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HISTORICAL PERSPECTIVE

# Maxwell Zombies: Mulling and Mauling the Second Law of Thermodynamics

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Abstract—Over the last decade two new classes of thermodynamic paradoxes have been investigated at the University of San Diego involving the recently identified phenomena of *epicatalysis* and *supradegeneracy*. These paradoxes add to a growing list of challenges to the second law of thermodynamics begun in the early 1990s. PACS numbers: 05.,05.70. Ce,05.20.-y

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## INTRODUCTION

The second law of thermodynamics—the principle that the entropy of closed systems never decreases in spontaneous processes—is perhaps the most widely applicable physical law, operating in virtually every system in the universe consisting of more than just a few particles, from subatomic to cosmological length scales. It is often said that it "holds . . . the supreme position among the laws of Nature" (Eddington, 1935).

The status of this law has been a subject of discussion for nearly 170 years. Due to its centrality to many branches of science and engineering, any exception to it would be fundamentally important, especially to physics and chemistry. The most celebrated second law challenge is Maxwell's demon, an intelligent microscopic creature that sorts molecules on an individual basis, creating pressure or temperature gradients from which work is derived (Maxwell, 1872). Various incarnations have been summoned and exorcised by scientists of each age, including Smoluchowski, Szilard, Brillouin, Gabor, Feynman, Penrose, Bennett, Landauer, and Zurek (Leff & Rex, 2003). By the early 1990s, the demon was pronounced dead. Cause of death: *the thermodynamics of information erasure* or, more colloquially, *thinking too much*. The demon may have died, but its progeny did not (Sheehan, 2018a).

Over the last 25–30 years the second law has faced unprecedented skepticism, led by several dozen challenges from researchers worldwide, international conferences (Sheehan, 2002, 2011, 2007a), as well as the first scientific monograph on the subject (Čápek & Sheehan, 2005). Unlike the original Maxwell demon, many contemporary challenges are *big* (macroscopic, hence not prone to failure via thermal fluctuations); *dumb* (do not carry out calculations, making information erasure irrelevant); and *durable* (more difficult to dispel than Maxwell's demon), hence their name: *Maxwell zombies* (Sheehan, 2018a). These have assumed the mantle of the demon, many stubbornly resisting resolution by the scientific community for decades. Several have been reviewed in this journal (Sheehan, 1998a, 2008). Their steadily increasing number and potency—in some cases corroborated by experiment (Sheehan, 1995, 1996, 2001, 2014, 2016)—strain the uncritical acceptance of the second law as absolute. Most are theoretical, but an increasing number are experimental, a few purporting actual violation (Sheehan et al., 2014).

The newest wave of Maxwell zombies is based on the recently identified phenomena called epicatalysis (Sheehan, 1998b, 2013) and supradegeneracy (Sheehan & Schulman 2019). This article considers them in both theoretical and practical terms. Just as it was necessary 150 years ago for Maxwell's demon to 'dirty its hands' with 19th-century work to make its point (e.g., pushing a piston in a cylinder), modern challenges sport 21st-century technologies to make theirs (e.g., lasers, thermophotovoltaics).

The 'second law' group at the University of San Diego (USD) has advanced roughly a dozen challenges since the early 1990s. The first four (plasma-electrical, plasma-pressure, chemical, and gravitational) were reviewed in *JSE* (Sheehan, 1998a) in 1998. It was shown that these—as well as later challenges—can be explained in terms of two broken symmetries: one geometric, one thermodynamic. In a second *JSE* review (Sheehan, 2008), another class of USD challenges was discussed, involving *nano-* and *microelectromechanical systems* (NEMS and MEMS). These microscopic, semiconductor-based, resonant oscillators had the advantage of operating at room temperature, as opposed to the earlier plasma and chemical ones that required temperatures in excess of 1000 K, plus they could be fabricated using well-established micro- and nano-fabrication techniques. Theoretical analysis, numerical simulations, and corroborating laboratory experiments mutually supported their potential viability. Theoretical upper-limit power densities were predicted to be prodigious ($\rho \geq 10^9$ W/m$^3$), as were fabrications costs.

Second law research at USD over the last 30 years has arced steadily from the *conceivable* toward the *realizable.* In the 1990s, challenges were mostly theoretical, but now, in 2020, commercial devices are being contemplated. The initial generation of USD challenges (Gen I) required either high temperatures ($T > 1000$ K), low pressures ($P \leq 10^{-4}$ Torr), exotic materials (e.g., tungsten, rhenium, tantalum), or astronomically large gravitational masses (e.g., mass of Moon). Although possible in principle, they had little commercial potential and were difficult to verify experimentally.

The second generation of USD challenges (Gen II) improved over Gen I in that they could operate at room temperature, and they relied on well-established solid state fabrication technologies. Still, they remained difficult and expensive to create.

This article reviews a third generation of challenges (Gen III). Like Gen II, these should operate at room temperature, but additionally they might be far less expensive to fabricate. Intellectual property protection has been sought for their core ideas (Sheehan, 2015, 2020a), unlike for Gen I and II, which were judged too academic and theoretical to be worth securing. Gen III are based on two recently recognized and broadly applicable physical phenomena: epicatalysis and supradegeneracy. Four distinct challenges involving them are reviewed here.

The remainder of this article is as follows. The next section reviews epicatalysis theory, experiment, and challenges, followed by a complementary discussion for supradegeneracy. The Discussion section considers general thermodynamic issues.

## EPICATALYSIS

The term *epicatalysis* was coined in 2013 (Sheehan, 2013), though its origins can be traced back at least a century; it was also tacitly invoked in Gen I challenges since the early 1990s. As its name implies, epicatalysis is related to standard catalysis, but with a twist. Conventional (positive) catalysts satisfy the three criteria, specifically they: (i) speed up their chemical reactions by providing low activation energy routes between reactants and products; (ii) participate in, but are not consumed by, their chemical reactions; and (iii) do not alter the final equilibria of their reactions. Epicatalysts abide by conditions (i) and (ii), but they break (iii). The concept of epicatalysis has been broadened by other researchers to encompass a wider array of phenomena and processes than originally envisioned, notably by J. Denur, who has applied it to gas-gravitational systems (Denur, 2018).

In USD challenges, epicatalysis applies to gas–surface reactions in which the gas-phase mean free path ($\lambda$) is comparable or long compared with the size of the confining vessel ($L$), whose walls presumably contain epicatalysts. (For comparison, the mean free path for air molecules at STP is roughly 70 nm, a hundred times smaller than a red blood cell.) Epicatalysts have strong physical or chemical affinities for the gas and are able to break chemical bonds or ionize atoms. Examples include molecular hydrogen dissociation on heated transition metals (e.g., tungsten, molybdenum, rhenium; $H_2 \rightarrow 2H$), and surface ionization of alkali metal or alkali earth metals (e.g., potassium, cesium, barium) on high-temperature, high work function metals (e.g., tantalum, tungsten; $Cs \rightarrow Cs^+ + e^-$). Because epicatalysts operate in the high Knudsen number regime ($\lambda \geq L$), the distinct gas phase products desorbing from the epicatalysts are not disposed to collide, hence react, in the gas phase. Thus, they are unable to attain standard gas phase equilibrium; instead, the gas phase retains the fingerprint of the epicatalytic surface from which it desorbs. (At everyday gas number densities, the mean free path is so short that gas phase equilibrium is quickly attained very near a surface even if epicatalytic effects are present.)

