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The Second Law of Thermodynamics: Foundations and Status

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Abstract Over the last 10–15 years the second law of thermodynamics has undergone unprecedented scrutiny, particularly with respect to its universal statue. This brief article introduces the proceedings of a recent symposium devoted to this topic, *The second law of thermodynamics*: *Foundations and Status*, held at University of San Diego as part of the 87th Annual Meeting of the Pacific Division of the AAAS (June 19–22, 2006). The papers are introduced under three themes: ideal gases, quantum perspectives, and interpretation. Roughly half the papers support traditional interpretations of the second law while the rest challenge it.

Keywords Second law of thermodynamics · Entropy · Thermodynamics · Statistical mechanics · Ideal gas

Perhaps more has been written about the second law of thermodynamics than about any other physical law. Direct and indirect references to it are found in all branches of science, engineering, economics, literature, psychology, philosophy, art and popular culture. It touches nearly everything from mundane folk wisdom[1] to the physical eschatology of the universe [1, 2]. In the scientific sphere, more memorable lines have been written about its universality than about the law itself. For instance:

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[1] For example: heat goes from hot to cold; a mess expands to fill the space available; if anything can go wrong it will; situations tend to progress from bad to worse; the only way to deal with a can of worms is to find a bigger can.

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> The second law of thermodynamics has the same degree of truth as the statement that if you throw a thimbleful of water into the sea, you cannot get the same thimbleful of water out again. (J.C. Maxwell [3])

> The law that entropy always increases—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation. (A. Eddington [4])

> [Classical thermodynamics] is the only theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown. (A. Einstein [5])

> Nobody can doubt the validity of the second principle, no more than he can the validity of the fundamental laws of mechanics. (L. Brillouin [6])

Unfortunately, such authoritative endorsements probably have done more to impede scientific progress than to advance it because they have fostered a second law mystique that has stifled inquiry into it for more than a century. While certainly the second law must be considered universal—since no experimental violation is currently recognized—it should be remembered that its universality is *contingent* rather than *necessary*. As for any physical law, the second law cannot be proven,[1] only verified in specific instances, and it is universal only insofar as it is experimentally observed to be so.

Over the last decade, roughly fifty papers covering two dozen challenges to second law universality have appeared in the refereed scientific literature; this is more than the combined total over its previous 150 years [7]. Most are purely theoretical, having no experimental embodiments, however some are experimentally testable and a few have laboratory tests either in progress or planned in the near future. At the very least they highlight fundamental issues that are not yet satisfactorily resolved; at worst (or best) they indicate the early stages of a paradigm shift.

Since 2002 several international conferences have addressed or have had special sessions devoted to the second law's status and its many foundational issues, e.g., [8–10]. This volume of Foundations of Physics is the proceedings of the most recent. *The Second Law of Thermodynamics: Foundations and Status* was held at University of San Diego as part of the 87th Annual Meeting of the Pacific Division of the AAAS (June 19–22, 2006). For the sake of this introduction, papers are organized into three categories: ideal gases, quantum perspectives, and interpretation.

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[1] Were the second law provable, it would be merely a theorem of deeper laws.

1 Ideal Gases

The ideal gas is a primary touchstone for the second law. Most modern scientists—as for the giants Maxwell, Boltzmann, Kelvin and Clausius—lean heavily on it for insight and support of their views. Here, three papers consider the ideal gas, however rather than finding support for the second law they find exception. Miller begins by analyzing gas cavities in the molecular flow regime in which anisotropic gas-surface interactions determine gas phase populations. He finds, under the standard constraints of particle flux, momentum and energy conservation, that nonequilibrium steady-state gas phase populations are possible, depending both on the cavity geometry and on the nature of gas-surface interactions.[2] Steady-state nonequilibria of this sort not only confound ordinary expectations for equilibrium, in principle they open the door for the extraction of work from a heat bath in violation of the second law. Miller proposes straightforward laboratory experiments by which his challenges can be tested.

