

Chapter 2

Stochastic Thermodynamics

Stochastic thermodynamics is an advancing field with many applications to small systems of current interest [1–5]. Its brief history is summarized in the Introduction. In this chapter we review the basic theoretical concepts involved in this domain. Specifically, in Sects. 2.1 and 2.2, we review the dynamical equations for the mesoscopic systems with discrete and with continuous state space, respectively. Further, in these two sections, we present equations which describe fluctuations of work, heat and internal energy of the system during isothermal processes. In Sect. 2.3 we give a short review of the celebrated work fluctuation relations [1, 6–9], which represent a generalization of the second law of thermodynamics. Finally, in Sect. 2.4, we review the recent results in the field of stochastic heat engines and present the theory needed to their analytical description.

2.1 Discrete Systems

Let us consider a general N -level system in contact with a thermal reservoir at the temperature T . We assume that the system is driven by an external agent. Let $\mathcal{G}_i = \mathcal{U}_i - k_B T \log \Omega_i$ denote free energy landscape (FEL) of the *system alone*, where \mathcal{U}_i (Ω_i) stands for the energies (degeneracies) of the individual levels and k_B is the Boltzmann constant. Moreover, let $\tilde{\mathcal{V}}_i[\mathbf{Y}(t)] = \mathcal{V}_i(t)$ denote an additional energy due to the interaction with the external agent. The discrete index $i = 1, 2, \dots, N$ labels the individual microstates (levels) available to the system and $\mathbf{Y}(t)$ stands for a vector of *control parameters* driven by the external agent. The FEL of the *compound system*, $\mathcal{F}_i(t)$, and the energies of its individual levels, $\mathcal{E}_i(t)$, read

$$\mathcal{F}_i(t) = \mathcal{G}_i + \tilde{\mathcal{V}}_i[\mathbf{Y}(t)] = \mathcal{G}_i + \mathcal{V}_i(t) \quad i = 1, 2, \dots, N, \quad (2.1)$$

$$\mathcal{E}_i(t) = \mathcal{U}_i + \tilde{\mathcal{V}}_i[\mathbf{Y}(t)] = \mathcal{U}_i + \mathcal{V}_i(t) \quad i = 1, 2, \dots, N. \quad (2.2)$$

Note that the external driving can not force the system to follow a specific sequence of microstates. It just influences, through the level free energies, the transition probabilities between the individual microstates.

2.1.1 Dynamics

At an arbitrary fixed time t , the state of the system is specified by the column vector $\mathbf{p}(t)$. The components of this vector $[\mathbf{p}(t)]_i = p_i(t)$, $i = 1, \dots, N$, are the occupation probabilities of the individual microstates (levels), i.e., the probabilities to find the system at the time t in the microstate i .

In many experimentally important situations, the time evolution of the system can be described as a Markov process. Such process is governed by the master equation [10]. The transition rates in the equation depend on the temperature of the bath and on the external parameters which influence the FEL of the system. Since the free energies depend on time, the rates must be time dependent as well. Hence the underlying Markov process is time inhomogeneous one.

One possible probabilistic approach [11, 12] to the analysis of a continuous time Markov process uses its decomposition into a discrete time Markov chain and a system of random points on the time axis. The transitions between the states of the Markov chain occur just at random instants. Usually, the time intervals between individual transitions are taken as independent exponentially distributed random variables. This decomposition can be used for simple and fast simulations of time inhomogeneous Markov processes. The details are discussed in Appendix C.

Formally speaking, the time evolution of the system is described by the time-inhomogeneous Markov process $\mathbf{D}(t)$, where $\mathbf{D}(t) = k$ if the system resides in the microstate k at the time t . The master equation can be written as

$$\frac{d}{dt} \mathbf{R}(t | t') = -\nu \mathbb{L}(t) \mathbf{R}(t | t'), \quad \mathbf{R}(t' | t') = \mathbb{1}, \quad (2.3)$$

where $\mathbb{1}$ is the $(N \times N)$ unity matrix, $\mathbb{L}(t)$ is the $(N \times N)$ matrix of transition rates, and $\mathbf{R}(t | t')$ is the $(N \times N)$ matrix of transition probabilities. ν^{-1} sets the elementary time scale. In the limit $\nu \rightarrow \infty$ ($\nu \rightarrow 0$) the relaxation processes are infinitely fast (slow).

If the transition rates would remain constant, the system should relax towards thermal equilibrium specified by the instantaneous values of the level free energies (2.1). In order to guarantee this behavior it is often assumed that the transition rates fulfill the so called (time local) detail balance condition

$$\exp[-\beta \mathcal{F}_j(t)] L_{ij}(t) = L_{ji}(t) \exp[-\beta \mathcal{F}_i(t)], \quad (2.4)$$

where $\beta = 1/(k_B T)$. The matrix of the transition probabilities, $\mathbb{R}(t | t')$, is a stochastic matrix [13]. Its elements are given by

$$R_{ij}(t | t') = \text{Prob} \{ D(t) = i | D(t') = j \}. \quad (2.5)$$

This means that the matrix $\mathbb{R}(t | t')$ evolves an arbitrary column vector of the initial occupation probabilities, $\mathbf{p}(t')$, as

$$\mathbf{p}(t) = \mathbb{R}(t | t') \mathbf{p}(t'). \quad (2.6)$$

Because this formula is valid for any initial vector $\mathbf{p}(t')$, it already suggests that the matrix $\mathbb{R}(t | t')$ fulfills the Chapman-Kolmogorov condition [10, 14]

$$\mathbb{R}(t | t') = \mathbb{R}(t | t'') \mathbb{R}(t'' | t'). \quad (2.7)$$

Here the matrix multiplication on the right hand side amounts for the summation over the intermediate states at the time t'' . This formula is valid for any intermediate time t'' and reflects the Markov property of the underlying stochastic process $D(t)$.

2.1.2 Energetics

The random internal energy of the system at the time t ,

$$U(t) = \mathcal{E}_{D(t)}(t), \quad (2.8)$$

changes according to the first law of thermodynamics as

$$\begin{aligned} \dot{U}(t) dt &= W(t + dt, t) + Q(t + dt, t) \\ &= [\mathcal{E}_{D(t)}(t + dt) - \mathcal{E}_{D(t)}(t)] + [\mathcal{E}_{D(t+dt)}(t) - \mathcal{E}_{D(t)}(t)], \end{aligned} \quad (2.9)$$

where we use the abbreviation $\dot{f}(t) = df(t)/dt$. The first (the second) term on the right hand side represents the random work (heat) accepted by the system during the infinitesimal time interval $[t, t + dt]$ [15]. Differently speaking, if the system dwells in the level i during the time interval $[t, t + dt]$ then the work done on the system *by the external agent*, $W(t + dt, t)$, equals $\mathcal{E}_i(t + dt) - \mathcal{E}_i(t)$ and no heat is accepted. On the other hand if the system changes its microstate from j to i during the infinitesimal time interval $[t, t + dt]$ and the level energies $\mathcal{E}_i(t)$, $\mathcal{E}_j(t)$ remain constant, then the heat accepted by the system *from the thermal environment*, $Q(t + dt, t)$, is $\mathcal{E}_i(t) - \mathcal{E}_j(t)$ and no work is done. These definitions are further discussed in detail in Sect. 2.2.3, also see Fig. 2.1.

The random work done on the system by the external agent when the control parameter is altered from $Y(t')$ to $Y(t)$ reads

$$W(t, t') = \int_{t'}^t dt'' \sum_{i=1}^N \dot{\mathcal{E}}_i(t'') \delta_{iD(t'')}, \quad (2.10)$$

and represents a *functional* of the stochastic process $D(t)$. Due to the first law of thermodynamics (2.9), the random heat accepted from the reservoir represents another functional of the process $D(t)$, specifically

$$Q(t, t') = U(t) - U(t') - W(t, t'). \quad (2.11)$$

For an analytical treatment of work and heat fluctuations it is useful to introduce the *augmented process* $\{W(t, t'), D(t)\}$ [16–18] which describes both the work and the microstate variable. This augmented process is again a time inhomogeneous Markov process and its two-time properties are described by the $(N \times N)$ matrix $G(w, t | w', t')$ with the matrix elements

$$G_{ij}(w, t | w', t') = \frac{1}{\epsilon} \text{Prob} \left\{ \begin{array}{c} W(t, 0) \in (w, w + \epsilon) \\ D(t) = i \end{array} \middle| \begin{array}{c} W(t', 0) = w' \\ D(t') = j \end{array} \right\}, \quad (2.12)$$

where $\epsilon \rightarrow 0$. The time evolution of $G(w, t | w', t')$ is given by [16–18]

$$\frac{\partial}{\partial t} G(w, t | w', t') = - \left[\frac{\partial}{\partial w} \dot{\mathbb{E}}(t) + \nu \mathbb{L}(t) \right] G(w, t | w', t') \quad (2.13)$$

with the initial condition $G(w, t' | w', t') = \delta(w - w') \mathbb{1}$. Here $\dot{\mathbb{E}}(t)$ is the diagonal matrix $\dot{\mathbb{E}}(t) = \text{diag}\{\dot{\mathcal{E}}_1(t), \dots, \dot{\mathcal{E}}_N(t)\}$. Note that $\mathbb{R}(t | t') = \int_{-\infty}^{\infty} dw G(w, t | 0, t')$ and that $G(w, t | w', t') = G(w - w', t | 0, t')$. Equation (2.13) represents a hyperbolic system of N^2 coupled partial differential equations with time-dependent coefficients. It can be derived in several ways. For example, as explained in reference [19], one considers at the time t the family of all realizations, which display at that time the work in the infinitesimal interval $(w, w + dw)$ and, simultaneously, which occupy a given microstate. During the infinitesimal time interval $(t, t + dt)$, the number of such paths can change due to two reasons. First, while residing in the given microstate, some paths enter (leave) the set, because the energy levels move and an additional work has been done. Secondly, some paths can enter (leave) the described family, because they jump out of (into) the specified level. These two contributions correspond to the two terms on the right hand side of Eq. (2.13). Another derivation [18] is based on an explicit probabilistic construction of all possible paths and their respective probabilities.

The Chapman-Kolmogorov condition for the augmented process assumes the form

$$G(w, t | w', t') = \int_{-\infty}^{\infty} dw'' G(w, t | w'', t'') G(w'', t'' | w', t'). \quad (2.14)$$

Here the matrix multiplication on the right hand side amounts for the summation over the intermediate states at the time t'' , and the integration runs over all possible intermediate values of the work variable w'' . The equation is valid for any intermediate time $t'' \in [t', t]$.

Equations (2.3) and (2.13) are exactly solvable only in several cases. Investigations have been conducted for simple spin systems driven by a time-dependent external field [11, 18–25]. As a result, analytical solutions are known for several two-level systems [11, 18, 23, 24, 26] and for systems composed of N_{sub} two-level subsystems in the limit of large N_{sub} [19, 25]. A generalization of these results and also some other exactly solvable models are presented in Chap. 3. Further, in Appendix A, we discuss the limit of infinitely fast (slow) relaxation ($\nu \rightarrow 0, \infty$). In these limiting cases Eqs. (2.3) and (2.13) can be solved for any model.

