

1-1-2008

Energy, Entropy and the Environment (How to Increase the First by Decreasing the Second to Save the Third)

D. P. Sheehan

University of San Diego, dsheehan@sandiego.edu

Follow this and additional works at: <http://digital.sandiego.edu/phys-faculty>



Part of the [Physics Commons](#)

Digital USD Citation

Sheehan, D. P., "Energy, Entropy and the Environment (How to Increase the First by Decreasing the Second to Save the Third)" (2008). *Physics and Biophysics: Faculty Publications*. 5.
<http://digital.sandiego.edu/phys-faculty/5>

This Article is brought to you for free and open access by the Department of Physics and Biophysics at Digital USD. It has been accepted for inclusion in Physics and Biophysics: Faculty Publications by an authorized administrator of Digital USD. For more information, please contact digital@sandiego.edu.

Energy, Entropy and the Environment (How to Increase the First by Decreasing the Second to Save the Third)

D. P. SHEEHAN

*Physics Department, University of San Diego, San Diego, CA 92110
e-mail: dsheehan@sandiego.edu*

Abstract—Energy is the lifeblood of civilization, but inexpensive, high energy density sources are rapidly being depleted and their exploitation is severely degrading the environment. This paper explores a radical solution to this energy-environmental dilemma. In the last 10–15 years, the universality of the second law of thermodynamics has fallen into serious theoretical doubt [1–3]. Should it prove experimentally violable, this would open the door to a nearly limitless reservoir of ubiquitous, clean, recyclable energy. If economical, it could precipitate paradigm shifts in energy production, utilization and politics. In this paper, recent challenges to the second law are reviewed, with focus given to one for which laboratory experiments are planned. Possible consequences of its violation for technology, society and the environment are explored.

Keywords: entropy—energy—second law of thermodynamics—climate change—environment—ecology—energy economy—famine

1 Introduction

Energy makes the world go round—physically, chemically, thermodynamically, industrially, economically, geopolitically. Current global consumption stands at roughly 1.5×10^{13} W, equivalent to the output of about fifteen thousand large nuclear power plants, or comparable to detonating a WWII-style atomic bomb every five seconds. This figure is expected to grow 50% in the next 20 years. About 20% of the world economy is devoted to the discovery and extraction of fuels, and to the generation, distribution, and consumption of energy. Economies are defined by it; wars are fought over it; nations rise and fall by it.

Presently, energy is derived primarily from non-renewable oil, natural gas, coal, and uranium, and to a lesser degree from renewable hydroelectricity, solar, wind and biofuels. The burning of fossil fuels is implicated in environmental pollution, global warming, climate change, and the degradation of the biosphere, all of which are expected to worsen in coming decades [4]. Recently, the tightening of global energy supplies has been linked to food shortages, affecting hundreds of millions of humans worldwide.

In fact, we are surrounded by a virtually limitless reservoir of energy: *thermal energy*. The total thermal energy content of the Earth's atmosphere is about

10^{24} J; the oceans' capacity is 500 times greater, and the Earth's crust holds an order of magnitude still more. At civilization's current rate of use, it would take millions of years to expend this amount, and even then, it is being replenished by solar radiation and the decay of radionuclides in the crust orders of magnitude faster than humanity could deplete it; in other words, the amount of thermal energy is effectively limitless. In magnitude, all the energy we could ever use already surrounds us; in form, however, it is largely beyond our reach – like a mirage in the desert – because of what is perhaps the most depressing law of nature: the second law of thermodynamics.

The second law has been called “the supreme law of nature” [5]. It governs our lives from the moments of our conception until our deaths; nearly every system in the universe, from an atomic nucleus to a galactic supercluster, is subject to it; the cosmos itself lives – and will eventually die – by it. Even the direction that time progresses, from past to present to future, has been attributed to it [6–9].

Among physical laws, arguably none is better tested than the second law. It has been verified in countless experiments for more than 150 years. Most scientists consider its universality beyond reproach; even to question it invites ridicule and ruin. Nonetheless, over the last 10–15 years, the second law has come under unprecedented scrutiny. More than 60 mainstream journal articles, monographs and conference proceedings have raised dozens of theoretical and experimentally-testable challenges to its universal status – more than the sum total during its previous 150-year history. From a Kuhnian perspective this suggests a paradigm shift might be on the horizon [10].

Given its central importance to the sciences, engineering and technology, in view of these recent theoretical developments, and in light of the current dilemmas facing world energy and environmental policies, it is timely to look ahead to possible changes that might result from second law violation. This paper briefly reviews recent second law challenges, and examines in detail one for which laboratory experiments are currently being mounted. Possible economic, geopolitical and environmental outcomes of second law violation are considered.

2 Second Law: Status and Challenges

2.1 Background

The second law was first enunciated by Clausius (1850) and Kelvin (1851), largely based on the work of Carnot 25 years earlier. There are several fine accounts of its history [11–14]. Once established, the second law settled down and multiplied wantonly¹; it has more common formulations than any other physical law. Some versions overlap, while others seem to be entirely distinct laws. Despite this Drinianian ambiguity, there is near universal agreement that, whatever it is, the second law is inviolable.

Here we introduce three standard formulations: two from classical thermo-

dynamics and a third from statistical mechanics. The first explicit and most widely cited formulation is due to Kelvin [15,16]:

Kelvin-Planck: No device, operating in a cycle, can produce the sole effect of extraction of a quantity of heat from a heat reservoir and the performance of an equal quantity of work.

In this, its most primordial form, the second law is an injunction against *perpetuum mobile* of the second type. Such a device could transform heat into useful work, in principle, indefinitely.

The second most cited version, and perhaps the most natural and experiential, is due to Clausius [17]:

Clausius-Heat: No process is possible for which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at a higher temperature.

In the vernacular: heat flows from hot to cold. A statistical formulation can be expressed in terms of entropy [16]:

Planck: For any spontaneous natural process, the entropy change of the universe is never negative; *i.e.*, $\Delta S_{\text{universe}} \geq 0$.

Though simply put, these statements are profound because they assert that work (organized energy) degrades inexorably into a disorganized, less useful form: thermal energy (heat). They guarantee that heat is difficult to reorganize back into work – and even trying just wastes more energy and generates more entropy than if the effort had never been made. Dealing with the second law is a “no win” situation. In truth, the best strategy against its ravages seems to be to do nothing at all.²

2.2 Recent Challenges

Although the question of second law universality has been considered settled by the wider scientific community for more than a century, there has always been an undercurrent of doubt, sustained by the unproven and admittedly incomplete foundations upon which it rests. In recent years this doubt has grown into a movement to examine more critically the second law foundations [18], integral to which has been the advancement of more than two dozen counter-examples to its universality by several research groups worldwide [1–3]. While *experimental* violation of the second law has not been claimed, experimentally testable challenges have been advanced, a number of which have laboratory corroboration of their critical underlying processes.

Second law challenges are diverse; they span classical and quantum mechanical regimes, range from nanoscopic to planetary in size, operate from above the melting point of steel down to a fraction of a degree above absolute zero. They make use of ideal gases, plasmas, semiconductors, superconductors, micro- and mesoscopic electrical circuits, chemical catalysts, and biologically-inspired structures. Perhaps not surprisingly, most inhabit physical regimes that were

unheard of when the second law was introduced by Clausius and Kelvin in the 1850s, but which are now routinely realized in the laboratory.

The modern second law movement began quietly 30 years ago with the seminal work of L. G. M. Gordon and J. Denur. Gordon considered theoretical chemical-mechanical systems apparently inspired by biological structures like cell membranes, molecular motors and ion channels. Through these he demonstrated that the principle of detailed balance was suspect [19–25]. Denur focused on the microscopic kinetics of ideal gases, which have traditionally been touchstones for second law universality, pointing out inconsistencies in the paradigmatic stance [26–30]. Most recently he has shown that at equilibrium, an ideal gas' velocity distribution spontaneously becomes weighted in favor of low-velocity particles, owing to their commensurately greater flight time between wall collisions [30]. Effectively, the bulk gas becomes cooler than the walls – a problem for the Clausius form of the second law. Both Gordon and Denur remain active in the field today.

