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Work, dissipation, and fluctuations in nonequilibrium physics

Comparison of far-from-equilibrium work relations

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Abstract

Recent theoretical predictions and experimental measurements have demonstrated that equilibrium free energy differences can be obtained from exponential averages of nonequilibrium work values. These results are similar in structure, but not equivalent, to predictions derived nearly three decades ago by Bochkov and Kuzovlev, which are also formulated in terms of exponential averages but do not involve free energy differences. In the present article the relationship between these two sets of results is elucidated, then illustrated with an undergraduate-level solvable model. The analysis also serves to clarify the physical interpretation of different definitions of work that have been used in the context of thermodynamic systems driven away from equilibrium. ***To cite this article: C. Jarzynski, C. R. Physique 8 (2007).***

Résumé

Comparaison des relations de travail loin de l'équilibre. De récentes prédictions théoriques et mesures expérimentales ont démontré que les différences d'énergie libre d'équilibre peuvent s'obtenir à partir de moyennes exponentielles des valeurs du travail de non-équilibre. Ces résultats sont semblables en structure mais non équivalents à des prédictions dérivées il y a près de trente ans par Bochkov et Kuzovlev, et qui sont aussi formulées en termes de moyennes exponentielles mais qui n'impliquent pas de différences d'énergie libre. Dans le présent article, la relation entre ces deux ensembles de résultats est élucidée et ensuite illustrée par un modèle soluble de niveau élémentaire. L'analyse sert aussi à clarifier les interprétations physiques des différentes définitions du travail qui ont été utilisées dans le contexte des systèmes thermodynamiques maintenus hors d'équilibre. ***Pour citer cet article : C. Jarzynski, C. R. Physique 8 (2007).***

Keywords: Nonequilibrium systems; Work relations

Mots-clés : Systèmes non-équilibres ; Relations de travail

1. Introduction

In recent years there has been considerable interest in the nonequilibrium statistical mechanics of small systems [1]. Among the results that have been derived and tested experimentally, the nonequilibrium work theorem [2,3],

$$\left\langle \mathrm{e}^{-\beta W} \right\rangle = \mathrm{e}^{-\beta \Delta F} \tag{1}$$

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relates fluctuations in the work W performed during a thermodynamic process in which a system is driven away from equilibrium, to a free energy difference ΔF between two equilibrium states of the system. Here, β specifies an inverse temperature, and the angular brackets denote an average over an ensemble of realizations (repetitions) of the process in question [4]. Eq. (1) and closely related results [5–7], along with experimental confirmations [8–12], have revealed that equilibrium free energy differences can be determined from distributions of nonequilibrium work values.

The recent progress in this area has drawn attention to a set of earlier papers by Bochkov and Kuzovlev [13–16], in which the authors had obtained—as one consequence of a more general analysis—the following result:

$$\left\langle \mathrm{e}^{-\beta W_0} \right\rangle = 1 \tag{2}$$

The angular brackets and inverse temperature β appearing here have the same meaning as in Eq. (1), and W_0 is identified as the work performed on the system.

Although Eqs. (1) and (2) are evidently similar in structure, they are not identical; most notably, ΔF does not appear, either explicitly or implicitly,[1] in Eq. (2). The precise relationship between these two results has not been clarified in the literature, nor is it immediately obvious from a quick comparison of the original derivations. The aim of the present paper is to fill this gap, first by deriving the two equalities within a single, Hamiltonian framework, and then by illustrating them both using the simple model of a perturbed harmonic oscillator. The conclusions that will emerge from this analysis are summarized by the following three points:

- Eqs. (1) and (2) apply to the same physical situation: a system, initially described by an unperturbed Hamiltonian H_0, is driven away from equilibrium by the application of a time-dependent perturbation. In principle, a single set of experiments could be used to test both predictions.
- While both W and W_0 are identified as *work* (in Refs. [2,3] and [13–16], respectively), the two quantities generally differ; see Eq. (15) below. The difference between them amounts to a matter of convention, related to whether we choose to view the perturbation as an external disturbance, or else as a time-dependent contribution to the internal energy of the system.
- For the special case of *cyclic* processes, in which the perturbation is turned on and then off, Eqs. (1) and (2) are equivalent.

This article is organized as follows. Section 2 establishes the Hamiltonian framework and the notation that will be used throughout the paper. In Section 3 we derive Eqs. (1) and (2) within this framework. Section 4 describes an exactly solvable model—a harmonic oscillator driven by a time-dependent external force—that illustrates the validity of these predictions and provides intuition regarding the two definitions of work, W and W_0. Finally, Section 5 presents an alternative derivation of Eqs. (1) and (2), by way of a stronger set of results (Eq. (57)). The paper concludes with a brief discussion.

2. Setup

To carry out a direct comparison between Eqs. (1) and (2), we will use the setup considered in Ref. [15]. Consider a classical mechanical system with D degrees of freedom, described by coordinates $\mathbf{q} = (q_1, \ldots, q_D)$ and momenta $\mathbf{p} = (p_1, \ldots, p_D)$, and let $z = (\mathbf{q}, \mathbf{p})$ denote a point in the phase space of this system. Consider also a number of external forces $X_1, X_2, \ldots$, which are under our direct control. We act on the system by manipulating these forces. The Hamiltonian that describes this system takes the form

$$H(z; X) = H_0(z) - \sum_k X_k \, Q_k(z) \tag{3}$$

(see Eq. 2.2 of Ref. [15]), where $Q_1(z), Q_2(z), \ldots$ denote the variables conjugate to the external forces:

$$Q_k = -\frac{\partial H}{\partial X_k} \tag{4}$$

[1] Rewriting Eq. (1) in terms of *dissipated* work [2], $W_d = W - \Delta F$, we obtain $\langle \exp(-\beta W_\mathrm{d}) \rangle = 1$, which bears an even stronger resemblance to Eq. (2). However, the quantity W_0 appearing in Eq. (2) is *not* equivalent to W_d, as apparent from the definitions provided in Section 2.

