The non-equilibrium work relation. Thermodynamic analysis and microscopic foundations

I. Santamaría-Holek †, A. Pérez-Madrid*

†Facultad de Ciencias, Universidad Nacional Autónoma de México. Circuito exterior de Ciudad Universitaria. 04510, D. F., México

*Facultat de Física, Universitat de Barcelona. Av. Diagonal 647, 08028, Barcelona, Spain

Abstract

We discuss the conditions for which the non-equilibrium work relation is valid by means of thermodynamic and microscopic arguments.

Key words: Nonequilibrium work relation, Dissipated work, Entropy production

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1 Introduction

The question of dissipation and the approach to equilibrium in mesoscopic and macroscopic systems has been a long standing problem since the early years of statistical mechanics as a science. Already at the beginning of the XX century Einstein and Ehrenfest were unsatisfied with the fundamental principles of statistical mechanics postulated by Boltzmann and Gibbs, since in their opinion those principles lack of a sound microdynamical basis. Their main idea was that the real problem concerns the approach towards the equilibrium state, and not equilibrium in itself. So, the knowledge of the dynamics of the irreversibility and the approach to equilibrium that follows enables one to draw the framework embodying equilibrium as a limiting behavior.

Email address: isholek.fc@gmail.com, agustiperezmadrid@ub.edu (I. Santamaría-Holek †, A. Pérez-Madrid* ).

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This subject has acquired a renewed interest, mainly due to the technological advances in biophysics and microrheology that make a more detailed analysis of the question possible. (4; 5)

Related to this problem, attempts have been made to go beyond equilibrium in order to establish some rules for extracting information from irreversible processes. (6; 7; 8; 9; 10; 11) Recently it has been claimed that there are only a few known relations in statistical mechanics that are valid for systems arbitrarily driven far from equilibrium. One of these relations is the one proposed by Jarzynski (12; 11) for which equilibrium properties can be obtained from non-equilibrium work measurements. For Hamiltonian isolated systems and systems in contact with a heat bath through weak interactions, theoretical justification for this assertion has been given in terms of ensembles of trajectories represented by means of a phase space density. (11) However, from the thermodynamic point of view this assertion seems to be true only for very specific situations. (13) As a consequence, it is important to stipulate the conditions in which one can make use of this relation. On the other hand, the knowledge of the range of applicability of this and other non-equilibrium relations is deeply rooted in the understanding of the microscopic bases of irreversibility. (6; 7; 8; 9; 10)

In this article, we will use thermodynamic and statistical arguments to show that the non-equilibrium work relation is valid only in isothermal and near-equilibrium conditions. Moreover, we will revise the validity of the original derivation of this non-equilibrium work relation (11) and then establish a quantitative criterion for determining these conditions by making use of a microscopic theory involving the BBGKY (Bogoliubov-Born-Green-Kirkwood-Yvon) hierarchy of equations (14).

The paper is organized as follows. In Section 2, we analyze the non-equilibrium work relation by considering the thermodynamic definition of the minimum work done on a system to change its state. After this, in Sec. 3 we analyze the problem of irreversibility in the context of a microscopic theory and propose the entropic time as a quantitative criterion to distinguish quasistatic and nonquasistatic processes. Finally, the last section is devoted to summarize and discuss our main results.

2 Thermodynamics and cumulants

In the very general case, a system driven out of equilibrium does not satisfy the condition of thermal equilibrium with the bath, since the temperature $T$ of the system differs from that of the bath $T_0$ (15). Among others, typical systems illustrating this situation are glasses and supercooled colloidal fluids. (16; 17)
Since irreversible processes are present in this general case, the total work $R$ performed on the system in order to change its state satisfies the relation (18)

$$R \geq \Delta E - T_0 \Delta S,$$

(1)

where $\Delta E$ and $\Delta S$ are the energy and the entropy variation of the system in the process. Hence, in the case of a reversible process, from Eq. (1) one can infer that the minimum amount of work $R_{\text{min}}$ necessary to reverse the state of the system is given by

$$R_{\text{min}} = \Delta E - T_0 \Delta S.$$  

(2)

In the isothermal case, when the system is in contact with a heat bath, $T = T_0$, Eq. (2) can be used to define the variation of the Helmholtz free energy of the system $\Delta F$

$$R_{\text{min}} = \Delta (E - T_0 S) = \Delta F.$$  

(3)

Therefore, thermodynamics requires that the change of the free energy of the system be equal to the work performed on it only in a reversible process in which at least the initial and final states satisfy the thermal equilibrium condition $T = T_0$.