Different epicatalytic surfaces can desorb distinct chemical products at the same temperature and gas number density. For instance, it has been known for decades that different transition

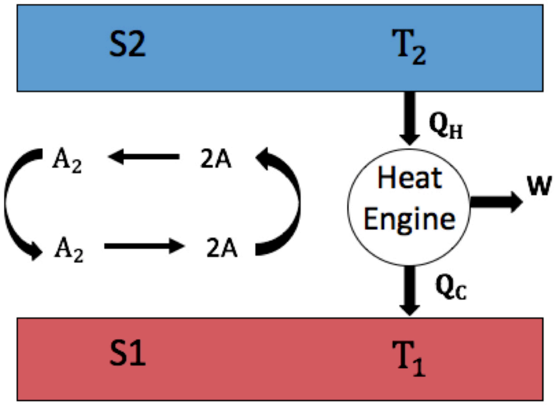


**Figure. 1. Epicatalysis Cycle. Molecule $A_2$ surface dissociates into monomers A, drawing thermal energy from S1, then 2A cycle to S2 where they recombine back into $A_2$, depositing thermal energy in S2 before cycling back to S1. Temperature differential $\Delta T = T_2 - T_1$ drives a heat engine.**

metals demonstrate different propensities for dissociating molecular hydrogen. For example, rhenium dissociates hydrogen better than tungsten at low pressures and high temperatures. Dissociation is an *endothermic* process (absorbs heat), thus, under otherwise identical conditions, rhenium tends to cool compared with tungsten when it dissociates hydrogen. Conversely, an *exothermic* process evolves heat such that a surface that recombines hydrogen well tends to heat relative to a surface that recombines hydrogen poorly.

Epicatalysis itself does not undermine the second law—in fact, it relies upon it—but when two or more epicatalysts operate upon the *same* gas in the *same* closed vessel, thermodynamic paradoxes can arise. Consider Figure 1, which depicts a cavity within which dimer gas $A_2$ circulates between two epicatalytic surfaces (S1 and S2). The gas $A_2$ preferentially dissociates on S1 ($A_2 + \Delta E \rightarrow 2A$, where $\Delta E$ is the dissociation energy for $A_2$), and then desorbs as two A atoms into the gas phase. These A species are then adsorbed on epicatalytic surface S2, where they preferentially recombine back into $A_2$ and desorb, releasing the recombination energy S2 ($A + A \rightarrow A_2 + \Delta E$). The result of this cycle is a net transfer of thermal energy from S1 to S2. (Gas phase reactions are not relevant here because this is an epicatalytic system with a long mean free path ($\lambda > L$).)

After many cycles of the gas through the cavity—absorbing, desorbing, dissociating, and recombining—an equilibrium is established, but one foreign to traditional thermodynamics. First, the gas phase is not described by normal gas phase equilibrium concentrations; rather, it bears the distinctive chemical imprints of S1 and S2. Second, and most critical to this study, the temperatures of S1 and S2 can be distinct. For the scenario pictured in Figure 1, one has $T_2 > T_1$ because S1 preferentially dissociates $A_2$, thereby cooling, while S2 preferentially recombines 2A into $A_2$, garnering thermal energy, and therefore heats. This 'equilibrium' is peculiar from the viewpoint of standard thermodynamics, which demands that closed systems like this settle down to a single temperature. This steady-state temperature difference by itself constitutes at least a *soft violation* of the second law (Moddel, 2019, personal communication), but this can become a *hard violation* if a heat engine (e.g., a thermoelectric generator) is attached between S2 and S1 such that heat flows and performs work (e.g., thermoelectricity).

The theory of epicatalysis was originally posed in terms of pressure differentials (Sheehan, 1998b), but temperature is a conjugate thermodynamic quantity, also able to perform work. Fifteen years later, the term *epicatalysis* was coined and the phenomenon explained in terms of kinetic theory (Sheehan, 2013). In 2017, a thermodynamic justification for epicatalysis was demonstrated using the symmetrized van 't Hoff equation (Sheehan, 2018b). This showed that neither kinetic theory nor microscopic analysis are necessary to challenge the second law; standard thermodynamics is sufficient. In this sense, traditional thermodynamics can be seen to be logically inconsistent. This author believes the inconsistency can be traced largely to an unrealistic idealization that permeates traditional thermodynamics, the so-called *thermodynamic* limit (Sheehan & Gross, 2006).

Experimental support for epicatalysis has been found in both plasma and chemical systems. In 2013, large steady-state temperature differences ($\Delta T \geq 120$ K) were measured in high-temperature hydrogen/W/Re blackbody cavity experiments; from these, areal power densities of roughly $10^4$ W/m$^2$ were inferred (Sheehan et al., 2014). Depending on one's tastes, this could be interpreted as either a hard or a soft (Moddel, 2019) violation. In 2015, evidence for *room–temperature* epicatalysis was discovered in hydrogen-bonded dimer systems (Sheehan et al., 2016) (e.g., formic acid dimers) reacting with hydrophilic surfaces (e.g., kapton). Although the room-temperature experiments were not conclusive concerning second law status—because temperature differentials were not measured (or sought)—their results raise hopes for a commercial second law technology in the form of an *epicatalytic thermal diode* (ETD), a device that rectifies thermal energy analogously to how an electrical diode rectifies electricity. This one-way valve for thermal energy can establish steady-state temperature differentials that, in principle, can be employed in a heat engine (Sheehan, 2015). ETDs are predicted to have applications across the entire energy sector (Sheehan, 2018a). Numerical simulations of room-temperature ETDs (Sheehan & Welsh, 2019), using realistic physical parameters and accounting for convective, conductive, and radiative heat transfers, predict temperature differentials in excess of 100 K and areal thermoelectric power densities up to several times $10^4$ W/m$^2$.

A practical ETD faces a number of potential hurdles. Although evidence has been found for room-temperature epicatalysis, temperature differentials and power extraction have not yet been demonstrated; even if they are, successful commercialization presents an entirely new set of conditions to be met.

Overall, epicatalysis undergirds potent thermodynamic challenges, some with attractive commercial prospects (Sheehan & Welsh, 2019). They have been demonstrated theoretically via microscopic analysis, kinetic theory, and traditional thermodynamics, experimentally verified and corroborated in plasma and chemical systems, and explored via numerical simulations. Many of the chemicals and surfaces necessary to construct ETDs are inexpensive and can be found in modern homes. Room-temperature epicatalysis experiments, seeking both soft and hard second law violations, are proceeding at USD.