H is a function on phase space, parametrized by the forces $X = (X_1, X_2, \ldots)$. We will refer to H_0 as the *bare*, or unperturbed, Hamiltonian, and to H as the *full* Hamiltonian.

If this system is brought into weak contact with a thermal reservoir at temperature T, with the external forces held fixed, then it will relax to an equilibrium state described by the Boltzmann–Gibbs distribution

$$P^{\mathrm{eq}}(z; X) = \frac{1}{Z(X)} \exp\bigl[-\beta H(z; X)\bigr] \tag{5}$$

where $\beta = (k_B T)^{-1}$. The corresponding classical partition function and free energy are:

$$Z(X) = \int \mathrm{d}z \exp\bigl[-\beta H(z; X)\bigr], \qquad F(X) = -\beta^{-1} \ln Z(X) \tag{6}$$

Now imagine that we subject this system to a thermodynamic process, defined by the following sequence of steps. Prior to time $t = 0$, the system is prepared in equilibrium, in the absence of external forces, i.e. at

$$X_0 = (0, 0, \ldots) \tag{7}$$

The reservoir is then removed. Subsequently, from $t = 0$ to a later time $t = \tau$, the external forces are turned on according to some arbitrary but pre-determined schedule, or *protocol*, X_t. The microscopic evolution of the system during this interval of time is described by a trajectory z_t evolving under Hamilton's equations,

$$\frac{\mathrm{d}\mathbf{q}}{\mathrm{d}t} = \frac{\partial H}{\partial \mathbf{p}}, \qquad \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = -\frac{\partial H}{\partial \mathbf{q}} \tag{8}$$

where $H = H(z; X_t)$. The protocol X_t effectively traces out a curve in 'force space', from the origin (Eq. (7)) to some final point X_τ. Let ΔF denote the free energy difference between two equilibrium states—both at the same temperature T—associated with the initial and final forces:

$$\Delta F = F(X_\tau) - F(X_0) = -\beta^{-1} \ln \frac{Z(X_\tau)}{Z(X_0)} \tag{9}$$

By repeatedly subjecting the system to this process—always first preparing the system in equilibrium, and always using the same protocol X_t—we generate a number of statistically independent *realizations* of the process, each characterized by a Hamiltonian trajectory z_t describing the microscopic response of the system to the externally imposed perturbation. Angular brackets $\langle \cdots \rangle$ will specify an ensemble average over such realizations.

For a given realization, let us now define W and W_0 appearing in Eqs. (1) and (2):

$$W_0 = \int_0^\tau \mathrm{d}t \sum_k X_k(t) \dot{Q}_k(z_t) \tag{10a}$$

$$W = -\int_0^\tau \mathrm{d}t \sum_k \dot{X}_k(t) Q_k(z_t) \tag{10b}$$

where the dots denote time derivatives, e.g. $\dot{Q}_k = (\mathrm{d}/\mathrm{d}t) Q_k(z_t)$. These two definitions are not equivalent: in general, $W \neq W_0$.

To gain some physical insight into these quantities, we rewrite them as follows:

$$W_0 = \int \mathrm{d}t\, X \cdot \dot{Q} = \int X \cdot \mathrm{d}Q \tag{11a}$$

$$W = -\int \mathrm{d}t\, \dot{X} \cdot Q = \int \mathrm{d}X \cdot \frac{\partial H}{\partial X} \tag{11b}$$

where $Q = (Q_1, Q_2, \ldots)$ is the vector of variables conjugate to the forces $X = (X_1, X_2, \ldots)$ (see Eq. (4)). The expression for W_0 is the familiar integral of force versus displacement found in introductory textbooks on mechanics [17], and corresponds to the definition of work used by Bochkov and Kuzovlev (Eq. 2.9 of Ref. [15]). By contrast, expressions equivalent to Eq. (11b) are often used to define work in discussions of the microscopic foundations of

macroscopic thermodynamics [18–20]; this is the definition that is used in the context of nonequilibrium work theorems (e.g. Eq. 3 of Ref. [2]). While it might seem unusual that two different quantities, W_0 and W, can both be interpreted as the work performed on a system, this ambiguity simply reflects the freedom we have to define what we mean by the internal energy of the system of interest. We discuss this point in some detail in the following two paragraphs.

What is the internal energy of the system when its microstate is $z = (\mathbf{q}, \mathbf{p})$, and the external forces are set at values $X = (X_1, X_2, \ldots)$? Eq. (3) suggests two natural ways to answer this question. (i) We can take the internal energy to be given by the value of the bare Hamiltonian, $H_0(z)$. From this perspective the system is imagined as a particle in a fixed energy landscape, H_0; we affect the particle's energy by varying the forces so as to move it from one region of phase space to another, but the forces X do not themselves appear in the definition of its energy. (ii) Alternatively, we can define the internal energy to be given by the value of the full Hamiltonian, $H = H_0 - X \cdot Q$. This point of view is captured by imagining an energy landscape that is not fixed, but changes with time as we manipulate the forces X. Let us refer to these two alternatives as the (i) *exclusive* and the (ii) *inclusive* frameworks, according to whether the term $-X \cdot Q$ is treated as a component of the internal energy of the system.

