Non-Equilibrium Thermodynamics and Stochasticity
A Phenomenological Look on Jarzynki’s Equality

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Abstract The theory of phenomenological Non-equlibrium Thermodynamics is extended by including stochastic processes in order to account for recently derived thermodynamical relations such as the Jarzynski equality. Four phenomenological axioms are postulated resulting in a phenomenological interpretation of Jarzynski’s equality. Especially, considering the class of Jarzynski processes Jarzynski’s equality follows from the axiom that the statistical average of the exponential work is protocol independent.

Keywords Non-equilibrium Thermodynamics · Jarzynski Equality · Stochasticity

1 Introduction

Among many branches of thermodynamics –such as Thermodynamics of Irreversible Processes, Rational Thermodynamics, Extented Thermodynamics, Endoreversible Thermodynamics, Finite Time Thermodynamics, Quantum Thermodynamics, Mesoscopic Theory, GENERIC [1]– Stochastic Thermodynamics is another branch which introduces probabilities into the thermodynamical description [2]. But in contrast to the above mentioned branches, Stochastic Thermodynamics allows processes of negative process entropy, some times called ”violations” of the Second Law. This item does not have any consequences on the phenomenological level because the negative process entropies vanish by establishing mean values using the introduced probabilities. Consequently it is obvious, how to obtain the phenomenological level in Stochastic Thermodynamics, but how vice-versa to incorporate stochastic processes with their probabilities and process entropies into phenomenological Non-equilibrium Thermodynamics is an open question which is investigated in this paper. This is not done in full generality, but only for a special process class –called the Jarzynski process class– because we want to clarify the status of the integral fluctuation theorem –the Jarzynski equality [3]– in the framework of Non-equilibrium Thermodynamics.

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The paper is organized as follows: After having introduced the Jarzynski process, a sketch of Non-equilibrium Thermodynamics of discrete systems is given for introducing the items which later on are needed. The Jarzynski process of phenomenological Non-equilibrium Thermodynamics is replaced by a set of stochastic processes which generate probability densities defined on the process work as a stochastic variable. These stochastic processes are decomposed into regular and non-regular processes distinguished by their process entropy production: regular ones have positive process entropy production, whereas that of the non-regular processes is negative. The mean values of process dissipation and work are considered with respect to the phenomenological Second Law. Two phenomenological axioms establish Jarzynski’s equality. The reversible case and equilibrium are shortly discussed. A summary and a discussion finish the paper.

2 The Jarzynski Process

We consider a discrete system\textsuperscript{1} which interacts with its environment by power and heat exchange performing a Jarzynski process. Such a process begins at time \( t = 0 \) in a fixed equilibrium state \( A^{eq} \) whose work variable (Jarzynski’s switching parameter) is \( \lambda = 0 \) and arrives at time \( t = \tau \) in a non-equilibrium state \( C^{neq} \) with the work variable \( \lambda = 1 \). During the time \( 0 \leq t \leq \tau \), the system exchanges irreversibly work and heat with its controlling equilibrium environment\textsuperscript{3} of constant thermostatic temperature \( T^* \). For times \( \tau < t \leq d \) the thermal contact with the controlling heat reservoir maintains, but the switching parameter is fixed at \( \lambda = 1 \), that means, no additional work, but heat is exchanged between the system and the reservoir during this time interval. Consequently, the final equilibrium state \( B^{eq} \) has the same work variable \( \lambda = 1 \) as \( C^{neq} \), and according to the process control by the heat reservoir its temperature is \( T^* \). Because the state space of the system in consideration is given by the work variable \( \lambda \) and by the contact temperature \( \Theta \), we can represent the Jarzynski process as follows

\[ J_\lambda : \quad t = 0 : \quad A^{eq}(\lambda = 0, T^*) \quad \rightarrow \quad [\dot{\lambda}(t), \dot{Q}(t)] \quad \rightarrow \quad (1) \]

\[ \quad \rightarrow \quad t = \tau : \quad C^{neq}(\lambda = 1, \Theta) \quad \rightarrow \quad [\dot{\lambda} = 0, \dot{Q}(t)] \quad \rightarrow \quad (2) \]

\[ \quad \rightarrow \quad t = d : \quad B^{eq}(\lambda = 1, T^*). \quad (3) \]

Here, the time-dependent work variable \( \lambda(t) \) –the protocol– is arbitrary, but controlled, whereas the heat exchange \( \dot{Q}(t) \) is uncontrolled and depends on the given protocol.

The interpretation of the work which is done during the transfer from \( \lambda = 0 \) to \( \lambda = 1 \) –during the protocol– is different in Non-equilibrium and Stochastic Thermodynamics: in Non-equilibrium Thermodynamics the work is a phenomenological variable, whereas in Stochastic Thermodynamics the work is introduced as a stochastic variable \( w \) generating a probability distribution \( p_\lambda(w) \), if identical protocols \( \lambda(t) \) are performed. Considering a

\textsuperscript{1}A so-called Schottky system\textsuperscript{4}: a “box” interacting with its environment which is not to be confused with discrete systems in Stochastic Thermodynamics which evolve on a discrete state space\textsuperscript{2}.

\textsuperscript{2}A so-called non-thermal state.

\textsuperscript{3}A heat reservoir.

\textsuperscript{4}The contact temperature is a non-equilibrium analogue of the thermostatic temperature. More details in sect.3.3 [5, 6, 7].
Jarzynski process \(\mathbf{1}\) to \(\mathbf{3}\) with a heat reservoir at inverse (thermostatic) temperature \(\beta\), the probability distribution is not arbitrary, but constrained by the relation which is known as Jarzynski equality

\[
\int_{-\infty}^{\infty} p_\lambda(w) \exp(-\beta w) dw = \exp(-\beta \Delta^{AB} F), \tag{4}
\]

where \(\Delta^{AB} F\) denotes the difference of the equilibrium free energy of the system between the states \(A^{eq}\) and \(B^{eq}\). Note that \(\mathbf{1}\) remains valid even if we only look at changes of the system from \(A^{eq}\) to \(C^{neq}\) because there is no work performed on the system from \(C^{neq}\) to \(B^{eq}\) and \(p_\lambda(w)\) remains unchanged during that part. Hence, \(\mathbf{4}\) teaches that non-equilibrium stochastic fluctuations contain valuable information about equilibrium quantities.

Jarzynski’s equality and was originally discovered in 1997 \[3, 8\]. Since then it was derived under many circumstances, for instance, it follows from the detailed (Crooks) fluctuation theorem \[9, 10, 11\], it is also valid in the strong coupling regime \[12\] or for quantum systems \[13, 14, 15\]. Furthermore, early experimental confirmations can be found in \[16, 17, 18\] and a recent review is given in \[19\]. In the next section we will look at the Jarzynski process from a purely phenomenological perspective (without probabilities and stochasticity) before we then ask how to incorporate the Jarzynski equality on a phenomenological level?

