Stochastic thermodynamics for kinetic equations.

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Stochastic thermodynamics is formulated for variables that are odd under time reversal. The invariance under spatial rotation of the collision rates due to the isotropy of the heat bath is shown to be a crucial ingredient. An alternative detailed fluctuation theorem is derived, expressed solely in terms of forward statistics. It is illustrated for a linear kinetic equation with kangaroo rates.

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The second law of thermodynamics is arguably one of the most general laws of nature. While originally stipulating the increase of total entropy in a closed isolated system $\Delta S_{\text{tot}} \geq 0$, it was reformulated by splitting the entropy change $\Delta S$ of an open system into the sum $\Delta S = \Delta_s + \Delta_e$ of a non-negative entropy production term $\Delta_s \geq 0$ plus an entropy exchange contribution $\Delta_e$. In particular when in contact with a single heat bath at temperature $T$, the exchange is given by $\Delta_e = Q/T$, where $Q$ is the amount of heat into the system. Over the past two decades, a much deeper formulation of the second law has been achieved by focusing on small open systems. One can still define all the above mentioned quantities, but they will now fluctuate from one measurement to another. Using lower the above mentioned quantities, but they will now fluctuate from one measurement to another. Using lower.

\begin{equation}
\left[ \frac{\partial}{\partial t} + v \frac{\partial}{\partial x} + a \frac{\partial}{\partial v} \right] P(x,v; t) = \int dv' \left[ k(v' \rightarrow v)P(x,v'; t) - k(v \rightarrow v')P(x,v; t) \right].
\end{equation}

Here $k(v' \rightarrow v)$ is the transition probability per unit time (rate) for a change of velocity from $v'$ to $v$. Formulation of the first law at the trajectory level is straightforward.

The energy $e(t)$ of a particle in the constant external force field $F$ is:

\begin{equation}
e(t) = -Fx(t) + \frac{1}{2}mv^2(t),
\end{equation}
where \(x(t)\) and \(v(t)\) are the position and velocity of the particle at time \(t\) in the given realization. The “ensemble” version of the first law is obtained by averaging with respect to the probability density \(P(x,v,t)\):

\[
E(t) = \langle e(t) \rangle = -F(x(t)) + \frac{1}{2} m \langle v^2(t) \rangle.
\]

In-between collisions, potential energy is converted into kinetic energy following Newton’s law \(m \dot{v}(t) = F\), hence this non-dissipative process produces no net energy \(\dot{e}(t) = 0\), and neither work nor heat are exchanged. The punctual collisions with the heat bath however lead to an instantaneous exchange of energy under the form of heat:

\[
\dot{e}(t) = \dot{q}(t),
\]

with \(\dot{q}(t)\) a sum of delta functions at the instants of the collision and with amplitude \(\frac{1}{2} m (v^2 - v'^2)\) for a collision changing the velocity from \(v'\) to \(v\). At the ensemble level, the resulting heat flux \(\dot{Q}(t)\) is obtained by averaging over the frequency of such collisions:

\[
\dot{E}(t) = \dot{Q}(t) = \int \int dv dv' k(v' \to v) P(v', t) \frac{1}{2} m (v^2 - v'^2).
\]

We next turn to the second law and formulate it first at the ensemble level. The “ensemble” entropy associated to the distribution \(P(x,v,t)\) is given by \(S(t) = -k_B \int P(x,v,t) \ln P(x,v,t)\), with \(k_B\) Boltzmann’s constant. When considering the time derivative of this quantity, we note that the motion is purely Hamiltonian in-between collisions. Following Liouville’s theorem, this part of the dynamics leaves the entropy invariant \([17]\). Hence, we need only to focus on the change of the entropy induced by the dissipative collisions, affecting solely the velocity variables. From:

\[
S(t) = -k_B \int P(v,t) \ln P(v,t)
\]

we find in combination with the evolution equation for \(P(v,t)\), obtained from Eq. \([1]\), and following some simple manipulations, that the rate of change of the entropy is given by:

\[
\dot{S} = k_B \int \int dv dv' k(v' \to v) P(v', t) \ln \frac{P(v', t)}{P(v, t)}.
\]

This rate of entropy change can thus be rewritten under the standard form \(\dot{S} = \dot{S}_d + \dot{S}_e\), with the rates of “entropy production” and “entropy exchange” given by:

\[
\dot{S}_d = \int \int dv dv' k(v' \to v) P(v', t) \ln \frac{k(v' \to v)}{k(v \to v')} \geq 0,
\]

\[
\dot{S}_e = \int \int dv dv' k(v' \to v) P(v', t) \ln \frac{k(v \to v')}{k(v' \to v)}.
\]