Denur's paper complements Miller's in that it concentrates on the bulk phase of the gas rather than on the gas-surface interface. Also treating the Knudsen regime, Denur shows that at equilibrium the bulk's velocity distribution spontaneously becomes weighted in favor of low-velocity particles, owing to their commensurately greater flight time between wall collisions. Effectively, the bulk gas becomes cooler than the walls, although temperature itself becomes problematic in this case. This challenges the second law both by maintaining a stationary temperature gradient between the walls and gas bulk (which might be harnessed for a heat engine) and because this non-Maxwellian distribution is not the maximum entropy state expected at equilibrium.

From here the discussion moves from the macroscopic down to the microscopic regime as Crosignani and Di Porto consider Callen's classic conundrum: the *adiabatic piston* [11]. In comparing the behavior of a gas cylinder divided by a adiabatic piston (perfect thermal insulator) with that of a diathermal piston (perfect thermal conductor), the authors illuminate the origin of the adiabatic piston's anomalously large random spatial displacements. In particular, they find an unexpected connection with the ratio of the piston mass to the gas particle mass. The adiabatic piston remains an outstanding theoretical problem and, as the art of nanofabrication matures, one with expanding opportunities for laboratory test.

2 Quantum Perspectives

Quantum theory was ignited by an ember of 19th-century thermodynamics: blackbody radiation theory. Here quantum mechanics returns the favor by providing new insights into thermodynamics.

As one of the most significant theoretical developments of the last thirty years, *decoherence* aims to explain the emergence of classicality from quantum reality, as well as to resolve the perennial quantum measurement problem. It is also central to

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[2] The traditional cosine distribution of molecular flux from surfaces is also questioned.

quantum thermodynamics and statistical mechanics. In this proceedings Schulman investigates the road to classical thermodynamic equilibrium via decoherence for pairs of interacting quantum harmonic oscillators.[3] He finds that the final equilibrium density matrices for the oscillators correspond to differing distributions (although their dropoffs are the same), depending on the initial conditions and interaction strengths. These distributions are non-Boltzmannian, indicating a failure of quantum oscillators to achieve equipartition, despite repeated scatterings.

Next, Burns considers the role of quantum vacuum fluctuations in establishing classical equilibrium. Under general conditions for solids, liquids or gases, it is shown that the randomizing effects of vacuum fluctuations over a particle's mean free path, when magnified by collisions at the ends of each path, are sufficient to guarantee an equilibrium bulk momentum distribution within just a few molecular collisions, even though there is no net energy or momentum exchange between vacuum fluctuations and the particle. This approach seems to justify Boltzmann's molecular chaos ansatz and, under appropriate interpretation, offers a general explanation for thermal fluctuations.

Lastly, Berger examines theoretically a system inspired by recent low-temperature condensed matter experiments whose results appear at odds with the second law [12]. Berger's model system consists of a non-uniform superconducting ring immersed in a heat bath near the superconducting transition temperature (hence sensitive to thermal fluctuations) and threaded with magnetic flux. Berger finds, both in analytic and numerical treatments, that the ring sustains a nonzero heat flow, in apparent conflict with the Clausius form of the second law. These results are related to experimental findings by Dubonos, et al. that show non-vanishing voltage drops around non-uniform superconducting rings [12].

3 Interpretation

Statistical physics has a rich interpretational structure, but at times this richness leads to ambiguity and confusion. Nowhere is this more evident than with the second law and the concept of entropy; more than a half dozen types of entropy and a dozen formulations of the second law are in common use [7].

In this proceedings, Leff considers the language and interpretation of entropy, first by examining its common metaphors—e.g., *disorder*, *multiplicity*, and *missing information*—and then, using trenchant examples, by showing that *spreading* (as applied to time, space and energy) offers new and superior insights, especially for the second law. He explores the thesis that *spreading* can be quantified and concludes that the function corresponding to it should have much in common mathematically with entropy.

