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On the work–Hamiltonian connection in manipulated systems

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Abstract. I examine the 'physical inconsistencies' pointed out in a recent work as deriving from the use of the expression $\mathrm{d}W/\mathrm{d}t = \partial H(x,t)/\partial t$ which appears in fluctuation relations for manipulated system, such as Jarzynski's equality. I show that these inconsistencies are illusory, since the 'arbitrary parameters' that appear in the expression of the free-energy difference obtained from this relation turn out to have a direct and simple physical interpretation connected with the physical setup needed to perform the manipulation.

Keywords: large deviations in non-equilibrium systems

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1. Introduction

An exciting scenario has recently been introduced for the investigation of nanosystems through the derivation of identities that relate the statistics of the fluctuating work in manipulated statistical mechanics systems with equilibrium properties. The most quoted of these relations is Jarzynski's equality (JE) [1]

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

which relates the fluctuating work W performed in a manipulation with the free-energy difference ΔF. A number of works [2] have shown how to harness these identities to explore the free-energy landscape of nanosystems via manipulations that do not necessarily maintain the systems at thermodynamic equilibrium. These suggestions have been explored experimentally with remarkable success [3].

A recent work [4] has challenged the possibility of evaluating free-energy differences in this way. The authors of this work state that 'Time-dependent Hamiltonians, however, provide the energy up to an arbitrary factor (*sic*) that typically depends on time and on the microscopic history of the system'. Such dependence prevents this approach from being generally applicable to compute thermodynamically consistent properties.

To arrive at this conclusion, they consider a system described by the Hamiltonian $H_0(x)$ under the effects of an external time-dependent force $f(t)$. The total Hamiltonian is given by

$$H(x,t) = H_0(x) - f(t)x + g(t), \tag{2}$$

where $g(t)$ is an arbitrary function of time. The function $g(t)$ does not affect the total force acting on the system, $F = -\partial H_0/\partial x + f(t)$, but it changes the Hamiltonian. Therefore, $g(t)$ has to be chosen so that the Hamiltonian can be identified with the energy of the system. Now the authors of [4] claim that the arbitrary time dependence of the Hamiltonian, $g(t)$, cannot be chosen so that the Hamiltonian gives a consistent energy.

I shall argue in the present work that the time-dependent Hamiltonian for a manipulated system can be consistently identified, and that the apparent disagreement between the results of [4] and the Jarzynski equality derives from the fact that different quantities are considered in the different works. Indeed, the manipulation of a system takes place by operating on a collection of bodies external to the system but which interact with

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it, which we shall call the *steering bodies*. It is therefore possible to define unambiguously (apart from a time-independent additive constant) the time-dependent Hamiltonian of a manipulated system by explicitly considering the energy of interaction between the observed system and the steering bodies. Now, the thermodynamical work performed on a system represents the work done *by it on the steering bodies*, rather than the work done on the system itself by the external bodies: a point stressed, e.g., by Gibbs in his founding book [5] on statistical mechanics. The connections between the different work concepts and their fluctuation relations have been recently thoroughly discussed by Jarzynski and Horowitz [6]. By these considerations, which are made more explicit in the following, one can see that the worries expressed in [4] are misplaced.

2. Work on the system and work by the system

Let us consider a system like the one considered by the authors of [4], which is described by a Hamiltonian $H_0(x)$ and is manipulated by moving some external bodies, whose positions are identified by $a = (a_i)$, and are assumed to be so large that the fluctuations of their coordinates can be safely neglected (cf [5, p 42]). Let the mutual interaction between these bodies and the system be described by a potential energy function $V(x, a)$, which does not explicitly depend on time. Let us moreover define a manipulation protocol, in which the coordinates a of the external bodies are expressed as functions of a parameter μ, and in which μ changes as a given function of the time t. Then the manipulated system is described by a Hamiltonian $H(x, t)$ which depends explicitly on time, and is given by

$$H(x, t) = H_0(x) + U(x, \mu(t)), \tag{3}$$

where $U(x, \mu) = V(x, a(\mu))$ is the mutual energy of the system and the manipulated bodies. This quantity is identified up to an additive constant which is independent of time. When the system undergoes a manipulation described by the change $\mu \longrightarrow \mu + \mathrm{d}\mu$ of the parameter, we can identify two different infinitesimal works:

- The work $\mathrm{d}W$ that the system performs on the external bodies, with the sign changed for later convenience. Since the force F_i that the system applies to the body described by the coordinate a_i is given by $F_i = -\partial V/\partial a_i$, we have

$$\begin{aligned}\mathrm{d}W &= -\sum_i F_i\,\mathrm{d}a_i = \sum_i \frac{\partial V(x,a)}{\partial a_i}\,\frac{\mathrm{d}a_i}{\mathrm{d}\mu}\,\mathrm{d}\mu \\ &= \frac{\partial U(x,\mu)}{\partial \mu}\,\mathrm{d}\mu = \frac{\partial U(x,\mu)}{\partial \mu}\,\dot{\mu}\,\mathrm{d}t = \frac{\partial H(x,t)}{\partial t}\,\mathrm{d}t.\end{aligned} \tag{4}$$

- The work $\mathrm{d}W_0$ that the external bodies perform on the system. This is given by

$$\mathrm{d}W_0 = -\frac{\partial V(x, a(\mu))}{\partial x}\,\mathrm{d}x = -\frac{\partial U(x,\mu)}{\partial x}\,\mathrm{d}x. \tag{5}$$

These two elementary works are not equal. It is easy to see, indeed, that

$$\mathrm{d}W_0 - \mathrm{d}W = -\frac{\partial U(x,\mu)}{\partial x}\,\mathrm{d}x - \frac{\partial U(x,\mu)}{\partial \mu}\,\mathrm{d}\mu = -\mathrm{d}U. \tag{6}$$

Let us now consider a quasistatic manipulation, in which the external bodies affecting the dynamics of the system are manipulated so slowly that the system can be considered to be at thermodynamical equilibrium at all times. In this situation, the infinitesimal work $\mathrm{d}W^{\mathrm{qs}}$ performed in an infinitesimal change $\mathrm{d}\mu$ of the parameter μ (i.e., for very small displacements $\mathrm{d}a_i = (\partial a_i/\partial\mu)\,\mathrm{d}\mu$ of the external bodies which interact with the system) does not fluctuate, and is equal to the average $\langle \mathrm{d}W\rangle$, given by

$$\langle \mathrm{d}W\rangle = \left\langle \frac{\partial U(x,\mu)}{\partial\mu}\right\rangle_{\mu} \mathrm{d}\mu. \tag{7}$$

Here $\langle\cdots\rangle_\mu$ is the canonical average with respect to the 'instantaneous' Hamiltonian $H_0(x) + U(x,\mu)$:

$$\langle A\rangle_\mu = \int \mathrm{d}x\; A(x)\,\frac{\mathrm{e}^{-\beta(H_0(x)+U(x,\mu))}}{Z_\mu}, \tag{8}$$

in which $\beta = 1/k_{\mathrm{B}}T$ and Z_μ is the μ-dependent partition function

$$Z_\mu = \int \mathrm{d}x\; \mathrm{e}^{-\beta(H_0(x)+U(x,\mu))}. \tag{9}$$

It is then a simple matter to see that, in these hypotheses, one has

$$\int_{\mu_0}^{\mu} \mathrm{d}W^{\mathrm{qs}} = -\beta^{-1}\int \mathrm{d}\mu\,\frac{\mathrm{d}\ln Z_\mu}{\mathrm{d}\mu} = -\beta^{-1}\left[\ln Z_\mu - \ln Z_{\mu_0}\right]. \tag{10}$$

Thus the total reversible work $W^{\mathrm{qs}} = \int \mathrm{d}W^{\mathrm{qs}}$ is related to the change of the partition function. We can express this change in terms of the *internal* free energy of the isolated system, F_0, defined as

$$F_0(\mu) = -\beta^{-1}\ln Z_\mu - \langle U(x,\mu)\rangle = \langle H_0\rangle_\mu - TS(\mu), \tag{11}$$

where $S(\mu)$ is the entropy of the system in the canonical equilibrium state defined by the 'instantaneous' Hamiltonian $H_0(x) + U(x,\mu)$.

For infinitely slow manipulations, because of equation (6), one has indeed

$$\langle W_0\rangle - W = \langle U(x,\mu_0)\rangle_{\mu_0} - \langle U(x,\mu)\rangle_\mu, \tag{12}$$

so that

$$\Delta F_0 = \int \langle \mathrm{d}W_0\rangle. \tag{13}$$

However, as soon as the manipulation takes place at a finite speed, so that the manipulated system drops out of equilibrium, the fluctuations of W and W_0 are different. The fluctuations of W obey Jarzynski's equality (1), which relates them to free-energy changes, while the fluctuations of W_0 obey a relation found long ago by Bochkov and Kuzovlev [7], namely

$$\left\langle \mathrm{e}^{-\beta W_0}\right\rangle_0 = 1, \tag{14}$$

where $\langle\cdots\rangle_0$ is the average over all paths followed by the system upon manipulation, when the initial state is described by the unperturbed Hamiltonian $H_0(x)$.