In Ref. (11), the following equation has been established

$$\Delta F = -k_B T_0 \ln \langle e^{-R/k_B T_0} \rangle,$$  

(4)

where $k_B$ is the Boltzmann constant and $\langle \rangle$ represents the average over an ensemble of measurements of the work $R$.

In view of the thermodynamic relations (1)-(3), one may legitimately ask about the conditions of validity of Eq. (4). To answer this question, it is very important to take into account that, in general, an arbitrary external perturbation will produce an internal irreversible process in which the system approaches equilibrium, in accordance with the Le Chatelier principle.(18)

For simplicity we will assume that work is done in isothermal conditions; therefore, we have

$$R = \Delta F + R_{\text{diss}},$$  

(5)

where $R_{\text{diss}}$ is the dissipated work.(18) Now, by taking the exponential of Eq.
one simply obtains
\[ e^{R/k_B T_0} = e^{\Delta F/k_B T_0} e^{R_{\text{diss}}/k_B T_0}. \] (6)

After averaging this expression over the ensemble of measurements of \( R \) one obtains
\[ \langle e^{-R/k_B T_0} \rangle = e^{-\Delta F/k_B T_0} \langle e^{-R_{\text{diss}}/k_B T_0} \rangle, \] (7)

where we have taken into account that \( \Delta F \) is a constant quantity between two equilibrium states. Therefore, from Eq. (7) it follows that the relation \( \langle e^{-R/k_B T_0} \rangle \simeq e^{-\Delta F/k_B T_0} \) is valid only if the time scales characterizing the variation of the external parameters are larger than the time scales characterizing the decay of the irreversible processes taking place within the system, since then \( R_{\text{diss}} \ll \Delta F \). A quantitative criterion for this time scale will be given in the following section, where these irreversible processes will be analyzed on microscopic basis.

For situations not far from equilibrium the implications of Eq. (6) can be viewed in the context of the linear response theory. Thus, by expanding the exponential containing \( R_{\text{diss}} \) and averaging over the ensemble of measurements of \( R \). Up to first order, the result is
\[ \langle e^{R/k_B T_0} \rangle \simeq e^{\Delta F/k_B T_0} \left[ 1 + \langle R_{\text{diss}} \rangle / k_B T_0 + O(2) \right], \] (8)

which seems to imply that Eq. (4) does not contain the first-order correction related to the response function of the system, included here in \( R_{\text{diss}} \).

This conclusion is in accordance with the requirement that Eq. (4) be valid for fluctuations of the work smaller than \( k_B T \) as assumed in Ref. (11): ”the fluctuations in the work \( R \) must not be much greater than \( k_B T \), if we are to have any hope of verifying Eq. (4) experimentally...” . A similar result can be obtained, for example, by expanding the average \( \langle e^{R/k_B T_0} \rangle \) around the mean value \( \langle R \rangle \) assuming that the distribution of work is a Gaussian. Due to the symmetry of this distribution one obtains
\[ \langle e^{R/k_B T_0} \rangle \simeq e^{\langle R \rangle / k_B T_0} \left[ 1 + \frac{\langle R^2 \rangle - \langle R \rangle^2}{2(k_B T_0)^2} + \ldots \right], \] (9)