The matrix $G(w, t | w', t')$ provides a complete description of the energetics of the process $D(t)$. The joint probability density for the internal energy $U(t)$ and the work $W(t, t')$ performed on the system during the time interval $[t', t]$, given the internal energy initially was u' , (regardless of the final state of the system at the time t) is given by

$$\xi(u, w, t; u') = \sum_{i,j=1}^N \delta[u - \mathcal{E}_i(t)] \delta[u' - \mathcal{E}_j(t')] G_{ij}(w, t | 0, t') p_j(t'). \quad (2.15)$$

Here $\delta(x)$ stands for the Dirac δ -function and $p_j(t')$ denotes the initial occupation probabilities. The function $\xi(u, w, t; u')$ already yields the probability density for the work,

$$\rho(w, t) = \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} du' \xi(u, w, t; u'). \quad (2.16)$$

An analogous integration over the variables u' and w gives the probability density for the internal energy $U(t)$,

$$\varsigma(u, t) = \int_{-\infty}^{\infty} du' \int_{-\infty}^{\infty} dw \xi(u, w, t; u'). \quad (2.17)$$

Furthermore, using the definition (2.11), the function $\xi(u, w, t; u')$ gives also the probability density for the heat $Q(t, t')$ transferred from the reservoir during the time interval $[t', t]$ [23]

$$\chi(q, t) = \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} du' \int_{-\infty}^{\infty} dw \delta[q - (u - u' - w)] \xi(u, w, t; u'). \quad (2.18)$$

The functions (2.16)–(2.18) yield all raw moments of internal energy (2.8), work (2.10) and heat (2.11) by single integration

$$\langle [\mathbf{U}(t)]^n \rangle = \int_{-\infty}^{\infty} du u^n \varsigma(u, t), \quad (2.19)$$

$$\langle [\mathbf{W}(t, t')]^n \rangle = \int_{-\infty}^{\infty} dw w^n \rho(w, t), \quad (2.20)$$

$$\langle [\mathbf{Q}(t, t')]^n \rangle = \int_{-\infty}^{\infty} dq q^n \chi(q, t). \quad (2.21)$$

Let us note that these moments can be also calculated directly from the definitions (2.8), (2.10) and (2.11) only using the solution of the master Eq. (2.3). This approach is convenient for the internal energy where one can use the identity $\int_{-\infty}^{\infty} du u^n \varsigma(u, t) = \sum_{i=1}^N [\mathcal{E}_i(t)]^n p_i(t)$. For the work and the heat the situation is more complicated and this approach is useful only for the first few moments. For example, the mean values of the internal energy, work and heat, are

$$U(t) = \langle \mathbf{U}(t) \rangle = \sum_{i=1}^N \mathcal{E}_i(t) p_i(t), \quad (2.22)$$

$$W(t, t') = \langle \mathbf{W}(t, t') \rangle = \sum_{i=1}^N \int_{t'}^t dt'' \dot{\mathcal{E}}_i(t'') p_i(t''), \quad (2.23)$$

$$Q(t, t') = \langle \mathbf{Q}(t, t') \rangle = \sum_{i=1}^N \int_{t'}^t dt'' \mathcal{E}_i(t'') \dot{p}_i(t''). \quad (2.24)$$

In order to calculate the second moments of the work and the heat without the probability densities (2.16) and (2.18), one needs the two-time correlation function

$$\langle h_{\mathbf{D}(t)} f_{\mathbf{D}(t')} \rangle_{\mathbf{C}} = \begin{cases} \sum_{i=1}^N \sum_{j=1}^N h_i f_j R_{ij}(t | t') p_j(t'), & t \geq t' \\ \sum_{i=1}^N \sum_{j=1}^N f_i h_j R_{ij}(t' | t) p_j(t), & t \leq t' \end{cases}. \quad (2.25)$$

The second raw moments of the work (2.10) and the heat (2.11) are then given by

$$\langle [W(t, t')]^2 \rangle = \int_{t'}^t dt'' \int_{t'}^t dt''' \left\langle \frac{\partial \mathcal{E}_{D(t'')}(t'')}{\partial t''} \frac{\partial \mathcal{E}_{D(t''')}(t''')}{\partial t'''} \right\rangle_C \quad (2.26)$$

and

$$\begin{aligned} \langle [Q(t, t')]^2 \rangle &= \langle [W(t, t')]^2 \rangle + \sum_{i, j=1}^N [\mathcal{E}_i(t) - \mathcal{E}_j(t')]^2 R_{ij}(t | t') p(t') \\ &- 2 \sum_{i, j, k=1}^N [\mathcal{E}_i(t) - \mathcal{E}_k(t')] \int_{t'}^t dt'' \frac{\partial \mathcal{E}_{D(t'')}(t'')}{\partial t''} \delta_{D(t'')j} R_{ij}(t | t'') R_{jk}(t'' | t') p_k(t'), \end{aligned} \quad (2.27)$$

where $\partial \mathcal{E}_{D(t)}(t)/\partial t \equiv d\mathcal{E}_i(t)/dt|_{i=D(t)}$. Obviously, in order to obtain the higher moments of the work and the heat, the higher time correlation functions must be defined and the resulting expressions become too complicated. Finally, let us define the variances of internal energy, heat and work which corresponds to the widths of the individual probability densities

$$[\Delta U(t)]^2 = \langle [U(t)]^2 \rangle - [U(t)]^2, \quad (2.28)$$

$$[\Delta W(t, t')]^2 = \langle [W(t, t')]^2 \rangle - [W(t, t')]^2, \quad (2.29)$$

$$[\Delta Q(t, t')]^2 = \langle [Q(t, t')]^2 \rangle - [Q(t, t')]^2. \quad (2.30)$$

The entropy of the system at the time t is given by the standard formula [15]

$$S_s(t) = -k_B \sum_{i=1}^N p_i(t) \log [p_i(t)]. \quad (2.31)$$

Its increment during the time interval $[t', t]$

$$S_s(t, t') = S_s(t) - S_s(t'), \quad (2.32)$$

together with the entropy transferred to the reservoirs during the time interval $[t', t]$

$$S_r(t, t') = -\frac{Q(t, t')}{T}, \quad (2.33)$$

determines the total entropy produced during the time interval $[t', t]$

$$S_{\text{tot}}(t, t') = S_s(t, t') + S_r(t, t') \geq 0. \quad (2.34)$$

2.2 Continuous Systems

Consider an externally driven one dimensional microscopic system in contact with a thermal reservoir at the temperature T . Let $\mathcal{G}(x) = \mathcal{U}(x) - k_B T \log \Omega(x)$ denote the FEL of the system alone, where $\mathcal{U}(x)$ denotes the energy of the x th microstate and $\Omega(x)$ stands for its multiplicity. Moreover, let $\tilde{\mathcal{V}}[x, \mathbf{Y}(t)] = \mathcal{V}(x, t)$ denote an additional energy due to the interaction with the external agent. The continuous index $x \in (-\infty, \infty)$ labels the individual microstates available to the system and $\mathbf{Y}(t)$ stands for the vector of the parameters controlled by the external agent. As in the discrete case, the external driving can not force the system to follow a specific sequence of microstates. It just influences, through the FEL, the transition probabilities between the individual microstates. The FEL, $\mathcal{F}(x, t)$, and the energy landscape, $\mathcal{E}(x, t)$, of the compound system read

$$\mathcal{F}(x, t) = \mathcal{G}(x) + \tilde{\mathcal{V}}[x, \mathbf{Y}(t)] = \mathcal{G}(x) + \mathcal{V}(x, t), \quad (2.35)$$

$$\mathcal{E}(x, t) = \mathcal{U}(x) + \tilde{\mathcal{V}}[x, \mathbf{Y}(t)] = \mathcal{U}(x) + \mathcal{V}(x, t). \quad (2.36)$$

Two examples of such setting are depicted in Figs. 4.1 and 4.2 and further discussed in Sect. 4.1.

2.2.1 Dynamics

In the present work we assume that the thermal forces can be described as the sum of the linear friction force and the Langevin white-noise force. We neglect the inertial forces. Then the equation of motion for the particle position (microstate of the system) is the stochastic differential equation [10, 14, 27]

$$\Gamma \frac{d}{dt} \mathbf{X}(t) = - \frac{\partial}{\partial x} \mathcal{F}(x, t) \Big|_{x=\mathbf{X}(t)} + \mathbf{N}(t), \quad (2.37)$$

with initial condition $\mathbf{X}(t') = x'$. In Eq. (2.37) Γ stands for the particle mass times the viscous friction coefficient, and $\mathbf{N}(t)$ represents the delta-correlated white noise, $\langle \mathbf{N}(t) \mathbf{N}(t') \rangle = 2D\Gamma^2 \delta(t - t')$. Here $D = k_B T / \Gamma$ denotes the diffusion constant. The Fokker-Planck equation corresponding to the stochastic differential Eq. (2.37) is [10, 14, 27]

$$\frac{\partial}{\partial t} R(x, t | x', t') = \left\{ D \frac{\partial^2}{\partial x^2} + \frac{1}{\Gamma} \frac{\partial}{\partial x} \left[\frac{\partial}{\partial x} \mathcal{F}(x, t) \right] \right\} R(x, t | x', t'), \quad (2.38)$$

with the initial condition $R(x, t' | x', t') = \delta(x - x')$. The conditional probabilities $R(x, t | x', t') dx$ play the same role as the matrix elements (2.5) for the discrete process $\mathbf{D}(t)$. More precisely, the function $R(x, t | x', t')$ evolves an arbitrary initial

probability distribution $p(x, t')$ as

$$p(x, t) = \int_{-\infty}^{\infty} dx' R(x, t | x', t') p(x', t'). \quad (2.39)$$

The function $p(x, t)$ specifies the state of the system at the time t . Concretely, the probability to find the system at the time t in a microstate which lies in an infinitesimal neighborhood of the microstate x reads $p(x, t) dx$, or, mathematically, $\text{Prob}\{\mathbf{X}(t) \in (x, x + dx)\} = p(x, t) dx$.

This setting represents a continuous analogy of the discrete one described in Sect. 2.1. However, it should be noted that the master equation formulation is more general than the continuous one, including the Langevin and Fokker-Planck cases as its special limits [10, 14]. The matrix multiplication (summation over the microstates) in the discrete model is now represented by x -integration. For example the Chapman-Kolmogorov Eq. (2.7) presently assumes the form

$$R(x, t | x', t') = \int_{-\infty}^{\infty} dx'' R(x, t | x'', t'') R(x'', t'' | x', t'). \quad (2.40)$$

2.2.2 Energetics

The random internal energy of the system at the time t ,

$$U(t) = \mathcal{E}[\mathbf{X}(t), t], \quad (2.41)$$

changes according to the first law of thermodynamics (2.11) as

$$\begin{aligned} \dot{U}(t) dt &= W(t + dt, t) + Q(t + dt, t) \\ &= \{\mathcal{E}[\mathbf{X}(t), t + dt] - \mathcal{E}[\mathbf{X}(t), t]\} + \{\mathcal{E}[\mathbf{X}(t + dt), t] - \mathcal{E}[\mathbf{X}(t), t]\}. \end{aligned} \quad (2.42)$$

The first (the second) term on the right hand side corresponds to the random work (heat) accepted by the system during the infinitesimal time interval $[t, t + dt]$ [15]. Differently speaking, if the system dwells at the position x during the time interval $[t, t + dt]$ then the work done on the system by the eternal agent, $W(t + dt, t)$, equals $\mathcal{E}(x, t + dt) - \mathcal{E}(x, t)$ and no heat is accepted. On the other hand if the system changes its position from x' to x during the infinitesimal time interval $[t, t + dt]$ and the energies $\mathcal{E}(x, t)$, $\mathcal{E}(x', t)$ remain constant, then the heat accepted by the system from the thermal environment, $Q(t + dt, t)$, is $\mathcal{E}(x, t) - \mathcal{E}(x', t)$ and no work is done.

As a result the random work satisfies the stochastic differential equation [28]

$$\frac{d}{dt}W(t, t') = \frac{\partial}{\partial t}\mathcal{E}[\mathbf{X}(t), t] \equiv \frac{d}{dt}\mathcal{E}(x, t) \Big|_{x=\mathbf{X}(t)} \quad (2.43)$$

with the initial condition $W(t', t') = 0$. Although this work definition, which we use in the whole thesis, naturally stems from the stochastic thermodynamic definition (2.10), it recently raised a heated discussion in the literature [29–32] and an alternative work definition was proposed [29]. This question is discussed in detail in Sect. 2.2.3.