These results are mathematically exact but, in order to achieve a correct thermodynamic interpretation of the entropy production and exchange, one needs in addition proper physical input about the collision mechanism, i.e. about the collision rate. We focus here on the simplest case in which the collision process represents energy exchange with a single isotropic thermal reservoir at temperature \(T\). As a result the collision process must induce, in absence of an external force, a relaxation to the Maxwell-Boltzmann distribution \(\varphi_0\), i.e., one has:

\[
\int dv' k(v \to v') \varphi_0(v) = \int dv' k(v' \to v) \varphi_0(v'),
\]

with \(\varphi_0(v) = \frac{e^{-v^2/2\sigma^2}}{\sigma \sqrt{2\pi}}\), \(\sigma^2 = mk_BT\).

As was realised first by Onsager \([17]\), micro-reversibility leads to a more stringent condition of detailed balance:

\[
k(v \to v') \varphi_0(v) = k(-v' \to -v) \varphi_0(-v').
\]

This detailed balance relation involves velocity inversion, and seems to be at variance with the condition Eq. \([9]\). The discrepancy is solved by making the crucial observation that, for a collision describing heat exchange with an isotropic bath, there is an additional symmetry requirement of invariance under reflection (and more generally under rotation \([13][19]\)):

\[
k(v \to v') \varphi_0(v) = k(-v' \to -v) \varphi_0(v).
\]

With this extra condition, the detailed balance relation Eq. \([11]\) implies Eq. \([9]\).

Eq. \([11]\) allows to make the consistent connection between first and second laws: the entropy exchange \(\dot{S}_e\) can be rewritten (\(\varphi_0(-v) = \varphi_0(v)\)):

\[
\dot{S}_e = k_B \int \int dv dv' k(v' \to v) P(v', t) \ln \frac{\varphi_0(v')}{\varphi_0(v)} = \frac{\dot{Q}}{T},
\]

where \(\dot{Q}\) is the rate of energy (heat) exchange from the bath to the particle, cf. Eqs. \([\text{9}][\text{10}]\). The entropy production is zero if and only if \(k(v' \to v) P(v') = k(v \to v') P(v)\), implying that \(P(v)/P(v') = \varphi_0(v)/\varphi_0(v')\) and hence \(P(v) = \varphi_0(v)\). We conclude that entropy production vanishes if and only if detailed balance is satisfied.

We now show that both Eq. \([11]\) and Eq. \([12]\) are crucial to formulate the second law at the trajectory level. The stochastic entropy for the velocity variables reads \([9]\):

\[
s(t) = -k_B \ln P(v(t), t).
\]

Note that this entropy still retains an ensemble character, as one needs to specify the probability distribution \(P(v,t)\), which is the probability to observe the particle with velocity \(v\) at time \(t\) starting from some specific initial probability distribution. This so-called forward experiment is ran from initial time \(t_i\) to some final time \(t_f\). We now write:

\[
\dot{s} = \dot{S}_d + \dot{S}_e,
\]

(15)
where the trajectory entropy exchange is the obvious analogue of the ensemble value given in Eq. (13): \( \delta s = \dot{q}/T \).

The meaning of the trajectory entropy production is most easily clarified by integrating Eq. (15) over a finite time, leading to the finite difference balance:

\[
\Delta s = \Delta_i s + \Delta_v s, \tag{16}
\]

with \( \Delta_v s = q/T \) and \( q \) is the total amount of heat received (by collisions) from the heat bath in the realization under consideration. An elegant derivation of the celebrated fluctuation theorem for the trajectory entropy production proceeds with the consideration of the probability for a trajectory in forward and reverse dynamics. We consider the simplest case of steady state operation, with the initial state of the forward experiment under acceleration \( a \) sampled from the steady state distribution \( P^a(v) \). The reverse trajectory proceeds under the same acceleration \( a \), starting with the final distribution of the forward probability, but with inverted speeds. Its properties will be identified with a superscript tilde. Let \( P(\Pi) \) and \( \bar{P}(\Pi) \) denote the probabilities for a forward and reverse trajectory, \( \Pi \) and \( \bar{\Pi} \), respectively. One now verifies the following striking equality:

\[
\Delta_i s = k_B \ln \frac{P(\Pi)}{\bar{P}(\Pi)}. \tag{17}
\]

