(\{y_i(\tau)\}) \equiv -\ln[p(\{y_i(\tau)\}, \tau) \det \{\partial y_i/\partial x\} \lambda_T^{3N}]. \]  

(19)

This correction with the Jacobian ensures that the entropy both on the trajectory as well as on the ensemble level is independent of the coordinates used to describe the stochastic motion. Of course, this statement is no longer true if the transformation from \( \{x_i\} \) to \( \{y_i\} \) is not one to one. Indeed, if some degrees of freedom are integrated out the entropy does and should change.

4 A unifying integral fluctuation theorem (IFT)

The IFT for entropy production (17) follows from a more general fluctuation theorem which unifies several relations previously derived independently. Based on the concept of time-reversed trajectories and time-reversed protocol [5, 10, 15], it is easy to prove the relation [2]

\[ \langle \exp[-\Delta s_m] \rangle p_1(x_t)/p_0(x_0) = 1 \]  

(20)

for any function \( p_1(x) \) with normalization \( \int dx \, p_1(x) = 1 \). Here, the initial distribution \( p_0(x) \) is arbitrary. By using the first law (8) this relation can also be written in the form

\[ \langle \exp[-(w - \Delta V)/T] \rangle p_1(x_t)/p_0(x_0) = 1 \]  

(21)

with no reference to an entropy change.

The arguably most natural choice for the function \( p_1(x) \) is to take the solution \( p(x, \tau) \) of the Fokker-Planck equation at time \( t \) which leads to the IFT (17) for the total entropy production. Other choices lead to the following relations originally derived differently.

4.1 Jarzynski relation (JR)

The Jarzynski relation [7]

\[ \langle \exp[-w/T] \rangle = \langle \exp[-\Delta F/T] \rangle \]  

(22)
expresses the free energy difference $\Delta F \equiv \mathcal{F}(\lambda_t) - \mathcal{F}(\lambda_0)$ between two equilibrium states as a non-linear average over the work required to drive the system from one equilibrium state to another. In the present formalism it follows for motion in a time-dependent potential $V(x, \lambda(\tau))$ without any additional non-conservative force $f \equiv 0$ by plugging into the general FT (21) the equilibrium initial distribution $p_0(x) = \exp[-(V(x, \lambda_0) - \mathcal{F}(\lambda_0))/T]$ and the function $p_1(x) = \exp[-(V(x, \lambda_t) - \mathcal{F}(\lambda_t))/T]$. It should be clear that this choice for $p_1(x)$ exploits a mathematical freedom. It does not imply that the system has acquired this new equilibrium distribution at the end of the process. In fact, the actual distribution at the end will be $p(x, t)$.

4.2 Bochkov-Kuzovlev relation (BKR)

For a system initially in equilibrium in a time-independent potential $V_0(x)$, which is for $0 \leq \tau \leq t$ subject to an additional space and time-dependent force $f(x, \tau)$, one obtains from (21) the relation

$$\langle \exp[-\tilde{w}/T] \rangle = 1$$

(23)

with

$$\tilde{w} \equiv \int_{x_0}^{x_t} f(x, \lambda(\tau)) dx$$

(24)

by choosing $p_1(x) = p_0(x) = \exp[-(V_0(x) - \mathcal{F}_0)/T]$. Under these conditions, the exponent $\tilde{w}$ is the work performed at the system. Since this relation derived much earlier by Bochkov and Kuzovlev [28, 29] looks almost like the Jarzynski relation there have been both claims that the two are the same and some confusion about the apparent contradiction that $\exp[-w/T]$ seems to be both $\exp[-\Delta \mathcal{F}/T]$ or 1.

The present derivation shows that the two relations are different since they apply a priori to somewhat different situations. The JR as discussed above applies to processes in a time-dependent potential, whereas the BKR relation as discussed here applies to a process in a constant potential with some additional force. If, however, in the latter case, this explicit force arises from a potential as well, $f(x, \tau) = -V_1'(x, \tau)$, there still seems to be an ambiguity. It can be resolved by recognizing that in this case the work entering the BKR (23)

$$\tilde{w} = \int dx f = -\int dx V_1'(x) = -\Delta V_1 + w$$

(25)

differs by a boundary term from the definition of work $w$ given in eq. (6) and used throughout this paper. Thus, if the force arises from a time-dependent but conservative potential both the BKR in the form $\langle \exp[-\tilde{w}/T] \rangle = 1$ and the JR (22) hold. The connection between the two relations has previously been discussed within a Hamiltonian dynamics approach [30].