3 A Thermodynamical Sketch

3.1 Basic phenomenological variables

The state of a discrete thermodynamical system is described by basic variables. Kind and number of these variables depend on the nature of the system under consideration and on the process going on in that system. The number of variables in non-equilibrium is clearly greater than in equilibrium. Therefore, equilibrium needs a minimal number of basic variables spanning the so-called equilibrium sub-space. According to a special formulation of the Zeroth Law \[20\], the equilibrium variables of a thermally homogeneous system are

\[
z_{eq} = (U, a, n) \quad \text{or} \quad z_{eq} = (T, a, n) \tag{5}
\]

(internal energy \(U\), work variables \(a\), mol numbers \(n\), thermostatic temperature \(T\)). In equilibrium, there exists an one-to-one mapping between the internal energy of the system and its thermostatic temperature \(U \leftrightarrow T\).

More basic variables than in equilibrium are needed in non-equilibrium

\[
z = (U, a, n, z_{neq}). \tag{6}
\]

The set of the non-equilibrium variables \(z_{neq}\) depends on the nature of the system in consideration: e.g. the orientation of needle-shaped molecules may be an example in the case of complex materials, time derivatives of the equilibrium variables and dissipative

\[5\]A system without adiabatic partitions.
fluxes are other examples. Here with regard to Jarzynski processes, we introduce the contact temperature $\Theta$ of the system as one non-equilibrium variable \cite{5, 6, 7}. Other basic non-equilibrium variables – e.g. the internal variables – are marked by a place-holder $\xi$. Consequently, the non-equilibrium variables are

\[ z_{\text{neq}} = (\Theta, \xi), \]  

and the basic variables spanning the state space of the system are

\[ z = (U, a, n, \Theta, \xi). \]

The non-equilibrium contact temperature $\Theta$ is independent of the other variables of the state space, especially independent of the internal energy \cite{21}.

### 3.2 Non-equilibrium entropy, First Law

A non-equilibrium entropy is a state function on the non-equilibrium state space \cite{8}. The time rate of this non-equilibrium entropy is an analogue to Gibbs’ fundamental equation \cite{7}:

\[ \dot{S} := \frac{1}{\Theta} \dot{Q} - \frac{A}{\Theta} \cdot \dot{a} - \frac{\mu}{\Theta} \cdot \dot{n} + \alpha \cdot \dot{\Theta} + \beta \cdot \dot{\xi} \]

The conjugate quantities to the state space variables are: the reciprocal contact temperature $1/\Theta$, the generalized forces $A$ over the contact temperature, the chemical potentials $\mu$ over the contact temperature and the conjugate quantities $\alpha$ and $\beta$ related to the contact temperature and to the internal variables.

Introducing the molar enthalpy $h$ and the external change of mol numbers $\dot{n}^e$ by the material exchange between system and environment \cite{22}, the First Law and the power $\dot{W}$ are

\[ \dot{U} = \dot{Q} + \dot{W} + h \cdot \dot{n}^e, \quad \dot{W} := A \cdot \dot{a}. \]

Approaching Jarzynski processes, we consider here closed discrete systems without chemical reactions

\[ \dot{n} = 0, \quad \dot{n}^e = 0. \]

By taking \cite{11} and \cite{11} into account, \cite{9} results for closed systems in

\[ \dot{S} = \frac{1}{\Theta} \dot{Q} + \alpha \cdot \dot{\Theta} + \beta \cdot \dot{\xi}. \]

This is the usual expression of decomposing the entropy time rate in phenomenological Non-equilibrium Thermodynamics \cite{23}: $\dot{Q}/\Theta$ is the entropy flux and $\alpha \cdot \dot{\Theta} + \beta \cdot \dot{\xi}$ the entropy production. Closing the system enforces vanishing of the entropy flux.

\textsuperscript{6}If the contact temperature $\Theta$ in \cite{9} is replaced by the thermostatic temperature $T^*$ of the controlling heat reservoir, the expression \cite{9} looses its property as state function because $T^*$ belongs to the controlling heat reservoir and is therefore not a state variable. In equilibrium, $\Theta$ is replaced by the thermostatic temperature $T$ of the system.
### 3.3 Contact temperature, free energy and work

We consider a closed non-equilibrium system which is in contact with a heat reservoir of thermostatic temperature $T^*$. The heat exchange between them is $\dot{Q}$. We now define the contact temperature $\Theta$ of the non-equilibrium system \[5\] \[6\] by the inequality

$$
\left( \frac{1}{\Theta} - \frac{1}{T^*} \right) \dot{Q} \geq 0.
$$

(13)

This “defining inequality of the contact temperature” states that $\Theta = T^*$ if and only if $\dot{Q} = 0$.

Taking (12), (10), (11) and (13) into account, we obtain

$$
\dot{S} - \alpha \dot{\Theta} - \beta \dot{\xi} \geq \frac{1}{T^*} \left( \dot{F} + (\Theta S) \right),
$$

(14)

an inequality which stems from introducing the contact temperature by (13) and which is independent of the Second Law. Here, $T^*$ is the constant thermostatic temperature of a controlling heat reservoir, such one which appears in the Jarzynski process.

Next, we define the state function of non-equilibrium free energy as \[7\]

$$
F(a, \Theta, \xi) := U - \Theta S \implies \dot{F} = \dot{U} - (\Theta S)\dot{\Theta}.
$$

(15)

Inserting (15) into (14) results in

$$
\dot{S} - \alpha \dot{\Theta} - \beta \dot{\xi} \geq \frac{1}{T^*} \left( \dot{F} + (\Theta S)\dot{\Theta} - \dot{W} \right).
$$

(16)

Integration along a Jarzynski process $J_\lambda : A^{eq} \rightarrow B^{eq}$ yields

$$
S_B - S_A - J_\lambda \int_A^B (\alpha \dot{\Theta} + \beta \dot{\xi}) dt \geq \frac{1}{T^*} \left( \Delta^{AB} F + \Theta_B S_B - \Theta_A S_A - W^{AB} \right).
$$

(17)

According to (11) and (3),

$$
\Theta_A = \Theta_B = T^*
$$

(18)

is valid\[8\], and we obtain an inequality valid along Jarzynski processes

$$
J_\lambda \int_A^B (\alpha \dot{\Theta} + \beta \dot{\xi}) dt =: \Sigma^{AB} \leq \frac{1}{T^*} \left( W^{AB} - \Delta^{AB} F \right) =: \frac{D^{AB}}{T^*}
$$

(19)

which stems as (14) from the defining inequality of the contact temperature (13). According to the decomposition of the entropy rate (12), the bracket in (19) is the entropy production, so that $\Sigma^{AB}$ becomes the process entropy production between $A^{eq}$ and $B^{eq}$, and $D^{AB}$ is the process dissipation which is in generally greater than $T^* \Sigma^{AB}$. Note that

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\[7\]This definition is in contrast to definitions used in Stochastic Thermodynamics \[24, 25, 26\] where the contact temperature is not used and is replaced by the thermostatic temperature $T^*$ of the controlling reservoir. Thus, $F$ becomes the free energy in the equilibrium state $B^{eq}$ \[3\], whereas (15) refers to $C^{neq}$.

\[8\]An integration only between $A^{eq}$ and $C^{neq}$ would not result in (18) because of $\Theta_C \neq T^*$. 

\[ D^{AB}/T^* \] is also sometimes called the entropy production because it coincides with the entropy increase of system and bath \([3, 2, 19]\).

