Correcting the Mistaken Identification of Nonequilibrium Microscopic Work

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Abstract

Nonequilibrium work-Hamiltonian connection at the level of a microstate plays a central role in diverse modern branches of statistical thermodynamics (fluctuation theorems, quantum thermodynamics, stochastic thermodynamics, etc.). The energy change $dE_k$ for the $k$th microstate is always but erroneously equated with the external work $dW_k$ done on the microstate, whereas the correct identification is $dE_k = -dW_k$, $dW_k$ being the generalized work done by the microstate; the average of $d_iW_k = dW_k + dW_k$ represents the dissipated work. We show that $dW_k$ is ubiquitous even in a purely mechanical system, let alone a nonequilibrium system. As $dW_k$ is not included in $dW_k$, the current identification $dE_k = dW_k$ does not account for irreversibility such as in the Jarzynski equality (JE). Using $dW_k$ to account for irreversibility, we obtain a new work relation that works even for free expansion, where the JE fails. In the new work relation, $\Delta E_k = -\Delta W_k$ depends only on the energies of the initial and final states and not on the actual process. This makes the new relation very different from the JE. Thus, the correction has far-reaching consequences and requires reassessment of current applications in theoretical physics.

I. INTRODUCTION

A. Motivation

In this work, we are mainly interested in an interacting system $\Sigma$ in the presence of a medium $\bar{\Sigma}$ as shown in Fig. [1]; the latter will be taken to be a collection of two parts: a work source $\bar{\Sigma}_w$ and a heat source $\bar{\Sigma}_h$, both of which can interact with the system $\Sigma$ directly but not with each other. We will continue to use $\bar{\Sigma}$ to refer to both of them together. The collection $\bar{\Sigma}_0 = \Sigma \cup \bar{\Sigma}$ forms an isolated system, which we assume to be stationary, with all of its observables such as its energy $E_0$, its volume $V_0$, its number of particles (we assume a single species) $N_0$ constant in time, even if there may be internal changes going on when its parts are out of equilibrium. These internal changes require some internal variables for their description [1-3]. In the following, we will assume $\bar{\Sigma}$ to be always in equilibrium (which requires it to be extremely large compared to $\Sigma$) so that any irreversibility going on within $\Sigma_0$ is ascribed to $\Sigma$ alone, and is caused by processes such as dissipation due to viscosity, internal inhomogeneities, etc. that are internal to the system. Moreover, we assume additivity of volume, a weak interaction between, and quasi-independence of, $\Sigma$ and $\Sigma_0$; the last two conditions ensure that the energies and entropies are additive [4-8] but also impose some restriction on the size of $\Sigma$ in that it cannot be too small. In particular, the size should be at least as big as the correlation length for quasi-independence as discussed earlier [5-8]. In this work, we will assume that all required conditions necessary for the above-mentioned additivity are met.

All quantities pertaining to $\Sigma$ carry no suffix; those for $\Sigma_0$ carry a tilde, while those of $\Sigma_0$ carry a suffix 0. As $\Sigma$ is always in equilibrium, all its fields have the same value as for $\Sigma_0$ so that its temperature, pressure, etc. are shown as $T_0$, $P_0$, etc. as seen in Fig. [1]. To simplify our discussion, we are going to mostly restrict our discussion to two parameters in the Hamiltonian; however, later in Secs. [IX-X] we will consider a general set $W$ of work parameters. In equilibrium (EQ), the state of $\Sigma$ is described by two observables $E$ and $V$ of which $V$ appears as a parameter in its Hamiltonian $H(z, V)$; here, $z$ is the collection of coordinates and momenta of the $N$ particles. Throughout this work, $N$ is kept fixed so we will not exhibit it unless necessary. We can manipulate $V$ from the outside through $\bar{\Sigma}_w$, which exerts an external "force" such as the pressure to do some "work." For this work, $V$ is a symbolic representation of an externally controlled parameter, which is commonly denoted by $\lambda$ in the current literature and whose nature is determined by the experimental setup. Thus, $V$ here should be considered a parameter in a wider sense than just the volume and $P$ its conjugate force; see Fig. [2].

Definition 1 At the microscopic level, the state of the system is specified by the set of microstates $\{m_k\}$, their energy set $\{E_k\}$ and their probability set $\{p_k\}$. For the same set $\{m_k, E_k\}$, different choices of $\{p_k\}$ describes different states, one of which corresponding to $\{p_{eq}\}$ uniquely specifies an EQ state; all other states are called nonequilibrium (NEQ) states.

The EQ entropy is a state function $S(E, V)$. Away from EQ, we also need an additional set of independent extensive internal variables to specify the state [1-3]; we take a single variable $\xi$ for our study to simplify the presentation [8]. In this case, $V$ and $\xi$ appear as parameters in the Hamiltonian $H(z, V, \xi)$. However, the discussion can be readily extended to many internal variables. The force conjugate to $\xi$ is known as the affinity and conventionally denoted by $A$ [1-3]. A NEQ state for which its entropy is a state function $S(E, V, \xi)$ is said to be an internal equilibrium (IEQ) state [1-3]. We will only consider IEQ states in this work for simplicity. It is well known that the energy $E = H_{\nu, \xi}$ does not change at fixed $V$ and $\xi$ as $z$ evolves in accordance with Hamilton’s equations of motion. Therefore, $z$ plays no role in the performance of work so we will usually not exhibit it unless clarity is needed.
FIG. 1: An isolated system $\Sigma_0$ consisting of the system $\Sigma$ in a surrounding medium $\Sigma$. The medium and the system are characterized by their fields $T_0, P_0, ...$ and $T(t), P(t), ...$, respectively, which are different when the two are out of equilibrium.

Focus on the Hamiltonian $\mathcal{H}(V, \xi)$ provides us with the advantage of obtaining a microscopic description of NEQ thermodynamics, where a central role is played by the microscopic work-Hamiltonian relation at the level of microstates $\{m_k\}$ of a NEQ system $\Sigma$. The work relation is a key ingredient in developing a microscopic NEQ statistical thermodynamics, where the emphasis is in the application of the first law in diverse branches including but not limited to nonequilibrium work theorems, 10–13 stochastic thermodynamics, 14, 15 and quantum thermodynamics, 16, 17 to name a few. Once microscopic work is identified, microscopic heat can also be identified by invoking the first law. This makes identifying work of primary importance in NEQ thermodynamics. Unfortunately, this endeavor has given rise to a controversy about the actual meaning of NEQ work, which apparently is far from settled 10, 13, 18, 28.

B. Mistaken Identity

The above controversy is distinct from the confusion about the meaning of work and heat in classical nonequilibrium thermodynamics 20, 30 involving a system-intrinsic (SI) or medium-intrinsic (MI) description, the latter only recently having been clarified 4, 8, 31, 32; see Sec. III for more details and clarification.

Definition 2 By a SI-description (MI-description), we mean a description that uses quantities associated with $\Sigma$ only (with $\Sigma$ only); see for example Eqs. 12 for $dW$ and 13 for $d\tilde{W}$.

The SI-work $dW$ is the work done by the system and the MI-work $d\tilde{W}$ is the work done by the medium. At the level of microstates, one is faced with the fact that both of these works $dW_k$ and $d\tilde{W}_k$ cannot be related to the change $dE_k$ in the microstate energy of $m_k$. Indeed, as pointed out recently 33, the identification of microscopic work has proven erroneous in that the external work $dW_k$, an MI quantity for $m_k$, is identified with the SI energy change $dE_k$ for $m_k$, whereas in a NEQ state, the thermodynamics of the medium and the system are very different. As pointed above, it is $\Sigma$ that experiences dissipation 29, 30, 34, which is partly responsible for the irreversible entropy generation $dS$ in the system. This dissipation is not captured by $d\tilde{W}_k$ in its current formulation as we will see in this work. This is related to a surprising fact hitherto unappreciated that at the microscopic level, $dW_k$ and $dE_k$ always differ in a thermodynamic system, even when dealing with a reversible process as shown by a thermodynamic example in Sec. VII B. In fact, they differ even for a purely mechanical system as shown by the mechanical example in Sec. VII A.

Jarzynski Equality: As we will show here (this has been briefly reported earlier 33), not recognizing this subtle fact has given rise to the "mistaken identity"

$$d\tilde{W}_k \neq dE_k,$$

between an MI-work and SI-energy change in the current literature; see for example Jarzynski 11 who exploits the mistaken identity to prove by now the famous Jarzynski equality (JE) discussed below in Sec. III C.

Following Prigogine 2, see also Fig. 1 and Sec. III for clarification, we partition

$$dE_k = d_e E_k + d_i E_k,$$

in which $d_e E_k \equiv d\tilde{W}_k$ represents the change caused by the exchange with $\Sigma$ through external work and $d_i E_k$ represents the change caused by internal processes going on within $\Sigma$. As the work $dW_k$ is the work done by $m_k$ at the expense of its energy loss, we have $dW_k = -dE_k$ as we will establish here. We will show by examples and arguments that $d_i E_k \neq 0$ is ubiquitous not only in purely mechanical systems but also in a reversible process and is necessary for dissipation. The main thesis of this work to be established here is the following

Proposition 3 It is the contribution $d_i E_k$ that is necessary but not sufficient to describe dissipation but is not captured by $dW_k = d_e E_k$. Therefore, assuming $dW_k = dE_k$ is to ignore dissipation completely regardless of the time dependence of the work protocol. The SI-work relation $dW_k = -dE_k$, which will be established here, contains dissipation and will provide the required NEQ work relation.

The same conclusion also applies to the accumulation $\Delta E_k \neq 0$ along a trajectory, which is the path $\gamma$ taken by the $k$th microstate $m_k$ during a NEQ process $P_0$ over
a time interval \((0, \tau)\). The energy changes \(dE_k, d_w E_k\) and \(d_r E_k\) occur during a segment of \(P_0\) between \(t\) and \(t + dt\), while \(\Delta E_k, \Delta_w E_k\) and \(\Delta_r E_k\) are cumulative changes over the entire trajectory \(\gamma\); see Sec. \([\n]\) for more details.

Quantum and Stochastic Thermodynamics: In a seminal paper laying down the foundation of quantum thermodynamics, Alicki \([17]\) cf. Eq. (2.4) there] identifies the average work \(dW\), the average of \(dW_k\), done by external forces with the average of \(dE_k\) in accordance with Eq. \([\\)`]. In a paper of similar importance for stochastic thermodynamics, Sekimoto \([14]\) cf. Eqs. (2.7)-(2.9) there] also identifies the change \(dE_k\) in the energy \(E_k\) by work variables with the work \(dW_k\) done by the external system.

What is Accomplished: The recent report \([33]\) was very compact. This work is designed to elaborate on what was reported, to provide the missing details and more. Throughout the work, we include an internal variable as a work variable. The main emphasis here will be to demonstrate the ubiquitous nature of \(dE_k\), whose existence has not been previously appreciated. Not recognizing its existence has resulted in the above mistaken identification. It is the force imbalance between the internal and external forces that generates \(dE_k\) and is very common in almost processes, even a reversible one as we will demonstrate. This is the most important outcome of the our approach, which emphasizes the importance of SI-quantities (such as \(dE_k = -dW_k\)) that are very different from the MI-quantities (such as \(d_r E_k = dW_k\)) in any process, even a reversible one. The use of generalized work as isentropic change \(dW = -dE_s\) allows us to calculate microscopic work \(dW_k\), which changes \(dE_k\) but not \(p_k\). On the other hand, the generalized heat \(dQ_k\) does not change \(dE_k\) but changes \(p_k\). This proves to be a great simplification and allows us to treat \(dW_k\) and \(dQ_k\) as purely a mechanical and a stochastic concept, respectively. In addition, as \(m_k\) uniquely determines \(E_k\) for a fixed work set \(W\), we find that \(dE_k\) is uniquely determined by \(dW\) and not by the nature of the work process. This provides a simplification in evaluating the cumulative change \(\Delta W_k\) and allows us to prove a new work theorem, both for the exclusive and the inclusive Hamiltonian. This work theorem is very general and we apply it successfully to the free expansion.

C. Layout

The layout of the paper is the following. In the next section, we introduce the extension of Prigogine’s notation as it may be unfamiliar to many readers. In Sec. \([III]\) three important concepts of NEQ quantities that will play a central role in this work: the concepts of SI- and MI-quantities, and that of microwork. In Sec. \([IX]\) we give two alternate versions of the first law using the MI- and SI-quantities, and introduce thermodynamic forces and their role in dissipation that does not seem to have been appreciated in the field. A new concept of force imbalance is also introduced that plays an important role in microscopic thermodynamics but has been hitherto overlooked. It is one of the central new quantities that is ubiquitous and needs to be incorporated in any process, EQ or NEQ. In Sec. \([X]\) we introduce a new approach to investigate NEQ thermodynamics at the microscopic level by using microstates. Here, we introduce a different way of looking at work and heat, which we call generalized work and generalized heat, that has only recently been developed but proves very useful for a microscopic understanding of statistical thermodynamics. The generalized work is isentropic and the generalized heat satisfies the Clausius equality \(dQ = TdS\) even for an irreversible process. This makes generalized work a purely mechanical quantity. The stochasticity arises from heat but not from work. This results in a clear division between work and heat, making them independent quantities as we explain here. In the next section, we introduce exclusive and inclusive Hamiltonians. It is the latter Hamiltonian that is used by Jarzynski, but we find basically no formal difference between the two. In Sec. \([VII]\) we consider two different models, a mechanical and a thermodynamic, to explain various different kinds of NEQ work and heat. In Sec. \([VIII]\) we show how internal variables emerge in a system’s Hamiltonian. We particularly pay attention to the relative velocity that induces a force that is dissipative, i.e., frictional and contributes to the dissipative work. In Sec. \([X]\) we finally develop our theoretical framework for NEQ statistical thermodynamics and introduce statistical formulation of various quantities. In Sec. \([X]\) we propose a new work theorem both for an exclusive and an inclusive Hamiltonian, which differs from the Jarzynski formulation. The latter is well known for its failure for free expansion. Therefore, we apply the new theorem to free expansion and show that it holds in Sec. \([XI]\) Indeed, we argue that the new theorem works for any arbitrary process and not just the free expansion. In the last section, we give a brief summary of our results.