Beginning in the mid-1990s, the number and variety of challenges burgeoned as multiple research teams entered the field. Čápek et al. were the most prolific, posing a broad spectrum of quantum theoretic challenges [31–46]. Their models are noteworthy for their formal, foundational approaches; however, they are also difficult to connect to concrete physical systems, making it difficult to assess their prospects for experimental verification. Allahverdyan and Nieuwenhuizen have written extensively on the limits to various formulations of the second law in the quantum regime, particularly quantum coherence and entanglement [47–52]. Among their significant contributions is the *spin boson model*, by which two-level systems that are quantum mechanically entangled with a bath of harmonic oscillators can extract work from a heat bath. They have also suggested experiments on mesoscopic or nanoscopic electrical circuits interacting with a low-temperature heat bath, which could pose a violation of the Clausius form of the second law in the quantum regime.

Several challenges connected with superconductivity have undergone exploratory laboratory experiments. Keefe proposes a simple thermodynamic process based on the magnetocaloric effect in which a small superconducting sample is cycled through field-temperature space and performs net work solely at expense from heat from a heat bath [53–56]. Nikulov, et al., have conducted experiments on mesoscopic, inhomogeneous superconducting loops that are interpreted as supporting the existence of a so-called *quantum force*, which arises due to fundamental differences between classical and quantum states of electrons (or Cooper pairs) in a conducting (superconducting) loop [57–60]. Significantly, independent theoretical work, by J. Berger, supports their hypothesis [61,62].

Second law non-idealities associated with gases have been pursued by other workers besides Denur. Crosignani, Di Porto and Conti have theoretically and numerically investigated the dynamical evolution of a frictionless, adiabatic piston in a gas-filled adiabatic cylinder subject to the Langevin force [63–67]. In the mesoscopic regime the piston can undergo sizable fluctuations in position

and display entropy decreases up to two orders of magnitude greater than those predicted from thermal fluctuations. The system also exhibits the disquieting property of failing to settle down to an equilibrium configuration.

Miller has theoretically analyzed gas cavities in the molecular flow regime in which anisotropic gas-surface interactions determine gas phase populations [68]. He finds that, under the standard constraints of particle flux, momentum and energy conservation, nonequilibrium steady-state gas phase populations are possible, depending both on cavity geometry and the nature of gas-surface interactions. From a theoretical standpoint, Miller's is one of the most compelling cases yet made. Outside the academic sphere there are many more challenges, but these will be left to the reader to explore.

In light of these many challenges, the status of the second law is uncertain. On one hand, universality advocates (*i.e.*, the broader scientific community) are unable to dispel the challenges, suggesting the law is likely either fundamentally flawed or incomplete. On the other hand, universality opponents, while having posed a number of *theoretical* challenges, have not yet delivered a decisive experiment to support their claims. Given the epistemic nature of physical law – that truth is ultimately decided by experiment rather than by theory – the burden of proof rests with the opponents. In the next section we review the largest class of experimentally testable challenges.

2.3 University of San Diego (USD) Challenges: Macroscopic Pressure Gradients (MPGs)

Over the last 18 years, a number of challenges have been investigated at USD, covering the fields of plasma, chemical, gravitational, biological and solid state physics [1–3,69–87]. Laboratory experiments have corroborated the key mechanisms upon which they depend. These have culminated in several micro- and nanoscopic solid state devices, one of which will soon undergo laboratory testing.

The USD challenges are joined by a common thread [72,86]. They exploit *equilibrium* MPGs, in particular, those found in the Debye sheaths at the edges of plasmas (electric field) [69–71]; nearby chemically active surfaces in low density gases (chemical potential field) [73,76,77,85]; in the curved spacetime around planets (gravitational field) [74,75,79,80]; and in the depletion regions of p-n junctions (electric field) [78,81–84,86]. They range in size from nanoscopic to planetary (10^{-7} – 10^7 m), occur over more than an order of magnitude in temperature (100–2000 K), and over more than eight orders of magnitudes in pressure ($\sim 10^3$ – 10^{-6} Torr).

Nearly all natural and technological processes are nonequilibrium in character and can be understood in terms of a working fluid moving under the influence of a *macroscopic* field expressible as the *gradient* of a *potential*. Examples are endless: water falling from the clouds under gravity; molecular hydrogen and oxygen combining in a fuel cell to form water; current in an electrical circuit.

Here *potential gradient* refers to any potential whose spatial derivative is capable of directing a fluid in a preferred spatial direction (*i.e.*, $\nabla\Phi = -\mathbf{F}$) and can transform equilibrium particle velocity distributions into nonequilibrium ones. (The Onsager relations embody this concept in the weakly nonequilibrium regime [88].) Directional, nonequilibrium particle fluxes are the hallmarks of standard work-producing processes.

While it is *nonequilibrium* MPG that drive natural processes, *equilibrium* MPG are also common. The crucial point is this: whereas nonequilibrium MPG derive their energy from exhaustible free energy sources (*e.g.*, nuclear reactions, sunlight, chemical reactions), equilibrium MPG derive their energy from purely thermal processes. Each USD system consists of a blackbody cavity surrounded by a heat bath, and a working fluid (*e.g.*, gas atoms, electrons, ions, holes) in which an *equilibrium* MPG forms (*e.g.*, gravitational field, electric field of a Debye sheath or depletion region). The following is a brief summary of the USD systems.

Plasma [69–71] Electrons and ions at a single temperature have different average thermal speeds $(kT/m)^{1/2}$, owing to their different masses. In a sealed blackbody cavity, in order to balance thermal flux densities in and out of a plasma, the plasma resides at an electrostatic potential (the so-called *plasma potential*, V_{pl}) with respect to the confining walls. This potential drop occurs across a thin layer between the plasma and the blackbody walls, called the Debye sheath (thickness λ_D). Typical plasma parameters render plasma potentials up to several times kT/q and gradients of order $\nabla V \sim V_{pl}/\lambda_D$. Sheath electrostatic gradients (electric fields) of the order of 10^3 V/m are common. Although the sheath is thin (but still macroscopic) in the direction of the electric field, in the other two dimensions it can extend over arbitrarily large distances, making this a full, three-dimensional macroscopic potential gradient. The other systems share this trait.

Chemical [73,76,77,85] In a sealed blackbody cavity, housing a low-density gas (*e.g.*, A_2) and two surfaces (S1 and S2) which are distinctly chemically reactive with respect to the gas-surface reaction ($2A \rightleftharpoons A_2$), a chemical potential gradient can be supported, expressed as steady-state differential atomic and molecular fluxes between the surfaces.

Gravitational [74,75,79,80] All finite masses exhibit gravitational potential gradients (gravitational fields) that can direct working fluids (gases) preferentially along field lines. No thermodynamic processes are required to sustain this MPG.

Solid State [78,81–84,86] When n- and p-doped semiconductors are joined (forming a standard p-n diode) an electrostatic potential difference (built-in potential, V_{bi}) arises between the two regions, across the so-called *depletion region* (thickness $x_{dr} \cong 1 \mu\text{m}$). In the depletion region, a balance is struck between electrostatic and chemical potentials. The equilibrium electrostatic potential gradient scales as $\nabla V \sim V_{bi}/x_{dr}$, which for typical p-n diodes is on the order of $V/10^{-6} \text{ m} = 10^6$ V/m. (The similarities between the plasma and solid state systems are not coincidental.) Applying these ideas to bio-membranes, a proposal has been made for a third category of life beyond the standard two – photosynthetic and chemosynthetic – that would rely on second law subversion: *thermosynthetic life* [87].

The above *equilibrium* MPG and their working fluids possess all the required physical characteristics by which everyday *nonequilibrium*, free-energy-driven MPG perform work in traditional thermodynamic cycles. Their potential

gradients are of sufficient magnitude and directionality to overcome thermal fluctuations and to perform macroscopic work. They differ from their non-equilibrium counterparts only in that they are generated and maintained under equilibrium conditions.

Work can be extracted from an equilibrium MPG system by allowing a fluid to cycle through the potential gradient. On one leg of its cycle the working fluid “falls” through the MPG and is transformed into a spatially-directed non-equilibrium flux, by which work is performed. On the return leg, the fluid and system returns to its original thermodynamic macrostate via standard thermal processes (*e.g.*, diffusion or evaporation).

3 Solid State Challenge

3.1 Electromechanical Oscillators

We begin our examination of a specific laboratory-testable solid-state second law challenge with a closely related system that does not challenge the second law whatsoever, one that is familiar in dozens of everyday guises: an electro-mechanical oscillator.

