Consequences of the Detailed Balance for the Crooks Fluctuation Theorem

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Abstract

We show that the assumptions of the detailed balance and of the initial equilibrium macrostate, which are central to the Crooks fluctuation theorem (CFT), lead to all microstates along a trajectory to have equilibrium probabilities. We also point out that the Crooks’s definition of the backward trajectory does not return the system back to its initial microstate. Once corrected, the detailed balance assumption makes the CFT a theorem only about reversible processes involving reversible trajectories that satisfy Kolmogorov’s criterion. As there is no dissipation, the CFT cannot cover irreversible processes, which is contrary to the common belief. This is consistent with our recent result that the JE is also a result only for reversible processes.

I. INTRODUCTION

A. Background

Crooks fluctuation theorem (CFT) [1,2] has become a central piece in the development of a microscopic theory of nonequilibrium thermodynamics (NEQT) expressed in terms of exchange quantities (such as exchange work $\Delta W$ or exchange heat $\Delta Q$ having the suffix e) with the medium $\Sigma$

which is external to the system $\Sigma$ but interacts with it. The exchange quantities are controlled by the medium-intrinsic (MI) properties of the medium and are easy to handle as the medium is normally taken to be in equilibrium with no irreversibility [3]; the irreversibility if present is always associated with the system $\Sigma$. This has made their usage very convenient so the CFT has attracted a lot of interest over the past two decades or so. We denote this particular thermodynamics here by $\mu$NEQT, with $\mu$ referring to its microscopic nature and the dot over it referring to the fact that it is based on extending the concept of macroscopic exchange quantities [4, 5, 8–10] to the microscopic level. This version extending the concept of macroscopic exchange quantities, see Sec. II for explanation. Because the conventional macroscopic NEQT also uses the exchange quantities, the $\mu$NEQT is supposed to be a direct extension of it [8–10] to the microscopic level but which does not directly involve any force imbalance between the external force and the internally induced restoring force necessary for irreversibility [3]; however, the extension provided by the $\mu$NEQT incorporates explicitly the irreversibility of the process [3,4] by directly involving the force imbalance. Within the $\mu$NEQT, the CFT provides a detailed stochastic description of work fluctuations to the situation where the final macrostate need not be in equilibrium (EQ). It also provides another proof of the Jarzynski identity (JE) [11]. The JE applies to the case where external driving is carried out in one shot, while it is applied several times during short durations in the approach taken by Crooks (the details are given later in Sec. III).

Definition 1 An extensive quantity defined for a microstate or a trajectory will be called a microquantity in this work, such as microentropy, microwork, microheat, etc. A thermodynamic average quantity will be called a macroquantity.

Definition 2 The time-evolution of a microstate $\mathbf{a}$ in a thermodynamic process is called the trajectory followed by $\mathbf{a}$ during the process. A deterministic or stochastic trajectory followed by a single microstate $\mathbf{a}$ will be denoted by $\gamma_a$, or simply $\gamma$.

Definition 3 A trajectory involving microstate transitions $\gamma_{ab}$ between distinct microstates will be denoted by $\gamma$ and called a mixed trajectory.

The difference between a deterministic and a stochastic $\gamma$ is that the probability of the microstate does not change in the former but changes in the latter trajectory. However, the microstate does not change. In the mixed trajectory, both the microstates and the probabilities change so $\gamma$ is always stochastic and so is the transition $\gamma_{ab}$.

Crooks consider a process involving mixed trajectories $\gamma$. The main idea behind Crooks’ approach is to identify a first-law-like statement for a trajectory $\gamma_{ab}$ between two macrostates $A$ and $B$ in a process $\mathcal{P}$, where $A$ and $B$ refer to some microstates of $A$ and $B$, respectively. The macrostates refer to a collection of $r$ microstates in the set $\{a_k\}$, $k = 1, \ldots, r$ and their energy and probability sets $E_A = \{E_{A_k}\}$, $p_A = \{p_{A_k}\}$ and $E_B = \{E_{B_k}\}$, $p_B = \{p_{B_k}\}$, respectively [12]. According to Crooks, the extension of the macroscopic first law (see Eq. 10 below) for the trajectory $\gamma_{C,ab}$ is

$$\Delta E(\gamma_{C,ab}) = \Delta_e Q_C(\gamma_{C,ab}) + \Delta_e R_C(\gamma_{C,ab});$$

(1)

here, $\Delta_e Q_C(\gamma_{C,ab})$ denotes the microheat exchanged with the medium $\Sigma$ that is added to the system and
\( \Delta_s R_C(\gamma_{C,ab}) \) the exchange microwork done on the system \( \Sigma \) by \( \Sigma'[4] \) over the trajectory \( \gamma_{C,ab} \); they are properly defined in Eqs. (35a) and (44a). The suffix \( C \) in various quantities is to emphasize the choice made by Crooks in his approach [12] described in Sec. IIII. From now on, we will use \( \Delta R_C \) for \( \Delta_s R_C \) as this work is always an exchange work.

For concreteness, we assume the work process \( P \) to change the extensive work parameter \( \lambda(t) \) like the volume \( V(t) \) of the system and take \( \Sigma \) from \( A \) to \( B \) over a time period \((0, \tau)\). Let \( t_m = m \delta t \), \( m = 0, 1, 2, \ldots, n \) denote a sequence of times over the duration \((0, \tau)\) so that \( t_0 = 0 \) and \( t_n = \tau \). We denote \( \lambda(t) \) by \( \lambda_m \) and the microstate by \( a_{k,m} \) at \( t = t_m \). It changes from \( \lambda_l \) to \( \lambda_{l+1} \) during the interval \( \delta_l = (t_l, t_{l+1}) \), \( l = 0, 1, 2, \ldots, n - 1 \). During the same interval, \( a_{k,m} \rightarrow a_{k_{l+1}} \) due to microheat exchange so that the microstate becomes \( a_{k_{l+1}} \) at \( t = t_{l+1} \). The final microstate at the end of \( P \) is \( a_{k_n} \). In the following, we will find it convenient to denote \( a_k \) simply by the index \( k \in (1, 2, \ldots, r) \) so that the subscript \( m \) on it \( (k_m) \) will denote the time \( t_m \) it appears in a realization of \( P \); the work parameter associated with \( k_m \) is \( \lambda_m \). In the transition \( k_l \rightarrow k_{l+1} \) during \( \delta_l \), \( k_l \) is the departing microstate and \( k_{l+1} \) is the arriving microstate.

Each realization of the process involves taking \( \Sigma \) from some initial \( k_0 = a \) through a sequence of intermediate microstates to the final microstate \( k_n = b \). The trajectory \( \gamma_{C,ab} \) refers to a chronological sequence of microstates \((k_0, k_1, k_2, \ldots, k_{n-1}, k_n)\) that the system \( \Sigma \) passes through at times \( t_m \), with \( k_m \in (1, 2, \ldots, r) \). We will refer to this as the forward trajectory \( \gamma_{C,ab} \) or simply \( \gamma_{C} \) when the context is clear, and the corresponding process \( P(F) \). In the backward trajectory \( \gamma_{C,ab} \) or simply \( \gamma_{C} \) for the backward process \( P(B) \) from \( B \) to \( A \), \( \Sigma \) passes the microstates through the reverse sequence \((k_n = b, k_{n-1}, k_{n-2}, \ldots, k_1, k_0 = a) \) so that the initial microstate \( k_0 \) of \( \gamma_{C,ab} \) is the terminal microstate of \( \gamma_{C,ba} \). There are \( r^n \) possible forward and backward trajectories for the process \( P(F) \) and \( P(B) \), respectively, with probabilities \( p(\gamma_{C,ab}) \) and \( p(\gamma_{C,ba}) \), respectively. The collection of all forward or backward trajectories will be denoted by the fold face \( \gamma_{C} \) or \( \gamma_{C} \), respectively. We will use \( P \) to denote both processes \( P(F) \) and \( P(B) \). Crooks derives the following relation for each of the forward trajectories and its associated backward trajectory:

\[ e^{\mathcal{E}_C(\gamma_{C})} = \frac{p(\gamma_{C,ab})}{p(\gamma_{C,ba})} = e^{\Delta S(\gamma_{C,ab}) - \beta_0 \Delta Q_C(\gamma_{C,ab})}, \tag{2} \]

where

\[ \Delta S(\gamma_{C,ab}) = \ln p(a) - \ln p(b) \tag{3} \]

is the change in the microscopic entropy (microentropy \( S(a) = -\ln p \) for a given microstate \( a \), which occurs with a probability \( p \)) of the forward trajectory \( \gamma_{C,ab} \)

\((k_0, k_1, k_2, \ldots, k_{n-1}, k_n)\) and \( \beta_0 \) is the inverse temperature of the heat bath. For a given \( a \) and \( b \), \( \Delta S(\gamma_{C,ab}) \) does not depend on various trajectories in \( \gamma_{C,ab} \). The exponent

\[ \omega_C(\gamma_{C,ab}) = \Delta S(\gamma_{C,ab}) - \beta_0 \Delta Q_C(\gamma_{C,ab}) \]

on the right side of Eq. (2) is supposed to denote the microentropy change \( \Delta_0 S(\gamma_{C,ab}) \) or simply \( \Delta_0 S(\gamma_{C}) \) of the isolated system \( \Sigma_0 = \Sigma \cup \Sigma \) along \( \gamma_{C,ab} \), whose thermodynamic average, see Sec. II.A, that is, the macroentropy

\[ \Delta_0 S(F) = \Delta_1 S(F) \geq 0. \tag{5} \]

For \( \Delta_1 S(F) > 0 \), the CFT represents a NEQ result. For \( \Delta_1 S(F) = 0 \), the CFT represents an EQ result. Crooks also emphasizes that the CFT is valid even if \( B \) is not an EQ-macrostate. If the final macrostate \( B \) denotes an EQ-macrostate, then one can easily derive a version of the JE.

**Remark 4** From the notation \( \Phi = \langle \Phi \rangle_{\gamma_{C}} \) indicating the average over \( \gamma_{C} \) in \( \gamma_{C} \), the function \( \Phi \) inside the angular brackets is a microfunction over the trajectory \( \gamma_{C} \) and should not be confused with the thermodynamic average, the macrofunction, on the left side. Thus, \( \Delta_0 S \) within the angular brackets in \( \langle \Delta_0 S(\gamma_{C}) \rangle \) stands for the trajectory microentropy change \( \Delta_0 S(\gamma_{C,ab}) \), and should never be confused with the macroentropy change \( \Delta_0 S(F) \), the entropy change of \( \Sigma_0 \).