Now we use the Hamiltonian identity

$$\frac{\partial H}{\partial z} \cdot \frac{\mathrm{d}z}{\mathrm{d}t} = \frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial H}{\partial \mathbf{p}} - \frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial H}{\partial \mathbf{q}} = 0 \tag{12}$$

(see Eq. (8)) to obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} H(z_t; X_t) = \frac{\partial H}{\partial z} \cdot \frac{\mathrm{d}z}{\mathrm{d}t} + \frac{\partial H}{\partial X} \cdot \frac{\mathrm{d}X}{\mathrm{d}t} = \dot{X} \cdot \frac{\partial H}{\partial X} = -\dot{X} \cdot Q \tag{13}$$

and therefore

$$\frac{\mathrm{d}}{\mathrm{d}t} H_0(z_t) = \frac{\mathrm{d}}{\mathrm{d}t}(H + X \cdot Q) = X \cdot \dot{Q} \tag{14}$$

Comparing with Eq. (11), we see that W_0 and W are equal to the net changes in the values of H_0 and H, respectively, during the interval of perturbation:

$$W_0 = \int_0^\tau \mathrm{d}t \, \frac{\mathrm{d}H_0}{\mathrm{d}t} = H_0(z_\tau) - H_0(z_0) \tag{15a}$$

$$W = \int_0^\tau \mathrm{d}t \, \frac{\mathrm{d}H}{\mathrm{d}t} = H(z_\tau; X_\tau) - H(z_0; X_0) \tag{15b}$$

Since the system is thermally isolated (i.e. not in contact with a heat reservoir) from $t = 0$ to $t = \tau$, it is natural to identify the work performed on it with the net change in its internal energy. With this in mind, Eq. (15) provides a simple interpretation of the difference between W and W_0. If we adopt the exclusive point of view and take the internal energy to be the value of the bare Hamiltonian H_0, then W_0 is the work performed on the system, by the application of external forces that affect its motion in a fixed energy landscape. If we instead choose the inclusive framework, using the full Hamiltonian $H = H_0 - X \cdot Q$ to define the internal energy of the system, then W is the appropriate definition of work. The distinction between these two frameworks is illustrated with a specific example in Section 4.

From Eq. (15) we obtain an explicit expression for the difference between W and W_0:

$$W_0 - W = X_\tau \cdot Q(z_\tau) = \sum_k X_k(\tau) Q_k(z_\tau) \tag{16}$$

since $X_0 = (0, 0, \ldots)$.

3. Derivations

Let us now compute the averages of $\mathrm{e}^{-\beta W_0}$ and $\mathrm{e}^{-\beta W}$, over an ensemble of realizations of the thermodynamic process described above. Since the system evolves under deterministic (Hamiltonian) equations of motion from $t = 0$

to $t = \tau$, a given realization is uniquely determined by the initial conditions z_0. We can therefore express $\langle e^{-\beta W_0} \rangle$ as an integral over an equilibrium distribution of initial conditions:

$$\left\langle e^{-\beta W_0} \right\rangle = \int dz_0 \, P^{\rm eq}(z_0; X_0) e^{-\beta W_0(z_0)} \tag{17}$$

where $W_0(z_0)$ denotes the value of W_0 for the trajectory launched from the microstate z_0. The first factor in the integrand is

$$P^{\rm eq}(z_0; X_0) = \frac{1}{Z(X_0)} e^{-\beta H_0(z_0)} \tag{18}$$

(note that $H(z_0; X_0) = H_0(z_0)$, by Eq. (7)). Using Eq. (15a), we have

$$W_0(z_0) = H_0\big(z_\tau(z_0)\big) - H_0(z_0) \tag{19}$$

where $z_\tau(z_0)$ indicates the final microstate of this trajectory, expressed as an explicit function of the initial microstate. Upon substituting these expressions into Eq. (17), a cancellation of terms occurs in the exponents, and we get

$$\left\langle e^{-\beta W_0} \right\rangle = \frac{1}{Z(X_0)} \int dz_0 \, e^{-\beta H_0(z_\tau(z_0))} \tag{20}$$

Since there is a one-to-one correspondence between the initial and final conditions of a given trajectory, we can change the variables of integration from z_0 to z_τ:

$$\left\langle e^{-\beta W_0} \right\rangle = \frac{1}{Z(X_0)} \int dz_\tau \left| \frac{\partial z_\tau}{\partial z_0} \right|^{-1} e^{-\beta H_0(z_\tau)} \tag{21}$$

We have inserted the determinant of the Jacobian matrix associated with this change of variables. By Liouville's theorem, this factor is identically unity, $|\partial z_\tau / \partial z_0| = 1$, which finally gives us

$$\left\langle e^{-\beta W_0} \right\rangle = \frac{1}{Z(X_0)} \int dz_\tau \, e^{-\beta H_0(z_\tau)} = 1 \tag{22}$$

by Eq. (6).

The exponential average of W (rather than W_0) follows from similar manipulations:

$$\begin{aligned} \left\langle e^{-\beta W} \right\rangle &= \int dz_0 \, P^{\rm eq}(z_0; X_0) e^{-\beta W(z_0)} \\ &= \frac{1}{Z(X_0)} \int dz_0 \, e^{-\beta H(z_\tau(z_0); X_\tau)} \\ &= \frac{1}{Z(X_0)} \int dz_\tau \, e^{-\beta H(z_\tau; X_\tau)} = \frac{Z(X_\tau)}{Z(X_0)} = e^{-\beta \Delta F} \end{aligned} \tag{23}$$

We have used $W(z_0) = H(z_\tau(z_0); X_\tau) - H(z_0; X_0)$ (Eq. (15b)) to get from the first line to the second, and a change of variables, $z_0 \to z_\tau$, to get to the third.

Eq. (22) was originally obtained by Bochkov and Kuzovlev [13–16], whereas Eq. (23) is the nonequilibrium work theorem of Refs. [2,3]. These results apply to two physically distinct quantities, W_0 and W, corresponding to different conventions for defining the internal energy of the system. In each case the exponential average of work reduces to a ratio of partition functions. In Eq. (22) the ratio is $Z(X_0)/Z(X_0)$, i.e. unity; while in Eq. (23) it is $Z(X_\tau)/Z(X_0)$, which yields the free energy difference ΔF.