The random work done on the system by the external agent when the control parameter is altered from $Y(t')$ to $Y(t)$ reads

$$W(t, t') = \int_{t'}^t dt'' \int_{-\infty}^{\infty} dx \dot{\mathcal{E}}(x, t'') \delta[x - \mathbf{X}(t'')]. \quad (2.44)$$

It represents a functional of the process $\mathbf{X}(t)$. Due to the first law of thermodynamics (2.42) the random heat accepted from the reservoir corresponds to another functional of the process $\mathbf{X}(t)$. This functional is given by (2.11).

The Fokker-Planck equation corresponding to the stochastic differential equations (2.37) and (2.43) reads [10, 27]

$$\begin{aligned} \frac{\partial}{\partial t}G(x, w, t | x', w', t') = & \left\{ D \frac{\partial^2}{\partial x^2} + \frac{1}{\Gamma} \frac{\partial}{\partial x} \left[\frac{\partial}{\partial x} \mathcal{F}(x, t) \right] \right. \\ & \left. - \dot{\mathcal{E}}(x, t) \frac{\partial}{\partial w} \right\} G(x, w, t | x', w', t'), \end{aligned} \quad (2.45)$$

with the initial condition $G(x, w, t | x', w', t') = \delta(x - x')\delta(w - w')$. The conditional probabilities $G(x, w, t | x', w', t') dx dw$ play similar role for the continuous process $\mathbf{X}(t)$ as the matrix elements (2.12) for the discrete process $\mathbf{D}(t)$.

Specifically, if we define the function $\xi(u, w, t; u')$ as

$$\begin{aligned} \xi(u, w, t; u') = & \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dx' \delta[u - \mathcal{E}(x, t)] \\ & \times \delta[u' - \mathcal{E}(x', t')] G(x, w, t | x', 0, t') p(x', t') \end{aligned} \quad (2.46)$$

the definitions (2.16)–(2.21) remain valid. In analogy with the discrete model the moments of the random variables in question can be also calculated from the definitions (2.41), (2.44) and (2.11) only using the solution of Eq.(2.38). One just substitutes the continuous variables in the formulas in question for their discrete equivalents and change the summations to the integrations. The raw moments of

the internal energy are now given by $\int_{-\infty}^{\infty} du u^n \varsigma(u, t) = \int_{-\infty}^{\infty} dx [\mathcal{E}(x, t)]^n p(x, t)$. The mean values of the internal energy, the work and the heat (2.22)–(2.24) now read

$$U(t) = \langle U(t) \rangle = \int_{-\infty}^{\infty} dx \mathcal{E}(x, t) p(x, t), \quad (2.47)$$

$$W(t, t') = \langle W(t, t') \rangle = \int_{-\infty}^{\infty} dx \int_{t'}^t dt'' \dot{\mathcal{E}}(x, t'') p(x, t''), \quad (2.48)$$

$$Q(t, t') = \langle Q(t, t') \rangle = \int_{-\infty}^{\infty} dx \int_{t'}^t dt'' \mathcal{E}(x, t'') \dot{p}(x, t''). \quad (2.49)$$

Similarly, the second moment of the work (2.26) is given by

$$\langle [W(t, t')]^2 \rangle = \int_{t'}^t dt'' \int_{t'}^t dt''' \left\langle \frac{\partial \mathcal{E}[\mathbf{X}(t''), t'']}{\partial t''} \frac{\partial \mathcal{E}[\mathbf{X}(t'''), t''']}{\partial t'''} \right\rangle_C, \quad (2.50)$$

with the two-time correlation function defined as

$$\begin{aligned} & \langle h[\mathbf{X}(t)] f[\mathbf{X}(t')] \rangle_C \\ &= \begin{cases} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' h(x) f(x') R(x, t | x', t') p(x', t'), & t \geq t' \\ \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' f(x) h(x') R(x, t' | x', t) p(x', t), & t \leq t'. \end{cases} \end{aligned} \quad (2.51)$$

The entropy of the system at the time t is given by the standard formula [15]

$$S_s(t) = -k_B \int_{-\infty}^{\infty} dx p(x, t) \log [p(x, t)]. \quad (2.52)$$

Its increase during the time interval $[t', t]$, $S_s(t, t')$, the entropy $S_r(t, t')$ transferred to the reservoirs during the time interval $[t', t]$ and the total entropy produced during the time interval $[t', t]$, $S_{\text{tot}}(t, t')$, are given by Eq. (2.32)–(2.34).

As in the discrete case, Eqs. (2.38) and (2.45) can be solved analytically only for few simple settings. Examples can be found in the works [4, 33–40]. In Chap. 4 we present a generic exactly solvable model—the “sliding parabola model”. Another exactly solvable model, an extension of the so called “breathing parabola model”, is discussed in Sect. 5.2.

2.2.3 On the Work Definition

Recently, an extensive criticism of the work definition has been raised (2.44) [29, 32]. The objections against the definition presented in [29] are:

- The work (2.44) done during a quasi-static process does not equal the free energy change of the system itself.
- After a gauge transformation $\mathcal{F}(x, t) \rightarrow \mathcal{F}(x, t) + g(t)$, $\mathcal{E}(x, t) \rightarrow \mathcal{E}(x, t) + g(t)$ one obtains a transformed system which possess the same dynamics as the original one, however, the work (2.44) done on the transformed system and that done on the original differ.
- The work should be defined in the traditional mechanical way as (force \times displacement). Using this definition, the random work done on the system by the external agent when the control parameter is altered from $Y(t')$ to $Y(t)$ reads¹

$$W_E(t, t') = - \int_{t'}^t dt'' \left. \frac{\partial}{\partial x} \mathcal{V}(x, t'') \right|_{x=X(t'')} \frac{dX(t'')}{dt''}, \quad (2.53)$$

where $-\partial \mathcal{V}(x, t)/\partial x = F(x, t)$ denotes the force applied on the system by the external agent. The work (2.53) done during a quasi-static process equals the free energy change of the system itself and is gauge invariant.

The papers [30, 31, 41] explain that the controversies caused by the above objections can be easily resolved. To this end we compare the the two work definitions on a specific, simple, example.

The thermodynamic work represents the work done by the external agent on the compound system system-interaction [30, 42, 43]. As an example consider the situation depicted in Fig. 2.1. The microscopic system (the black ball) is driven by an external agent (the car). The interaction between the car and the ball is realized by the spring with zero unloaded length, which contains the interaction energy $\mathcal{V}(x, t)$ and acts on the ball (car) by the force $F(x, t)$ [$-F(x, t)$]. The ball is surrounded by thermal environment and the impacts of its molecules (small arrows) can cause that the ball moves against the force applied. In such case the energy of the impacts [the heat (2.11)] is stored in the spring and the internal energy of the compound system (ball-spring), $\mathcal{E}(x, t)$, increases. If the spring moves the ball, its kinetic energy immediately dissipates into the environment. Part of the energy $\mathcal{E}(x, t)$ is transferred as heat (2.11) into the bath. Another way how to increase (decrease) the energy $\mathcal{E}(x, t)$ is to drive the car [externally manipulate with the interaction potential $\mathcal{V}(x, t)$]. Assume that the impacts of the molecules from the environment cause the ball to stand still. If one drives the car to the left, the spring must be stretched and the work (2.44) is done on the compound system [$\mathcal{E}(x, t)$ increases and the petrol is consumed].

¹ Note that the generalization of this definition for the discrete models is not very natural, because, in such case, one has to substitute a finite difference for the position derivative in the force definition.

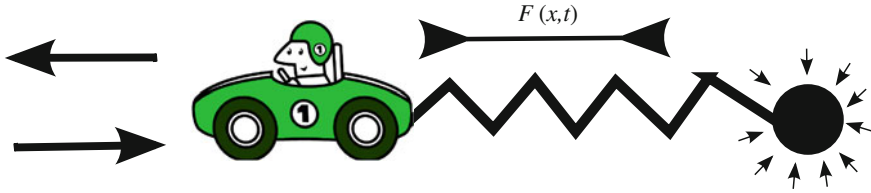


Fig. 2.1 Sketch illustrating the meaning of thermodynamic work (2.44) and that of the mechanical work (2.53)

However, if one drives to the right, the spring pulls the car and the compound system does the work (2.44) on the car [$\mathcal{E}(x, t)$ decreases and one can store the energy in an accumulator].

Contrary to the thermodynamic work (2.44), the mechanical work (2.53) describes the work done by the external agent on the system itself [30, 42, 43]. Consider again the situation depicted in Fig. 2.1. If the ball moves towards the car, the energy $\mathcal{E}(x, t)$ decreases at the expense of the ball kinetic energy which is quickly (immediately) transferred as heat into the bath. The work (2.53) is done on the ball by the spring, it causes its movement against the friction. Similarly, if the distance between the ball and the car decreases the heat is transferred into the spring and the ball (the thermal environment via the ball) does the work on the spring.

From the last two paragraphs one can deduce that the work definition (2.53) is similar to the definition of heat (2.11). Indeed the mechanical work can be rewritten as

$$W_E(t, t') = -\mathcal{V}[X(t), t] + \mathcal{V}[X(t'), t'] + W(t, t') \quad (2.54)$$

and thus, using Eqs. (2.11) and (2.36), we have $W_E(t, t') = \mathcal{U}[X(t)] - \mathcal{U}[X(t')] - Q(t, t')$. For freely diffusing particle [$\mathcal{U}(x) = 0$] the mechanical work thus equals the (minus) heat transferred from the compound system to the thermal environment, $W_E(t, t') = -Q(t, t')$. This is not surprising. If one neglects the inertia and sets $\mathcal{U}(x) = 0$, the only agent which protects the system from moving freely (without consuming work) is the thermal environment.

In [44] the thermodynamic work (2.44) is referred to as the *inclusive work*. Similarly, the mechanical work (2.53) was called the *exclusive work*. The reason for these terms is the following. During a quasi-static isothermal process the inclusive work is trajectory independent and it equals the change of the Helmholtz free energy $F(t)$ of the system described by the full free energy landscape (2.35), i.e.,

$$[W(t, t')]_{\text{eq}} = \Delta F(t, t') = F(t) - F(t') = -\frac{1}{\beta} \ln \frac{Z(t)}{Z(t')}, \quad (2.55)$$

where $F(t) = -\ln[Z(t)]/\beta$ and the partition function $Z(t)$ reads

$$Z(t) = \int_{-\infty}^{\infty} dx \exp[-\beta \mathcal{F}(x, t)]. \quad (2.56)$$

The free energy obtained from the inclusive work thus *includes* the terms which stem from the interaction with the external agent. A general proof is presented for example in [30] a proof using Eq. (2.13) for discrete systems is presented in Appendix A. The gauge transformation $\mathcal{F}(x, t) + g(t)$ changes the quasi-static work as $[\mathbf{W}(t, t')]_{\text{eq}} \rightarrow [\mathbf{W}(t, t')]_{\text{eq}} + g(t) - g(t')$ and the free energy difference as $\Delta F(t, t') \rightarrow \Delta F(t, t') + g(t) - g(t')$, indeed. However, the possibility to insert a function $g(t)$ into $\mathcal{F}(x, t)$ is not unphysical—the work can be done on the system without changing its dynamics. For instance the function $g(t)$ may represent an energy input which is the same for all microstates of the system. Consider that the one dimensional microscopic system from Fig. 2.1 is putted into an elevator placed in a gravitational field. If one neglects the inertial effects, the energy flow into the system caused by the elevator movement up and down would be described exactly by the gauge therm $g(t)$.