**Remark 5** While \( \Delta_1 S(F) \geq 0 \) is nonnegative because of the second law, there is no such restriction for individual trajectory microentropy \( \Delta_0 S(\gamma_{C,ab}) \); the latter can be of any sign.

**B. Motivation**

The derivation of Eq. (2) is based on treating the sequence \((k_0, k_1, k_2, \ldots, k_{n-1}, k_n)\) as a Markov chain satisfying the principle of detailed balance. This is surprising as the principle is known to only hold for reversible changes [13, 14], i.e., the system will show no irreversibility. Therefore, it is important to understand how the derivation by Crooks overcomes this limitation. It is this desire that has motivated this work. Moreover, there seems to be an asymmetry between \( \gamma_{C} \) and \( \gamma_{C,ba} \). For \( \gamma_{C} \), the initial transition \( k_0 \rightarrow k_1 \) occurs at fixed
\( \lambda = \lambda_1 \) associated with the arriving microstate \( k_1 \) at \( t_1 \), and the final transition \( k_{n-1} \rightarrow k_n \) occurs at fixed \( \lambda = \lambda_n \) associated with the arriving microstate \( k_n \) at \( t_n \). Thus, the work parameter for \( k_l \rightarrow k_{l+1} \) is fixed at \( \lambda = \lambda_{l+1} \) the associated with the arriving microstate at \( t = t_{l+1} \) in \( \gamma_c^{(F)} \). However, for \( \gamma_c^{(B)} \), the initial transition \( k_n \rightarrow k_{n-1} \) occurs at fixed \( \lambda = \lambda_n \) associated with the departing microstate \( k_n \). Similarly, the final transition \( k_1 \rightarrow k_0 \) occurs at fixed \( \lambda = \lambda_1 \) associated with the departing microstate \( k_1 \). Thus, the work parameter for \( k_{l+1} \rightarrow k_l \) is at fix \( \lambda = \lambda_{l+1} \) associated with the departing microstate \( k_{l+1} \) in \( \gamma_c^{(B)} \). This asymmetry appears innocuous but is not as \( \gamma_c^{(B)} \) does not bring the system back to the equilibrium microstate \( k_0 \) as will be discussed later; see Sec. VII.

This requires carefully identifying the correct backward trajectory.

C. New Results

We always assume \( k_0 = a \) to have the equilibrium probability associated with the equilibrium macrostate \( A \). We show that the assumption of the principle of detailed balance, when carefully analyzed, requires the new microstates \( \{k_m\}_{m=1,\ldots,n} \) to have equilibrium probabilities \( \{\gamma_m\}_{m=1,\ldots,n} \) so that the final macrostate \( B \) is also an EQ-macrostate. The fact that the sequence \( \{k_m\}_{m=1,\ldots,n} \) belonging to \( \mathcal{P}^{(F)} \) is a sequence of EQ-microstates, see Definition 11, having equilibrium probabilities does not rule out by itself that \( \mathcal{P}^{(F)} \) is not irreversible as one can imagine an irreversible process between two equilibrium macrostates. Therefore, we need some additional argument to establish that \( \mathcal{P}^{(F)} \) is reversible. For this we need to consider the backward process. We show that when we carefully identify the backward process, we find that

\[
\omega(\gamma_{ab}^{(F)}) \equiv \Delta_i S(\gamma_{ab}^{(F)}) = 0, \forall \gamma_{ab}^{(F)}
\]

so that the thermodynamic average over the set \( \gamma_{ab}^{(F)} \) also vanishes identically

\[
\Delta_i S^{(F)} = 0;
\]

compare with Eq. 5 and the discussion following it. Note that the forward trajectory \( \gamma_{ab}^{(F)} \) introduced above and the associated backward trajectory \( \gamma_{ab}^{(B)} \) are not identical to the Crooks forward and backward processes \( \gamma_{C,ab}^{(F)} \) and \( \gamma_{C,ab}^{(B)} \) respectively, as we will explain later; see Eqs. 56a and 56b. This then completes the demonstration that the CFT, when properly defined, only covers reversible processes, contrary to what is conventionally accepted in the field. This is consistent with our previous conclusion that the JE is also restricted to reversible processes only.

D. Layout

The layout of the paper is as follows. In the next section, we briefly review the two versions of the microscopic NEQT. In particular, we show that the generalized SI-work is carried out isentropically, while the generalized SI-heat is always given by \( TdS \) no matter how irreversible the transformation is provided we can identify the temperature \( T \). This ensures that the generalized work \( (dS = 0) \) and generalized heat \( (dS \neq 0) \) are independent contributions in the first law that could never be confused. At the macrostate or trajectory level, this means that the generalized microwork is carried out at fixed probabilities \( (dp = 0) \), while the generalized microheat requires changes in the probabilities \( (dp \neq 0) \). This distinct separation proves useful for calculating various trajectory quantities as no confusion can arise between the generalized microwork and microheat. We summarize Crooks’s approach in Sec. III. We partition the medium \( \Sigma \) into two separate and mutually noninteracting parts, the external work source \( \Sigma_w \) and an external heat source \( \Sigma_h \). Crooks simplifies his approach and allows the system \( \Sigma \) to undergo interactions with each one at different times; we call these \( \Sigma_w \)-interactions to perform external work \( \Sigma_h \)-interactions to exchange microheat. The principle of microscopic detailed balance is treated in Sec. IV. This is an important section where attention is drawn to the fact that the acceptance of the principle results in the transition matrix elements \( \{T_{ij}\} \) being determined by the equilibrium probabilities of the arriving state \( j \), see Eqs. 12 and 17, and has no memory of the departing state \( i \). The same conclusion follows if we treat the transition matrix to be balanced. It follows from this conclusion that all microstates after \( \Sigma_h \)-interactions become EQ-microstates (see Definition 11). We then show in Sec. VII, see Conclusion 16, that \( \Sigma_w \)-interactions must precede \( \Sigma_h \)-interactions during each interval \( \delta_i \) of the process \( \mathcal{P}^{(F)} \) if we require a terminal EQ-microstate at \( t = t_{l+1} \); the order cannot be reversed. The following section, Sec. VIII, is devoted to the consequences of the detailed balance. Sec. IX is also very important, where we show that the Crooks’s backward trajectory does not satisfy the basic requirement that the reverse process brings the system back to its initial macrostate. We introduce a novel trick to identify the reverse process in a transparent manner, which we use to introduce the corrected form of the backward trajectory that satisfies this basic requirement. If accepted, we find that the Markov chain becomes \( \text{reversible} \). We then demonstrate that \( \omega(\gamma_{C,ab}^{(F)}) = 0 \), see Eq. 6, which is simply an extension of Kolmogorov’s Criterion for conventional reversible Markov chain to the present work where two different interactions are involved. The extended Kolmogorov criterion shows that there is no irreversible entropy generation \( (\Delta_i S^{(F)} = 0) \) and finally proves that the corrected CFT only applies to reversible processes. It cannot apply to irreversible processes because of the
acceptance of the principle of detailed balance. This conclusion is consistent with our recent result \([6, 7]\) that the JE is also restricted to reversible processes. Thus, they both fail to account for any irreversibility in \(\mathcal{P}^{(F)}\), contrary to the popular belief.

II. MICROSCOPIC NEQ THERMODYNAMICS

In this section, we briefly review the two versions: \(\mu\)NEQT and \(\bar{\mu}\)NEQT and show how they will be used in understanding the consequences of the CFT. As noted above, \(\mu\)NEQT exploits exchange quantities that are determined by the properties of the medium \(\Sigma\) (see below for more details). Therefore, the \(\mu\)NEQT is governed by medium-intrinsic (MI) quantities \([4–7]\) so care must be taken to bring in indirectly the force imbalance necessary for irreversibility \([5]\) in any consideration. In contrast, the \(\mu\)NEQT based on SI-quantities already includes irreversible contributions to the system due to force imbalance; see Sec. III and \([5]\). Therefore, the two approaches are very different when irreversibility is present.

A. Thermodynamic Averages

In general, an equilibrium or nonequilibrium ensemble average (EA) is defined instantaneously, and requires identifying (a) the elements (microstates \(\{a_k\}\) ) of the ensemble and (b) their instantaneous probabilities \(\{p_k\}\).

The average is uniquely defined over \(\{a_k\}\) using \(\{p_k\}\) at each instant, which we identify as the instantaneous ensemble average (IEA). Let \(O_k\) be some extensive microquantity pertaining to \(a_k\) and \(dO_k\) the change in it during some infinitesimal process \(d\mathcal{P}\). The instantaneous thermodynamic averages \(\langle O \rangle\) and \(\langle dO \rangle\) are defined \([3, 10]\) as

\[
\langle O(t) \rangle = \sum_k O_k(t) p_k(t),
\]

\[
\langle dO(t) \rangle = \sum_k dO_k(t) p_k(t),
\]

and define the corresponding macroquantities. We will usually not show the time \(t\) unless clarity is needed. In thermodynamics, it is common to simply use \(O\) and \(dO\) for the average also. Therefore, we will be careful to avoid this simplification if it may cause confusion. The average energy \(E \equiv \langle E \rangle\) and entropy \(S \equiv \langle S \rangle\) are such instantaneous average SI-quantities, where \(E_k\) and \(S_k = -\ln p_k \equiv -\eta_k\) denote the microenergy and microentropy of the microstate \(a_k\); we have also introduced Gibbs probability index \(\eta_k = \ln p_k\). The infinitesimal thermodynamic MI-work \(dR \equiv \langle dR \rangle\) done on the system and the SI-work done by the system \(dW \equiv \langle dW \rangle\) also represent such an average instantaneous quantity. They involve the microwork \(dR_k\) and \(dW_k\) associated with \(a_k\) during \(d\mathcal{P}\).

We can extend the average notion in Eq. \((8b)\) to the trajectory average \(\langle \Delta O \rangle_{\tau_{ab}}\):

\[
\Delta O_{\tau_{ab}} \equiv \sum_{\tau_{ab}} \Delta O(\tau_{ab}) p(\tau_{ab}),
\]

in terms of the probabilities \(p(\tau_{ab})\) of \(\tau_{ab} \in \mathcal{T}_{ab}\); here \(\Delta O(\tau_{ab})\) denotes the accumulated microvalue of \(O\) along \(\tau_{ab}\)

\[
\Delta O(\tau_{ab}) = \int_{\tau_{ab}} dO_k(t),
\]

where \(dO_k(t)\) refers to the instantaneous microstate \(a_k\) along \(\tau_{ab}\). All quantities related to the trajectory are microquantities as opposed to the macroquantities \(\langle O \rangle\) and \(\langle dO \rangle\) above. These are the quantities that are relevant in \(\mu\)NEQT and \(\bar{\mu}\)NEQT.