The proof goes as follows. The probability of a trajectory involves the initial probability, the probability for not having collisions in-between the transitions, and the probability for transitions. Since the starting probability of the reverse dynamics is equal to the final probability of the direct dynamics, the log ratio of the initial probability contributions reproduces \( \Delta s = k_B \ln P(v(t_f), t_f) - k_B \ln P(v(t_i), t_i) \), cf. Eq. (14). Due to the detailed balance condition Eq. (11), the log ratio of probabilities for collisions in forward and backward dynamics, cf. \( \ln k(v' \rightarrow v)/k(-v \rightarrow -v') = \ln \varphi_0(v)/\varphi_0(v') = (v^2 - v'^2)/(2k_B T) \), reproduces \( \Delta_v s = -q/T \). Finally, due to the reflection symmetry Eq. (12), the probability for having no collisions, determined by the rates \( k(v' \rightarrow v) \) and \( k(-v' \rightarrow -v) \) when we have a velocity \( v' \) and \( -v' \), respectively, is the same in forward and backward trajectories. Hence the corresponding terms cancel out, and we have \( \Delta_i s = \Delta s - \Delta_v s \) as required. We conclude that both at the ensemble level and at the trajectory level, the combination of detailed balance condition with the reflection symmetry are essential for a consistent stochastic thermodynamic interpretation. The implications of Eq. (17) are well known [20]: the probability distributions \( P(\Delta_i s) \) and \( \bar{P}(-\Delta_i s) \) for observing an entropy production \( \Delta_i s \) in the forward process and minus this value in the backward process obey a detailed fluctuation theorem:

\[
\frac{P(\Delta_i s)}{P(-\Delta_i s)} = \exp(\Delta_i s), \tag{18}
\]

from which follows the integral fluctuation theorem: \( \langle \exp(-\Delta_i s) \rangle = 1 \). A comment concerning the interpretation of Eq. (18) is in place, for more details see [10, 11, 21–23]. In general \(-\Delta_i s \) is not the entropy production of the reverse trajectory. This will only be the case if the inverse “tilde” process is an involution, i.e., twice this operation is equal to the identity. In particular, the final probability distribution of the reverse process should be equal to the initial distribution of the forward process. In the case of even variables, a sufficient condition is that the forward process starts and ends in a steady state. For odd variables, this condition is not sufficient as is illustrated by the above example: the velocity inversion at the end of the forward process produces a probability distribution that is no longer at the steady state when \( a \neq 0 \). There is however a simple procedure to cure this problem and to obtain a detailed fluctuation theorem which is, just like the integral fluctuation theorem, expressed solely in terms of a (slightly modified) forward process. At the end of the forward process, one performs an instantaneous switch of the probability distribution from \( P(v_f) \) to \( P(-v_f) \), implying and entropy change of \( \Delta_v s = \ln P(v_f)/P(-v_f) \). This is, on average (with respect to \( P(v_f) \)), an irreversible entropy producing step. With this additional step, velocity inversion at the end of the forward will reproduce the steady state distribution, which is also in the case considered here the initial distribution of the forward process. In conclusion the corrected entropy production \( \Delta_i s_c = \Delta s + \Delta_v s \) will obey a symmetric detailed fluctuation theorem:

\[
\frac{P(\Delta_i s_c)}{P(-\Delta_i s_c)} = \exp(\Delta_i s_c), \tag{19}
\]

which can conveniently be verified by considering statistics of the forward experiment alone.

To illustrate the above formalism, we focus on the simple case of a “kangaroo” kinetic equation with a rate \( k(v' \rightarrow v) \) [14]:

\[
k(v' \rightarrow v) = \lambda(v')\varphi(v). \tag{20}
\]

One verifies that the detailed balance symmetry Eq. (11) implies in this case that the collision rate \( \lambda = 1/\tau \) is a constant, independent of \( v' \), and hence \( k(v' \rightarrow v) = \varphi_0(v)/\tau \). The reflection symmetry Eq. (12) is, in this case, an automatic consequence of the detailed balance condition Eq. (11). Numerical simulations of the stochastic process Eq. (1) allow us to compute the probability distribution \( P(\Delta_i s_c) \), see Fig. 1 and test the validity of the fluctuation theorem, cf. Fig. 3. In the inset of Fig. 1 we plot the large deviation function \( \Phi_\delta(x) \) that results of the fit \( P(\delta_i s_c) \sim \exp(-\Phi_\delta(\delta_i s_c)) \), with \( t_f - t_i = \delta_i s_c \). We have also considered the case \( \lambda(v) = a|v| \) whose corresponding results for \( P(\Delta_i s_c) \) are shown in Fig. 2. Interestingly, the reflection symmetry property is still satisfied, and the detailed fluctuation
the theorem is formally recovered. However the detailed balance condition is violated. The steady state solution is not Maxwellian, and the interpretation of $\Delta s_c$ as thermodynamic entropy production is false.