The process work \(W^{AB}\) along the Jarzynski process \(J_\lambda\) is related to the given protocol \(\lambda(t)\) according to (1) and to the generalized forces \(L(\lambda, \Theta)\)

\[ W^{AB}_\lambda = J_\lambda \int_A^B L(\lambda, \Theta) \lambda (t) dt. \quad (20) \]

This quantity will become a key position when stochastic processes are introduced below. We now take the Second Law into account.

### 3.4 Second Law

According to the Second Law, the entropy production

\[ \alpha \dot{\Theta} + \beta \cdot \dot{\xi} \geq 0, \quad (21) \]

is not negative in phenomenological Non-equilibrium Thermodynamics \([23]\). Thus, (12) and (19) become with (13) and (21)

\[ \dot{S} \geq \frac{1}{\Theta} \dot{Q} \geq \frac{1}{T^*} \dot{Q}, \quad 0 \leq \Sigma^{AB} \leq \frac{D^{AB}}{T^*}. \quad (22) \]

From (19) and (22) follows the well known fact which is also valid for Jarzynski processes

\[ W^{AB} \geq \Delta^{AB} F. \quad (23) \]

The reversible case is defined by

\[ (\alpha \dot{\Theta} + \beta \cdot \dot{\xi})^{rev} = 0, \quad \text{and} \quad \Theta = T^* = \text{const}. \quad (24) \]

Consequently, we obtain according to (19) and (24) for the reversible case

\[ \Sigma^{AB}_{rev} = D^{AB}_{rev} = 0 \quad \rightarrow \quad W^{AB}_{rev} = \Delta^{AB} F. \quad (25) \]

This sketch outlines the tools which we need in the sequel.

### 4 Introducing Stochasticity

In contrast to macroscopic systems, the behaviour of small (mesoscopic) systems is inherently stochastic: for describing them, stochastic variables have to be used generating probability distributions. Although the average behaviour of stochastic systems still obeys the phenomenological laws of thermodynamics, there is much more to discover as Stochastic Thermodynamics lets suppose. Here, for the special example of Jarzynski processes, we are interested in a “top-down” approach, i.e., we ask how to modify phenomenological Non-equilibrium Thermodynamics in order to account for fluctuations and stochasticity. This is in contrast to Stochastic Thermodynamics, which follows rather from a “bottom-up” approach by relying on microscopically derived equations of motion (e.g., Langevin or master equations) \([2]\).
4.1 Process work as a stochastic variable

We consider one of the numerous protocols \( \lambda(t) \) performing a Jarzynski process. According to (20), the work \( W_{\lambda}^{AB} \) is required. Whenever the same protocol is used in Non-equilibrium Thermodynamics, the same work is required for performing the corresponding Jarzynski process. This situation is totally different for stochastic systems: several experiments, all performed with the same given protocol \( \lambda(t) \) require several different works for performing the Jarzynski process with the result, that (20) cannot hold true for stochastic systems. Consequently, we postulate that the process work is a stochastic quantity.

4.1.1 The first basic axiom

■ First Basic Axiom: The process work along a Jarzynski process is a stochastic variable given by a stochastic equation

\[
W_{\lambda}^{AB} = \mathcal{J}_\lambda \int_{A}^{B} L(\lambda, \Theta) \dot{\lambda}(t) dt \in \mathbb{R} \rightarrow p_{\lambda}(W_{\lambda}^{AB}) \tag{26}
\]

replacing (20). Performing the same protocol numerously, the values of the process works generate a probability distribution function \( p_{\lambda} \) on \( W_{\lambda}^{AB} \).

The same protocol \( \lambda(t) \) generates by the stochastic properties of the material – introduced by the stochastic mapping \( L(\lambda, \Theta) \) for the generalized forces [27] – different process works \( W_{\lambda}^{AB} \) which all together implement a probability distribution function \( p_{\lambda}(W_{\lambda}^{AB}) \) on the stochastic variable of the process work. Consequently, in the framework of Non-equilibrium Thermodynamics, the probability distribution function \( p_{\lambda}(W_{\lambda}^{AB}) \) is a measurable quantity which can be found out by performing a sufficiently high number of Jarzynski processes always using the same protocol \( \lambda(t) \). Not only the work becomes a stochastic quantity but also related quantities such as heat, entropy and entropy production.

4.1.2 Jarzynski process class

We can suppose, that by replacing the phenomenological quantities of Non-equilibrium Thermodynamics by stochastic ones, some results of the phenomenological theory will change: Stochastic and Non-equilibrium Thermodynamics are different to each other, and the following question arises: What are the phenomenological conditions under which Non-equilibrium Thermodynamics turns out to be a special case of Stochastic Thermodynamics? For instance, it is easy to see that, taking Jarzynski’s inequality into account, processes of negative process dissipation appear in Stochastic Thermodynamics, a fact which is strictly forbidden in Non-equilibrium Thermodynamics.

Up to now, we considered one arbitrary, but fixed protocol belonging to a special Jarzynski process. According to (13) and (23), Jarzynski processes can be performed with several different protocols. All these protocols together form the (stochastic) Jarzynski process class

\[
\{ \mathcal{J}_\lambda \} := \{ \wedge \lambda : \lambda(t) \in \mathcal{J}_\lambda, p_{\lambda}(W_{\lambda}^{AB}) \} \tag{27}
\]

The introduction of this process class allows to derive connections between the probability densities of different protocols in the sequel.
4.2 Exponential mean process work

Approaching Jarzynski’s equality, we start out with Jensen’s inequality 9

\[ \int p(x) \exp(-\beta x) \, dx \geq \exp \left( -\beta \int p(x) \, dx \right), \]  
\[ \int p(x) \, dx = 1, \quad p(x) \geq 0, \quad \beta > 0, \]  

and we identify \( x \) with the stochastic process work, and the probability function \( p_\lambda(x) \) belongs to an arbitrary protocol \( \lambda(t) \)

\[ x \equiv W^{AB}_\lambda, \quad \int p_\lambda(x) \, dx =: W^{AB}_\lambda. \]  

Here, the phenomenological process work \( W^{AB}_\lambda \) is introduced as the mean value over all stochastic process works \( W^{AB}_\lambda \). According to this setting, Jensen’s inequality (28) results in

\[ \int p_\lambda(W^{AB}_\lambda) \exp(-\beta W^{AB}_\lambda) \, dW^{AB}_\lambda \geq \exp \left( -\beta W^{AB}_\lambda \right). \]  

As already mentioned, the theoretical concept of process work is different in Stochastic and Non-equilibrium thermodynamics: according to (30), we have to distinguish between stochastic and phenomenological work: \( W^{AB}_\lambda \neq W^{AB}_\lambda \) [27].