## SUPRADEGENERACY

The phenomenon *supradegeneracy* has produced a variety of second law challenges, involving lasers, chemical membranes, thermophotovoltaics, and perhaps applications to biology. Its formal derivation is relatively recent (2016) (Sheehan & Shulman, 2019), but its roots can be traced back at least a decade (Sheehan, 2007b). In fact, supradegeneracy could have been discovered at the dawn of statistical mechanics,perhaps 140 years ago, but somehow it was overlooked, perhaps because no natural systems exhibited it.

Supradegeneracy can be understood heuristically as follows. Imagine a particle placed on a multiply forked path (Figure 2), subject to Brownian motion, that is, to random thermal excursions. The path bifurcates, trifurcates, or multifurcates. At each node the particle's next step is chosen randomly from its possibilities, one to the left and three to the right. Over time, the particle drifts to the right for purely statistical reasons because there are more ways for it to move to the right than for it to move to the left. This preference is a manifestation of the *entropic force*, $F_{\nabla S}$, which is defined as the product of temperature ($T$) and an entropy gradient ( $\nabla S \sim \frac{\delta S}{\delta x}$ ), i.e., $F_{\nabla S} = T\,\nabla S$. This statistically-based force is well-established (Neumann, 1980; Sokolov, 2010), especially in biological systems where it is critical to a number of phenomena, including diffusion, osmotic pressure, and polymer folding and coiling (Nelson, 2004).[29]

Now consider the energy levels of an arbitrary quantum-thermodynamic system (Figure 3). The number of states at a given energy level ($E_n$) is called its degeneracy, $g_n$. In Figure 3, for example, the degeneracies of levels 3 and 4 are two and five, respectively. The energy difference between the two levels is $\epsilon \equiv E_4 - E_3$.

It is a central maxim of statistical physics that, at equilibrium and at temperature, the ratio of occupation probability for two arbitrary levels n+1 and n is given by (Pathria, 1985; Reif, 1965; Schroeder, 2000)[1]

$$\frac{P_{n+1}}{P_n} = \frac{g_{n+1}}{g_n}\, e^{-\epsilon/kT}, \qquad (1)$$

where $k$ is the Boltzmann constant. For the case of energy levels 3 and 4 in Figure 3, one has $\frac{P_4}{P_3} = \frac{5}{2}\, e^{-(E_4 - E_3)/kT}$ .

For most thermodynamic systems the uppermost levels are less populated than lower ones (i.e., $\frac{P_{n+1}}{P_n} < 1$) because level degeneracies are typically of order unity $\frac{g_{n+1}}{g_n}$, while energy differences between

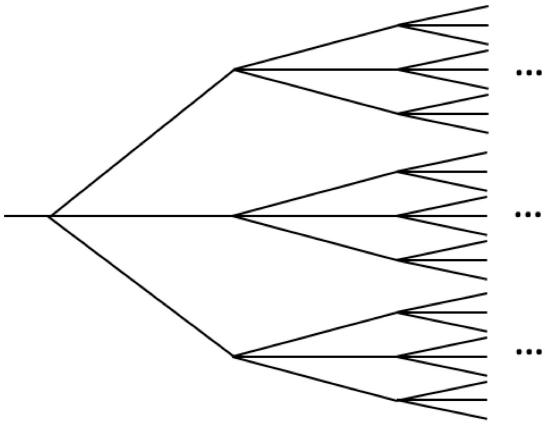


**Figure 2. Heuristic model of supradegeneracy.**

them are much greater than thermal increments $\left(\frac{\in}{kT}\right) \gg 1$ so that the Boltzmann exponential (factor) is much less than one $\left(e^{-\in/KT} \ll 1\right)$, therefore it dominates the overall probability ratio, giving $\frac{P_{n+1}}{P_n} < 1$. Only in special circumstances is it found that $\frac{P_{n+1}}{P_n} > 1$ in the uppermost levels, e.g., with population inversion in lasers, but these usually require some sort of nonequilibrium pumping, for instance chemical reactions, electrical discharge, or optical pumping with a flash lamp or laser.

But there's a catch. Notice that the probability ratio in Equation (1) can be written in a more suggestive form:

$$\frac{P_{n+1}}{P_n} = \frac{g_{n+1}}{g_n} e^{-\in/kT} = exp\left[\ln\left(\frac{g_{n+1}}{g_n}\right) - \in/kT\right] = e^{\gamma} \cdot \qquad (2)$$

Note that if $\ln\left(\frac{g_n + 1}{g_n}\right) > \in/kT$, then $e^{\gamma} > 1$, which means that the higher levels can be more populated than the lower ones $\left(\frac{P_{n+1}}{P_n} > 1\right)$. In other words, if level degeneracies increase rapidly enough, degeneracy can dominate the Boltzmann factor to create

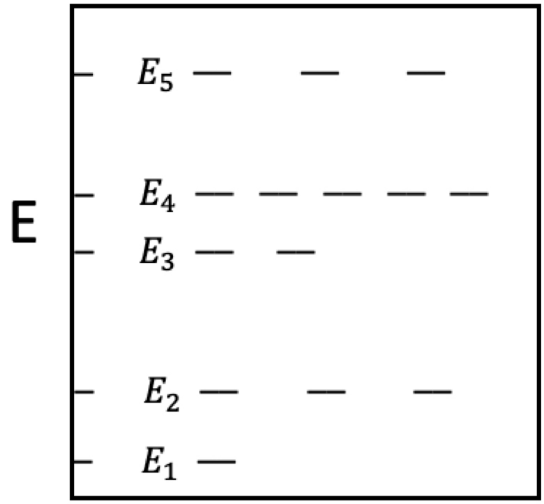


**Figure 3. Energy level diagram with conventional degeneracies.**

what amounts to population inversion *at equilibrium* without requiring *nonequilibrium* pumping. This is supradegeneracy (Sheehan & Schulman, 2019).

A *supradegenerate energy ladder* is depicted in Figure 4, where $\epsilon$ is taken to be the same between levels, and degeneracy increases exponentially as $g_n \sim p^n$ with $p > 1$ and $n$ is an integer. Analysis (Sheehan & Schulman, 2019) indicates that if viable transitions exist between the upper states of the energy ladder and lower states (Path 2 in Figure 4), then in principle steady-state particle currents can circulate in the system: particles climbing the energy ladder, falling down Path 2 back down to the ladder base (with switch open), then climbing up again. Steady-state currents are hallmarks of non-equilibrium (Attard, 2012; Gaveau et al., 2009; de Groot & Mazur, 1984; Zwanzig, 2001) and can lead to second law challenges, especially if the descending particles (Path 2) carry suprathermal energy ($E \gg kT$). Numerical studies corroborate the potential for such supradegenerate currents and predict they should be maximized for $\epsilon\beta \sim 1$. That is, energy steps of roughly $kT$ optimize upward energy currents, an intuitively satisfying result.[2]

To be clear, the *net* currents to and from the ground level and the upper energy level are nonequilibrium ones for both Paths 1 and 2.

