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Comment on "Nonequilibrium Equality for Free Energy Differences"

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The existence of Jarzynski *"equality"* is a direct threat to the second law of thermodynamics. Jarzynski [Phys. Rev. Lett. **78**, 2690 (1997)] uses Liouville equation of motion in dissipative system and derives a relation between ir-reversible work and change in Helmholtz free energy. In this comment, we will underline the flaw that exists in Jarzynski analysis, and thus, we will show that exact relation between ir-reversible works and change in Helmholtz/Gibbs free energy is impossible in any real thermodynamical system.

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Zarzynski derives two contentious equation $(2a, 2b)$ for any thermodynamical system under reversible and in ir-reversible condition. He ignores the fundamental concept in thermodynamics that every directional process evolves under the presence of finite chemical/electrical/magnetic/gravitational potential-energy-gradient. The evolution of any thermodynamics process under the presence of finite-gradient (any-type) in every time-step are highly non-linear and very ir-reversible in nature. Work-done under these schemes are highly speed, path and surrounding configuration dependent. The work done in any ir-reversible process will be *"strictly-greater"* than the change in Gibbs or Helmholtz free energy of the system. Therefore, no direct relation can be obtained between work done under arbitrary condition and the change in Gibbs or Helmholtz free energy. In ir-reversible system, generally, Hamiltonian is not uniquely defines, and thus, calculation of work-done using equation 3, is prohibited. Liouville equation of motion $\frac{\partial f}{\partial t} + \{f, H_\lambda\} = 0$, and phase-space volume conservation are not applicable in any real directional thermodynamic system due to the presence of unavoidable dissipative forces (sink term), which arises after surrounding interaction. In Nose-Hoover (NH) thermostat, the phase-space distribution is stationary till the thermostat present. Thermostat provides the required dissipative energy in ever time-steps and maintain the phase-space volume of dissipative-system. If thermostat is removed, then volume of the phase-space will be shrink. If any physical reservoir supply dissipative energy to the system and maintain volume of phase-space, then, reservoir should also needed to be refiled by some external agency, otherwise reservoir energy will be drained-away and it will not in position to maintain the volume of phase-space. Also, equation $2a, 2b, 3, 4, 6, 7, 8, 9$ and 10, are only applicable in a conservative system in which only conservative force can appear. Every real thermodynamics system (at any-length and time-scale) is a non-conservative, dissipative system, and thus, unique-potentials are not defined. If $t_s \to 0$, then, thermodynamics process will be highly non-linear and concluding anything using equation 5, will be absurd. Equation 11, has no physical explanation that why work done in n^{th}-step should be divided by factorial n. In non-conservative system, equation 13 and 14, have no real physical significance. Also, $\Phi_\lambda(q)$ and $Q_\lambda(\mathbf{z}, \zeta)$ are non-defined in any non-conservative, ir-reversible thermodynamical system (strictly speaking, every thermodynamical system is inherently non-conservative and ir-reversible). Also, perfectly closed and isolated system are impossible in real-life.