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3-1-2004

# The Second Law Mystique

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### Digital USD Citation

Nikulov, Alexey V. and Sheehan, D. P., "The Second Law Mystique" (2004). *Physics and Biophysics: Faculty Publications*. 21.  
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*Editorial*

## The Second Law Mystique

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*Received: 1 March 2004 / Accepted: 10 March 2004 / Published: 31 March 2004*

Over fifty years ago Arthur Eddington wrote [1]: “*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 do 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*”.

Although this is perhaps the most famous endorsement of the second law, it is certainly not the only one; in the works of Einstein, Planck, Maxwell, and other luminaries one can find similarly strong imprimaturs. Common to them is an almost mystical faith in the law's inviolability. Aside perhaps from the standard conservation laws, no physical axiom engenders more support from the scientific community. The reasons are not hard to list. No experimental violation of the second law has been recognized by the scientific community in over 150 years; meanwhile, it has been confirmed in countless experiments and natural phenomena. Absolute inviolability is intellectually satisfying. One should also not discount the power of peer pressure; like most paradigms, the second law is understood deeply by few and taken on faith by most. Such faith is cemented by many famous endorsements and is so deeply rooted in a century and a half of cultural legacy that it has put the second law nearly beyond the reach of serious scientific discussion. Taken together, these constitute what may be called the second law mystique.

Despite the deeply rooted belief in its absolute status, the second law has always had surprisingly shallow roots. Despite vaunted claims to the contrary, it does not have a fully satisfactory theoretical proof; therefore, its absolute status has always been questionable and contingent and, like all good

laws, it is falsifiable in the Popperian sense. Second, since its discovery, physics has undergone multiple paradigm shifts - e.g., quantum mechanics, relativity, chaos - that have revolutionized our view of reality, and yet the second law has emerged essentially unchanged from its classical roots and has been inadequately tested in many new experimental regimes where it should apply. Lacking full theoretical or experimental support, it is epistemologically unsound to presume it at the level to which the scientific community has become accustomed. Third, there are more than a half dozen common statements of it - dating back to Clausius and Thomson and, in spirit, to Carnot 180 years ago - not all of which are equivalent. As quipped by Clifford Truesdell, "Every physicist knows exactly what the first and second law mean, but it's my experience that no two physicists agree on them". From a purely logical standpoint, this Babel-like understanding is intolerable - but this situation has not only been tolerated by the scientific community, it has been embraced. Sensing some of these difficulties, there have been some serious attempts to render the second law axiomatic in recent years [2,3].

The foundation of the second law mystique rests on the presumed impossibility of the perpetual mobile. The belief in its impossibility can be traced back to Leonardo da Vinci and before. It guided the development of thermodynamics in the 19th century and much of statistical physics since. Carnot's principle (1824) is such a statement [4]: Useful work cannot be obtained from heat without a temperature difference since such possibility implies the possibility of a perpetual mobile. It was obvious in Carnot's time that heat could be employed to perform work and it was obvious that kinetic energy degraded spontaneously into heat; it was also understood that if heat could be regraded into directed kinetic energy that a perpetual mobile would be possible. Thus, the impossibility of a perpetual mobile requires that heat cannot be transformed solely into work; rather, work requires a temperature gradient be present and that waste heat result.

Thus, a very tidy formulation of the second law can be established from Carnot's investigations: "A perpetual mobile is impossible because of the irreversibility of thermodynamic processes". The utility and power of this formulation rests in the thrift and clarity of its terms. In contrast, both the Clausius (1850) and Thomson (1851) formulations are couched in terms of irreversible thermodynamic processes that require additional definitions. In the Clausius formulation, heat energy cannot be transferred from a cold body to a hot body without an expense of additional energy. In the Thomson formulation it is impossible to obtain useful work by cooling of a body with lowest temperature. These formulations depend on the terms "hot," "cold," and "a body with lowest temperature." These formulations are not equivalent. A challenge to the temperature determination may threaten, for example, the Clausius formulation but not the Carnot one.

