On the Crooks fluctuation theorem and the Jarzynski equality

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The Jarzynski equality (JE) and the undergirding Crooks fluctuation theorem (CFT) have generated intense interest recently among researchers in physical and biological sciences. It has been held that the CFT has wider applicability than the JE. This note shows that the two are equally applicable and that their applicability is possibly limited to near-equilibrium processes, where the linear fluctuation-dissipation theorem holds. © 2008 American Institute of Physics.

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The Jarzynski equality¹ (JE) and the undergirding Crooks fluctuation theorem² (CFT) have summoned much interest from researchers in physical and biological sciences. See, for example, Refs. 3–8. This note examines the self-consistency requirements of the CFT and shows that the CFT's applicability is not wider than the JE's. For systems whose dynamics are microscopically reversible, CFT leads to the following formula:²

$$e^{-\beta\Delta G} = \langle f(W_{A\rightarrow B}) \rangle_F / \langle f(-W_{B\rightarrow A}) e^{-\beta W_{B\rightarrow A}} \rangle_R \quad (1)$$

for the equilibrium free energy difference, $\Delta G = G_B - G_A$, between states A and B . Here $\beta = 1/k_B T$. k_B is the Boltzmann constant. T is the absolute temperature. $W_{A\rightarrow B(B\rightarrow A)}$ is the work done to the system when it is driven from state A to state B (driven back from state B to state A). The brackets in the numerator represent the statistical mean among all the forward paths (from state A to state B), and their counterparts in the denominator represent the same among the reverse paths (from state B to state A).

The CFT, referring to Eq. (1), is very remarkable because it holds for an arbitrary finite function $f(W)$. This fact makes it straightforward to check its self-consistency and thus its range of applicability. The well-known choice of $f(W) = e^{-\beta W}$ leads to the JE,

$$e^{-\beta\Delta G} = \langle e^{-\beta W_{A\rightarrow B}} \rangle_F. \quad (2)$$

Now, if one chooses $f(W) = 1$, the same free energy difference must be given by

$$e^{-\beta\Delta G} = 1 / \langle e^{-\beta W_{B\rightarrow A}} \rangle_R. \quad (3)$$

Equations (2) and (3) combine to place a very strong constraint on the system's statistics,

$$\langle e^{-\beta W_{A\rightarrow B}} \rangle_F \langle e^{-\beta W_{B\rightarrow A}} \rangle_R = 1. \quad (4)$$

Equation (4) must be satisfied for the CFT to be valid. Therefore, it gives a range of the CFT's applicability. A model system that violates Eq. (4) will be studied in the latter part of this note.

In order to avoid the difficulty of a formal discussion of CFT's validity based on Eq. (4), one can consider the Gaussian approximation of the statistics. In such a limit, the JE becomes

$$e^{-\beta\Delta G} = \exp\left(-\beta\langle W_{A\rightarrow B} \rangle_F + \frac{1}{2}\beta^2\langle\delta W^2 \rangle_F\right). \quad (5)$$

Meanwhile, the self-consistency requirement, Eq. (4), demands

$$\langle W_{A\rightarrow B} \rangle_F + \langle W_{B\rightarrow A} \rangle_R = \frac{1}{2}\beta(\langle\delta W^2 \rangle_F + \langle\delta W^2 \rangle_R). \quad (6)$$

This is simply the linear fluctuation-dissipation theorem (FDT). Note that the left-hand side gives the dissipative work $\langle W_{A\rightarrow B} \rangle_F + \langle W_{B\rightarrow A} \rangle_R = 2\langle W_d \rangle$. Moreover it is not unusual for the variances over the forward and reverse paths to be equal: $\langle\delta W^2 \rangle_F = \langle\delta W^2 \rangle_R = \langle\delta W^2 \rangle$. In this, one has the familiar form of the linear FDT,⁹

$$\langle\delta W^2 \rangle = 2k_B T \langle W_d \rangle. \quad (7)$$

It should be pointed out that within this range of applicability, the JE gives a result for the free energy difference,

$$\Delta G = \langle W_{A\rightarrow B} \rangle_F - \frac{1}{2}\langle\delta W^2 \rangle_F = \frac{1}{2}(\langle W_{A\rightarrow B} \rangle_F - \langle W_{B\rightarrow A} \rangle_R). \quad (8)$$

Equation (8) is identical to the FR result of Ref. 10 that was derived by using the CFT but without invoking the JE. At this point, it is clear that the range of JE's applicability is not narrower than CFT's. Although JE may be numerically less efficient than CFT, its range of applicability could be, in principle, wider than CFT's. The validity of CFT guarantees the validity of JE, but not vice versa.

Equation (6) does not prove but suggests that the CFT is self-consistent and applicable only when the processes driving a system between states A and B are quasi-equilibrium. This conclusion is consistent with what is concluded on the JE in Ref. 11. In the rest of this note, it will be shown that the self-consistency requirement, Eq. (4) or (6), is violated by a simple system that is driven far from equilibrium.

Reference 12 considers a one-dimensional system consisting of a particle (mass m) attached to a spring (elastic constant k). Its coordinate is $x(t)$ at a given time t . The particle is also subject to stochastic random forces from the environment of temperature T . Therefore, its dynamics is Brownian. A constant force, $\lambda(t) = f_0$ for $0 \leq t \leq \tau$, is applied

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to the system to stretch the particle from state A ($\langle x(0) \rangle = 0$) to state B ($\langle x(\tau) \rangle = f_0/k$). The potential energy is $U(x) = kx^2/2 - \lambda x$. Since the system is linear, its Brownian dynamics is analytically solvable. The free energy difference can be found exactly as

$$\Delta G = f_0^2/2k. \quad (9)$$

Using the conventional force-displacement definition of work, $W_{A \rightarrow B} = \int_0^\tau dt \dot{x}(t) \lambda(t)$, the JE was found¹² to produce an erroneous result for the free energy $\Delta G_B^{(\text{JE})} = 0$.

Now let us examine the self-consistency requirement of the CFT on this model system. Sampling the stochastic paths of transition from state A to state B , the statistical average among the forward paths gives

$$\langle W_{A \rightarrow B} \rangle_F = f_0^2/k, \quad \langle \delta W_{A \rightarrow B}^2 \rangle_F = 2k_B T f_0^2/k. \quad (10)$$

In the same manner, sampling the stochastic paths of transition from state B to state A , the statistical average among the reverse paths yields

$$\langle W_{B \rightarrow A} \rangle_R = 0, \quad \langle \delta W_{B \rightarrow A}^2 \rangle_R = 2k_B T f_0^2/k. \quad (11)$$

Combining Eqs. (10) and (11), one sees that Eq. (6) does not hold for the system. Recalling the Gaussianness of the model system, it is straightforward that the general form of the self-consistency condition, Eq. (4), is violated by the model system.

In summary, this note shows that the CFT does not have a wider range of applicability compared to the JE. An analysis of the CFT's self-consistency suggests that its validity is limited to the near-equilibrium regime. CFT and JE are both invalid for a simple model system driven far from equilib-

rium. This unexpected inapplicability of the CFT may stem from the assumption of microscopic reversibility of the system's dynamics—that the set of forward paths is the same as the set of reverse paths. In the quasi-equilibrium regime, all the important paths are in the close vicinity of the reversible (infinitely slow) path. The assumption of microscopic reversibility should be a good approximation. When the system is driven far from equilibrium, however, such a strong assumption does not seem to be valid. New approaches beyond the CFT and JE are therefore needed.

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