

Comment on “Experimental violations of the second law of thermodynamics for small systems and short timescales”

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The experimental verification of the Fluctuation Theorem by Wang et al. is not a violation but even a confirmation of the second law, resulting from their observations in a proper interpretation.

In a recent paper Wang et al.¹ consider a colloidal system and test the validity of the Fluctuation Theorem

$$\frac{\Pr(\Sigma_t = A)}{\Pr(\Sigma_t = -A)} = \exp(A), \quad (1)$$

where Σ_t is the entropy production of a given trajectory of a colloidal particle, equal to the ratio of the dispersed energy and $k_B T$.

This equality is a strong statement about the second law, a field often described by inequalities. It says that the probability for trajectories with positive entropy production is larger than the one with negative production. As such, the theorem and the data of Wang et al show that the *average* entropy production is positive. Indeed, a small exercise yields from Eq. (1)

$$\begin{aligned} \langle \Sigma_t \rangle &= \int_{-\infty}^{\infty} dA A \Pr(\Sigma_t = A) \\ &= \int_0^{\infty} dA A (1 - e^{-A}) \Pr(\Sigma_t = A) \end{aligned} \quad (2)$$

which is obviously positive. The positivity is also clear

from the date presented in ¹.

The statement made by the second law concerns the *average* entropy production, because the second law is related to the *average* heat transfer between system and bath. Thus, opposite to what the authors claim, their data fully confirm the validity of the second law.

This insight in the meaning of the second law goes back to Maxwell, who invented his so-called Maxwell demon with the motivation *to pick a hole in the second law of thermodynamics*, or, more precisely, *to show that the second law has only a statistical nature*^{2,3}. The aim of that exercise was of course that by proving the non-existence of the demon, the second law in its statistical nature would be proven.

It remains to stress that none of formulations of the second law known to us ever claimed that unaveraged entropy production or unaveraged work must be positive; see e.g.^{4,5,6,7,8,9,10}.

We conclude that the statement “violation of the second law” made by Wang et al is not an adequate term for the observed physics.

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¹⁰ A.E. Allahverdyan, and Th.M. Nieuwenhuizen, Physica A **305**, (2002) 542.