The first and second laws are the bones and the flesh of thermodynamics; by comparison, the zeroth and third laws are mere hat and slippers. The first gives structure and the second gives life. With regard to the first law, energy is sufficiently malleable a concept that the first law is essentially inviolable; that is, were a first law violation to loom, energy could be simply redefined to make it go away. In other words, since energy is essentially a bookkeeping device for describing physical processes, one can always 'cook the books' to guarantee first law compliance. Such a trick is not so easy with the second

law. Granted, entropy is at least as slippery a concept as energy, but there are plenty of second law formulations that do not appeal to entropy and that make reference to sufficiently well-defined physical processes that there is little room for equivocation. Thus, in terms of falsifiability and applicability, the second law stands above the rest.

Violation of the second law would allow construction of a perpetual mobile. Ostwald called such a device a perpetual mobile of the second type. His formulation of the second law in terms of its impossibility (1877) is operationally equivalent to Carnot's over five decades earlier (1824). If one traces the development of the second law and various formulations of it, virtually all lead back to the belief in the impossibility of perpetual mobile. In this sense, it is the gold standard of second law formulations.

The demand for irreversibility stemming from the impossibility of perpetual mobile underlies the well known collision between dynamics and thermodynamics in the late 19th century. Most 19th century scientists rejected the atomic-kinetic theory of the heat proposed by Maxwell and Boltzmann [5] in part because of this collision. The probabilistic interpretation of the second law championed by Maxwell and Boltzmann overcame this impasse and their interpretation has come to dominate present day thinking [6]. Indeed, their reasoning is convincing: it is not every microscopic state of a macroscopic system that will evolve in accordance with the second law, but that the majority of states will, and since this majority becomes so overwhelming when the number of atoms in the system becomes very large, irreversible behavior of a macroscopic system becomes a near certainty [6].

But does a very large number of degrees of freedom (atoms) for a system ensure the absolute validity of the second law? Maxwell wrote [7], "the second law is drawn from our experience of bodies consisting of an immense number of molecules". Ironically, this same Maxwell raised the first challenge to its absolute status. Initially, Maxwell's doubts about the compatibility of dynamics and thermodynamics were connected with his belief that the temperature of a gas under gravity should vary inversely with the height of the column [8]. Second law debates about the role of gravity on gas velocity distributions were continued by Loschmidt, Boltzmann and others, and they continue to the present day [9].

Maxwell's most famous challenge was his "neat-fingered being" who could make a hot system hotter and a cold system colder without performing any work via the sorting atoms on a microscopic level. In 1874, Thomson christened it Maxwell's "demon" - although it is really more of just a heat fairy. Various incarnations of this demon have appeared in the scientific literature for more than 130 years. It has become one of the most beloved and productive touchstones in science, sparking important contributions and insights not only in thermodynamics but also in disparate other fields including information theory, biology, computer science, philosophy, and economics. H. Leff and A. Rex have compiled two fine anthologies on the subject [10,11].

Most authors of this special issue of Entropy were participants in the First International Conference on Quantum Limits to the Second Law (QLSL2002) held at the University of San Diego, July 29-31, 2002, which brought together over 120 researchers, representing 25 countries to discuss the current

status of the law in light of recent theory and experiment. That it appears to have been the first conference of its type in history is telling, given the central role the second law plays in all fields of science. That challenges can finally be discussed openly suggests the emergence of a new field of study. In some sense, this special issue of Entropy can be considered as a continuation of the San Diego discussions.

