Chapter 5
Basics of Stochastic Thermodynamics

Stochastic thermodynamics is a discipline exhibiting a rapid development over the past two decades. The progress is driven by many applications to small (nano-sized) systems of current interest (such as individual Brownian particles, biomolecules, quantum dots) and, from the theoretical point of view, by recent discoveries of rather general relations called fluctuation theorems. The adjective "stochastic" in the name of the field means that the dynamics of the system under consideration is governed by stochastic evolution equations, which in our case is the Langevin equation. The key quantities of the classical thermodynamics such as heat, work and entropy are (within the framework of the stochastic thermodynamics) defined along individual trajectories of the system. Thus defined quantities are valid for *finite*, and even small systems which are driven *arbitrarily far from equilibrium*, in contrast to their classical counterparts which are used for *macroscopic* systems *in equilibrium* (or in a linear-response regime).

The main aim of the present chapter is to introduce basic concepts and relations which are necessary for the study presented in Chap. 6. First, we identify the work and the heat for the system whose dynamics obeys the Langevin equation (Sect. 5.1), second we introduce two fluctuation theorems which proved to be useful in experiments (Sect. 5.2), and third, we provide references to several reviews and to just a few selected original works in the field (Sect. 5.3).

5.1 Definition of Stochastic Work and Heat

Nonequilibrium processes in biology and nanosystems are generally strongly affected by thermal fluctuations. A paradigmatic model for gaining a better understanding of nonequilibrium processes in such systems is a colloidal particle diffusing in water and driven by an externally controlled potential. In the overdamped regime (characterized by low Reynolds numbers) the position of the particle evolves according to the Langevin equation

© Springer International Publishing Switzerland 2016

A. Ryabov, *Stochastic Dynamics and Energetics of Biomolecular Systems*,
Springer Theses, DOI 10.1007/978-3-319-27188-0_5

$$\mathrm{d}\mathbf{X}(t) = \mathcal{F}(\mathbf{X}(t), t)\mathrm{d}t + \sqrt{2D}\,\mathrm{d}\mathbf{B}(t), \tag{5.1}$$

where D controls the strength of the thermal noise and $\mathbf{B}(t)$ is the standard Wiener process. Specifically, in the present case of a thermal environment, the noise strength is proportional to the heat-bath temperature, $D = k_\mathrm{B}T$ (the particle mobility is set to one). The external force, $\mathcal{F}(x, t)$, is derived from the potential $U(x, t)$, $\mathcal{F}(x, t) = -\partial U/\partial x$, which represents, e.g., the confinement imposed by an optical trap.

If the potential is modulated in time following a given externally imposed protocol, the position of the particle evolves along a stochastic trajectory. Any single trajectory of the particle in the time interval $[0, t]$ yields a single value of the work $\mathbf{W}(t)$ done on the particle by an external filed. The work $\mathbf{W}(t)$ is a *functional* of the position process $\mathbf{X}(t')$, $0 \le t' \le t$, and it is distributed with a probability density function $p(w, t)$. The probability $p(w, t)\mathrm{d}w$ that the work $\mathbf{W}(t)$ falls into an infinitesimal interval $(w, w + \mathrm{d}w)$ equals the probabilistic weight of all trajectories giving work values in that interval. Analogical reasoning holds true for the heat exchanged with the heat reservoir, $\mathbf{Q}(t)$.

The stochastic heat and work are identified with the aid of the first law of thermodynamics. In the overdamped regime which we consider here, the "internal energy" of the particle is given by its mean potential energy $\langle U(\mathbf{X}(t), t)\rangle$. The total differential of the potential energy

$$\mathrm{d}U = \left(\frac{\partial U}{\partial x}\right)_t \mathrm{d}x + \left(\frac{\partial U}{\partial t}\right)_x \mathrm{d}t \tag{5.2}$$

is decomposed into two parts. If we substitute into the above expression the (random) position of the particle at time t, $x \to \mathbf{X}(t)$, the following interpretation emerges [1, 2]. The first term on the right-hand side describes the infinitesimal increment of the potential energy due to the particle relaxation in the *time-independent* potential. We identify this term with the heat accepted by the system from heat bath:

$$\delta\mathbf{Q}(t) = -\mathcal{F}(\mathbf{X}(t), t)\mathrm{d}\mathbf{X}(t). \tag{5.3}$$

This relation is physically plausible since in the overdamped regime the total mechanical force times the displacement corresponds to dissipated energy. The minus sign corresponds to the convention that the heat transferred into the system is positive.

