Nonequilibrium Work and its Hamiltonian Connection for a Microstate in Nonequilibrium Statistical Thermodynamics: A Case of Mistaken Identity

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Abstract

Nonequilibrium work-Hamiltonian connection for a microstate plays a central role in diverse branches of statistical thermodynamics (fluctuation theorems, quantum thermodynamics, stochastic thermodynamics, etc.). We show that the change in the Hamiltonian for a microstate should be identified with the work done by it, and not the work done on it. This contradicts the current practice in the field. The difference represents a contribution whose average gives the work that is dissipated due to irreversibility. As the latter has been overlooked, the current identification does not properly account for irreversibility. As an example, we show that the corrected version of Jarzynski’s relation can be applied to free expansion, where the original relation fails. Thus, the correction has far-reaching consequences and requires reassessment of current applications.

The work-Hamiltonian relations at the level of microstates play a central role in the application of the first law to a system $\Sigma$ under nonequilibrium conditions in a medium $\bar{\Sigma}$ in diverse branches of nonequilibrium (NEQ) statistical thermodynamics including but not limited to nonequilibrium work theorems [1–4], stochastic thermodynamics [5, 6] and quantum thermodynamics [7, 8]. Once work is identified, heat is identified by invoking the first law. Unfortunately, this endeavor has given rise to a controversy about the actual meaning of work, which apparently is far from settled [1, 4, 9–19]. The controversy is distinct from the confusion about the meaning of work and heat in classical nonequilibrium thermodynamics [20–22, for example, and references therein] involving a system-intrinsic (SI) or medium-intrinsic (MI) description, the latter only recently been clarified [23, 24]. For example, the classical thermodynamic formulations of work in the two descriptions take the form $dW$ or $P_0 dV$, respectively, in terms of the instantaneous pressure $P$ of $\Sigma$ or $P_0$ of $\bar{\Sigma}$ and their volume change $dV$ or $-dV$, respectively. As usual, $\Sigma$ and $\bar{\Sigma}$ form an isolated system $\Sigma_0$. Throughout this work, we will assume that $\Sigma$ and $\Sigma_0$ are statistically quasi-independent [25, 26] so that their entropies are additive.

In equilibrium (EQ), the state of $\Sigma$ is described by its set of extensive observables, or state variables, such as its energy $E$, volume $V$, the number of particles $N$, etc. We collectively denote them by $X$. They are controllable from outside by an observer and appear as parameters in the Hamiltonian $H$ of $\Sigma$. The equilibrium entropy is a state function $S(X)$ of $X$. Away from equilibrium, we also need an additional set of extensive internal variables $\xi$ [23, 24, 26, 32] to specify the state of a NEQ system so that $Z = (X, \xi)$ denotes the set of state variables. The internal variables are not controllable from outside by an observer. A NEQ state for which its entropy is a state function $S(Z)$ of $Z$ is said to be an internal equilibrium (IEQ) state [23, 26]; if not, the entropy $S(Z, t)$ is an explicit function of time $t$. If we do not use $\xi$ to specify a NEQ state, then the entropy $S(X, t)$ again is not a state function even if we have an IEQ state. In any NEQ state, there are going to be internal processes that are beyond the control of an observer, but have to be accounted for a proper thermodynamic description.

The MI-description always refers to exchange quantities (work or heat, to be denoted here by their modern notation $dW$ or $dQ$ [30, 31, 32], respectively) between the medium and the system and involve quantities referring to the medium and are readily identifiable and measurable. No internal variables are required since their affinities vanish for the medium as it is always in equilibrium. The SI-description always refers to quantities (work or heat, to be denoted here by $dW$ or $dQ$, respectively) intrinsic to the system, i.e. they contain quantities pertaining to the system alone. These quantities represent SI quantities and may include internal variables as their affinities do not vanish for $\Sigma$; in many cases, they may not be readily measurable or even identifiable and require care in interpreting results. Therefore, the use of exchange quantities is quite widespread. Despite this, we have concluded [23, 24] that the SI-description is more appropriate to study nonequilibrium processes, even if we do not use $\xi$, since $H$ plays a central role for dynamics.