Consider the simple electrical circuit depicted in Figure 1, consisting of a battery, a capacitor, a switch and ground. In Figure 1a, the capacitor is fully charged and in a stable, high-energy equilibrium state, while in Figure 1b, it is fully discharged to ground (which is assumed to have zero resistance) and in a stable, low-energy equilibrium state. Since there is no electrical resistance in the circuit, the charging and discharging are instantaneous. While it is straightforward to switch between these two equilibrium states, there is no practical mechanism for auto-switching or work extraction. In Figure 1c both shortcomings are resolved. Here is added a mechanical spring that doubles as a resistor. It simultaneously permits the top capacitor plate to discharge against the other – thereby acting as a switch – while also executing mechanical motion whereby mechanical work can be extracted from the moving upper plate, for example, by lifting a weight or running an electrical generator. Such electro-mechanical oscillators are ubiquitous in everyday life; battery-driven electric clocks and watches are common examples.

The device in Figure 1c, called the *hammer-anvil*, is a hybrid of well-known mechanical and electrical oscillators. The hammer (top capacitor plate) moves with respect to the anvil (lower plate). The electromechanics of the hammer is described by the following coupled pair of equations:

$$F = F_{diss} + F_{sp} + F_{es} = m\ddot{x} = -\frac{1}{Q_m}\dot{x} - kx - \frac{q^2}{2\epsilon_0 A}. \quad (1)$$

Here x is the instantaneous excursion of the top plate from its equilibrium separation, A is the plate area, Q_m is the mechanical quality factor, k is the spring

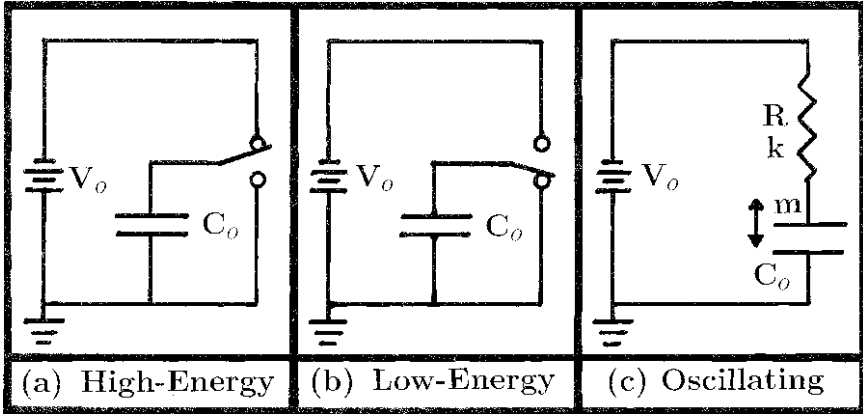


Fig. 1. Electrical equilibria for capacitors, (a) High-energy state, (b) Low-energy state, (c) Auto-switching resonant electromechanical oscillator (hammer-anvil).

constant, ϵ_o is the permittivity of free space, and q is the instantaneous charge on the plates. The charge satisfies:

$$\dot{q} = \left(V_o - \frac{q(x_g - x)}{\epsilon_o A} \right) \frac{1}{R}; \quad q < q_{sat}, \tag{2}$$

where R is electrical resistance, and $\dot{q} = 0$ for $q \geq q_{sat}$. Here the right-hand side of (1) gives of the dissipative, spring, and electrostatic forces, respectively. In (2) q_{sat} is the maximum (saturated) charge on the plates, x_g is the equilibrium gap width between plates, and $\epsilon_o A / (x_g - x) = C_o$ is the capacitance.

Two independent time constants characterize this system: one electrical ($\tau_e \sim RC_o$) and one mechanical ($\tau_m = 2\pi\sqrt{m/k}$). This system is electromechanically unstable: if the charged capacitor plates electrostatically draw together and electrically discharge, the attractive electric field collapses, the spring retracts the plates, the plates recharge on time scale τ_e , and the cycle can repeat. If the hammer’s mechanical oscillation time constant τ_m is comparable to the circuit’s electrical time constant τ_e and if the quality factor, Q_m , is sufficiently large, then the system can execute resonant, sustained electromechanical oscillation, converting the electrical energy of the battery into mechanical energy. Laboratory scale models of this oscillator have been co-built by the author and silicon-based microelectromechanical system (MEMS) versions, incorporating cantilever springs, have been demonstrated by others [89].

Ideally, this resonant electromechanical oscillator cycles between the two equilibrium states (Figure 1a and b) and some mechanical energy can be siphoned off in the process, so long as the extra load does not damp the oscillator beyond its ability to self-discharge. (Work load is modeled as an additional damping term in (1).) Clearly, this oscillator derives its energy from the battery; as it runs down, the electric field in the capacitor subsides and eventually the electromechanical oscillation cannot be sustained. This system also complies

completely with the second law since work (chemical energy in the battery) is steadily degraded into heat via mechanical-aerodynamic-electrical damping.

It is crucial to notice that the mechanical part of the oscillator, the part that performs work, is oblivious to the source of the electric field that drives it. It could originate with a battery – as is the case here – or from a less familiar source, say the built-in potential associated with the depletion region of a p-n diode. Herein lies the rub.

3.2 Solid State Electromechanical Oscillator

In this section, a solid state version of the traditional resonant electro-mechanical oscillator is described that, in theory, undermines the universality of the second law. We begin with a review of pertinent solid state concepts.

3.2.1 Intrinsic Bias. The depletion region of a standard p-n diode represents a minimum free energy state in which bulk electrostatic and diffusive forces are balanced. Typical depletion regions are narrow, ranging from $10\ \mu\text{m}$ for lightly-doped semiconductors to $0.01\ \mu\text{m}$ for heavily-doped ones. The potential drop across a region, the built-in potential V_{bi} is given approximately by [90]:

$$V_{bi} = \frac{kT}{q} \ln\left(\frac{N_A N_D}{n_i^2}\right) \quad (3)$$

Here kT is thermal energy; q is electric charge; n_i is intrinsic carrier concentration (for silicon ($n_i \cong 1.2 \times 10^{16}\ \text{m}^{-3}$ at 300K); and $N_{A,D}$ are acceptor and donor concentrations. For dopant concentrations $N_A = N_D = N = 10^{21}\ \text{m}^{-3}$, one has $V_{bi} \cong 0.6\ \text{V}$, a typical value.

Consider the horseshoe-shaped p-n diode with a vacuum gap (Figure 2a). At the left junction (J-I) is a regular p-n diode depletion region, while at the right (J-II) there is a vacuum gap. (Notice the similarities between Figures 1 and 2.) The built-in potential of the depletion region V_{bi} will be expressed across the vacuum gap; this can be argued either via energy conservation (Kirchhoff's loop law) or via Faraday's law. Numerical models using semiconductor device simulators (*e.g.*, Silvaco International – Atlas) corroborate this gap electric field [78,84], as have numerous condensed matter experiments.

Although V_{bi} is small, the gap width x_g can also be made small such that the electric field – and therefore the electrostatic pressure – can be sizable. For example, for $V_{bi} = 0.6\ \text{V}$ and gap width $x_g = 3 \times 10^{-8}\ \text{m}$, the gap field is $E \cong V_{bi}/x_g = 2 \times 10^7\ \text{V/m}$ and pressure $P \equiv (\epsilon_o/2)E^2 \sim 10^3\ \text{Pa}$. The open-gap configuration is a high-energy equilibrium state. If the gap is closed (Figure 2b) a new equilibrium state is created, characterized by a new depletion region. The net energy released by gap closure, between Figure 2a and 2b, can be shown to be:

$$\Delta\mathcal{E} \simeq \frac{16\upsilon\epsilon_o^2}{qN} \left\{ \frac{kT}{q} \ln\left[\frac{N}{n_i}\right] \right\}^3 \left\{ \frac{1}{x_g} - \frac{2}{3}\eta \left(\frac{2\eta\epsilon_o}{Nq} \left(\frac{kT}{q} \right) \ln\left[\frac{N}{n_i}\right] \right)^{-1/2} \right\}, \quad (4)$$

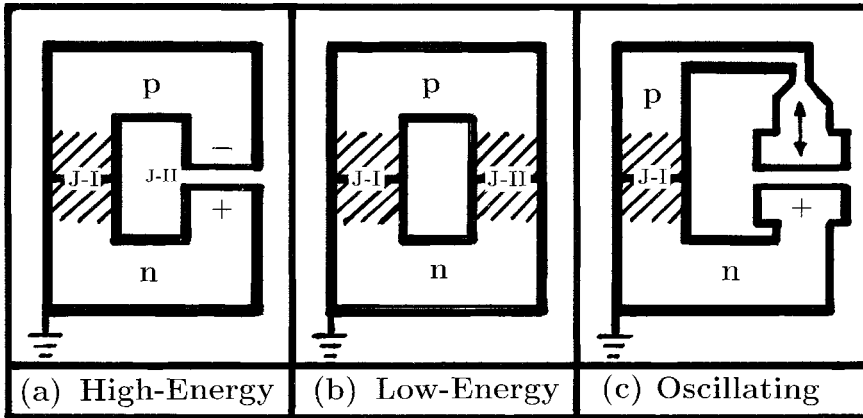


Fig. 2. Electrical solid state equilibria for p-n diode, (a) High-energy state with open p-n junction, (b) Low-energy state with closed p-n junction, (c) Auto-switching resonant electromechanical oscillator (hammer-anvil). Slashed areas indicate depletion regions.

where η is the dielectric constant ($\eta_{silicon} = 11 - 12$). In principle, this energy difference $\Delta\mathcal{E}$ can be used to perform useful work. A more detailed account of the gap electric field is presented elsewhere [78,84].