Between one and two dozen challenges to the second law have been proposed over the last 10 years. These represent the work of about a dozen independent research groups and individuals worldwide and can be found in roughly 40 papers in the refereed scientific literature. The reader is directed to the Bibliography at <http://www.sandiego.edu/secondlaw2002/>, the AIP Conference Proceedings 643 "Quantum Limits to the Second Law" <http://proceedings.aip.org/proceedings/confproceed/643.jsp> and the papers at <http://www.ipmt-hpm.ac.ru/SecondLaw/>. Limits to the second law were discussed in the last year at the Workshop "Hot Topics in Quantum Statistical Physics: q-Thermodynamics, q-Decoherence and q-Motors" (Leiden University, August 11 -16, 2003) <http://www.lc.leidenuniv.nl/lc/web/2003/20030811/info.php3?wsid=77>. Further discussion are expected this year at the EPS Satellite Conference "Frontiers of Quantum and Mesoscopic Thermodynamics" (Prague, 26-29 July 2004) <http://www.fzu.cz/activities/conferences/fqmt04/index1.php>. Finally, a monograph entitled "Challenges to the Second Law of Thermodynamics" is slated to appear as part of Kluwer's "Fundamental Theories of Physics" series in 2004 [12].

The first article of this special issue, Craig Callender's ("A collision between dynamics and thermodynamics") maps "the logical geography of the underworld of physics," the realm of Maxwell's demon. Although largely philosophical and historical in content, this lively article lays bare some of the fundamental logical-philosophical issues that both sides of the debate have often preferred to sweep under the rug. As such, he performs perhaps the most critical of jobs: exposing presuppositions and logical inconsistencies such that a sound debate can occur. The author notes that the arguments by defenders of the second law are often flawed, incomplete, or even circular. (For example, the exorcisms of the Maxwell demon by Szilard [13] and Landauer [14] are based on the inadmissibility of second law violation - circular reasoning.) Meanwhile, he cautions detractors of the law not to fall into the same types of traps as the defenders. As he notes, there's something here to 'offend everyone.'

Circular arguments about impossibility of second law violation abound. For a modern case in point, consider the quantum mesoscopic phenomenon of persistent current, i.e. direct current observed under equilibrium conditions investigated by one of the editorial authors (A.N.). It has been known for over forty years that persistent currents can be observed at non-zero resistance. Based on quantum theory and as corroborated in numerous experiments, a direct current in the equilibrium state can be maintained at non-zero power dissipation [15]. This is a clear threat to the second law, however, when confronted with this persistent current observed at non-zero resistance, the author found that most scientists simply stated that such an equilibrium phenomenon could not threaten the second law since no work can be extracted from the equilibrium state (see Discussion in [16]). Clearly, the defending statement is itself a formulation of the second law, rendering the argument circular. The free energy  $F =$

$E - ST$  has minimum value in the equilibrium state and it is impossible to decrease in value below its minimum. But the internal energy  $E$  can be decrease without any decrease of the free energy at non-zero temperature  $T > 0$  if the entropy  $S$  decreases at the same time. As this anecdote shows, in defending the second law, one must be careful not to implicitly assume it, but this is often not as easy at it looks. As recounted by Callender, even luminaries such as Szilard - in his analysis of a mechanical Maxwell demon - fell prey to such circular reasoning.

In the second paper "The deep physics behind the second law: Information and energy as independent forms of bookkeeping" by T. L. Duncan and J. S. Semura discuss the possibility that the foundation of the second law may lie the finite capacity of nature to store information about its own state. They propose a classification of second law challenges within this context. This is a necessary project, given the many various and disparate second law challenges that currently exist. At present, challenges span classical and quantum physics; they can be found from temperature approaching absolute zero to high temperature plasma systems; in size they have been considered from molecular to planetary dimensions. Hopefully, all can be understood under some general rubric.

The their paper, "Thomson's formulation of the second law for macroscopic and mesoscopic work sources," A.E. Allahverdyan, R. Balian, and Th. M. Nieuwenhuizen present a simple proof of the Thomson version of the second law -- no work can be extracted from an equilibrium system by means of a cyclic process generated by an external work source - for macroscopic systems and contrasts it with the results for finite systems, comparing it to the Clausius formulation. These researchers have been among the most fastidious in discriminating between the various second law formulations. In doing so, they are laying a solid, logical groundwork upon which valid future debates can be conducted.

