Title
Comment regarding "On the Crooks fluctuation theorem and the Jarzynski equality" [J. Chem. Phys. 129, 091101 (2008)] and "Nonequilibrium fluctuation-dissipation theorem of Brownian dynamics" [J. Chem. Phys. 129, 144113 (2008)]

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Comment regarding "On the Crooks fluctuation theorem and the Jarzynski equality" [J. Chem. Phys. 129, 091101 (2008)] and "Non-equilibrium fluctuation-dissipation theorem of Brownian dynamics" [J. Chem. Phys. 129, 144113 (2008)].

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Abstract

The incongruous "unexpected inapplicability of the CFT [Crook's Fluctuation Theorem]" is due to an inexplicable, inappropriate use of inconsistent expressions. The girding is secure.

An important principle of thermodynamics is that the change in internal energy U of a system can be separated (under suitably idealized circumstances) into separate components, heat and work. The essential distinction is that heat flow is associated with a change in entropy of the environment, whereas work is not. For a classical system, in the continuous limit, we can typically write

$$\Delta U(x,\lambda) = \underbrace{\int \left(\frac{\partial U}{\partial \lambda}\right)_x \frac{d\lambda}{dt} dt}_{\text{work, } W} + \underbrace{\int \left(\frac{\partial U}{\partial x}\right)_\lambda \frac{dx}{dt} dt}_{\text{heat, Q}} \ . \tag{1}$$

Here, t is time, W is work, the flow of energy into the system due to a systematic manipulation of a controllable parameter $\lambda(t)$, and Q is heat, the flow of energy from the environment due to an uncontrolled change in the internal microscopic state of the system x. For a fuller discussion, see for example[1].

As an illustrative example, suppose our system-of-interest consists of a rubber band, or, on a microscopic scale, a single polymer, and that we can experimentally control the end-to-end distance L. The work applied to the system due to a controlled change in length is

$$W_L = \int \left(\frac{\partial U}{\partial L}\right)_x \frac{dL}{dt} dt = - \int \mathcal{T} dL \ . \tag{2}$$

In the second equality, we recognize that the change in internal energy U due to an infinitesimal change in length is the tension $\mathcal{T}$, the force the polymer exerts on our apparatus.

On the other hand, suppose that the controllable parameter is the applied tension. The internal energy has the form $U(x,f) = u(x) - \mathcal{T} L(x)$ and the applied work is

$$W_f = \int \left(\frac{\partial U}{\partial \mathcal{T}}\right)_x \frac{d\mathcal{T}}{dt} dt = - \int L d\mathcal{T} \ . \tag{3}$$

Note that the specific functional dependance of work depends on the details of the system. (As, of course, does the free energy change and equilibrium ensemble.) The form of Eq. 2, the integral of force times displacement, is perhaps most familiar. But this form is neither universal nor truly fundamental, since it implicitly requires either, (a) that displacement is under control, or (b) that the system is macroscopic, since in the thermodynamic limit (where fluctuations are relatively small) (2) and (3) are numerically almost identical. In order to obtain consistent results in the general case, we need to refer to the thermodynamic work defined by Eq. 1.

In a recent paper[2], Prof. Chen applied the aforementioned eponymous fluctuation theorem[3] to a rather trivial system, a harmonic spring with an applied, controllable external force. Regrettable, instead of using Eq. 3, the value of work clearly dictated for this system by a careful reading of the original papers, Chen instead calculates work as if the control parameter were length. One can, of course, have a reasonable disagreement over the definition of various terms. But changing definitions half-way through a derivation, as between the implicit definition of work in Chen's Eq. 1, and actually inserted after Eq. 9, leads to erroneous and unwarranted conclusions.

In another recent contribution[4], Prof. Chen considers work for a discrete time Markov dynamic. Here, Prof. Chen's expressions for work fails a basic symmetry requirement; the work is not odd under a time reversal (Eq. 21). Once more, Prof. Chen has inserted his own understanding into the Jarzynski identity and related undergirding, rather than the actual expressions clearly defined in the original papers[3,5,6]. Given inconsistent definitions, any and all conclusion about the applicability of the girding is invalid.

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