which as compared with Eq. (8), leads to the estimate
\[ \frac{\langle R_{\text{diss}} \rangle}{k_B T_0 \sim} \frac{\langle R^2 \rangle - \langle R \rangle^2}{2(k_B T_0)^2}. \] (10)
This is precisely the result obtained in Ref. (11) in the paragraph that follows Eq. (12) in this reference. In addition, given that \( \langle R \rangle = \Delta F + \langle R_{\text{diss}} \rangle \), by subtracting (8) from (9) and taking into account (10), one obtains \( e^{(R_{\text{diss}})/k_B T_0} = 1 \), which means that \( \langle R_{\text{diss}} \rangle / k_B T_0 \simeq 0 \). Our linear response analysis, although it may seem naive, runs parallel to the one underlying in the assumptions concerning the work fluctuations in Ref. (11). A more elaborated linear response analysis has been done in Ref. (19), in which the authors conclude that what the non-equilibrium work relation really offers is not the thermodynamic free energy difference but merely an upper bound: ”most significantly, \( \Delta A_j \) is not the free energy change predicted by thermodynamics.....”. This assertion is relevant since it also indicates that Eq. (4) gives only an approximate value of \( \Delta F \), thus implying that this is not valid in general, contrary to what is commonly claimed. This is a widely extended misinterpretation which we attempt to clarify here.

The previous results highlight the thermodynamic implications of the two assumptions underlying Eq. (4). However, a deeper analysis can be performed by noticing that \( \langle e^{R/k_B T_0} \rangle \) is the moment-generating function of the probability distribution of \( R \). Hence, in a general case we get more clarity if we perform a series expansion of the quantity \( -k_B T_0 \ln(e^{-R/k_B T_0}) \),

\[
-k_B T_0 \ln(e^{-R/k_B T_0}) = -k_B T_0 \sum_{n=1}^{\infty} \frac{1}{n!} \kappa_n (-k_B T_0)^n. \tag{11}
\]

where \( \kappa_n \) is the n-th order cumulant.

Using now the theory of Thiele semi-invariants, (20; 22) we can define the n-th order cumulant in terms of the moments of \( \langle R^k \rangle \). For the first few values of \( n \), we have

\[
\kappa_1 = \langle R \rangle \tag{12}
\]
\[
\kappa_2 = \langle R^2 \rangle - \langle R \rangle^2 \tag{13}
\]
\[
\kappa_3 = \langle R^3 \rangle - 3\langle R \rangle^2 \langle R \rangle + 2 \langle R \rangle \tag{14}
\]
\[
\kappa_4 = \langle R^4 \rangle - 4 \langle R^3 \rangle \langle R \rangle - 3 \langle R^2 \rangle^2 + 12 \langle R \rangle^2 \langle R \rangle - 6 \langle R \rangle \tag{15}
\]

It can be shown(21) that for a Gaussian distribution, \( \kappa_n = 0 \) for \( n > 2 \). So, the value of the quantity \( -k_B T_0 \ln(e^{-R/k_B T_0}) \) depends on the probability distribution, and therefore cannot coincide with the thermodynamic free energy since the thermodynamic free energy must be independent from the statistics. As we have shown above, this coincidence occurs only in the Gaussian case when the system is not arbitrarily far away from equilibrium (i.e., in the fluctuation-dissipation regime). A cumulant analysis has been also performed...
in several papers, in Ref. (11) itself or in Refs. (19; 23) just to cite a few examples. Nonetheless, the approach in these works differs from ours since in these the non-equilibrium work relation is taken for granted and the cumulant expansion serves to test how great the statistic must be to compute the free energy. For us however, the cumulant expansion is less restrictive since the only thing that this gives us for sure is information about the probability distribution of work fluctuations and very little else.