This structure constitutes an *intrinsically-biased* capacitor since no external voltage source is used, this in contradistinction to the traditional *externally-biased* capacitor in Figure 1. In principle, the intrinsic capacitor can store electrostatic energy indefinitely, purely by thermal means.

3.2.2 Work Cycle. Now consider the following thermodynamic work cycle (Figure 3), appropriate to closing and then reopening the vacuum gap in Figure 2c. (Compare this with Figure 1c.) The ordinate is the electrostatic force F_{es} on the gap face (area A), which is:

$$F_{es} = \frac{\epsilon_o}{2} E^2 A = \frac{\epsilon_o}{2} \left[\frac{V_{bi}}{x} \right]^2 A. \quad (5)$$

The abscissa is the instantaneous width of the vacuum gap x . The cycle proceeds counterclockwise: $a \rightarrow b \rightarrow c \rightarrow a$. The cycle in Figure 3 runs as follows:

($a \rightarrow b$): The gap closes quasi-statically, performing work, $\int_{x_o}^0 F_{es} dx$. Since V_{bi} across the vacuum gap is fixed by the left depletion region (J-I), in principle, the electric field, energy density and total energy increase at J-II during gap closure. In theory, the work integral diverges, but in practice it does not because the gap electric field saturates at a finite value (e.g., $E_{max} \cong 2 \times 10^7$ V/m for silicon which, as expected, is below its dielectric strength). Quantum tunneling of charge across the gap might occur in the last several angstroms of the stroke, allowing some pre-contact discharge.

($b \rightarrow c$): The apposing gap faces of J-II make contact ($x = 0$), precipitating rapid and irreversible electron-hole recombination at the gap faces, formation of a depletion region in the bulk like the one at J-I, and elimination of the gap electric field. The diode

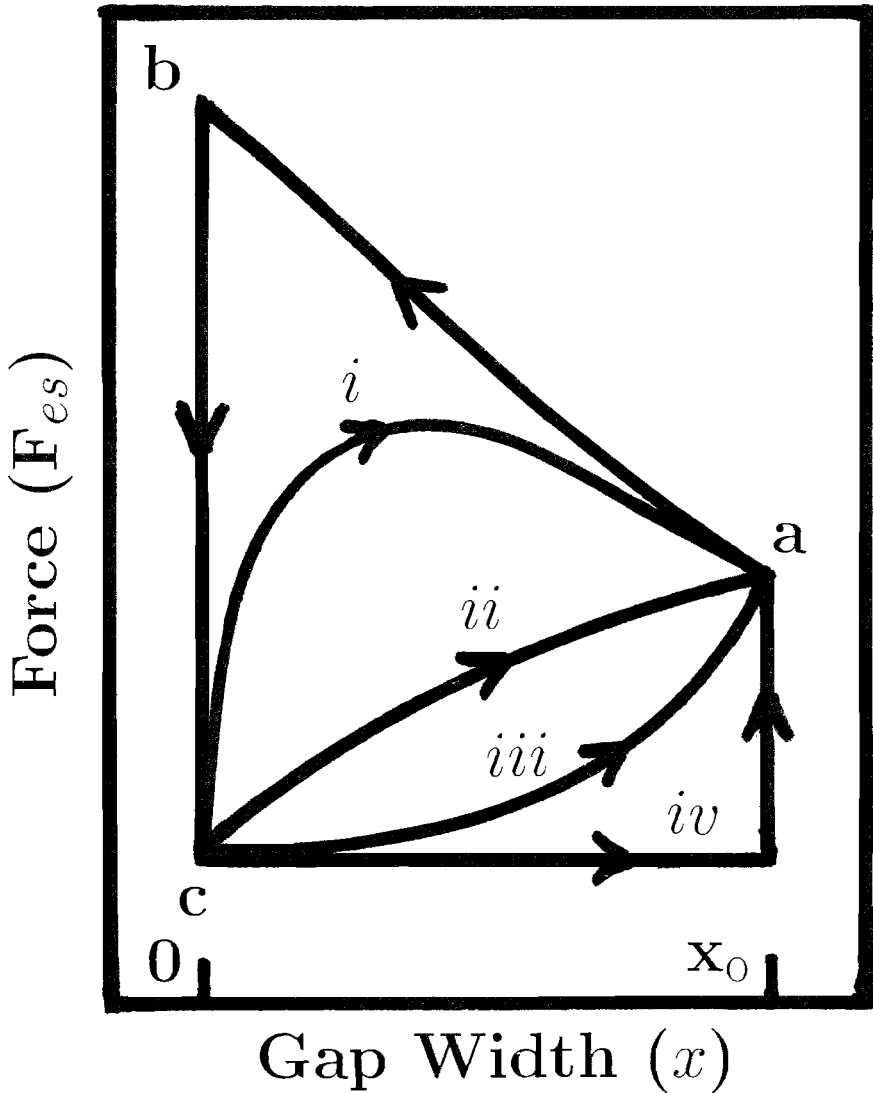


Fig. 3. Work cycle for p-n diode with vacuum gap. Paths (*i-iii*) are realistic for semiconductor resonators.

system falls from its high-energy equilibrium (Figure 2a) to its low-energy equilibrium (Figure 2b).

(*c* → *a*): The route taken to complete the cycle determines the net work output. If the gap opening is performed quasi-statically, then the cycle retraces in reverse its original path exactly (*c* → *b* → *a*), in which case the area enclosed by the cycle is zero and no work is performed. (This is also the path taken if the semiconductor were replaced with perfect conductors.) Along other paths (*i-iv*) non-zero area is enclosed and, thus,

net work is performed. Of these, only path (iv) is unrealistic since it indicates no recharging during gap opening, hence presumes instantaneous opening. Path (iii) is physically realistic for a semiconducting hammer-anvil and corresponds to near maximum work extraction.

It is emphasized that only with semiconductors can this cycle realistically have positive gain; neither perfect conductors (*e.g.*, metals) nor nonconductors will work. Perfect conductors discharge and recharge instantaneously, making a cycle of zero area, while nonconductors might allow a single discharge, but would take an infinite time to recharge, therefore they are not feasible for a continuous work cycle. Semiconductors, on the other hand, can spontaneously develop the necessary built-in potential, discharge, and then thermally recharge in a sufficiently long time to allow for mechanical motion of the faces (cases (i–iii) in Figure 3).

Second law universality is theoretically challenged by the steady-state operation of this device. This can be shown by pitting the first law of thermodynamics against the second. Let the universe consist of the hammer-anvil (plus its work extraction apparatus), plus a surrounding heat bath. Let the system settle into a thermodynamic steady-state (actually a steady-state nonequilibrium). If the hammer-anvil performs steady-state work, but remains in a thermodynamic steady-state (neither heating nor cooling), then the energy of the work it performs must come from somewhere other than itself. Since the first law demands that energy (heat + work) must be conserved universally, this leaves the heat bath as the source of energy. But a heat bath does not perform work; it provides only heat. Thus, by logical exclusion, the work performed by the hammer-anvil operating in its thermodynamic steady-state must come solely from the heat bath. This violates the Kelvin-Planck formulation of the second law. This device can also be shown to challenge any other standard formulation of the second law.

3.2.3 Solid State Hammer and Anvil. The rigid silicon horseshoe (Figure 2c) is not practical for work extraction, but realistic physical embodiments have been proposed [81,87] and laboratory studies of them are in progress.

Consider the electromechanical device depicted in Figure 4, a solid state torsional version of the hammer-anvil discussed previously. The top piece (all p-type semiconductor), which consists of an oscillator mass, two flexible torsional springs and the surrounding ledges, rests on an n-type base, thus forming a p-n diode. Comparing Figures 1c and 2c, the top-center p-semiconductor mass acts as the hammer in Figure 4; likewise, the lower stationary n-semiconductor in Figure 4 acts as the lower, fixed anvil. The spring is replaced by two torsional fibers³.