The second term on the right-hand side of Eq. (5.2) describes the increment of the potential energy due to the time-variation of the potential while the particle position is held constant. In this case, the potential energy of the particle is either raised or lowered purely due to the externally controlled modulation of potential U. Correspondingly, this term describes as the work performed on the particle:

$$\delta\mathbf{W}(t) = \left(\frac{\partial U}{\partial t}\right)_{\mathbf{X}(t)} \mathrm{d}t, \tag{5.4}$$

and hence altogether we have

$$\mathrm{d}U(\mathbf{X}(t), t) = \delta\mathbf{Q}(t) + \delta\mathbf{W}(t). \tag{5.5}$$

The above definition of the stochastic work is in agreement with the definition of "thermodynamic work" used in equilibrium theory [3]. However, the definition is not identical to that used in introductory courses of classical mechanics, where to "work = force times displacement".[1] For the discussion of (un)ambiguity of the definition used see Refs. [4–7] and references therein. See also Refs. [8, 9] for implications of different work definitions in context of fluctuation relations.

5.2 Crooks Fluctuation Theorem and Jarzynski Equality

Many important processes in biophysics take place in the liquid environment which is maintained at a constant temperature. In classical thermodynamics, work w required to transfer the system from the specified initial equilibrium state i to the specified final equilibrium state f by the means of an *isothermal* process is equal to the increase of the system's free energy ΔF, $\Delta F = F_f - F_i$, only if the process is carried out *quasistatically*. That is the variation of the external parameters must be so slow that the system is at any instant in the state of thermodynamic equilibrium with the heat bath (the environment). Theoretically such a process would take an infinite time. Contrary to this, any finite-time process is accompanied by the dissipation and the required work fulfills $w \geq \Delta F$. The extra amount of work performed on the system during the nonequilibrium process as compared to the equilibrium one is dissipated as heat which is accepted by the heat bath. The Crooks fluctuation theorem [10, 11] states something remarkable. Consider the process $i \to f$, carried out at *an arbitrary rate*. At the initial state i the system resides in a thermal equilibrium and the external potential is equal to $U(x, 0)$. Afterwards, in a finite time interval $[0, t]$, the potential is varied according to a given (forward) protocol $U(x, \tau)$, $\tau \in [0, t]$. Then the PDF of the work performed on the particle during the described nonequilibrium process fulfills

$$\frac{p(w, t)}{p_{\mathrm{R}}(-w, t)} = \exp[\beta(w - \Delta F)]\,, \tag{5.6}$$

where $1/\beta = k_{\mathrm{B}}T$ is the thermal energy, and $p_{\mathrm{R}}(w, t)$ stands for the PDF of the work performed on the particle during the *reversed process*: the process that departs from the equilibrium state f (in this state the potential is equal to $U(x, t)$) and, during the process, the potential is varied according to the time-reversed protocol $U(x, t - \tau)$, $\tau \in [0, t]$.

If we multiply the both sides of the Crooks theorem by $p_{\mathrm{R}}(-w, t)\mathrm{e}^{-\beta w}$ and then integrate over all possible values of w we obtain perhaps the most widely known

[1]The mechanical definition of work is used whenever it is meaningful to split the total potential energy U into two contributions: $U = U_0(x) + U_{\mathrm{ext}}(x, t)$, the first being an intrinsic time-independent potential and the second describes the external driving. Then the "mechanical work", $\delta W_{\mathrm{mech}} = -(\partial U_{\mathrm{ext}}/\partial x)\mathrm{d}x$, satisfies the integrated first law of the form $\Delta U_0 = Q(t) + W_{\mathrm{mech}}(t)$.

fluctuation theorem, the Jarzynski equality [12]

$$\int_{-\infty}^{+\infty} \mathrm{d}w \, \mathrm{e}^{-\beta w} p(w,t) = \left\langle \mathrm{e}^{-\beta \mathbf{W}(t)} \right\rangle = \mathrm{e}^{-\beta \Delta F}. \tag{5.7}$$

The equality relates the free energy difference between two equilibrium configurations of the system to the exponential average of the work done during a finite-time far-from-equilibrium (forward) process.