Let us illustrate our point with a simple example which shows that Eq. (4) is not general. A typical distribution in non-equilibrium situations is the chi-squared or gamma distribution, (24) for which

\[- k_B T_0 \ln \langle e^{-R/k_B T_0} \rangle = -k_B T_0 \ln \langle e^{-\langle R/\Delta F \rangle (\Delta F/k_B T_0)} \rangle = \]

\[\frac{k_B T_0 \langle R \rangle}{2} \sum_{n=1}^{\infty} \frac{1}{n} \left( \frac{2 \Delta F}{k_B T_0} \right)^n,\]  

(16)

(17)

where work has been measured in units of $\Delta F$. The sum in Eq. (17) is a Mercator series which is convergent when $2\Delta F/k_B T_0 < 1$. Hence in this case, we obtain

\[- k_B T_0 \ln \langle e^{-R/k_B T_0} \rangle = -\frac{k_B T_0 \langle R \rangle}{2} \Delta F \ln \left( 1 - 2 \frac{\Delta F}{k_B T_0} \right) \approx \]

\[\langle R \rangle = \langle R_{\text{diss}} \rangle + \Delta F = \Delta F \left( 1 + \frac{\langle R_{\text{diss}} \rangle}{\Delta F} \right) \neq \Delta F.\]  

(18)

(19)

Therefore, clearly the non-equilibrium work relation is not satisfied in this case. Thus, by considering nonequilibrium situations where the distribution of $R_{\text{diss}}$ can be fitted to a chi-square distribution

\[F(x)dx = 1/[2\Gamma(f/2)] (x/2)^{f/2-1} e^{-x/2}dx,\]  

(20)

with variance $\sigma_x^2 = 2f$ and mean $m_x = f$, with $x \equiv R_{\text{diss}}/k_B T_0$ and $f \sim \langle x \rangle$, we can compute

\[\langle e^{-x} \rangle = \int_0^\infty e^{-x} F(x)dx = (1/3)^{f/2} \neq 1\]  

(21)

Hence, since according to Eq. (21) $\langle e^{-x} \rangle \neq 1$ one concludes that $\langle e^{-R/k_B T_0} \rangle \neq e^{-\Delta F/k_B T_0}$ which violates the conditions we have found through Eqs. (8)-(10). These results clearly show that unlike what is claimed in the current literature (12), for arbitrary large fluctuations the non-equilibrium work relation is not applicable and thus is only valid for equilibrium fluctuations.
Experimentally, the mean value $\langle R \rangle$ is obtained through an arithmetic mean. A Gaussian distribution centered in $\langle R \rangle$ is used to account for data dispersion. Since the number of experiments performed is finite, this distribution corresponds to the statistical distribution of frequencies of the measured values of $R$. However, as is emphasized in Fig. 1, this statistical distribution does not necessarily coincide with the limiting distribution whose maximum value corresponds to the free energy difference $\Delta F$. As a consequence, it is quite possible that the measurements will have values near those of the limiting distribution, and any difference will be interpreted as a statistical error and not due to other kind of bias.

To conclude our analysis of Eq. (4), we will consider a system far from equilibrium which is in contact with a heat bath, whose entirety constitutes an isolated system(11). Under these conditions, it is very important to note that the temperature $T \propto \beta^{-1}$ is a function of the energy, (25; 26) regardless of the size of the system (27). There is also more recent literature emphasizing this fact, (28; 29; 30). Therefore, for a time-dependent Hamiltonian system, $T$ is not a thermodynamic variable in itself but rather a time-dependent parameter. Hence, the use of a constant equilibrium temperature $T_0 \propto \beta_0^{-1}$ as a prefactor in the exponentials of Eqs. (7) and (8) of Ref. (11) is not appropriate, since its time dependence must be taken into account. In our opinion this non-adequate treatment of the temperature is also present in Ref. (31). It should be noted that our perception about the temperature is coincident with the same objection raised in Refs. (13; 32). In view of this, we may follow Ref. (11) in order to write

$$f(z; t)e^{-\beta_0 w(z; t)} = Z_0^{-1}e^{-\beta_0 H_0(z_0)}e^{-\beta_0 w(z; t)} = Z_0^{-1}e^{-\beta_0 H(z; t)},$$