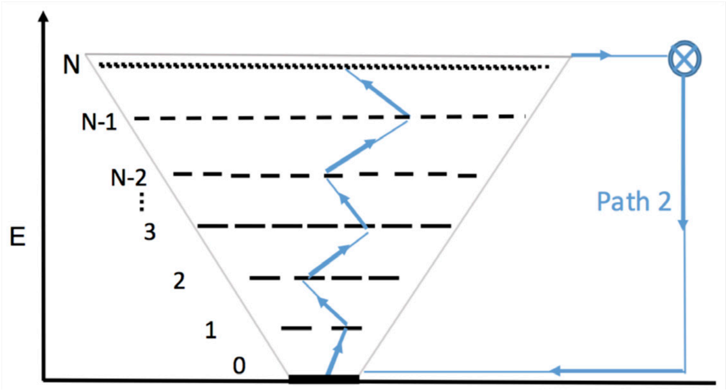


**Figure 4. Supradegenerate energy ladder. State degeneracy increases as $g_n \sim p^n$, satisfying Equation (2). Direct (single-step) path down from top rung indicated (Path 2 with switch ⊗).**

The climb up the energy ladder (Path 1) is a nonequilibrium process because it is time irreversible; that is, it is highly probable for it to climb up, but it is very improbable for it to climb down. Additionally, starting from the ground level, it is highly improbable for the system to thermally jump up to the upper-most level, either via Path 1 or 2. In contrast, the nonequilibrium flux downward along Path 2 is favored, both energetically and statistically, plus it is nonequilibrium since, presumably, suprathermal work can be extracted in the fall. In effect, the net fluxes up Path 1 and down Path 2 are nonequilibrium ones—constituting a net circular current—and a second law paradox if work is derived from the downward current.

Denur (personal communication) noted that some naturally occurring systems exhibit many of the features of supradegeneracy, for example a gas in a uniform gravitational field confined to an upwardly rising, flaring conical chamber (like a birch trumpet) whose flare rate is large enough that the gas particle number versus altitude satisfies the supradegeneracy statistical criterion ($e^{\gamma} > 1$). Particles climb the energy ladder using thermal energy; the upper energy levels can be considered a population inversion and their energies suprathermal. Unfortunately, the practicalities of such a scenario make it very unlikely that it could arise *naturally* on any planet or satellite. This gas (atmosphere) would be driven away from equilibrium by solar irradiance and the cone (on Earth) would likely have to extend nearly into space to satisfy the supratherm-al criterion($E \gg kT$).[3] Additionally, the conical gas provides no clear route to a second law challenge.

The energy ladder must be capped at a finite maximum ($n = N$), otherwise the system can achieve infinite energy, clearly an unphysical result.[4] No naturally-occurring supradegenerate systems are known—and this itself is mysterious[5]—but manmade supradegenerate systems seem achievable. Two are presently being pursued at USD.

An early form of supradegeneracy appeared in a proposal for a new (third) category of life (Sheehan, 2007b). At present only two categories are recognized: (a) chemosynthetic life, which is animated by chemical reactions (e.g., animals); and (b) photosynthetic life, which is powered by light (e.g., plants). In 2006, a third category was proposed (*thermosynthetic life*) that would be driven by thermal energy from the environment, contravening the second law (Sheehan, 2007b). (It is easily shown that the thermal energy inside and closely surrounding any cell is more than enough to power it, were the second law violable.) The best candidates for thermosynthetic life are predicted to be single-celled, superthermophilic, hyperbarophilic anaerobes confined several kilometers down in the earth's crust where it might have an energetic advantage over traditional *free-energy* life forms. Crucial to its proposed operation is a multi-tiered supradegenerate energy ladder constructed inside its cell membrane. Recently, the intriguing proposal has been advanced that everyday cellular life might already be harvesting thermal energy from its surroundings, using standardcell membrane machinery (Lee, 2019).

Man-made supradegenerate systems appear possible, and these could constitute the most eclectic class of second law challenges yet proposed. We now review three of the most promising.

## Laser

Dozens of types of lasers are known (Milonni & Eberly, 1988; Saleh & Teich, 1991), and many more are possible.[6] Conventional lasers (Figure 5) require at least three quantum states: (1) ground state (g.s.), a low-energy state where the majority of molecules reside at equilibrium; (2) a long-lived metastable state (m.s.) that acts as

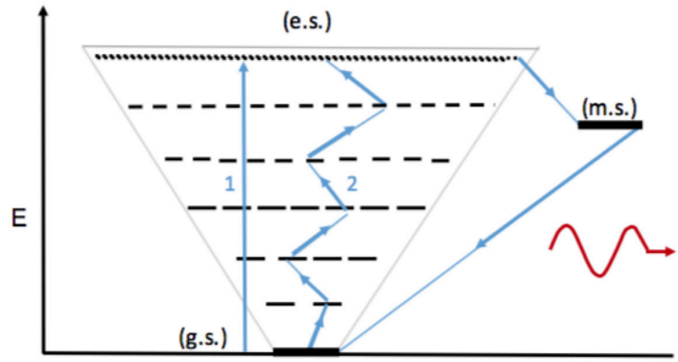


**Figure 5. Three-level laser. Conventional single-step non-equilibrium pumping (Path 1); and pumping via multi-step supradegenerate energy ladder (Path 2). Laser light (red) emitted in (m.s. ⟶ g.s.) transition.**

a reservoir of energy for the lasing transition (m.s. ⟶ g.s.); and (3) an excited state (e.s.) that feeds the metastable state and is pumped from the ground state by a nonequilibrium process, like a chemical reaction, electrical discharge, or optical pumping from another laser. The pump step in a traditional laser is accomplished via a single large, suprathermal transition ($\Delta E \gg kT$), as indicated by Path 1 in Figure 5. The excited state partially decays to the metastable, where a population inversion builds, and from there decays en masse, via stimulated emission, to create laser light.

A *supradegenerate laser* operates similarly to this conventional laser but with a major distinction: The supradegenerate laser makes the (g.s. ⟶ e.s.) transition via an energy ladder consisting of a series of small, roughly thermal increments ($\Delta E \sim kT$), as indicated by Path 2. One can liken the difference between these two paths to the difference between ascending a tall building in a single bound (Path 1) versus via the stairs (Path 2). Both achieve the same end, but by very different thermodynamic processes. Conventional lasers require *nonequilbrium* processes that entail external energy inputs (pumping), while the supradegenerate laser draws thermal energy directly from its environment *near equilibrium* to reach the excited state. More importantly, the conventional laser upholds the second law, whereas the supradegenerate laser violates it. Specifically, it contravenes the Kelvin–

Planck form of the law, which forbids transforming a quantity of heat solely into work (e.g., laser light) in a thermodynamic cycle.