4.3 Hummer and Szabo relation

As an important application, the Jarzynski relation can be used to reconstruct the free energy landscape of a biomolecule $G(x)$ where $x$ denotes a “reaction coordinate” like the end-to-end distance in forced protein folding as reviewed in [19]. If one end of such a protein is attached to an AFM tip or an optical trap via a potential $(k/2)(x - \lambda(\tau))^2$ where $k$ is the stiffness of the cantilever or trap and $\lambda(\tau)$ the time-dependent center, the total potential reads

$$V(x, \lambda(\tau)) = G(x) + (k/2)(\lambda(\tau) - x)^2.$$  

(26)

The initial distribution $p_0(x) = \exp[-(V(x, \lambda_0) - \mathcal{F}(\lambda_0))/T]$ and the choice

$$p_1(x) = \delta(x - z)\exp[-[V(x, \lambda_t)/T]/\exp[-[V(z, \lambda_t)/T]$$

(27)

plugged into (20) leads to the potential reconstruction formula

$$e^{-G(x)} = \langle \delta[z - x(t)]e^{-w(t)} \rangle e^{(k/2)(z - \lambda(t))^2} e^{\mathcal{F}(\lambda_0)}$$

(28)

first derived by Hummer and Szabo [31] using a Feynman-Kac approach. Thus to get the potential $G(z)$ it is sufficient to select those trajectories that have reached $z$ after time $t$ and record the corresponding work $w(t) = k \int_0^t d\tau (\lambda(\tau) - x(\tau))$ accumulated up to time $t$. An experiment on unfolding RNA has been one of the first real-world test of this $z$-resolved Jarzynski relation [32].

4.4 Integral “end-point” relations

A variety of “end-point” relations can be generated from (20) as follows.

By choosing $p_1(x) = p(x, t)g(x)/\langle g(x) \rangle$, one obtains

$$\langle g(x_t) \exp[-\Delta s_{tot}] \rangle = \langle g(x_t) \rangle$$

(29)

for any function $g(x)$ [33]. Likewise, for $f \equiv 0$ and $V(x, \lambda(\tau))$, by choosing $p_1(x) = g(x)\exp[-(V(x, \lambda_t) - \mathcal{F}(\lambda_t))/\langle g(x) \rangle_{eq, \lambda_t}$, one obtains

$$\langle g(x_t) \exp[-(w - \Delta \mathcal{F})/T] \rangle = \langle g(x) \rangle_{eq, \lambda_t}$$

(30)

which has been first derived by Crooks [10]. Here, the average on the right hand side is the equilibrium average at the final value of the control parameter.

In the same fashion, one can derive

$$\langle g(x_t) \exp[-\tilde{w}/T] \rangle = \langle g(x) \rangle_{eq, \lambda_0}$$

(31)

by choosing $p_1(x) = g(x)\exp[-(V(x, \lambda_0) - \mathcal{F}(\lambda_0))/\langle g(x) \rangle_{eq, \lambda_0}$ for a time-independent potential and arbitrary force $f(x, \tau)$ which is the end-point relation corresponding to the BKR.

5 Non-equilibrium steady states (NESSs)

5.1 Characterization

Non-equilibrium does not necessarily require that the system is driven by time-dependent potentials or forces as discussed so far. A non-equilibrium steady state (NESS) is
generated if time-independent but non-conservative forces $f(x)$ act on the system. Such systems are characterized by a time-independent or stationary distribution

$$p^s(x) \equiv \exp[-\phi(x)].$$

(32)

As a fundamental difficulty, there seems to be no simple way to calculate $p^s(x)$ or, equivalently, the “non-equilibrium potential” $\phi(x)$. In one dimension, it follows from quadratures but for more degrees of freedom, setting the right-hand-side of the Fokker-Plank equation (3) to zero represents a formidable partial differential equation. Physically, the complexity arises from the presence of a non-zero stationary current (in the full configuration space)

$$j^s(x) = \mu F(x)p^s(x) - D\partial_x p^s(x) \equiv v^s(x)p^s(x)$$

(33)

which defines the mean local velocity $v^s(x)$. This current leads to a mean entropy production rate

$$\sigma \equiv \langle \Delta s_{\text{tot}} \rangle / t = \int dx j^s D^{-1} j^s / p^s.$$  

(34)

Even though the stationary distribution and currents can not be calculated in general, a variety of exact relations concerning entropy production and heat dissipation have been derived.