Applying the mean value theorem on the lhs of (31), we obtain

\[ \int p_\lambda(x) \exp(-\beta x) \, dx = \exp(-\beta M_\lambda) \geq \exp(-\beta W^{AB}_\lambda) \]  

Here, \( M_\lambda \) is the exponential mean process work which is different from the phenomenological one according to (32)

\[ M_\lambda \leq W^{AB}_\lambda. \]  

We now consider the exponential mean process work in two special cases of the probability distribution: the non-stochastic case and the reversible one.

4.2.1 The non-stochastic case

If in every repetition of the same protocol we measure the same work value \( W^{AB}_{\lambda\text{nst}} \), we refer to this case as “non-stochastic” and the corresponding probability density is

\[ p^{\text{nst}}_\lambda(x) = \delta \left( x - W^{AB}_{\lambda\text{nst}} \right). \]  

Then, according to (32) we obtain

\[ \exp(-\beta W^{AB}_{\lambda\text{nst}}) = \exp(-\beta M^{\text{nst}}_\lambda) \geq \exp(-\beta W^{AB}_{\lambda\text{nst}}), \]  

resulting in

\[ M^{\text{nst}}_\lambda = W^{AB}_{\lambda\text{nst}} \geq \Delta^{AB} F, \]  

because the phenomenological process work obeys the Second Law (23) also for non-stochastic processes.

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9Jensen’s inequality states that for any convex function \( f \) and random variable \( X \) we have \( \mathbb{E}[f(X)] \geq f[\mathbb{E}(X)] \) where \( \mathbb{E}[..] \) denotes an expectation value. Since \( f(x) = e^{-\beta x} \) is convex, Eq. (28) follows.
4.2.2 The reversible case

According to (25), the reversible case is defined by

\[ W^{AB}_{\text{rev}} = \Delta^{AB}F. \]  

(37)

Thus, (32) yields

\[
\int p^\text{rev}_\lambda(x) \exp(-\beta x) dx = \exp(-\beta M^\text{rev}_\lambda) \geq \exp(-\beta \Delta^{AB}F) \]  

(38)

resulting in \( M^\text{rev}_\lambda \leq \Delta^{AB}F \). In comparison with (36) and (37), we obtain the chain of inequalities

\[ M^\text{rev}_\lambda \leq \Delta^{AB}F = W^{AB}_{\text{rev}} \leq M^{\text{nst}}_\lambda = W^{AB}_{\text{nst}}. \]  

(39)

Consequently, the exponential mean process work \( M_\lambda \) is process-dependent – reversible or non-stochastic – for the present.\(^{10}\)

4.3 Regular and non-regular processes

The stochastic process work (26) takes values which can be greater or smaller than the free energy difference \( \Delta^{AB}F \). Consequently, the integral in (32) can be decomposed into two parts

\[
\int_{x \geq \Delta} p_\lambda(x) \exp(-\beta x) dx + \int_{x < \Delta} p_\lambda(x) \exp(-\beta x) dx = \exp(-\beta M_\lambda). \]  

(40)

We now denote processes with \( W^{AB}_\lambda \geq \Delta^{AB}F \) as regular processes and such with \( W^{AB}_\lambda < \Delta^{AB}F \) as non-regular ones. Consequently, the first integral of (40) runs over the regular processes, whereas the second one runs over the non-regular processes.

Application of the mean value theorem to the lhs of (40) is possible and results by use of (32) in

\[
\exp(-\beta M^+_\lambda) P^+_\lambda + \exp(-\beta M^-_\lambda) P^-_\lambda = \exp(-\beta M_\lambda) \geq \exp(-\beta W^{AB}_\lambda), \]  

(41)

\[
P^+_\lambda := \int_{x \geq \Delta} p_\lambda(x) dx, \quad P^-_\lambda := \int_{x < \Delta} p_\lambda(x) dx, \quad P^+_\lambda + P^-_\lambda = 1. \]  

(42)

By construction, we obtain

\[ M^-_\lambda < \Delta^{AB}F \leq M^+_\lambda. \]  

(43)

More specifically, the exponential mean process works \( M^+_\lambda \) and \( M^-_\lambda \) of the regular and the non-regular processes depend on the precise form of the probability densities. According to (41), (40) and (42), we obtain

\[
M^+_\lambda = \frac{1}{\beta} \left[ \ln \int_{x \geq \Delta} p_\lambda(x) dx - \ln \int_{x \geq \Delta} p_\lambda(x) \exp(-\beta x) dx \right], \]  

(44)

\[
M^-_\lambda = \frac{1}{\beta} \left[ \ln \int_{x < \Delta} p_\lambda(x) dx - \ln \int_{x < \Delta} p_\lambda(x) \exp(-\beta x) dx \right]. \]  

(45)

\(^{10}\)This process dependence vanishes by introducing Jarzynski’s equality in sect.5, giving rise to the second basic axiom in sect.5.2.
Together with (43) and (42), this yields after a short algebraic manipulation

$$\frac{P^-}{P^+} < \frac{\int_{x<\Delta} p_\lambda(x) \exp(-\beta x)dx}{\int_{x\geq\Delta} p_\lambda(x) \exp(-\beta x)dx}. \quad (46)$$

With the help of (44) and the normalization condition (42), we can solve for $P^\pm_\lambda$. This results in

$$P^+_\lambda = \frac{\exp(-\beta M^-_\lambda) - \exp(-\beta M_\lambda)}{\exp(-\beta M^-_\lambda) - \exp(-\beta M^+_\lambda)}, \quad (47)$$

$$P^-_\lambda = \frac{\exp(-\beta M_\lambda) - \exp(-\beta M^+_\lambda)}{\exp(-\beta M^-_\lambda) - \exp(-\beta M^+_\lambda)}. \quad (48)$$

From the positivity of $P^\pm_\lambda$ we further obtain

$$M^-_\lambda \leq M_\lambda, \quad M_\lambda \leq M^+_\lambda. \quad (49)$$

4.4 Mean process work

Up to now, the exponential mean process work was considered in sect. 4.2. Let us now go one step back and look at the mean value of the stochastic work itself. Starting out with (30) and decomposing its lhs according to (42), we obtain by use of the mean value theorem and (23)

$$W^+_\lambda P^+_\lambda + W^-_\lambda P^-_\lambda = W^{AB}_\lambda \geq \Delta^{AB} F. \quad (50)$$

According to the decomposition (42), we have for the mean values of the process works belonging to the regular (+) and non-regular (-) processes

$$W^-_\lambda \leq \Delta^{AB} F \leq W^+_\lambda. \quad (51)$$

From (50) follows

$$(W^+_\lambda - W^{AB}_\lambda)P^+_\lambda + (W^-_\lambda - W^{AB}_\lambda)P^-_\lambda = 0, \quad \rightarrow \quad 1 = \frac{(W^{AB}_\lambda - W^-_\lambda)P^-_\lambda}{(W^+_\lambda - W^{AB}_\lambda)P^+_\lambda}. \quad (52)$$