(22)

where $w(z; t) = H_A(z; t) - H_0(z_0)$ is the work done along a trajectory $z(z_0, t)$ with initial condition $z_0$. However, since for a finite switching time $t_s \beta(t_s) = \beta_1 \neq \beta_0$, one obtains

$$\int dz \exp[-\beta_0 H_1] \neq Z_1 \equiv \int dz \exp[-\beta_1 H_1],$$

(24)

in contradiction with the result given in Ref. (11). Additionally, it must be emphasized that the definition of work $w$ in Eq. (23) is not consistent with the one corresponding to thermodynamic processes. The consistency between these two definitions arises only when the processes considered are slow enough, i.e., for adiabatic processes for which the entropy is a constant and therefore constitute reversible processes.(18)

As a consequence of the previous analysis, it follows that it is not correct to identify the quantity $w(11)$ with the thermodynamic work $R$ which, through
Eqs. (3) and (5), constitutes the definition of the free energy difference $\Delta F$. Thus, after using Eq. (7), one can write

$$\Delta F = -k_B T_0 \ln \frac{\langle e^{-R/k_B T_0} \rangle}{\langle e^{-R_{\text{diss}}/k_B T_0} \rangle},$$

(25)

which is the general relation arising from thermodynamic arguments.

3 Microscopic analysis: The entropic time

The discussion in the previous section allows us to conclude that, far away from equilibrium, the approximations made in order to derive non-equilibrium work relation’s (4) are no longer valid. Hence, the evaluation of the dissipate d work becomes necessary.

In order to achieve this objective and to obtain a quantitative criterion establishing when Eq. (4) can be applied, we will write the work dissipated by a system in contact with a heat bath and due to the action of an external force $X_j$ in the form

$$R_{\text{diss}} = X_j \Delta \xi_j,$$

(26)

where $\xi_j$ is an internal parameter characterizing the state of the system. Since in view of Eq. (26) $R_{\text{diss}}$ is related to the entropy production of the system $\dot{\sigma}$, we may write Eq. (7)

$$\langle e^{-R/k_B T_0} \rangle \simeq e^{-\Delta F/k_B T_0} \left[ 1 - \frac{\dot{\sigma} \tau_s}{k_B} + O(2) \right],$$

(27)

where $\tau_s$ is an elapsed time. From this equation it follows that it is necessary to estimate the characteristic relaxation time of the entropy production in order to determine when Eq. (4) is valid.

This task can be accomplished by means of a microscopic theory that we will summarize here. For an isolated N-body system, in Ref. (34; 35; 36) it was postulated the non-equilibrium entropy $S$ in the BBGKY scenario as a functional of the set of $s$-particle reduced distribution functions ($s \leq N$), represented in the distribution vector $f$

$$S = -k_B tr \left\{ f \ln \left( f^{-1} f_{\text{eq}} \right) \right\} + S_{\text{eq}} =$$

(28)
\[-k_B \sum_{s=1}^{N} \frac{1}{s!} \int f_s \ln \frac{f_s}{f_{eq,s}} dx_1...dx_s + S_{eq}, \quad (29)\]

which generalizes the Gibbs entropy postulate (7; 8; 9). In this relation \(S_{eq}\) is the (thermodynamic) entropy at equilibrium and \(f_{eq}\) is the distribution vector that corresponds to the equilibrium state. Hence, \(f_{eq}\) is the equilibrium solution of the BBGKY hierarchy, in other words this is a solution of the YBG (Yvon-Born-Green) hierarchy (14; 37), and therefore is not a Boltzmann-like function. Additionally, the non-equilibrium entropy (28) reaches its maximum value at equilibrium, when \(f = f_{eq}\).

In the framework of the BBGKY description, the system is assumed to be a mixture of \(s\)-particle interacting fluids in the phase space and each fluid is made up of particle-clusters of equal size (34). As a consequence of the interaction among those fluids a compressible multiphase flow is established in the phase space, so it has been proved (34) that Eq. (28) is a monotonically increasing function in time that properly describes the regression to equilibrium of a system originally under non-equilibrium conditions.