B. The First Law

The first law during an infinitesimal process \(d\mathcal{P}\) is expressed as a sum of two SI-contributions \([18]\)

\[
d\langle E \rangle = \sum_k E_k dp_k + \sum_k p_k dE_k.
\]

The first sum represents the generalized heat

\[
dQ = \sum_k E_k dp_k,
\]

while the second sum represents \(-dW\), the generalized work \([6, 7, 18]\)

\[
dW = -\sum_k p_k dE_k.
\]

We have shown elsewhere \([13, 17]\) that the generalized heat can be used to turn the conventional Clausius inequality into a generalized Clausius equality

\[
dQ = T dS;
\]

here \(T\) denotes the temperature of the system, which may or may not equal the temperature \(T_0\) of the medium. The Clausius equality is consistent with \(dQ\) being an SI-quantity. Thus, the final form of the first law in terms of the SI-quantities becomes

\[
d\langle E \rangle = dQ - dW.
\]

It is this formulation of the first law that forms the cornerstone of the \(\mu\)NEQT \([6, 7]\) and will guide us in this work for the simple reason that it provides a straightforward description of the microstates and trajectories as noted above.

The first law in Eq. \((10)\) is in terms of the SI-quantities \(E_k\) and \(p_k\). However, its important lies in its ability to clearly distinguish the concept of generalized heat and work. The origin of the generalized heat \(dQ\) is the change in the microstate probabilities, while their microenergies remain fixed, and the origin of the generalized work \(dW\) is the change in the microenergies, while their probabilities remain fixed. For fixed probabilities, the entropy
\( S = -\sum_k p_k \ln p_k \) remains constant. Therefore, the generalized work is the isentropic change in the macroenergy change \( d \langle E \rangle \), and the change in \( d \langle E \rangle \) due to \( dS \) alone is the generalized heat. This clearly shows the two distinct sources for \( dQ \) and \( dW \) and provides a clear distinction between the two quantities as said above.

The important point to remember is that these SI-microquantities include the contributions that arise from the mismatch between the system's and medium's quantity expressed by the force imbalance \([5]\). This is easily seen by observing that these generalized quantities differ from the exchanged heat and work \( d_e Q \) and \( d_e W \), respectively:

\[
dQ = d_e Q + d_i Q, dW = d_e W + d_i W, \tag{14}
\]

with \( d_i W = -dR \). The differences \( d_i Q \) and \( d_i W \) are generated within the system and denote irreversible quantities; see Remark \([8]\). They satisfy an important identity of their magnitude

\[
d_i Q = d_i W \geq 0 \tag{15}
\]

but not the source: While \( d_i Q \) is generated by the internal changes in the probabilities at fixed \( E = \{ E_k \} \), \( d_i W \) is generated by the internal changes in the energies at fixed \( P = \{ p_k \} \).

The equality in Eq. (14) ensures that the first law can also be expressed in terms of the MI-quantities \( d_e Q \) and \( d_e W = -dR \):

\[
d \langle E \rangle = d_e Q - d_e W = d_e Q + dR. \tag{16}
\]

It is this formulation that is employed in the \( \mu \)NEQT and in the CFT as we will discuss below.

### C. Microquantities

Using Eq. (8d), we can identify microheat and microwork \([7,17]\) from Eq. (10). They are

\[
dQ_k = E_k d\eta_k, dW_k = -dE_k, \tag{17}
\]

that are associated with \( a_k \). We also note that they have distinct sources (fixed \( E_k \) versus fixed \( p_k \)). Let us look at \( dW_k \), which is part of the summand in the second sum in Eq. (10). This summand requires no change in the probability. Therefore, \( dE_k = -dW_k \) is the deterministic change in the energy \( E_k \) of \( a_k \). This explains the deterministic contribution along \( \gamma \) in Definition \([3]\). The contribution \( dQ_k \) is part of the summand in the first sum in Eq. (10). This summand requires changes in the probabilities but not in \( E_k \). This, therefore, represents the stochastic contribution.

We also observe that both \( dQ_k \) and \( dW_k \) refer to the microchanges associated with a single microstate \( a_k \), except that \( dQ_k \) is a stochastic variable as it involves probability change \( d\eta_k \), while \( dW_k \) is a deterministic variable as it involves no probability change. Therefore, to determine their accumulation using Eq. (9), we must replace \( \gamma_{ab} \) by \( \gamma_a \). This is a tremendous simplification due to the concept of microheat \( dQ_k \) in the \( \mu \)NEQT compared to the Crooks approach which uses the mixed trajectory \( \gamma_{ab} \), where one is forced to introduce transition probabilities; see Secs. [III] and [IV].

The thermodynamic averages of microheat and microwork following Eq. (5b) are

\[
dQ = \langle dQ \rangle, dW = \langle dW \rangle. \tag{18}
\]

It is these microquantities that lend them useful to study quantities relevant for a trajectory \( \gamma \).

From Eq. (17), we find that the irreversible work is given by

\[
d_i W = dW + dR \geq 0, \tag{19a}
\]

where we have used the identification \( d_i W = -dR \). We are now ready to understand the physical significance of \( d_i W \). Its microscopic analog \( d_i W_k \) for a given microstate \( a_k \) is the work done by the force imbalance such as \( P_k - P_0 \) as shown elsewhere \([3,7]\) so that

\[
d_i W_k = \sum_k p_k d_i W_k = \langle dW \rangle. \tag{19b}
\]

The microwork \( d_i W_k \) denotes an internal microwork and not an irreversible microwork; see Remark \([8]\).

The inequality in Eq. (15) or in Eq. (19a) is related to the second law \([17]\). It is easy to show that

\[
d_i Q = d_i W = (T - T_0)d_e S + T d_i S \geq 0, \tag{20a}
\]

in which each term of the second equation must be non-negative to satisfy the second law \([7]\). For an isothermal change \( (T = T_0) \), we have

\[
d_i Q = d_i W = T_0 d_i S \geq 0. \tag{20b}
\]

The irreversibility \( (d_i S > 0) \) in this case is due to the irreversible causability of the performance of work. The term \( (T - T_0)d_e S \) is the irreversibility caused by heat transfer at different temperature \( (T \neq T_0) \) in addition to the work irreversibility. For a reversible process, \( d_i Q = d_i W = 0 \). In that case, \( T = T_0, d_i S = 0, dQ = d_e Q = T_0 d_e S \) and \( dW = d_e W = -dR \).

The microscopic version of Eq. (20b) gives rise to

\[
d_i W_k = d_i Q_k. \tag{21}
\]

It follows from Eq. (20b) that the corresponding microrelation is \( d_i Q_k = T_0 d_i S_k, d_i S = \langle d_i S \rangle \); compare with Eq. (19b). This microrelation can be used to relate the microwork \( d_i W_k \) with the internal microentropy change \( d_i S_k \) associated with \( a_k \):

\[
d_i W_k = T_0 d_i S_k, \tag{22}
\]

except that there is no restriction on the sign of \( d_i W_k \) or \( d_i S_k \) at the microstate level.
Remark 6 If a theory does not allow for any force imbalance for \( a_k \), \( d_i W_k \) will be identically zero for \( \forall k \). If the process is isothermal, we see from Eq. \( 23 \) that \( d_i S_k \equiv 0 \). Consequently,

\[
d_i S \equiv \langle d_i S \rangle = 0, \tag{23}
\]

which implies that the process is a reversible process. However, as discussed in Remark 7, there are no fluctuations in \( d_i S_k \).

We will see later how Eqs. \( 22 \) and \( 23 \) are fulfilled in the CFT.

Remark 7 With hindsight, we will only be interested in treating processes for the CFT that satisfy Eq. \( 33 \). This means that Crooks does not allow any force imbalance as we discuss below.

D. Work-Energy Theorem

From now on, we will usually refer to the generalized (macro)work and (macro)heat simply as work and heat for simplicity as the notation will be explicit and no confusion can arise. The work \( dW \) done by the system is an SI-quantity, which is distinct from the MI-work \( dR \) done on the system by the medium during an infinitesimal process \( dP \). They are related by \( 15–17 \):

\[
dW = -dR + d_i W, \quad d_i W \geq 0, \tag{24}
\]

along some infinitesimal process \( dP \); see Eq. \( 19a \). By introducing the accumulation \( \Delta \Psi \) of some extensive (SI- or MI-) quantity \( \Psi \) along a process \( P \) defined by

\[
\Delta \Psi \equiv \int_P d\Psi, \tag{25}
\]

the above relationship becomes

\[
\Delta W = -\Delta R + \Delta_i W, \tag{26a}
\]

where the meaning of various accumulated quantities follows Eq. \( 25 \).

We now describe how to evaluate microwork \( \Delta W(\tau_{ab}) \) for a mixed trajectory. As the initial and final microstates can be different, we need to divide \( \tau_{ab} \) into a disjoint collection of several \( \gamma_a \)'s whose union gives \( \tau_{ab} \):

\[
\tau_{ab} \equiv \bigcup_i \gamma_{a_i}. \tag{27}
\]

For each \( \gamma_{a_i} \), we are dealing with a single microstate \( a_i \) so we define

\[
\Delta W(\tau_{ab}) \equiv \sum_i \Delta W(\gamma_{a_i}). \tag{28a}
\]

We similarly define

\[
\Delta R(\tau_{ab}) \equiv \sum_i \Delta R(\gamma_{a_i}). \tag{28b}
\]

In the Hamiltonian formulation used at the microscopic level so that it becomes relevant for microstates \( a \) or their trajectories \( \gamma \) along \( P \), we are interested in microquantities and their fluctuations. For example, we are interested in SI-microquantities such as \( \Delta W(\tau_{ab}) \), the work done by the system along the trajectory \( \tau_{ab} \) or the MI-microwork \( \Delta R(\tau_{ab}) \) done on the system; see Eq. \( 9 \) for the definition. Their relationship follows from Eq. \( 20 \):

\[
\Delta W(\tau_{ab}) = -\Delta R(\tau_{ab}) + \Delta_i W(\tau_{ab}), \tag{29}
\]

where \( \Delta_i W(\tau_{ab}) \) is the internal microwork due to force imbalance that must be present for irreversibility and strongly depends on the nature of the trajectory. However, there is no restriction on the sign of \( \Delta_i W(\tau_{ab}) \) as is for \( \Delta_i W \geq 0 \).

Remark 8 We will always call any \( \Delta_i \)-microquantity an internal microquantity since its sign is not restricted. The thermodynamic average of such a quantity satisfies the restriction imposed by the second law and has a particular sign. We can call such a macroquantity an irreversible quantity. We will always make this distinction. Thus, \( \Delta_i W(\tau_{ab}) \) is an internal microquantity with no sign restriction, but the average \( \Delta_i W \) satisfies the restriction due to the second law and is called the irreversible work.