Traditional formulation of nonequilibrium statistical mechanics and thermodynamics [34, 35] starts with a mechanistic approach in which $\Sigma$, or more precisely its microstate $M$, follows its classical or quantum mechanical evolution in time, which will require focusing on the Hamiltonian $H$ of the system, a SI quantity; the interaction with $\Sigma$ is usually treated as a very weak stochastic perturbation on it. This immediately suggests adopting a SI-description. Unfortunately, this description has been overlooked by the current practitioners in the field who have consistently used a MI-description such as in Jarzynski’s nonequilibrium work relation

$$\langle e^{-\beta_0 \Delta W_i} \rangle_0 \equiv e^{-\beta_0 \Delta F} = \langle e^{\beta_0 \Delta W_i} \rangle_0 \quad (1)$$

to be explained below. In Eqs. (1), the question mark on the first (and currently widely accepted) equality implies that it may be questionable in all cases. We will establish that an appreciation of the SI-description will paved the way for a correct work-Hamiltonian relation for a microstate resulting in the last equality in Eqs. (1) in...
all cases. This is the main point of this paper. We then draw attention to some of its consequences. We have applied this approach to the set \( \{M_k\} \) of microstates to obtain a microscopic representation of work and heat in terms of the set of microstate probabilities \( \{p_k\} \), which will be exploited here. As we will be dealing with microstates, we will mostly use their energy set \( \{E_k\} \) instead of \( \mathcal{H} \) in the following.

In Eq. (1), \( \langle \rangle_0 \) refers to averaging with respect to the canonical probability distribution \( \{e^{-\beta_0 E_k} / Z_{\text{eq}}(\beta_0)\} \) of the initial equilibrium state \( \Lambda_{\text{eq}}, Z_{\text{eq}}(\beta_0) \) the initial equilibrium partition function for the system, \( \Delta W'_{\gamma} \) the work done on the \( k \)th microstate by the external working medium \( \Sigma \) during a process \( \gamma \) (not necessarily reversibly) connecting the terminal states, both at the same inverse temperature \( \beta_0 \), and \( \Delta F' \) is the change in the free energy between those states. (The mystery behind the prime will become clear later.) However, the average \( \langle \rangle_0 \) in Eq. (1) does not represent a thermodynamic average over \( \gamma \). The inverse temperature along \( \gamma \) may not always exist or may be different than \( \beta_0 \) due to irreversibility [2, 22].

The differential external work \( d\tilde{W}_k \) done on the \( k \)th microstate \( M_k \) during a segment of the path \( \gamma \) between \( t \) and \( t + dt \) is identified as the change \( dE_k = E_k(t + dt) - E_k(t) \) in its energy \( E_k(Z) \) as parameters in \( Z \) change:

\[
d\tilde{W}_k = \frac{\partial E_k}{\partial Z} dZ \equiv dE_k \quad (= -dW_k). \tag{2}
\]

Observe that the microstate \( M_k \) does not change during the performance of the above work, only its energy changes as \( Z \) changes. The relation is common to all of the three domains of activities [2, 3, 8] for example except that \( Z \) is replaced by \( X \). The net external work done on the system is the integral over the path \( \gamma \)

\[
\Delta \tilde{W}_k = \int_\gamma \frac{\partial E_k}{\partial Z} dZ = \int_\gamma dE_k \quad (= -\Delta W_k). \tag{3}
\]

The thermodynamic works \( d\tilde{W} \) and \( \Delta \tilde{W} \) are averages over \( \{p_k\} \) (not to be confused with \( \langle \rangle_0 \) in Eq. (1)):

\[
d\tilde{W} \equiv \sum_k p_k dE_k \quad (= -dW), \quad \Delta \tilde{W} \equiv \int_\gamma \sum_k p_k dE_k \quad (= -\Delta W). \tag{4}
\]

Before proceeding further, we introduce various notions of work that are relevant here by two simple examples.