Let us now consider the special case in which the external forces vanish both at $t = 0$ and at $t = \tau$:

$$X_0 = X_\tau = (0, 0, \ldots) \tag{24}$$

This corresponds to a *cyclic* process, for which the Hamiltonian begins and ends at H_0. In this case we have, identically, $W = W_0$ (Eq. (16)) and $\Delta F = 0$ (Eq. (6)). Thus, Eqs. (22) and (23) are equivalent when the Hamiltonian is varied cyclically.

Finally, it is instructive to consider a process during which the external forces are switched on *suddenly* at $t = 0$, from $X_0 = (0, 0, \ldots)$ to $X_\tau = (X_1, X_2, \ldots)$. Since the process occurs instantaneously ($\tau \to 0$), the system has no opportunity to evolve, hence $z_\tau = z_0$. Thus, Eq. (15) gives us

$$W_0 = 0, \qquad W = \Delta H(z_0) \tag{25}$$

where $\Delta H(z) \equiv H(z; X_\tau) - H(z; X_0)$. Eq. (22) is immediately satisfied, and Eq. (23) reduces to Zwanzig's perturbation formula [21],

$$\left\langle \mathrm{e}^{-\beta \Delta H} \right\rangle_0 = \mathrm{e}^{-\beta \Delta F} \tag{26}$$

where $\langle \cdots \rangle_0$ denotes an average over microstates sampled from the $X = (0, 0, \ldots)$ canonical distribution.

4. An example

Let us now illustrate the general analysis presented above, using the example of a one-dimensional harmonic oscillator perturbed by a uniform external force. We take the bare Hamiltonian

$$H_0(z) = \frac{1}{2m} p^2 + \frac{m\omega^2}{2} q^2 \tag{27}$$

and we consider a perturbation

$$-X Q(z) = -Xq \tag{28}$$

Thus, $H = H_0 - Xq$. The perturbation describes a force X acting along the direction of the coordinate q. The canonical distribution at a given force X is

$$P^{\mathrm{eq}}(z; X) = \frac{1}{Z(X)} \exp\bigl[-\beta(H_0 - Xq)\bigr] \tag{29}$$

and by direct evaluation of Eq. (6) we get

$$F(X) = F(0) - \frac{X^2}{2m\omega^2} \tag{30}$$

Now imagine a process during which the perturbing force is linearly ramped up from zero to some positive value χ:

$$X_t = \frac{\chi t}{\tau}, \quad 0 \leqslant t \leqslant \tau \tag{31}$$

To simplify the calculations below, we take τ to be the period of the unperturbed oscillator:

$$\tau = \frac{2\pi}{\omega} \tag{32}$$

The evolution of the system satisfies Hamilton's equations,

$$\dot{q} = \frac{p}{m}, \qquad \dot{p} = -m\omega^2 q + \frac{\chi t}{\tau} \tag{33}$$

which can readily be solved. For initial conditions (q_0, p_0), we get a trajectory

$$q_t = q_0 \cos(\omega t) + \frac{p_0}{m\omega} \sin(\omega t) + \frac{\chi}{m\omega^3 \tau}\bigl[\omega t - \sin(\omega t)\bigr] \tag{34a}$$

$$p_t = p_0 \cos(\omega t) - m\omega q_0 \sin(\omega t) + \frac{\chi}{\omega^2 \tau}\bigl[1 - \cos(\omega t)\bigr] \tag{34b}$$

hence

$$q_\tau = q_0 + \frac{\chi}{m\omega^2}, \qquad p_\tau = p_0 \tag{35}$$

The quantities W_0 and W then follow from Eq. (15):

$$W_0 = \chi q_0 - \Delta F, \qquad W = \Delta F \tag{36}$$

where

$$\Delta F = F(\chi) - F(0) = -\frac{\chi^2}{2m\omega^2} \tag{37}$$

From Eq. (36) we obtain explicit expressions for the distributions of work values, $\rho_0(W_0)$ and $\rho(W)$, assuming initial conditions (q_0, p_0) sampled from equilibrium. Since $W = \Delta F$ for every realization, we have

$$\rho(W) = \delta(W - \Delta F) \tag{38}$$

In turn, since W_0 is a linear function of q_0 (Eq. (36)), which is sampled from a thermal, Gaussian distribution with mean $\langle q_0 \rangle = 0$ and variance $\sigma_{q_0}^2 = (m\omega^2\beta)^{-1}$, it follows that W_0 is also distributed as a Gaussian, with mean and variance $\langle W_0 \rangle = -\Delta F$, $\sigma_{W_0}^2 = \chi^2 \sigma_{q_0}^2$. Explicitly,

$$\rho_0(W_0) = \sqrt{\frac{m\omega^2\beta}{2\pi\chi^2}} \exp\left[-\frac{m\omega^2\beta}{2\chi^2}(W_0 + \Delta F)^2\right] \tag{39}$$

It is now straightforward to verify by inspection and Gaussian integration that Eqs. (1) and (2) are satisfied:

$$\left\langle e^{-\beta W} \right\rangle = \int dW\, \rho(W) e^{-\beta W} = e^{-\beta \Delta F} \tag{40}$$

$$\left\langle e^{-\beta W_0} \right\rangle = \int dW_0\, \rho_0(W_0) e^{-\beta W_0} = 1 \tag{41}$$

The very simple expressions obtained above for W_0 and W are consequences of our choice for τ, Eq. (32). The model remains solvable for arbitrary τ; in that case both ρ and ρ_0 are Gaussian distributions, satisfying Eqs. (1) and (2), but the expressions for their means and variances are more complicated.