L.G.M. Gordon is one of the pioneers in second law studies, having raised several biochemically-inspired challenges for the last 25 years. In his paper "The decrease in entropy via fluctuations" he argues that the intelligence in the Szilard's device can be quite generally replaced by an unintelligent mechanism. The information gathering or measurement are not essential in this case, thus sidestepping issues of information theory, and thereby reducing the problem to one similar to the ratchet-pawl combinations considered by Feynman [17] and Smoluchowski [5]. In "Maxwellian valves based on centrifugal forces," Gordon explores the hypothesis that centrifugal forces can trigger conformational changes in large enzymatic biomolecules such as to create Maxwellian-like one-way valves for molecules at a single temperature. Via appropriate valving, this can result in spontaneous density gradients, in violation of the second law. Gordon continues his attack with "Smoluchowski's trapdoor," in which he argues that a simple gate biomembrane could also generate spontaneous density gradients. One of the signatures of Gordon's programme is to take dead-aim on the principle of detailed balance. Later workers like Capek and Sheehan independently raised second law challenges with anti-detailed balance themes, but Gordon must be acknowledged as the prime exponent of this approach. His arguments are compelling and, if correct, open the door to biologically-based second law challenges. Taken to their logical conclusion, they suggest that life itself might have the capacity to subvert the second law under suitable conditions.

The interpretation of the second law and its violations continue to be sources of confusion and controversy. For example, the authors of [18] purport to demonstrate experimental violations of the second law in small systems for short time scales, whereas others claim these experimental results are not a violation of the law, but actually confirm it [19]. The system in [18] does not differ qualitatively from the one considered by M. Smoluchowski ninety years ago in "Validity limits of the second law of thermodynamics" [5]. Random entropy decreases by small systems for short times does not contradict the modern interpretation of thermodynamics and is not considered by most scientists to be a threat to the second law; only systematic reductions in total entropy are generally considered valid challenges. Such systematic reductions are possible if Brownian motion is not quite chaotic or could be made ordered under equilibrium conditions.

Whether the random molecular motion of heat can be rectified into the ordered motion of work is perhaps the single most pressing question involving the second law. Theoretical systems for achieving this can be divided into nonsentient types (e.g., the ratchet-pawl) and sentient types (e.g., the classical Maxwell demon). Information gathering and measurement are not essential for the first type and are critical problems for the second. The nonsentient types have become increasingly popular in recent years largely because advances in information theory over the last few decades (e.g., Landauer principle) have essentially put to rest the possibility for sentient demons. Nonsentient types are considered in the papers: "The adiabatic piston: a perpetuum mobile in the mesoscopic realm" by B. Crosignani, P. Di Porto, and C. Conti; "Langevin approach to the Porto system" by J. Bok, V. Capek; "From randomness to order" by J. Berger; "Modified Feynman ratchet with velocity - dependent fluctuations" by J. Denur, "A Maxwellian valve based on centrifugal forces" and "Smoluchowski's trapdoor" by L.G.M. Gordon. The problem of the entropy change during information gathering and measurement is considered by M. Devereux in "A modified Szilard's engine: measurement, information, and Maxwell's demon".

Theory and experiment reveal a profound logical connection between the second law and symmetry. For instance, because of spatial symmetry the velocity distribution function in the standard equilibrium state does not depend on the velocity direction of particles. Therefore, the average velocity should be zero for a continuous spectrum of permitted states; that is, for any state with velocity  $v$ , there should also be a permitted state with velocity  $-v$  with equal probability. Or, for instance, the Nyquist noise has the same power density  $W_{Nyq} = k_B T \Delta \omega$  at any frequency  $\omega$  up to the quantum limit  $\omega \ll (k_B T)^2 / \hbar$ ; that is, no frequency dominates in an equilibrium noise spectrum. For such reasons as these, symmetry is a powerful argument against attempted second law violations consisting of directed motion or preferred states at thermal equilibrium. Jorge Berger considers several, including Smoluchowski's trapdoor, Brownian motors, and Parrondo's games, but finds them wanting. He likens the Brownian motion in a classical, asymmetric, time-changing potential to the quantum phenomenon observed in an asymmetric superconducting loop [20], but there are fundamental and crucial differences between these two cases. The Brownian motor achieves ordered motion because the asymmetric, time-varying potential drives particles in one direction, whereas in superconducting loop the ordered motion of the persistent current exists without any directed force; rather, it arises because of a discrete spectrum of permitted states in