Notice that the both above relations are perfectly consistent with the classical thermodynamics. If the process $i \to f$ is reversible, then the work done during the reversed process has exactly the same distribution as that in the forward one and the Crooks relation implies that $w = \Delta F$. This should be understood in the sense that the work loses its stochastic nature and it simply becomes a number. On the other hand, for an arbitrary process the Jensen relation $\langle \mathrm{e}^x \rangle \geq \mathrm{e}^{\langle x \rangle}$ applied on the Jarzynski equality gives us $\langle \mathbf{W}(t) \rangle \geq \Delta F$.

The both fluctuation theorems provide us a completely new possibility how to measure equilibrium thermodynamic properties of small systems. Instead of trying to perform an equilibrium manipulation e.g. with the single RNA macromolecule, one can carry out a far-from-equilibrium experiment and use one of the fluctuation theorems to recover the free energy differences. The latter procedure is favorable in systems with complex free-energy landscapes where the condition of equilibrium manipulation cannot be achieved in a reasonable time. Indeed, the Crooks fluctuation theorem has been experimentally used e.g. in RNA pulling experiments with optical tweezers [13] proving to be a reliable tool for extracting the free energy differences. In the (bidirectional) experiment the both distributions $p(w,t)$ and $p_{\mathrm{R}}(-w,t)$ are measured, then, according to Eq. (5.6), ΔF equals to value of w at which the two histograms $p(w,t)$, $p_{\mathrm{R}}(-w,t)$ intersect when plotted against the common w axis.

In situations when the forward and reverse work distributions are separated by a large gap on the w axis the above bidirectional method is biased by a rather large error [14]. In these cases, the Jarzynski equality, or its modification due to Hummer and Szabo [15] can be used to extract ΔF from a unidirectional experiment only [16–22]. In general, however, the application of Eq. (5.7) can be difficult, because the exponential average $\langle \exp[-\beta \mathbf{W}(t)] \rangle$ is dominated by rare trajectories with exceptionally low work values $w \ll \Delta F$. In experiments these rare trajectories are almost never observed and even in computer simulations it is difficult to generate them with a sufficient statistical weight. A possible solution is to extend measured histograms to the tail regime $w \ll \Delta F$ by fitting to theoretical predictions. To this end, some generic behavior in the tail regime needs to be assumed and attempts have been made recently in this direction [23–25]. For example, in the case of DNA/RNA unfolding, Palassini and Ritort [23] suggested that the lower tail of the work distribution is unbounded and decays as

$$p(w,t) \sim \frac{q}{\Omega} \left(\frac{|w - w_c|}{\Omega} \right)^{\nu} \mathrm{e}^{-\left(\frac{|w-w_c|}{\Omega}\right)^{\delta}}, \qquad w \to -\infty, \tag{5.8}$$

with $q > 0$ and $\Omega > 0$, w_c is a characteristic work value. For the Jarzynski equality (5.7) to hold, it needs to be either $\delta > 1$, or $\Omega < 1$ and $\delta = 1$. Interestingly, the asymptotic behavior of the work distribution for a driven Brownian particle in a harmonic potential was found to satisfy Eq. (5.8) with $\delta = 1$ and $\nu = -1/2$ [25, 26]. One of the important results of the analysis presented in the next chapter is that Eq. (5.8) holds with $\delta = 1$ also for an asymmetric and anharmonic potential, the exponent ν in this case quantifies a degree of anharmonicity.