Fig. 1 depicts the distributions ρ_0 and ρ. Note that W is negative, while the mean value of W_0 is positive. We can understand this sign difference as follows. Suppose we adopt the exclusive convention and take the internal energy of the system to be given by H_0. We imagine that the particle evolves in a fixed harmonic well

$$U_0(q) = m\omega^2 q^2/2 \tag{42}$$

under the influence of a time-dependent external force X_t. The initial position q_0 is sampled from a Gaussian distribution centered at $q = 0$, and as we turn on the perturbing force from 0 to χ, we displace the particle rightward by a net amount $\Delta q = q_\tau - q_0 = \chi/m\omega^2$ (Eq. (35)). The final condition q_τ is then distributed as a Gaussian whose mean no longer coincides with the center of the fixed harmonic well, but rather has shifted by a distance Δq, as shown in Fig. 2. In effect, the perturbation pushes the particle distribution rightward along the q-axis, and 'up' the quadratic potential energy landscape, resulting in a positive value for the average work, $\langle W_0 \rangle > 0$.

Now suppose that we instead choose the inclusive convention and use the full Hamiltonian $H = H_0 - Xq$ to define the internal energy of the system. Thus we imagine a particle moving in a time-dependent potential,

$$U_t(q) = U_0(q) - X_t q = \frac{m\omega^2}{2}\left(q - \frac{\Delta q}{\tau}t\right)^2 + \Delta F \cdot \frac{t^2}{\tau^2} \tag{43}$$

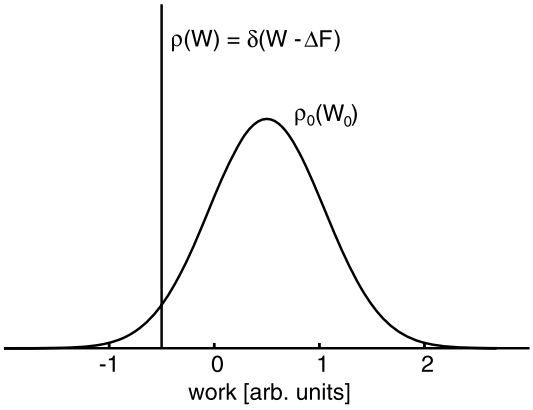

Fig. 1. Distributions of work values W_0 and W for the harmonic oscillator example, with $\chi = m = \omega = 1.0$ and $k_B T = 0.3$. The distribution ρ is a delta-function at $\Delta F = -0.5$, while ρ_0 is a Gaussian whose mean is at $-\Delta F$.

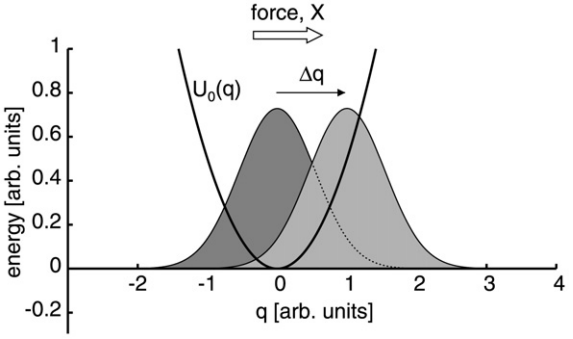

Fig. 2. The bare harmonic potential U_0 is shown, along with the distributions of initial particle positions (dark gray) and final particle positions (light gray). As we turn on the force X, we shift the distribution by an amount $\Delta q = \chi/m\omega^2 = 1.0$ away from the minimum of the potential, resulting in an average increase in the value of U_0.

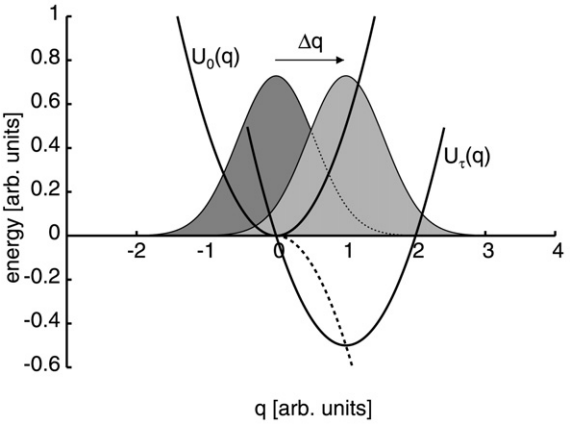

Fig. 3. Same as Fig. 2, only now we think in terms of a time-dependent potential well rather than an externally applied force. From $t = 0$ to $t = \tau$ the minimum of the harmonic well moves along the path depicted by the thick dashed line. During a given realization, the particle suffers a net displacement $q_\tau - q_0 = \Delta q$, hence $W = U_\tau(q_\tau) - U_0(q_0) = \Delta F$.

where $\Delta q = \chi/m\omega^2$ and $\Delta F = -\chi^2/2m\omega^2$, as above. Eq. (43) describes a harmonic well that moves rightward along the q-axis with a velocity $\Delta q/\tau$, and slides downward in energy, as depicted in Fig. 3. We can now appreciate why $W = \Delta F$ for every realization of the process. From $t = 0$ to $t = \tau$ the particle moves by a net amount Δq; simultaneously, the well shifts by the same amount, and acquires an energy offset ΔF:

$$U_\tau(q) = \frac{m\omega^2}{2}(q - \Delta q)^2 + \Delta F \tag{44}$$

The particle thus ends with the same displacement relative to the minimum of the well as it began with, so the net change in its energy is just the offset ΔF.

In summary, in the exclusive framework, we picture a particle that is pushed rightward by an external force in a fixed harmonic well ($\langle W_0 \rangle > 0$); while in the inclusive framework we imagine a particle that is dragged rightward in space and 'downward' in energy by a moving harmonic well ($W < 0$).

5. Weighted distributions

Here we sketch an alternative derivation of Eqs. (1) and (2).