II. GENERALIZATION OF PRIGOGINE’S PARTITION

Any extensive SI quantity \(X(t)\) of \(\Sigma\), see Fig. \([II]\) can undergo two distinct kinds of changes in time: one due to the exchange with the medium and another one due to internal processes. Following modern notation \([12, 13]\) exchanges of \(X\) (we will suppress the time argument unless clarity is needed) with the medium and changes within the system carry the suffix e and i, respectively:

\[
dX \equiv d_e X + d_i X; \tag{3}
\]

here

\[
dX(t) = X(t + dt) - X(t).
\]

For the medium, we must replace \(X\) by \(\tilde{X}\) so that

\[
d\tilde{X}(t) = (\tilde{X}(t + dt) - \tilde{X}(t)).
\]

For \(\Sigma_0\), we must use \(X_0\).
so that \( dX_0(t) \equiv X_0(t + dt) - X_0(t) \). We will assume additivity of \( X \) for \( \Sigma_0 \):

\[
X_0 = X(t) + \tilde{X}(t).
\]

For this to hold, we need to assume that \( \Sigma \) and \( \tilde{\Sigma} \) interact so weakly that their interactions can be neglected; recall that \( E \) is one of the possible \( X \). As there is no irreversibility within \( \tilde{\Sigma} \), we must have \( d_\xi \tilde{X}(t) = 0 \) for any medium quantity \( \tilde{X}(t) \) and

\[
d_\xi X = -d\tilde{X} = -d_\xi \tilde{X}. \tag{4}
\]

It follows from additivity for \( \Sigma_0 \) that

\[
dX_0 \equiv dX + d\tilde{X} = d_\xi X. \tag{5}
\]

This means that any irreversibility in \( \Sigma_0 \) is ascribed to \( \Sigma \), and not to \( \tilde{\Sigma} \), as noted above. In a reversible change, \( d_\xi X \equiv 0 \). The additivity of entropy

\[
S_0(t) = S(t) + \tilde{S}(t)
\]

requires \( \Sigma \) and \( \tilde{\Sigma} \) to be quasi-independent as said earlier so that

\[
dS_0 = dS + d\tilde{S}.
\]

As an example of the Prigogine’s notation, the entropy change \( dS \) is written as

\[
dS \equiv d_\varepsilon S + d_\xi S \tag{6}
\]

for \( \Sigma \); here,

\[
d_\varepsilon S = -d_\varepsilon \tilde{S}
\]

is the entropy exchange with the medium and

\[
d_\xi S \geq 0
\]

is irreversible entropy generation due to internal processes within \( \Sigma \) and is nonnegative in accordance with the second law. It follows from Eq. \( \text{(5)} \) that \( d_\varepsilon S \) is also the entropy change \( dS_0 \) of \( \Sigma_0 \). For the energy change \( dE \), we write

\[
dE \equiv d_\varepsilon E + d_\xi E, \tag{7}
\]

compare with Eq. \( \text{(2)} \), except that

\[
d_\xi E \equiv 0, \tag{8}
\]

since no internal process, even chemical reaction, can change the energy of the system. [The surprising fact is that \( d_\xi E_k \neq 0 \), as we will establish below; see Eq. \( \text{(61)} \).] Similarly, if \( dW \) and \( dQ \) represent the SI work done by and the heat change of the system, then

\[
dW \equiv d_\varepsilon W + d_\xi W, dQ \equiv d_\varepsilon Q + d_\xi Q.
\]

Here, \( d_\varepsilon W \) and \( d_\varepsilon Q \) are the work exchange and heat exchange with the medium, respectively, and \( d_\xi W \equiv d_\xi W_0 \) and \( d_\xi Q \equiv d_\xi Q_0 \) are irreversible work done and heat generation due to internal processes in \( \Sigma \). For an isolated system such as \( \Sigma_0 \), the exchange quantity vanishes so that \( dX_0 = d_\xi X_0 \). In particular,

\[
dS_0 = d_\xi S_0; dE_0 = d_\varepsilon E_0 \equiv 0, dW_0 = d_\xi W_0; dQ_0 = d_\xi Q_0. \tag{9}
\]

Thus, a description in terms of SI quantity alone can describe an isolated and an open system, whether in equilibrium or not. This makes the SI description highly desirable.

The use of exchange quantities results in an MI-description for \( \Sigma \). No internal variables are required to determine the exchange quantities since their affinities for \( \Sigma \) vanish \([1, 2]\), which is always assumed to be in equilibrium. The SI-description always refers to SI quantities (\( dW, dQ, \text{ etc.} \)). The SI quantities may include internal variables as their affinities need not vanish for \( \Sigma \); in many cases, they may not be readily measurable or even identifiable and require care in interpreting results \([3]\).

Therefore, the use of exchange quantities (MI) is quite widespread. Despite this, the SI-description, which we call the internal approach, is more appropriate to study nonequilibrium processes at the microscopic level, even if we do not use \( \xi \), since \( \xi \), itself an SI quantity, plays a central role. In contrast, the MI-description is called the external approach here.

**Intuitive Meaning:** Intuitively, \( dW \) denotes the work done by the system, a part \( d_\varepsilon W (\equiv p_0 dV) \) of which is transferred to \( \tilde{\Sigma}_w \) through exchange and \( d_\xi W \) is spent to overcome internal dissipative forces. Of \( dQ \), a part \( d_\varepsilon Q \) is transferred from \( \tilde{\Sigma}_h \) through exchange and \( d_\xi Q = d_\varepsilon W \) is generated by internal dissipative forces.

The modern notation requires three different operators \( d, d_\varepsilon \) and \( d_\xi \) having the additive property

\[
d \equiv d_\varepsilon + d_\xi, \tag{10}
\]

acting on any extensive quantity. They are linear differential operators, which satisfy

\[
d_\alpha (aX + bX') = ad_\alpha X + bd_\alpha X',
\]

\[
d_\alpha (X X') = Xd_\alpha X' + (d_\alpha X)X';
\]

here \( d_\alpha \) stands for \( d, d_\varepsilon \) and \( d_\xi \). \( X \) and \( X' \) are two extensive quantities, and \( a \) and \( b \) are two pure numbers. These operators also work on microstate quantities as well and will prove very useful. We have already seen its use for \( E_k \) in Eq. \( \text{(2)} \).

Treating microstate probabilities \( \{ p_k \} \) as fractions \( \mathcal{N}_k / \mathcal{N} \) of the number of replicas in the \( k \)th microstate out of a large but fixed number \( \mathcal{N} \) of replicas of the same system, we can also apply \( d_\alpha \) on \( p_k \) with the result

\[
dp_k = d_\varepsilon p_k + d_\xi p_k, \tag{11}
\]

that will be very useful later.
III. NEW CONCEPTS

A. SI- and MI-works

In a NEQ state, the thermodynamics of the medium and the system are very different. As pointed above, it is $\Sigma$ that experiences dissipation [29, 30, 34], which is partly responsible for the irreversible entropy generation $d_tS$ in the system as we will see in Eq. (35). To clarify the difference between the SI-description and the MI-description, we consider the pressure-volume work and the work done by some internal variable $\xi$ as an example: see the gas confined in a cylinder with one end closed and a movable piston on the other end in Fig. 2(a). The internal variable may describe the nonuniformity of the gas in an irreversible process. It should be recalled that a system in EQ must be uniform [5, 35] so any nonuniformity will result in a NEQ state. The work in the two descriptions is the

SI-work $dW = PdV + Ad\xi$ \hspace{1cm} (12)

done by $\Sigma$ (SI) or the

MI-work $d\tilde{W} = -P_0dV$ \hspace{1cm} (13)
done by $\tilde{\Sigma}$ (MI) in terms of the instantaneous pressure $P$ of $\Sigma$ or $P_0$ of $\tilde{\Sigma}$, and their volume change $dV$ or $-dV$, respectively, where we have used the additivity of the volume $V_0 = V + \tilde{V}$ and the fact that $d\tilde{V} = -dV$ to ensure a constant $V_0$. Notice that $d\tilde{W}$ does not contain any contribution from the internal variable since $A_0 = 0$ [1, 2]. It represents the MI-work done on the system by $\Sigma$ and its negative denotes the exchange work between $\Sigma$ and $\tilde{\Sigma}$ as the MI-work done by $\Sigma$ against $\tilde{\Sigma}$; we denote it by

\[
d_eW = -d\tilde{W} = P_0dV.\]

Let $d\tilde{Q}$ denote the heat added to the medium $\tilde{\Sigma}$, here by the system. Then, $d_eQ = -d\tilde{Q}$ is the heat transferred (exchanged) to $\Sigma$ by $\tilde{\Sigma}$ and $d_eW = -d\tilde{W}$ is the work transferred (exchanged) by $\tilde{\Sigma}$ to $\Sigma$. Both $d_eQ$ and $d_eW$ refer to energy flows across the boundary between $\Sigma$ and $\tilde{\Sigma}$ (see the exchange $d_eX$ in Fig. 1), and are determined by the process of transfer that depends on the combined properties of $\Sigma$ and $\tilde{\Sigma}$. They are customarily used to express the first law for $\Sigma$

\[
dE = d_eQ - d_eW \hspace{1cm} (14)\]

Our sign convention is that $d_eQ$ is positive when it is added to $\Sigma$, and $d_eW$ is positive when it is transferred to $\Sigma$. Once, work has been identified, the use of the first law allows us to uniquely determine the heat.

B. Microwork

The above macroscopic concepts of work represent thermodynamic averages (this will become more clear later) [31, 34, 36]. This allows us to identify the microscopic analogs $dW_k$ and $d\tilde{W}_k$ of $dW$ and $d\tilde{W}$, respectively, at the level of kth microstates $m_k$. The thermodynamic average connection, see also Sec. V, is the following:

\[
dW = \langle dW \rangle = \sum_k p_k dW_k, \hspace{0.5cm} d\tilde{W} = \langle d\tilde{W} \rangle = \sum_k p_k d\tilde{W}_k, \hspace{1cm} (15)\]

which also introduces thermodynamic averaging $\langle \cdot \rangle$ with respect to the instantaneous microstate probabilities $\{p_k\}$. For the energy change $dE_k$, we have its average given by

\[
dE_S = \langle dE \rangle = \sum_k p_k dE_k; \hspace{1cm} (16)\]

the reason for the special symbol becomes once we recall the definition of entropy $S$:

\[
S = - \langle \ln p \rangle = - \sum_k p_k \ln p_k. \hspace{1cm} (17)\]

As the above three averages are at fixed $p_k$’s, they are evaluated at fixed entropy. This is shown by the suffix $S$ in $dE_S$. This quantity will turn out to have an important role in our theory.

We will refer to $dW_k$ in the following as microstate work or microwork in short (but not $d\tilde{W}_k$). One can then determine the accumulated work $\Delta W_k, \Delta \tilde{W}_k$ and $\Delta E_k$ along some path $\gamma$ followed by the microstate in some process $P_0$ by simply integrating $dW_k$ but without the probabilities:

\[
\Delta W_k \doteq \int_{\gamma} dW_k, \hspace{0.5cm} \Delta \tilde{W}_k \doteq \int_{\gamma} d\tilde{W}_k, \hspace{0.5cm} \Delta E_k \doteq \int_{\gamma} dE_k. \hspace{1cm} (18)\]
We observe that \( dW_k, \Delta W_k \) and \( dE_k \) are defined regardless of the probability \( p_k \). Because of this, we wish to emphasize the following important point, which we present as a

**Condition 4** The cumulative quantities \( \Delta W_k, \Delta W_k \) or \( \Delta E_k \) exist or are defined regardless of \( p_k \). Thus, they exist or defined even if \( p_k = 0 \).

This condition will prove useful when we consider free expansion of a classical gas in Sec. [XI].

Traditional formulation of NEQ statistical mechanics and thermodynamics [35, 36] takes a mechanical approach in which \( \Sigma \) follows its classical or quantum mechanical evolution dictated by its SI-Hamiltonian \( H(V, \xi) \); the interaction with \( \Sigma \) is usually treated as a very weak stochastic perturbation. However, investigating microwork (SI approach) is very convenient as \( p_k \)'s do not change. Unfortunately, this description has been overlooked by the current practitioners in the field who have consistently used a MI-description for work by using the external approach but then mistakenly confuse it with its SI-analog; see Eq. (1).

