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More on the Demons of Thermodynamics

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LETTERS

More on the demons of thermodynamics

In her November 2021 article (page 44), Katie Robertson presents an elegant synthesis of Maxwell's, Loschmidt's, and Laplace's demons. Implicit in the text—and explicit in the conclusion—is the thesis that the second law of thermodynamics remains above reproach. Although that might have appeared to be the case at the close of the 19th and 20th centuries, it is not in the 21st. Since the mid 1990s, at least three dozen potent second-law challenges have advanced into the literature, some with strong experimental support, more than the total proposed during the previous century and a half.[1] One example involves two opposing filaments, each formed from a different material, in a diatomic gas atmosphere at uniform temperature.[2] Due to the different dissociation rates for the diatomic gas at the two surfaces, permanent gradients in pressure and temperature are formed, in apparent conflict with the second law.

The most successful of the newer demons do not suffer the ailments of their ancestors: They are macroscopic in size rather than microscopic, they operate on molecules wholesale rather than individually, and they don't think too much. Typically, they involve thermodynamic spatial asymmetries by which macroscopic energy reservoirs, which are regenerable thermally[2,3] or by other means,[4] are created at one or more of the system boundaries, standard hallmarks of discontinuities in chemical potential. Evidence for such demons should not be overlooked here, especially considering that they undercut the primary thesis of the work.

References

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THE FLAMMARION ENGRAVING has often been used to symbolize humanity's quest for scientific knowledge. (Engraving from Camille Flammarion, *L'atmosphère: météorologie populaire*, 1888, p. 163/public domain.)

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In her article "The demons haunting thermodynamics" (Physics Today, November 2021, page 44), Katie Robertson concludes the introductory historical summary by saying that modern developments in quantum foundations have banished the demons "once and for all." Unfortunately, no explanation or reference is given for that optimistic but controversial conclusion.

Robertson presents Erwin Hahn's 1950 spin-echo experiments[1] as the realization of Josef Loschmidt's vision of reversing momentum. But Hahn clearly described his spin-echo experiments as the effect of traditional spin dynamics for noninteracting spins in a spatially inhomogeneous magnetic field. Although the detailed explanation involves many particular subtleties of NMR dynamics in liquids, Hahn's interpretation does not imply any violation of the "second law"; it uses only the mild assumption that the spin observables are at thermal equilibrium before each start signal. Robertson's misunderstanding clearly appears when she writes that "atomic spins that have dephased and become disordered are taken back to their earlier state by an RF pulse" and, a few lines later, "it turns out that the spin-echo experiment is a special case; most systems approach equilibrium instead of retracing their steps back to nonequilibrium states." The spins have not become disordered: The phase of each spin remains directly related to the magnetic field at the spin's location, and that relationship explains the echo.

Two illuminating articles by Won-Kyu Rhim, Alexander Pines, and John Waugh describe spin-echo experiments in which the irreversible time evolution of a coupled nuclear spin system in solids is apparently "reversed" for a limited duration.[2] As the authors explain, the results arise from uniform spin manipulation and are still consistent with the laws of thermodynamics.

Another aspect of Robertson's article that disturbed me is the lack of discussion of the relations between the actual experiments performed on large (macro-