The supradegenerate laser energy ladder has partial precedents with multiphoton pumping of organic dyes (He et al., 2002; Zhang et al., 2019; Zheng et al., 2013), nanocrystal systems (Li et al., 2015; Wang et al., 2014; Xing et al., 2012) and atoms (Garrett et al., 1996), which sometimes use intermediate states and multiple frequencies, but these adhere to the second law. Attractive candidates for supradegenerate laser ladders include impurity states in the bandgaps of insulators (e.g., alumina, quartz, titanium dioxide) and semiconductors (e.g., silicon, germanium, gallium arsenide). Particular incarnations of the supradegenerate laser are not known but are under study.

## Concentration-Graded Chemical Membrane

Capacitors are mainstays for electronic energy storage. The archetypal version consists of two parallel plates that are charged (energized) by an external power supply. It appears possible to create *thermally charged capacitors* using energy ladders built into concentration-graded chemical membranes, as depicted in Figure 6.

The supradegenerate capacitor could consist of a series of layers whose chemical concentrations of a charge-transfer molecule or polymer, e.g., ionomer (Eisenberg & Kim, 1998; Kreuer, 2003; Rogers & Ubbelohde, 1950) vary exponentially from bottom to top, satisfying the supradegeneracy condition, Equation (2). An attractive candidate is the *proton exchange membrane* (PEM) polymer nafion, which conducts hydrogen ions (protons)—not electrons—and whose number density of charge-transfer sites (sulfonic acid groups) can be varied widely and continuously. If the concentration of nafion is varied from low to high from the bottom to top layers of the membrane stack, an upward-pointing entropy gradient is created that should operate as an energy ladder for protons. Protons introduced at the bottom of the ladder (e.g., an acid bath, HCl) should experience an entropic force upward, such that $H^+$ ions accumulate at the top of the ladder, leaving negative counterions (e.g., $Cl^-$) at the base.

The stack generates an electrostatic potential up to a value at which further charge separation stops due to a balance between entropic and electrostatic forces. Analysis indicates that this can be

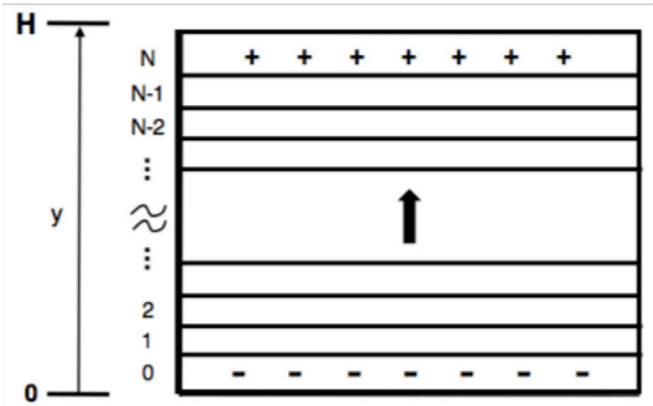


**Figure 6. Supradegenerate thermally charged capacitor. Discrete energy ladder with N + 1 levels, energy increment ∈ , maximum energy $E_{max}$ = ∈*N*, and degeneracy increasing vertically, with $g_n = p^n$. Charge separation (+/–) due to positive charge transport up ladder, leaving negative counter ions at base.**

up to several hundred millivolts. Analogous thermally generated, self-limiting electrostatic potentials and energies are well-known in plasma (Chen, 1984; Debye & Hückel, 1923; Ichimaru, 1980) and semiconductor (Neudeck, 1989; Mouthaan, 1999; Dimitrijev, 2000) systems, so this supradegenerate one is not surprising.

This arrangement constitutes a *thermally-charged capacitor*. Its capacitive energy can be written, $U = \frac{1}{2} CV^2$, where *V* is the net voltage across the membrane; capacitance is $C = \frac{\kappa \in_0 A}{d}$, with $\kappa$ the effective dielectric constant of the membrane, $\in_0$ the permittivity of free space, *A* the cross-sectional area of the membrane, and *d* its thickness. Electromechanical means to exploit this capacitive energy—while undermining the second law—has been explored in the context of MEMS/NEMS semiconductor oscillators (Sheehan et al., 2002; Sheehan et al., 2005).

A nafion capacitor energy ladder is currently under experimental investigation at USD. Initial experiments involving discrete nafion ladders corroborate the polarity and approximate magnitudes predicted for supradegenerate membrane voltages.

## Thermophotovoltaics

*Photovoltaics* (PV) convert light into electricity (Mertens, 2014; Smets et al., 2016). Solar PVs, for example, utilize the blackbody (thermal) radiation from the Sun ($T$ = 5800 K). *Thermophotovoltaics* (TPV) (Bauer, 2011) also convert light into electricity, but typically use cooler thermal sources (e.g., hot filament or rod), usually with $T$ < 2000 K. Though closely related, TPV is the poor cousin of solar PV, principally due to the technical difficulties connected with producing, maintaining, and powering the TPV radiation source; by contrast, the thermal radiation for solar PV (sunlight) arrives freely. Typical TPV semiconductors include germanium, gallium antimonide, indium gallium arsenide antimonide, or other narrow- or medium-gap semiconductors.

A conventional TPV/PV converter is a p-n diode, pictured in Figure 7. A photon (red squiggly arrow in Figure 7) excites an electron in a single transition from the valence band of the p-region into the conduction band, as indicated by Path 1, leaving behind a hole in the valence band. The electron is swept to the negative electrode by the electric field of the depletion region and the hole to the positive electrode. The electrodes can be connected across an electrical load to perform work. Here the electron recombines with the hole, and the cycle can repeat with another photon. In sum, photonic energy is converted into electrical energy.

The *supradegenerate thermophotovoltaic* (STPV) operates almost identically to the standard TPV, with one exception. In the STPV, the electron crosses from the valence band to the conduction band via a series of small, incremental steps ($\Delta E \sim kT$) up a supradegenerate energy ladder constructed across the bandgap (Path 2, Figure 7), rather than via a single large jump as in a standard TPV. Once across, the electron and hole should proceed as in a conventional TPV, performing work on the load. This scenario, however, conflicts with the Kelvin–Planck statement of the second law.