5.2 Detailed fluctuation theorem (DFT)

In a NESS, the (detailed) fluctuation theorem

$$p(-\Delta s_{\text{tot}})/p(\Delta s_{\text{tot}}) = \exp[-\Delta s_{\text{tot}}]$$

(35)

expresses a symmetry which the probability distribution $p(\Delta s_{\text{tot}})$ for the total entropy production after time $t$ in the steady state obeys. This relation has first been found in simulations of two-dimensional sheared fluids [3] and then proven by Gallavotti and Cohen [4] using assumptions about chaotic dynamics. A much simpler proof has later been given by Kurchan [5] and Lebowitz and Spohn [6] using a stochastic dynamics for diffusive motion. Strictly speaking, in all these works the relation holds only asymptotically in the long-time limit since entropy production had been associated with what is here called entropy production in the medium. If one includes the entropy change of the system (11), the DFT holds even for finite times in the steady state [2]. This fact shows again the advantage of the entropy definition introduced above.

While the DFT for (medium) entropy production has been tested experimentally for quite a number of systems, a first test including the system entropy has recently been achieved for a colloidal particle driven by a constant force along a periodic potential [34]. This experimental set-up constitutes the simplest realization of genuine NESS. The same set-up has been used to test other recent aspects of stochastic thermodynamics like the possibility to infer the potential $V(x)$ from the measured stationary distribution and current [35] or a generalization of the Einstein relation beyond the linear response regime [36,37].

The DFT for total entropy production holds even under the more general situation of periodic driving $F(x,\tau) = F(x,\tau + \tau_p)$, where $\tau_p$ is the period, if (i) the system has settled into a periodic distribution $p(x,\tau) = p(x,\tau + \tau_p)$, and (ii) the trajectory length $t$ is an integer multiple of $\tau_p$.

For the distribution of work $p(W)$, a similar DFT can be proven provided the protocol is symmetric $\lambda(\tau) = \lambda(t - \tau)$, the non-conservative force zero, and the systems starts in equilibrium initially. For such conditions, the DFT for work was recently tested experimentally using a a colloidal particle pushed periodically by a laser trap against a repulsive substrate [26].

5.3 Transitions between different NESSs

Just as a system can be driven from one equilibrium state to another by a time dependent potential $V(x,\lambda(\tau))$, one can generate a transition from one NESS characterized by $f_1(x)$ to another one at $f_2(x)$ by a time-dependent force $f(\tau)$. For the thermodynamic analysis of such a transition, it has become convenient to split the dissipated heat quite generally into two contributions,

$$\Delta q \equiv \Delta q_{\text{hk}} + \Delta q_{\text{ex}}$$

(36)

where the house keeping heat

$$q_{\text{hk}} \equiv \int_0^t d\tau \dot{x}(\tau) \mu^{-1} v^s(x(\tau))$$

(37)

is the heat inevitably dissipated in maintaining a NESS [38,39]. For a transition from one NESS to another, one has both the IFT for the house keeping heat [40]

$$\langle \exp[-q_{\text{hk}}/T] \rangle = 1$$

(38)

and the Hatano-Sasa relation [39]

$$\langle \exp[-(q_{\text{ex}}/T + \Delta \phi(x,\lambda)) \rangle = 1.$$  

(39)

The latter relation allows one to obtain Clausius-type inequalities for the minimal entropy change related to transitions between different NESSs. Experimentally, the Hatano-Sasa relation has been verified for a colloidal particle pulled through a viscous liquid at different velocities which corresponds to different steady states [41].

6 General stochastic dynamics

6.1 Entropy production

For the mechanically driven systems described so far the identification of a first law is simple since both internal energy and applied work are rather clear concepts. On the other hand the proof of both the IFT and the DFT shows that the first law does not crucially enter. In fact,
the proof of these theorems exploits only the fact that under time-reversal entropy production changes sign. If the changes in the medium entropy are written in the form (9, 10) only transition rates enter. Likewise, the identification of system entropy requires only a solution of the Fokker-Plank equation. Therefore, similar relations should hold for a much larger class of stochastic dynamic models without reference to a first law.