Let us consider in particular the effects of a sudden displacement of the steering bodies (represented by $\mu_0 \longrightarrow \mu$), so fast that the system does not have time to change its coordinates. In this case one has of course $W_0 = 0$, and Bochkov and Kuzovlev's relation

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is trivially satisfied, as noticed in [4]. But in order to displace the steering bodies, some work has to be done on them. This work is equal to the change in the potential energy of interaction of the system with the steering bodies:

$$W = U(x, \mu) - U(x, \mu_0). \tag{15}$$

As shown in [1], the Jarzynski equality follows immediately from this relation and the assumption that the system was at equilibrium before the manipulation.

Let us point out that Gibbs explicitly remarks [5, p 4, footnote] that the energy function of a statistical system should include 'that energy which might be described as mutual to that system and external bodies,' and that it is clear from Gibbs's treatise [5, p 42] that his definition of the thermodynamic work corresponds to what I have denoted by W rather than to W_0.

3. An elementary example

We shall now make these considerations more explicit, by considering a simple thermodynamical system, i.e., a one-dimensional oscillator characterized by its mass m and spring constant k, kept at a fixed temperature T. This system has also been examined in detail by the authors of [4]. It is described by the Hamiltonian

$$H(p, x) = \frac{p^2}{2m} + \frac{1}{2}kx^2. \tag{16}$$

In the following we shall focus only on the *displacement* degree of freedom, namely x. Its equilibrium distribution is given by

$$p^{\mathrm{eq}}(x) = \frac{\mathrm{e}^{-kx^2/2k_{\mathrm{B}}T}}{Z}, \tag{17}$$

where Z is given by

$$Z = \int \mathrm{d}x\ \mathrm{e}^{-kx^2/2k_{\mathrm{B}}T} = \sqrt{2\pi k_{\mathrm{B}}T/k}. \tag{18}$$

We shall now apply a uniform, but time-varying, force $f(t)$ to the system. We wish to evaluate the thermodynamical work performed on it, as the applied force changes from $f_0 = 0$ to f, so slowly that the system can be considered to remain at thermodynamical equilibrium at all times.

One then proceeds as follows:

(1) One writes down the Hamiltonian of the system in the presence of the applied force:

$$H(x, f) = \tfrac{1}{2}kx^2 - f\,(x - \gamma)\,. \tag{19}$$

Here γ is defined as the point at which the potential of the applied force vanishes. This point might depend on f, but we shall here assume that it is fixed. It is determined by the actual device used to apply the constant force on the system, as discussed in the following.

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(2) One applies either Gibbs' equation (117) [5, p 45], or Tolman's equation (124.1) [8, p 542], to obtain the quasistatic thermodynamical work $\mathrm{d}W^{\mathrm{qs}}$ associated with a small variation $\mathrm{d}f$ of the applied force:

$$\mathrm{d}W^{\mathrm{qs}} = \left\langle \frac{\partial H}{\partial f} \right\rangle \mathrm{d}f = -\langle (x-\gamma)\rangle\, \mathrm{d}f = -\left(\langle x\rangle - \gamma\right) \mathrm{d}f. \tag{20}$$

In this equation, $\langle A\rangle$ is the canonical average of the function $A(x)$:

$$\langle A\rangle = \frac{1}{Z}\int \mathrm{d}x\; A(x)\, \mathrm{e}^{-H(x,f)/k_{\mathrm{B}}T}. \tag{21}$$

In our case, one obtains

$$\langle x\rangle = \frac{f}{k}, \tag{22}$$

from which $\mathrm{d}W^{\mathrm{qs}}$ can be calculated via equation (20).