5 Jarzynki’s Equality

5.1 Two phenomenological lemmata

Approaching Jarzynski’s equality, an axiom is needed which postulates suitable properties of the exponential mean process work $M_\lambda$ which is up to now protocol dependent according to (39). For more physical elucidation, we formulate this axiom in two steps by two lemmata, so to say as auxiliary axioms. Although the exponential mean process work $M_\lambda$ is smaller than $W^{AB}_\lambda$ according to (33), we demand that it satisfies the Second Law (23) like the phenomenological process work:

**Lemma I:**

$$\Delta^{AB} F \leq M_\lambda. \quad (53)$$
Lemma I together with the inequalities (33), (43), and (49) can be summarized as

\[ M^{-\lambda} < \Delta^{AB} F \leq M_{\lambda} \left\{ \begin{array}{c} \leq W_{\lambda}^{AB} \\ \geq M_{\lambda}^{+} \end{array} \right\} \]  

(54)

or, equivalently,

\[ \exp(-\beta M^{-\lambda}) > \exp(-\beta \Delta^{AB} F) \geq \exp(-\beta M_{\lambda}) \left\{ \begin{array}{c} \geq \exp(-\beta W_{\lambda}^{AB}) \\ \geq \exp(-\beta M_{\lambda}^{+}) \end{array} \right\}. \]  

(55)

Because Lemma I is demanded for all protocols – also for reversible ones – we obtain from (39) in comparison with (53)

\[ M_{\lambda}^{ABrev} = \Delta^{AB} F, \]  

(56)

and (38) results in

\[ \int p_{\lambda}^{rev}(x) \exp(-\beta x) dx = \exp(-\beta \Delta^{AB} F). \]  

(57)

That is to say, Lemma I implies the Jarzynski equality (4) for reversible protocols. Taking the second inequality of (55) into account, (48) results in

\[ P^{-\lambda} \leq \frac{\exp(-\beta \Delta^{AB} F) - \exp(-\beta M^{+}_{\lambda})}{\exp(-\beta M^{-\lambda}) - \exp(-\beta M^{+}_{\lambda})}. \]  

(58)

that means, Lemma I gives also a constraint on the integrated probability \( P^{-\lambda} \) of the non-regular processes, an inequality which we need later on.

Now, to extend the validity of the Jarzynski equality to arbitrary protocols we introduce a second Lemma, which states that the non-regular admixture (48) should have an influence as great as possible by choosing \( M_{\lambda} \) independently of the special protocol. Hence, we demand

\[ \text{Lemma II:} \]

\[ \left( P^{-\lambda} \rightarrow \text{max, for all protocols} \right) \rightarrow \left( \exp(-\beta M_{\lambda}) \rightarrow \text{max} \right) \rightarrow \left( M_{\lambda} \overset{\ast}{=} \Delta^{AB} F \right). \]  

(59)

Note that Lemma II implies Lemma I, but we found it intuitive to start with Lemma I separately. Furthermore, the second inequality of (55) and the inequality (58) change into equations by Lemma II. Now, multiplication of (32) \( \text{I} \) with \( \exp(\beta M_{\lambda}) \) and taking Lemma II into account results in a phenomenological vindication of Jarzynski’s equality

\[ \{J_{\lambda} : \int p_{\lambda}(x) \exp \left( -\beta (x - \Delta^{AB} F) \right) dx = 1 \]  

(60)

including (57) which can be derived without using Lemma II.
Finally, taking Jarzynski’s equality into account, from (47) and (48) follows with (59) for the admixtures of the regular and non-regular processes

\[ P^+_\lambda = \frac{\exp(-\beta M^+_\lambda) - \exp(-\beta \Delta^{AB} F)}{\exp(-\beta M^+_\lambda) - \exp(-\beta M^+_\mu)}, \]

\[ P^-_\lambda = \frac{\exp(-\beta \Delta^{AB} F) - \exp(-\beta M^-_\lambda)}{\exp(-\beta M^-_\lambda) - \exp(-\beta M^-_\mu)}, \]

resulting in

\[ \frac{P^-_\lambda}{P^+_\lambda} = \frac{1 - \exp\left(-\beta (M^+_\lambda - \Delta^{AB} F)\right)}{\exp\left(-\beta (\Delta^{AB} F - M^-_\lambda)\right) - 1}. \]

Note that the restriction on the probability densities \( p_\lambda(W^{AB}_\lambda) \) by the phenomenological Lemmata I and II generating Jarzynski’s equality can be tested by experimental investigation according to our basic assumption that these probability densities are experimentally given in the view of Non-equilibrium Thermodynamics. Especially, testing the restrictions on \( P^\pm_\lambda \) might require much less statistics than the validation of the Jarzynski equality itself for which it is extremely important to sample the very rare events where the dissipated work is much smaller than the free energy difference [28, 29].

5.2 The Second Basic Axiom

Because \( \Delta^{AB} F \) is a constant belonging to all Jarzynski processes between \( A \) and \( B \), we obtain from (60) for two different protocols \( \lambda(t) \) and \( \mu(t) \) of \( \{J_\lambda\} \)

\[ \int p_\lambda(x) \exp(-\beta x) dx = \int p_\mu(x) \exp(-\beta x) dx = \exp(-\beta \Delta^{AB} F). \]

That means, the expectation value of the exponential process work \( \exp(-\beta W^{AB}_\lambda) \) is protocol-independent, and all protocols of the Jarzynski process class have to satisfy Jarzynski’s equality, a fact which restricts the possible probability densities. Consequently, Jarzynski’s equality is an object of experimentally testing because in Non-equilibrium Thermodynamics we do not start out with special given probability densities \( p_\lambda(W^{AB}_\lambda) \).

Jarzynski’s equality is here established by the two phenomenological lemmata [53] and [59], whereby the second one includes the first. The two-step procedure is chosen because of the more evident physical interpretation. The main result of Jarzynski’s equality is that the mean value of the exponential process work is protocol-independent according to Lemma II [59],. This fact can be used for replacing the two phenomenological lemmata by another basic axiom:

**Second Basic Axiom:**

The mean value of the exponential process work is protocol-independent.

Using this axiom, (59) follows immediately from (59), because protocol independence of
the mean value of the exponential process work means $M_{\lambda}^{\text{rev}} = M_{\lambda}^{\text{nst}}$. This more formal axiom allows to establish Jarzynski’s equality with out use of Lemmata I and II which can be regarded as physical interpretation behind the Second Basic Axiom.

