Comment on "Failure of the Work-Hamiltonian Connection for Free-Energy Calculations"

Nonequilibrium work relations establish a connection between nonequilibrium work values and equilibrium free energies. In a recent Letter, Vilar and Rubi [1] (VR) argue that the definition of work used in these relations,

$$W = \int dt \frac{\partial H}{\partial t} = \int dt \dot{\lambda} \frac{\partial H}{\partial \lambda}, \tag{1}$$

is incorrect, and therefore the relations themselves are fundamentally flawed. In our investigations, however, we have reached the opposite conclusion [2], as have Imparato and Peliti [3] in direct response to VR.

In Eq. (1), λ represents generalized coordinates $(a_1, a_2, \cdots)$ describing the external bodies that we manipulate to act on the system of interest; W is the integral of force, multiplied by the displacements of these bodies [4]. Referring to Refs. [2–4] for a broader discussion, in this Comment we illustrate that W has exactly the properties we associate with thermodynamic work.

We consider the model system analyzed in Ref. [1], described by the Hamiltonian

$$H(x; f) = \tfrac{1}{2}kx^2 - fx, \tag{2}$$

and evolving under Langevin dynamics with friction coefficient $\gamma = 1$. The force $f(t)$ is switched on uniformly, from $f(0) = 0$ to $f(\tau) = f_0$; outside the time interval $0 < t < \tau$ the force is held constant. This system evolves from equilibrium state A in the distant past ($f = 0$), to equilibrium state B in the distant future ($f = f_0$). The initial and final Hamiltonian functions and canonical distributions are shown in Fig. 1. Since $H(x; f(t))$ is constant for $t < 0$ and $t > \tau$, its value during these times is identified with the energy of the system [1]. Using the equilibrium distribution $p \propto \exp(-\beta H)$, we compute the internal energy ($E = \int pH$) and the entropy ($S = -\int p \ln p$) for states A and B: $E_A = (2\beta)^{-1}$, $E_B = (2\beta)^{-1} - f_0^2/(2k)$, $S_A = S_B = [1 - \ln(\beta k/2\pi)]/2$. From the thermodynamic definition of free-energy, $G = E - ST$ [5], we then get

$$\Delta G = G_B - G_A = -\frac{f_0^2}{2k}. \tag{3}$$

The negative value of ΔG reflects a decrease in internal energy, with no change in entropy (see Fig. 1).

For this model, the distribution of work values over an ensemble of realizations of the process, $\rho(W)$, can be obtained using the approach of Ref. [6]. This distribution is a Gaussian with mean and variance,

$$\langle W \rangle = -\frac{f_0^2}{2k} + \frac{\beta \sigma_W^2}{2}, \qquad \sigma_W^2 = \frac{2f_0^2}{\beta k^2 \tau}\left[1 + \frac{e^{-k\tau} - 1}{k\tau}\right]. \tag{4}$$

This result implies that: $W \to \Delta G$ for every realization in the reversible limit ($\tau \to \infty$); $\langle W \rangle > \Delta G$ in the irreversible case (finite τ); and $\langle e^{-\beta W} \rangle = e^{-\beta \Delta G}$ for any value of τ. Thus the work defined by Eq. (1) is consistent with the second law of thermodynamics, and its exponential average correctly gives ΔG, when the free-energy is defined by the expression $G = E - ST$.

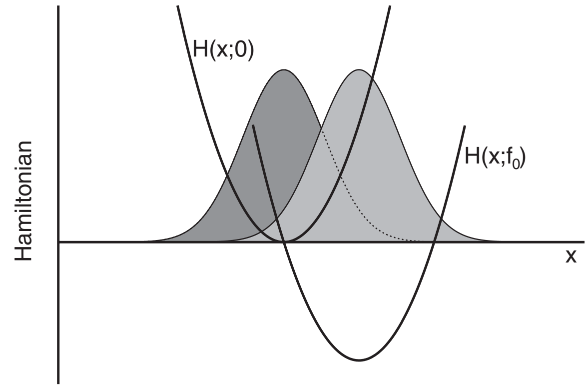

FIG. 1. The Hamiltonian functions and equilibrium distributions (shaded) at $f = 0$ and $f = f_0$.

By contrast, VR obtain $\Delta G > 0$ for this model (Eq. 4 of Ref. [1]), and assert that a negative value would be "inconsistent with a nonspontaneous process." We disagree. An undisturbed system certainly seeks to minimize its free-energy (e.g., after the removal of a constraint), but when an external agent varies a parameter of the system, such as the field f above, then there is no universal restriction on the sign of the free-energy change. For instance, by manipulating a piston we can either increase or decrease the Helmholtz free-energy of a gas, according to whether we compress or expand the gas.

J. Horowitz and C. Jarzynski
University of Maryland
College Park, Maryland 20742, USA

Received 29 January 2008; published 26 August 2008
DOI: 10.1103/PhysRevLett.101.098901
PACS numbers: 05.70.Ln, 05.20.−y, 05.40.−a

[1] J. M. G. Vilar and J. M. Rubi, Phys. Rev. Lett. **100**, 020601 (2008).
[2] C. Jarzynski, C.R. Physique **8**, 495 (2007); J. Horowitz and C. Jarzynski, J. Stat. Mech. (2007) P11002.
[3] A. Imparato and L. Peliti, arXiv:0707.3802v1; L. Peliti, J. Stat. Mech. (2008) P05002.
[4] See, e.g., J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Scribner's, New York, 1902), p. 42; K. Sekimoto, Prog. Theor. Phys. Suppl. **130**, 17 (1998).
[5] The distinction between Gibbs and Helmoltz free energies is not relevant for this model.
[6] O. Mazonka and C. Jarzynski, arXiv:cond-mat/9912121.