Continuing in this vein, Duncan and Semura view entropy from the dualistic perspective of information and energy. Specifically, they propose that "energy and information dynamics are independent but coupled" and that "the foundational principle underlying the second law can be expressed: …*No process can result in a net gain*

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[3] These oscillators could model, for instance, atoms in an electromagnetic field or a heat bath.

of information." This formulation mirrors the Kelvin-Planck formulation of the second law in terms of entropy: *No spontaneous process can result in a net decrease in entropy*; however, the authors argue that the information formulation "appears to be deeper and more universal than standard formulations of the second law."

In the final paper, second law status intersects biology. Life on Earth is a 3.8 billion year-old unbroken chain of steady-state nonequilibrium carbon-based systems that has transformed the landscape of our planet with geologic force. It is the second law's greatest creation. In the final paper, a case is made for a third category of life—thermosynthetic life—which, unlike the two traditional types (photosynthetic and chemosynthetic), does not rely on free energy sources (light or high-energy chemical reactions); rather, it relies solely on thermal energy from its environment. If the second law is indeed violable, then it is plausible that life has found ways to exploit its loopholes. Building upon known biochemical mechanisms and biological structures, as well as upon ideas from recent second law challenges [13, 14], Sheehan presents a plausibility argument for thermosynthetic life and suggests how it might be sought among currently known extremophiles.

4 Conclusion

The nine papers of these proceedings trace the temporal arc of the second law, from Boltzmann's 19th-century molecular chaos ansatz through 21st-century decoherence theory. They reaffirm the worth of its touchstones, while at the same time question its foundations. Although the sway of the second law now spans three centuries, its ongoing universal status is more in question today than at any time since it was enunciated by Kelvin and Clausius. Perhaps this is as it should be since, for any vital science, *…the end of all our exploring will be to arrive where we started and know the place for the first time* [15].

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References

1. Dyson, F.J.: Time without end: physics and biology in an open universe. Rev. Mod. Phys. **51**, 447 (1979)
2. Adams, F.C., Laughlin, G.: A dying universe: the long-term fate and evolution of astrophysical objects. Rev. Mod. Phys. **69**, 337 (1997)
3. Maxwell, J.C.: In Strutt, R.J. (ed.) Life of John William Strutt, Third Baron Rayleigh, pp. 47–48. Arnold, London (1924)
4. Eddington, A.: The Nature of the Physical World. Everyman's Library, London (1929)
5. Einstein, A.: Autobiographical notes. In Schilpp, P.A. (ed.) Albert Einstein: Philosopher-Scientist, vol. 2, Cambridge University Press, Cambridge (1970)
6. Brillouin, L.: Life, thermodynamics, and cybernetics. Am. Sci. **37**, 554 (1949)
7. Čápek, V., Sheehan, D.P.: Challenges to the Second Law of Thermodynamics: Theory and Experiment. Fundamental Theories of Physics Series, vol. 146. Springer, Dordrecht (2005)

8. Sheehan, D.P. (ed.) AIP Conference, vol. 643, First International Conference on Quantum Limits to the Second Law, University of San Diego, 28–31 July, 2002, AIP Press, Melville (2002)
9. Nieuwenhuizen, Th.M., Keefe, P.D., Špička, V. (eds.) Physica E **29**(1–2), Frontiers of Quantum and Mesoscopic Thermodynamics, Prague, Czech Republic, 26–29 July, 2004, Elsevier, Amsterdam (2005)
10. Meeting the Entropy Challenge, Massachusetts Institute of Technology, 4–5 October 2007
11. Callen H.B.: Thermodynamics. Wiley, New York (1960) p. 321
12. Dubonos, S.V., Kuznetsov, V.I., Nikulov, A.V.: Observation of dc voltage on segments of an inhomogeneous superconducting loop, http://arxiv.org/abs/physics/0105059
13. Sheehan, D.P., Wright, J.H., Putnam, A.R., Perttu, E.K.: Intrinsically biased, resonant NEMS-MEMS oscillator and the second law of thermodynamics. Physica E **29**, 87 (2005)
14. Sheehan, D.P., Wright, J.H., Putnam, A.R.: A solid state Maxwell demon. Found. Physics **32**, 1557 (2002)
15. Eliot, T.S.: Four Quartets. Harcourt Brace and Co., San Diego (1943)