Let \( \Sigma \) be described by its Hamiltonian \( \mathcal{H}(\lambda) \) in which the work parameter \( \lambda \) can be manipulated from the outside through the medium by applying a "force" \( F_\lambda \). A particular realization of the system corresponds to a microstate \( a_k \) of the system so the discussion below should be taken for at the microstate level. We denote the value of the Hamiltonian for \( a_k \) by \( E_k \). The restoring force in the system conjugate to \( \lambda \) is given by the SI-force

\[
F_\lambda = -\partial E_k(\lambda)/\partial \lambda, \tag{30}
\]

which need not be equal to \( F_0 \) in magnitude. The SI-microwork \( dW_k = F_\lambda d\lambda \) is given by

\[
dW_k = -d\lambda E_k(\lambda), \tag{31}
\]

the negative of the change \( d\lambda E_k(\lambda) \) in the energy \( E_k(\lambda) = \mathcal{H}_k(\lambda) \) due to the variation of \( \lambda \) as exemplified by the derivative operator \( d_\lambda \). We consider a trajectory \( \gamma_k \) associated with \( a_k \) during which \( \lambda \) changes from its initial value \( \lambda_{in} \) to its final value \( \lambda_{fn} \). The above definition of the SI-force \( F_\lambda \) and the microwork \( dW_k \) above justifies Eq. \( 32 \), which appears as an identity due to the definition of the force \( F_k \).

Theorem 9 It is the SI-microwork that is directly related to the change in the Hamiltonian \( \mathcal{H}_k(\lambda) \), known as the Work-Energy Theorem \( G \) \( G \):

\[
\Delta W(\gamma_k) \equiv -\Delta \mathcal{H}_k(\lambda) \equiv \mathcal{H}_k(\lambda_{fn}) - \mathcal{H}_k(\lambda_{in}), \tag{32}
\]

whether internal work \( \Delta_i W_k \) is present or not.
Proof. The theorem follows trivially and directly from the definition of the SI-force and work; see Eqs. (31) and 32 for \( F_k \) and \( dW_k \), respectively. Accumulating \( dW_k \) along \( \gamma_i \) immediately proves Eq. (32) as an identity.

The proof does not require any relation between \( F_k \) and \( F_0 \) so force imbalance can exist, which will result in a nonzero internal microwork \( \Delta W(\gamma_k) \).

Remark 10 It is clear that

\[
\Delta R(\gamma_k) = H_k(\lambda_m) - H_k(\lambda_m)
\]

only if \( \Delta_i W(\gamma_k) \equiv 0 \). While \( \Delta_i W(\gamma_k) \equiv 0 \) implies \(
\Delta_i W = 0 \), the converse is not always true as it is possible to have several nonzero \( \Delta_i W(\gamma_k) \) and yet have their thermodynamic average \( \Delta_i W = 0 \). In the former case, there is no fluctuation in \( \Delta_i W(\gamma_k) \), while the fluctuations are present in the latter case. Therefore, the validity of Eq. (33) requires a very strong statement about the absence of fluctuations [2, 7].

We clearly see that the \( \mu \text{NEQT} \) is more appropriate than the \( \mu \text{NEQT} \) to deal with microscopic fluctuations and force imbalance.

III. CROOKS’ APPROACH

We now review and elaborate the approach taken by Crooks. Let us consider a finite segment of the process \( \Sigma \) and force imbalance.}

During the exchange of energy \( \Delta E \), only microwork is exchanged and during \( \delta_t \), only microheat is exchanged. The trajectory \( \tau_{CG} \equiv \tau_{Gab} \) is uniquely specified by the chronologically ordered microstate sequence \( \{k_0, k_1, k_2, \ldots, k_{m-1}, k_m \equiv b\} \), in which \( k_m, m = 0, 1, 2, \ldots, n \) refers to the microstate \( a_{k_m}(t_m) \) at time \( t_m \). The time \( t_m \) also specifies the value of \( \lambda = \lambda_m \) and the corresponding probability \( p_{k_m}(t_m) \); here \( k_m \equiv k(t_m) \in \{1, 2, \ldots, r\} \) indexes the \( r \) microstates. Crooks further assumes that the sequence \( \{k_m\} \) (along with the associated sequence \( \{p_{k_m}(t_m)\} \)) forms a (time-inhomogeneous) Markov chain, which is divided into \( n \) contiguous segments \( \{k_i, k_{i+1}\} \) in one-to-one correspondence with the \( n \) intervals \( \delta_i \) so that the integration over \( (0, \tau) \) is approximated by a sum over these intervals, its accuracy getting better as \( n \) increases. Each microstate is specified by its energy and work parameter at time \( t_m \). The probability \( p_{k_m} \) of a microstate \( k_m \) may or may not have its equilibrium value.

Definition 11 We will call a microstate (by an abuse of the concept only valid for macrostates) an EQ-microstate or a NEQ-microstate if the corresponding probability is the equilibrium probability or not, respectively; the latter will be denoted by appending a prime on the microstate label such as \( k' \).

Crooks does not make any such distinction but we will find it very useful in our discussion and also when identifying the backward trajectories. During \( \delta_t \) over which \( \Sigma \) interacts with \( \Sigma_w, \lambda \) changes to \( \lambda_{i+1} \) but not the microstate \( k_i \). During this interval, microwork done on the system is taken to be the energy change of the microstate:

\[
\Delta R_C((k_l, \lambda_t \rightarrow \lambda_{i+1}) \equiv E(k'_l, \lambda_{i+1}) - E(k_l, \lambda_l)
\]

with no change in the probability \( p(k_l, \lambda_l) \). This is inconsistent with the work-energy theorem according to which

\[
\Delta W_C(k_l, \lambda_t \rightarrow \lambda_{i+1}) \equiv E(k_l, \lambda_l) - E(k'_l, \lambda_{i+1})
\]

as follows from Eq. (32). We have also used the notation \( k'_l \) above to denote the microstate \( k_l(t'_l+1) \) that results at the end of the work protocol at \( t'_l+1 \). It represents a NEQ-microstate as will become clear in Sec. [15] see also Conclusion [15]. The only difference between \( k_l \) and \( k'_l \) is in their probabilities. At present, this difference is not relevant so we can overlook the prime for the moment. The work \( \Delta e R_C(\gamma_{Gab}) \) in Eq. (1) is given by

\[
\Delta e R_C(\gamma_{Gab}) = \sum \Delta R_C(k_l, \lambda_t \rightarrow \lambda_{i+1}),
\]

with fixed probability set \( \{p(k_l, \lambda_l)\}_{l=1, \ldots, n-1} \); compare with Eq. (28). Comparing \( \Delta R_C((k_l, \lambda_t \rightarrow \lambda_{i+1}) \) with the energy change in Eq. (31), we conclude that Crooks has implicitly assumed that Eq. (33) remains valid so no force imbalance is allowed; see Remark [10]. The work parameter \( \lambda(t) = \lambda_{i+1} \) is held fixed over \( \delta_t^l \) during which the microstate changes from \( k_l \) to \( k_{l+1} \) by exchanging energy with \( \Sigma_b \) in the form of microheat

\[
\Delta e Q_C(k_l \rightarrow k_{l+1}, \lambda_{i+1}) = E(k_{l+1}, \lambda_{i+1}) - E(k_l, \lambda_{i+1}));
\]

\[
(33a)
\]
this exchange occurs in conjunction with probability change as will be discussed in Sec. IV, the latter is however not involved in $\Delta_c Q_C(k_l \rightarrow k_{l+1}, \lambda_{l+1})$. The exchange heat $\Delta_c Q_C(\gamma_{C,\text{ab}})$ in Eq. (1) is given by

$$\Delta_c Q_C(\gamma_{C,\text{ab}}) = \sum l \Delta Q_C^l(k_l \rightarrow k_{l+1}, \lambda_{l+1}). \quad (35b)$$

The forward trajectory is specified uniquely by the following sequence of microstates, where we reinsert the prime on the microstates as necessary:

$$\tau^{(F)} : k_0 \xrightarrow{\circ} k'_0 \xrightarrow{h} k_1 \xrightarrow{\circ} k'_1 \xrightarrow{h} k_2 \xrightarrow{\circ} k'_2 \xrightarrow{h} k_3 \cdots$$

$$\cdots \xrightarrow{\circ} k_{n-1} \xrightarrow{h} k'_n \xrightarrow{\circ} k_n,$$  \(36\)

in which the triplet $k_l \xrightarrow{\circ} k'_l \xrightarrow{h} k_{l+1}$ corresponds to the interval $\delta_l$: the $w$-arrow $k_l \xrightarrow{\circ} k'_l$ refers to the deterministic interaction with $\Sigma_w$ during $\delta_l'$ and the $h$-arrow $k'_l \xrightarrow{h} k_{l+1}$ to the stochastic interaction with $\Sigma_h$ during $\delta_l''$. We remark that in each interval $\delta_l$, microwork is performed before microheat is exchanged. These two interactions are similar to the driven and reequilibration stages used in the derivation of the JE in Eq. (11). Thus, the Crooks process is a sequence of $n$ different Jarzynski processes $\delta P_l$ occurring during $\delta_l$, $l = 0, 1, \ldots, n - 1$. As we will see in Sec. IV, the driven stage brings an EQ-microstate $k_l$ to a NEQ-microstate $k'_l$, which is then brought to an EQ-microstate $k_{l+1}$ during the equilibration stage, which means that each Jarzynski process $\delta P_l$ takes an EQ-microstate to an EQ-microstate. We summarize this as a

**Conclusion 12** The $w$-arrow $\xrightarrow{\circ}$ always takes an EQ-microstate to a NEQ-microstate, whereas the $h$-arrow $\xrightarrow{h}$ always takes a NEQ-microstate to an EQ-microstate in a forward trajectory; the two arrows denote the interactions with $\Sigma_w$ and $\Sigma_h$, respectively.

We also note that because of the presence of intermediate NEQ-microstates $k'_l$, $\tau^{(F)}$ contains more information than the original Crooks trajectory $\tau^{(C)}$.

**IV. MICROSCOPIC DETAILED BALANCE**

As introduced above, the microwork during $\delta_l'$ is purely mechanical, and is carried out at fixed $p_{k_l}(E_l, \lambda_l, t_l)$. Even if $k_l$ is an EQ-microstate at $t_l$ $p_{k_l}(E_l(\lambda_l), \lambda_l, t_l) = p_{k_{eq}}(E_l(\lambda_l), \lambda_l)$. At $t_{l+1}$ has $p_{k_l}(E_l(\lambda_{l+1}), \lambda_{l+1})$ as its probability, which is not the equilibrium probability $p_{k_{eq}}(E_l(\lambda_{l+1}), \lambda_{l+1})$ at $\lambda_{l+1}$. Therefore, the microstate $k_l$ at $t_{l+1}$ after microwork has been performed is a NEQ-microstate, and should be denoted with a prime following our convention; See Definition 11. This explains the reason for introducing $k'_l$ in Eq. (35).