(3) One integrates the result with a variable force f' from the initial value $f_0 = 0$ to the final value f, obtaining

$$\Delta F = \int_0^f \left\langle \left.\frac{\partial H}{\partial f}\right|_{f'} \right\rangle \mathrm{d}f' = -\int_0^f \left(\frac{f'}{k} - \gamma\right) \mathrm{d}f' = -\frac{f^2}{2k} + \gamma f. \tag{23}$$

In this expression, ΔF is the change in the Helmholtz free energy, $F = E - TS$. Since it is easy to see that in the present system the entropy S does not change during the manipulation, we can equate it with the change in the *internal* energy E. We have therefore

$$\Delta E = -\frac{f^2}{2k} + \gamma f. \tag{24}$$

The authors of [4] find that this result is not physically acceptable. They raise the following objections: setting first $\gamma = 0$, one obtains $\Delta E = -f^2/2k$, which is a negative value inconsistent with a non-spontaneous process. More generally, the change ΔE can be positive or negative depending on the value of γ, which is a constant parameter which does not affect the dynamics of the system. Therefore they conclude that these estimates are not suitable for obtaining thermodynamics properties, such as whether or not a given process occurs spontaneously.

I shall now show that the expression (24) corresponds to the actual change of energy of the system upon manipulations, when the mutual energy of the system and the manipulating bodies is taking into account. Indeed, in order to apply uniform but time-varying forces to the system, it is necessary to act on it by manipulating external bodies. I shall consider two possible conceptual setups: one electrostatic and one exploiting the Earth's gravitational field.

Electrostatic device

Let us assume that the mass of the oscillator carries a small charge q. We place two point-like charged bodies on the x-axis at $\pm\infty$, one carrying a charge $+Q$ and the other carrying a charge $-Q$. We then let these two charged bodies come closer and closer to the origin (the equilibrium point of the oscillator), by letting the charge $+Q$ be situated at the point $-X+\gamma$, and the charge $-Q$ at the point $X+\gamma$. Thus the electric field acting on the oscillator at point x is given by

$$\begin{aligned} E &= \frac{Q}{4\pi\epsilon_0}\left[\frac{1}{(x-X-\gamma)^2}+\frac{1}{(x+X-\gamma)^2}\right] \\ &= \frac{Q}{2\pi\epsilon_0}\frac{(x-\gamma)^2+X^2}{[(x-\gamma)^2+X^2]^2-4(x-\gamma)^2X^2} \\ &\simeq \frac{Q}{2\pi\epsilon_0}\left\{\frac{1}{X^2}+\frac{3(x-\gamma)^2}{X^4}+\frac{5(x-\gamma)^4}{X^6}+\cdots\right\}. \end{aligned} \tag{25}$$

If X is large enough, then all terms beyond the first one are negligible, for the expected excursions of the oscillator from the origin. Then the force applied by the charge Q is given by

$$f = \frac{qQ}{2\pi\epsilon_0}\frac{1}{X^2}. \tag{26}$$

Let us choose Q such that, even for the largest force f_1 which we wish to apply, X is so large that the terms beyond the first in equation (25) are negligible. Thus by moving the charges $\pm Q$ from infinity to $\pm X+\gamma$, always symmetrically around the point γ, we can apply a uniform but time-varying force to our oscillator. It is now clear that γ, far from being a fictitious parameter, corresponds to the location of the center of the device by which a uniform force is applied to the system we are studying. In order to change γ, external work must be supplied to the apparatus.

Let us now evaluate the internal energy of the system as a function of X. We have

$$\begin{aligned} E &= \left\langle \tfrac{1}{2}kx^2+U(x,X)\right\rangle \\ &= \frac{1}{Z}\int \mathrm{d}x\ \mathrm{e}^{-H(x,X)/k_\mathrm{B}T}\left[\frac{1}{2}kx^2+\frac{qQ}{4\pi\epsilon_0}\left(\frac{1}{x+X-\gamma}-\frac{1}{X-x+\gamma}\right)\right]. \end{aligned} \tag{27}$$

The first term yields

$$\left\langle\frac{1}{2}kx^2\right\rangle = \frac{1}{2}k\left[\left\langle(x-\langle x\rangle)^2\right\rangle+\langle x\rangle^2\right] = \frac{1}{2}k_\mathrm{B}T+\frac{1}{2}\frac{f^2}{k}. \tag{28}$$

The first term is given by the equipartition theorem, and the second by equation (22). One can expand the second term in powers of $1/X$, obtaining

$$\langle U(x,X)\rangle = -\frac{qQ}{2\pi\epsilon_0}\left[\frac{1}{X^2}\langle(x-\gamma)\rangle+\frac{1}{X^4}\left\langle(x-\gamma)^3\right\rangle+\cdots\right]. \tag{29}$$

Thus, if $\langle(x-\gamma)^2\rangle/X^2 \ll 1$, we have

$$\langle U(x,X)\rangle = -\frac{qQ}{2\pi\epsilon_0}\frac{\langle(x-\gamma)\rangle}{X^2} = -\frac{f^2}{k}+\gamma f, \tag{30}$$

where we have exploited (26) and (22). Summing up, we obtain

$$E = \frac{1}{2}k_\mathrm{B}T-\frac{f^2}{2k}+\gamma f, \tag{31}$$

in agreement with equation (24).