In Ref. (34), it was also shown that the dynamics of the non-equilibrium entropy (28) follows from the dynamics of the distribution vector \(f\) given through

\[\frac{\partial f(t)}{\partial t} = \mathcal{L}f(t), \quad (30)\]

which is the generalized Liouville equation expressing the BBGKY hierarchy in a compact way, where \(\mathcal{L}\) is the generalized Liouvillian. As it is known, Eq. (30) is obtained by projecting adequately the Liouville equation onto each one of the \(s\)-particle phase space. Therefore, using Eqs. (28) and (30) one can compute the entropy production

\[\dot{\sigma} \equiv \frac{\partial S}{\partial t} = -\frac{1}{T} \sum_{s=1}^{N} \frac{1}{s!} \sum_{j=1}^{s} \int J_j \Delta F_j dx_1...dx_s, \quad (31)\]

where \(\Delta F_j\) is the averaged non-equilibrium force between the \(j\)-th particle and the particles of the remaining fluids. Moreover, \(J_j\) arises from deviations of the distribution function with respect to equilibrium.

From Eq. (31) we may estimate the relaxation time of the irreversible processes taking place in the system. To this end, note that the product \(J_j dx_1...dx_s\) has dimensions of velocity whereas \(\Delta F\) has dimensions of force. Introducing the characteristic velocity \(\overline{v}\) and taking into account that \(\Delta F\) contains the interaction forces among the components of the system, then \(\Delta F \sim \phi_0/r_0\) with \(\phi_0\) and \(r_0\) being the characteristic energy and the characteristic length.
of the interaction potential. Thus, the entropic time scale \( \tau_s = m v r_0 / \phi_0 \) (with \( m \) the mass of the system) related to the approach to equilibrium is the time associated to the relaxation of the non-equilibrium entropy to its equilibrium value. If we assume that \( \bar{v} \sim \sqrt{k_B T / m} \) with \( m \) the mass of the system, we finally obtain

\[
\tau_s \simeq \sqrt{mk_B T} (r_0 / \phi_0),
\]

which has the expected physical limits at low and high temperatures. Eq. (32) implies that experimental measurements can be interpreted in the context of Eq. (4) only if the time elapsed before taking a measurement in each point of the trajectory is larger than \( \tau_s \). It is important to note that the dependence on mass of Eq. (32) implies that the time of decay of irreversible processes in nanoscale systems could be very short, thus making them appropriate candidates to make the misleading interpretation that Eq. (4) is a far-from-equilibrium relation.

Here, it is convenient to consider that the thermodynamics of small systems,\(^{(27)}\) introduces corrections to the thermodynamic variables and state functions which make them different from their corresponding macroscopic counterparts. The magnitude of these corrections depend directly on the size of the ensemble of systems which is considered.\(^{(27)}\) From a dynamical point of view, for small systems these deviations from the macroscopic behavior are not small and may affect, in general, not only the extensive quantities but also the intensive ones (as, for example, the Massieu function). This fact is important, since these fluctuations modify the dynamics in such a way that may introduce multiplicative stochastic noises in the corresponding evolution equations for the variables determining the state of the system. Often, these multiplicative fluctuations lead to polynomial corrections to the local Gaussian distributions associated with the fluctuating quantities. As shown in the previous section, these corrections will affect the cumulant expansion of the corresponding distribution. The assumption that for arbitrary nonequilibrium processes the higher order terms of Eqs. (8)-(13) cancel between them in general, seems to be incorrect.

In the previous paragraph we analyzed the irreversible behavior of an isolated system. However, since most of the experiments are performed in the presence of a bath, we should generalize our analysis.

In the case when the system is in contact with a bath, it is necessary to extend the full phase-space in order to account for the presence of the bath. In this framework, the volume elements of the new phase space are conserved and therefore the Liouville theorem is satisfied. Thus, we will include a set of pairs of conjugated generalized coordinates \((\lambda, \dot{\lambda})\) so that the Hamiltonian is now a function of \( \lambda \) and \( \dot{\lambda} \), \( H(p, q, \lambda, \dot{\lambda}) \).\(^{(18)}\) Here, \( \lambda \) represents the set of
external parameters determining the state of the system and accounting for
the interaction with the bath and $\dot{\lambda}$ the set of conjugated generalized momenta
(which can be also understood as external currents).