We close with a few remarks. Stochastic thermodynamics has been developed in great detail for Langevin equations, see e.g. [9, 24], both in the over-damped and underdamped. A well documented case is a chain of harmonic oscillators in contact with two heat baths, see [25–28]. One may wonder why the symmetry property Eq. (11) has not been discussed in this context. By making the diffusion approximation on the master equation (1) [29], one easily verifies that Eq. (11) requires that the drift term be uneven in the velocity and the noise term even. These conditions are met in a generic Langevin equation, explaining why this issue has not appeared in this context. The formalism presented above can be easily extended to more complicated situations, such as multiple particles with vectorial velocities in contact with several reservoirs of heat, particles or momentum and with time-dependent external forcing. Also the splitting of the entropy production in several components, such as the adiabatic and non-adiabatic contribution, proceeds as before [20].

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[1] C. Jarzynski, Physical Review Letters 78, 2690 (1997).
[2] R. Kawai, J. M. R. Parrondo, and C. V. den Broeck, Physical Review Letters 98, 80602 (2007).
[3] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Physical Review Letters 71, 2401 (1993).
[4] G. Gallavotti, Physical Review Letters 77, 4334 (1996).
[5] G. Crooks, Journal of Statistical Physics 90, 1481 (1998).
[6] J. Kurchan, Journal of Physics A: Mathematical and General 31, 3719 (1998).
[7] J. Lebowitz and H. Spohn, Journal of Statistical Physics 95, 333 (1999).
[8] S. Sekimoto, Stochastic Energetics (Springer, NewYork, 2010).
[9] U. Seifert, Reports on Progress in Physics 75, 126001 (2012).
[10] C. Van den Broeck, in Proceedings of the International School of Physics “Enrico Fermi”, Course CLXXXIV “Physics of Complex Colloids”, edited by C. Bechinger, F. Sciortino, and Zicherl P. (Italian Physical Society, 2013).
[11] C. Van den Broeck and M. Esposito, *Physica A: Statistical Mechanics and its Applications* (2014), 10.1016/j.physa.2014.04.035.

[12] R. E. Spinney and I. J. Ford, *Physical Review Letters* 108, 170603 (2012).

[13] H. K. Lee, C. Kwon, and H. Park, *Physical Review Letters* 110, 50602 (2013).

[14] C. Van den Broeck and R. Toral, *Physical Review E* 89, 062124 (2014).

[15] G. Gradiniego, A. Puglisi, A. Sarracino, and U. M. B. Marconi, *Physical Review E* 85, 031112 (2012).

[16] G. Gradiniego, A. Sarracino, A. Puglisi, and H. Touchette, *Journal of Physics A: Mathematical and Theoretical* 46, 335002 (2013).

[17] R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1975).

[18] P. Gaspard, *Physica A: Statistical Mechanics and its Applications* 392, 639 (2013).

[19] B. Gaveau and M. Moreau, *EPJST*, special issue in memory of J. Yvon.

[20] M. Esposito and C. Van den Broeck, *Physical Review Letters* 104, 90601 (2010).

[21] R. Spinney and I. Ford, in *Nonequilibrium Statistical Physics of Small Systems: Fluctuation Relations and Beyond*, edited by W. Klaes and C. Jarzinsky (Wiley, 2013).

[22] T. Becker, T. Willaert, B. Cleuren, and C. V. den Broeck, *Physical Review Letters* (2014) [arXiv:1405.6064].

[23] R. J. Harris and G. M. Schütz, *Journal of Statistical Mechanics: Theory and Experiment* 2007, P07020 (2007).

[24] T. Tomé and M. J. de Oliveira, *Physical Review Letters* 99, 180601 (2007).

[25] K. Saito and A. Dhar, *Physical Review E* 83, 041121 (2011).

[26] R. J. Harris and G. M. Schütz, *Journal of Statistical Mechanics: Theory and Experiment* 2011, P03007 (2011).

[27] H. C. Fogedby and A. Imparato, *Journal of Statistical Mechanics: Theory and Experiment* 2012, P04005 (2012).

[28] N. van Kampen, *Stochastic Processes in Physics and Chemistry*, 3rd ed. (North-Holland, Amsterdam, 2007).