The STPV energy ladder is conceptually simple. Impurities in semiconductors can express themselves as energy states in the bandgap (Ibach & Lüth, 2009; Milnes, 1973; ). For example, with a silicon substrate (bandgap width 1.1 eV) the acceptor (p-type) impurities boron, gallium, and indium create energy states 0.045 eV, 0.072 eV,

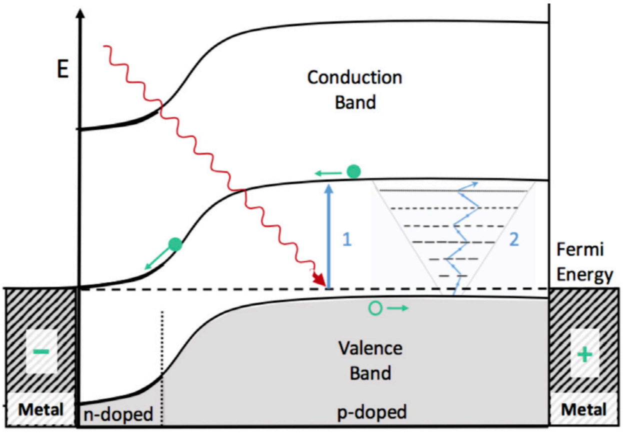


**Figure 7. Conventional and supradegenerate thermophotovoltaic (STPV). In conventional PV or TPV, a photon excites an electron directly from the valence band to the conduction band. In STPV, an electron climbs the energy ladder to the conduction band using only ambient thermal energy.**

and 0.16 eV, respectively, in the bandgap just above the valance band edge. If the impurity concentrations are set at roughly $10^{15}$ cm$^{-3}$, $10^{16}$ cm$^{-3}$, and $10^{17}$ cm$^{-3}$, respectively, these three impurities could constitute an elementary, three-tier energy ladder roughly 1/7 of the way up into the silicon bandgap. The supradegeneracy condition, Equation (2), is approximately satisfied. This silicon energy ladder is currently under experimental investigation at USD.[7]

Should this test ladder succeed, a 4–5 rung ladder will be attempted across a so-called *narrow-gap semiconductor* whose bandgap is $E_{bg} \leq 0.3$ eV. Candidate narrow-gap semiconductors (Dornhaus et al., 1983; McGill & Collins, 1993) include indium antimonide ($E_{bg} = 0.17$ eV), lead selenide ($E_{bg} = 0.27$ eV), and mercury cadmium telluride ($0 \leq E_{bg} \leq 1.5$ eV). As shown elsewhere (Sheehan, 2020b), a p–n diode with an ~0.3 eV bandgap, a 4–5 rung energy ladder (with appropriate concentration jumps between impurities), might operate as a *room-temperature* STPV. Assuming that rung spacings are roughly $\in \simeq 1 - 2kT$, the InSb bandgap could be completely bridged by just 2–4 well-placed impurities. These STPVs would contravene the second law because thermal energy (driving electrons up the ladder) has been converted solely into electrical energy. (Even if it fails as a second law challenge, the STPV ladder could improve the efficiency of standard PVs and TPVs by providing additional stepping stones by which a broader portion of solar or thermal spectra could be harvested (Sheehan, 2019).)

Refrigeration is a natural byproduct of supradegenerate (and epicatalytic) work cycles. If work is produced at the expense of the system's ambient thermal energy, then the first law of thermodynamics requires that the device cool, especially if it is thermally isolated from its heat reservoir. As one application, high-performance computer chips are often compromised by ohmic heating and require heroic cooling measures. On-chip supradegenerate refrigerators might not only offset ohmic heating but in principle also contribute to the chip's electrical power. Such zero–net-power, perpetual computing has been proposed (Sheehan, 2010; Yeung, 2002). As a bonus, this application could help answer longstanding questions at the intersection between thermodynamics and information theory (Shannon, 1948; Yeung, 2002), such as the fate of Maxwell's demon (Bennett, 1982; Leff & Rex, 2003; Maxwell, 1872) and the physics of Landauer's principle (Earman & Norton, 1998, 1999; Landauer, 1961).

## DISCUSSION

Epicatalysis and supradegeneracy are foundational to Gen III challenges, but they themselves do not conflict with the second law. In fact, the peril posed by the Maxwell zombies depends critically on the faithful operation of the second law.[8] Remarkably, in each step of the zombic thermodynamic cycles, the second law is satisfied, and its violation cannot be pinned on any individual step; rather, it is only in assessing the cycle in toto that the law is contravened. An analogous claim can be made of the classic Carnot work cycle: Each individual step satisfies the second law and no individual operation depends directly on any of the others, but together in proper sequence and subject to suitable boundary conditions and constraints, they complete a work cycle. The difference between the Carnot and Maxwell zombie cycles is that the former generates net entropy, while the latter consumes it.

One might suspect, especially given the omniscience often ascribed to it, that the second law should be able to look ahead in a zombic cycle and somehow find a way to foil it, but this mistakes the law's modus operandi. The second law neither remembers the past nor plans for the future: It operates strictly in the present, maximizing the entropy of its immediate environment as quickly as possible, subject to its boundary conditions and physical constraints. As such, it is blind to higher-order, meta-phenomena like the overall thermodynamic cycle. (It is blind in an analogous way that natural selection is blind in its support of the meta-phenomenon, evolution.) Maxwell zombies use the second law's temporal shortsightedness and entropic greed against it.

Ultimately, the second law is a physical axiom based on experimental observations of Nature; it is true only because it is observed to be so. Likewise, Maxwell zombies, no matter how compelling, cannot be considered actual violations until they are successfully reduced to practice. Although claims to this effect have been made (Sheehan et al., 2014), they have not been accepted by the scientific community. It is the opinion of this author that such claims will continue to be dismissed or ignored until a commercial application is realized, at which point the scientific community's imprimatur becomes superfluous. It is here that Gen III devices find their value because of their commercial potential.

Gen III challenges are the culmination of the previous two generations. It would have been difficult to arrive at them ex nihilo; actually, the shortcomings of Gens I and II were their spur. In particular, Gen I suffer from one or more of the following limitations: (1) high temperatures; (2) low pressures; (3) exotic materials; (4) low power densities; (5) astronomical size; (6) difficult or expensive manufacture. Generation II eliminates or reduces shortcomings (1–5) but exacerbates (6). Generation III again sidesteps (1–5) and mostly resolves (6).[9]

## CONCLUSIONS

Epicatalysis and supradegeneracy have been recognized as physical phenomena only in the last several years, but they could have been discovered 100–150 years ago, as could have many of their physical embodiments. In this sense, Gen III challenges are underwhelming; after all, they do not involve exotic materials or extreme thermodynamic conditions. In another sense, however, this is encouraging because they should not be overly difficult to explore; after all, many involve 19th-century technology and methods.

Science is littered with former 'laws': Newton's law of gravitation, law of mass action, conservation of mass, ideal gas law, Avogadro's, Boyle's, Charles's, Dalton's, Euler's, Fourier's, Gay-Lussac's, Ohm's, Kirchhoff's, Darcy's, Petit-Dulong, Curie's, Raoult's, Snell's, Stokes', and many more. Though still widely applicable, these 'laws' are now understood to be merely handy approximations. Their demotions did not reduce their usefulness; rather, they cleared the way for more comprehensive, precise, and accurate descriptions of Nature. Newton's gravity, for instance, gave way to Einstein's general relativity; the ideal gas law was superceded by van der Waals equation; and conservation of mass was replaced by conservation of mass–energy. Perhaps it's time to reconsider the universality of the 19th-century's most famous law. Should Maxwell zombies fail, the domain of the second law is extended; should they succeed, new thermodynamic horizons appear. Win, lose, or draw, something surprising will be learned and new technologies and applications likely result.[10] In the end, science proceeds by paradox, not dogma.[11]

## NOTES

1 The canonical ensemble is considered here, but this discussion also applies to the microcanonical or grand canonical ensembles.