**C. Jarzynski Process**

As \( \Delta \tilde{W}_k \) is not affected by the internal state \( \{P, \Sigma \} \) of \( \Sigma \), it is a choice candidate for studying work fluctuations and for the Jarzynski process. By setting the MI-works \( d\tilde{W}_k, \Delta \tilde{W}_k \) equal to the SI-changes \( dE_k, \Delta E_k \), respectively,

\[
d\tilde{W}_k = dE_k, \Delta \tilde{W}_k = \Delta E_k, \tag{19}
\]

[compare with Eq. (1)] Jarzynski developed the following famous nonequilibrium work relation, the JE, using a very clever averaging \( \langle \cdot \rangle_0 \)

\[
\langle e^{-\beta_0 \Delta \tilde{W}'} \rangle_0 \equiv \sum_k p_{k0} e^{-\beta_0 \Delta \tilde{W}'_k} = e^{-\beta_0 \Delta F'} \tag{20}
\]

for a Jarzynski process (we use a prime now reserved for the inclusive approach discussed in Sec. [XI]). In Eq. (20), where an externally driven nonequilibrium process \( \mathbb{P}_0 \) between two equilibrium states, the initial state \( \mathbb{A}_{\text{eq}} \) and the final state \( \mathbb{B}_{\text{eq}} \), at the same inverse temperature \( \beta_0 \) is considered, \( \langle \cdot \rangle_0 \) refers to a special averaging with respect to the canonical probabilities of the initial state \( \mathbb{A}_{\text{eq}} \):

\[
p_{k0} \equiv e^{-\beta_0 E_k} / Z_{\text{in}}'(\beta_0);
\]

here, the suffix 0 refers to the initial state \( \mathbb{A}_{\text{eq}} \), \( Z_{\text{in}}'(\beta_0) \) the initial equilibrium partition function for the system, \( \Delta \tilde{W}'_k \) the cumulative work done on \( m_k \) during \( \mathbb{P}_0 \), and \( \Delta F' \) the change in the free energy over \( \mathbb{P}_0 \). However, the average \( \langle \cdot \rangle_0 \) in Eq. (20) does not represent a thermodynamic average [compare with Eq. (53)] over \( \mathbb{P}_0 \) as recently pointed out [37]. The inverse temperature along \( \mathbb{P}_0 \) may not always exist or may be different than \( \beta_0 \) due to irreversibility [18, 38]. The process \( \mathbb{P}_0 \) consists of two stages: in the driving stage \( \mathbb{P} \), external work is done \( (\Delta \tilde{W}_k' \neq 0) \), and the reequilibration stage \( \mathbb{P}_0 = \mathbb{P}_0 \setminus \mathbb{P} = \mathbb{P} \cap \mathbb{P} \) in which \( \Sigma \) is in thermal contact with the heat bath \( \Sigma_h \) at \( \beta_h \), during which no work is done \( (\Delta \tilde{W}_k'' = 0) \); \( \Sigma_h \) may or may not be present during \( \mathbb{P} \). The equality is not obeyed for free expansion of a classical gas for which \( \Delta \tilde{W}'_k = 0 \) but \( \Delta F' \neq 0 \) as previously observed [20, 22].

**IV. THE FIRST AND SECOND LAWS, THERMODYNAMIC FORCES AND DISSIPATION**

**A. Gibbs Fundamental Relation**

For the IEQ entropy \( S(E, V, \xi) \), the Gibbs fundamental relation [30] is given by

\[
dS = (dE + PdV + Ad\xi)/T, \tag{21}
\]

where

\[
1/T = \partial S/\partial E, P = T\partial S/\partial V, A = T\partial S/\partial \xi
\]

are the inverse temperature, pressure and the affinity of the system that represent its fields. As \( S \) is a SI-quantity, the above fields are also SI-quantities. In Eq. the affinity vanishes, which means that \( S \) no longer depends on \( \xi \). In other words, \( \xi \) is no longer independent of \( E \) and \( V \) in EQ so we can write it as \( \xi_{\text{eq}} \equiv \xi(E, V) \). Otherwise, \( \xi \) is an independent variable in NEQ states. We can rewrite Eq. (21) as

\[
dE = TdS - PdV - Ad\xi. \tag{22}
\]

We see that the first term on the right side of the equation represents the change in the energy due to the entropy, while the last two terms represent the isentropic change \( dE_S \) in the energy; see Eq. (12). These changes represent SI-changes in \( E \) and play an important role in our approach. In particular, as \( V \) and \( \xi \) are work variables that we collectively denote by \( \mathbf{W} \), we see from Eq. (12) that \( dE_{\mid S} \) is nothing but the SI-work \( dW \). Thus,

\[
TdS = dE - dE_S \equiv dE_{\mathbf{W}}, \tag{23}
\]

where \( dE_{\mathbf{W}} \) represents the change \( dE \) at fixed \( \mathbf{W} \). For brevity, we will call \( dE_{\mathbf{W}} \) the isometric change in which all work variables are held fixed. Thus, we arrive at the following conclusion:

**Conclusion 5** The change \( dE \) consists of two independent contributions- an isentropic change \( dW = dE_S \), and an isometric change \( TdS = dE_{\mathbf{W}} \).

The conclusion allows us to express the first law in an alternative form using SI-quantities as we discuss below.
B. The First Law

Using the exchange work $d_{e}W = -d\tilde{W} = P_{0}dV$, the (MI) work done by $\Sigma$ against $\tilde{\Sigma}$, and the work partition

$$dW = d_{e}W + d_{i}W,$$

we identify $d_{i}W$. We also introduce the exchange heat $d_{e}Q = -d\tilde{Q} = T_{0}d_{e}S$ between $\tilde{\Sigma}$ and $\Sigma$, which represents a MI-quantity. Defining

$$d_{i}Q \equiv d_{i}W$$

(25)

to emphasize the well-known fact that internal work can also be treated as internal heat, we introduce

$$dQ = d_{e}Q + d_{i}Q$$

(26)

so that the conventional MI-form of the first law in Eq. (14) can also be written in an SI-form

$$dE = dQ - dW.$$

(27)

From now on, we will refer to $dW$ and $dQ$ ($d_{e}W$ and $d_{i}Q$) as generalized work and generalized heat (exchange work and exchange heat), respectively, so that no confusion can arise.

If we compare this form with Eq. (22), we recognize that the last two terms there is $dW$ above. Hence, the first term $TdS$ there is nothing but $dQ$ introduced above. This provides us with an important consequence of our approach [4–8, 31, 32] in which

$$dQ = TdS;$$

(28)

compare with Eq. (23). In other words, $dQ$ is nothing but the isometric change $dE|_{W}$ in $E$: it is the change when no work is done ($dW = 0$). The relation $dQ = TdS$ is very interesting in that it not only turns the well-known Clausius inequality $d_{i}Q = T_{0}d_{e}S \leq T_{0}dS$ into an equality but also makes the generalized work $dW$ in Eq. (27) isentropic, whereas $d_{i}W = -d\tilde{W}$ is not. This aspect of $dW$ will prove useful later. Moreover, Eq. (24) allows us to uniquely identify generalized heat and work: this work is always isentropic and this heat is always isometric. On the other hand, the MI-heat and the MI- work suffer from ambiguity; see, for example, Kestin [31]. We summaries these important observations here as

**Conclusion 6** The generalized work $dW$ is isentropic change in the energy, while the generalized heat $dQ = TdS$ is the isometric change in the energy.

It is important to draw attention to the following important fact. We first recognize that the first law in Eq. (14) really refers to the change in the energy caused by exchange quantities. Therefore, $dE$ on the left truly represents $d_{e}E$; see Eq. (17). Accordingly, we write Eq. (14) as

$$d_{i}E = d_{e}Q - d_{e}W.$$  

(29)

Subtracting this equation from Eq. (27), we obtain the identity

$$d_{i}E = d_{i}Q - d_{i}W \equiv 0,$$

(30)

where we have used Eq. (8). The above equation is nothing but the identity in Eq. (25). However, the analysis also demonstrates the important fact that the first law can be applied either to the exchange process or to the interior process. In the last formulation, it is also applicable to an isolated system.

The analog of $dW$ between two nearby equilibrium states is well known in classical thermodynamics and is usually called the dissipated work; see for example, p. 12 in Woods [34]. The dissipated work $(P - P_{0})dV$ is the difference between the generalized work $dW = PdV$ and the reversible work $dW_{rev} = P_{0}dV$ done by $\Sigma$ between the same two equilibrium states and is always nonnegative in accordance with Theorem 17 that will be proved later in its general form (which refers to $dW$ between any two nearby arbitrary states that need not necessarily be equilibrium states). If they are not, then the procedure described by Wood to determine dissipated work cannot work as there is no reversible path connecting two nonequilibrium states. This makes our approach for introducing $dW = dW - d_{e}W$ much more general.

C. The Second Law

We rewrite $dE$ in Eq. (27) as

$$dW = TdS - dE = -dF + (T - T_{0})dS,$$

where

$$F = E - T_{0}S$$

(31)

is the Helmholtz free energy; note the presence of $T_{0}$ and not $T$ in $F$. As $(T - T_{0})dS \leq 0$ established later, see Eq. (71), we conclude

$$dW \leq -dF,$$

(32)

as a consequence of the second law. It is also easy to see from this that

$$\tilde{dW} \geq dF,$$

(33)

where we have used the fact that $d_{i}W \geq 0$, which is again a consequence of the second law as shown in Theorem 17. Similar inequalities also hold in the inclusive approach:

$$dW' \leq -dF', \tilde{dW'} \geq dF'.$$

(34)

D. Dissipation and Thermodynamic Forces

We first return to the relationship of dissipation with the entropy generation $d_{i}S$ for $\Sigma$. The general result for the present case is

$$Td_{i}S = \frac{(T_{0} - T)}{T_{0}}d_{i}Q + (P - P_{0})dV + Ad\xi \geq 0;$$

(35)
In accordance with the second law in Eq. (6), each term on the right of the first equation must be nonnegative. The first term is due to heat exchange \( d_\text{Q} \) with \( \Sigma \) at different temperatures, the second term is the irreversible work due to pressure imbalance and the third term is the irreversible work due to \( \xi \). It is customary to think of \( A \) as the instantaneous "force" associated with the "displacement" \( d\xi \). As the affinity \( A_0 = 0 \) for \( \Sigma, A - A_0 \equiv A \) also denotes the affinity imbalance. Therefore, the last two terms above denote dissipated work, which is customarily called dissipation; the first term is not considered part of it. Therefore, in this work, we will use dissipation to denote the dissipated work.

It is clear that the root cause of dissipation is a "force imbalance" \( P(t) - P_0, A(t) - A_0 \equiv A(t) \), etc. \([4,5,31,34]\) between the external and the internal forces performing work, giving rise to an internal work \( dW \) due to all kinds of force imbalances, which is not captured by using the MI-work \( d\tilde{W} \) unless we recognize that there must be some nonvanishing force imbalance to cause dissipation. The irreversible or dissipated work is \([2,30,34]\)

\[
d_W = (P - P_0)dV + Ad\xi \geq 0,
\]

which is generated within \( \Sigma \); we give a general proof of this result (see Eq. (31)) in Theorem 17. The pressure and affinity imbalance \( P - P_0 \) and \( A - A_0 \equiv A \) are commonly known as thermodynamic forces driving the system towards equilibrium.

If we include the relative velocity between the subsystem \( \Sigma_p \) formed by the piston and the subsystem \( \Sigma_{gc} \) of the gas and the cylinder (\( \Sigma = \Sigma_p \cup \Sigma_{gc} \)), we must account for an additional term \(-V \cdot d\mathbf{P}_p \) in \( d_W \) due to the relative velocity \( V \):

\[
d_W = (P - P_0)dV - V \cdot d\mathbf{P}_p + Ad\xi.
\]

This is reviewed in Sec. VIII. We will come back to this term later when we consider the motion of a particle attached to a spring; see Fig. 2b.

The irreversible work is present even if there is no temperature difference such as in an isothermal process as long as there exists some nonzero thermodynamic force. The resulting irreversible entropy generation is then given by

\[
T dS = d_W \geq 0.
\]

We summarize this as a conclusion [2]:

**Conclusion 7** To have dissipation, it is necessary and sufficient to have a nonzero thermodynamic force. In its absence, there can be no dissipation regardless of the time-dependence of the work process.

## V. MICROSTATE THERMODYNAMICS

We have applied the internal approach microscopically to the set \( \{m_k\} \) of microstates \([7,8,31]\) to obtain a microscopic representation of (generalized) work and heat in terms of the set of microstate probabilities \( \{p_k\} \) and other SI-quantities. We expand on this approach here and exploit it. As we will be dealing with microstates, we will mostly use their energy set \( \{E_k\} \) instead of \( \mathcal{H} \).