1. Consider our system a general but purely a classical mechanical one-dimensional spring of arbitrary Hamiltonian \( \mathcal{H}(x, p) \) with one end fixed at an immobile wall and the other end of mass \( m \) free to move. The free end is pulled by an external force (not necessarily a constant) \( F_0 \) applied at time \( t = 0 \). A microstate \( M \) can be thought of as a small phase space area with its center at \( k \equiv (x, p) \). However, we will not show the index \( k \) below for simplicity. Initially the spring is undisturbed and has zero SI restoring spring force \( F = -\partial \mathcal{H} / \partial x \). The total force \( F = F_0 + F \) acts like the force imbalance \( F_i \leq 0 \). There is no mechanical equilibrium unless \( F_i = 0 \) and the spring continues to stretch or contract. The SI work done by \( F \) is identified as the work \( d\tilde{W} = Fdx \) performed by the spring, while the work performed by \( F_0 \) is identified as the work \( d\tilde{W} = F_0 dx \) transferred to the spring; its negative \( d_iW = -F_0 dx \) is identified as the work performed by the spring against the external force. As this is a purely mechanical example, there is no dissipation. Despite this, we can introduce using the modern notation [33]

\[
d_iW = dW - d_iW \equiv dW + d\tilde{W} \equiv F_i dx, \tag{5}
\]

which can be of either sign and represents the work done by the imbalance \( F_i \). Thus, \( dW, d_iW = -d\tilde{W} \) and \( d_iW \) represent different works, a result that has nothing to do with irreversibility but only with the imbalance; among these, only \( dW \) is a SI work. The change in the Hamiltonian \( \mathcal{H} = E \) of the spring due to a variation in the work variable \( x \) is \( d\mathcal{H}|_w = dE|_w = Fdx = -dW \neq d\tilde{W} \), where we have used a suffix \( w \) to refer to the change caused by the performance of work.

Above, we have considered the exclusive Hamiltonian \( \mathcal{H} \). Let us consider the inclusive Hamiltonian \( \mathcal{H}' = E' = E - F_0 x \) used in deriving Eq. (1); this explains the presence of a prime there. For the inclusive energy \( E' = E - dF_0 x = -F_0 dx + xdF_0 \), \( \partial E'/\partial x = -F_0 \) does not identically vanish, \( E'(x, F_0) \) is a function of two work parameters \( x \) and \( F_0 \). As \( \partial E'/\partial F_0 = -x, x \) is the generalized force conjugate to \( F_0 \). The corresponding SI work \( dW' \) consists of two contributions due to variations in \( x \) and \( F_0 \): \( dW' = dW'_x + dW'_{F_0} = F_t dx + xdF_0 \) and satisfies \( dW' = -dE'|_w \) just as above with the exclusive Hamiltonian \( \mathcal{H} \). Furthermore, the contribution \( dW'_x \equiv xdF_0 \) represents the exchange work \( d_iW' \) with the medium so that \( dW' = -xdF_0 \neq dE'|_w \) represents the exchange work that appears in the left side of Eq. (1). The following identities are always satisfied:

\[
dW'_x \equiv dE|_w \equiv dW' - d\tilde{W} \equiv -d(F_0 x),
\]

\[
dW' - d\tilde{W} \equiv d_iW' - d_iW \equiv -d(F_0 x). \tag{6}
\]

Let us investigate the case \( F_0 = 0 \). In this case, \( F_i = F \) and \( dW = dW' = F dx \neq 0 \) and \( dW = d\tilde{W} = 0 \) 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 \( F \).

2. To incorporate dissipation, we consider a thermodynamic analog of the above example: a gas in a cylinder, closed at one end and a movable piston at the other end. 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 \( x \to V, F \to P \) (or \( P_k \) when considering \( M_k \)) and \( F_0 \to -P_0 \). The gas expands (\( dV \geq 0 \)) and \( P \cap P_0 \). The SI work done by the gas is 
\[ dW = PdV, \]
while 
\[ d\tilde{W} = -P_0dV = -dW. \]
The difference 
\[ d_1W = dW - d_\tilde{W} = (P - P_0)dV \geq 0 \]
appears as the work that is dissipated in the form of heat (\( d_1Q \geq d_1W \) as will be shown below) either due to the friction between the piston and the cylinder or other dissipative forces like the viscosity of the gas.