From Eq. (2.54) one can see that the exclusive work done during a quasi-static isothermal process equals $[\mathbf{W}_E(t, t')]_{\text{eq}} = -\mathcal{V}[\mathbf{X}(t), t] + \mathcal{V}[\mathbf{X}(t'), t'] + \Delta F(t)$. Note that, in contrary to the equilibrium inclusive work, $[\mathbf{W}_E(t, t')]_{\text{eq}}$ still depends on the random initial and final states of the system, $\mathbf{X}(t)$ and $\mathbf{X}(t')$. Nevertheless, its average value equals to the increase of the free energy $F_0(t, t')$ of the system alone, i.e.,

$$\begin{aligned} \left\langle [\mathbf{W}_E(t, t')]_{\text{eq}} \right\rangle &= \Delta F(t) - \int_{-\infty}^{\infty} dx \mathcal{V}(x, t) \frac{\exp[-\beta \mathcal{F}(x, t)]}{Z(t)} \\ &+ \int_{-\infty}^{\infty} dx \mathcal{V}(x, t') \frac{\exp[-\beta \mathcal{F}(x, t')]}{Z(t')} = F_0(t) - F_0(t') = \Delta F_0(t, t'), \end{aligned} \quad (2.57)$$

where the free energy of the unperturbed system at the time t reads

$$F_0(t) = \mathcal{G}(\langle [\mathbf{X}(t)]_{\text{eq}} \rangle). \quad (2.58)$$

Here $\langle [\mathbf{X}(t)]_{\text{eq}} \rangle$ stands for the mean equilibrium state of the system corresponding to the instantaneous FEL $\mathcal{F}(x, t)$. It is given by

$$\langle [\mathbf{X}(t)]_{\text{eq}} \rangle = \int_{-\infty}^{\infty} dx x \frac{\exp[-\beta \mathcal{F}(x, t)]}{Z(t)}. \quad (2.59)$$

The free energy obtained from the exclusive work thus *excludes* the terms which stem from the interaction with the external agent and therefore it is also invariant with respect to the gauge transformation $\mathcal{F}(x, t) + g(t)$.

Let us stress that the both equilibrium works can be used for measuring the free energy differences between the states of the system alone, $\Delta F_0(t)$. The average equilibrium exclusive work is exactly $\Delta F_0(t, t')$. The average equilibrium inclusive work yields the free energy difference of the compound system, $\Delta F(t, t')$, which

translates to $\Delta F_0(t, t')$ as

$$\Delta F_0(t, t') = -\mathcal{V}(\langle [\mathbf{X}(t)]_{\text{eq}} \rangle, t) + \mathcal{V}(\langle [\mathbf{X}(t')]_{\text{eq}} \rangle, t') + \Delta F(t, t'). \quad (2.60)$$

The formula (2.60) can be used once one knows the correct form of the interaction energy $\mathcal{V}(x, t)$. However, in most experimentally relevant situations this function is known indeed. In Sect. 4.1 we illustrate the connection between the exclusive and inclusive work in the form of a specific, physically relevant, model.

2.3 Work Fluctuation Relations

Investigation of dynamics and thermodynamics of mesoscopic systems under influence of (external) time dependent forces is of great interest over last two decades [45, 46]. As we mentioned in the Introduction, one of the most interesting theoretical result in this field was the discovery of the so called fluctuation theorems [1, 47, 48, 48–52]. General relations depicting time-irreversibility of various non-equilibrium stochastic processes occurring in microscopic systems exposed to non-equilibrium conditions, such as entropy production [8, 15, 53–59] and work done on the environment [15, 44, 48, 60, 61].

In this section, we focus on the theorems involving the two work definitions (2.44) and (2.53) presented in Sect. 2.2.² The two works represent different random variables and hence they possess different probability densities [44]. Fluctuation theorems for the thermodynamic work (2.44) are studied in detail for last two decades [15, 48, 60, 61]. The most important results in the field are Jarzynski equality [1, 48]

$$\langle \exp[-\beta \mathbf{W}(t, t')] \rangle = \exp[-\beta \Delta F(t, t')] \quad (2.61)$$

and Crooks fluctuation theorem [7–9]

$$\frac{\rho_F(w)}{\rho_R(-w)} = \exp\{-\beta[\Delta F(t, t') - w]\}. \quad (2.62)$$

The average on the right-hand side of Eq. (2.61) is taken over the work distribution (2.16) given that the system is initially in equilibrium, i.e., $p(x, t') = \pi(x, t') = \exp[-\beta \mathcal{F}(x, t')] / Z(t')$. In Eq. (2.62) this work distribution is denoted as $\rho_F(w)$. By the subscript F (*forward*) we stress that the externally controlled parameters are driven from $\mathbf{Y}(t')$ to $\mathbf{Y}(t)$, $t' < t$. $\rho_R(w)$ in Eq. (2.62) stands for the work probability distribution for the *time-reversed* process. Here the externally controlled parameters are driven from $\mathbf{Y}(t)$ to $\mathbf{Y}(t')$ and the system starts from the equilibrium state corresponding to the FEL of the compound system at the time t , $\mathcal{F}(x, t)$. The free energy

² In this section, we use the notation introduced in Sect. 2.2 for the continuous models, nevertheless the results remains valid also for the discrete models described in Sect. 2.1, indeed.

difference $\Delta F(t, t')$ in Eqs. (2.61) and (2.62) is given by (2.55). The only assumption needed for validity of Eqs. (2.61) and (2.62) is the microscopic reversibility of the underlying dynamics. The discrete models (Sect. 2.1) are reversible if the detailed balance condition (2.4) is fulfilled. The time-reversibility for the continuous models is already incorporated in the Langevin Eq. (2.37). The theorems (2.61) and (2.62) represent an elegant refinement of the second law of thermodynamics. For example, using Jensen's inequality, the well known form of the second law, $\Delta F(t, t') \leq W(t, t')$, follows from Eq. (2.61). Note that Eq. (2.61) is a corollary of Eq. (2.62), but not vice versa.

Equivalent fluctuation theorems for the mechanical work (2.53) were discovered nearly three decades earlier [43, 44, 62, 63]

$$\langle \exp[-\beta W_E(t, t')] \rangle = 1, \quad (2.63)$$

$$\frac{\bar{\rho}_F(w)}{\bar{\rho}_R(-w)} = \exp(\beta w). \quad (2.64)$$

Here the average in Eq. (2.63) is taken over the probability density for the work (2.53) given that the system starts at the time t' from the state $\bar{\pi}(x) = \exp[-\beta \mathcal{G}(x)] / Z_0$, $Z_0 = \int_{-\infty}^{\infty} dx \exp[-\beta \mathcal{G}(x)]$, the thermal equilibrium state corresponding to the FEL of the unperturbed system, $\mathcal{G}(x)$. This probability density is in Eq. (2.64) denoted by $\bar{\rho}_F$. The subscripts F and R have the same meaning as in Eq. (2.62) with the difference that the system starts the reversed process again from the state $\bar{\pi}(x)$.

The theorems for the thermodynamic work (2.44) relate, different from the theorems for the mechanical work (2.53), the work done during a *non-equilibrium* process (easy to measure experimentally) to the increase of the *equilibrium* free energy of the compound system (sometimes hard to measure experimentally), and thus they received much more attention in the literature. The obtained free energy difference $\Delta F(t, t')$ can be interesting in itself or can be used for calculating the increment of the free energy of the unperturbed system, $\Delta F_0(t, t')$, via Eq. (2.60). Moreover, another generalization of Eq. (2.61) allows the reconstruction of the whole FEL of the unperturbed system, $G(z)$, using the work measurements. This result is called Hummer-Szabo relation and reads [64]

$$Z(t') \exp \left\{ \beta \tilde{\mathcal{V}}[z, \mathbf{Y}(t)] \right\} \langle \delta[\mathbf{X}(t) - z] \exp[-\beta W(t, t')] \rangle = \exp[-\beta \mathcal{G}(z)]. \quad (2.65)$$

The knowledge of $\mathcal{G}(z)$ allows to calculate the equilibrium free energy differences $\Delta F(t, t')$ and $\Delta F_0(t, t')$ from their definitions (2.55) and (2.58). Here we have to stress that there exist also different, and often more accurate, methods which allow to obtain $\mathcal{G}(z)$ etc experimentally. One possibility is to measure the time which the system needs to leave the individual microstates (survival probability), see, for example, [65, 66].

Validity of the equalities (2.61), (2.62) and (2.65) was confirmed in various theoretical models [23, 33, 67], in many experiments [68–71] and also in numerous numerical simulations [72, 73]. They can be derived for thermostated reversible

Table 2.1 The values of the arbitrary functions $p_F(x)$ and $p_B(x)$ that yield the individual relations (2.61), (2.63) and (2.65) from Eq. (2.66)

| Equation | $p_F(x)$ | $p_B(x)$ |
|----------|--|--|
| (2.61) | $\frac{\exp[-\beta\mathcal{F}(x, t')]}{\int_{-\infty}^{\infty} dx \exp[-\beta\mathcal{F}(x, t')]}$ | $\frac{\exp[-\beta\mathcal{F}(x, t)]}{\int_{-\infty}^{\infty} dx \exp[-\beta\mathcal{F}(x, t)]}$ |
| (2.63) | $\frac{\exp[-\beta\mathcal{G}(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta\mathcal{G}(x)]}$ | $\frac{\exp[-\beta\mathcal{G}(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta\mathcal{G}(x)]}$ |
| (2.65) | $\frac{\exp[-\beta\mathcal{F}(x, t')]}{\int_{-\infty}^{\infty} dx \exp[-\beta\mathcal{F}(x, t')]}$ | $\delta[X(t) - z] \frac{\exp\{-\beta\mathcal{F}[X(t), t]\}}{\exp[-\beta\mathcal{F}(z, t)]}$ |

deterministic systems [74], and also for microscopically reversible stochastic dynamics using both the Langevin equation [8], and the Master equation formulation [48]. In single-molecule experiments [75], all the relations (2.61), (2.62) and (2.65) are used for reconstructing free energy profiles of biomolecules [68, 69]. Influence of the experimental errors originating both from the instrument noise and from the uncertainty of measurements on the free energy difference estimate was studied in [76, 77]. It was found that the obtained free-energy difference is correct if the stochastic errors are statistically the same for the conjugate forward and reverse protocols [76], cf. the example in Appendix C. The discussion about the correct work definition also occurred in the field of fluctuation relations [44, 78]. The result is that the correct work definition, which fulfills the experimentally useful fluctuation theorems (2.61), (2.62) and (2.65), is the definition of the thermodynamic work (2.44).

In order to close this section let us note that the *integral* fluctuation theorems (2.61), (2.63) and (2.65) can be immediately derived from the single relation [15]

$$\left\langle \exp \left[\frac{-S_r(t, t')}{k_B} \right] \frac{p_B(x)}{p_F(x)} \right\rangle = 1, \quad (2.66)$$

where

$$S_r(t, t') = -\frac{Q(t, t')}{T} \quad (2.67)$$

is the (random) entropy transferred from the system into the thermal environment during the time interval $[t', t]$ and the auxiliary function $p_B(x)$ fulfills the normalization condition $\int_{-\infty}^{\infty} dx p_B(x) = 1$. The average in Eq. (2.66) is taken over all trajectories of the stochastic process $X(t)$ that depart at the time t' with an arbitrary probability $p_F(x) dx$ from the position that lies in the infinitesimal interval $(x, x + dx)$. The values of the arbitrary functions $p_B(x)$ and $p_F(x)$ that yield the individual relations (2.61), (2.63) and (2.65) are given in Table 2.1. Even more general formula, which contains *all* the presented fluctuation relations, was derived by Harris [49].