Therefore, in this case equation (30) is rewritten in the form

$$\frac{d\lambda f(t)}{dt} \equiv \left( \frac{\partial}{\partial t} + \dot{\lambda} \frac{\partial}{\partial \lambda} \right) f(t) = \mathcal{L}f(t), \quad (33)$$

where $d\lambda/dt$ is the convective derivative associated with the external currents.
Following the procedure that bring us Eq. (31), equations (28) and (33) lead to

$$\frac{d\lambda S}{dt} = \dot{\sigma}_\lambda + \frac{\dot{Q}}{T_0}, \quad (34)$$

with $\dot{Q}$ being the rate of heat exchange between the system and the bath.
In addition, $\dot{\sigma}_\lambda$ stands for the entropy production of the system at a given
value of the external parameter $\lambda$ imposed by the bath. In this case Eq. (27)
is written as

$$\langle e^{-R/k_BT_0} \rangle \simeq e^{-\Delta F/k_BT_0} \left[ 1 - \frac{\dot{\sigma}_\lambda \tau_s}{k_B} + O(2) \right]. \quad (35)$$

In addition, when the internal irreversible processes in the system have decayed
($t \geq \tau_s$), Eq. (34) reduces to the well known Clausius relation $\delta S = \delta Q/T_0$,
valid for quasistatic processes.

4 Conclusions

In this article, we have analyzed the non-equilibrium work relation on the
grounds of equilibrium thermodynamics and in terms of the underlying micro-
scopic dynamics based on the BBGKY description. Our analysis is applicable
no matter how distant from equilibrium the system is.

We have shown that, in general, in order to be valid non-equilibrium work
relation’s (4) should include a correction taking into account the internal dissipa-
tion in the system. Additionally, we have shown that Eq. (4) corresponds
to the zero order term in a linear response analysis and thus is merely a near
equilibrium result (i.e., it applies when the fluctuations are gaussian, in the
fluctuation-dissipation regime).
From the microscopic dynamics of the system, given through the generalized Liouville equation and from the entropy postulate (28), we have computed the entropy production and provide an estimate of the characteristic time scale for the irreversible process taking place in the system, the entropic time \( \tau_s \). This quantity depends on the mass, the temperature, the characteristic length and the magnitude of the interaction potential and therefore establishes the criterion that must be satisfied by a process in order to be quasistatic. This phase-space analysis is the most appropriate for small systems characterized by smooth phase-space distribution functions.

Once again to avoid misunderstandings we emphasize that our microscopic analysis is based on a generalization of the Gibbs entropy postulate defined through Eq. (28) which is a functional of the distribution vector \( f(t) \). This distribution vector represents the whole set of \( s \)-particle reduced distribution functions with \( s = 0, \ldots, N \) whose dynamics is given by the generalized Liouville equation (30). Therefore, our entropy (28) is not a constant of motion under the generalized Liouville dynamics (30) as repeatedly has been shown in several applications (34; 35; 36; 38). Also incorporated in the theory is the presence of a bath which introduces a drive. This has been carried out by including the degrees of freedom of the bath into the full phase space through the external parameters used to characterize the state of the system. In this way, the volumes of the phase space are conserved and the generalized Liouville equation (33) remains valid. These external parameters originate currents entering the generalized Liouville equation and consequently also in the distribution function. In this scenario, the non-equilibrium entropy depends on the external currents through the distribution functions.

The present discussion establishes \( \tau_s \) as a useful quantitative criterion to implement experiments in good agreement with the theory.

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Fig. 1. Limiting (solid line) and frequency (dashed line) distributions as a functions of the reduced work $R^* = R/k_BT$. The figure shows that $\langle R \rangle \simeq \Delta F$ only when the number of experimental measurements $N \to \infty$ and the internal irreversible processes of the system have relaxed.
Fig. 1.