Complementary expressions for the entropy-from-work theorem

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We establish an expression of the entropy-from-work theorem that is complementary to the one originally proposed by Talkner, Hanggi, and Morillo [Phys. Rev. E **77**, 051131 (2008)]. In the original expression the final energy is fixed, whereas in the present expression the initial energy is fixed.

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In a recent and very interesting work [1] Talkner *et al.* have established the microcanonical quantum fluctuation theorem. They proved that in quantum mechanics one obtains the same fundamental equation that one finds classically: namely,

$$\omega_E(t_0)p_{t_f,t_0}(E,w) = \omega_{E+w}(t_f)p_{t_0,t_f}(E+w,-w), \tag{1}$$

where $\omega_E(t_0)$ and $\omega_{E+w}(t_f)$ are the densities of states at energies E and $E+w$ at times t_0 and t_f, respectively. The symbol $p_{t_f,t_0}(E,w)$ denotes the probability of moving from energy E at time t_0 to energy $E+w$ at time t_f, as a result of a protocol that changes the Hamiltonian from $H(t_0)$ to $H(t_f)$. The symbol $p_{t_0,t_f}(E+w,-w)$ denotes the probability of starting from $E+w$ at t_f and ending up at E at t_0 when the reversed protocol is acted on the system.

Using Boltzmann's definition of entropy,[1]

$$S(E,t) = \ln \omega_E(t), \tag{2}$$

Talkner *et al.* reexpressed Eq. (1) as the microcanonical quantum version of Crook's theorem:

$$\frac{p_{t_f,t_0}(E,w)}{p_{t_0,t_f}(E+w,-w)} = e^{[S(E+w,t_f)-S(E,t_0)]}. \tag{3}$$

Then, by expressing the final energy in terms of the initial energy and work and by integrating the exponentiated initial entropy in Eq. (3) over all possible values of work they were able to prove the following *entropy-from-work* theorem:

$$e^{S(E_f,t_f)} = N_{\rightarrow}(E_f)\langle e^{S(E,t_0)}\rangle_{E_f}, \tag{4}$$

where

$$N_{\rightarrow}(E_f) = \int dE p_{t_f,t_0}(E,E_f-E). \tag{5}$$

We label $N_{\rightarrow}$ with a right arrow to indicate that p_{t_f,t_0} in the integrand refers to the forward protocol.

Note that the entropy-from-work theorem of Eq. (4) is an equality that allows one to extract an equilibrium property (the final entropy) in terms of nonequilibrium work measurements. In particular, by running many experiments that end up with the same energy E_f and by measuring the work that has been performed in each experiment, one is able to extract the value of the final entropy. Of course, since w is a stochastic variable, the initial energy of each experiment is not fixed and one has to sample a certain range of initial energies.

In this Brief Report we would like to point out another nonequilibrium equality that follows from Eq. (3). In this equality the initial energy is fixed rather than the final, and we look for the average exponentiated negative final entropy. We have

$$\begin{aligned}\langle e^{-S(E+w,t_f)}\rangle_E &= \int dw\, p_{t_f,t_0}(E,w)e^{-S(E+w,t_f)} \\ &= \int dw\, p_{t_f,t_0}(E,w)\omega^{-1}_{E+w}(t_f) \\ &= \int dw\, p_{t_0,t_f}(E+w,-w)\omega^{-1}_{E}(t_0) \\ &= e^{-S(E,t_0)}\int dE_f p_{t_0,t_f}(E_f,E-E_f).\end{aligned} \tag{6}$$

By defining

$$N_{\leftarrow}(E) = \int dE_f p_{t_0,t_f}(E_f,E-E_f), \tag{7}$$

we obtain:

$$\langle e^{-S(E+w,t_f)}\rangle_E = N_{\leftarrow}(E)e^{-S(E,t_0)}. \tag{8}$$

This constitutes a second entropy-from-work theorem by means of which we can express the average exponentiated negative final entropy in terms of nonequilibrium measurements of work. The left arrow indicates that p_{t_0,t_f} in the integrand refers to the backward protocol.

So we have established a second entropy-from-work theorem which is not opposed but rather complementary to the theorem (4) provided in [1]. The two complementary theorems can be put in the following symmetric form:

$$\langle e^{-\Delta S}\rangle_{E_f} = N^{-1}_{\rightarrow}(E_f), \tag{9}$$

$$\langle e^{-\Delta S}\rangle_{E} = N_{\leftarrow}(E), \tag{10}$$

where $\Delta S = S(E_f,t_f) - S(E,t_0)$. In the expression given by Talkner *et al.* the final energy E_f is fixed and the average is taken over all processes that would end at that energy. In the expression given here the initial energy E is fixed and the average is over all the processes that start from that energy.

[1] For convenience, we set k_B, Boltzmann's constant, equal to 1.

It is interesting to study the relations between the entropy-from-work theorem and the second law of thermodynamics. With reference to the form in Eq. (8), using the Jensen equality one finds

$$\langle S(E+w,t_f)\rangle_E - S(E,t_0) \geqslant -\ln N_{\leftarrow}(E). \tag{11}$$

Note that the previous equation does not ensure the positivity of the entropy change. In fact, $N_{\leftarrow}(E)$ can be larger than 1, so that $-\ln N_{\leftarrow}(E)$ can be negative. This means that the final expectation of the Boltzmann entropy in Eq. (2) can be lower than the initial value. One example where this happens is the one-dimensional harmonic oscillator with changing frequency. For this system the density of states does not depend on energy and is proportional to the inverse of the frequency. Thus for any protocol of increasing frequency the change in Boltzmann entropy is negative. Recent works [2,3] suggest that the final expectation of microcanonical entropy could be proved to be always larger than the initial value if the alternative definition where the density of states is replaced by the volume of phase space is employed. This has been already proved in general for the canonical initial condition [2,4] and in high-dimensional chaos for the microcanonical initial condition [3]. Nonetheless, no associated entropy-from-work theorem has been reported yet that employs this alternative definition of entropy.

With reference to the form of Talkner *et al.*, Eq. (4), in an analogous way one also finds

$$S(E_f,t_f) - \langle S(E,t_0)\rangle_{E_f} \geqslant \ln N_{\rightarrow}(E_f), \tag{12}$$

which again does not put any constraint to the positivity of averaged entropy change.

To summarize, we have established another form of the entropy-from-work theorem that refers to the case of fixed initial energy. This is complementary to the expression given by Talkner *et al.* where instead the final energy is fixed. The relations between the entropy-from-work theorems and the second law of thermodynamics have been discussed too.

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