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Gravity-field device

A simpler conceptual experiment can be set up, imagining that the oscillator mass is constrained to move along a rectilinear frictionless guide, which can rotate around a point H in a vertical plane. Let us set a fixed, two-dimensional coordinate system, with ξ and ζ denoting horizontal and vertical position respectively. When the guide is horizontal, the equilibrium position of the spring coincides with the coordinate origin O. We shall denote by x the displacement of the mass along the guide with respect to the equilibrium point of the spring. Let m be the oscillator mass, g the acceleration of gravity, and let the hinge H be placed at $(\xi = \gamma, \zeta = 0)$, corresponding to $x = \gamma$. If the guide is now rotated clockwise by an angle θ, the oscillator mass will be acted upon by a uniform force, directed towards increasing values of x, and of intensity $mg \sin\theta$. On the other hand, if the mass is at location x along the guide, its height is given by $\zeta = -(x - \gamma)\sin\theta$. It is then a simple matter to evaluate the average of $U(x, \theta)$:

$$\langle U(x,\theta)\rangle = mg\langle\zeta\rangle = -mg\sin\theta\langle x-\gamma\rangle = -\frac{f^2}{k} + \gamma f. \tag{32}$$

Adding to it the average elastic energy $\frac{1}{2}k\langle x^2\rangle$ we recover equation (24) again. But it is amusing to verify that this result does indeed correspond to the work done by the system on the external device. Let us consider the line to be tilted by θ, and the position of the oscillator to be x. Then the oscillator applies to the rectilinear guide a torque

$$\tau = mg\cos\theta(x-\gamma). \tag{33}$$

As the angle changes by $\mathrm{d}\theta$, this torque executes on the guide a work $\tau\,\mathrm{d}\theta = mg(x - \gamma)\,\mathrm{d}\sin\theta$. The infinitesimal quasistatic work performed by the system on its environment is given by the average of this expression, namely

$$-\mathrm{d}W^{\mathrm{qs}} = \langle\tau\rangle\,\mathrm{d}\theta = mg\left(\langle x\rangle - \gamma\right)\,\mathrm{d}\sin\theta. \tag{34}$$

The change in the internal energy due to the transformation is given by $\mathrm{d}W^{\mathrm{qs}}$, integrated between 0 and the final value of θ. It is easy to check that it yields again the result (24).

When the rectilinear guide is tilted, the oscillator spring is stretched and its elastic energy is increased. On the other hand, the potential energy of the mass in the gravity field can either increase or decrease, and the resulting total energy change can be of either sign. If $\gamma = 0$, one has, for instance,

$$\Delta E = -\frac{m^2g^2\sin^2\theta}{2k} = -\frac{f^2}{2k}. \tag{35}$$

The authors of [4] claim that this result is inconsistent, because a negative free-energy change (which coincides in our case with the energy change) would imply that the process is spontaneous, and that the spring is unstable, in contradiction with elementary physics. It is clear however that, *if the rectilinear guide is free to rotate around the origin*, the system is indeed unstable: the guide would rotate until it reaches a vertical stand, with the oscillator mass hanging on the spring. Thus, far from being unphysical, the result yields the correct prediction for the physical setup that one is considering. Of course, in an actual experiment, one would *constrain* the guide to being at a given angle θ, and the oscillator will find equilibrium around a point $\langle x\rangle$ given by equation (22).

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I should also like to mention that Mazonka and Jarzynski [9] have exactly evaluated some time ago the distribution of W in the model which the authors of [4] attempt to solve numerically in their letter. It turns out that this distribution identically satisfies Jarzynski's equality.

4. Closing remarks

Following similar reasonings, one is also led to conclude that there is no need to worry even about the presence of an additive time-dependent constant like $g(r)$, which may be safely subtracted out from the estimated free-energy change, if one wishes to get rid of it. I leave the interested readers to work out the details for themselves. We can be assured, therefore, that the misgivings of the authors of [4] are misplaced. The time-dependent Hamiltonian of manipulated systems can be unambiguously defined, and the thermodynamical work is more closely related to the quantity W that appears in Jarzynski's equality than to the one, W_0, that appears in Bochkov and Kuzovlev's one.

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