### A. General Discussion

As \( \mathcal{H} \) depends on \( V \) and \( \xi \) as parameters, \( E_k \) also depends on them as parameters so we write it as \( E_k(V,\xi) \). Then the thermodynamic energy is given by

\[
E = \langle E \rangle = \sum_k p_k E_k(V,\xi).
\]

The dependence of \( p_k \) is not important. Now, we have

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

here,

\[
dE_k = (\partial E_k/\partial V) dV + (\partial E_k/\partial \xi) d\xi.
\]

As \( \{p_k\} \) is not changed in the first sum, it is evaluated at fixed entropy of \( \Sigma \) \([8,31]\) so this isentropic sum must be identified with \(-dW\):

\[
dW = -\langle dE \rangle = -\sum_k p_k dE_k;
\]

the summand must denote \( dW_k \); compare with Eq. (15):

\[
dW_k = -dE_k.
\]

It follows from Eq. (2) that

\[
d_eW_k = -d_eE_k, dW_k = -d_iE_k.
\]

We also find that \( dW \) only changes \( E_k \)'s but not \( p_k \)'s. The second sum in \( dE \) must be identified with the generalized heat \( dQ \)

\[
dQ = \sum_k E_k dp_k = T dS,
\]

see Eq. (27). It is possible to express \( dQ \) also as an average by introducing Gibbs index of probability \([36]\)

\[
\eta_k \equiv \ln p_k.
\]

We have

\[
dQ = \langle dQ \rangle = \langle d\eta \rangle = \sum_k p_k E_k d\eta_k,
\]

so that we can formally introduce a quantity

\[
dQ_k = E_k d\eta_k
\]

for \( m_k \), which we will refer to as microstate heat or micro-heat in short. It also changes the probability at fixed \( E_k \). Thus, both \( dQ \) and \( dQ_k \) are stochastic quantities. We should emphasize that our concept of microstate heat is very different from the concept of heat currently used in the literature.

We also observe that the generalized heat \( dQ \) and \( dQ_k \) only changes \( p_k \)'s, but not \( E_k \)'s. Therefore, the following aspects of the generalized quantities will be central in our discussion later, which we present as two conclusions:
Conclusion 8 The microwork $dW_k$ changes $E_k$ without changing $p_k$. Thus, a purely mechanical approach can be used for microwork. The effect of microheat is to change $p_k$ but not $E_k$ so it is microheat that makes a thermodynamic process stochastic by changing $p_k$.

Conclusion 9 While the microheat $dQ_k$ do not change $E_k$, it does contribute to the energy change $dE$ through $dQ = \sum_k E_k dp_k$ as $p_k$’s change.

The following conclusion also follows from the above general discussion.

Conclusion 10 Comparing $\langle dE \rangle$ in Eq. (40) with $\langle dE \rangle = -dW$ given above, we conclude that

$$d\langle E \rangle \neq \langle dE \rangle.$$  

The difference is $dQ$ above.

B. Microscopic Force Imbalance

The force imbalance necessary for irreversibility has its root in a similar imbalance at the microstate level. We only have to recall Eq. (12) and to recognize that

$$P = \sum_k p_k P_k, A = \sum_k p_k A_k,$$

where $P_k = -\frac{\partial E_k}{\partial V}$, $A_k = -\frac{\partial E_k}{\partial \xi}$ are the instantaneous pressure and affinity associated with $m_k$ at that time $t$. (We can similarly introduce $V_k$ if we are interested in it.) It follows from Eq. (11) that $dE_k = -dW_k$. Using Eqs. (43) and (44), along with (12), (13), (24) and (40), we conclude that

$$dW_k = -dE_k = P_k dV + A_k d\xi,$$

$$\tilde{dW}_k = -dW_k = d_eE_k = -P_0 dV,$$

$$dI_k = -dI_e = (P_k - P_0) dV + A_k d\xi.$$  

The important point to note is that the force imbalances $P_k - P_0$ and $A_k$ determine the internal changes $d_eE_k$ or $dI_k$ for $m_k$. On the other hand, $dE_k$ is determined by the SI-fields $P_k$ and $A_k$, while $d_eE_k$ is determined by the MI-field $P_0$. From now on, we will reserve the use of force imbalance to denote it only at the microstate level. At this level, it appears as a mechanical force imbalance. In contrast, we will refer to macroscopic force imbalance from now on as thermodynamic forces. We will in the following see that there are reasons to make a clear distinction between the two; compare Conclusion 7 with Conclusion 11.

The following comment for various microscopic works in Eq. (41) should be obvious: the average of Eq. (51a) gives Eq. (42), the average of Eq. (51b) yields Eq. (43), and the average of Eq. (51c) gives Eq. (40). This helps us extend Conclusion 7 for thermodynamic forces to a new conclusion valid only for mechanical force imbalances $P_k - P_0$ and $A_k$ to accommodate the possibility when they result in

$$\sum_k p_k (P_k - P_0) = 0, \sum_k p_k A_k = 0,$$

even if $P_k - P_0$ and $A_k$ are nonzero. In this case, the system is in EQ despite the fact that the force imbalance is present. Indeed, we will see later that the presence of force imbalance is a ubiquitous phenomenon and must be incorporated even if they result in zero thermodynamic forces. The new conclusion is the following:

Conclusion 11 To have dissipation, it is necessary but not sufficient to have a nonzero mechanical force imbalance. Even in its presence, there may be no dissipation if Eq. (52) is satisfied. Nevertheless, it must be incorporated for a consistent theory.

C. Accumulation of thermodynamic work along a Trajectory

Consider a path $\gamma$ taken by the $k$th microstate $m_k$ during a NEQ process $P_0$ and $dW_k$ and $d\tilde{W}_k$ during $t$ and $t + dt$ along $\gamma$. The net works $\Delta W_k$ and $\Delta \tilde{W}_k$ is the integral over $\gamma$ as shown in Eq. (15). The thermodynamic works are averages $\langle \cdot \rangle$ over $\{p_k\}$ not to be confused with $\langle \cdot \rangle_0$ in Eq. (20):

$$dW = \langle dW \rangle = \sum_k p_k dW_k, \quad \tilde{dW} = \langle \tilde{dW} \rangle = \sum_k p_k d\tilde{W}_k,$$

$$\Delta W = \int_\gamma dW = \int_\gamma \langle dW \rangle = \int_\gamma \sum_k p_k dW_k,$$

$$\Delta \tilde{W} = \int_\gamma \tilde{dW} = \int_\gamma \langle \tilde{dW} \rangle = \int_\gamma \sum_k p_k d\tilde{W}_k.$$  

D. Exchange and Irreversible Components

Let us focus on the exclusive approach and express exchange quantities microscopically. Using the partition of $dE_k$ in $dW_k$, we have

$$d_eW = -\sum_k p_k d_eE_k, \quad d_I = -\sum_k p_k d_I.$$  

Similarly, using $dp_k = d_e p_k + d_p p_k$ from Eq. (11), we have

$$d_eQ = \sum_k E_k d_e p_k, \quad d_I = \sum_k E_k d_p p_k,$$

and

$$d_eS = -\sum_k \ln p_k d_e p_k, \quad d_I = -\sum_k \ln p_k d_p p_k.$$  

We finally have

$$\Delta_e W = -\sum_k \int_\gamma p_k d_e E_k, \quad \Delta_I = -\sum_k \int_\gamma p_k d_I E_k,$$

$$\Delta_e Q = \sum_k \int_\gamma E_k d_e p_k, \quad \Delta_I = \sum_k \int_\gamma E_k d_p p_k,$$

$$\Delta W = -\sum_k \int_\gamma p_k E_k dE_k, \quad \Delta Q = \sum_k \int_\gamma E_k dp_k.$$  

9
along with \( \Delta W = \Delta Q \). The equation for \( \Delta W \) above and its differential form \( dW \) provide the correct identification at the microscopic level of the SI-quantities, and must be used to account for irreversibility.

Furthermore, using Eq. (2) in Eq. (10), we have

\[
\begin{align*}
    d_iE & \doteq \sum_k p_k d_iE_k + \sum_k E_k d_ip_k = 0, \quad (55) \\
    dE & \doteq d_iE \doteq \sum_k p_k dE_k + \sum_k E_k d_p k, \quad (56)
\end{align*}
\]

where we have used the identity \( d_iW = d_iQ \) from Eq. (25) in the top equation to show consistency of the above approach with the important identity in Eq. (8): the first term here represents \( (-d_iW) \) and the second term stands for \( d_iQ \).

Claim 12 Most important conclusion of our approach is that even if \( d_iE_k \neq 0, d_iE = 0 \) as is well known; see Eq. (6).

The Eq. (56) reproduces Eq. (14), which again shows consistency of our approach with thermodynamics.

VI. EXCLUSIVE AND INCLUSIVE HAMILTONIANS

The Hamiltonian \( \mathcal{H}(V, \xi) \) above is given in terms of SI-variables and has no information about the medium. Because of this, it has become customary to call it the exclusive Hamiltonian. However, as \( V \) is coupled to the external pressure \( P_0 \), it is also useful to introduce another Hamiltonian in which \( V \) is replaced by \( P_0 \). This is a well-known trick in classical equilibrium thermodynamics (\( P = P_0 \)), where such a transformation is known as the Legendre transform. Instead of considering the energy \( E(V) \), we consider its Legendre transform \( E(V) + P_0 V = E(V) + PV \). It is well known that in equilibrium, this transform is nothing but the enthalpy \( H(P) \).

A simple example is to consider the situation in Fig. 2(a) in which the system \( \Sigma \) is formed by the gas in the left chamber delimited by the cylinder and the right chamber with the movable piston and the cylinder is connected to a large sealed container with a gas at pressure \( P_0 \neq P \); the right chamber and the sealed container along with the cylinder and the piston forms \( \Sigma \).

Taking this cue of the EQ Legendre transform, the inclusive Hamiltonian \( \mathcal{H}' \) is defined as

\[
\mathcal{H}'(V, \xi, P_0) = \mathcal{H}(V, \xi) + P_0 V, \quad (57)
\]

even when we are dealing with a NEQ situation such as when \( P \neq P_0 \) and/or \( A \neq 0 \); here

\[
P_0 \doteq -\partial E/\partial V
\]

is the conjugate field of the medium; compare this with \( P \doteq -\partial E/\partial V \). As we have shown \[3, 6\], the NEQ Legendre transform has a very different property. We find that

\[
V = \frac{\partial \mathcal{H}'}{\partial P_0}, A = -\frac{\partial \mathcal{H}'}{\partial \xi}, P' \doteq \frac{\partial \mathcal{H}'}{\partial V} = P - P_0 \neq 0 \quad (58)
\]

so that \( V, \xi \) and \( P_0 \) are parameters in \( \mathcal{H}' \) unless \( P' \) vanishes, which will happen only under mechanical equilibrium. Therefore, we can think of \( \mathcal{H}'(V, \xi, P_0) \) as another Hamiltonian with the three parameters \( V, \xi \) and \( P_0 \); each parameter will have its own contribution to work \( dW \) for the inclusive Hamiltonian \( \mathcal{H}'(V, \xi, P_0) \). However, the main difference is that \( P_0 \) is not an extensive parameter. As it will be treated as a work variable, the conjugate field will be an extensive variable. The change \( dE' \) in the inclusive Hamiltonian \( \mathcal{H}' \) is

\[
dE' = -P'dV - A d\xi + V dP_0, \quad (59)
\]

which will reduce to the EQ form \( dE' = V dP_0 \) for the EQ enthalpy. As has already been discussed in the literature \[10, 11\], the inclusive Hamiltonian \( \mathcal{H}' \) should be thought of as referring to a different system \( \Sigma' \). This means that \( \mathcal{H}' \) or the corresponding energy \( E' \) is an SI quantity for \( \Sigma' \). Thus, there are SI analogs of generalized work \( dW' \), generalized heat \( dQ' \), etc. along with MI analogs like \( dW/ \), etc. Indeed, there is no fundamental difference between the exclusive and inclusive approaches. All results for the inclusive Hamiltonian can be simply converted for the inclusive Hamiltonian by simply adding a prime on all the quantities and adding the contribution from the parameter \( P_0 \). This will become clear as we go along.

We see from Eqs. (59) and (22) that

\[
d(E' - E) = d(P_0 V). \quad (60)
\]

This is basically what we see from the definition of \( \mathcal{H}' \) in Eq. (57): the difference \( \mathcal{H}' - \mathcal{H} \) is nothing but \( P R_0 \). This remains true also for the accumulated change

Comparison with Jarzynski’s Approach: Finally, we remark that Jarzynski’s discussion \[11\] of the inclusive Hamiltonian differs from our discussion in that Jarzynski overlooks the first term \( -P'dV \) in \( dE' \) above. Accordingly, he assumes the thermodynamic force \( P' = 0 \), which makes his conclusion very different from us; see Conclusion \[17\]. As this is an important difference, we state it as a

Conclusion 13 Jarzynski’s approach to the inclusive Hamiltonian sets \( P' = P - P_0 = 0 \). This results in the complete absence of dissipation as he does not consider any internal variable \( \xi \) in his analysis.