Consider an ensemble of realizations of the process described in Section 2. Let us picture this ensemble as a swarm of Hamiltonian trajectories evolving in phase space, represented by a density[2]

$$f(z,t) = \big\langle \delta(z - z_t) \big\rangle \tag{45}$$

which satisfies the Liouville equation,

$$\frac{\partial f}{\partial t} = \{H, f\} \tag{46}$$

Here we use the convenient Poisson bracket notation: $\{A, B\} = (\partial A/\partial \mathbf{q}) \cdot (\partial B/\partial \mathbf{p}) - (\partial A/\partial \mathbf{p}) \cdot (\partial B/\partial \mathbf{q})$. In general, Eq. (46) does not yield a simple solution; the evolution of $f(z,t)$ can be very complicated, particularly if the underlying Hamiltonian dynamics are chaotic.

[2] See Ref. [22] for a brief discussion of the ordering of limits implied in Eqs. (45) and (49).

For a given trajectory z_t, let

$$w_0(t) = \int_0^t \mathrm{d}t' \sum_k X_k(t')\,\dot{Q}_k(z_{t'}) \tag{47}$$

denote the amount of work performed on the system to time t, using the definition of work corresponding to the exclusive framework (Eq. (10a) and Refs. [13–16]). Since the rate of change of the observable Q_k along a trajectory z_t is given by $\dot{Q}_k = \{Q_k, H\}$ [23], we can rewrite Eq. (47) as

$$w_0(t) = \int_0^t \mathrm{d}t' \{X \cdot Q, H\} = \int_0^t \mathrm{d}t' \{X \cdot Q, H_0\} \tag{48}$$

The last equality follows from the identity $\{X \cdot Q, X \cdot Q\} = 0$. Now consider a *weighted* phase space density

$$g_0(z,t) = \big\langle \delta(z - z_t) \exp\big[-\beta w_0(t)\big] \big\rangle \tag{49}$$

in which each trajectory carries a statistical weight, $\exp[-\beta w_0(t)]$ (see the discussion below). This density satisfies

$$\frac{\partial g_0}{\partial t} = \{H, g_0\} - \beta \{X \cdot Q, H_0\} g_0 \tag{50}$$

where the second term on the right accounts for the evolving statistical weights. The derivation of this equation is very similar to those found in Section II of Ref. [3] and Section 4.1 of Ref. [22].

Since $w_0(0) = 0$ identically, and since we assume our ensemble is initially prepared in equilibrium, we have $g_0(z,0) = f(z,0) = P^{\mathrm{eq}}(z; X_0)$. Given these initial conditions, the unique solution of Eq. (50) is the time-*independent* distribution

$$g_0(z,t) = \frac{1}{Z(X_0)} \exp\big[-\beta H_0(z)\big] = P^{\mathrm{eq}}(z; X_0) \tag{51}$$

To see this, note that

$$\big\{H, \mathrm{e}^{-\beta H_0}\big\} = -\beta \{H, H_0\} \mathrm{e}^{-\beta H_0} = \beta \{X \cdot Q, H_0\} \mathrm{e}^{-\beta H_0} \tag{52}$$

using the derivative rule for Poisson brackets, and the identity $\{H_0, H_0\} = 0$. From this result it follows by inspection that Eq. (51) satisfies Eq. (50).

The functions $f(z,t)$ and $g_0(z,t)$ are two different statistical representations of the same ensemble of realizations. Continuing to picture this ensemble as a swarm of trajectories evolving in phase space, f (Eq. (45)) can be viewed as a number density, which simply counts how many trajectories are found in the vicinity of z at time t; while g_0 (Eq. (49)) can be interpreted as a mass density, if we imagine that each realization carries a fictitious, time-dependent mass $\exp[-\beta w_0(t)]$. Eq. (51) then has the following interpretation: when the initial conditions are sampled from equilibrium, the 'mass density' of trajectories remains constant in time, even as the 'number density' evolves in a possibly complicated way. Thus while the number of trajectories found near a given point z changes with time, these fluctuations are balanced by the evolving statistical weights (fictitious masses) of those trajectories, in precisely such a way as to keep the local mass density constant.

We can obtain analogous results in the inclusive framework (Eq. (10b) and Refs. [2,3]). Introducing

$$w(t) = -\int_0^t \mathrm{d}t' \sum_k \dot{X}_k(t')\,Q_k(z_{t'}) = -\int_0^t \mathrm{d}t'\, \dot{X} \cdot Q \tag{53}$$

along with the corresponding weighted density

$$g(z,t) = \big\langle \delta(z - z_t)\, \exp\big[-\beta w(t)\big] \big\rangle \tag{54}$$

we obtain the equation of motion [3,22]

$$\frac{\partial g}{\partial t} = \{H, g\} + \beta \dot{X} Q g \tag{55}$$

For initial conditions $g(z,0) = f(z,0) = P^{\rm eq}(z; X_0)$, the unique solution is

$$g(z,t) = \frac{1}{Z(X_0)} \exp\bigl[-\beta H(z; X_t)\bigr] = \frac{Z(X_t)}{Z(X_0)}\, P^{\rm eq}(z; X_t) \tag{56}$$

The weighted density is no longer constant in time (as was the case with g_0), but rather is proportional to the equilibrium distribution corresponding to the current value of the parameters X.

The results just obtained are summarized as follows:

$$\bigl\langle \delta(z - z_t) \exp\bigl[-\beta w_0(t)\bigr]\bigr\rangle = P^{\rm eq}(z; X_0) \tag{57a}$$

$$\bigl\langle \delta(z - z_t) \exp\bigl[-\beta w(t)\bigr]\bigr\rangle = \frac{Z(X_t)}{Z(X_0)}\, P^{\rm eq}(z; X_t) \tag{57b}$$

Eqs. (1) and (2) now follow immediately by evaluating Eq. (57) at $t = \tau$ and integrating both sides over phase space. While the derivations presented here are less elementary than those of Section 3, we ultimately gain a stronger set of results. By a simple trick of statistical reweighting, we transform an equation of motion that we cannot solve (Eq. (46)) into one that is easily solved (Eq. (50) or (55)). The result, Eq. (57), allows us to reconstruct equilibrium distributions $P^{\rm eq}$ using trajectories driven away from equilibrium.