Jarzynski’s equality, derived in the framework of Stochastic Thermodynamics [3, 2], is an integral fluctuation relation with regard to the Jarzynski process class. Whatever its derivation in Stochastic Thermodynamics may be, from the point of view of Non-equilibrium Thermodynamics, Jarzynski’s equality can be phenomenologically established by the Second Basic Axiom. The procedure for implementing stochastic processes into Non-equilibrium Thermodynamics is totally different from that used in Stochastic Thermodynamics because we neither make use of any underlying equation of motion nor any specific Hamiltonian in our framework. In Non-equilibrium Thermodynamics non-regular processes appear instead of reversed processes with the difference that non-regular processes are measurable contributions to the non-regular admixture. The Second Basic Axiom which allows to establish Jarzynski’s equality is a phenomenological statement on the protocol-independence of the mean values of the exponential process works.

6 Some Results

6.1 Dissipation and non-stochasticity

Jarzynski’s equation allows to express the dissipation. Starting out with (60) and (31)

$$\int p_{\lambda}(x) \exp(-\beta x) dx = \exp(-\beta \Delta^{AB} F) \geq \exp(-\beta W^{AB}_{\lambda}),$$

we obtain

$$\int p_{\lambda}(x) \exp(-\beta(x - W^{AB}_{\lambda})) dx = \exp(\beta(W^{AB}_{\lambda} - \Delta^{AB} F)) \geq 1,$$

and the dissipation is

$$D^{AB}_{\lambda} := \beta(W^{AB}_{\lambda} - \Delta^{AB} F) = \ln \int p_{\lambda}(x) \exp(-\beta(x - W^{AB}_{\lambda})) dx \geq 0.$$ (67)

The phenomenological process work $W^{AB}_{\lambda}$ is given by (30)$_2$.

A further result due to Jarzynski’s equality is obtained for non-stochastic processes: taking (59)$_3$ into account, (66) yields

$$\Delta^{AB} F = M^{\text{nst}}_{\lambda} = W^{AB\text{nst}}_{\lambda} \geq \Delta^{AB} F \rightarrow \Delta^{AB} F = W^{AB\text{nst}}_{\lambda},$$ (68)

that means, non-stochastic processes are always reversible, if Jarzynski’s equality holds:

$$\text{Jarzynski’s equality} \rightarrow \left\{\begin{array}{ccc}
\text{non-stochastic} & \rightarrow & \text{reversible} \\
\text{stochastic} & \leftarrow & \text{irreversible}
\end{array}\right\}$$ (69)

Because reversible ”processes” are defined as trajectories in the equilibrium sub-space [30], [31] [32], they are idealized objects which do not exist in nature. Nevertheless, the reversible
processes have to be included into the theoretical framework because they belong to it as a closure of the theory. According to (69), all irreversible processes create stochasticity in the sense that the work distribution is different from a delta distribution, but why was this not recognized so far within the framework of phenomenological Non-equilibrium Thermodynamics? This is due to the fact that most experiments were carried out on macroscopic systems where the number of repetitions of the experiment as well as the measurement device is not sensible enough to discriminate between different work values for a given protocol. Hence, the different process works appear as being equal according to (20) and (26)

\[ J \int_A^B \left[ L(\lambda, \Theta) - L(\lambda, \Theta) \right] \lambda(t) dt \approx 0. \]  

(70)

Consequently, conventional Non-equilibrium Thermodynamics is a special case of Stochastic Thermodynamics, if Jarzynski’s equality holds and the stochasticity of the irreversible processes is ignored. Another possibility to ignore stochasticity is to remove the non-regular processes from the theoretical concept, discussed in the next section.

6.2 Stochasticity without ”violations”?

Taking lemma II (59) into account, Jarzynski’s equality writes according to (40)

\[ \int_{x \geq \Delta} p_\lambda(x) \exp(-\beta x) dx + \int_{x < \Delta} p_\lambda(x) \exp(-\beta x) dx = \exp(-\beta \Delta^{AB} F). \]  

(71)

Here, the \((x \geq \Delta)\)-terms belong to the regular processes. According to (42), the non-regular admixture includes all experiments belonging to protocols \(\lambda(t)\) whose process work \(x\) is smaller than the difference \(\Delta^{AB} F\) of the free energy. These experiments are some times denoted as ”violations” of the Second Law. This expression should be used with care because the phenomenological Second Law is not a statement valid for stochastic variables.

We now investigate the consequences, if the non-regular processes are eliminated and only the regular processes are considered. Thus, we set

\[ x < \Delta^{AB} F : \quad p_\lambda(x) \leftarrow 0 \quad \rightarrow \quad \int_{x \geq \Delta} p_\lambda(x) dx = 1, \]  

(72)

and a naive application of Jarzynski’s equality (71) becomes

\[ \int_{x \geq \Delta} p_\lambda(x) \left( \exp(-\beta x) - \exp(-\beta \Delta^{AB} F) \right) dx = 0. \]  

(73)

Because the big bracket in (73) is negative, the probability density is

\[ x \geq \Delta^{AB} F : \quad p_\lambda(x) = \delta(x - \Delta^{AB} F), \]  

(74)

that means: if Jarzynski’s equality holds and if the non-regular admixture vanishes, the stochastic process works \(x = W_\lambda^{AB}\) have for all protocols the same value \(\Delta^{AB} F\). Consequently, the regular processes are non-stochastic according to (34) and reversible according to (69). Thus, we proved the following statement:
If Jarzynski’s equality holds and the non-regular admixture vanishes, all regular processes are non-stochastic and reversible.

or shorter in other words: irreversible processes generate stochasticity and no stochasticity without non-regular processes.

6.3 A special family of probability densities

In principle, there are many different probability distributions possible which satisfy the Jarzynski equality. But of course, these probability distributions are not arbitrary because they have to satisfy Jarzynski’s equality as a constraint. We now are going to consider a special, but characteristic family for which the non-regular processes are much less frequent than the regular ones. For this purpose we start out with Jarzynski’s equality \[60\] written down in the special decomposition into regular and non-regular processes

\[
\int_{x \geq \Delta} p_\lambda(x) \exp \left( -\beta (x - \Delta^{AB} F) \right) dx + \int_{x < \Delta} p_\lambda(x) \exp \left( -\beta (x - \Delta^{AB} F) \right) dx = 1 = \int_{x \geq \Delta} p_\lambda(x) dx + \int_{x < \Delta} p_\lambda(x) dx,
\]

resulting in

\[
\int_{x \geq \Delta} p_\lambda(x) \left[ \exp \left( -\beta (x - \Delta^{AB} F) \right) - 1 \right] dx = \int_{x < \Delta} p_\lambda(x) \left[ 1 - \exp \left( -\beta (x - \Delta^{AB} F) \right) \right] dx.
\]

By changing the integral limits: first integral \( x =: \Delta^{AB} F + y, y \geq 0 \)

\[
\int_0^\infty p_\lambda \left( \Delta^{AB} F + y \right) \left[ \exp(-\beta y) - 1 \right] dy = \int_0^\infty p_\lambda \left( \Delta^{AB} F - y \right) \left[ 1 - \exp(\beta y) \right] dy.
\]

A special probability density obeying \[77\] and consequently also satisfying Jarzynski’s equality is

\[
p_\lambda \left( \Delta^{AB} F - x \right) = \frac{1 - \exp(-\beta x)}{\exp(\beta x) - 1} p_\lambda \left( \Delta^{AB} F + x \right), \quad x > 0.
\]

Because

\[
\frac{1 - \exp(-\beta x)}{\exp(\beta x) - 1} = \exp(-\beta x), \quad x > 0,
\]

we obtain for the probability density \[78\]

\[
p_\lambda \left( \Delta^{AB} F - x \right) = \exp(-\beta x) p_\lambda \left( \Delta^{AB} F + x \right), \quad x > 0.
\]
showing that the probability density belonging to the non-regular processes is exponentially smaller than that belonging to the regular ones. This special chosen case motivates to formulate a further axiom in the next section which holds generally for all probability densities and all protocols of the Jarzynski process class and not only for the special chosen case.