VII. SOME CLARIFYING EXAMPLES

Before proceeding further, we clarify the distinction between various thermodynamic works \( dW, d_iW \) and \( dW' \) or their microstate analogs by two simple examples. It is also clear from the previous section that the pressure difference \( P' \) plays an important role in capturing dissipation; see Conclusion \[13\] Only under mechanical equilibrium do we have \( P' = 0 \). The following examples will make this point abundantly clear that a nonzero force imbalance like \( P' \) is just as common even in classical mechanics whenever there is absence of mechanical equilibrium.
A. Force Imbalance in a Mechanical System: A Microstate Approach

1. Exclusive Approach

Consider as our system a general but a purely classical mechanical one-dimensional massless spring of arbitrary exclusive Hamiltonian $\mathcal{H}(x)$ with one end fixed at an im-mobile wall on the left and the other end with a mass $m$ free to move; see Fig. 2(b). The center of mass of $m$ is located at $x$ from the left wall. For the moment we consider a vacuum instead of a fluid filling system so we do not need to worry about any frictional drag; we will consider this complication in Sec. VIII. The free end is pulled by an external force (not necessarily a constant) $F_0$ applied at time $t = 0$; thus $x$ acts as a work parameter. We do not show the center-of-mass momentum $p$ as it plays no role in determining work. We treat the system purely mechanically. Therefore, the exercise here should be considered as discussing a microstate of the system.

Initially the spring is undisturbed and has zero SI restoring spring force

$$F_s = -\partial \mathcal{H}/\partial x.$$  

The total force

$$F_t = F_0 + F_s$$

is the force imbalance $F_t \leq 0$. There is no mechanical equilibrium unless $F_t = 0$ and the spring continues to stretch or contract, thereby giving rise to an oscillatory motion that will go on forever. During each oscillation, $F_t$ is almost always nonzero. The SI work done by $F_s$ is the spring work $dW \equiv F_s dx$ performed by the spring (internal approach), while the work performed by $F_0$ is $d\tilde{W} = F_0 dx$ transferred to the spring; its negative $d_s W = -F_0 dx$ is the exchange work (external approach). The kinetic energy plays no role in determining work and is not considered. Being a purely mechanical example, there is no dissipation. Despite this, we can introduce using the modern notation

$$d_i W \equiv dW - d_s W \equiv dW + d\tilde{W} \equiv F_t dx,$$  

which can be of either sign (no second law here) and represents the work done by $F_t$. Thus, $dW, d_s W = -d\tilde{W}$ and $d_i W$ represent different works, a result that has nothing to do with dissipation but only with the imbalance; among these, only the generalized work $dW$ is an SI work. The change in the Hamiltonian $\dot{\mathcal{H}} = E$ of the spring due to a variation in the work variable $x$ is

$$d\mathcal{H}\big|_w = dE\big|_w = -F dx = -dW \neq d\tilde{W};$$

the suffix $w$ refers to the change caused by the performing work by varying $x$ here. We thus conclude that

$$dW = -dE\big|_w + d\tilde{W} = dE\big|_w + F_t dx,$$  

which shows the importance of the force imbalance $F_t$ and also shows that $dW \neq -d\tilde{W}$ almost always.

2. Inclusive Approach

Let us consider the inclusive Hamiltonian $[11] \mathcal{H}' = E' \equiv E - F_0 x$ used in deriving Eq. (20); it also explains the prime there. We have

$$dE' = dE - d(F_0 x) = -F_0 dx - xdF_0.$$  

As the force $F_t = -\partial E'/\partial x$ conjugate to $x$ does not identically vanish, $E'(x, F_0)$ is a function of two work parameters $x$ and $F_0$. However, Jarzynski, see Conclusion[13] neglects $F_t$ so $E'(F_0)$ becomes a function of only $F_0$. We will see below that the existence of $F_t$ is very common. As $x = -\partial E'/\partial F_0$, $x$ is the generalized force conjugate to $F_0$. The SI work $dW'$ consists of two contributions:

$$dW' = dW'_x + dW'_{F_0} = F_t dx + xdF_0$$

and satisfies

$$dW' = -dE|_w,$$  

as in the exclusive approach. Furthermore, $dW'_{F_0} = xdF_0$ represents the external work

$$d_s W' = dW'_{F_0} = xdF_0;$$

hence,

$$d_i W' = dW'_x = F_t dx$$

represents the internal work due to $F_t$, and which appears in the left side of Eq. (20).

The following identities are always satisfied, whether we consider a mechanical system as in this subsection or a thermodynamic system as in the next subsection:

$$dE'|_w - dE|_w = dW - dW' \equiv -d(F_0 x),$$  

$$d\tilde{W}' - d\tilde{W} = d_s W - d_s W' \equiv -d(F_0 x).$$  

$$d_i W' \equiv d_i W \equiv F_t dx.$$  

For a mechanical system like a microstate $\omega$, we should append a subscript $k$ to each of the quantities in Eq. (64).

For a thermodynamic system, each of the quantities also refer to thermodynamic average quantities.

Let us investigate the case $F_0 = 0$: $F_t = F_s$, and $dW = dW' = F_s dx \neq 0$ and $d\tilde{W} = d\tilde{W}' = 0$ as a consequence of $\mathcal{H} = \mathcal{H}'$. Such a situation arises when the spring, which is initially kept locked in a compressed (or elongated) state is unlocked to let go without applying any external force. Here, $dW = dW' \neq 0$, while $d\tilde{W} = d\tilde{W}' = 0$ as the spring expands (or contracts) under the influence of its spring force $F_s$. The reader should notice a similarity with the free expansion noted above.

Comparison with Jarzynski’s Approach: The difference between our approach and that by Jarzynski should be mentioned. As said earlier, Jarzynski does not allow the contribution $dW'_x = F_t dx$ in $dE'$ as he
treats $E'(F_0)$ as a function of a single work parameter $F_0$. Therefore,

$$d_1 W^{(3)} = 0 \text{ and } d_1 W'_{(3)} = -zdF_0 = dE'_{w}(J); \quad (65)$$

we have used a superscript $(J)$ as a reminder for the microstate since we have already studied it earlier. This is no different from the one shown in Fig. 2(b). This example is no different from the one shown in Fig. 2(a). We will actually discuss this gas-piston system since we have already studied it earlier. This is easily converted to the spring-mass system by a suitable change in the vocabulary as we will elaborate below.

**B. Force Imbalance in a Thermodynamic System**

1. **Exclusive Approach**

To incorporate dissipation, we consider a thermodynamic analog of the above example by replacing the vacuum with a fluid in the example discussed above; see Fig. 2(b). This example is no different from the one shown in Fig. 2(a). We will actually discuss this gas-piston system since we have already studied it earlier. This is easily converted to the spring-mass system by a suitable change in the vocabulary as we will elaborate below.

The piston is locked and the gas has a pressure $P$. We first focus on various work averages to understand the form of dissipation. At time $t = 0$, an external pressure $P_0 < P$ is applied on the piston and the lock on the piston is released. We should formally make the substitution $x \rightarrow V, F \rightarrow P$ (or $P_k$ when considering $m_k$) and $F_0 \rightarrow -P_0$. At the same time, we will also invoke $\xi$. The gas expands $(dV \geq 0)$ and $P \gg P_0$. The SI work done by the gas is $dW = PdV + Ad\xi$, while $d\tilde{W} = -P_0 dV = -d_W W$. The difference $d_1 W = (P - P_0)dV + Ad\xi \geq 0$ appears as the irreversible work that is dissipated in the form of heat $(d_1 Q = d_1 W)$ either due to friction between the moving piston and the cylinder or other dissipative forces like the viscosity; including them does not change the first two equations but supplements the meaning of $F_1$ in the last equation in Eq. (64); it must include all possible force imbalance as clearly seen in Sec. VII. We will see how internal processes such as friction give rise to internal variables. Assuming this to be the case, our assumption of the presence of an internal variable should not come as a surprise.

Let us analyze this model more carefully at a microstate level. Let $\mathcal{H}(V, \xi) = E(V, \xi)$ be the exclusive Hamiltonian of the gas. Let $E_k(V, \xi)$ denote the energy in the inclusive approach of some $m_k$; let $E(V, \xi) \equiv \langle E \rangle$ and $P(V, \xi) \equiv \langle P \rangle$ be their statistical average over microstates. We use Eq. (2), and use Eq. (51) to identify

$$dW_k = -dE_k, \quad d_1 W_k = -d_1 E_k, \quad d_1 W'_{k} = -d_1 E_k,$$

giving the three work-Hamiltonian relations for a microstate. The statistical averaging gives

$$dW \equiv -dE_{w} = PdV + Ad\xi; \quad d_e W \equiv -d_e E_{w} = P_0 dV \quad d_1 W \equiv -d_1 E_{w} = (P - P_0)dV + Ad\xi$$

just as discussed above; the suffix $w$ refers to these averages determined by the work variables $V$ and $\xi$.

There is no reason for $P_k = P_0, A_k = 0, \forall k$, even in a reversible process for which $P = P_0$ and $A = 0$. As there are pressure fluctuations even in equilibrium,

$$\sum_k P_k (P_k - P_0)^2 \geq 0. \quad (66)$$

For the same reason, we expect affinity fluctuations also in equilibrium. Thus, $P_k - P_0 \neq 0$ and $A_k \neq 0$ in general; hence $d_1 W_k \neq 0$.

2. **Inclusive Approach**

The inclusive Hamiltonian for $m_k$ appears similar to the microstate analog of the NEQ enthalpy $[5, 6]$ $E_k'(V, \xi, P_0) = E_k(V, \xi) + P_0 V$. It is a function of $V, \xi$ and $P_0$ as was discussed in Sec. VII. Therefore,

$$dW_k' = -(\partial E_k'/\partial V) dV - (\partial E_k'/\partial \xi) d\xi - (\partial E_k'/\partial P_0) dP_0 = (P_k - P_0)dV + A_k d\xi - V dP_0$$

of this, $d_e W_k' = -dW_k' = -V dP_0$ is spent to overcome the external force $-V \equiv - (\partial E_k'/\partial P_0)$ conjugate to the work variable $P_0$ and the balance is the irreversible work

$$d_1 W_k' = (P_k - P_0)dV + A_k d\xi = d_1 W_k.$$

Since $d_1 W_k' = -P_0 dV$, Eq. (61) remains satisfied for each microstate, and also for the averages. As we have seen above that $d_1 W_k \neq 0$ in general. Thus, we come to the very important conclusion

**Conclusion 14** The presence of $d_1 W_k \equiv d_1 W_k'$ is ubiquitous and must be accounted for even in a reversible process, let alone an irreversible process; see Eq. (60). This clearly shows that $dW_k (dW_k')$ does not vanish even if $dW_k = -d_1 W_k (dW_k' = -d_1 W_k')$ vanishes.

**Conclusion 15** The microwork $dW_k$ or $dW_k'$ continues to contribute to $dE_k$ (such as during $\overline{P}$ in the Jarzynsky process) even if $dW_k$ or $dW_k'$ has ceased to exist (during $\overline{P}$). Therefore, $dW_k$ or $dW_k'$ contributes over the entire process $P_0$.

**Remark 16** The evaluation of $\Delta W_k$ or $\Delta W_k'$ becomes extremely easy as we need to focus on the entire process and do not have to consider the driving and reequilibration stages of the process separately. As a consequence,
we need to determine $\Delta E_k$ between the final and initial states of $\mathcal{P}_0$. As $E_k$ is an SI-quantity, its value depend on the state, see Definition 1, so the value of $\Delta E_k$ does not depend on the actual process $\mathcal{P}_0$. In other words, $\Delta W_k = -\Delta E_k$ is the same for all possible processes $\mathcal{P}_0$ between the same two states. This observation clarifies a very important Conclusion 12 obtained later.

A third example is the spring-mass problem in Fig. 2(b), where we consider the relative motion of the particle. This example can be considered a prototype of a manipulated Brownian particle undergoing a relative motion with respect to the rest of the system and is treated within our internal approach in Sec. VIII. As we will see, the irreversible work done by the frictional force is properly accounted by the generalized work and, in particular, the frictional work is part of $d_iW$ or of $d_iW_k$.

VIII. EMERGENCE OF INTERNAL VARIABLES IN THE HAMILTONIAN

We wish to show that including other dissipation or internal variables does not alter the first two equations of Eq. (64). However, the third equation needs to incorporate additional contributions due to new forms of dissipation such as new internal variables. The discussion also shows how the Hamiltonian becomes dependent on internal variables, and how the system is maintained stationary despite motion of its parts.