For long, thin fibers ($w_f, t_f \ll l_f$) and for small angular displacements ($\theta \ll 1$), a linear torsional constant can be defined: $\kappa = (3/10)(S/l_f)([w_f^3 t_f^3]/[w_f^2 + t_f^2])$ where l_f , w_f , and t_f are length, width and thickness of the torsion fiber, and S is its shear modulus ($S_{silicon} = 7.9 \times 10^{10} \text{ N/m}^2$). The device's depletion region imposes its built-in voltage across the vacuum gap between the p-type hammer and the n-type anvil base, as in Figure 2c. The mechanical frequency of the torsion

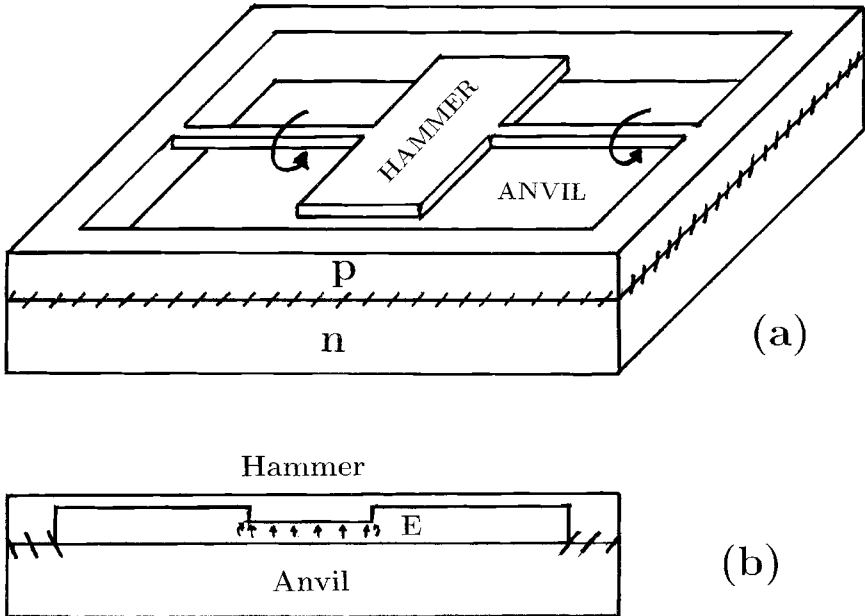


Fig. 4. Solid-state, torsional hammer-anvil oscillator, (a) Perspective view, (b) Cutaway side view. Slashed areas indicate depletion regions. "E" denotes gap electric field.

oscillator is given by $\omega = \sqrt{\kappa/I} = 2\pi f$ where $I = (1/12)ML^2$ is the moment of inertia of the oscillating mass about its axis of rotation, with M its mass and L its total length. The fiber must be given an initial twist to kick-start the oscillation.

The electric field in the hammer-anvil gap provides negative electrostatic pressure that drives and sustains the mechanical oscillations. It has been shown elsewhere [2,87] that, for sustained oscillation, three criteria must be met. (These criteria are also met by the macroscopic electromechanical resonator in Figure 1.)

- (I) The electrical and mechanical time constants must be comparable to achieve electromechanical resonance ($\tau_e \sim \tau_m$).
- (II) The hammer's mechanical energy gain per cycle must equal or exceed its mechanical dissipation per cycle, otherwise the oscillation will damp out.
- (III) The torque retracting the hammer after contact with the anvil must exceed the maximum torque exerted by van der Waals and electrostatic attractive forces, otherwise the hammer will stick to the anvil.

For Criterion I ($\tau_e \sim \tau_m$), the electrical time constant τ_e for the hammer-anvil p-n junction should be on the order of the inverse-slew rate of a comparably-sized p-n diode. This is typically 10^{-6} – 10^{-8} sec for micron-size silicon diodes, corresponding to frequencies of $f_e \sim 1$ –100 MHz. Mechanical resonant

frequencies for cantilevers in excess of 10^9 Hz have been achieved. Since f_m can be made comparable to f_e , the first criterion can be met. Alternatively, a resistor can be inserted between the hammer and anvil to establish a resistor-capacitor (RC) circuit. In this case a physically larger, lower frequency oscillator is possible, still satisfying $\tau_e \sim \tau_m$.

Regarding Criterion II, NEMS-MEMS oscillators have documented Qs as high as $Q \sim 10^5$ in vacuum [94]. This implies that a small energy gain per cycle (e.g., $\sim 10^{-5}$ total mechanical energy) should be sufficient to sustain oscillation. Numerical simulations verify that this condition also can be met for the torsional oscillator.

Finally, regarding Criterion III, it has been shown [2,84] that with sufficiently stiff cantilevers, the van der Waals and electrostatic forces can be overcome, while satisfying the other two criteria.

In all, detailed analysis indicates that high-Q MEMS-NEMS torsion oscillators and linear cantilevers, in principle, can achieve self-sustained resonant oscillation, utilizing intrinsic bias from a p-n depletion region. Simulations indicate a broad, physically realistic and experimentally accessible parameter space in which the torsional hammer-anvil should be viable that is squarely within the current art of MEMS fabrication.

The torsion oscillator we will investigate experimentally (Figure 4) will be relatively slow ($f \sim 10^4$ Hz) and large ($L \sim 10^{-2}$ m); nonetheless, its hammer-anvil gap distance must be minute ($x_{gap} \sim 10^{-7}$ m), thus requiring extremely fine mechanical tolerances ($x_{gap}/L \cong 10^{-5}$). Phosphorus and boron doping will be in the $N \cong 10^{21} \text{ m}^{-3}$ range, resulting in 0.6 V built-in voltages and electric fields near that of silicon's dielectric strength.

3.2.4 Practical Considerations. The useful work derived from *second law devices* (SLDs) can take many forms; proposals include mechanical, chemical, gaseous pressure gradients, osmotic pressure; temperature gradients, light and electrical. The most immediately convenient will probably be electrical, although chemical possibilities might also be competitive [85,87].

For the electrostatically driven hammer anvil devices, the theoretical maximum power density (\mathcal{P}) should scale as $\mathcal{P} \sim \rho_e f$, where ρ_e is the electrostatic energy density ($\rho_e = (\epsilon_0/2)E^2(\text{J/m}^3)$) and f (Hz) is the oscillation frequency. Taking E to be the dielectric strength of silicon (3×10^7 V/m) and the frequency to be the maximum of state-of-the-art NEMS resonators ($f \sim 5$ GHz), one finds that the maximum theoretical power density for electromechanical SLDs should be a staggering $2 \times 10^{13} \text{ Wm}^{-3}$. In other words, one cubic meter of SLDs could, in theory, supply civilization's power requirements. Realistically, however, one must consider: (a) the device's mechanical support volume not devoted to vacuum electric fields; and (b) heat transfer into the SLDs, both of which will greatly reduce this maximum theoretical power density. With regard to (a), based on advanced SLD designs, the actual fractional volume of an SLD array devoted to electric fields will likely be $\leq 10^{-2}$, thus lowering \mathcal{P} to $\leq 500 \text{ GWm}^{-3}$.

Consideration (b) is even more limiting. To review, there are three types of heat transfer: convection, conduction, and radiation. Under their anticipated operating conditions it can be shown that convection will probably dominate heat transfer for SLDs. Consider fluid flow with velocity v through one face of a matrix of SLDs and let the temperature drop be ΔT between the fluid's entrance and exit. The net output power flux density (Wm^{-2}) for the matrix is given by

$$F = \rho v C \Delta T - \frac{1}{2} \rho v^3, \quad (6)$$

where ρ is the mass density of the fluid and C is its specific heat. The first term is the SLD output power derived from the conversion of heat (see cycle in Figure 3) and the second is the kinetic energy vested in the fluid, assumed to be supplied by the SLDs. The condition for positive flux density is that: $v \leq \sqrt{2C\Delta T}$. The maximum flux density with respect to velocity ($\partial F/\partial v = 0$) occurs at $v_{max} = \sqrt{(2/3)C\Delta T}$. For water with $\Delta T = 10$ K, this is $v_{max} = 160$ m/s, and for air with $\Delta T = 100$ K, $v_{max} = 230$ m/s.