Eqs. (57a) and (57b) are in fact equivalent. Multiplying both sides of Eq. (57a) by $\exp[+\beta X_t \cdot Q(z)]$ and pulling this factor inside the angular brackets, we obtain Eq (57b). Conversely, multiplication by $\exp[-\beta X_t \cdot Q(z)]$ leads us from Eq. (57b) to Eq. (57a). However, this equivalence is lost once we integrate over phase space: Eqs. (1) and (2) do not imply one another.

Eq. (57b) can be viewed as a direct consequence of the Feynman–Kac theorem; this observation by Hummer and Szabo serves as a starting point for their method of reconstructing equilibrium potentials of mean force from single-molecule manipulation experiments carried out away from equilibrium [7]. Moreover, Eq. (57a) is essentially a special case of Eq. 12 of Ref. [7] (with W_0 as generalized by Eq. (59) below), if we assume that their confining potential is initially turned off: $u(z,0) = 0$. For an alternative approach to estimating potentials of mean force from similar experiments, see the 'clamp-and-release' method proposed by Adib [24].

6. Discussion

The nonequilibrium work theorem, Eq. (1), has generated interest (and controversy [25–27]) primarily for two reasons. First, along with the *fluctuation theorem* for entropy production [28–33], it is one of relatively few equalities in statistical physics that apply to systems far from thermal equilibrium. Note that the term 'fluctuation theorem' has also been used to specify a relation between the response of a system to external perturbations, and a correlation function describing fluctuations of the unperturbed system [34,35]. Second, Eq. (1) predicts that equilibrium free energy differences can be determined from irreversible processes, counter to expectations that irreversible work values can only place *bounds* on ΔF [36]. Eq. (2) shares the first feature—it remains valid far from equilibrium—but not the second; it does not seem to be the case that ΔF can be determined solely from a distribution of values of W_0.

A crucial distinction in this paper has been the difference between the quantities W and W_0. The recognition that, in the literature, various meanings are assigned to the term *work*, might at first come as an unwelcome surprise. Work is a concept of such central importance in thermodynamics that it ought to be unambiguously defined! However, in dealing with a physical situation that involves the mechanical perturbation of a system, the perturbation is often accomplished by coupling externally controlled variables $(X_1, X_2, \ldots)$ to generalized system coordinates $(Q_1, Q_2, \ldots)$. This coupling is represented by a term of the form $-\sum_k X_k Q_k$ (or a nonlinear generalization thereof, see below) in the full Hamiltonian that governs the evolution of the system and its surroundings. We are then faced with the question of whether or not to view this term as part of the internal energy of the system of interest. As stressed in this paper, either choice is acceptable—this is a question of book-keeping rather than principle—but it is precisely this freedom that leads to the ambiguity in the definition of work. For related discussions of this issue, particularly in the context of interpretation of experimental data, see Refs. [37–39,9].

Throughout this paper it has been assumed, following Refs. [13–16], that the coupling between the forces X and the observables Q is linear: $H = H_0 - X \cdot Q$. However, as already observed by Bochkov and Kuzovlev, this assumption can easily be relaxed. Had we written the Hamiltonian as

$$H(z; X) = H_0(z) - h(Q; X) \tag{58}$$

and assumed $h(Q; X_0) = 0$, then the entire analysis leading to Eqs. (1) and (2) would have remained valid, provided the following definitions of work:

$$W = \int_0^\tau \mathrm{d}t\, \dot{X} \cdot \frac{\partial H}{\partial X}, \qquad W_0 = \int_0^\tau \mathrm{d}t\, \dot{Q} \cdot \frac{\partial h}{\partial Q} \tag{59}$$

We recover Eqs. (3) and (11) with a linear perturbation $h = X \cdot Q$.

The definition of W_0 depends explicitly on the manner in the which the full Hamiltonian is decomposed into a bare term and a perturbation. Such a decomposition is often natural. For instance, in single-molecule manipulation experiments we normally take H_0 to be the undisturbed molecule, while a harmonic interaction term $-h$ represents the perturbation due to an AFM cantilever or optical trap [7]. In this context it is important to keep in mind that the derivation of Eq. (2) explicitly assumes that the perturbation is initially 'off' (e.g. Eq. (7)). If this assumption is violated, as is often the case in single-molecule experiments [8,10], then Eq. (2) generally does not hold, although Eq. (1) remains valid.[3]

While the analysis here has been carried out using Hamiltonian dynamics, the conclusions remain valid under other frameworks for modeling the evolution of the system. The connection to the stochastic approach taken in Ref. [7] has already been noted. Moreover, Eqs. 33 and 34 of Ref. [38], derived for inertial Langevin dynamics, are equivalent to Eqs. (1) and (2) of the present paper. For non-inertial (overdamped) Langevin dynamics, similar results follow directly from the Onsager–Machlup expressions for path-space distributions [40,41].

Finally, recall the Crooks fluctuation theorem [5],

$$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\bigl[\beta(W - \Delta F)\bigr] \tag{60}$$

where the subscripts refer to two thermodynamic process (*forward* and *reverse*) that are related by time-reversal of the protocol used to perturb the system. The Bochkov–Kuzovlev papers contain results that are reminiscent of Eq. (60), for instance Eq. 7 of Ref. [13] and Eq. 2.12 of Ref. [15]. However, while Crooks uses a definition of work corresponding to W of the present paper, Bochkov and Kuzovlev use W_0, and their results do not involve ΔF. Moreover, in Refs. [13–16] the derivations seem to assume that the initial conditions are sampled from the same, unperturbed equilibrium distribution for both the forward and the reverse process (see e.g. Eq. 2.6 of Ref. [15]). Crooks, by contrast, assumes that the forward and reverse processes are characterized by different initial equilibrium states, both represented by canonical distributions [42]. It would be useful to clarify more precisely the relationship between these sets of results.