A further information on experiments with single biomolecules (mechanical manipulation of biomolecules by optical tweezers, or an atomic force microscope) can be found e.g. Refs. [27–33]. Recent progress in fluctuation theorems and free energy recovery is reviewed in Ref. [14].

The above discussion may evoke an impression that the work fluctuations are observable in small systems only. Notice, however, that both the Jarzynski equality and the Crooks theorem does not refer explicitly to the system size. As a matter of fact, the two fluctuation theorems have been confirmed in an experiment involving a macroscopic torsional pendulum [34, 35]. See also Ref. [36] for an experiment with a granular gas.

5.3 Further Reading

The stochastic thermodynamics, despite its long history [37], experiences a rather rapid development in recent years. The growing interest in the field is certainly stimulated by discoveries of fluctuation theorems (FTs). Two prominent examples of FTs, the Crooks theorem and the Jarzynski equality, have been discussed in Sect. 5.2. The theorems are remarkable for their generality and they extend our understanding of thermodynamics far beyond its original area of validity (i.e., to small systems driven arbitrarily far from the thermal equilibrium). Besides new relationships for free-energy differences, the theorems resulted in a long-awaited breakthrough in our understanding of how macroscopic irreversibility (dictated by the second law) emerges from a time-reversal symmetric microscopic dynamics [38].

Probably the first appearance of fluctuation relations in the literature can be found in papers by Bochkov and Kuzovlev [39, 40]. The two works, however, have remained unnoticed until recently, see Refs. [8, 9, 41] for detailed discussion. A fluctuation theorem for entropy production was first observed in simulations of sheared fluids by Evans et al. [42, 43]. Shortly after that a related FT for the deterministic dynamics has been proven by Gallavotti and Cohen [44], for the Langevin dynamics by Kurchan [45], and for fairly general Markov processes by Lebowitz and Spohn [46] and Maes [47]. The (experimental) usefulness of fluctuation relations has been recognized after Jarzynski [12, 48] and Crooks [10, 11] demonstrated how to relate equilibrium quantities to non-equilibrium work measurements. A fluctuation theorem (analogous to Jarzynski equality) that applies to transitions between two different non-equilibrium steady states has been derived by Hatano and Sasa [49].

Since 2000 a number of significant contributions to stochastic thermodynamics and to fluctuation theorems have been published (see e.g. Refs. [50–61] to name just a few). Fortunately, the rapidly growing amount of literature has became a subject of numerous reviews, lecture notes and introductory texts [38, 62–77]. In particular, for a pedagogical introduction to fluctuation relations and related topics we recommend recent book [76]. For a comprehensive overview of the stochastic thermodynamics including the fluctuation relations, their classification and interrelations see the review by Seifert [75], which is possibly the most complete survey in the field. Further, nonequilibrium work relations for Langevin dynamics are summarized by Kurchan [68]. Fluctuation theorems for the systems governed by the Master equation are reviewed by Harris and Schütz [69]. For other reviews focusing on different aspects related to fluctuation relations we refer to Van den Broeck [73] (performance of Brownian machines), Sevick et al. [38] (irreversibility of macroscopic dynamics), Maes [63, 64] (entropy in out-of-equilibrium systems), Ritort [30, 65] and Bustamante et al. [66] (FTs from experimental perspective), and Gaspard [67] (statistical mechanics based on Hamiltonian dynamics).

Finally, it should be noted that also quantum versions of FTs are nowadays subject to an active (mainly theoretical) development. For the reviews we refer to Refs. [78, 79].