The microheat transfer over $\delta_l''$ is accompanied by probability changes as we now discuss using the Markovian property encoded in the transition matrix $T^{(1)}(\lambda')$.

The transition matrix tells us how a NEQ-microstate $k'_l$ transforms into $k_{l+1}$. Suppressing $l$ for the moment, we introduce its matrix elements, the one-step transition probabilities $T_{ij}(\delta'') \equiv T(j | i | \delta'')$ from microstate $i' \equiv i(t')$ to a microstate $j(t' + \delta'')$ at given $E_j$ and $\lambda'$; here, $E_j$ and $\lambda'$ refer to the microstate $i'$ at time $t'$. Recall that $\lambda'$ is held fixed during $\delta''$ so $\lambda' \equiv \lambda(t') \equiv \lambda(t' + \delta'')$. Similarly, $E'_j \equiv E_j(t' \equiv E_j(t' + \delta'')$. With hindsight, we are using $j$ for the arriving microstate as we will see that it an EQ-microstate. We are also suppressing the prime on $i$ in the subscript of $T_{ij}(\delta'')$. The matrix elements satisfy

$$\sum_j T_{ij}(\delta'') = 1, \quad (37)$$

and determine the probabilities at the next time $t'' \equiv t' + \delta''$ in the sequence

$$p_j(t'') = \sum_i p_i(t') T_{ij}(\delta''). \quad (38)$$

Given $T(\delta'')$, we can determine the new probability at $t''$ in terms of the set $\{p_i(t')\}$, where $p_i(t')$ stands for $p_i(E_i', \lambda', t' \equiv p_i(E_i' (\lambda'), \lambda', t')$ and denotes the probability of $i'$ at given $E_i' (\lambda') = E_i(t')$ and $\lambda' = \lambda(t')$. If we introduce a row probability vector $p(t') = \{p_i(t')\}$, we can express the above relation using matrix multiplication

$$p(t'') = p(t') T(\delta'') \quad (39)$$

for the given $E_i' (\lambda') \equiv \{E_i' (\lambda')\}$ and $\lambda'$. It is evident that $T(\delta'')$ depends on $\delta''$ in some fashion. The dependence is not important to know for the discussion here. From these conditions, we find that

$$p_j(t'') - p_j(t') = \sum_i [p_i(t') T_{ij}(\delta'') - p_j(t') T_{ji}(\delta'')] \quad (40)$$

It is clear that in the Markovian approximation, we need to know $T_{ij}(\delta'')$ to determine the probability change. To make further progress, we need to make some assumption. It is convenient and very common in the field to determine $T_{ij}(\delta'')$ by accepting the condition of microscopic reversibility, also known as the condition of the detailed balance, which is valid for equilibrium probabilities at fixed $\lambda'$ at $t''$:  

$$p_{eq}(E'_j, \lambda') T_{ij}(\delta'') - p_{eq}(E'_i, \lambda') T_{ji}(\delta'') = 0, \forall (i, j). \quad (41)$$

where we have used the double arrow to indicate the condition of microscopic reversibility, and have used the fact that the equilibrium probabilities do not depend on time. We remark that $p_{eq}(E'_i, \lambda')$ at $t''$ must not be confused with $p_i(E'_i(\lambda'), \lambda', t')$ at $t'$. So that there cannot be any confusion, we write $p_{eq}(E'_i, \lambda') as $p_{eq}(E_i, \lambda')$ since $E'_i(\lambda') at $t'$ and $E_i(\lambda') at $t'' are the same. The use of Eq. (41) now determines the elements $T_{ij}(\delta'')$ as follows. We first conclude that

$$T_{ij}(\delta'') / T_{ji}(\delta'') = p_{eq}(E_j, \lambda') / p_{eq}(E_i, \lambda').$$
It then follows from this that the choice
\[
\overrightarrow{T}_{ij}(\delta'') = p_{eq}(E_j, \lambda'), \overrightarrow{T}_{ji}(\delta'') = p_{eq}(E_i, \lambda'), \tag{42}
\]
is consistent with the condition of the detailed balance. A direct proof comes from Theorem 13. We can summarize the above as the following claim:

**Claim 13** The matrix element \( T_{ij}(\delta'') \) for the transition \( i' \rightarrow j \) is equal to the equilibrium probability \( p_{eq}(E_j, \lambda') \), i.e., \( p_{eq}(E_j(\lambda'), \lambda') \) of the arriving microstate \( j \) at \( t'' \) under the assumption of the detailed balance given in Eq. (47). As \( p_{eq}(E_j, \lambda') \) is time-independent, \( T_{ij}(\delta'') \) is also time independent so it must have no dependence on \( \delta'' \).

We see that under the assumption of the detailed balance, each row of the matrix \( T \) is the equilibrium row vector \( p_{eq}(\lambda') \):
\[
\overrightarrow{T} = \begin{pmatrix}
p_{eq}(E(\lambda'), \lambda') \\
p_{eq}(E(\lambda'), \lambda') \\
\vdots \\
p_{eq}(E(\lambda'), \lambda')
\end{pmatrix}, \tag{43}
\]
where the equilibrium vector refers to \( p_{eq}(E(\lambda'), \lambda') \) to \( p_{eq}(E_j(\lambda'), \lambda') \) at \( t'' \), which is invariant under the transition matrix \( \overrightarrow{T} \):
\[
p_{eq}(E(\lambda'), \lambda') = p_{eq}(E(\lambda'), \lambda') \overrightarrow{T}, \tag{44}
\]
for each interval \( \delta'' \). Such a transition matrix is said to be balanced over \( \delta'' \). It is easy to conclude from the above invariance equation that \( \overrightarrow{T} \) must be a stationary transition matrix. It is known from the theory of Markov chains that such a matrix is the limiting matrix; see Eq. (45).

While the form of Eqs. (43) and (44) is trivial based on Eq. (41), it is well known that a balanced \( \overrightarrow{T} \) in Eq. (43) also has the same form as in Eq. (44); see the Fundamental Limit theorem or Doeblin’s theorem of Markov chains [19, 20]. We simply state the theorem below:

**Theorem 14 Fundamental Limit Theorem:** For the transition matrix \( T \) for a regular Markov chain with finite number of states \( r < \infty \),
\[
\lim_{k \to \infty} T^k \overrightarrow{\lambda} = \overrightarrow{T} \overrightarrow{\lambda}, \tag{45}
\]
given in Eq. (43) and satisfying the balanced condition in Eq. (44). In particular,
\[
\lim_{k \to \infty} T^k_{ij} = \overrightarrow{T}_{ij} = p_{eq} > 0 \quad \text{for all} \quad k. \tag{46}
\]

**Proof.** For proof, see Refs. [19, 20] or any other textbook on Markov chains.

Therefore, from now on, we will take the balanced \( \overrightarrow{T} \) to be given by Eq. (43).

We now insert the index \( l \) so that the matrix elements of such a transition matrix (recall that \( \lambda' = \lambda(t'_{l+1}) = \lambda(t_{l+1}) = \lambda_{l+1} \) and \( E_j = E_j(t_{l+1}) = E_j(t_{l+1}) = E_j(t_{l+1}) + 1 \)) is uniquely determined and given by
\[
\overrightarrow{T}_{i,j}(l) = p_{eq}(E_j(\lambda(t_{l+1}), \lambda_{l+1}), \forall i, l, \tag{47}
\]
where \( p_{eq}(E_j, \lambda_{l+1}) \) is the equilibrium probability of the equilibrium \( j \)th microstate at time \( t_{l+1} \); see Eq. (43). Using the above transition matrix \( \overrightarrow{T}(l) \), we can determine how any arbitrary row probability vector \( \overrightarrow{p} \) changes over \( \delta_l' \):
\[
\overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) = p(E_{l+1}, \lambda_{l+1}, t_{l+1}) \overrightarrow{T}(l), \tag{48}
\]
where \( \overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) \) is used as a short hand notation for the vector \( \{p_j(E_j(\lambda_{l+1}), \lambda_{l+1}, t_{l+1})\} \) as above. We first recognize that each row in \( \overrightarrow{T}(l) \) is the same row vector \( p_{eq}(\lambda_{l+1}) \) in accordance with Eq. (49), a fact that does not seems to have been recognized in the current literature. This means that the \( j \)th column in \( \overrightarrow{T}(l) \) has the same entry \( p_{eq}(\lambda_{l+1}) \) for all rows. The effect of this is the following surprising observation that, after evaluating the right side of the above equation, we obtain
\[
\overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) = \overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) \overrightarrow{T}(l), \tag{49}
\]
for any arbitrary row probability vector \( \overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) \), not necessarily an equilibrium vector \( \overrightarrow{p}_{eq}(E_{l+1}, \lambda_{l+1}) \) at \( t_{l+1} \). Despite the arbitrary \( \overrightarrow{p}(E_{l+1}, \lambda_{l+1}, t_{l+1}) \), the result of \( \overrightarrow{T}(l) \) on it is to yield the equilibrium vector \( \overrightarrow{p}_{eq}(E_{l+1}, \lambda_{l+1}) \). We illustrate this by a simple example for \( r = 2 \) and some arbiter \( l \), which we again suppress. The corresponding \( \overrightarrow{T} = \overrightarrow{T}(l) \) is written as (we suppress \( l, E_j \) and \( \lambda_{l+1} \))
\[
\overrightarrow{T} = \begin{pmatrix}
p_{1eq} & p_{2eq} \\
p_{1eq} & p_{2eq}
\end{pmatrix},
\]

We consider an arbitrary probability vector \( \overrightarrow{p} = (p_1, p_2) \) to find that
\[
(p_1, p_2) \begin{pmatrix}
p_{1eq} & p_{2eq} \\
p_{1eq} & p_{2eq}
\end{pmatrix} = (p_{1eq}, p_{2eq}),
\]
where we have used the fact that \( p_1 + p_2 = 1 \). This thus justifies using the the microstate \( j \) as an EQ-microstate in the notation \( \overrightarrow{T}(l) \) as noted above.

**V. ORDER FOR MICROWORK AND MICROHEAT**

We have seen in the previous section that the microstate \( k' \) at \( t_{l+1} \) is a NEQ-microstate. However, the interaction with \( \Sigma_h \) during \( \delta_l' \) ensures that the probability at \( t_{l+1} \) is the equilibrium probability in accordance with Eq. (49). Thus, we conclude that
Conclusion 15 The microstates $k_l(t_l)$ and $k_{l+1}(t_{l+1})$ are EQ-microstates, but the intermediate microstate $k_{l+1}'(t_{l+1})$ is not.