2.4 Heat Engines

One of the hot topics in the field of stochastic thermodynamics are stochastic heat engines [23, 28, 79–87]. The variety of models can be roughly classified according to the dynamical laws involved. In the case of the classical stochastic heat engines, the state space can either be discrete [23, 86–89] or continuous [80–82, 85–87]. Examples of the quantum heat engines are studied, e.g., in [90–93].

In the present work we consider periodically operating classical stochastic heat engines which communicate with two baths at the temperatures T_+ and T_- . Let t_p denote the duration of one operational cycle, $W_{\text{out}} \equiv -W(t_p, 0)$ stands for the (mean) work performed by the engine during one period and

$$Q_{\text{in}} = \int_0^{t_p} dt \frac{dQ(t, 0)}{dt} \Theta \left[\frac{dQ(t, 0)}{dt} \right], \quad (2.68)$$

where the function $\Theta(\bullet)$ equals to 1 for a positive argument and to 0 otherwise, denotes the heat transferred into the engine from the reservoirs per cycle. The engine efficiency is then defined by the standard formula

$$\eta = \frac{W_{\text{out}}}{Q_{\text{in}}}. \quad (2.69)$$

Similarly, the (mean) power output of the engine reads

$$P_{\text{out}} = \frac{W_{\text{out}}}{t_p}. \quad (2.70)$$

The traditional consideration of efficiency of heat engines operating between the two baths leads to the Carnot's upper bound³

$$\eta_C = 1 - \frac{T_-}{T_+}. \quad (2.71)$$

This bound is only achieved under reversible conditions where the state changes require infinite time and hence the power output is zero. Real heat engines generate a finite power output (2.70), i.e., they perform finite work W_{out} during a cycle of a finite duration t_p . The Carnot's inequality $\eta \leq \eta_C$ was recently generalized by Sinitsyn [94] (see also [95]) who derived a fluctuation theorem which relates the statistics of the (random) heat extracted from the hot reservoir during the cycle and that of the (random) work performed by the engine per cycle.

An alternative way to classify the performance of the heat engines is to compare their efficiencies at maximum power. On the macroscopic level, the first works on

³ Without loose of generality we assume that $T_+ > T_-$.

this subject were performed by Chambadal [96] and Novikov [97]. They studied, in the framework of endoreversible thermodynamics, the efficiency of nuclear power plants and derived the famous formula for the efficiency at maximum power

$$\eta_{\text{CA}} = 1 - \sqrt{\frac{T_-}{T_+}}. \quad (2.72)$$

This result have been referred to as the Curzon-Ahlborn efficiency since it was, nearly twenty years later, independently rediscovered by Curzon and Ahlborn [98]. After the derivation of η_{CA} , the discussion whether or not it represents the upper bound for the efficiency at maximum power has been initiated. The result was negative. The efficiency at maximum power is always *model dependent* and no universal upper bound was discovered, yet (see, for example, the reviews [87, 99]).

Nevertheless Tu [100] recently realized that large variety of heat engines [82, 89, 98, 100] (see also the reviews [86, 87]) exhibit similar efficiency at maximum power in the case of small difference between the two reservoir temperatures (i.e., η_{C} is small). Later it was proven [83] that the Taylor expansion of the efficiency at maximum power

$$\eta_{\text{P}} \approx \frac{\eta_{\text{C}}}{2} + \frac{\eta_{\text{C}}^2}{8} + o\left(\eta_{\text{C}}^3\right) \quad (2.73)$$

is general for “strong coupling” models (the term $\eta_{\text{C}}/2$) that possess a “left-right symmetry” (the term $\eta_{\text{C}}^2/8$). In the strong coupling models the energy (heat) flow is proportional to the flow that performs the work (matter flow). The left-right symmetry means that the heat flow through the system changes its sign when the two heat reservoirs are interchanged. If the second assumption is relaxed, only the term $\eta_{\text{C}}/2$ of the expansion (2.73) remains generally valid.

The authors of the study [83] also derived a lower and an upper bound for the efficiency at maximum power for a non-equilibrium analogue of the Carnot’s cycle [84], the cycle which consists of two non-equilibrium isotherms (say branches I and III) and two non-equilibrium adiabatic branches. More precisely, assume that the durations of the two isothermal branches are t_+ and t_- and that the total entropies produced during those isotherms are S_+ and S_- , respectively. If these variables fulfill the relations $t_{\text{p}} \approx (t_+ + t_-)$, $S_+ \approx 1/t_+ \geq 0$ and $S_- \approx 1/t_- \geq 0$, then the efficiency at maximum power is bounded by the inequalities

$$\frac{\eta_{\text{C}}}{2} \leq \eta_{\text{P}} \leq \frac{\eta_{\text{C}}}{2 - \eta_{\text{C}}}. \quad (2.74)$$

In Chap. 5 we present two examples of stochastic heat engines [23, 85, 86]. An engine based on the two-level system, which is introduced in Sect. 3.1.2, is investigated in Sect. 5.1 (see also [23]). An engine based on a particle diffusing in an external log-harmonic potential is studied in Sect. 5.2. The both models represent examples of the above mentioned non-equilibrium Carnot’s cycle. The second one

demonstrates the validity of the relations (2.73) and (2.74). In the next section we describe the generic periodic driving used in the two models.

2.4.1 Limit Cycle

An important part of the driving of a heat engine is represented, except the externally controlled parameters $Y(t)$, by the time dependence of the reservoir temperature $T = T(t)$. Under a periodic driving, $Y(t) = Y(t + t_p)$, $T(t) = T(t + t_p)$, the state of the system eventually, after a transient regime, becomes also periodic. The system attains an uniquely defined *limit cycle*, the operational cycle of the engine. An example of such cycle is depicted in Fig. 5.8. As mentioned above, the generic driving used in the models presented in this thesis consists of two adiabatic branches and two isotherms. Specifically, we assume the following driving:

- *Branch I (isothermal)*: The temperature equals T_+ and the control parameters changes smoothly from $Y(0)$ to $Y(t_+^-)$.
- *Branch II (adiabatic)*: The temperature and the control parameters changes rapidly from T_+ to T_- and from $Y(t_+^-)$ to $Y(t_+^+)$, respectively. We assume that the process is so fast that the state of the system remains unchanged (no heat is exchanged with the reservoir). The work done on the system $W(t_+^+, t_+^-)$ equals $U(t_+^+) - U(t_+^-)$ and no entropy is produced.
- *Branch III (isothermal)*: The temperature equals T_- and the control parameters changes smoothly from $Y(t_+^+)$ to $Y(t_p^-)$.
- *Branch IV (adiabatic)*: The temperature and the control parameters changes rapidly back from T_- to T_+ and from $Y(t_p^-)$ to $Y(t_p) = Y(0)$, respectively. We assume that the process is so fast that the state of the system remains unchanged (no heat is exchanged with the reservoir). The work done on the system $W(t_p, t_p^-)$ equals $U(t_p) - U(t_p^-)$ and no entropy is produced.

Up to now, both the master Eq. (2.3) and the Fokker-Planck Eq. (2.38) have been considered only for an isothermal process. However, neither in the case of Eq. (2.3) nor in the case of Eq. (2.38) the time dependence of the temperature does not break the Markov property of the underlying stochastic dynamics. Therefore one can use the Chapman-Kolmogorov Eqs. (2.7) and (2.40) to compose the solution of Eqs. (2.3) and (2.38) for the periodic driving above from their solutions for the isotherms I and III (during the adiabatic branches II and IV the system state does not change). In the next two paragraphs we execute the proposed procedure for the systems with discrete and with continuous state space, respectively.

2.4.1.1 Discrete Systems

Let $\mathbb{R}_+(t | t') = \mathbb{R}(t | t')$, $t', t \in (0, t_+^+)$ and $\mathbb{R}_-(t | t') = \mathbb{R}(t | t')$, $t', t \in (t_+^+, t_p)$ denote the solution of Eq. (2.3) during the isothermal branches I and III, respectively.

Using the Chapman-Kolmogorov Eq. (2.7) the solution of the master Eq. (2.3) for the above described periodic driving reads⁴

$$\mathbb{R}_p(t | t') = \begin{cases} \mathbb{R}_+(t | t'), & t', t \in [0, t_+^+], \\ \mathbb{R}_-(t | t_+^+) \mathbb{R}_+(t_+^+ | t'), & t' \in [0, t_+^+], \wedge t \in [t_+^+, t_p], \\ \mathbb{R}_-(t | t'), & t', t \in [t_+^+, t_p]. \end{cases} \quad (2.75)$$

The matrix $\mathbb{R}_p(t | t')$ can be used for calculation of the time correlation function (2.25) during the cycle. Further we focus on the matrix $\mathbb{R}_p(t) \equiv \mathbb{R}_p(t | 0)$, which evolves any initial state of the system as $\mathbf{p}(t) = \mathbb{R}_p(t) \mathbf{p}(0)$. The system states at the ends of the individual periods form a Markov chain and, in order to obtain the periodic state of the system during the limit cycle, $\mathbf{p}(t) = \mathbf{p}(t + t_p)$, we are interested in its fixed point behavior $\lim_{n \rightarrow \infty} [\mathbb{R}_p(t_p)]^n \mathbf{p}(0)$. If we take the stationary state as the initial condition, $\mathbf{p}(0) = \mathbf{p}^{\text{stat}}$, the system revisits this special state after each period of the driving. Therefore, to find the vector \mathbf{p}^{stat} , it suffices to solve the eigenvalue problem [13]

$$\mathbf{p}^{\text{stat}} = \mathbb{R}_p(t_p) \mathbf{p}^{\text{stat}}. \quad (2.76)$$

Similarly, let the matrix $\mathbb{G}_+(w, t | w') = \mathbb{G}(t, w | w', 0)$, $t \in (0, t_+^+)$ and the matrix $\mathbb{G}_-(w, t | w') = \mathbb{G}(t, w | w', t_+^+)$, $t \in (t_+^+, t_p)$ denote the solution of Eq. (2.13) during the isothermal branches I and III, respectively. According to the Chapman-Kolmogorov Eq. (2.14) the solution of Eq. (2.13) for the periodic driving reads

$$\mathbb{G}_p(w, t) = \begin{cases} \mathbb{G}_+(w, t | 0), & t \in [0, t_+^+], \\ \int_{-\infty}^{\infty} dw' \mathbb{G}_-(w, t | w') \mathbb{G}_+(w', t_+^+ | 0), & t \in [t_+^+, t_p]. \end{cases} \quad (2.77)$$

These results completely describe dynamics and energetics of the engine during the limit cycle. Specifically, the system state during the cycle reads

$$\mathbf{p}(t) = \mathbb{R}_p(t) \mathbf{p}^{\text{stat}} \quad (2.78)$$

and the energetics of the engine during the cycle is determined by the function

$$\xi(u, w, t; u') = \sum_{i,j=1}^N \delta[u - \mathcal{E}_i(t)] \delta[u' - \mathcal{E}_j(0)] [\mathbb{G}_p(w, t)]_{ij} p_j^{\text{stat}} \quad (2.79)$$

which enters Eqs. (2.16)–(2.18).

⁴ It is important to note that the matrix $\mathbb{R}_p(t) \equiv \mathbb{R}_p(t | 0)$ is, contrary to the driving $\mathbf{Y}(t)$, always continuous, i.e., $\mathbb{R}_p(t_+^+) = \mathbb{R}_p(t_+^+)$ and $\mathbb{R}_p(t_p^-) = \mathbb{R}_p(t_p)$.