References

1. K. Sekimoto, Kinetic characterization of heat bath and the energetics of thermal ratchet models. J. Phys. Soc. Jpn. **66**, 1234 (1997). doi:10.1143/JPSJ.66.1234
2. K. Sekimoto, Langevin equation and thermodynamics. Prog. Theor. Phys. Suppl. **130**, 17 (1998). doi:10.1143/PTPS.130.17
3. F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGrow-Hill Inc., New York, 1965). Section 6.6. ISBN 07-051800-9
4. J.M.G. Vilar, J.M. Rubi, Failure of the work-Hamiltonian connection for free-energy calculations. Phys. Rev. Lett. **100**, 020601 (2008). doi:10.1103/PhysRevLett.100.020601
5. L. Peliti, On the work–Hamiltonian connection in manipulated systems. J. Stat. Mech. P05002 (2008). doi:10.1088/1742-5468/2008/05/P05002
6. J. Horowitz, C. Jarzynski, Comment on "Failure of the work-Hamiltonian connection for free-energy calculations". Phys. Rev. Lett. **101**, 098901 (2008). doi:10.1103/PhysRevLett.101.098901
7. E.N. Zimanyi, R.J. Silbey, The work-Hamiltonian connection and the usefulness of the Jarzynski equality for free energy calculations. J. Chem. Phys. **130**, 171102 (2009). doi:10.1063/1.3132747
8. J. Horowitz, C. Jarzynski, Comparison of work fluctuation relations. J. Stat. Mech. P11002 (2007). doi:10.1088/1742-5468/2007/11/P11002
9. C. Jarzynski, Comparison of far-from-equilibrium work relations. C. R. Physique **8**, 495 (2007). doi:10.1016/j.crhy.2007.04.010
10. G.E. Crooks, Nonequilibrium measurements of free energy differences for microscopically reversible Markovian systems. J. Stat. Phys. **90**, 1481 (1998). doi:10.1023/A:1023208217925
11. G.E. Crooks, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences. Phys. Rev. E **60**, 2721 (1999). doi:10.1103/PhysRevE.60.2721
12. C. Jarzynski, Nonequilibrium equality for free energy differences. Phys. Rev. Lett. **78**, 2690 (1997). doi:10.1103/PhysRevLett.78.2690