For a water-powered SLD matrix with a 1 m^2 intake ($v = v_{max} = 160$ m/s, $\Delta T = 10$ K, $C = 4.2 \times 10^3 \text{ J[kgK]}^{-1}$), Eq. (6) predicts $P \cong 5 \times 10^9$ W, the equivalent output of several modern nuclear power plants. As a convecting fluid, air has advantages over water in being easier to handle and more ubiquitous, and it also allows greater temperature variations ΔT ; on the other hand, it has lower density and specific heat ($C_{air}/C_{water} \cong 0.2$). For air, letting $\Delta T = 100$ K and $v = v_{max} = 230$ m/s, Eq. (6) predicts $P = 2 \times 10^7 \text{ Wm}^{-2}$. Notice that the power flux density for the SLD can be several orders of magnitude greater than those possible by wind or solar, which are fundamentally limited by wind speed or the solar constant, as well as by their availability during the hours of the day and by the season.

To be viable for large-scale power production, microscopic SLDs, like the torsional hammer-anvil, must efficiently transduce their energy to macroscopic scales. Analysis indicates that massive series-parallel arrays operating in unison should be possible. The detailed engineering and economics are beyond the scope of this paper, however, several transduction mechanisms suggest themselves:

Piezoelectricity: For SLDs with flexing mechanical structures, like the double-cantilever or torsional versions of the hammer-anvil, piezoelectric elements might be built into the device, or perhaps the entire device might be fabricated from a piezoelectric material, with output electrodes situated at locations of maximum mechanical strain.

Thermoacoustics: Here, SLDs' mechanical vibrations would generate sound waves in a background gas, by which thermoacoustic heating and cooling could be used to run a heat engine. Thermoacoustic motors and refrigerators are commercially available.

Faraday Induction: In this scenario, microscopic magnets would be affixed to the hammer. Via Faraday induction, an ac electromotive force (emf) is induced in a nearby coil via time-changing magnetic flux coupled through it. While this scheme would require substantial ancillary magnetic and electrical hardware – especially compared with

the piezoelectric scenario for which the mechanical and electrical elements could be the same structure – the high frequencies typical of NEMS are advantageous since induced emf is proportional to the time rate of change of magnetic flux.

4 Ramifications of Second Law Violation

The second law is so ingrained in human experience that its violation should lead to unexpected and counterintuitive results. Consider SLDs at home. For example, a household SLD power generator might consist of a tube about the size of a coffee can. On one end could be a fan to draw the air through the tube over a series of baffles – like a radiator – packed with millions of SLDs. The SLDs convert atmospheric heat into electricity, some of which powers the fan, but the vast majority of which is available to run household appliances and utilities. For modest, self-generated air flow (5 m/s) and modest heat recovery ($\Delta T \cong 20$ K), Eq. (6) predicts that this coffee-can-sized generator should produce between 1 and 2 kilowatts of electricity nonstop – roughly enough to power an average US household.

On the road and in the sky, SLD automobiles and planes could *run on air*, taking in air at the front, passing it through internal SLD baffles, converting heat into electricity for electric motors, and finally exhausting colder air out the back. They would consume no fuel and produce no pollution, aside from trailing plumes of cold air. In principle, almost any technological device could be redesigned to be energy self-reliant. Further, since nearly all electricity is eventually degraded into heat, it can be recycled again and again. Homes, businesses and industries could become energy self-sufficient. The power grid would become superfluous.

Thermal energy should be superior to almost any other energy resource. First, the terrestrial thermal energy reserves in the atmosphere, ocean and crust alone exceed by orders of magnitude all presently exploited energy reserves combined (coal, oil, gas, uranium) and are exceeded only by the potential energy of thermonuclear fusion of light elements, a prospect still decades away from commercial viability. Thermal energy is also ubiquitous so SLDs should operate anywhere, anytime. Second, unlike any other energy source, it should be completely recyclable and renewable; in this sense, thermal energy is effectively limitless.

Third, thermal energy is clean, *green* energy. Aside from the products of their manufacturing, SLDs should create no chemical wastes and no pollution since they consume no material fuel, only heat. Fourth, in principle, their power flux densities are compatible with virtually any modern mechanical or electronic device, from lightbulb to locomotive. (Only for the most power-intensive systems, *e.g.*, rockets, would they be infeasible.)

If they prove economically competitive, SLDs could precipitate a shift in the world's energy paradigm. Unlike traditional energy sources, thermal energy does not require discovery and extraction since it is found in abundance everywhere.

Large generation plants or transmission infrastructure would be unnecessary since heat-to-electricity conversion could be accomplished locally. Energy storage (*e.g.*, batteries, flywheels) would be unnecessary for all but the highest power applications. Furthermore, unlike other renewable energy sources (*e.g.*, solar, hydroelectric, or wind) SLD can support very high power densities. And, thermal energy is not simply *renewable*, it is *perpetually recyclable*.

The short-term economic and political impacts of cheap and abundant SLDs could be dire. Vast personal, corporate and national fortunes in mineral wealth would be wiped out. Middle Eastern energy empires would collapse as oil and gas became nearly worthless, their use restricted largely to plastics, fertilizers, lubricants and asphalt. The energy exploration, extraction and delivery industries would implode; gas and oil wells, coal mines, tanker fleets and gas stations would be idled; pipelines, refineries, power plants and power grids would be scavenged for spare parts. The economic clout and political leverage derived from energy resources would largely vanish, restructuring economic and political landscapes across the globe, for instance, those between gas-rich Russia and energy-poor Europe.

After these shocks, the economic, political and ecological benefits of SLDs could be profound and salutary. The release of the world economy from the constraints of limited and expensive energy should be invigorating. Energy-shackled economies, like India and China, could flourish. Cheap energy should reduce the cost of virtually all products. The costs of recycling material resources like metals, plastics and paper should also be reduced.

Inexpensive energy should help unlock other critical resources, for instance, possibly allowing widespread desalination of seawater and its pumping over long distances to thirsty lands and populations. Most recently, the world has experienced a tight coupling between energy and food markets, resulting in global shortages in basic foodstuffs like rice, wheat and corn, affecting hundreds of millions of humans. If energy can be made sufficiently inexpensive, these two markets should decouple, thereby stabilizing food supplies. (Of course, cheap energy should also reduce the cost of producing and transporting food, as well.)

Eliminating these energy-related shortages should, in turn, reduce political and economic tensions leading to war and civil strife. The necessities for military interventions to control energy reserves would end; armies could come home. Politically and militarily, there would be one less critical resource to fight over.

Pollution from fossil fuel burning and nuclear fission could be eliminated. Land scarred and ecosystems maimed by civilization's thirst for energy could be left to heal. (It has been suggested that greenhouse gases might be scrubbed from the atmosphere, but these proposals are energy-intensive. SLVs might be employed here since scrubbing would now be an energy-neutral proposition.⁴)

Of course, the virtues of this technology could become a vice if taken to extremes. Abundant, inexpensive energy would lift a fundamental constraint on humankind's exploitation of Nature. Mining, fishing and logging could be conducted non-stop, further stripping the world's natural resources and

accelerating environmental destruction. Wars could be conducted by tanks, ships and planes without need of refueling. The fault of these dangers rests, of course, not in the technology but in ourselves.

At present the immediate specters of global food shortages, climate change, pollution, ecosystem destruction and species extinctions, driven largely by humanity's thirst for energy, seem to require rapid and radical solutions. If the second law can be violated in an economically and ecologically viable manner, then I believe it should be pursued vigorously.

5 Outlook

The energy paradigm under which civilization has traditionally operated but which now threatens the environment and civil society – that free-energy sources are absolutely required – is now being challenged. The experiment described in this paper is merely a test of principle. If successful, hopefully it will inspire more efficient, higher power density and economical versions. Certainly, any experimental violation of the second law would fundamentally alter the landscape of physics and the pure sciences, but its potential for positive societal change is perhaps even more profound.

In the next several years, as laboratory SLDs are tested at USD and other institutions, *the heat will be turned up* on the second law. If successful, they promise to change humankind's relationship to energy perhaps as fundamentally as it was by the taming of fire 400,000 years ago.

Acknowledgments

The author thanks P. Sturrock for his kind invitation to write this article based on an invited talk at the 26th Annual Meeting of the Society for Scientific Exploration in East Lansing, Michigan, June, 2007. The author thanks P. C. J. Sheehan and W. F. Sheehan for stimulating conversations. The referees are thanked for their critical comments. This work was performed in part at the Center for Integrated Nanotechnologies, Office of Basic Energy Sciences user facility, at Los Alamos National Laboratory (Contract DE-AC52-06NA25396) and Sandia National Laboratories (Contract DE-AC04-94AL85000). This paper is dedicated to the memories of M.P.S, M.J.S., P.C.S. and W.F.S., and to Shannon's dream.