2.4.1.2 Continuous Systems

The description for the continuous systems is similar. Let $R_+(x, t | x', t') = R(x, t | x', 0)$, $t', t \in (0, t_+^+)$ and $R_-(x, t | x', t') = R(x, t | x', t_+^+)$, $t', t \in (t_+^+, t_p)$ denote the solution of Eq. (2.38) during the isothermal branches I and III, respectively. Using the Chapman-Kolmogorov Eq. (2.40) the solution of the Fokker-Planck Eq. (2.38) for the periodic driving above reads

$$\begin{cases} R_+(x, t | x', t'), & t', t \in [0, t_+^+], \\ \int_{-\infty}^{\infty} dx'' R_-(x, t | x'', t_+^+) R_+(x'', t_+^+ | x', t'), & t' \in [0, t_+^+] \wedge t \in [t_+^+, t_p], \\ R_-(x, t | x', t'), & t', t \in [t_+^+, t_p]. \end{cases} \quad (2.80)$$

The eigenvalue problem (2.76) now translates into the integral Eq.

$$\int_{-\infty}^{\infty} dx' R_p(x, t_p | x', 0) p^{\text{stat}}(x') = p^{\text{stat}}(x). \quad (2.81)$$

The dynamics of the engine is described by the (periodic) state of the system during the limit cycle

$$p(x, t) = \int_{-\infty}^{\infty} dx' R_p(x, t | x', 0) p^{\text{stat}}(x'). \quad (2.82)$$

The energetics of the engine is determined by the function $p(x, t)$, which enters Eqs. (2.48)–(2.49) for the mean values of the work, the heat and the internal energy and by the functions $R_p(x, t | x', t')$ and $p^{\text{stat}}(x)$, which yield the time correlation function (2.51) and hence describe the fluctuations of the work and the heat.

2.4.2 Diagrams of the Limit Cycle

In this section we discuss the possibility to depict the limit cycle of an engine in a diagram similar to the pressure volume (PV) diagram known from classical thermodynamics. The mean work done per cycle by a discrete system can be rewritten as [cf. Eqs. (2.23) and (2.48)]

$$\begin{aligned}
W_{\text{out}} &= -W(t_p, 0) = - \int_0^{t_p} dt \sum_{i=1}^N \left[\frac{d}{dt} \mathcal{E}_i(t) \right] p_i(t) \\
&= - \int_{Y(0)}^{Y(t_p)} dY \sum_{i=1}^N \left[\frac{d}{dY} \tilde{\mathcal{V}}_i(Y) \right] \tilde{p}_i(Y) \\
&= - \sum_{j=1}^K \int_{Y_j(0)}^{Y_j(t_p)} dY_j \sum_{i=1}^N \left[\frac{\partial}{\partial Y_j} \tilde{\mathcal{V}}_i(Y_1, \dots, Y_K) \right] \tilde{p}_i(Y) \\
&= \sum_{i=1}^K \int_{Y_i(0)}^{Y_i(t_p)} dY_i f_i(Y_i), \tag{2.83}
\end{aligned}$$

where K stands for the number of components of the external driving $Y(t)$ and $\tilde{p}_i[Y(t)] = p_i(t)$. The individual terms on the right-hand side of Eq.(2.83) correspond to the work done by the individual components of the driving. For the continuous models the functions $f_i(Y_i)$ are given by $(p(x, t) = \tilde{p}[x, Y(t)])$

$$\begin{aligned}
f_i(Y_i) &= - \int_{-\infty}^{\infty} dx \left[\frac{\partial}{\partial Y_i} \tilde{\mathcal{V}}(x, Y) \right] \tilde{p}(x, Y) \\
&= - \int_{-\infty}^{\infty} dx \left[\frac{\partial}{\partial Y_i} \tilde{\mathcal{V}}(x, Y_1, \dots, Y_K) \right] \tilde{p}(x, Y). \tag{2.84}
\end{aligned}$$

Since $Y(t_p) = Y(0)$, each of the K contributions on the right-hand side of Eq.(2.83) equals the *oriented* area enclosed by the parametric plot of the system response, represented by the average $f_i(Y_i)$, versus the i th component of the driving, $Y_i(t)$. The parameter t runs from 0 to t_p . Similar decomposition of work is well known from classical thermodynamics. As an example consider a magnetic gas and let the driving possess two components, the volume $Y_1 = V$ and the magnetic field (spatially homogeneous magnetic flux density) $Y_2 = B$. The thermodynamic work done by the system per cycle then reads [101]

$$W_{\text{out}} = \int_{V(0)}^{V(t_p)} dV p(V) - \int_{B(0)}^{B(t_p)} dB I(B), \tag{2.85}$$

where $f_1 = p$ denotes the gas pressure and $-f_2 = I$ stands for the component of the total magnetic moment of the gas parallel to the external magnetic field. The parametric plots corresponding to the individual terms on the right-hand side of

Eq. (2.83) thus represent an analogy of the well known PV diagrams. In the field of stochastic thermodynamics such diagrams were used for the first time in the works [23, 102, 103]. Several examples of the diagrams are presented in Chap. 5 (see Figs. 5.1, 5.4, 5.9 and 5.11).

Important eye-guides in the diagrams can be formed by the so called *equilibrium isotherms*. The curves corresponding to the values of the functions f_i if a given cycle would be carried out quasi-statically. They are given by

$$f_i^{\text{eq}}[Y_i(t)] = \sum_{j=1}^N \left\{ \frac{\partial \tilde{\mathcal{V}}_j[Y_1(t), \dots, Y_K(t)]}{\partial Y_i(t)} \right\} \frac{\exp[\beta(t)\mathcal{F}_j(t)]}{\sum_{j=1}^N \exp[\beta(t)\mathcal{F}_j(t)]} \quad (2.86)$$

and

$$f_i^{\text{eq}}[Y_i(t)] = \int_{-\infty}^{\infty} dx \left[\frac{\partial \tilde{\mathcal{V}}(x, Y_1(t), \dots, Y_K(t))}{\partial Y_i(t)} \right] \frac{\exp[\beta(t)\mathcal{F}(x, t)]}{\int_{-\infty}^{\infty} dx' \exp[\beta(t)\mathcal{F}(x', t)]} \quad (2.87)$$

for the discrete and for the continuous models, respectively. The equilibrium isotherm corresponding to the first isothermal branch is obtained if one takes in Eqs. (2.86) and (2.87) $t \in (0, t_+^-)$ and $\beta(t) = 1/(k_B T_+)$. Similarly, the equilibrium isotherm corresponding to the second isothermal branch is obtained if one assumes $t \in (t_+^+, t_p^-)$ and $\beta(t) = 1/(k_B T_-)$. In Figs. 5.1, 5.4, 5.9 and 5.11 it can be clearly seen that the non-equilibrium functions f_i are “attracted” to the equilibrium isotherms, which represent the carrot (the banana) in the horse-carrot (banana-monkey) analogy depicted in Fig. 2.44. The more “reversible” the individual non-equilibrium isotherms are the stronger this attraction is (cf. Fig. 5.11).

References

1. Jarzynski, C. (1997). Nonequilibrium equality for free energy differences. *Physical Review Letters*, 78, 2690–2693, doi:[10.1103/PhysRevLett.78.2690](https://doi.org/10.1103/PhysRevLett.78.2690).
2. Carberry, D. M., Reid, J. C., Wang, G. M., et. al. (2004). Fluctuations and irreversibility: An experimental demonstration of a second-law-like theorem using a colloidal particle held in an optical trap. *Physical Review Letters*, 92, 140601, doi:[10.1103/PhysRevLett.92.140601](https://doi.org/10.1103/PhysRevLett.92.140601).
3. Hänggi, P., & Marchesoni, F. (2009). Artificial Brownian motors: Controlling transport on the nanoscale. *Reviews of Modern Physics*, 81, 387–442, doi:[10.1103/RevModPhys.81.387](https://doi.org/10.1103/RevModPhys.81.387).
4. Speck, T. (2011). Work distribution for the driven harmonic oscillator with time-dependent strength: Exact solution and slow driving. *Journal of Physics A: Mathematical and Theoretical*, 44(30), 305001, <http://stacks.iop.org/1751-8121/44/i=30/a=305001>.
5. Bressloff, P. C., & Newby, J. M. (2013). Stochastic models of intracellular transport. *Reviews of Modern Physics*, 85, 135–196, doi:[10.1103/RevModPhys.85.135](https://doi.org/10.1103/RevModPhys.85.135).
6. Jarzynski, C. (1997). Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach. *Physical Review E*, 56, 5018–5035, doi:[10.1103/PhysRevE.56.5018](https://doi.org/10.1103/PhysRevE.56.5018).

7. Crooks, G. (1998). Nonequilibrium measurements of free energy differences for microscopically reversible Markovian systems. *Journal of Statistical Physics*, 90(5–6), 1481–1487. ISSN 0022–4715, doi:[10.1023/A:1023208217925](https://doi.org/10.1023/A:1023208217925).
8. Crooks, G. E. (1999). Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences. *Physical Review E*, 60, 2721–2726, doi:[10.1103/PhysRevE.60.2721](https://doi.org/10.1103/PhysRevE.60.2721).
9. Crooks, G. E. (2000). Path-ensemble averages in systems driven far from equilibrium. *Physical Review E*, 61, 2361–2366, doi:[10.1103/PhysRevE.61.2361](https://doi.org/10.1103/PhysRevE.61.2361).
10. Van Kampen, N. (2011). *Stochastic processes in physics and chemistry*. North-Holland Personal Library: Elsevier Science. ISBN 9780080475363, <http://books.google.cz/books?id=N6II-6HIPxEC>.
11. Chvosta, P., Reineker, P., & Schulz, M. (2007). Probability distribution of work done on a two-level system during a nonequilibrium isothermal process. *Physical Review E*, 75, 041124, doi:[10.1103/PhysRevE.75.041124](https://doi.org/10.1103/PhysRevE.75.041124).
12. Chvosta, P., & Reineker, P. (1999) Dynamics under the influence of semi-Markov noise. *Physica A: Statistical Mechanics and its Applications*, 268, 103–120, ISSN 0378–4371. doi:[10.1016/S0378-4371\(99\)00021-7](https://doi.org/10.1016/S0378-4371(99)00021-7), <http://www.sciencedirect.com/science/article/pii/S0378437199000217>.
13. Motl, L., & Zahradník, M. (1995). *Pěstujeme lineární algebru*. Karolinum. ISBN 9788071841869, <http://books.google.cz/books?id=0shyAAAACAAJ>.
14. Gillespie, D. T. (1992). *Markov processes: An introduction for physical scientist*. San Diego: Academic press, Inc.
15. Seifert, U. (2008). Stochastic thermodynamics: Principles and perspectives. *The European Physical Journal B: Condensed Matter and Complex Systems*, 64, 423–431. ISSN 1434–6028, doi:[10.1140/epjb/e2008-00001-9](https://doi.org/10.1140/epjb/e2008-00001-9).
16. Imparato, A., & Peliti, L. (2005). Work probability distribution in single-molecule experiments. *EPL (Europhysics Letters)*, 69(4), 643, <http://stacks.iop.org/0295-5075/69/i=4/a=643>.
17. Imparato, A., & Peliti, L. (2005) Work distribution and path integrals in general mean-field systems. *EPL (Europhysics Letters)*, 70(6), 740, <http://stacks.iop.org/0295-5075/70/i=6/a=740>.
18. Šubrt, E., & Chvosta, P. (2007). Exact analysis of work fluctuations in two-level systems. *Journal of Statistical Mechanics: Theory and Experiment*, 2007(09), P09019. <http://stacks.iop.org/1742-5468/2007/i=09/a=P09019>.
19. Imparato, A., & Peliti, L. (2005). Work-probability distribution in systems driven out of equilibrium. *Physical Review E*, 72, 046114, doi:[10.1103/PhysRevE.72.046114](https://doi.org/10.1103/PhysRevE.72.046114).
20. Chatelain, C., & Karevski, D. (2006). Probability distributions of the work in the two-dimensional Ising model. *Journal of Statistical Mechanics: Theory and Experiment*, 2006(06), P06005, <http://stacks.iop.org/1742-5468/2006/i=06/a=P06005>.
21. Híjar, H., Quitana-H, J., & Sutmann, G. (2007). Non-equilibrium work theorems for the two-dimensional using model. *Journal of Statistical Mechanics: Theory and Experiment*, 2007(04), P04010, <http://stacks.iop.org/1742-5468/2007/i=04/a=P04010>.
22. Einax, M., & Maass, P. (2009). Work distributions for Ising chains in a time-dependent magnetic field. *Physical Review E*, 80, 020101. doi:[10.1103/PhysRevE.80.020101](https://doi.org/10.1103/PhysRevE.80.020101), <http://link.aps.org/doi/10.1103/PhysRevE.80.020101>.
23. Chvosta, P., Einax, M., Holubec, V., et al., et al., (2010). Energetics and performance of a microscopic heat engine based on exact calculations of work and heat distributions. *Journal of Statistical Mechanics*, 2010(03), P03002, <http://stacks.iop.org/1742-5468/2010i=03/a=P03002>.
24. Verley, G., Van den Broeck, C., & Esposito, M. (2013). Modulated two-level system: Exact work statistics. *Physical Review E*, 88, 032137, doi:[10.1103/PhysRevE.88.032137](https://doi.org/10.1103/PhysRevE.88.032137).
25. Ritort, F. (2004). Work and heat fluctuations in two-state systems. *Journal of Statistical Mechanics: Theory and Experiment*, 2004(10), P10016, <http://stacks.iop.org/1742-5468/2004/i=10/a=P10016>.