2 By analogy, it is relatively easy to climb a tall building taking the stairs, while rather difficult to leap it in a single bound.

3 The e-folding distance for an ideal gas column on Earth is roughly 8.6 km, thus to attain suprathermal gravitational energy (e.g., $E = mgz \simeq 10kT$ with T = 300 K) would require a cone height of roughly 85 km, which is just shy of the von Karman line, the rough boundary between the atmosphere and space.

4 Real energy ladders will be capped by such things as the finite size and number of atoms in the system.

5 A number of natural systems (e.g., the hydrogen atom and other hydrogenic systems) narrowly avoid the supradegeneracy condition for reasons not understood, but currently under investigation.

6 The opportunities for lasing are so ubiquitous that it is said that strawberry jam (or a solution of it) could be made to lase.

7 This research is conducted in collaboration with Pacific Integrated Energy, San Diego, California, USA.

[8] For example, in the ETD (Figure 1), the second law guarantees the operation of the heat engine by which its violation is consummated.

[9] It is the opinion of this author that the ETD is the simplest, potentially highest power density, most versatile, and perhaps least expensive second law device yet devised.

[10] Rarely do novel physical phenomenon (e.g., supradegeneracy, epicatalysis) not result in new technologies or applications.

[11] It is hoped Bohr's dictum holds: "How wonderful that we have met with a paradox. Now we have some hope of making progress" (Moore, 1966).

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## REFERENCES

Attard, P. (2012). *Non-equilibrium thermodynamics and statistical mechanics: Foundations and applications.* Oxford University Press.

Bauer, T. (2011). *Thermophotovoltaics: Basic principles and critical aspects of system design.* Springer.

Bennett, C. H. (1982, December). The thermodynamics of computation—A review. *International Journal of Theoretical Physics, 21*(12), 905–940.

Cápek, V., & Sheehan, D. P. (2005). *Challenges to the second law of thermodynamics (Theory and experiment).* Fundamental Theories of Physics Series 146. Springer.

Chen, F. F. (1984). *Introduction to plasma physics and controlled fusion: Volume 1: Plasma physics* (2nd ed.). Plenum.

Debye, P., & E. Hückel, E. (1923). The theory of electrolytes. *Physikalische Zeitschrift, 24,* 185–206.

de Groot, S. R., & P. Mazur, P. (1984). *Non-equilibrium thermodynamics.* Dover.

Denur, J. (2018). Epicatalysis in a simple mechanical–gravitational system: A second-law paradox? *Journal of Thermodynamics and Catalysis, 9.* DOI:10.4172/2157-7544.1000200; researchgate.net/publication/334811479

Dimitrijev, S. (2000). *Understanding semiconductor devices.* Oxford University Press.

Dornhaus, R., Nimtz, G., & Schlicht, B. (1983). *Narrow-gap semiconductors.* Springer.

Earman, J., & Norton, J. D. (1999). Exorcist XIV: The wrath of Maxwell's demon. *History and Philosophy of Modern Physics, 29*(4), 435–471; *30*, 1.

Eddington, A. S. (1935). *New pathways in science.* Cambridge University Press.

Eisenberg, A., & Kim, J.-S. (1998). *Introduction to Ionomers.* Wiley.

Garrett, W. R., Zhu, Y., Deng, L., & Payne, M. G. (1996). Multi-photon excitation through a resonant intermediate state: Unique separation of coherent and incoherent contributions. *Optics Communications, 128,* 66.

Gaveau, B., & Schulman, L. S. (2009). Generalized Clausius relation and power dissipation in nonequilibrium stochastic systems. *Physics Review E, 79*(1), 021112.

He, G. S., Markowicz, P. P., Lin, T. C., & Prasad, P. N. (2002). Observation of stimulated emission by direct three-photon excitation [Letter]. *Nature, 415,* 767–770.

Ibach, H. & Lüth, H. (2009). *Solid-state physics* (4th ed.) Springer.

Ichimaru, S. (1980). *Basic principles of plasma physics: A statistical approach.* Benjamin-Cummings.

Kreuer, K. D. (2003). Proton-conducting oxides. *Annual Review of Materials Research, 33,* 333.

Landauer, R. (1961). Irreversibility and heat generation in the computing process. *IBM Journal of Research and Development, 5,* 183–191. http://dx.doi.org/10.1147/rd.53.0183

Lee, J. W. (2019). Electrostatically localized proton bioenergetics: Better understanding membrane potential. *Heliyon, 4,* e01961.

Leff, H. S., & Rex, A. F. (2003). *Maxwell's demon 2: Entropy, classical and quantum information, computing.* Institute of Physics Publishing.

Li, M., et al. (2015). Ultralow-threshold multiphoton-pumped lasing from colloidal nanoplatelets in solution. *Nature Communications.* DOI: 10.1038/ncomms9513

Maxwell, J. C. (1872). *Theory of heat* (Chapter 12). Longmans, Green, and Co.

McGill, T. C., & Collins, D. A. (1993). Prospects for the future of narrow bandgap materials. *Semiconductor Science Technology, 8,* S1.

Mertens, K. (2014). *Photovoltaics: Fundamentals, technology and practice.* John Wiley.

Milnes, A. G. (1973). *Deep impurities in semiconductors.* Wiley-Interscience.

Milonni, P. W., & Eberly, J. H. (1988). *Lasers.* John Wiley & Sons.

Moore, R. E. (1966). *Niels Bohr: The man, his science & the world they changed.* Knopf.

Mouthaan, T. J. (1999). *Semiconductor devices explained: Using active simulation.* Wiley.

Nelson, P. (2004). *Biological physics: Energy, information, life.* W. H. Freeman.

Neudeck, G. W. (1989). *The PN junction diode* (2nd ed.). Addison-Wesley.

Neumann, R. M. (1980). Entropic approach to Brownian movement. *American Journal of Physics, 48*(5), 354–357. https://doi.org/10.1119/1.12095

Pathria, R. K. (1985). *Statistical mechanics.* Pergamon.

Reif, F. (1965). *Fundamentals of statistical and thermal physics.* McGraw-Hill.

Rogers, S. E., & Ubbelohde, A. R. (1950). Melting and crystal structure. III.—Low-melting acid sulphates. *Transactions of the Faraday Society, 46*, 1051–1061. https://doi.org/10.1039/TF9504601051

Saleh, B. E. A., & Teich, M. C. (1991). *Fundamentals of photonics.* John Wiley & Sons.

Schroeder, D. V. (2000). *An introduction to thermal physics.* Addison Wesley Longman.