References

- [1] Sheehan, D. P. (Ed.) (2002). *First International Conference on Quantum Limits to the Second Law*. AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [2] Čápek, V., & Sheehan, D. P. (2005). *Challenges to the Second Law of Thermodynamics, of Fundamental Theories of Physics* (Vol. 146). Springer.
- [3] Sheehan, D. P. (Ed.) (2007). *The Second Law of Thermodynamics: Foundations and Status*. Proceedings of Symposium at 87th Annual Meeting of the Pacific Division of AAAS, University of San Diego, June 19–22, 2006. Special Issue of *Foundations of Physics*, 37(12).
- [4] Andrews, J., & Jelley, N. (2007). *Energy Science: Principles, Technologies, and Impacts*. Oxford University Press.

- [5] Eddington, A. S. (1929). *The Nature of the Physical World*. New York: Macmillan.
- [6] Davies, P. C. W. (1974). *The Physics of Time Asymmetry*. University of California Press.
- [7] Mackey, M. C. (1992). *Time's Arrow: The Origins of Thermodynamic Behavior*. Springer-Verlag.
- [8] Zeh, H. D. (2007). *The Physical Basis of the Direction of Time* (5th ed.). Springer-Verlag.
- [9] Sheehan, D. P. (Ed.) (2006). *Frontiers of Time: Retrocausation – Experiment and Theory*. Proceedings of symposium at 87th Annual Meeting of the Pacific Division of AAAS, University of San Diego, June 19–22, 2006. AIP Conference Proceedings (Vol. 863). Melville, NY: American Institute of Physics.
- [10] Kuhn, T. S. (1962). *The Structure of Scientific Revolutions*. University of Chicago Press.
- [11] Brush, S. (1976). *The Kind of Motion We Call Heat*. North-Holland.
- [12] von Baeyer, H. C. (1998). *Warmth Disperses and Time Passes | The History of Heat*. Modern Library.
- [13] Uffink, J. (2001). Bluff your way into the second law of thermodynamics. *Studies in History and Philosophy of Modern Physics*, 32, 305–394.
- [14] Kestin, J. (1976). *The Second Law of Thermodynamics*. Stroutsburg, PA: Dowden, Hutchinson, and Ross.
- [15] Kelvin, Lord (Thomson, W.) (1882). *Mathematical and Physical Papers* (Vol. I). Cambridge University Press.
- [16] Planck, M. (1906). *Vorlesungen über die Theorie der Wärmestrahlung*. Leipzig, Germany: Barth. (1945) *Treatise on Thermodynamics* (7th ed.). Translated by Ogg, A. New York: Dover.
- [17] Clausius, R. (1879). *The Mechanical Theory of Heat*. Macmillan.
- [18] Leff, H. S., & Rex, A. F. (2003) *Maxwell's Demon 2: Entropy, Classical and Quantum Information, Computing*. Bristol: Institute of Physics. (1990) *Maxwell's Demon. Entropy, Information, Computing*. Bristol: Hilger & IOP Publishing.
- [19] Gordon, L. G. M. (1981). Brownian movement and microscopic irreversibility. *Foundations of Physics*, 11, 103–113.
- [20] Gordon, L. G. M. (1983). Maxwell's demon and detailed balancing. *Foundations of Physics*, 13, 989–997.
- [21] Gordon, L. G. M. (1994). The molecular-kinetic theory and the second law. *Journal of Colloid and Interface Science*, 162, 512–513.
- [22] Gordon, L. G. M. (2002). Perpetual motion with Maxwell's demon. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 242–247). AIP Conference Proceedings, Vol. 643. Melville, NY: AIP Press.
- [23] Gordon, L. G. M. (2004). The decrease in entropy via fluctuations. *Entropy*, 6, 38–49.
- [24] Gordon, L. G. M. (2004). A Maxwellian valve based on centrifugal forces. *Entropy*, 6, 87–95.
- [25] Gordon, L. G. M. (2004). Smoluchowski's trapdoor. *Entropy*, 6, 96–101.
- [26] Denur, J. (1981). The Doppler demon. *American Journal of Physics*, 49, 352–355.
- [27] Denur, J. (1989). Velocity-dependent fluctuations: Breaking the randomness of Brownian motion. *Physical Review A*, 40, 5390–5399.
- [28] Denur, J. (2002). Modified Feynman ratchet with velocity-dependent fluctuations. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 326–331). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [29] Denur, J. (2004). Modified Feynman ratchet with velocity-dependent fluctuations. *Entropy*, 6, 76–86.
- [30] Denur, J. (2007). Speed-dependent weighting of the Maxwellian distribution in rarefied gases: A second law paradox? *Foundations of Physics*, 37, 1685–1706.
- [31] Čápek, V. (1997). Isothermal Maxwell daemon and active binding pairs of particles. *Journal of Physics A: Mathematical and General*, 30, 5245–5258.
- [32] Čápek, V. (1997). Isothermal Maxwell daemon. *Czechoslovak Journal of Physics*, 47, 845–849.
- [33] Čápek, V. (1998). Isothermal Maxwell daemon: Swing (fish-trap) model for particle pumping. *Czechoslovak Journal of Physics*, 48, 879–901.
- [34] Čápek, V., & Bok, J. (1998). Isothermal Maxwell daemon: Numerical results in a simplified model. *Journal of Physics A: Mathematical and General*, 31, 8745–8756.
- [35] Čápek, V., & Maňcal, T. (1999). Isothermal Maxwell daemon as a molecular rectifier. *Europhysics Letters*, 48, 365–371.
- [36] Čápek, V., & Bok, J. (1999). A thought construction of working perpetuum mobile of the second kind. *Czechoslovak Journal of Physics*, 49, 1645–1652.

- [37] Čápek, V., & Tributsch, H. J. (1999). Particle (electron, proton) transfer and self-organization in active thermodynamic reservoirs. *Journal of Physical Chemistry B*, *103*, 3711–3719.
- [38] Čápek, V., & Frege, O. (2000). Dynamical trapping of particles as a challenge to statistical thermodynamics. *Czechoslovak Journal of Physics*, *50*, 405–423.
- [39] Čápek, V., & Bok, J. (2001). Violation of the second law of thermodynamics in the quantum microworld. *Physica A*, *290*, 379–401.
- [40] Čápek, V. (2001). Twilight of a dogma of statistical thermodynamics. *Molecular Crystals and Liquid Crystals*, *335*, 13–24.
- [41] Čápek, V., & Bok, J. (2002). A model of spontaneous generation of population inversion in open quantum systems. *Chemical Physics*, *277*, 131–143.
- [42] Čápek, V., & Maňal, T. (2002). Phonon mode cooperating with particle serving as Maxwell gate and rectifier. *Journal of Physics A: Mathematical and General*, *35*, 2111–2130.
- [43] Čápek, V., & Sheehan, D. P. (2002). Quantum mechanical model of a plasma system: A challenge to the second law of thermodynamics. *Physica A*, *304*, 461–479.
- [44] Čápek, V. (2002). Zeroth and second law of thermodynamics simultaneously questioned in the quantum world. *European Physical Journal B*, *25*, 101–113.
- [45] Čápek, V. (2003). Dimer as challenge to the second law. *European Physical Journal B*, *34*, 219–223.
- [46] Bok, J., & Čápek, V. (2004). Langevin approach to the Porto system. *Entropy*, *6*, 57–67.
- [47] Allahverdyan, A. E., & Nieuwenhuizen, Th. M. (2000). Extraction of work from a single thermal bath in the quantum regime. *Physical Review Letters*, *85*, 1799–1802.
- [48] Allahverdyan, A. E., & Nieuwenhuizen, Th. M. (2001). Breakdown of the Landauer bound for information erasure in the quantum regime. *Physical Review E*, *64*, 056117.
- [49] Pombo, C., Allahverdyan, A. E., & Nieuwenhuizen, Th. M. (2002). Bath-generated work extraction in two-level systems. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 254–258). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [50] Nieuwenhuizen, Th. M., & Allahverdyan, A. E. (2002). Statistical thermodynamics of quantum Brownian motion: Construction of perpetuum mobile of the second kind. *Physical Review E*, *66*, 036102.
- [51] Allahverdyan, A. E., & Nieuwenhuizen, Th. M. (2003). Testing the violation of the Clausius inequality in nanoscale electric circuits. *Physical Review B*, *66*, 115–309.
- [52] Allahverdyan, A. E., & Nieuwenhuizen, Th. M. (2004). Bath-generated work extraction and inversion-free gain in two-level systems. *Journal of Physics A: Mathematical and General*, *36*, 875–882.
- [53] Keefe, P. (2002). Coherent magneto-caloric effect heat engine process cycle. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 213–218). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [54] Keefe, P. (2003). Coherent magneto-caloric effect superconductive heat engine process cycle. *Journal of Modern Optics*, *50*, 2443–2454.
- [55] Keefe, P. (2004). Second law violation by magneto-caloric effect adiabatic phase transition of type I superconductor particles. *Entropy*, *6*, 116–127.
- [56] Keefe, P. (2005). Quantum limit to the second law by magneto-caloric effect, adiabatic phase transition of mesoscopic-size type I superconductor particles. *Physica E*, *29*, 104–110.
- [57] Nikulov, A. V., & Zhilyaev, I. N. (1998). The Little-Parkes effect in an inhomogeneous superconducting ring. *Journal of Low Temperature Physics*, *112*, 227–236.
- [58] Nikulov, A. V. (2001). Quantum force in a superconductor. *Physical Review B*, *64*, 012505.
- [59] Nikulov, A. V. (2002). About perpetuum mobile without emotions. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 207–212). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [60] Dubonos, S. V., Kuznetsov, V. I., & Nikulov, A. V. (2002). In *Proceedings of 10th International Symposium ‘‘Nanostructures: Physics and Technology’’* (p. 350). St. Petersburg Ioffe Institute.
- [61] Berger, J. (2005). The Chernogolovka experiment. *Physica E*, *29*, 100–103.
- [62] Berger, J. (2007). A nonconventional scenario for thermal equilibrium. *Foundations of Physics*, *37*, 1738–1743.
- [63] Crosignani, B., & Di Porto, P. (1996). Approach to thermal equilibrium in a system with adiabatic constraints. *American Journal of Physics*, *64*, 610–613.
- [64] Crosignani, B., & Di Porto, P. (2001). On the validity of the second law of thermodynamics in the mesoscopic realm. *Europhysics Letters*, *53*, 290–296.