the momentum circulation of quantum particles [15]. Fundamentally, the Brownian motor is classical mechanical, while the persistent supercurrent is inherently and uniquely quantum mechanical. In their contribution "Langevin approach to the Porto system," Jiri Bok and Vladislav Capek consider the possibility of unidirectional motion under equilibrium conditions for a molecular rotor along a linear track due to Coulomb interactions. (Vladislav Capek was outstanding scientist whose challenges to the second law (for example [21-30]) were visionary and whose significance will become increasingly apparent with time.) Jack Denur considers broken velocity symmetries leading to second law violations in "Time evolution of a modified Feynman ratchet with velocity-dependent fluctuations and the second law of thermodynamics". This is a continuation of a theoretical research programme spanning over 20 years. Like Gordon, Denur is one of the pioneers in the field. Here he presents his clearest and most detailed challenge yet.

Low-temperature quantum systems have emerged in the last several years as some of the most cogent challenges to the second law. Among these, superconductors have been at the forefront. In "Second law violation by magneto-caloric effect adiabatic phase transition of type I superconductor particles," P. Keefe presents an experimentally-testable challenge. In reviewing Keefe's proposal several years ago, one of the authors of the modern theory of superconductivity - the "B" in BCS, John Bardeen -believed superheating should be present at any first order phase transition. Indeed, appropriate superheating resulting from latent heat would prevent the second law from being broken at this transition. However, it is not clear that a first order phase transition would generate the necessary superheating in this case since Keefe's transition is a coherent quantum mechanical process. Anomalous magnetization behavior in small superconductor particles has been recognized recently (see for example [31]).

The Carnot principle - arising from a historic resistance to perpetuum mobile - has profound consequences for vast areas of the physical sciences, engineering and technology. The second law bears on classical and quantum physics, problems of phase transition and gravity, stars and biological systems. The paper "A Concise Equation of State for Aqueous Solutions of Electrolytes Incorporating Thermodynamic Laws and Entropy" by Raji Heyrovska is devoted to thermodynamics of a classical system. The problem of irreversibility in view of decoherence, dephasing and dissipation in quantum systems is explored by H. Yamada in "Delocalization and sensitivity of quantum wavepacket in coherently perturbed kicked Anderson model." The close connections between the second law, entropy and gravitation are discussed by S. De Filippo and F. Maimone in "Entropic localization in non-unitary Newtonian gravity." A generalization of thermodynamics with an eye toward the origin of irreversibility and the second law is illuminated by D.H.E. Gross in "A new thermodynamics from Nuclei to Stars." R. Leandre develops a mathematical description of Brownian motion in "Markov property and operads." The thermodynamics of zero-point electromagnetic radiation is considered by Jiri Mares, Vaclav Spicka, Jozef Kristofik and Pavel Hubik in "On Expansion of a Spherical Enclosure Bathed in Zero-Point Radiation". Can order arise from disorder without an external influence? This is one of the deepest questions connecting Nature to the second law. A part of this question – the



possibility of the Darwinian mechanism of the evolution as a random process - is evaluated in the paper "Internal Structure of Elementary Particle and Possible Deterministic Mechanism of Biological Evolution" by Alexei Melkikh.

When Arthur Eddington wrote, "The second law of thermodynamics holds the supreme position among the laws of Nature," he did so with an appreciation of its universal applicability, but also under the assumption of its absolute validity. Now nearly a century separated from him, we affirm his appreciation, but question his assumption. The present status of second law research, both theoretical and experimental, is such that one can no longer legitimately or unequivocally claim its absolute validity in all physical regimes. Every major formulation of it has come under credible theoretical attack; several experiments are currently either in progress or are planned, one or more of which could soon provide strong evidence either second law violability (in principle) or outright violation. After more than a century of presumption, the second law's absolute status is now properly an open question. It is to this question that this special issue is devoted.

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