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References

[1] C. Bustamante, J. Liphardt, F. Ritort, Phys. Today 58 (2005) 43.
[2] C. Jarzynski, Phys. Rev. Lett. 78 (1997) 2690.
[3] C. Jarzynski, Phys. Rev. E 56 (1997) 5018.
[4] For pedagogical derivations of Eq. (1) and related results, see for instance Section 7.4.1 of D. Frenkel, B. Smit, Understanding Molecular Simulation: from Algorithms to Applications, second ed., Academic Press, San Diego, 2002; or
S. Park, K. Schulten, J. Chem. Phys. 120 (2004) 5946; or
G. Hummer, A. Szabo, Acc. Chem. Res. 38 (2005) 504.
[5] G.E. Crooks, Phys. Rev. E 60 (1999) 2721.
[6] G.E. Crooks, Phys. Rev. E 61 (2000) 2361.
[7] G. Hummer, A. Szabo, Proc. Nat. Acad. Sci. 98 (2001) 3658.
[8] J. Liphardt, et al., Science 296 (2002) 1832.

[3] In some situations the difference between W_0 and W is relatively small, and one can be used as a substitute for the other in Eq. (1) [10]. However, this issue is separate from the validity of Eq. (2), which requires $X_0 = 0$ (Eq. (7)), or more generally $h(Q; X_0) = 0$.

[9] F. Douarche, S. Ciliberto, A. Petrosyan, I. Rabbiosi, Europhys. Lett. 70 (2005) 593.
[10] D. Collin, et al., Nature 437 (2005) 231.
[11] V. Blickle, et al., Phys. Rev. Lett. 96 (2006) 070603.
[12] C.H. Kiang, N. Harris, in preparation.
[13] G.N. Bochkov, Yu.E. Kuzovlev, Zh. Eksp. Teor. Fiz. 72 (1977) 238; Sov. Phys. JETP 45 (1977) 125.
[14] G.N. Bochkov, Yu.E. Kuzovlev, Zh. Eksp. Teor. Fiz. 76 (1979) 1071; Sov. Phys. JETP 49 (1979) 543.
[15] G.N. Bochkov, Yu.E. Kuzovlev, Physica A 106 (1981) 443.
[16] G.N. Bochkov, Yu.E. Kuzovlev, Physica A 106 (1981) 480.
[17] D. Halliday, R. Resnick, J. Walker, Fundamentals of Physics, seventh ed., John Wiley and Sons, 2005.
[18] J.W. Gibbs, Elementary Principles in Statistical Mechanics, Scribner's, New York, 1902, pp. 42–44.
[19] E. Schrödinger's, Statistical Thermodynamics, Cambridge, 1962. See the paragraphs found between Eqs. (2.13) and (2.14).
[20] G.E. Uhlenbeck, G.W. Ford, Lectures in Statistical Mechanics, Amer. Math. Soc., Providence, 1963, Chapter I, Section 7.
[21] R. Zwanzig, J. Chem. Phys. 22 (1954) 1420.
[22] C. Jarzynski, in: P. Garbaczewski, R. Olkiewicz (Eds.), Lecture Notes in Physics, vol. 597, Springer Verlag, Berlin, 2002.
[23] H. Goldstein, Classical Mechanics, second ed., Addison–Wesley, Reading, MA, 1980, Chapter 9.5.
[24] A.B. Adib, J. Chem. Phys. 124 (2006) 144111.
[25] E.G.D. Cohen, D. Mauzerall, J. Stat. Mech.: Theor. Exp. (2004) P07006.
[26] E.G.D. Cohen, D. Mauzerall, Mol. Phys. 103 (2005) 2923.
[27] J. Sung, cond-mat/0506214v2.
[28] D.J. Evans, E.G.D. Cohen, G.P. Morris, Phys. Rev. Lett. 71 (1993) 2401–2404.
[29] D. Evans, D. Searles, Phys. Rev. E 50 (1994) 1645.
[30] G. Gallavotti, E.G.D. Cohen, Phys. Rev. Lett. 74 (1995) 2694–2697.
[31] J. Kurchan, J. Phys. A 31 (1998) 3719.
[32] J.L. Lebowitz, H. Spohn, J. Stat. Phys. 95 (1999) 333.
[33] See also numerous references in D.J. Evans, D. Searles, Adv. Phys. 51 (2002) 1529.
[34] P. Hänggi, Helv. Phys. Acta 51 (1978) 202.
[35] P. Hänggi, H. Thomas, Phys. Rep. 88 (1982) 207.
[36] W.P. Reinhardt, M.A. Miller, L.M. Amon, Acc. Chem. Res. 34 (2001) 607.
[37] J.M. Schurr, B.S. Fujimoto, J. Phys. Chem. B 107 (2003) 14007.
[38] O. Narayan, A. Dhar, J. Phys. A 37 (2004) 63.
[39] A. Dhar, Phys. Rev. E 71 (2005) 036126.
[40] L. Onsager, S. Machlup, Phys. Rev. 91 (1953) 1505.
[41] R. Dean Astumian, personal correspondence and cond-mat/0608352.
[42] Recently Eq. (60) has been recovered as the limiting case of an analogous microcanonical result, derived within a Hamiltonian formulation; see B. Cleuren, V. Van den Broeck, R. Kawai, Phys. Rev. Lett. 96 (2006) 050601.