The result (80) is here derived by a phenomenological procedure. As Crooks found out in Stochastic Thermodynamics [9, 10, 11], the distribution belonging to the non-regular processes can be linked to the experiment by considering the inverse protocol of $\lambda(t)$, defined by $\lambda^\dagger(t) \equiv \lambda(\tau - t)$, $t \in [0, \tau]$, and the inversion of any magnetic field and rotation. (80) is then known as a special case of the so-called detailed fluctuation theorem [2].

7 The Non-regular Admixture

In the last section, a special class of probability densities was distinguished by an arbitrary choice which results in the fact that the probability density of the non-regular processes is smaller than that of the regular processes. This statement has to be generalized for other process quantities presupposing Jarzynski’s equality.

7.1 The third axiom

Inspired by the last section, we postulate the third axiom:

\[ P_\lambda^- \leq P_\lambda^+ \quad \rightarrow \quad P_\lambda^- \leq \frac{1}{2}, \quad P_\lambda^+ \geq \frac{1}{2}. \quad \text{ Third Axiom: } \]

This axiom goes beyond the Jarzynski equality or the Crooks fluctuation theorem because we postulate it for every protocol of the Jarzynski process class.

A first consequence of (81) is according to (52)

\[ W^{AB}_\lambda - W^-_\lambda \geq W^+_\lambda - W^{AB}_\lambda \quad \rightarrow \quad 2W^{AB}_\lambda \geq W^+_\lambda + W^-_\lambda. \quad (82) \]

This result (82) is pretty clear: the difference between the phenomenological process work and the mean value of the process works of the non-regular admixture is not smaller than that for the regular processes. This statement is so evident that it could serve as an axiom instead of (81). We now go back to the exponential mean values of the process work.

Introducing the abbreviations according to (43)

\[ a := \beta(M^\dagger_\lambda - \Delta^{AB}F) \geq 0, \quad b := \beta(\Delta^{AB}F - M^-_\lambda) \geq 0, \]

we obtain from (83) and (81)

\[ \frac{P^-}{P^+} = \frac{1 - \exp(-a)}{\exp b - 1} \leq 1 \quad \rightarrow \quad 2 \leq \exp b + \exp(-a) \quad \rightarrow \ln \left(2 - \exp(-a)\right) \leq b, \]

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an inequality connecting $M^+_\lambda$, $M^-\lambda$ and $\Delta^{AB}F$ according to the third axiom. Because of

\[ 2 - \exp(-a) \leq \exp a \]  

(85)

results in

\[ \ln \left( 2 - \exp(-a) \right) = b_{\text{min}}(a) \leq a. \]  

(86)

Consequently, if $a$ is given, two kinds of $b$ ($b^-$ and $b^+$) are possible satisfying (84) in accordance with the third axiom (81)

\[ b_{\text{min}}(a) \leq b^- \leq a \leq b^+. \]  

(87)

Inserting the abbreviations (83), we obtain inequalities which have $M^+_\lambda$, $M^-\lambda$ and $\Delta^{AB}F$ to satisfy so that the third axiom (81) is true

\[ \ln \left[ 2 - \exp \left( -\beta(M^+_\lambda - \Delta^{AB}F) \right) \right] \leq \begin{cases} \beta(\Delta^{AB}F - M^-\lambda) \\ \beta(M^+_\lambda - \Delta^{AB}F) \leq \beta(\Delta^{AB}F - M^-\lambda) \end{cases} \]  

(88)

In any case, the third axiom enforces

\[ \ln \left[ 2 - \exp \left( -\beta(M^+_\lambda - \Delta^{AB}F) \right) \right] \leq \beta(\Delta^{AB}F - M^-\lambda), \]  

(89)

an inequality which can be tested by experiments.

The third axiom allows an estimation of the non-regular admixture. Starting out with (84), a $y$ exists

\[ \frac{P^-}{P^+} = \frac{1 - \exp(-a)}{\exp b - 1} \leq \exp(-y) \leq 1, \quad y \geq 0, \]  

(90)

and we obtain

\[ \ln \frac{\exp b - 1}{1 - \exp(-a)} \geq y. \]  

(91)

We now apply the estimation

\[ \ln x \geq 2 \frac{x - 1}{x + 1}, \quad x > 0. \]  

(92)

Inserting

\[ x - 1 \rightarrow \frac{\exp b - 1}{1 - \exp(-a)} - 1 = \frac{\exp b + \exp(-a) - 2}{1 - \exp(-a)} \]  

(93)

\[ x + 1 \rightarrow \frac{\exp b - 1}{1 - \exp(-a)} + 1 = \frac{\exp b - \exp(-a)}{1 - \exp(-a)} \]  

(94)

into (92), we obtain by taking (84) into consideration

\[ \ln \frac{\exp b - 1}{1 - \exp(-a)} \geq 2 \frac{\exp b + \exp(-a) - 2}{\exp b - \exp(-a)} =: y \geq 0. \]  

(95)
Consequently, (90) results in
\[
\frac{P^-}{P^+} \leq \exp \left[ 2 \frac{- \exp b - \exp(-a)}{\exp b - \exp(-a)} \right] = \exp \left[ 2 \frac{- \exp (\beta(\Delta^{AB}F - M^-_\lambda)) - \exp \left( - \beta(M^+_\lambda - \Delta^{AB}F) \right)}{\exp (\beta(\Delta^{AB}F - M^-_\lambda)) - \exp \left( - \beta(M^+_\lambda - \Delta^{AB}F) \right)} \right], \tag{96}
\]

(97)

\[
= \exp \left[ \frac{2 - \exp \left( \beta(\Delta^{AB}F - M^-_\lambda) \right) - \exp \left( - \beta(M^+_\lambda - \Delta^{AB}F) \right)}{\exp \left( \beta(\Delta^{AB}F - M^-_\lambda) \right) - \exp \left( - \beta(M^+_\lambda - \Delta^{AB}F) \right)} \right], \tag{97}
\]

if (83) is inserted.

We now investigate the consequences of the third axiom (81) for equilibrium and in the case of reversible protocols.