Indeed, one can derive these relations for stochastic dynamics on an arbitrary set of states \{n\} where transitions between states m and n occur with a rate \(w_{mn}(\lambda)\), which may depend on an externally controlled time-dependent parameter \(\lambda(\tau)\). The master equation for the time-dependent probability \(p_n(\tau)\) then reads

\[
\frac{\partial \tau}{\partial \tau} p_n(\tau) = \sum_{m \neq n} [w_{mn}(\lambda)p_m(\tau) - w_{nm}(\lambda)p_n(\tau)].
\] (40)

The analogue of the fluctuating trajectory \(x(\tau)\) in the mechanical case becomes a stochastic trajectory \(n(\tau)\) that starts at \(n_0\) and jumps at times \(\tau_j\) from \(n_j^{-}\) to \(n_j^{+}\) ending up at \(n_t\). As entropy along this trajectory, one defines [2]

\[
s(\tau) \equiv -\ln p_n(\tau)
\] (41)

where \(p_n(\tau)\) is the solution \(p_n(\tau)\) of the master equation (40) for a given initial distribution \(p_n(0)\) taken along the specific trajectory \(n(\tau)\). As above, this entropy will depend on the chosen initial distribution.

The entropy \(s(\tau)\) becomes time-dependent due to two sources. First, even if the system does not jump, \(p_n(\tau)\) can be time-dependent either for time-independent rates due to possible relaxation from a non-stationary initial state or, for time-dependent rates, due to the explicit time-dependence of \(p_n(\tau)\). Including the jumps, the change of system entropy reads

\[
\dot{s}(\tau) = -\frac{\partial \tau}{\partial \tau} p_n(\tau) - \sum_j \delta(\tau - \tau_j) \ln \frac{p_{n_j^+}}{p_{n_j^-}}
\] (42)

\[
\equiv \dot{s}_{\text{tot}}(\tau) - \dot{s}_m(\tau),
\] (43)

where we define the change in medium entropy to be

\[
\dot{s}_m(\tau) \equiv \sum_j \delta(\tau - \tau_j) \ln \frac{w_{n_j^-} n_j^+}{w_{n_j^+} n_j^-}.
\] (44)

For a general system, associating the logarithm of the ratio between forward jump rate and backward jump rate with an entropy change of the medium seems to be an arbitrary definition. Two facts motivate this choice. First, it corresponds precisely to what has been identified as exchanged heat in the mechanically driven case (9,10). Second, one can easily show [2] that with this choice the total entropy production \(\Delta s_{\text{tot}}\) fulfills both the IFT (20) for arbitrary initial condition, arbitrary driving and any length of trajectory and the DFT (35) in the steady state, i.e. for constant rates. Of course, in a general system, there is no justification to identify the change in medium entropy with an exchanged heat.

### 6.2 Two classes of systems

For a discussion, it is appropriate to distinguish two classes of systems based on whether or not their stationary distribution \(p_n^s\) for fixed \(\lambda\) obeys the detailed balance condition

\[
p_n^s(\lambda)w_{nm}(\lambda) = p_m^s(\lambda)w_{mn}(\lambda).
\] (45)

#### 6.2.1 Detailed balanced systems

System which obey detailed balance formally resemble mechanically driven systems without non-conservative force since for the latter, at fixed potential, detailed balance holds as well. Exploiting this analogy, one can assign a (dimensionless) internal “energy”

\[
e_n(\lambda) \equiv -\ln p_n^s(\lambda)
\] (46)

to each state. The ratio of the rates then obeys

\[
\frac{w_{nm}(\lambda)}{w_{mn}(\lambda)} = \exp[e_n(\lambda) - e_m(\lambda)]
\] (47)

which looks like the familiar detailed balance condition in equilibrium. For time-dependent rates \(w_{nm}(\lambda(\tau))\), one can now formally associate a first law along the trajectory as follows. The analogue of the work is written in the form

\[
w \equiv \int_0^t \partial \lambda e_n(\lambda(t)) = \sum_j \ln \frac{w_{n_j^-} n_j^+}{w_{n_j^+} n_j^-} + e_n(t)(\lambda_t) - e_n(0)(\lambda_0)
\] (48)