The order of the interactions with $\Sigma_w$ and $\Sigma_h$ during $\delta_1$ is important to ensure that $k_l(t_l)$ and $k_{l+1}(t_{l+1})$ remain EQ-microstates. Suppose we interchange their order so that the interaction with $\Sigma_h$ occurs during $\delta_1'$ followed by the interaction with $\Sigma_w$ during $\delta_1''$ with the final effect $\lambda_l(t_l) \rightarrow \lambda_{l+1}(t_{l+1}), k_l(t_l) \rightarrow k_{l+1}'(t_{l+1})$ at the end of $\delta_1'$; here, we have used the fact to be established below that $k_l(t_l)$ and $k_{l+1}(t_{l+1})$ are NEQ-microstates so we will denote their energies with a prime in the following. As the change $\lambda_l \rightarrow \lambda_{l+1}$ is a consequence of the $\Sigma_w$-interaction, the $\Sigma_h$-interaction resulting in $k_l(t_l) \rightarrow k_{l+1}'(t_{l+1})$ (as shown below, $k_{l+1}'(t_{l+1})$ is an EQ-microstate after this interaction so its energy is denoted without a prime) must occur at fixed $\lambda_l$. From the discussion above, we conclude that for the transition $i' \rightarrow k_{l+1}'(t_{l+1})$, the matrix element $\widetilde{T}_{ij}^{(l)}(\delta_l')$ (we use $i$ instead of $i'$ in the subscript) is given by

$$\widetilde{T}_{ij}^{(l)}(\delta_l') = p_{eq}(E_j(\lambda_l), \lambda_l), \forall i', l,$$

which is different from the matrix elements in Eq. (47); here $E_j(\lambda_l)$ is the energy of $j(t_{l+1}')$, which is the same as the energy $E_j(\lambda_l)$ at $t_l$. As a consequence, Eq. (49) is replaced by

$$p(E(\lambda_l), \lambda_l, t_{l+1}') = p(E'(\lambda_l), \lambda_l, t_l) \widetilde{T}^{(l)} = p_{eq}(E(\lambda_l), \lambda_l).$$

(51)

This means that the probability of the arriving microstate $j$ with $\lambda(t_{l+1}') = \lambda_l$ is the equilibrium probability of $j$ at $t_{l+1}'$, even though $i'$ at the start of $\delta_l$ is a NEQ-microstate as we now demonstrate.

The $\Sigma_w$-interaction with $k_{l+1}$ at $t_{l+1}'$ results in $\lambda_l \rightarrow \lambda_{l+1}$ and changes its energy to $E_{k_{l+1}'}(\lambda_{l+1})$ from $E_{k_{l+1}}(\lambda_l)$ due to the microwork $\Delta R_C^{(l)}(k_{l+1}, \lambda_l) \rightarrow \lambda_{l+1}$) without changing its probability so that $p_{\Sigma_w}(E_{k_{l+1}'}(\lambda_{l+1}), \lambda_{l+1}, t_{l+1}) = p_{\Sigma_w}(E_{k_{l+1}}(\lambda_l), \lambda_l) \neq p_{\Sigma_w}(E_{k_{l+1}'}(\lambda_{l+1}), \lambda_{l+1})$. This explains why the resulting NEQ-microstate at $t_{l+1}$ is denoted by $k_{l+1}'$. Using the same argument by replacing $l$ by $l - 1$, we will conclude that the final microstate $k_l'$ at the end of $\delta_{l-1}$ is also a NEQ-microstate, which finally proves our assertion that both $k_l'$ and $k_{l+1}'$ are NEQ-microstates, with the intermediate microstate $k_{l+1}$ an EQ-microstate.

It should be evident that in order to obtain an EQ terminal microstate $k_0$, we must always have the $\Sigma_w$-interaction followed by the $\Sigma_h$-interaction during $\delta_0$. Similarly, if we wish to start from an EQ-microstate $k_0$, we must use the same order of the two interactions in $\delta_0$. Recursively, this is true for all other intervals, which means that the order of the two interactions in each interval $\delta_l$ must not be reversed. Thus, we come to the following

Conclusion 16 In each interval $\delta_l$, we must have the $\Sigma_w$-interaction followed by the $\Sigma_h$-interaction.

VI. CONSEQUENCES OF DETAILED BALANCE

We now follow the consequence of Eq. (49). We start with $l = 0$ and focus on the initial EQ-microstate $k_0$ during the interval $\delta_0$ of $\mathbf{F}$; see Eq. (49). It is turned into a NEQ-microstate $k_0'$ at $t_0'$ after microwork has been performed during $\delta_0'$ so that $E'_{k_0}(\lambda_l) = E(k_0, \lambda_0) + \Delta R_C^{(0)}(k_0, \lambda_0) \rightarrow \lambda_1)$ at $t_0'$, which we will simply denote by $E'_{k_0}(\lambda_1)$ so that we can use the notation $E'(\lambda_1)$ for the set $\{E'_{k_0}(\lambda_1)\}$; recall that we suppress the prime on the subscript $k_0'$ in $E'_{k_0}(\lambda_1)$. The probability of the initial microstate $k_0$ is $p_{base}(E_{k_0}(\lambda_0), \lambda_0)$. At $t_0'$, $k_0'$ has the same probability as this initial probability: $p_{base}(E'_{k_0}(\lambda_1), \lambda_1) = p_{base}(E_{k_0}(\lambda_0), \lambda_0)$. Interaction with $\Sigma_h$ does not change the energies of the microstates but only their probabilities. Therefore, $E(\lambda_0, \lambda_1) = E(k_0, \lambda_0) \neq E(k_0', \lambda_1)$ but $E(\lambda_0, \lambda_1) \equiv E(\lambda_0, \lambda_1), \forall \lambda_0 \neq 0$ at time $t_0$; in particular, $E(\lambda_1, \lambda_1) \equiv E(\lambda_1, \lambda_0)$. This is because as no microwork is done on these microstates $k_0$. Thus, $E'(\lambda_1) = E(\lambda_1) = E(\lambda_0)$, except for the initial microstate $k_0$. As we have seen in the previous section, $\mathbf{T}^{(l)}$ is determined by $p_{eq}(E', \lambda_1)$; the set $\{E_{k_0}(\lambda_1)\}$ corresponding to the initial microstate is not an invariant probability vector. Therefore, $p_{eq}(E, \lambda_0)$ represents an arbitrary probability vector in Eq. (48). It now follows from Eq. (49) that

$$p(E', \lambda_1, t_1') \mathbf{T}^{(0)} = p_{eq}(E, \lambda_1).$$

We also know that $p(E', \lambda_1, t_1') \equiv p_{eq}(E, \lambda_0)$, the initial probability vector of the EQ-macrostate $\mathbf{A}$. Therefore, we can equivalently say that the effect of $\mathbf{T}^{(0)}$ on $p_{eq}(E, \lambda_0)$ results in $p_{eq}(E', \lambda_1)$, which is the equilibrium probability vector for the arriving macrostate at the end $t_1 \equiv t_0 + \delta t$ of $\delta_0$ or the start of $\delta_1$. This is the macrostate that is arrived at after the successive interactions, first with $\Sigma_w$ and then with $\Sigma_h$. It is obviously an EQ-macrostate as its probability vector is $p_{eq}(E, \lambda_1)$. It arises when we consider all the trajectories starting with any of the $r$ possible microstates $\{a_k\}$ for $k_0$. In other words, all possible microstates at $t_1$ represent EQ-microstates, i.e., an EQ-macrostate. However, we should not forget that $\mathbf{T}^{(0)}$ only acts during $\delta_0$ and not over the entire duration $\delta_0$. This also means that $k_0$ does not have to be an EQ-microstate or that $\mathbf{A}$ does not have to be an EQ-macrostate for the macrostate at $t = t_1$ to be an EQ-macrostate.

It now follows that applying Eq. (49) along with the above argument for $l = 1, 2, \ldots, n - 1$ successively, we see that

$$p(E_{l+1}, \lambda_{l+1}, t_{l+1}) = p_{eq}(E_{l+1}, \lambda_{l+1}), l = 0, 1, 2, \ldots, n - 1,$$

(52)
where $E_{t+1}$ really stands for $E(\lambda_{t+1}) \equiv E(\lambda_t)$ at the end of the interval $\delta_t$. We are now set for drawing one of our most important conclusions based on the principle of detailed balance or the use of the particular transition matrix $T^{(l)}$.

**Conclusion 17** Due to the requirement of the principle of detailed balance and having the $\Sigma_k$-interaction always occur in the second-half of each interval $\delta_t$, the successive probability vectors at times $t_m, m = 1, \ldots, n$ are $p_{eq}(E(\lambda_1), \lambda_1), p_{eq}(E(\lambda_2), \lambda_2), \ldots, p_{eq}(E(\lambda_n), \lambda_n)$, respectively, for the process $p^{(F)}$: we do not have to assume that $A$ must be an EQ-macrostate. Thus, all intermediate macrostates and the final macrostate $B$ must be EQ-macrostates, contrary to what is usually claimed.

By requiring the initial macrostate $A$ to be also an EQ-macrostate, we can also add $p_{eq}(E(\lambda_0), \lambda_0)$ in the above sequence, but this requirement is not essential. However, the most important conclusion is about the final macrostate $B$ being an EQ-macrostate. As EQ-macrostates imply EQ-microstates, the above Conclusion means that not only the last microstate but every intermediate microstate in the Crooks’ approach is an equilibrium microstate, which contradicts the common understanding of the Crooks approach in which the final macrostate does not have to be an EQ-macrostate as is the case with the Jarzynski process. This also justifies why $\tau$ should really be thought of as representing $\tau_{eq}$.