A. Piston-Gas System

We consider the second example, which is depicted in Fig. 2(a), for this exercise. To describe dissipation, we need to treat the motion of the piston by including its momentum $P_p$ in our discussion. The gas, the cylinder and the piston constitute the system $\Sigma$. We have a gas of mass $M_g$ in the cylindrical volume $V_g$, the piston of mass $M_p$, and the rigid cylinder (with its end opposite to the piston closed) of mass $M_c$. However, we will consider the composite subsystem $\Sigma_{gc} = \Sigma_g \cup \Sigma_c$ so that with $\Sigma_p$ it makes up $\Sigma$. The Hamiltonian $\mathcal{H}$ of the system is the sum of $\Sigma_{gc}$ of the gas and cylinder, $H_p$ of the piston, the interaction Hamiltonian $H_{int}$ between the two subsystems $\Sigma_{gc}$ and $\Sigma_p$, and the stochastic interaction Hamiltonian $H_{stoc}$ between $\Sigma$ and $\Sigma_p$. As is customary, we will neglect $H_{stoc}$ here. We assume that the centers-of-mass of $\Sigma_{gc}$ and $\Sigma_p$ are moving with respect to the medium with linear momentum $P_{gc}$ and $P_p$, respectively. We do not allow any rotation for simplicity. We assume that

$$P_{gc} + P_p = 0,$$  \hspace{1cm} (67)

so that $\Sigma$ is at rest with respect to the medium. Thus,

$$\mathcal{H}(x|V,P_{gc},P_p) = \sum_{\lambda} \mathcal{H}_\lambda(x_\lambda|V_\lambda,P_\lambda) + H_{int},$$

where $\lambda = gc,p$, $x_\lambda = (r_\lambda, p_\lambda)$ denotes a point in the phase space $\Gamma_\lambda$ of $\Sigma_\lambda$; $V_\lambda$ is the volume of $\Sigma_\lambda$, and $V = V_{gc} + V_p$ is the volume of $\Sigma$. We do not exhibit the number of particles $N_g, N_c, N_p$ as we keep them fixed. We let $x$ denote the collection $(x_g, x_c, x_p)$. Thus, the system Hamiltonian $\mathcal{H}(x|V,P_{gc},P_p)$ and the average energy $E$ depend on the parameters $V, P_{gc}, P_p$. Accordingly, the system entropy, which we assume is a state function, is written as $S(E,V,P_{gc},P_p)$. Hence, the corresponding Gibbs fundamental relation becomes

$$dS = \beta [dE + PdV - V_{gc}dP_{gc} - V_p dP_p],$$

where we have used the conventional conjugate fields

$$\beta \equiv \partial S/\partial E, \beta P \equiv \partial S/\partial V,$$

$$\beta V_{gc} \equiv -\partial S/\partial P_{gc}, \beta V_p \equiv -\partial S/\partial P_p$$  \hspace{1cm} (68)

as shown elsewhere and references therein. Using Eq. (67), we can rewrite this equation as

$$dS = \beta [dE + PdV - \mathbf{V} \cdot d\mathbf{P}]$$  \hspace{1cm} (69)

in terms of the relative velocity, also known as the drift velocity $\mathbf{V} \equiv V_p - V_{gc}$ of the piston with respect to $\Sigma_{gc}$. We can cast the drift velocity term as $\mathbf{V} \cdot d\mathbf{P}_p = \mathbf{F}_p \cdot d\mathbf{R}$, where $\mathbf{F}_p \equiv d\mathbf{P}_p/\partial P_p$ is the force and $d\mathbf{R} = \mathbf{V} dt$ is the relative displacement of the piston. The first law applied to the stationary $\Sigma$ gives

$$dE = T_0 dE_S - P_0 dV,$$  \hspace{1cm} (70)

in terms of the temperature $T_0$ and the pressure $P_0$ of the medium.

The internal motions of $\Sigma_{gc}$ and $\Sigma_p$ is not controlled by any external agent so the relative motion described by the relative displacement $\mathbf{R}$ represents an internal variable so that the corresponding affinity $F_{p0} = 0$ for $\Sigma$. Because of this, Eq. (70) does not contain the relative displacement $\mathbf{R}$. We now support this claim using our approach in the following. This also shows how $\mathcal{H}(x|V,P_{gc},P_p)$ develops a dependence on the internal variable $\mathbf{R}$. We manipulate $dS$ in Eq. (69) by using the above first law for $dE$ so that

$$TdS = T_0 dE_S + (P - P_0) dV - \mathbf{F}_p \cdot d\mathbf{R},$$

which reduces to

$$T_0 dE_S = (T_0 - T) dS + (P - P_0) dV - \mathbf{F}_p \cdot d\mathbf{R}.$$  \hspace{1cm} (71)

This equation expresses the irreversible entropy generation as sum of three distinct and independent irreversible entropy generations. To comply with the second law, we conclude that for $T_0 > 0$,

$$(T_0 - T) dS \geq 0, (P - P_0) dV \geq 0, \mathbf{F}_p \cdot d\mathbf{R} \leq 0,$$

which shows that each of the components of $d_iS$ is non-negative. In equilibrium, each irreversible component vanishes, which happens when

$$T \to T_0, P \to P_0, \text{ and } \mathbf{V} \to 0 \text{ or } \mathbf{F}_p \to 0.$$  \hspace{1cm} (72)
The inequality \( F_p \cdot dR \leq 0 \) shows that \( F_p \) and \( dR \) are antiparallel, which is what is expected of a frictional force. This causes the piston to finally come to rest. As \( F_p \) and \( V \) vanish together, we can express this force as

\[
F_p = -\mu V f(V^2),
\]

(73)

where \( \mu > 0 \) and \( f \) is an even function of \( V \). The medium \( \Sigma \) is specified by \( T = T_0, P = P_0 \) and \( V_0 = 0 \) or \( F_p = 0 \).

We will take \( F_p \) and \( dR \) to be collinear and replace \( F_p \cdot dR \) by \(-F_t dx \) (\( F_t dx \geq 0 \)), where the magnitude \( F_t \) is written as \( F_t \) as a reminder that this force is responsible for the frictional force and \( dx \) is the magnitude of the relative displacement \( dR \). The sign convention is that \( F_t \) and increasing \( x \) point in the same direction. We can invert Eq. (69) to obtain

\[
dE = TdS - PdV - F_t dx
\]

(74)

in which \( dQ = TdS \) from our general result in Eq. (28).

Comparing the above equation with the first law in Eq. (74), we conclude that

\[
dW = PdV + F_t dx.
\]

(75)

The important point to note is that the friction term \( F_t dx \) properly belongs to \( dW \). As \( d_e W = P_0 dV \), we have

\[
d_e W = (P - P_0)dV + F_t dx.
\]

(76)

Both contributions in \( d_e W \) are separately nonnegative. The corresponding inclusive Hamiltonian is given by \( \mathcal{H}' = \mathcal{H} + P_0 V \). We can easily verify that the first two equations in Eq. (64) in the main text remain valid with \( x \rightarrow V, F_0 \rightarrow -P_0 \) without any modification. The right-side of the last equation, however, is modified to \((P - P_0) dV + F_t dx \) and now contains the internal variable.

We can determine the exchange heat \( d_e Q = dQ - d_e W \)

\[
d_e Q = TdS - (P - P_0)dV - F_t dx
\]

(77)

We can now consider a microstate \( m_k \). For this we need to consider \( dE_k \equiv dE|_{m_k} \), from which we determine

\[
dE_k = -dW_k = P_0 dV + F_{ik} dx,
\]

where \( F_{ik} \) is frictional force associated with \( m_k \). As \( d_e E_k = -d_e W_k = -P_0 dV \), we also conclude that

\[
d_e E_k = -d_e W = -(P_0 - P_0) dV - F_{ik} dx.
\]

It should be emphasized that in the above discussion, we have not considered any other internal motion such as between different parts of the gas besides the relative motion between \( \Sigma_{ge} \) and \( \Sigma_p \). These internal motions within \( \Sigma_g \) can be considered by following the approach outlined elsewhere [3]. We will not consider such a complication here.

### B. Particle-Spring-Fluid System

It should be evident that by treating the piston as a mesoscopic particle such as a pollen or a colloid, we can treat its thermodynamics using the above procedure. This allows us to finally make a connection with the system depicted in Fig. (2b) in which the particle (a pollen or a colloid) is manipulated by an external force \( F_0 \). We need to also consider two additional forces \( F_s \) and \( F_t \), both pointing in the same direction as increasing \( x \); the latter is the frictional force induced by the presence of the fluid in which the particle is moving around. The analog of Eq. (70) for this case becomes

\[
d_i W = (F_s + F_0) dx + F_t dx = F_t dx,
\]

(78)

where \( F_i = F_s + F_0 + F_t \). The other two works are \( dW = (F_s + F_t) dx \) and \( d\tilde{W} = F_0 dx = -d_e W \). In EQ, \( F_i = 0 \) and \( F_s + F_0 = 0 \) \((F_0 \neq 0)\) to ensure \( d_i W = 0 \). In this case, \( d\tilde{W} = -dW = F_0 dx = dE_S \), but this will not be true for a NEQ state.

### C. Particle-Fluid System

In the absence of a spring in the previous subsection, we must set \( F_s = 0 \) so

\[
dW = F_t dx, d\tilde{W} = F_0 dx = -d_e W, d_i W = (F_0 + F_t) dx.
\]

(79)

In EQ, \( F_0 + F_t = 0 \) so that \( F_t = -F_0 \). This means that in EQ, the particle’s nonzero terminal velocity is determined by \( F_0 \) as expected. In this case, \( d\tilde{W} = -dW = F_0 dx = dE_S \), but this will not be true for a NEQ state.

### IX. THEORETICAL CONSIDERATION

In this section, we allow not just \( V \) and \( \xi \) as the two work variables in the exclusive Hamiltonian \( \mathcal{H} \) but an arbitrary number of work variables \( \mathbf{W} \), out of which we single out one special work variable \( V \) that is used to define the exclusive Hamiltonian \( \mathcal{H}' = \mathcal{H} + P_0 V \). (One can construct NEQ Legendre transform with more than one variable, but we will not consider such a complication here.) The lesson from Conclusion [14] is that \( d_i W_k = d_i W_k' \) does not normally vanish. It is this Conclusion that forms a central core of the theoretical development in this section along with the concept of SI-quantities. The importance of both these ideas have not been appreciated to the best of our knowledge but will play a central role in our discussion below.
A. Thermodynamic Work-Energy Principle

We first consider the exclusive Hamiltonian $\mathcal{H}$ and consider its change $d\mathcal{H}_{|\text{w}}$ due to work variables

$$d\mathcal{H}_{|\text{w}} = (\partial \mathcal{H}/\partial \mathbf{W}) \cdot d\mathbf{W} = -\mathbf{F} \cdot d\mathbf{W}, \quad (80)$$
due to all work variables in $\mathbf{W}$; here

$$\mathbf{F} \equiv -\partial \mathcal{H}/\partial \mathbf{W}$$

is the generalized force, from which it follows that the SI-work is

$$dW \equiv \mathbf{F} \cdot d\mathbf{W} = -d\mathcal{H}_{|\text{w}}. \quad (81)$$

It is important to recall that $d\mathcal{H}_{|\text{w}}$ is the change in $\mathcal{H}$ at fixed $\mathbf{W}$ and should not be confused with the change $d\mathcal{H}_{|\text{w}}$ due to changes in the work variables in $\mathbf{W}$. Indeed, $d\mathcal{H}_{|\text{w}} = d\mathcal{H}_S$, which follows from Eq. (10), but we use the current notation $d\mathcal{H}_{|\text{w}}$ instead to emphasize the role of work parameters in $\mathbf{W}$.

We first recognize that $d\mathcal{H}_{|\text{w}}$ represents the change in a microstate energy $E_k$ so we will always think of $d\mathcal{H}_{|\text{w}}$ as $dE_k$ for some $m_k$. Following Sec. II, we break $d\mathcal{H}_{|\text{w}}$ into two parts, as we did for $dE_k$ for $m_k$ above:

$$d\mathcal{H}_{|\text{w}} = d_e\mathcal{H}_{|\text{w}} + d_i\mathcal{H}_{|\text{w}}, \quad (82)$$

and apply it to some $m_k$ so that $d_e\mathcal{H}_{|\text{w}} = d_eE_k \equiv -d_eW_k \equiv d\tilde{W}_k$ is due to the exchange work $d\tilde{W}_k$ and $d_i\mathcal{H}_{|\text{w}} = d_iE_k \equiv -d_iW_k$ is due to the internal work $d_iW_k$ performed by the generalized force $\mathbf{F}$ imbalance on $m_k$. We now make the following claim in the form of a

Theorem 17 Thermodynamic Work-Energy Principle

The change $d\mathcal{H}_{|\text{w}} = dE_k$ in the Hamiltonian $\mathcal{H}$ due to work only must be identified with the SI-work $dW_k$ and not with $d\tilde{W}_k$ for $m_k$; see Eq. (82). It has two contributions; see Eq. (82). The first one corresponds to the external work $d\tilde{W}_k = -d_eW_k$ performed by the medium on $m_k$ and the second one to the negative internal work $-d_iW_k$ due to the imbalance in the generalized forces. After statistical averaging,

$$d_eE_{|\text{w}} = (d_e\mathcal{H}_{|\text{w}}) \equiv -d_eW \equiv -\sum_k p_k d_iW_k \leq 0$$
results in dissipation in the system.