13. D. Collin, F. Ritort, C. Jarzynski, S.B. Smith, I. Tinoco, C. Bustamante, Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies. Nature **437**, 321 (2005). doi:10.1038/nature04061
14. A. Alemany, M. Ribezzi-Crivellari, F. Ritort, Recent progress in fluctuation theorems and free energy recovery, eds. by R. Klages, W. Just, C. Jarzynski. Nonequilibrium Statistical Physics of Small Systems. Reviews of Nonlinear Dynamics and Complexity, Chap. 5, pp. 155–180 (Wiley-VCH, Weinheim, Germany, 2013). ISBN: 978-3-527-41094-1
15. G. Hummer, A. Szabo, Free energy reconstruction from nonequilibrium single-molecule pulling experiments. PNAS **98**, 3658 (2001). doi:10.1073/pnas.071034098
16. J. Liphardt, S. Dumont, S.B. Smith, I. Tinoco, C. Bustamante, Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality. Science **296**, 1832 (2002). doi:10.1126/science.1071152
17. F. Ritort, C. Bustamante, I. Tinoco, A two-state kinetic model for the unfolding of single molecules by mechanical force. PNAS **99**, 13544 (2002). doi:10.1073/pnas.172525099
18. C. Danilowicz, V.W. Coljee, C. Bouzigues, D.K. Lubensky, D.R. Nelson, M. Prentiss, DNA unzipped under a constant force exhibits multiple metastable intermediates. PNAS **100**, 1694 (2003). doi:10.1073/pnas.262789199
19. D.M. Zuckerman, T.B. Woolf, Theory of a systematic computational error in free energy differences. Phys. Rev. Lett. **89**, 180602 (2002). doi:10.1103/PhysRevLett.89.180602
20. J. Gore, F. Ritort, C. Bustamante, Bias and error in estimates of equilibrium free-energy differences from nonequilibrium measurements. PNAS **100**, 12564 (2003). doi:10.1073/pnas.1635159100
21. N.C. Harris, Y. Song, C.-H. Kiang, Experimental free energy surface reconstruction from single-molecule force spectroscopy using Jarzynski's equality. Phys. Rev. Lett. **99**, 068101 (2007). doi:10.1103/PhysRevLett.99.068101
22. S. Engel, A. Alemany, N. Forns, P. Maass, F. Ritort, Folding and unfolding of a triple-branch DNA molecule with four conformational states. Philos. Mag. **91**, 2049 (2011). doi:10.1080/14786435.2011.557671
23. M. Palassini, F. Ritort, Improving free-energy estimates from unidirectional work measurements: theory and experiment. Phys. Rev. Lett. **107**, 060601 (2011). doi:10.1103/PhysRevLett.107.060601
24. A. Engel, Asymptotics of work distributions in nonequilibrium systems. Phys. Rev. E **80**, 021120 (2009). doi:10.1103/PhysRevE.80.021120
25. D. Nickelsen, A. Engel, Asymptotics of work distributions: the pre-exponential factor. Eur. Phys. J. B **82**, 207 (2011). doi:10.1140/epjb/e2011-20133-y
26. A. Ryabov, M. Dierl, P. Chvosta, M. Einax, P. Maass, Work distribution in a time-dependent logarithmic-harmonic potential: exact results and asymptotic analysis. J. Phys. A: Math. Theor. **46**, 075002 (2013). doi:10.1088/1751-8113/46/7/075002
27. A. Janshoff, M. Neitzert, Y. Oberdörfer, H. Fuchs, Force spectroscopy of molecular systems—single molecule spectroscopy of polymers and biomolecules. Angew. Chem. Int. Ed. **39**, 3212 (2000). doi:10.1002/1521-3773(20000915)39:18<3212::AID-ANIE3212>3.0.CO;2-X
28. J. Liphardt, B. Onoa, S.B. Smith, I. Tinoco, C. Bustamante, Reversible unfolding of single RNA molecules by mechanical force. Science **292**, 733 (2001). doi:10.1126/science.1058498
29. X. Zhuang, M. Rief, Single-molecule folding. Curr. Opin. Struct. Biol. **13**, 88 (2003). doi:10.1016/S0959-440X(03)00011-3
30. F. Ritort, Single-molecule experiments in biological physics: methods and applications. J. Phys.: Condens. Matter **18**, R531 (2006). doi:10.1088/0953-8984/18/32/R01
31. A. Mossa, M. Manosas, N. Forns, J.M. Huguet, F. Ritort, Dynamic force spectroscopy of DNA hairpins: I. Force kinetics and free energy landscapes. J. Stat. Mech. P02060 (2009). doi:10.1088/1742-5468/2009/02/P02060
32. A. Mossa, M. Manosas, N. Forns, J.M. Huguet, F. Ritort, Dynamic force spectroscopy of DNA hairpins: II. Irreversibility and dissipation. J. Stat. Mech. P02061 (2009). doi:10.1088/1742-5468/2009/02/P02061