26. Manosas, M., Mossa, A., Forns, N., et al. (2009). Dynamic force spectroscopy of DNA hairpins: II. Irreversibility and dissipation. *Journal of Statistical Mechanics: Theory and Experiment*, 2009(02), P02061, <http://stacks.iop.org/1742-5468/2009/i=02/a=P02061>.
27. Risken, H. (1985). *The Fokker-Planck equation: Methods of solution and applications*. Berlin: Springer.
28. Sekimoto, K. (1997). Kinetic characterization of heat bath and the energetics of thermal ratchet models. *Journal of the Physical Society of Japan*, 66(5), 1234–1237, doi:10.1143/JPSJ.66.1234.
29. Vilar, J. M. G., & Rubi, J. M. (2008). Failure of the Work-Hamiltonian connection for free-energy calculations. *Physical Review Letters*, 100, 020601, doi:10.1103/PhysRevLett.100.020601.
30. Peliti, L. (2008). On the work-Hamiltonian connection in manipulated systems. *Journal of Statistical Mechanics: Theory and Experiment*, 2008(05), P05002, <http://stacks.iop.org/1742-5468/2008/i=05/a=P05002>.
31. Zimanyi, E. N., & Silbey, R. J. (2009). The work-Hamiltonian connection and the usefulness of the Jarzynski equality for free energy calculations. *Journal of Chemical Physics*, 130(17), 171102, doi:10.1063/1.3132747.0902.3681.
32. Vilar, J. M. G., & Rubi, J. M., (2011). Work-Hamiltonian connection for anisoparametric processes in manipulated microsystems. *Journal of Non-Equilibrium Thermodynamics*, 36, 123–130. doi:10.1515/jnetdy.2011.008, <http://www.degruyter.com/view/j/jnet.2011.36.issue-2/jnetdy.2011.008/jnetdy.2011.008.xml>.
33. Mazonka, O., & Jarzynski, C. (1999). Exactly solvable model illustrating far-from-equilibrium predictions. eprint [arXiv:cond-mat/9912121](https://arxiv.org/abs/cond-mat/9912121), [arXiv:cond-mat/9912121](https://arxiv.org/abs/cond-mat/9912121), <http://arxiv.org/abs/cond-mat/9912121>.
34. Baule, A., & Cohen, E. G. D. (2009). Fluctuation properties of an effective nonlinear system subject to Poisson noise. *Physical Review E*, 79, 030103, doi:10.1103/PhysRevE.79.030103.
35. Engel, A. (2009). Asymptotics of work distributions in nonequilibrium systems. *Physical Review E*, 80, 021120. doi:10.1103/PhysRevE.80.021120, <http://link.aps.org/doi/10.1103/PhysRevE.80.021120>.
36. Ryabov, A., Dierl, M., Chvosta, P., et. al. (2013). Work distribution in a time-dependent logarithmic-harmonic potential: Exact results and asymptotic analysis. *Journal of Physics A: Mathematical and Theoretical*, 46(7), 075002, <http://stacks.iop.org/1751-8121/46/i=7/a=075002>.
37. Nickelsen, D., & Engel, A. (2011). Asymptotics of work distributions: the pre-exponential factor. *The European Physical Journal B*, 82(2011), 207–218. ISSN 1434–6028, doi:10.1140/epjb/e2011-20133-y.
38. van Zon, R., & Cohen, E. G. D. (2003). Stationary and transient work-fluctuation theorems for a dragged Brownian particle. *Physical Review E*, 67, 046102, doi:10.1103/PhysRevE.67.046102.
39. van Zon, R., & Cohen, E. G. D. (2004). Extended heat-fluctuation theorems for a system with deterministic and stochastic forces. *Physical Review E*, 69, 056121, doi:10.1103/PhysRevE.69.056121.
40. Cohen, E. G. D. (2008). Properties of nonequilibrium steady state: A path integral approach. *Journal of Statistical Mechanics: Theory and Experiment*, 2008(07), P07014, <http://stacks.iop.org/1742-5468/2008/i=07/a=P07014>.
41. Campisi, M., Hänggi, P., & Talkner, P. (2011). Colloquium: Quantum fluctuation relations: Foundations and applications. *Reviews of Modern Physics*, 83, 771–791, doi:10.1103/RevModPhys.83.771.
42. Gibbs, J. (2010). *Elementary principles in statistical mechanics: Developed with especial reference to the rational foundation of thermodynamics*. Cambridge University Press: Cambridge Library Collection—Mathematics. ISBN 9781108017022, <http://www.google.cz/books?id=7VbC-15f0SKC>.
43. Schurr, J. M., & Fujimoto, B. S. (2003). Equalities for the nonequilibrium work transferred from an external potential to a molecular system. Analysis of single-molecule extension

- experiments. *The Journal of Physical Chemistry B*, 107(50), 14007–14019, doi:[10.1021/jp0306803](https://doi.org/10.1021/jp0306803).
44. Jarzynski, C. (2007). Comparison of far-from-equilibrium work relations. *Comptes Rendus Physique*, 8, 495–506. doi:[10.1016/j.crhy.2007.04.010](https://doi.org/10.1016/j.crhy.2007.04.010), arXiv:cond-mat/0612305.
 45. Bustamante, C., Liphardt, J., & Felix, R. (2005). The nonequilibrium thermodynamics of small systems. *Physics Today*, 58, 43, <http://dx.doi.org/10.1063/1.2012462>.
 46. Ritort, F. (2006). Single-molecule experiments in biological physics: Methods and applications. *Journal of Physics: Condensed Matter*, 18(32), R531, <http://stacks.iop.org/0953-8984/18/i=32/a=R01>.
 47. Schuler, S., Speck, T., Tietz, C., et. al. (2005). Experimental test of the fluctuation theorem for a driven two-level system with time-dependent rates. *Physical Review Letters*, 94, 180602, doi:[10.1103/PhysRevLett.94.180602](https://doi.org/10.1103/PhysRevLett.94.180602).
 48. Ritort, F. (2008). Nonequilibrium fluctuations in small systems: From physics to biology. In *Advances in chemical physics* (Vol.137, pp. 31-123). John Wiley & Sons Inc., ISBN 9780470238080, doi:[10.1002/9780470238080.ch2](https://doi.org/10.1002/9780470238080.ch2).
 49. Harris, R. J., & Schü, G. M. (2007). Fluctuation theorem for stochastic dynamics. *Journal of Statistical Mechanics: Theory and Experiment*, 2007(07), P07020, <http://stacks.iop.org/1742-5468/2007/i=07/a=P07020>.
 50. Esposito, M., & Van den Broeck, C. (2010). Three detailed fluctuation theorems. *Physical Review Letters*, 104, 090601, doi:[10.1103/PhysRevLett.104.090601](https://doi.org/10.1103/PhysRevLett.104.090601).
 51. Sagawa, T., & Ueda, M. (2010). Generalized jarzynski equality under nonequilibrium feedback control. *Physical Review Letters*, 104, 090602, doi:[10.1103/PhysRevLett.104.090602](https://doi.org/10.1103/PhysRevLett.104.090602).
 52. Sagawa, T., & Ueda, M. (2012). Nonequilibrium thermodynamics of feedback control. *Physical Review E*, 85, 021104, doi:[10.1103/PhysRevE.85.021104](https://doi.org/10.1103/PhysRevE.85.021104).
 53. Kurchan, J. (1998). Fluctuation theorem for stochastic dynamics. *Journal of Physics A: Mathematical and General*, 31(16), 3719, <http://stacks.iop.org/0305-4470/31/i=16/a=003>.
 54. Searles, D. J., & Evans, D. J. (1999). Fluctuation theorem for stochastic systems. *Physical Review E*, 60, 159–164, doi:[10.1103/PhysRevE.60.159](https://doi.org/10.1103/PhysRevE.60.159).
 55. Hatano, T., & Sasa, S.-I. (2001). Steady-state thermodynamics of Langevin systems. *Physical Review Letters*, 86, 3463–3466, doi:[10.1103/PhysRevLett.86.3463](https://doi.org/10.1103/PhysRevLett.86.3463).
 56. Seifert, U. (2005). Entropy production along a stochastic trajectory and an integral fluctuation theorem. *Physical Review Letters*, 95, 040602, doi:[10.1103/PhysRevLett.95.040602](https://doi.org/10.1103/PhysRevLett.95.040602).
 57. Esposito, M., & Van den Broeck, C. (2010). Three faces of the second law. I. Master equation formulation. *Physical Review E*, 82, 011143, doi:[10.1103/PhysRevE.82.011143](https://doi.org/10.1103/PhysRevE.82.011143).
 58. Van den Broeck, C., & Esposito, M. (2010). Three faces of the second law. II. Fokker-Planck formulation. *Physical Review E*, 82, 011144, doi:[10.1103/PhysRevE.82.011144](https://doi.org/10.1103/PhysRevE.82.011144).
 59. García-García, R., Domínguez, D., Lecomte, V., et. al. (2010). Unifying approach for fluctuation theorems from joint probability distributions. *Physical Review E*, 82, 030104, doi:[10.1103/PhysRevE.82.030104](https://doi.org/10.1103/PhysRevE.82.030104).
 60. Kurchan, J. (2007). Non-equilibrium work relations. *Journal of Statistical Mechanics: Theory and Experiments*, 2007(07), P07005, <http://stacks.iop.org/1742-5468/2007/i=07/a=P07005>.
 61. Baule, A., & Cohen, E. G. D. (2009). Steady-state work fluctuations of a dragged particle under external and thermal noise. *Physical Review E*, 80, 011110, doi:[10.1103/PhysRevE.80.011110](https://doi.org/10.1103/PhysRevE.80.011110).
 62. Bochkov, G., & Kuzovlev, Y. (1981). Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics: I. Generalized fluctuation-dissipation theorem. *Physica A: Statistical Mechanics and its Applications*, 106(3), 443–479, ISSN 0378–4371, doi:[10.1016/0378-4371\(81\)90122-9](https://doi.org/10.1016/0378-4371(81)90122-9).
 63. Bochkov, G., & Kuzovlev, Y. (1981). Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics: II. Kinetic potential and variational principles for nonlinear irreversible processes. *Physica A: Statistical Mechanics and its Applications*, 106(3), 480–520, ISSN 0378–4371, doi:[10.1016/0378-4371\(81\)90123-0](https://doi.org/10.1016/0378-4371(81)90123-0).