Proof. Based on the three examples, and the general relation in Eq. (80) or the earlier result in Eq. (43), the proof for

$$d\mathcal{H}_{|\text{w}} = dE_k = -d\tilde{W}_k$$
is almost trivial. We only have to recognize that both $dE_k$ and $d\tilde{W}_k$ are SI-quantities as they appear in the identity in Eq. (80). The proof here is not restricted to only two work variables. We consider an arbitrary number of work variables in $\mathbf{W}$. Consider the first law representation using the MI-quantities in Eq. (27). The isentropic change $dE_S$ is identified with

$$dE_S = -dW = -\mathbf{F} \cdot d\mathbf{W}.$$ 

It represents the average of $-d\tilde{W}_k = dE_k$ with

$$dE_k \equiv (\partial E_k/\partial \mathbf{W}) \cdot d\mathbf{W} \equiv d_eE_k + d_iE_k.$$ 

We thus identify $d_eW_k = -d_iE_k$ and $d_iW_k = -d_iE_k$. This proves the first part. The isometric change in $dE$ represents the generalized heat $dQ$, as discussed earlier. To proceed further and better understand the above result and prove the last part, we turn to the thermodynamics of the system, which we now require to be in internal equilibrium so that $dQ = TdS$. We rewrite $dE = TdS - dW$ as

$$dE = T_0d_iS - d_iW + T_0d_iS + (T - T_0)dS - d_iW;$$

which leads to

$$T_0d_iS = (T_0 - T)dS + d_iW; \quad (83)$$

which is a different way to write Eq. (83). Each term on the right side, being independent of each other, must be nonnegative separately to ensure the second law in Eq. (6); compare with Eq. (71). This proves the last part

$$d_iW \geq 0. \quad (84)$$



B. Equivalence of Exclusive and Inclusive Approaches

The discussion above can be extended to the inclusive energy. Indeed, all relations derived in the exclusive approach have analogs in the inclusive approach: all we need to do is to insert a prime on each quantity. It should be stressed that

$$-(\partial E_k/\partial \mathbf{W}) \text{ or } -(\partial E_k'/\partial \mathbf{W}'), \mathbf{W}' = (\mathbf{W}, P_0)$$
represents the "generalized force" and the work has the conventional form: "force" x "distance," contrary to what is commonly stated. According to the theorem, only SI-works $(-dW_k, -\Delta W_k, -dW, -\Delta W, \text{ and } -\Delta W'_k)$ must be used on the left sides in Eq. (1) or its analogs and as shown in Eq. (51a) and its cumulative analog. It is easy to convince that the Eq. (61) holds in all cases; see the discussion in Sec. VI.

X. A NEW NEQ WORK THEOREM

In a quantum system, the index $k$ denotes a set of quantum numbers, which we take to be a finite set, i.e., having a finite number of quantum numbers so that the
set \( \{ m_k \} \) is countable infinite. Such is the case for a particle in a box treated quantum mechanically that we investigate in Sec. XI. The energy \( E_k(W) \) of a microstate \( m_k \) depends on the work parameter \( W \) so it changes as \( W \) changes during a process \( P_0 \) according to Eq. (80) but the set \( k \) does not change. This means that \( m_k \) keeps its identity, while its energy changes during the work protocol \( P_0 \). The change of energy during this protocol is related to the microwork

\[
\Delta W_k = -(E_{k_{\text{fin}}} - E_{k_{\text{in}}}),
\]

where we have set

\[
E_{k_{\text{fin}}} = E_k(\tau), E_{k_{\text{in}}} = E_k(0);
\]

here, \( \tau \) is the duration of the process \( P_0 \). As we discussed in reference to Eq. (80), the change \( \Delta E_k = E_{k_{\text{fin}}} - E_{k_{\text{in}}} \) occurs at fixed \( p_k \) and equals \( -\Delta W_k \). Any change in \( p_k \) requires the microheat \( \Delta Q_k \), i.e., either \( \Delta e_kQ_k \) or \( \Delta s_kQ_k \). We finally conclude that

**Conclusion 18** If we are interested in knowing the cumulative change \( \Delta W_k \), we only need to determine \( \Delta E_k \) by following the same \( m_k \) mechanically during a work protocol \( P_0 \). The probability plays no role as \( \Delta Q_k \) is of no concern.

**Remark 19** It should be stated here that for all different processes \( P_0(A_{\text{fin}} | A_{\text{in}})'s \) between the same two states \( A_{\text{fin}} \) and \( A_{\text{in}} \), not necessarily EQ states, \( E_{k_{\text{fin}}} \) and \( E_{k_{\text{in}}} \) are the same, see Definition 7 so

\[
\Delta W_k(P_0) = -\Delta E_k(A_{\text{fin}}, A_{\text{in}}), \quad \forall P_0(A_{\text{fin}} | A_{\text{in}}).
\]

This allows us to determine the dissipated work

\[
\Delta^\text{r}W_k(P_0) = -\Delta E_k(A_{\text{fin}}, A_{\text{in}}) - \Delta W_k(P_0)
\]

in which \( \Delta^\text{r}W_k(P_0) = -\Delta \tilde{W}_k(P_0) \) in terms of the external work \( \Delta W_k(P_0) \).

What the above remark implies is the following: Different processes between the same two states \( A_{\text{fin}} \) and \( A_{\text{in}} \) differ not in \( \Delta W_k(P_0) \) but in \( \Delta \tilde{W}_k(P_0) \) or in \( \Delta^\text{r}W_k(P_0) \). This makes microwork unique in that it does not depend on the nature of \( P_0(A_{\text{fin}} | A_{\text{in}}) \). Despite this, it contains the contribution of dissipation in it given by the average (\( \Delta W_k(P_0) \)).

However, the property of a quantum \( m_k \) maintaining its identity during \( P_0 \) is different from the property of a microstate \( m_k \) in a classical system, for which \( m_k \) is a small dimensionless volume element \( \delta z_k \) in the phase space \( \Gamma \) surrounding a point \( z_k \); the collection \( \{ \delta z_k \} \) covers the entire phase space \( \Gamma \). This microstate changes its identity \( (\delta z_k \rightarrow \delta z_l, k \neq l) \) as it evolves in time following its Hamiltonian dynamics; recall that \( dH_W = 0 \) during this dynamics. Despite this, the evolution is unique so there is a 1-to-1 mapping between \( m_k(t) \rightarrow \delta z_k(t) \) and \( m_k(t') \rightarrow \delta z_l(t') \). This causes no problem as the change \( \Delta W_k = -\Delta E_k \) is not affected by the microstate evolution past \( \tau \), the duration of \( P_0 \); see Conclusions 8 and 9 for more details. In this case, introducing

\[
E_k(\tau) = E(\delta z_k(\tau)), E_k(0) = E(\delta z_k(0)),
\]

we can write \( \Delta W_k \) as in Eq. (85). Thus, whether we are considering a classical system or a quantum system, we can always express \( \Delta W_k \) as in Eq. (85).

**A. Derivation**

Let us evaluate the particular average \( \langle \cdot \rangle_0 \) in Eq. (20) but of \( e^{\beta_0 \Delta W_k} \) using Eq. (85). We first consider the exclusive approach. We have

\[
\langle e^{\beta_0 \Delta W} \rangle_0 = \sum_k e^{-\beta_0 E_k(0)} e^{\beta_0 \Delta W_k} = \sum_k \frac{e^{-\beta_0 E_k(0)}}{Z(\beta_0)} e^{-\beta_0 (E_{k_{\text{fin}}} - E_{k_{\text{in}}} - \Delta W_k)},
\]

which leads to

\[
\langle e^{\beta_0 \Delta W} \rangle_0 = \sum_k \frac{e^{-\beta_0 E_{k_{\text{fin}}}}}{Z(\beta_0)} = \frac{Z(\beta_0)}{Z(\beta_0)} = e^{-\beta_0 \Delta F},
\]

where \( Z(\beta_0) \) and \( Z(\beta_0) \) are initial and final canonical partition functions. Introducing the free energy difference \( \Delta F \equiv F_{\text{fin}} - F_{\text{in}} \), we finally have

\[
\langle e^{\beta_0 \Delta W} \rangle_0 = e^{-\beta_0 \Delta F}.
\]

This is our new work theorem involving microworks. The same calculation can be carried out for the inclusive Hamiltonian, with a similar result except all the quantities must be replaced by their prime analog as said earlier:

\[
\langle e^{\beta_0 \Delta W'} \rangle_0 = e^{-\beta_0 \Delta F'}.
\]

This fixes the original Jarzynski relation in Eq. (20) by accounting irreversibility in both approaches, and is valid in all cases, reversible or otherwise.

**XI. THE FREE EXPANSION**

Consider the case of a free expansion \((P_0 = 0) \) of a gas in an isolated system of volume \( V_{\text{fin}} \), divided by an impenetrable partition into the left (L) and the right (R) chambers as shown in Fig. 3(a). Initially, all the \( N \) particles are in the left chamber of volume \( V_{\text{in}} \) in an equilibrium state at temperature \( T_0 \); there is vacuum in the right chamber. At time \( t = 0 \), the partition is suddenly removed, shown by the broken partition in Fig. 3(b) and the gas is allowed to undergo free expansion to the final volume \( V_{\text{fin}} \) during \( P \). After the free expansion, the gas is in a NEQ state and is brought in contact with \( \Sigma_h \) during \( P \) to come to equilibrium at the initial temperature.
$T_0$. If the gas is ideal, there is no need to bring in $\bar{\Sigma}_h$ for reequilibration; we can let the gas come to equilibrium by itself as it is well known that the temperature of the equilibrated gas after free expansion is also $T_0$. It should be stated, which is also evident from Fig. 3(b), that while the removal of the partition can be instantaneous, the actual process of gas expanding in the right chamber is continuous and gradually fills it. Therefore, at each instant, it is possible to imagine a front of the expanding gas shown by the solid vertical line enclosing the largest among smallest possible volumes containing all the particles so that there are no particles to the right of it in the right chamber in all possible realization of the expanding gas. By this we mean the following: we consider all possible realizations of the expanding gas at a particular time $t > 0$ and locate the front corresponding to the smallest volume containing all the gas particles to its left. Then we choose among all these fronts that particular front that results in the smallest volume on its right or the largest volume on its left. In this sense, this front is an average concept and is shown in Fig. 3(b). We have identified the volume to its right as "vacuum" in the figure. This means that at each instant when there is a vacuum to the right of this front, the gas is expanding against zero pressure so that $d\tilde{W} = 0$. Despite this, as the expansion is a NEQ process, $dW = d_qW > 0$.

A. Quantum Free Expansion

We now apply Eq. (87) to the free expansion of a one-dimensional ideal gas of classical particles, but treated quantum mechanically as a particle in a box with rigid walls, which has studied earlier [39], see also Bender et al [40]. We assume that the gas is thermalized initially at some temperature $T_0 = 1/\beta_0$ and then isolated from the medium so that the free expansion occurs in an isolated system. After the free expansion from the box size $L_{in}$ to $L_{fin} > L_{in}$, the box is again thermalized at the same temperature $T_0$. The role of $V$ is played by the length $L$ of the box. This will also set the stage for the classical treatment later.

As discussed in Sec. VII.A for $F_0 = 0$, $\Delta W_k \neq 0$ even though $\Delta \tilde{W}_k = 0$. Since we are dealing with an ideal gas, we do not need to bring $\bar{\Sigma}_h$, see below, so we let the gas to come to equilibrium as an isolated system. As there is no inter-particle interaction, we can focus on a single particle for our discussion; its energy levels are in appropriate units

$$E_k = k^2/L^2,$$

where $L$ is the length of the box. We assume that the gas is thermalized initially at some temperature $T_0 = 1/\beta_0$. It is isolated from the medium so that the free expansion occurs in an isolated system, during which, we have $\Delta_e Q = \Delta_e W = 0$ (but $\Delta_i Q = \Delta_i W \neq 0$) so that $\Delta E_{\text{free}}(L_{fin}, L_{in}) = 0$; see Eq. (14). After the free expansion from the box size $L_{in}$ to $L_{fin} > L_{in}$, the box is allowed to come to equilibrium in isolation so that we have $\Delta E_{\text{reeq}}(L_{fin}) = 0$. Accordingly, $\Delta E_{\text{eq}}(L_{fin}, L_{in}) = 0$ after reequilibration.

The initial partition function is given by

$$Z_{\text{in}}(\beta_0, L) = \sum_k e^{\beta_0 E_k_{\text{in}}}.$$  

Approximating the sum by an integration over $k$ as is common, we can evaluate $Z_{\text{in}}(\beta_0, L)$ from which we find that the free energy $F_{\text{eq}}$ and the average energy $E_{\text{eq}}$ are given by

$$\beta_0 F_{\text{eq}} = -(1/2) \ln(L^2 \pi/4 \beta_0), \quad E_{\text{eq}} = 1/2 \beta_0;$$

while $F_{\text{eq}}$ depends on $\beta_0$ and $L$, $E_{\text{eq}}$ depends only on $\beta_0$ but not on $L$ so that $E_{\text{eq}}$ has the same value in the final EQ state. This means that the final equilibrium state has the same temperature $T_0$. This explains why we did not need to bring $\bar{\Sigma}_h$ in play for reequilibration as assumed above.

As we have discussed in reference to Eq. (40) and concluded in Conclusions [8] 9 and [15] and summarized in Remark 19, $\Delta E_k = -\Delta W_k$ regardless of whether $P_0$ is irreversible or not. Below we will show that the present calculation here is dealing with an irreversible $P_0$. The energy change between two EQ states is

$$\Delta E_k = k^2(1/L_{fin}^2 - 1/L_{in}^2).$$

Let us determine the microwork done to take the initial microstate to the final microstate by using the internal pressure

$$P_k = -\partial E_k/\partial L = 2E_k/L \neq 0 \tag{89}$$
irreversible. This is also evident from the observation that the expansion we are studying is isothermic and Eq. (88) with
\[\int_{\Gamma_{in}} P_k dL.\] (90)

It is easy to see that this microwork is precisely equal to \(-\Delta E_k\) in accordance with Theorem 17, as expected. It is also evident from Eq. (89) that for each \(L\) between \(L_{in}\) and \(L_{fin}\),
\[P = \sum_k p_k P_k = 2E/L \neq 0.\]

We can use this average pressure to calculate the thermodynamic work
\[\Delta W = \int_{L_{in}}^{L_{fin}} P dL = 2\sum_k \int_{L_{in}}^{L_{fin}} p_k E_k dL/L \neq 0.\]
as expected. As \(\Delta E = 0\), it means that \(\Delta Q = \Delta W \neq 0\), which really means \(\Delta_e Q = \Delta_e W \neq 0\) in this case. This establishes that the expansion we are studying is irreversible. This is also evident from the observation that \(P \neq P_0 = 0\).