- [65] Crosignani, B., Di Porto, P., & Conti, C. (2002). The adiabatic piston and the second law of thermodynamics. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 267–272). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [66] Crosignani, B., Di Porto, P., & Conti, C. (2004). The adiabatic piston: A perpetual mobile in the mesoscopic realm. *Entropy*, 6, 50–56.
- [67] Crosignani, B., & Di Porto, P. (2007). Random fluctuations of diathermal and adiabatic pistons. *Foundations of Physics*, 37, 1707–1715.
- [68] Miller, S. L. (2007). Insights into the second law of thermodynamics from anisotropic gas-surface interactions. *Foundations of Physics*, 37, 1660–1684.
- [69] Sheehan, D. P. (1995). A paradox involving the second law of thermodynamics. *Physics of Plasmas*, 2, 1893–1898.
- [70] Sheehan, D. P. (1996). Another paradox involving the second law of thermodynamics. *Physics of Plasmas*, 3, 104–110.
- [71] Sheehan, D. P., & Means, J. D. (1998). Minimum requirement for second law violation: A paradox revisited. *Physics of Plasmas*, 5, 2469–2471.
- [72] Sheehan, D. P. (1998). Four paradoxes involving the second law of thermodynamics. *Journal of Scientific Exploration*, 12, 303–314.
- [73] Sheehan, D. P. (1998). Dynamically maintained steady-state pressure gradients. *Physical Review E*, 57, 6660–6666.
- [74] Sheehan, D. P., Glick, J., & Means, J. D. (2000). Steady-state work by an asymmetrically inelastic gravitator in a gas: A second law paradox. *Foundations of Physics*, 30, 1227–1256.
- [75] Sheehan, D. P., & Glick, J. (2000). Gravitationally-induced, dynamically-maintained, steady-state pressure gradients. *Physica Scripta*, 61, 635–640.
- [76] Sheehan, D. P. (2000). Reply to “Comment on ‘Dynamically-maintained steady-state pressure gradients.’” *Physical Review E*, 61, 4662–4665.
- [77] Sheehan, D. P. (2001). The second law and chemically-induced, steady-state pressure gradients: controversy, corroboration and caveats. *Physica A*, 280, 185–190.
- [78] Sheehan, D. P., Wright, J. H., & Putnam, A. R. (2002). A solid-state Maxwell demon. *Foundations of Physics*, 32, 1557–1595.
- [79] Sheehan, D. P., Glick, J., Duncan, T., Langton, J. A., Gagliardi, M. J., & Tobe, R. (2002). Phase space portraits of an unresolved gravitational Maxwell demon. *Foundations of Physics*, 32, 441–462.
- [80] Sheehan, D. P., Glick, J., Duncan, T., Langton, J. A., Gagliardi, M. J., & Tobe, R. (2002). Phase space analysis of a gravitationally-induced, steady-state nonequilibrium. *Physica Scripta*, 65, 430–437.
- [81] Wright, J. H. (2002). A novel sub-micron electrostatic motor. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 308–313). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [82] Putnam, A. R. (2002). Two-dimensional numerical simulations of a solid state Maxwell demon motor. In Sheehan, D. P. (Ed.), *Quantum Limits to the Second Law* (pp. 314–319). AIP Conference Proceedings (Vol. 643). Melville, NY: AIP Press.
- [83] Wright, J. H., Sheehan, D. P., & Putnam, A. R. (2003). Modeling a submicrometer electrostatic motor. *Journal of Nanoscience and Nanotechnology*, 3, 329–334.
- [84] Sheehan, D. P., Wright, J. H., Putnam, A. R., & Perttu, A. K. (2005). Intrinsically-biased, resonant NEMS-MEMS oscillator and the second law of thermodynamics. *Physica E*, 29, 87–99.
- [85] Sheehan, D. P., & Seideman, T. (2005). Intrinsically biased electrocapacitive catalysis. *Journal of Chemical Physics*, 122, 204713.
- [86] Sheehan, D. P., & Gross, D. H. E. (2006). Extensivity and the thermodynamic limit: Why size really does matter. *Physica A*, 370, 461–482.
- [87] Sheehan, D. P. (2007). Thermosynthetic life. *Foundations of Physics*, 37, 1774–1797.
- [88] Onsager, L. (1931). Reciprocal relations in irreversible processes, I. *Physical Review*, 37, 405–426.
- [89] Bienstman, J., Vandewalle, J., & Puers, R. (1998). The autonomous impact resonator: A new operating principle for a silicon strain gauge. *Sensors and Actuators, A* 66, 40–49.
- [90] Neudeck, G. W. (1989). *Vol. II: The pn junction diode* (2nd ed). In Pierret, R. F., & Neudeck, G. W. (Eds.) *Modular series on solid state devices*. Addison-Wesley.
- [91] Roukes, M. L. (2000). *Tech. Dig. of the 2000 Solid-State Sensor and Actuator Workshop*. Hilton Head Island, SC, June.

- [92] MacDonald, N. C. (1999). In Timp, G. (Ed.), *Nanotechnology*. AIP-Springer Verlag.
- [93] Pelesko, J. A., & Bernstein, D. H. (2003). *Modeling MEMS and NEMS*. Chapman and Hall/CRC.
- [94] Mohanty, P., Harrington, D. A., Ekinci, K. L., Yang, Y. T., Murphy, M. J., & Roukes, M. L. (2002). Intrinsic dissipation in high-frequency micromechanical resonators. *Physical Review B*, *66*, 085416.

Notes

- ¹ Čápek and Sheehan list 21 different versions in [2], without exhausting the possibilities.
- ² When he was younger the author argued with his mother that he shouldn't clean his room so as to spare the universe further disorganization. He was unsuccessful. Perhaps he should have appealed to his father, a physical chemist.
- ³ This hammer-anvil is a relative of well-studied NEMS and MEMS (Micro-Electro-Mechanical Systems/Nano-Electro-Mechanical Systems) cantilever oscillators. Cantilever oscillators have many proven and potential applications, including as accelerometers, motors, clocks, sensors (*e.g.*, temperature, pressure, electronic charge, magnetic fields, environmental contaminants, microbes), beam steerers, choppers, and modulators, computing elements and switches [91–93]. Cantilevers are usually driven by AC electrical signals whose frequencies are commensurate with their mechanical oscillation frequencies, but DC signals can also drive them.
- ⁴ In the near term, SLDs might actually exacerbate global warming by replacing energy devices whose emitted particulates cause {\em solar dimming} and the {\em Twomey indirect effect}, both of which probably offset the warming effects of greenhouse gases.