Shannon, C. E. (1948, July, October). A mathematical theory of communication. *Bell System Technical Journal, 27, 379–423*, 623–656. http://people.math.harvard.edu/~ctm/home/text/others/shannon/entropy/entropy.pdf

Sheehan, D.P. (1995). A paradox involving the second law of thermodynamics. *Physics of Plasmas, 2*(6), 1893–1898. https://doi.org/10.1063/1.871276

Sheehan, D. P. (1996). Another paradox involving the second law of thermodynamics. *Physics of Plasmas, 3*(1), 104–110. https://doi.org/10.1063/1.871834

Sheehan, D. P. (1998a, June). Four paradoxes involving the second law of thermodynamics. *Journal of Scientific Exploration, 12*(2), 303–314. https://www.scientificexploration.org/docs/12/jse_12_2_sheehan.pdf

Sheehan, D. P. (1998b, June). Dynamically maintained steady-state pressure gradients. *Physical Review E, 57*(6), 6660–6666. https://digital.sandiego.edu/cgi/viewcontent.cgi?article=1003&context=phys-faculty

Sheehan, D. P. (2001, February). The second law and chemically-induced, steady-state pressure gradients: Controversy, corroboration and caveats. *Physics Letters A, 280*(4), 185–190. https://doi.org/10.1016/S0375-9601(01)00060-3

Sheehan, D. P. (Ed.) (2002, July). *First international conference on quantum limits to the second law*, San Diego, CA, July 28–31,2002; *American Institute of Physics 643*.

Sheehan, D. P. (Guest Ed.). (2007a). The second law of thermodynamics: Foundations and status. *Proceedings of AAAS Symposium*, June 19–22, 2006, University of San Diego, CA; Special Issue of *Foundations of Physics, 37*(12).

Sheehan, D. P. (2007b, December). Thermosynthetic life. *Foundations of Physics, 37*(12), 1774–1797. https://doi.org/10.1007/s10701-007-9168-y

Sheehan, D. P. (2008, December). Energy, entropy, and the environment (how to increase the first by decreasing the second to save the third). *Journal of Scientific Exploration, 22*(4), 459–480. https://www.scientificexploration.org/docs/22/jse_22_4_sheehan.pdf

Sheehan, D. P. (2010). *Look mom, no batteries: Perpetual computing and the second law*. Technical presentations at Microsoft and Google.

Sheehan, D. P. (Ed.). (2011). Second law of thermodynamics: Status and challenges. *Proceedings of symposium at 92nd Annual Meeting of Pacific Division of AAAS*, 14–15 June 2011, University of San Diego; *American Institute of Physics 1411*.

Sheehan, D. P. (2013). Nonequilibrium heterogeneous catalysis in the long mean-free-path regime. *Physical Review E, 88*, 032125. https://doi.org/10.1103/PhysRevE.88.032125

Sheehan, D. P. (2015, December). United States Patent, US 9,212,828, *Epicatalytic Thermal Diode*. U.S. Patent Office.

Sheehan, D. P. (2018a, July–August). Maxwell zombies: Conjuring the thermodynamic undead. *American Scientist, 106*(4), 234–241. https://doi.org/10.1511/2018.106.4.234

Sheehan, D. P. (2018b). Asymmetric van't Hoff equation and equilibrium temperature gradients. *Journal of Non-Equilibrium Thermodynamics, 43*(4), 301–315. https://doi.org/10.1515/jnet-2017-000

Sheehan, D. P. (2019, December). Advancing photovoltaics and thermophotovoltaics with supradegeneracy. *Sustainable Energy Technologies & Assessment, 36*, 100539.

Sheehan, D. P. (2020a). Thermal energy extraction and utilization using supradegeneracy. U.S. patent pending.

Sheehan, D. P. (2020b). Supradegeneracy and the second law of thermodynamics. *Journal of Non-Equilibrium Thermodynamics, 45*(2), 121–132. https://doi.org/10.1515/jnet-2019-0051

Sheehan, D. P., & Gross, D. H. E. (2006, October 15). Extensivity and the thermodynamic limit: Why size really does matter. *Physica A, 370*(2), 461–482. https://doi.org/10.1016/j.physa.2006.07.020

Sheehan, D. P., & Schulman, L. S. (2019, June 15). 'Population inversion' at equilibrium. *Physica A, 524,* 100–105. https://doi.org/10.1016/j.physa.2019.03.022

Sheehan, D. P., & Welsh, T. M. (2019, February). Epicatalytic thermal diode: Harvesting ambient thermal energy. *Sustainable Energy Technologies & Assessments, 31,* 355–368. https://doi.org/10.1016/j.seta.2018.11.007

Sheehan, D. P., Putnam, A. R., & Wright, J. H. (2002, October). A solid-state Maxwell demon. *Foundations of Physics, 32*(10), 1557–1595. https://doi.org/10.1023/A:1020479302947

Sheehan, D. P., Wright, J. H., Putnam, A. R., & Perttu, E. K. (2005, October). Intrinsically biased, resonant NEMS-MEMS oscillator and the second law of thermodynamics. *Physica E, 29*(1–2), 87–99.

Sheehan, D. P., Mallin, D. J., Garamella, J. T., & Sheehan, W. F. (2014, March). Experimental test of a thermodynamic paradox. *Foundations of Physics, 44*(3), 235–247. https://doi.org/10.1007/s10701-014-9781-5

Sheehan, D. P., Zawlacki, T. A., & Helmer, W. H. (2016, July). Apparatus for testing gas–surface reactions for epicatalysis. *Review of Science Instruments, 87*(7), 074101. https://doi.org/10.1063/1.4954971

Smets, A., Jäger, K., Isabella, O., Van Swaaij, R., & Zeman, M. (2016). *Solar energy: The physics and engineering of photovoltaic conversion technologies and systems.* UIT Cambridge.

Sokolov, I. M. (2010, November). Statistical mechanics of entropic forces: Disassembling a toy. *European Journal of Physics, 31*(6), 1353–1367.

Wang, Y. et al. (2014, May 14). Stimulated emission and lasing from CdSe/CdS/ZnS core-multi-shell quantum dots by simultaneous three-photon absorption. *Advanced Materials, 26,* 2954–2961.

Xing, G., et al. (2012). Ultralow-threshold two-photon pumped amplified spontaneous emission and lasing from seeded CdSe/CdS nanorod heterostructures. *ACS Nano, 6*(12), 10835–10844.

Yeung, R. W. (2002). *A first course in information theory.* Kluwer Academic/Plenum.

Zhang, F.-D., et al. (2019, September). Dynamic properties of ultrashort two-photon pumped transient cavityless lasing in a Coumarin-dye solution, *Journal of Optics, 21*(10), 105502. https://doi.org/10.1088/2040-8986/ab3e23

Zheng, Q., et al. (2013, March). Frequency-upconverted stimulated emission by simul-taneous five-photon absorption. *Nature Photonics 7,* 234–239. https://doi.org/10.1038/nphoton.2012.344

Zwanzig, R. (2001). *Nonequilibrium statistical mechanics.* Oxford University Press.