Despite this, \(\Delta W_k\) is always equal to the same \((-\Delta E_k)\) regardless of the nature of irreversibility of \(P_0\), which is consistent with Conclusion 18 and Remark 19. The same \(\Delta W_k\) will also apply to a reversible \(P_0\) as we are considering the energy change between two EQ states. The only difference is that now \(\Delta Q = \Delta W \neq 0\) will mean \(\Delta_e Q = \Delta_e W \neq 0\). It is trivially seen that Eq. (87) is satisfied for all \(P_0\), not just the free expansion.

As \(P_0 = 0\), there is no difference between the exclusive Hamiltonian and the inclusive Hamiltonian. Thus, the discussion above is also valid for the inclusive Hamiltonian and Eq. (88) with \(E'_k = E_k\) and \(F' = F\).

**B. Classical Free Expansion**

We will consider the free expansion of an isolated classical gas in a vacuum \((P_0 = 0)\), see Fig. 3. We set \(V_{in}\) and \(V_{fin}\) for simplicity. The initial phase space is denoted by the interior of the solid red ellipse \(\Gamma_{in}\) on the left side in Fig. 4. The final phase space is shown by the interior of the broken red ellipse on the left and the solid red ellipse \(\Gamma_{fin}\) on the right in Fig. 4. The gas is in a "restricted (i.e., being confined in the left chamber)" equilibrium state with equilibrium microstate probability
\[f_0(\delta z_0) = e^{-\beta_0 E(z_0)} / Z_{in}(\beta_0, V_{in})\] (91)
at \(t = 0\); here, the initial partition function in the initial volume \(V_{in}\) is
\[Z_{in}(\beta_0, V_{in}) = \sum_{\delta z_0 \in \Gamma_{in}} e^{-\beta_0 E(z_0)}.\] (92)

We consider the set of microstates in the final phase space \(\Gamma_{fin}\) and pick two microstates \(\delta z_0\) and \(\delta z\) associated with \(z_0 \in \Gamma_{in}\) and \(z \in \bar{\Gamma} = \Gamma_{fin} \setminus \Gamma_{in}\); here, \(\bar{\Gamma} = \Gamma_{fin} \setminus \Gamma_{in}\) denotes the difference set of \(\Gamma_{fin}\) and \(\Gamma_{in}\). We use the notation \(z_0 = (z_0, z)\) to denote the two points. Let us identify \((z_0, z')\) as the unique 1-to-1 phase points obtained by the deterministic Hamiltonian evolution of \((z_0, z)\) along the deterministic or mechanical trajectories \(\gamma = \gamma(z_0)\) and \(\gamma' = \gamma'(z)\) corresponding to a given work protocol \(P_0\); see Fig. 4. The probabilities of the two paths are irrelevant for the microworks
\[\Delta W_{\gamma}(z_0) = - (E(z) - E(z_0)),\]
\[\Delta W_{\gamma'}(z) = - (E(z') - E(z));\] (93)
see Conclusions 8 and 9.

While the initial EQ probability distribution \(f_0(\delta z_0)\) is nonzero for \(\delta z_0 \in \Gamma_{in}\), it is common to think of \(f_0(\delta z) = 0\) for \(z \in \bar{\Gamma}\). This is an ideal situation and requires taking the energy \(E(z) = \infty\), but in reality, \(f_0(\delta z)\) falls rapidly as we move into the right chamber away from the left one in the initial macrostate. Moreover, during free expansion, \(f(\delta z)\) at \(t > 0\) is not going to remain zero. Therefore, we formally assume that the initial probability distribution \(f_0(\delta z)\) is infinitesimally small by assigning to it a very large positive energy
\[E(z) = \varepsilon(z)/\varepsilon > 0, z \in \bar{\Gamma} \text{ at } t = 0\] (94)

by introducing an infinitesimal positive quantity \(\varepsilon\). At the end of the calculation, we will take the limit \(\varepsilon \to 0^+\), which simply means \(\varepsilon \to 0\) from the positive side. Under this limit, the contribution from \(e^{-\beta_0 E(z)}\) will vanish:
\[e^{-\beta_0 E(z)} \varepsilon \to 0^+ \to 0.\]

This allows us to recast the initial partition function as a sum over all microstates \(z \in \Gamma_{fin}\):
\[\lim_{\varepsilon \to 0^+} Z_{in}(\beta_0, V_{fin}, \varepsilon) = \lim_{\varepsilon \to 0^+} \sum_{z \in \Gamma_{fin}} e^{-\beta_0 E(z)} = Z_{in}(\beta_0, V_{in});\] (95)
Thus, we can focus on \(\Gamma_{fin}\) as the phase space to consider during any work protocol \(P_0\) instead of \(\Gamma_{in}\). This allows
us to basically use a 1-to-1 mapping between initial microstates \( \mathbf{z}_0 \equiv (z_0, \mathbf{z}) \) and final microstates \( \mathbf{z}_\gamma \equiv (z_\gamma, \mathbf{z}_\gamma) \) discussed above. We simply denote \( \mathbf{z}_0 \) or \( \mathbf{z} \) by \( \mathbf{z} \in \Gamma_{\text{fin}} \) or \( \mathbf{z}_\gamma \in \Gamma_{\text{fin}} \) for the Hamiltonian evolution of \( \mathbf{z} \) along the microwork protocol from now on. We consider the Jarzynski average of the exponential work in Eq. (87) for the exclusive Hamiltonian and write it as

\[
\lim_{\varepsilon \to 0^+} \left\langle e^{\beta_0 \Delta W} \right\rangle_0 = \lim_{\varepsilon \to 0^+} \frac{\sum_{\mathbf{z} \in \Gamma_{\text{fin}}} e^{-\beta_0 E(\mathbf{z})} e^{-\beta_0 [E(\mathbf{z}) - E(\mathbf{z})]} Z_{\text{fin}}(\beta_0, V_{\text{fin}}, \varepsilon)}{Z_{\text{fin}}(\beta_0, V_{\text{fin}}, \varepsilon)},
\]

where we have used \( \Delta W_{\gamma}(\mathbf{z}) = -(E(\mathbf{z}) - E(\mathbf{z})) \) in accordance with Eq. (83). The initial partition function in the original volume \( V_{\text{fin}} \) because of the vanishing probabilities to be outside this volume. Because of the 1-to-1 mapping to \( \mathbf{z}_\gamma \), we can replace the sum to a sum over \( \mathbf{z}_\gamma \), and at the same time cancel the initial energy \( E(\mathbf{z}) \) in the exponent; the cancellation is exact even for \( \mathbf{z} = \mathbf{z} \) for which \( E(\mathbf{z}) \rightarrow +\infty \) in the limit \( \varepsilon \to 0^+ \). Because of this, the lim operation has no effect in the numerator. The partition function in denominator reduces to \( Z_{\text{fin}}(\beta_0, V_{\text{fin}}) \) as shown in Eq. (95). We finally find

\[
\left\langle e^{\beta_0 \Delta W} \right\rangle_0 = \frac{\sum_{\mathbf{z} \in \Gamma_{\text{fin}}} e^{-\beta_0 E(\mathbf{z})} Z_{\text{fin}}(\beta_0, V_{\text{fin}})}{Z_{\text{fin}}(\beta_0, V_{\text{fin}})},
\]

which is precisely what we wish to prove in Eq. (87).

The situation with the inclusive Hamiltonian is the same as \( \mathcal{H}' = \mathcal{H} \) as before. This allows us to also prove \( \mathcal{Q}_2 \). Moreover, as in the previous subsection, the demonstration of Eqs. (87) and (88) is valid for any arbitrary process, not just the free expansion, the title of this section.

It should be emphasized that allowing for a negligible probability is a common practice even in EQ statistical mechanics where we evaluate the partition function by considering all microstate, regardless of how negligibly small the corresponding statistical weight is. This probability could even be zero. The only difference is that the microstate is defined over the volume of the system and not outside. We have allowed microstates in deriving Eqs. (87) and (88) with vanishing small or zero probabilities. Here, we are considering microstates outside the volume of the system, but mathematically, there is no difference.

By allowing such microstates in \( \overline{\Gamma} \), we have shown that Eqs. (87) and (88) hold even for free expansion of a classical or quantum gas, where the Jarzynski equality fails.

XII. CONCLUSION

The present work is motivated by a desire to clarify the connection between work and energy change at the mechanical level. The goal is summarized in Proposition 3. The use of SI-quantities proves useful in expressing the First law in which the generalized heat \( dQ \) is proportional to \( dS \), while the generalized work \( dW = -dE_S \) is isentropic change in the energy \( E \). This ensures that \( dW \) and \( dQ \) change \( E \) independently so that we need not consider any effect of \( dQ \) while considering the change \( dE_S \); see Conclusion 5.

As the probability during microwork does not change, a microstate can also be treated as a mechanical system during microwork; see Conclusion 6. As the change \( \Delta E_k \) is an SI-quantity, it must be related to the work that is also an SI-quantity. This gives \( \Delta E_k = -\Delta_k W \) (internal scheme), which contradicts the current but erroneous practice of using \( \Delta E_k = \Delta_k \tilde{W} \) (external scheme) in diverse applications in nonequilibrium statistical thermodynamics mentioned earlier; see the discussion in Sec. 11. The mistake results in setting

\[
\Delta W_k = 0,
\]

which contradicts the most important result of this work that \( \Delta W_k \neq 0 \) in almost all cases as concluded in Conclusion 11. This has been justified by a purely mechanical system in Sec. VIIA which shows that Eq. (88) holds only when there is mechanical equilibrium. This equilibrium occurs under a very special condition of zero force balance \( F_i \). However, as shown in Sec. VIIA, Eq. (88) does not hold in general for a mechanical system. The thermodynamic system investigated in Sec. VIIIB also shows that Eq. (88) does not hold in general.

As Conclusion 11 shows, the presence a nonzero force imbalance is necessary (but not sufficient) for dissipation in the system. The force imbalance is what gives rise to thermodynamic forces, whose importance does not seem to have been acknowledged by many workers that consistently use the mistaken identity \( \Delta E_k = \Delta_k \tilde{W} \) in Eq. (1). This means that the Eq. (88) holds in these studies, which cannot include any dissipation. This is consistent with Theorem 17 that there is no irreversibility (\( \Delta W = 0 \)) if we accept \( \Delta E_k = \Delta_k \tilde{W} \). This also shows that the JE is not a valid identity.

The existence of \( \Delta_k E_k = -\Delta_k W_k \) is one of the most surprising result of our approach, which appears almost counter-intuitive and has remain hitherto unrecognized in the field because of it. It is so because it is well known that it is impossible to have \( \Delta_k E \neq 0 \), where

\[
\Delta_k E = \int_i d_i E,
\]

in terms of \( d_i E \) is given in Eq. (55). However, we have shown, see Claim 12 that even if \( d_i E_k \neq 0 \), \( d_i E \) always vanishes.

As we see from Remarks 10 and 11, the determination of the SI-work \( \Delta W_k \) or \( \Delta W_k' \) over the entire process \( P_0 \) is extremely easy as it is independent of the nature of the actual process \( P_0 \); it is the same for all processes between the same two states since \( \Delta E_k' \) or \( \Delta E_k \) is an SI-quantity and is determined by the initial and the final states but
not on the nature of the process. Because of this, Eqs. \[87\] and \[88\] hold for all processes between the same two states. This is very different from \(\Delta_w k = -\Delta q W\)
or \(\Delta w W' = -\Delta k W'\), which depends strongly on \(\mathcal{P}\) during which it is nonzero and vanishes during \(\overline{\mathcal{P}}\). The difference is \(\Delta_k W_k = \Delta_k W_k'\).

The correct identification \(\Delta W_k = -\Delta E_k\) or \(\Delta W_k' = -\Delta E_k'\) ensures that

\[\Delta_k W_k = \Delta_k W_k' \geq 0\]

in conformity with its ubiquitous nature as is evident from the existence of pressure fluctuations in Eq. \[66\]; see Conclusion \[14\]. With this identification, Eqs. \[87\] and \[88\] always hold in the exclusive and inclusive approaches, respectively. They hold not only for free expansion, but also for any arbitrary process \(\mathcal{P}_0\) as we show in Sec. \[XI\] Thus, our theorem differs from the JE, which fails for free expansion.

With the ubiquitous nature of \(d_i W_k = -d_i E_k\) and the SI-equivalence of \(dW_k = -dE_k\) as opposed to the mistaken identity \(d\tilde{W}_k = dE_k\), we believe that the correction requires complete reassessment of current applications; see Sec. \[13\]. In particular, we need to recognize the importance of \(d_i W_k = -d_i E_k\), which has not been hitherto recognized. Without acknowledging this fact in any theory results in a total absence of dissipation regardless of the time dependence the work protocol such as in the Jarzynski equality.