33. J.M. Huguet, C.V. Bizarro, N. Forns, S.B. Smith, C. Bustamante, F. Ritort, Single-molecule derivation of salt dependent base-pair free energies in DNA. PNAS **107**, 15431 (2010). doi:10.1073/pnas.1001454107
34. F. Douarche, S. Ciliberto, A. Petrosyan, I. Rabbiosi, An experimental test of the Jarzynski equality in a mechanical experiment. Europhys. Lett. **70**, 593 (2005). doi:10.1209/epl/i2005-10024-4
35. S. Ciliberto, S. Joubaud, A. Petrosyan, Fluctuations in out-of-equilibrium systems: from theory to experiment. J. Stat. Mech. P12003 (2010). doi:10.1088/1742-5468/2010/12/P12003
36. A. Naert, Experimental study of work exchange with a granular gas: the viewpoint of the fluctuation theorem. Europhys. Lett. **97**, 20010 (2012). doi:10.1209/0295-5075/97/20010
37. C. Van den Broeck, Stochastic thermodynamics, eds. by W. Ebeling, H. Ulbricht, Selforganization by nonlinear irreversible processes. Springer series in synergetics, pp. 57–61 (Springer, Berlin, 1986). ISBN-13: 978-3-642-71006-3, doi:10.1007/978-3-642-71004-9
38. E.M. Sevick, R. Prabhakar, S.R. Williams, D.J. Searles, Fluctuation theorems. Annu. Rev. Phys. Chem. **59**, 603 (2008). doi:10.1146/annurev.physchem.58.032806.104555
39. G.N. Bochkov, Y.E. Kuzovlev, General theory of thermal fluctuations in nonlinear systems. Sov. Phys. JETP **45**, 125 (1977). http://www.jetp.ac.ru/cgi-bin/e/index/e/45/1/p125?a=list
40. G.N. Bochkov, Y.E. Kuzovlev, Fluctuation-dissipation relations for nonequilibrium processes in open systems. Sov. Phys. JETP **49**, 543 (1979). http://www.jetp.ac.ru/cgi-bin/e/index/e/49/3/p543?a=list
41. G.N. Bochkov, Y.E. Kuzovlev, Fluctuation-dissipation relations. Achievements and misunderstandings. Physics-Uspekhi **56**, 590 (2013). doi:10.3367/UFNe.0183.201306d.0617
42. D.J. Evans, E.G.D. Cohen, G.P. Morriss, Probability of second law violations in shearing steady states. Phys. Rev. Lett. **71**, 2401 (1993). doi:10.1103/PhysRevLett.71.2401
43. D.J. Evans, D.J. Searles, Equilibrium microstates which generate second law violating steady states. Phys. Rev. E **50**, 1645 (1994). doi:10.1103/PhysRevE.50.1645
44. G. Gallavotti, E.G.D. Cohen, Dynamical ensembles in nonequilibrium statistical mechanics. Phys. Rev. Lett. **74**, 2694 (1995). doi:10.1103/PhysRevLett.74.2694
45. J. Kurchan, Fluctuation theorem for stochastic dynamics. J. Phys. A: Math. Gen. **31**, 3719 (1998). doi:10.1088/0305-4470/31/16/003
46. J.L. Lebowitz, H. Spohn, A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics. J. Stat. Phys. **95**, 333 (1999). doi:10.1023/A:1004589714161
47. C. Maes, The fluctuation theorem as a Gibbs property. J. Stat. Phys. **95**, 367 (1999). doi:10.1023/A:1004541830999
48. C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: a master-equation approach. Phys. Rev. E **56**, 5018 (1997). doi:10.1103/PhysRevE.56.5018
49. T. Hatano, S. Sasa, Steady-state thermodynamics of Langevin systems. Phys. Rev. Lett. **86**, 3463 (2001). doi:10.1103/PhysRevLett.86.3463
50. G.E. Crooks, Path-ensemble averages in systems driven far from equilibrium. Phys. Rev. E **61**, 2361 (2000). doi:10.1103/PhysRevE.61.2361
51. C. Maes, K. Netočný, Time-reversal and entropy. J. Stat. Phys. **110**, 269 (2003). doi:10.1023/A:1021026930129
52. U. Seifert, Entropy production along a stochastic trajectory and an integral fluctuation theorem. Phys. Rev. Lett. **95**, 040602 (2005). doi:10.1103/PhysRevLett.95.040602
53. A. Imparato, L. Peliti, Fluctuation relations for a driven Brownian particle. Phys. Rev. E **74**, 026106 (2006). doi:10.1103/PhysRevE.74.026106
54. B. Cleuren, C. Van den Broeck, R. Kawai, Fluctuation and dissipation of work in a Joule experiment. Phys. Rev. Lett. **96**, 050601 (2006). doi:10.1103/PhysRevLett.96.050601
55. C. Maes, K. Netočný, Minimum entropy production principle from a dynamical fluctuation law. J. Math. Phys. **48**, 053306 (2007). doi:10.1063/1.2738753
56. M. Esposito, K. Lindenberg, Continuous-time random walk for open systems: fluctuation theorems and counting statistics. Phys. Rev. E **77**, 051119 (2008). doi:10.1103/PhysRevE.77.051119