**VII. BACKWARD TRAJECTORY AND DETERMINATION OF $\omega(\lambda_{ab})$**

**A. Limitations of the Crooks’ Approach**

Crooks identifies the forward trajectory by the sequence of microstates

$$\omega^{(F)}_{IC}: k_0 \xrightarrow{\lambda_1} k_1 \xrightarrow{\lambda_2} k_2 \xrightarrow{\lambda_3} k_3 \cdots k_{n-1} \xrightarrow{\lambda_n} k_n, \quad (53a)$$

and defines the backward trajectory as

$$\omega^{(B)}_{IC}: k_0 \xleftarrow{\lambda_1} k_1 \xleftarrow{\lambda_2} k_2 \xleftarrow{\lambda_3} k_3 \cdots k_{n-1} \xleftarrow{\lambda_n} k_n, \quad (53b)$$

which seems a natural choice by reversing the transitions; we have suppressed the suffix $ab$ for simplicity. The backward trajectory for a Markov chain has been an actively investigated topic [21]. We will simply quote some relevant results. The transition matrix element $T^{(B)}_{ij}$ for the backward trajectory is given by

$$T^{(B)}_{ij} = \frac{T^{(F)}_{ji} p_{eq}}{p_{eq}} = p_{j\rightarrow i} = T^{(F)}_{ij}, \quad (54)$$

where we have used twice Eq. (47), which is valid in the Crooks’s approach. Such a Markov chain for which the forward and backward trajectories (chains) have the same transition probabilities is said to be reversible, and there is no need to use the two superscripts $F$ and $B$ on $T^{(F)}_{ij}$. In this case, the principle of detailed balance is satisfied. Thus, the Crooks approach results in a reversible trajectory. According to Kolmogorov’s criterion [21], p. 21), we must have

$$T_{k_0 k_1} T_{k_1 k_2} \cdots T_{k_{n-1} k_n} T_{k_n k_0} = T_{k_0 k_n} T_{k_n k_{n-1}} \cdots T_{k_{2} k_1} T_{k_1 k_0}. \quad (55)$$

This merely expresses the fact that by adding the initial microstate $k_0$ after $k_n$ and pictorially thinking of all the microstates to be on a closed loop, we can traverse the loop from $k_0$ in either directions, one which we identify as the forward and the other backward. Therefore, the equivalence of the two transition matrices allows us to think of the backward trajectory as the continuation of the forward trajectory with additional microstates $\{a_k\}$ with the microstate index $k = n + 1, n + 2, \ldots, 2n$ and use the transformation $k' = 2n - k$ to put them on a loop as shown below:

$$k_0 \xleftarrow{\lambda_1} k_1 \xleftarrow{\lambda_2} k_2 \xrightarrow{\lambda_3} k_3 \cdots k_{n-1} \xrightarrow{\lambda_n} k_n,$$

except for the mismatch for the index for the work parameter $\lambda$. The transformation $k \rightarrow k'$ would have required $\lambda_{n+1}$ for $k_n$ to be transformed to $\lambda_{n-1}$ and to the transition $k_{n-1} \leftarrow \lambda^{-1}_{n-1} k_n$. But Crooks takes it to be $k_{n-1} \xleftarrow{\lambda_{n-1}} k_n$, see Eq. (55b). This casts doubt on the backward trajectory in Eq. (53b) not forming a reversible trajectory, which would then violate Kolmogorov’s criterion.

The significance of the transition $k_1 \xrightarrow{\lambda_1} k_{l+1}$ or its reverse $k_1 \xleftarrow{\lambda_1} k_{l+1}$ is that the work parameter $\lambda_{l+1}$ is kept fixed during the transition $k_1 \rightarrow k_{l+1}$ or $k_1 \leftarrow k_{l+1}$. It is with this choice that the CFT in Eq. (2) has been derived. It should be evident from the discussion earlier that each transition refers to a $\Sigma_k$-interaction, whether the transition is forward or backward. Since we have required the initial microstate $k_0$ of $T^{(F)}$ to be an EQ-microstate, we need to follow Conclusion 16 so that each $\Sigma_k$-interaction is preceded by a $\Sigma_{w}$-interaction in each interval $\delta_t$, even for the continuation of the forward trajectory described above. This is consistent with the first transition $k_0 \xrightarrow{\lambda_1} k_1$ in Eq. (53a), where we fix $\lambda = \lambda_1$ after $\lambda_0 \rightarrow \lambda_1$ due to the $\Sigma_{w}$-interaction. This is true of all the transitions in Eq. (53a). Therefore, according to Conclusion 17, the end microstate $k_n$ with $\lambda = \lambda_n$ for $T^{(F)}$ is an EQ-microstate.

We are now ready to introduce the backward trajectory $\omega^{(B)}$ for which the EQ-microstate $k_n$ with $\lambda = \lambda_n$ must play the role of the initial microstate. The final microstate of the backward trajectory must be the initial EQ-microstate $k_0$ of $T^{(F)}$. This allows us to reverse
the sequence \((k_0, k_1, k_2, \ldots, k_{n-1}, k_n)\) for \(\gamma^{(F)}\) to the sequence \((k_n, k_{n-1}, k_{n-2}, \ldots, k_1, k_0)\) for \(\gamma^{(B)}\) as used in the definition of \(e^{\omega(\gamma^{(F)})}\) in Eq. (2). Both trajectories sample the same two EQ-macrostates \(A\) and \(B\) in reverse order by going through the same intermediate microstates.

Let us first consider the backward trajectory \(\gamma^{(B)}\) specified in Eq. (53b), which does not mention the \(\Sigma_w\)-interactions, but which can be deduced from the above specification of \(\gamma^{(C)}\). It is clearly seen from \(k_{n-1} \lambda_n = k_n\) at fixed \(\lambda = \lambda_n\) that it represents a \(\Sigma_n\)-interaction, which then must be followed by a \(\Sigma_w\)-interaction in which \(\lambda_n \rightarrow \lambda_{n-1}\) so that we can follow the next \(\Sigma_h\)-interaction specified by \(k_{n-2} \lambda_{n-1} = k_{n-1}\). We see that the order of the two interactions are, therefore, reversed for \(\gamma^{(B)}\) compared to that for \(\gamma^{(C)}\). Following this argument recursively, we come to the last \(\Sigma_h\)-interaction specified by \(k_0 \lambda_1 = k_1\) for \(\gamma^{(B)}\). This cannot be the last interaction as it will leave the value of the work parameter at \(\lambda = \lambda_1\), while \(\lambda = \lambda_0\) for the macrostate \(A\). Therefore, there must be another \(\Sigma_w\)-interaction to ensure that \(\lambda_1 \rightarrow \lambda_0\). However, this makes the last microstate a NEQ-microstate \(k_0^*\) whose probability is not the equilibrium probability \(p_{k_0^{eq}}(E_0, \lambda_0)\). Thus, the proposed backward trajectory \(\gamma^{(B)}\) does not bring back the system to the EQ-macrostate \(A\).

**B. New Approach**

**Claim 18** In order to define a backward trajectory properly, it is important to have \(A\) an EQ-macrostate.

Therefore, we will assume as is commonly done that \(A\) is an EQ-macrostate.

We have uniquely identified the forward trajectory in Eq. (55) involving the intermediate NEQ-microstates \(\{k_2^*\}\), and can symbolically represent as an interaction sequence (we suppress \(w\) and \(h\) above the arrows as they can be uniquely deciphered from the sequence)

\[
\gamma^{(F)} : k_0 \rightarrow k'_0 \rightarrow k_1 \rightarrow k'_1 \cdots k_{n-1} \rightarrow k'_{n-1} \rightarrow k_n.
\] (56a)

This trajectory starts at the EQ-microstate \(k_0\) and terminates in the EQ-macrostate \(k_n\). We can now uniquely identify the backward trajectory \(\gamma^{(B)}\) that starts in the EQ-microstate \(k_0\) and terminates in the EQ-macrostate \(k_0\) by the pictorial continuation described above as follows:

\[
\gamma^{(B)} : k_0 \leftarrow k'_0 \leftarrow k_1 \leftarrow k'_1 \leftarrow \cdots k_{n-1} \leftarrow k'_{n-1} \leftarrow k_n.
\] (56b)

By suppressing all of the \(\Sigma_w\)-interactions, we can rewire the above sequences as

\[
\gamma^{(F)} : k'_0 \lambda_1 k_1 \lambda_2 k_2 \cdots k'_{n-1} \lambda_{n-1} k_{n-1} \lambda_n k_n,
\]

\[
\gamma^{(B)} : k_0 \lambda_0 k'_1 k_1 \lambda_1 k'_2 \cdots k'_{n-1} \lambda_{n-1} k_{n-1} \lambda_n \lambda_{n-1} k_n.
\] (57)

If we compare the above sequences with the sequences in Eqs. (55a) and (55b), we observe that while the sequence of the work parameters are the same for the forward trajectories, they are displaced by one unit for the backward trajectories. However, \(\gamma^{(B)}\) brings the system back to the EQ-macrostate \(k_0\) with \(\lambda = \lambda_0\) as required.

**Remark 19** We see that the order of the two interactions in Conclusion 12 must also be maintained in the backward trajectories to ensure that the backward trajectories bring the system back to the initial EQ-macrostate \(k_0\).

This also means that the backward trajectories bring the system back to the EQ-macrostate \(A\).

We are now prepared to evaluate \(\omega(\gamma^{(F)})\) that is defined similar to the definition of \(\omega_C(\gamma^{(F)}_C)\) in Eq. (2):

\[
e^{\omega(\gamma^{(F)})} = \frac{p(\gamma^{(F)}_C)}{p(\gamma^{(F)}_B)}.
\] The probability \(p(\gamma^{(F)})\) is

\[
p_{k_{0^{eq}}}(E_0, \lambda_0)p_{k_{1^{eq}}}(E_1, \lambda_1)p_{k_{2^{eq}}}(E_2, \lambda_2) \cdots p_{k_{n^{eq}}}(E_n, \lambda_n),
\]

where we have used the transition matrix elements given in Eq. (17). Comparing this with the left side of Eq. (57) and recalling that \(\gamma^{(F)}_{k, k_0} = p_{k_{0^{eq}}}(E_0, \lambda_0)\), we see that they are identical. We similarly find for \(p(\gamma^{(B)}_B)\) the value

\[
p_{k_{n^{eq}}}(E_n, \lambda_n)p_{k_{n-1^{eq}}}(E_{n-1}, \lambda_{n-1}) \cdots p_{k_{0^{eq}}}(E_0, \lambda_0),
\]

which is the same as for \(p(\gamma^{(F)}_F)\) and the right side of Eq. (57). Therefore, we finally obtain a new FT

\[
e^{\omega(\gamma^{(F)})} = 1, \forall \gamma^{(F)} \in \gamma^{(F)}_F,
\] (58)

which is different from the CFT derived by Crooks. Our derivation also shows that

\[
\beta_0 \Delta Q_C(\gamma^{(F)}) \equiv \Delta S(\gamma^{(F)}), \forall \gamma^{(F)}.
\] (59)

As \(\Delta S(\gamma^{(F)})\), see Eq. (8), is different for different choices of \(k_0, k_n \in \{1, 2, \ldots, r\}\) but the same for all forward trajectories \(\gamma^{(F)} \in \gamma^{(F)}_F\) between \(k_0\) and \(k_n\), it is not a function of the trajectories but only of \(k_0\) and \(k_n\). Thus, it follows from Eq. (8) that \(\Delta Q_C(\gamma^{(F)})\) is also a function of \(k_0\) and \(k_n\) but not of various \(\gamma^{(F)} \in \gamma^{(F)}_F\). As \(\omega(\gamma^{(F)}) = 0\) is supposed to denote the microentropy \(\Delta S_0(\gamma^{(F)}) \equiv \Delta_i S(\gamma^{(F)})\) of \(\Sigma_0\) for all possible forward trajectories, we have

\[
\omega(\gamma^{(F)}) \equiv \Delta_i S(\gamma^{(F)}) \equiv 0, \forall \gamma^{(F)} \in \gamma^{(F)}_F,
\]

where \(\Delta_i S(\gamma^{(F)})\) is the internally generated microentropy in the system over \(\gamma^{(F)}\). We thus conclude that
1. the thermodynamic average $\Delta_i S^{(F)}$ of $\Delta_i S^{(\gamma^{(F)})}$ also vanishes for the entire process $\mathcal{P}^{(F)}$;

2. there are no fluctuations in $\Delta_i S^{(\gamma^{(F)})}$ over all possible forward trajectories as $\Delta_i S^{(\gamma^{(F)})} \equiv 0, \forall \gamma^{(F)}$;

3. it is easy to establish that the same two conclusions are also valid for all backward trajectories in $\gamma^{(B)}$.