where the second lines identifies the “heat” with the medium entropy change and the last term represents a change in “internal energy”. Even though one should not put physical meaning into these definitions for an abstract stochastic dynamics, the analogy helps to see immediately that the fluctuation relations quoted above for zero non-conservative force hold for these more general systems as well. Specifically, one has the “generalized” JR (22) and the corresponding end-point relation (30) with \(\Delta F = 0\) and \(T = 1\). Similarly, with the identification

\[
\tilde{w} \equiv \sum_j [e_{n_j^+}(\tau_j) - e_{n_j^-}(\tau_j)] - [e_{n_j^+}(0) - e_{n_j^-}(0)]
\] (49)

both (23) and (31) with \(T = 1\) hold for such a master equation dynamics. The initial state in all cases is the steady state corresponding to \(\lambda_0\).

The simplest realization of such a detailed-balanced system is any two-level system with time-dependent rates. In recent experiments [42,43], an optically driven defect center in diamond has been used to test the IFT for total entropy production and the analogy of the Jarzynski relation for such a general stochastic dynamics [44].
6.2.2 Unbalanced systems

The more interesting class of networks, however, are those for which at constant λ the detailed balance condition (45) is not fulfilled. Within the mechanical analogy, they correspond to systems with non-vanishing non-conservative force \( f \neq 0 \). For a mapping to this case, one would have to find the analogy of the conservative potential and the force \( f \) which is responsible for breaking detailed balance. The apparent arbitrariness of such a division is resolved by forming the analogy of the house-keeping heat (37) as

\[
q_{hk}[n(\tau)] = \sum_j \ln \frac{p_{n_j}^+ w_{n_j^-} n_j^+}{p_{n_j}^- w_{n_j^+} n_j^-}. \tag{50}
\]

For detailed balanced systems, this expression vanishes identically. With this identification, it is clear that the fluctuation relations (39) hold as well using these definitions (and \( T = 1 \)). For further fluctuation relations in such systems, see the comprehensive review [22].

7 (Bio)chemically driven systems

Biochemical reactions constitute another important class of systems for which an embedding heat bath provides the source of stochastic dynamics. Therefore, the concepts reviewed so far are ideally suited to develop a stochastic thermodynamics of such systems. Conceptually, two situations should be distinguished described here only briefly.

7.1 A single enzym or motor

An enzym or molecular motor can be considered as a system which stochastically undergoes transitions from one state \( m \) to another state \( n \). In such a transition, a chemical reaction may be involved like hydrolysis which transforms one molecule ATP to ADP and a phosphate. These three molecular species are externally maintained at non-equilibrium conditions thereby providing a source of chemical energy, i.e., chemical work, to the system. In each transition, this work will be transformed into mechanical work, dissipating heat, or changes in the internal energy (with any combination of positive and negative contributions). The formalism of stochastic thermodynamics allows to identify work, heat, and internal energy for each single transition [33, 45] in close analogy to the mechanically driven case, thus illustrating the concepts described above for a more general stochastic dynamics.

7.2 Chemical reaction networks

Chemical reaction networks consist of a number of possible reactions taking place between different types of reactants. The rates for each reaction are proportional to the number of possible reaction partners thus involving the stochiometric coefficients. In order to describe such a network under non-equilibrium conditions, one should separate the reactants into two classes. The first class comprise species whose concentration, i.e., chemical potentials, are fixed externally at constant values (like the ATP concentration in the cell). The second species comprises molecules whose number is traced along a trajectory. Under such conditions, chemical work, dissipating heat and changes in internal energy can be identified on the level of a single reaction trajectory for which the general formalism yields IFTs, generalization of the Jarzynski relation and other relations [46]. So far, no experiments illustrating these concepts seem to have been reported.

8 Stochastic dynamics of fields

The Langevin dynamics discussed for the mechanically driven case can easily be generalized to \( N \) coupled degrees of freedom [33, 47]. A further generalization to the dynamics of stochastic fields, which as an exciting perspective looks obvious, seems not yet to been explored systematically.