Let us analyze this model more carefully at a microstate level but without using any \( \xi \) for the sake of simplicity. Let the Hamiltonian of the gas be denoted by \( \mathcal{H}(X) = E(X) \). In the following, we will only show \( V \) and keep all other parameters held fixed. Therefore, the only work we will consider is due to the generalized force conjugate to \( V \). Let \( E_k(V) \) denote the energy of some \( M_k \) and \( P_k \) due to work only must be identified with the SI-work and the second one to the internal work 
\[ W. \]
This proves the first part. As \( \{ E_k \} \) is unchanged in the second sum, it refers to an isometric process at fixed \( Z \) and represents generalized heat \( dQ = d_\tilde{Q} + dQ. \) Thus, 
\[ dE = d\tilde{Q} - dW. \]

As \( \{ p_k \} \) is not changed in the first sum, it is evaluated at fixed entropy of \( \Sigma \). This isentropic sum \( -dW \) is an average of \( -dW_k = dE_k \equiv (\partial E_k / \partial \tilde{Z}) \cdot \tilde{Z} = d_\tilde{Q} + dQ_k. \) This proves the first part. \( \Box \)

Let us rewrite the energy 
\[ dE = \sum_k p_k dE_k + \sum_k E_k dp_k. \]

**Proof.** Based on the two examples, the proof is almost trivial. For the average energy \( E \), we have 
\[ dE = \sum_k p_k dE_k + \sum_k E_k dp_k. \]

This proves the last part. 

It should be stressed that \(- (\partial E_k / \partial Z) \) or \(- (\partial E_k / \partial Z') \) represents the generalized force and the work has the conventional form: "force" \( \times \) "distance," contrary to what is commonly stated. According to the claim, we must use 
\[ -d\Delta W' - d\tilde{W}_k = -d\Delta W. \]
This proves the right sides, being independent of each other, must be non-negative separately to ensure the second law (\( dS \geq 0 \)). This proves the last part. 

The lesson from the two examples is that 
\[ \{ E_k \} \] and not with 
\[ \{ \tilde{E}_k \} \]
and not with 
\[ \{ \tilde{E}_k \} \]

**Theorem 1** 

**Thermodynamic Work-Energy Principle** The change \( d\mathcal{H} = dE_k \) 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 \( M_k \). It has two contributions as shown in Eq. (7). The first one corresponds to the external work 
\[ d_1W = d_1W \]
performed by \( M_k \) against the medium and the second one to the internal work 
\[ d_\tilde{W}_k \]
performed by the imbalance in the generalized forces. After a statistical averaging over all microstates for a system, 
\[ d_1E \equiv \langle d_1\mathcal{H} \rangle \equiv -d_1W \equiv -\sum_k p_k d_1W_k \leq 0 \]
results in dissipation in the system with the inequality referring to irreversibility.

\[ dE = \sum_k p_k dE_k + \sum_k E_k dp_k. \]

As \( \{ p_k \} \) is not changed in the first sum, it is evaluated at fixed entropy of \( \Sigma \). This isentropic sum \( -dW \) is an average of \( -dW_k = dE_k \equiv (\partial E_k / \partial \tilde{Z}) \cdot \tilde{Z} = d_\tilde{Q} + dQ_k. \) This proves the first part. As \( \{ E_k \} \) is unchanged in the second sum, it refers to an isometric process at fixed \( Z \) and represents generalized heat \( dQ = d_\tilde{Q} + dQ_k. \) Thus, 
\[ dE = d_\tilde{Q} - dW. \]

Since \( dE = d_\tilde{Q} - dW \) also, we \( dW \equiv d_1Q. \) To prove the last part, we turn to thermodynamics. It can be shown that the temperature of any thermodynamic state can be defined by 
\[ dQ = T dS \]
so we can write 
\[ dE = -T dS - dW. \]

We rewrite this as 
\[ dE = T d_\tilde{Q} - dW_k - \Delta W_k \]
and \( -d\Delta W \) on the left sides in Eqs. (11), respectively, as shown by the enclosed parentheses.