7.2 Equilibrium: the fourth axiom

Equilibrium and reversible processes are two different concepts which should be distinguished properly: whereas reversible ”processes” as trajectories in the equilibrium subspace are defined by (57), equilibrium is defined by equilibrium conditions which by definition are also valid for reversible processes. In more detail: taking into account that (52) is also valid for reversible processes, we obtain by use of (37)

\[
1 = \frac{(W^{AB}_{\lambda_{rev}} - W^{-}_{\lambda_{rev}})P^{-}_{\lambda_{rev}}}{(W^{+}_{\lambda_{rev}} - W^{AB}_{\lambda_{rev}})P^{+}_{\lambda_{rev}}} = \frac{(\Delta^{AB}F - W^{-}_{\lambda_{rev}})P^{-}_{\lambda_{rev}}}{(W^{+}_{\lambda_{rev}} - \Delta^{AB}F)P^{+}_{\lambda_{rev}}}. \tag{98}
\]

We now have to postulate the equilibrium condition in agreement with the definition of reversible processes:

■ Fourth Axiom (Equilibrium): In equilibrium –and consequently also for reversible processes– regular and non-regular processes are equally frequent: according to (98), we obtain

\[
\frac{P^-_{\lambda_{eq}}}{P^+_{\lambda_{eq}}} = 1 \iff \frac{\Delta^{AB}F - W^{-}_{\lambda_{rev}}}{W^{+}_{\lambda_{rev}} - \Delta^{AB}F} = 1 \iff 2\Delta^{AB}F = W^{+}_{\lambda_{rev}} + W^{-}_{\lambda_{rev}}. \tag{99}
\]

The fourth axiom (99) points out that in equilibrium the regular processes are equalized by the non-regular ones. This corresponds to the assumption in Stochastic Thermodynamics that in equilibrium the global detailed balance is satisfied and that probability fluxes are balanced and no net currents appear. Here, the non-regular processes come into consideration by splitting the process integrals according to (40) and (42).

According to the fourth axiom (99) and (84), we obtain by taking (83) and (86) into account

\[
\ln \left[ 2 - \exp(-a_{rev}) \right] = b_{rev} \leq a_{rev}, \tag{100}
\]

\[
\ln \left[ 2 - \exp \left( - \beta(M^+_\lambda_{rev} - \Delta^{AB}F) \right) \right] = \beta(\Delta^{AB}F - M^-_{\lambda_{rev}}), \tag{101}
\]

\[
\frac{b_{rev}}{\beta} = \Delta^{AB}F - M^-_{\lambda_{rev}} \leq M^+_{\lambda_{rev}} - \Delta^{AB}F = \frac{a_{rev}}{\beta}, \tag{102}
\]

\[\text{In Stochastic Thermodynamics, this axiom runs: Forward and backward path probabilities are equal in equilibrium.} \tag{33}\]

11 In Stochastic Thermodynamics, this axiom runs: Forward and backward path probabilities are equal in equilibrium.
and from \((99)\) and \((102)\) follows
\[
2\Delta^{AB}F = W_{\lambda_{\text{rev}}}^+ + W_{\lambda_{\text{rev}}}^- \leq M_{\lambda_{\text{rev}}}^+ + M_{\lambda_{\text{rev}}}^-.
\] (103)

The fourth axiom \((99)\) enforces the equality in \((89)\)
\[
\ln \left[ 2 - \exp \left( -\beta (M_{\lambda_{\text{rev}}}^+ - \Delta^{AB}F) \right) \right] = \beta (\Delta^{AB}F - M_{\lambda_{\text{rev}}}^-).
\] (104)

which also can be experimentally tested, if the corresponding protocol is reversible, that means, if the protocol of the Jarzynski process \((1)\) to \((3)\) is sufficiently slow \(\lambda(\alpha t), \alpha \to 0\), for approximating reversibility.

8 Summary

- Processes of a closed discrete system between to fixed equilibrium states controlled by a heat reservoir and divided into two parts—the first part with power exchange caused by fixed initial and fixed final work variables, the second one as relaxation by constant work variables to the final equilibrium state—constitute the Jarzynski process class \((1)\) to \((3)\) and \((27)\).

- Experimental fact is that the process work is different for several identical Jarzynski processes enforcing to treat the process work as a stochastic variable whose different values establish the domain of a probability density \((26)\).

- The processes of the Jarzynski process class fall into two branches: regular processes of non-negative process dissipation \((42)\) and non-regular processes of negative process dissipation \((42)\).

- Although the process dissipation is negative for non-regular processes, the mean value of all Jarzynski processes—the phenomenological dissipation—is not negative \((22)\).

- Two phenomenological lemmata
  I) the exponential mean process work obeys the Second Law and
  II) the non-regular processes have an extent as great as lemma I) allows, are the phenomenological back-ground of the basic axiom

\[
\text{The mean value of the exponential process work is independent of the Jarzynski process class.}
\]

This basic axiom implements Jarzynski’s inequality straightforward, \((59)\) and \((60)\).

- If Jarzynski’s equality holds, non-stochastic processes are always reversible.

- If Jarzynski’s equality holds, irreversible processes generate stochasticity.

- Beyond Jarzynski’s equality: the extent of the non-regular processes is not greater than that of the regular ones \((81)\)
• Beyond Jarzynski’s equality: in equilibrium –and consequently for reversible ”processes” – the fractions of non-regular and regular processes are equal, [32].

9 Discussion

The tools of Stochastic Thermodynamics are based on Statistical Mechanics, whereas Non-equilibrium Thermodynamics is a purely phenomenological theory. Both theories describe phenomenological processes, Stochastic Thermodynamics by mean values over its statistical back-ground and Non-equilibrium Thermodynamics by phenomenological Laws. For a special class of processes –the Jarzynski process class– an equality, called Jarzynski’s equality, was derived in 1997 by a statistical procedure containing a probability density stemming from the statistical back-ground. Now the question arises: can Jarzynski’s equality be derived phenomenologically, if Non-equilibrium Thermodynamics is equipped with stochastic processes?

Considering the Jarzynski process class, an experimental fact is that the process work is a stochastic variable, that means, performing a Jarzynski process identically repeated, the process work fluctuates, and a probability density is experimentally generated. What are now the phenomenological axioms which this probability density has to obey, so that Jarzynski’s equality is valid? The answer –based on two phenomenological axioms– is easy: the mean value of the stochastic exponential process work is the same for all Jarzynski processes.

The Jarzynski processes which are identically repeated can be split into regular and non-regular ones. By definition, the process dissipation of the non-regular processes is smaller than the corresponding difference of the free energy. By contrast, the process dissipation of the regular processes is not smaller than the free energy difference as it is valid for all non-stochastic processes. The non-regular processes are sometimes confusingly called “violations” of the second law of thermodynamics.

Finally statement: Non-equilibrium Thermodynamics of the Jarzynski process class can be extended by stochastic processes satisfying Jarzynski’s equality which obeys phenomenological axioms.

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