64. Hummer, G., & Szabo, A. (2001). Free energy reconstruction from nonequilibrium single-molecule pulling experiments. *Proceedings of the National Academy of Sciences*, 98(7), 3658–3661. doi:[10.1073/pnas.071034098](https://doi.org/10.1073/pnas.071034098), <http://www.pnas.org/content/98/7/3658.full.pdf+html>, <http://www.pnas.org/content/98/7/3658.abstract>.
65. Mossa, A., Manosas, M., Forns, N., et al. (2009). Dynamic forces spectroscopy of DNA hairpins: I. Force Kinetics and free energy landscapes. *Journal of Statistical Mechanics: Theory and Experiment*, 2009(02), P02060, <http://stacks.iop.org/1742-5468/2009/i=02/a=P02060>.
66. Nostheide, S., Holubec, V., Chvosta, P., et. al. (2013). Unfolding kinetics of periodic DNA hairpins. arXiv preprint [arXiv:1312.4146](https://arxiv.org/abs/1312.4146), arxiv.org/abs/1312.4146.
67. Crooks, G. E., & Jarzynski, C. (2007). Work distribution for the adiabatic compression of a dilute and interacting classical gas. *Physical Review E*, 75, 021116, doi:[10.1103/PhysRevE.75.021116](https://doi.org/10.1103/PhysRevE.75.021116).
68. Liphardt, J., Dumont, S., Smith, S. B., et. al. (2002). Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality. *Science*, 296(5574), 1832–1835. doi:[10.1126/science.1071152](https://doi.org/10.1126/science.1071152), <http://www.sciencemag.org/content/296/5574/1832.full.pdf>, <http://www.sciencemag.org/content/296/5574/1832.abstract>.
69. Collin, D., Ritort, F., Jarzynski, C., et al. (2005). Verification of the crooks fluctuation theorem and recovery of RNA folding free energies. *Nature*, 437, 231, <http://dx.doi.org/10.1038/nature04061M3>.
70. Blickle, V., Speck, T., Helden, L., et. al. (2006). Thermodynamics of a colloidal particle in a time-dependent nonharmonic potential. *Physical Review Letters*, 96, 070603, doi:[10.1103/PhysRevLett.96.070603](https://doi.org/10.1103/PhysRevLett.96.070603).
71. Gomez-Solano, J. R., Bellon, L., Petrosyan, A. et. al. (2010). Steady-state fluctuation relations for systems driven by an external random force. *EPL (Europhysics Letters)*, 89(6), 60003, <http://stacks.iop.org/0295-5075/89/i=6/a=60003>.
72. Xiao, T. J., Hou, Z., & Xin, H. (2008). Entropy production and fluctuation theorem along a stochastic limit cycle. *The Journal of Chemical Physics*, 129(11), 114506. doi:[10.1063/1.2978179](https://doi.org/10.1063/1.2978179), <http://link.aip.org/link/?JCP/129/114506/1>.
73. Holubec, V., Chvosta, P., Einax, M., et al. (2011). Attempt time Monte Carlo: An alternative for simulation of stochastic jump processes with time-dependent transition rates. *EPL (Europhysics Letters)*, 93(4), 40003, <http://stacks.iop.org/0295-5075/93/i=4/a=40003>.
74. Sevick, E., Prabhakar, R., Williams, S. R., et. al. (2008). Fluctuation theorems. *Annual Review of Physical Chemistry*, 59(1), 603–633. doi:[10.1146/annurev.physchem.58.032806.104555](https://doi.org/10.1146/annurev.physchem.58.032806.104555), <http://www.annualreviews.org/doi/pdf/10.1146/annurev.physchem.58.032806.104555>.
75. Manosas, M., & Ritort, F. (2005). Thermodynamic and kinetic aspects of RNA pulling experiments. *Biophysical Journal*, 88(5), 3224–3242, ISSN 0006–3495. doi:[10.1529/biophysj.104.045344](https://doi.org/10.1529/biophysj.104.045344), <http://www.sciencedirect.com/science/article/pii/S0006349505733749>.
76. Maragakis, P., Ritort, F., Bustamante, C., et. al. (2008). Bayesian estimates of free energies from nonequilibrium work data in the presence of instrument noise. *The Journal of Chemical Physics*, 129(2), 024102. doi:[10.1063/1.2937892](https://doi.org/10.1063/1.2937892), <http://link.aip.org/link/?JCP/129/024102/1>.
77. Calderon, C. P., Harris, N. C., Kiang, C.-H., et. al. (2009). Quantifying multiscale noise sources in single-molecule time series. *The Journal of Physical Chemistry B*, 113(1), 138–148, doi:[10.1021/jp807908c](https://doi.org/10.1021/jp807908c).
78. Alemany, A., Ribezzi, M., Ritort, F. (2011). Recent progress in fluctuation theorems and free energy recovery. *AIP Conference Proceedings*, 1332(1), 96–110. doi:[10.1063/1.3569489](https://doi.org/10.1063/1.3569489), <http://link.aip.org/link/?APC/1332/96/1>.
79. Takagi, F., & Hondou, T. (1999). Thermal noise can facilitate energy conversion by a ratchet system. *Physical Review E*, 60, 4954–4957, doi:[10.1103/PhysRevE.60.4954](https://doi.org/10.1103/PhysRevE.60.4954).
80. Sekimoto, K., Takagi, F., & Hondou, T. (2000). Carnot's cycle for small systems: Irreversibility and cost of operations. *Physical Review E*, 62, 7759–7768, doi:[10.1103/PhysRevE.62.7759](https://doi.org/10.1103/PhysRevE.62.7759).
81. Van den Broeck, C., Kawai, R., & Meurs, P. (2004). Microscopic analysis of a thermal Brownian motor. *Physical Review Letters*, 93, 090601, doi:[10.1103/PhysRevLett.93.090601](https://doi.org/10.1103/PhysRevLett.93.090601).

82. Schmiedl, T., & Seifert, U. (2008). Efficiency at maximum power: An analytically solvable model for stochastic heat engines. *EPL (Europhysics Letters)*, 81(2), 20003, <http://stacks.iop.org/0295-5075/81/i=2/a=20003>.
83. Esposito, M., Lindenberg, K., & Van den Broeck, C. (2009). Universality of Efficiency at Maximum Power. *Physical Review Letters*, 102, 130602, doi:10.1103/PhysRevLett.102.130602.
84. Esposito, M., Kawai, R., Lindenberg, K., et. al. (2010). Efficiency at maximum power of low-dissipation carnot engines. *Physical Review Letters*, 105, 150603, doi:10.1103/PhysRevLett.105.150603.
85. Blickle, V., & Bechinger, C. (2011). Realization of a micrometre-sized stochastic heat engine. *Nature Physics*, 8(2), 143–146, doi:10.1038/nphys2163.
86. Seifert, U. (2012). Stochastic thermodynamics, fluctuation theorems and molecular machines. *Reports on Progress in Physics*, 75(12), 126001, <http://stacks.iop.org/0034-4885/75/i=12/a=126001>.
87. Zhan-Chun, T. (2012). Recent advance on the efficiency at maximum power of heat engines. *Chinese Physics B*, 21(2), 020513, <http://stacks.iop.org/1674-1056/21/i=2/a=020513>.
88. Arnaud, J., Chusseau, L., & Philippe, F. (2010). A simple model for Carnot heat engines. *American Journal of Physics*, 78(1), 106–110. doi:10.1119/1.3247983, <http://link.aip.org/link/?AJP/78/106/1>.
89. Esposito, M., Kawai, R., Lindenberg, K., et. al. (2010). Quantum-dot carnot engine at maximum power. *Physical Review E*, 81, 041106, doi:10.1103/PhysRevE.81.041106.
90. Rezek, Y., & Kosloff, R. (2006). Irreversible performance of a quantum harmonic heat engine. *New Journal of Physics*, 8(5), 83, <http://stacks.iop.org/1367-2630/8/i=5/a=083>.
91. Henrich, M. J., Rempp, F., & Mahler, G. (2007). Quantum thermodynamic Otto machines: A spin-system approach. *The European Physical Journal Special Topics*, 151(1), 157–165, ISSN 1951–6355. doi:10.1140/epjst/e2007-00371-8. <http://dx.doi.org/10.1140/epjst/e2007-00371-8>.
92. Allahverdyan, A. E., Johal, R. S., & Mahler, G. (2008). Work extremum principle: Structure and function of quantum heat engines. *Physica Review E*, 77, 041118, doi:10.1103/PhysRevE.77.041118.
93. Abah, O., Roßnagel, J., Jacob, G., et. al. (2012). Single-Ion heat engine at maximum power. *Physical Review Letters*, 109, 203006, doi:10.1103/PhysRevLett.109.203006.
94. Sinitsyn, N. A. (2011). Fluctuation relation for heat engines. *Journal of Physics A: Mathematical and Theoretical*, 44(40), 405001, <http://stacks.iop.org/1751-8121/44/i=40/a=405001>.
95. Lahiri, S., Rana, S., & Jayannavar, A. M. (2012). Fluctuation relations for heat engines in time-periodic steady states. *Journal of Physics A: Mathematical and Theoretical*, 45(46), 465001, <http://stacks.iop.org/1751-8121/45/i=46/a=465001>.
96. Chambadal, P. (1957). *Les Centrales nucléaires*. Colin: Collection Armand Colin, <http://books.google.cz/books?id=TX8KAAAAMAAJ>.
97. Novikov, I. I. (1958). The efficiency of atomic power stations. *Journal of Nuclear Energy II*, 7, 125.
98. Curzon, F. L., & Ahlborn, B. (1975). Efficiency of a Carnot engine at maximum power output. *American Journal of Physics*, 43(1), 22–24. doi:10.1119/1.10023, <http://link.aip.org/link/?AJP/43/22/1>.
99. Durmayaz, A., Sogut, O. S., Sahin, B., et. al. (2004). Optimization of thermal systems based on finite-time thermodynamics and thermoeconomics. *Progress in Energy and Combustion Science*, 30(2), 175–217, ISSN 0360–1285. doi:10.1016/j.pecs.2003.10.003, <http://www.sciencedirect.com/science/article/pii/S0360128503000777>.
100. Tu, Z. C. (2008). Efficiency at maximum power of Feynman's ratchet as a heat engine. *Journal of Physics A: Mathematical and Theoretical*, 41(31), 312003, <http://stacks.iop.org/1751-8121/41/i=31/a=312003>.
101. Callen, H. (2006). *Thermodynamics & an intro to thermostatics*. (Student ed.), New York: Wiley India Pvt. Limited, ISBN 9788126508129. http://books.google.cz/books?id=uOiZB_2y5pIC.

102. Holubec, V. (2009). Nonequilibrium thermodynamics of small systems. Diploma Thesis, Charles University in Prague, Faculty of Mathematics and Physics.
103. Chvosta, P., Holubec, V., Ryabov, A., et. al. (2010). Thermodynamics of two-stroke engine based on periodically driven two-level system. *Physica E: Low-dimensional Systems and Nanostructures*, 42(3), 472–476, ISSN 1386–9477. <http://dx.doi.org/10.1016/j.physe.2009.06.031>; *Proceedings of the International Conference Frontiers of Quantum and Mesoscopic Thermodynamics FQMT '08*, <http://www.sciencedirect.com/science/article/pii/S1386947709002380>.

Non-equilibrium Energy Transformation Processes
Theoretical Description at the Level of Molecular
Structures

Holubec, V.

2014, XIV, 152 p. 29 illus., 22 illus. in color., Hardcover

ISBN: 978-3-319-07090-2