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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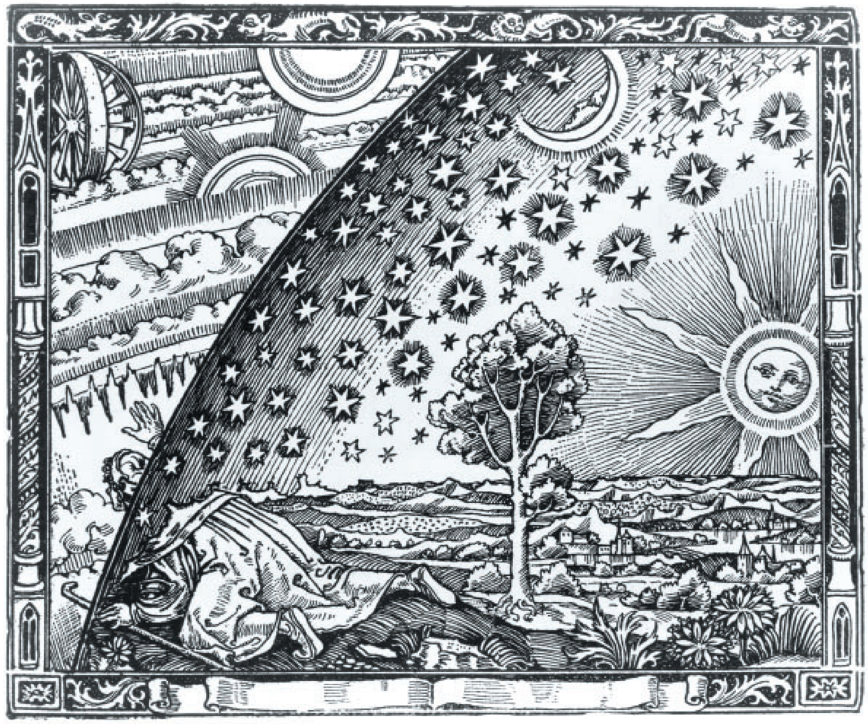

THE FLAMMARION ENGRAVING has often been used to symbolize humanity's quest for scientific knowledge. (Engraving from Camille Flammarion, *L'atmosphère: météorologie populaire*, 1888, p. 163/public domain.)

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 (macroscopic) systems and the microscopic-scale models used in attempts to make predictions about those results.

Consider a mixture of oxygen and hydrogen at atmospheric pressure and room temperature. Standard thermodynamics and statistical mechanics will lead to excellent predictions of the equation of state, specific heat, and the like. But the standard models ignore the possibility of the chemical reaction producing water. Improved models are needed if one is to allow for, say, a slow, isothermal catalytic reaction or—much more complicated—an explosion in an isolated system at constant volume. Spin systems offer a rich variety of experimental possibilities for external manipulation and observation, but the corresponding models are related to the real experimental situations by complicated transformations and approximations that must be chosen according to the situation under study.

Robertson invokes two models in the context of Maxwell's demon. One is a biological machine using a ratchet-style mechanism. But in the cited article, the abstract carefully indicates that the evolution does not violate the second law because the microscopic mechanism is coupled to the exterior of the system.[3] In the demon-style experiment of Robertson's figure 3, a complete realistic discussion of an actual implementation of the experiment leads to the similar conclusion that the second law is not violated.

My conclusion is that demons and the related controversies are features of models and that the interpretation of actual experiments should be subjected to critical examination, preferably by those who performed the experiment and have a complete knowledge of all details.

References

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Katie Robertson's article gives a delightful overview of the vanquishing of demons haunting thermodynamics (Physics Today, November 2021, page 44). We want to add that Maxwell's demon plays a special role in physics apart from concerns about vanquishing. Maxwell's demon reveals a subtle link between information acquisition and thermodynamics.

Over the past two or so decades, that link has provided inspiration for the development of a robust field, stochastic thermodynamics, which enables analysis of the energetics of nonmacroscopic systems with information feedback. Stochastic thermodynamics formalizes what the demon has taught us informally—namely, that information is a resource that can enhance the ability of a system to do work, and erasure of each bit of information in the demon's memory increases entropy by $k_B \ln 2$ (with k_B being Boltzmann's constant), assuring the sanctity of the second law. Without Maxwell's demon, it is questionable whether stochastic thermodynamics and a host of interesting nonmacroscopic experimental results would exist today.

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► **Robertson replies:** Daniel Sheehan, Garret Moddel, and James Lee draw attention to an interesting book, *Challenges to the Second Law of Thermodynamics: Theory and Experiment*, which provides a survey of recent work that throws doubt on the inviolability of the second law. Do those avenues resurrect Maxwell's demon? Do they conjure new ones?

Of course, no scientific law is immutably beyond reproach, no matter how many famous physicists have sworn by it. But in considering the avenues suggested in the book, it can be helpful to scrutinize what we mean by the "second law."[1] If the second law is that entropy—of which there are many forms—cannot decrease, then it can surely be violated; the Boltzmann entropy decreases in macroscopically indeterministic processes. But if the second law is taken to be that no engine is more efficient than a Carnot engine, then at least the previous example is not necessarily a violation.

As David Wallace said in a talk at the University of Cambridge in November 2015, the distinction is between whether we can find ingenious and cunning devices or whether we can solve the energy crisis! The faith in the implausibility of the latter—that we will not find a perpetual motion machine of the second kind—is what those aggrandizing thermodynamics attest to. I meant to have captured that distinction between different kinds of "violations" of the second law in my discussion of "deft illusionists" versus "true magicians." But that may have sounded dismissive; to be clear, important insights are revealed by studying the cases that Sheehan, Moddel, and Lee highlight, especially with respect to how the macroscopic domain may differ from the mesoscopic and microscopic ones. And if there were a true magician, then that would be welcome news in the current energy crisis.

Similarly, whether the spin-echo experiment counts as a violation depends on precisely what we mean by the second law—no one is expecting to create a greater-than-Carnot efficiency engine out of that scenario. The point is merely that a system "retracing its steps" may have seemed nigh on impossible to Josef Loschmidt, but the spin-echo case provides a nice illustration of its feasibility. I am sympathetic to Jean Jeener's view that the spin echo is not a case of increasing and then decreasing entropy, but then again, if we just look at the unitary dynamics, then entropy is neither increasing nor decreasing.

One feature absent from my original article—as rightly emphasized by Harvey Leff and Andrew Rex—is the connection between thermal physics and information forged by Maxwell's demon. That is often the lynchpin or starting place for those interested in quantum thermodynamics (referenced as "quantum steampunk" in my article) and, as Leff and Rex emphasize, stochastic thermodynamics. That brings up a question though: If information is central to thermodynamics, does that raise the specter of anthropocentrism?

Reference

1. For more on this theme, see J. Uffink, in *Time and History: Proceedings of the 28 International Ludwig Wittgenstein Symposium; Kirchberg am Wechsel, Austria 2005*, F. Stadler, M. Stöltzner, eds., De Gruyter (2006), p. 275.

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