57. M. Esposito, C. Van den Broeck, Three faces of the second law. I. Master equation formulation. Phys. Rev. E **82**, 011143 (2010). doi:10.1103/PhysRevE.82.011143
58. M. Esposito, C. Van den Broeck, Three faces of the second law. II. Fokker-Planck formulation. Phys. Rev. E **82**, 011144 (2010). doi:10.1103/PhysRevE.82.011144
59. U. Seifert, T. Speck, Fluctuation-dissipation theorem in nonequilibrium steady states. Europhys. Lett. **89**, 10007 (2012). doi:10.1209/0295-5075/89/10007
60. S. Rahav, C. Jarzynski, Nonequilibrium fluctuation theorems from equilibrium fluctuations. New J. Phys. **15**, 125029 (2013). doi:10.1088/1367-2630/15/12/125029
61. C. Maes, K. Netočný, A nonequilibrium extension of the Clausius heat theorem. J. Stat. Phys. **154**, 188 (2014). doi:10.1007/s10955-013-0822-9
62. D.J. Evans, D.J. Searles, Fluctuation theorems. Adv. Phys. **51**, 1529 (2002). doi:10.1080/00018730210155133
63. C. Maes, On the origin and use of fluctuation relations for entropy. Sém. Poincaré **2**, 29 (2003). http://www.bourbaphy.fr/maes.pdf
64. C. Maes, Nonequilibrium entropies. Phys. Scr. **86**, 058509 (2012). doi:10.1088/0031-8949/86/05/058509
65. F. Ritort, Work fluctuations and transient violations of the second law: perspectives in theory and experiments. Sém. Poincaré **2**, 63 (2003). http://www.bourbaphy.fr/ritort.pdf
66. C. Bustamante, J. Liphardt, F. Ritort, The nonequilibrium thermodynamics of small systems. Phys. Today **58**, 43 (2005). doi:10.1063/1.2012462
67. P. Gaspard, Hamiltonian dynamics, nanosystems, and nonequilibrium statistical mechanics. Physica A **369**, 201 (2006). doi:10.1016/j.physa.2006.04.010
68. J. Kurchan, Non-equilibrium work relations. J. Stat. Mech. P07005 (2007). doi:10.1088/1742-5468/2007/07/P07005
69. R.J. Harris, G.M. Schütz, Fluctuation theorems for stochastic dynamics. J. Stat. Mech. P07020 (2007). doi:10.1088/1742-5468/2007/07/P07020
70. C. Maes, K. Netočný, B. Wynants, On and beyond entropy production: the case of Markov jump processes. Markov Processes Relat. Fields **14** 445 (2008). http://arxiv.org/abs/0709.4327
71. U. Seifert, Stochastic thermodynamics: principles and perspectives. Eur. Phys. J. B **64**, 423 (2008). doi:10.1140/epjb/e2008-00001-9
72. J. Prost, J.-F. Joanny, J.M.R. Parrondo, Generalized fluctuation-dissipation theorem for steady-state systems. Phys. Rev. Lett. **103**, 090601 (2009). doi:10.1103/PhysRevLett.103.090601
73. C. Van den Broeck, The many faces of the second law. J. Stat. Mech. P10009 (2010). doi:10.1088/1742-5468/2010/10/P10009
74. M. Campisi, P. Hänggi, Fluctuation, dissipation and the arrow of time. Entropy **13**, 2024 (2011). doi:10.3390/e13122024
75. U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines. Rep. Prog. Phys. **75**, 126001 (2012). doi:10.1088/0034-4885/75/12/126001
76. R. Klages, W. Just, C. Jarzynski (eds.), *Nonequilibrium Statistical Physics of Small Systems, Reviews of Nonlinear Dynamics and Complexity* (Wiley-VCH, Weinheim, Germany, 2013)
77. V. Holubec, *Non-equilibrium Energy Transformation Processes*, Springer Theses (Springer, New York, 2014)
78. M. Esposito, U. Harbola, S. Mukamel, Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems. Rev. Mod. Phys. **81**, 1665 (2009). doi:10.1103/RevModPhys.81.1665
79. M. Campisi, P. Hänggi, P. Talkner, Colloquium: Quantum fluctuation relations: foundations and applications. Rev. Mod. Phys. **83**, 771 (2011). doi:10.1103/RevModPhys.83.771