It is remarkable that $\Delta_i S^{(\gamma^{(F,B)})}$ is neither positive nor negative but identically zero. The most certain consequence of $\Delta_i S^{(\gamma^{(F,B)})} \equiv 0$ is that there is no irreversible entropy generated during $\mathcal{P}$: $\Delta_i S^{(\gamma^{(F,B)})} \equiv 0$. Hence, the CFT only covers reversible processes; it cannot cover irreversible processes. However, $\Delta_i S^{(\gamma^{(F,B)})} \equiv 0$ is also consistent with some $\Delta_i S^{(\gamma^{(F,B)})}$ being positive and negative in such a way that the averages vanish. This does not happen in the new FT in Eq. (58) due to the absence of fluctuations in $\Delta_i S^{(\gamma^{(F,B)})}$.

VIII. DISCUSSION AND CONCLUSIONS

The derivation of the CFT is based on two assumptions, the first of which has never been mentioned to date:

A1. the energy change $\Delta E(a, \lambda) \equiv E(a, \lambda + \Delta \lambda) - E(a, \lambda)$ of a microstate $a$ due to the change $\Delta \lambda$ in the work parameter $\lambda$ is equal to the exchange work $\Delta R_C(a, \lambda \rightarrow \lambda + \Delta \lambda)$, see Remark [10] and Eq. (34a), and not the generalized work $[-\Delta W(a, \lambda \rightarrow \lambda + \Delta \lambda)]$, see Eq. (31);

A2. the transition between microstates $k$ and $j$ forms a Markov chain described by a balanced transition matrix, which has the form given in Eq. (13).

The two assumptions seem to be independent. But this is not the case under closer scrutiny as we show now. It follows from Assumption A1 that Crooks does not allow for the possibility of any force imbalance, which is equivalent to assuming that the internal microwork $\Delta_i W_a = \Delta_i W(a, \lambda \rightarrow \lambda + \Delta \lambda) = 0$. It follows from Eq. (21), which is the microscopic version of Eq. (15) that $\Delta_i Q_a = 0$ so that $\Delta Q_a = \Delta_a Q_a$. In other words, there is no irreversible heat exchange. This is true of the two interactions within each interval $\delta_i$. To ensure $\Delta_i Q_a = 0$, we need to impose the requirement of a balanced transition matrix in each $\delta_i$. If, on the other hand, we allow force imbalance so that $\Delta_i W_a \neq 0$ by relaxing A1, then we cannot continue to use balanced transition matrix, since that would ensure $\Delta_i Q_a = 0$, which would then violate the thermodynamic requirement $\Delta_i W_a = \Delta_i Q_a$; see Eq. (21). Thus, A2 must also be relaxed. This thus proves our claim.

Note that the above conclusion about the absence of irreversibility refers to the forward trajectories and, by extension, to backward trajectories independently and has nothing to do with the Kolmogorov criterion in Eq. (55) or the derivation of the CFT, although they are both consistent with the lack of irreversibility. In other words, the approach taken by Crooks cannot capture any irreversibility so it is limited to reversible processes only.

In summary, we have shown that the use of the principle of detailed balance results in the microstates $k_1, k_2, \cdots, k_n$ being EQ-microstates, even if the initial microstate $k_0$ is not an EQ-microstate. However, per convention, we ensure that even $k_0$ is an EQ-microstate. This consequence of the principle of detailed balance by itself does not mean that the process during each interval $\delta_i$ is reversible. We can use the above discussion regarding A1 and A2 to show

$$\Delta_i W_a \equiv \Delta_i Q_a \equiv 0.$$

Instead, we have followed Crooks and look at the backward trajectories. We find that the definition of the backward trajectory $\gamma^{(B)}$ fails to reproduce the EQ-microstate $k_0$. We provide a modified version of the backward trajectory $\gamma^{(B)}$ that ensures to reproduce the EQ-microstate $k_0$. We then find that the ratio of the probabilities of the forward and backward trajectories turns out to be unity, in accordance with the Kolmogorov criterion for a reversible Markov chain. From this, we finally conclude that the adimensional Crooks microheat function $\beta_0 \Delta Q_C^{(\gamma^{(F)})} \equiv \Delta_0 S^{(\gamma^{(F)})}$ so that the average irreversible entropy generation $\Delta_i S^{(F)}$ vanishes precisely so that the CFT is a result valid only for a reversible process and not for an irreversible process. This result is consistent with our previous result that the JE is also valid only for a reversible process.

Let us try to understand the reason for the above limitation of the modified CFT. There are two steps that are responsible for the new result.

1. By not allowing any force imbalance in the work protocol (see A1), allows Crooks to accept Eq. (55) to identify $\Delta R_C^{(\gamma^{(C,ab)})}$. This, according to Remark [10] implies that there is no internal microwork, a necessity for irreversibility. From the identity in Eq. (21), this also means that there is no internal microheat generated within the system. Thus, we must allow for force imbalance in the work protocol. The force imbalance can be identified as giving rise to an internal variable $15$.

2. By treating the transition matrix as balanced or accepting the principle of the detailed balance, the temperature of the system is always taken to be $T_0$, the temperature of the medium. This means that the exchanged heat is reversible. As there is no internal microheat also, there is again no irreversibility. Therefore, one must abandon balanced transition matrix to allow for possible heat exchange at different temperatures and make the process irreversible. The temperature imbalance can be identified as giving rise to an internal variable $15$. 

13
3. The rate of exchange of heat depends very strongly on the physical properties such as heat conductivity, etc. of Σ so whether the heat transfer is isothermal or not strongly depends on how large or small is the duration δ二是; we are suppressing the index i. This means that it is determined by the dependence of $T_{\beta}(\delta'')$ on δ''. We see from Eq. (13) that

$$\frac{dp(t'')}{d\delta''} = \frac{dp(t'')}{dt} = p(t') \frac{dT(\delta'')}{d\delta''}.$$  

Since $T = \tilde{T}$ has no dependence on δ'', as shown in Claim 13, $dp(t'')/dt''$ also vanishes, which is consistent with the conclusion in Eq. (13), regardless of $p(t')$. Therefore, the acceptance of the principle of detailed balance does not allow for the rate of heat transfer to depend on δ'', which explains why there is no irreversibility due to heat transfer. To describe irreversible heat transfer, we must abandon the principle of detailed balance.

It would be interesting to follow the consequences of abandoning the principle of detailed balance, the lack of fluctuations of $\Delta_i(\Psi_{\beta}(F,B))$, and how $\Delta Q_{C}(F,B)(\delta'')$ relates to $\Delta Q_{k}(\delta'')$ in Eq. (17). We hope to return to these issues in a separate publication.

Valuable communications with G. Crooks are gratefully acknowledged.

[1] G.E. Crooks, J. Stat. Phys. 90, 1481 (1998).
[2] G.E. Crooks, Phys. Rev. E 61, 2361 (2000).
[3] We will use the following notation in this work. We consider a system Σ, which is in thermal contact with a heat bath (heat medium) $\Sigma_h$ for energy exchange and interacts with a working medium $\Sigma_w$ during the performance of work done by it. The two media do not interact with each other but interact with the system directly. We denote their combination by $\Sigma = \Sigma_h \cup \Sigma_w$ and the combination $\Sigma \cup \Sigma$ by $\Sigma_0$, which forms an isolated system. All quantities pertaining to Σ have no suffix, and those pertaining to $\Sigma(\Sigma_0)$ with a tilde (suffix 0). We assume that Σ is very small compared to $\Sigma$. The medium $\Sigma$ is always taken to be in equilibrium so its fields are not affected by the presence of Σ; as these fields are the same for the isolated system $\Sigma_0$, we do not use tilde and denote them by $T_0, P_0, F_0$, etc.

[4] Any macroscopic extensive or intensive quantity such as the energy E, entropy S, volume V, temperature $T$, pressure P, restoring force F, generalized work dW and heat dQ, etc. that depend on the system $\Sigma$ alone are called system-intrinsic (SI) quantities. The external temperature $T_0$, pressure $P_0$, force $F_0$, etc. are not SI quantities; they are medium-intrinsic (MI) quantities $\Theta$ that control the exchange (suffix e) quantities $d_e Z, d_e F, d_e P, d_e T$ for the system and determine the thermodynamic forces $\Xi$ such as $T - T_0, P - P_0, F + F_0$, etc. which control the system’s approach to equilibrium. The exchange work $d_e W = P_0 d_e V + F_0 d_e \lambda$, the exchange heat $d_e Q = T_0 d_e S$, etc. depend on the MI-quantities $P_0, T_0$, etc. and must be distinguished from SI-analogs $dW = PdV - Fd\lambda$ and $dQ = TdS$. The $\mu$NEQT is based on using the MI-quantities. Adopting the use of the SI-quantities $dW, dQ$, etc. gives rise to a microscopic thermodynamics, which we denote by $\mu$NEQT. It is straightforward to express the force imbalance at a microstate level in the $\mu$NEQT $\Xi$ by considering the difference $d_e W \neq dW - d_e W \geq 0, d_e Q \neq dQ - d_e Q \geq 0$, etc. that are determined by thermodynamic forces $\Xi$. The inequalities are the consequence of the second law.

[5] In a nonequilibrium process, $T - T_0, P - P_0, F + F_0$, etc. act as thermodynamic forces, which drive the system towards equilibrium when they finally vanish $\Xi$ [10]. The
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