We assume a dynamical equation for a field \( \phi(r, \tau) \) with \( r \in \mathbb{R}^2 \) of the type

\[
\partial_\tau \phi(r, \tau) = F[\phi(r, \tau)] + \zeta(r, \tau) \tag{51}
\]

where \( F[\phi(r, \tau)] \) is an arbitrary possibly non-linear functional and \( \zeta(r, \tau) \) Gaussian white noise of strength

\[
\langle \zeta(r, \tau) \zeta(r', \tau') \rangle = 2D (r-r') \delta(\tau-\tau') \tag{52}
\]

with a spatial correlation \( D(r-r') \). Motivated by the mechanically driven case, one defines a change in medium entropy

\[
\Delta s_m \equiv \int_0^t d\tau \int dr \int dr' \partial_\tau \phi(r, \tau) D^{-1} (r-r') F[\phi(r', \tau)]. \tag{53}
\]

and a change in entropy of the field

\[
\Delta s \equiv -\ln p(\phi(r, \tau), \tau) \big|_{0}^{t} \tag{54}
\]

where \( p(\phi(r, \tau), \tau) \) is the evolving probability distribution for the field.

The validity of the IFT for total entropy production (20) for arbitrary initial state and arbitrary length \( t \) of the trajectory is obvious. If the dynamics settles into a steady state \( p^*(\phi(r, \tau)) \), the DFT (35) also holds.

As an illustrative example consider the KPZ equation

\[
\partial_\tau h = \lambda (\nabla h)^2 + \nu \nabla^2 h + \zeta \tag{55}
\]

for the height field \( h(r, \tau) \) of a growing interface where \( \lambda \) measures the strength of the non-linearity and \( \nu \) corresponds to a surface tension [48]. The white noise is uncorrelated in space and time \( \langle \zeta(r, \tau) \zeta(r', \tau') \rangle = 2D (r-r') \delta(\tau-\tau') \) (setting \( D \) to 1 for notational simplicity).
In the steady state, the total entropy production becomes
\[
\Delta s_{\text{tot}} = \lambda \int_0^t \int d\tau (\partial_\tau h)(\nabla h)^2
\]
\[- \left[ (\nu/2) \int d\tau (\nabla h)^2 + \ln p^*(h) \right]_0^t. \quad (56)
\]
In one dimension, the known stationary distribution \(p^*(h) \sim \exp[-(\nu/2) \int d\tau (\nabla h)^2]\) cancels the boundary term of the medium entropy so that the total entropy production over a time \(t\) along a trajectory in the steady state is given exactly by
\[
\Delta s_{\text{tot}} = \lambda \int_0^t d\tau (\partial_\tau h)(\nabla h)^2. \quad (57)
\]

The DFT (35) now makes a statement about the probability distribution of the time integral of this particular product involving three powers of the field. By expanding the exponent, one can generate relations between particular three point, six point, nine point functions and so on. While the immediate benefit of such relations is not obvious, it looks worthwhile to explore the consequences of this symmetry for correlations functions.

In higher dimensions, the stationary distribution is unknown and the exact statement holds only for the sum of the three terms in (56). Clearly, only the term in the first line is extensive in time so one might expect that focussing on this term in the long time limit may be admissible but one should be aware of corrections arising from the two boundary terms. In any case, one could speculate whether the DFT restricts exponents or scaling functions if a suitable scaling ansatz for correlation functions is put into it.

If useful information can be extracted from such an approach for the KPZ equation, one might afterwards be tempted to look at other stochastic field equations. A particularly intriguing case are the Navier Stokes equations with noise terms used to stochastically drive the system on large scales to model turbulence. In fact, for two-dimensional turbulence such an approach has been applied to the enstrophy cascade [49].

9 Concluding remark

The notion “stochastic thermodynamics” had been introduced two decades ago for an interpretation of chemical reaction networks in terms of thermodynamic notions on the ensemble level [50]. From the present perspective, it seems even more appropriate to use this term for the refined description along the fluctuating trajectory. Both for mechanically and chemically driven systems in a surrounding heat bath, the thermodynamic concepts can literally and consistently be applied on this level. As a generalization to arbitrary stochastic dynamics, analogues of work, heat and internal energy obey similar exact relations which ultimately all arise from the behaviour of the dynamics under time-reversal. How much closer such an approach can lead us towards a systematic understanding of non-equilibrium phenomena in general is a question too early to be answered yet.

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