Let us rewrite \( dE \) as follows: 
\[ dW = T d_\tilde{Q} - dF = -T d_\tilde{Q} - (T - T_0)dS, \]
where \( F = E - T_0 S \). As shown in the proof above, \( (T - T_0)dS \leq 0 \). Thus, we conclude that 
\[ dW \leq -dF. \]

It is also easy to see that \( d\tilde{W} = dF + T_0 d_\tilde{Q} \). To obtain the partition of \( dE \) in \( dW \), we have 
\[ dW_k = \sum_k p_k dE_k, \]
\[ dW = \sum_k p_k dE_k. \]

Similarly, using the partition 
\[ d_\tilde{W}_k = dE_k + d_\tilde{Q} \]
and 
\[ d_\tilde{W}_k = dE_k + d_\tilde{Q} \]

we have 
\[ d\mathcal{H} = dE_k + d_\tilde{Q} \]
for \( M_k \) into two parts 
\[ d\mathcal{H} = dE_k \]
and 
\[ d\mathcal{H} = d_\tilde{Q} \]
for \( M_k \) into two parts.

where 
\[ d_\mathcal{H} = dE_k \equiv dW_k \]
and 
\[ d\mathcal{H} = dE_k \equiv dW_k \]
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\[ d\mathcal{H} = dE_k \equiv dW_k \]
Even if $d_{i}E_{k} \neq 0$, $d_{i}E = 0$; thus, $E$ cannot change by internal processes as is well known. The second equation gives the conventional form of the second law in terms of the exchange quantities: $dE = d_{i}E \equiv d_{i}Q - d_{i}W$.

Let us evaluate the particular average considered in Eq. (1) but of $e^{\beta_{0}\Delta W}$

$$
\langle e^{\beta_{0}\Delta W} \rangle_{0} \equiv \sum_{k} \frac{e^{-\beta_{0}E_{k,in}}}{Z_{in}(\beta_{0})} e^{\beta_{0}W_{k}} = \sum_{k} \frac{e^{-\beta_{0}E_{k,in}}}{Z_{in}(\beta_{0})} e^{-\beta_{0}\Delta E_{k}|w}.
$$

As the terminal states are equilibrium states, we have $\Delta E_{k}|_{w} = E_{k,fn} - E_{k,in}$. Therefore,

$$
\langle e^{\beta_{0}\Delta W} \rangle_{0} = \sum_{k} \frac{e^{-\beta_{0}E_{k,in}}}{Z_{in}(\beta_{0})} = Z_{in}(\beta_{0})^{-1} e^{-\beta_{0}\Delta F}; \quad (11)
$$

here $F = E - T_{0}s$ for the exclusive Hamiltonian. 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. This fixes the first equation, the original Jarzynski relation, in Eq. (1) by the second equation in enclosed parentheses.

Let us apply Eq. (11) to the example of a free expansion of a one-dimensional ideal gas of classical particles, but treated quantum mechanically as a particle in a box with rigid walls. We assume that the gas is thermalized initially at some temperature $T_{0}$. It is isolated from the medium so that the free expansion occurs in an isolated system. After the expansion from the box size $L_{i} \rightarrow L_{f}$, $L_{f} > L_{i}$, the box is again thermalized at the same temperature $T_{0}$. As discussed at the end of the first example for $F_{0} = 0$, we note that $dW_{k} \neq 0$ even though $dW_{k} = 0$. Since we are dealing with an ideal gas, we can focus on a single particle whose energy levels are in appropriate units $E_{k} = k^{2}/L^{2}$, where $L$ is the length of the box. The change is due only to the work as no heat is allowed. Therefore, $\Delta E_{k}|_{w} = \Delta E_{k} = k^{2}(1/L_{i}^{2} - 1/L_{f}^{2})$. The partition function is given by $Z_{i}(\beta_{0}) = \sum_{k} e^{\beta_{0}E_{k,i}}$. It is trivially seen that Eq. (11) is satisfied, whereas the first equation in Eq. (1) due to Jarzynski fails in this case.

To conclude, we find that the change $\Delta H|_{w}$ in the Hamiltonian due to changes in its parameter is negative of the work $\Delta W$ done by the system, which contradicts the current practice in diverse applications in nonequilibrium statistical thermodynamics such as fluctuation theorems, quantum thermodynamics, stochastic thermodynamics, etc. where $\Delta H|_{w}$ is related to the work $\Delta W$ done on the system; see the left hand and right hand sides in Eqs. (11). The correction ensures that Eq. (11) holds even for free expansion. We believe that the correction requires complete reassessment of current applications.

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