

10

Special Topics

Four special topics are discussed: (i) two proposals for a common rubric for classical second law challenges; (ii) speculation on a third type of life — *thermosynthetic* — which would sustain itself by converting heat into biochemical energy; (iii) speculations on the far future (physical eschatology); and finally, (iv) a collection of quotations from the sciences and humanities pertaining to the second law.

10.1 Rubrics for Classical Challenges

Of the several second law challenges that have been advanced over the last 20-25 years, the majority have been forwarded as independent counterexamples, narrow in their thermodynamic regimes of validity and specific in their physical constructions. No attempt has been made to place all under a single theoretical rubric. Perhaps such an enterprise is misguided. Just as the many attempts over the last 150 years to produce a general proof of the second law have failed — it has been proven only for a few highly idealized systems — so too, perhaps, a general theory of second law exceptions might prove equally elusive. Surely, one valid counterexample suffices to refute absolute validity, but finding the common thread among the many would be both satisfying and useful to future investigations.

In this section, we explore the similarities among the several ostensibly disparate challenges investigated at the University of San Diego (USD) since the early 1990's [1-9]. Several common threads bind them: geometric and thermody-

System	Temp (K)	Pressure (Torr)	Power Density (W/m ³)
Plasma I (electrostatic)	> 1500	< 10 ⁻³	10 ⁻²
Plasma II (chemical/electrostatic)	> 1500	< 10 ⁻³	10 ⁻²
Chemical (chemical)	> 1000	< 1	10 ⁻³
Gravitational (gravitational)	> 10	< 10 ⁻¹⁰	10 ⁻⁹
Solid State (chemical/electrostatic)	100 < T < 1000	—	> 10 ⁸

Table 10.1: USD challenges, comparing viable temperature and pressure ranges and estimated power densities. MPG listed below the system name.

namic asymmetries, macroscopic potential gradients, and asymmetric momentum fluxes. A notable theorem by Zhang and Zhang [10] asserts that the latter of these threads should bind *all* second law challenges to date.

10.1.1 Macroscopic Potential Gradients (MPG)

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.

For this discussion, *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. Directional, nonequilibrium particle fluxes are the hallmarks of standard work-producing processes. *Macroscopic* refers to length scales long compared to atomic dimensions and to those of statistical fluctuations. In order to extract wholesale work, a system's potential gradients should be *macroscopic*.

Working fluids can be transformed from one MPG to another, descending a ladder, starting from high-grade directed energy to lower-grade undirected energy (heat), ending in a maximum entropy state (equilibrium). For practice, it is instructive to trace the million year journey of energy via various working fluids and MPGs, starting from hydrogen fusion in the Sun's core, to its release as light from

the solar photosphere, its absorption by chloroplasts and conversion into carbohydrates in Iowan corn fields, to its ultimate exhaustion as frictional heat as a child pedals down a country road in rural Indiana after a breakfast of corn flakes. Here one can identify a dozen different fluids and MPGs. It is fair to say that *nonequilibrium macroscopic potential gradients make the world go round*.

So far, only *nonequilibrium* MPGs have been considered, but *equilibrium* MPGs are also common. 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 (or none at all). As a result, their exploitation to perform work can imply the use of heat from a heat bath, and thereby a challenge to the second law.

Each USD challenge consists of (i) a blackbody cavity surrounded by a heat bath; (ii) a working fluid (*e.g.*, gas atoms, electrons, ions, holes); (iii) a work extraction mechanism (*e.g.*, electrical generator, piston); and (iv) an equilibrium MPG (*e.g.*, gravitational field, electric field of a Debye sheath or depletion region). Work is extracted as the working fluid cycles through the potential gradient. On one leg of its cycle the working fluid ‘falls’ through the MPG and is transformed into a spatially-directed nonequilibrium flux, by which work is performed. On the return leg, the fluid and system returns to its original thermodynamic macrostate via thermal processes (*e.g.*, diffusion, evaporation). The work performed by exploiting the MPG (either intermittently or in steady state) represents a *large, local* excursion from equilibrium, but only a *small* excursion for the system *globally*. The USD challenges range in size from nanoscopic to planetary ($10^{-7} - 10^7$ m), operate over more than an order of magnitude in temperature (100 - 2000 K), and over more than 8 orders of magnitudes in pressure ($\sim 10^3 - 10^{-6}$ Torr). They span chemical, plasma, gravitational and solid state physics.

A summary of the USD challenges can be found in Table 10.1, comparing their viable temperature and pressure regimes, and theoretical achievable power densities. The following is a summary of the *equilibrium* MPG that are discussed in Chapters (6-9).

Plasma (Chapter 8; [1, 2, 3]) Electrons and ions at a single temperature have different average thermal speeds $(\frac{kT}{m})^{1/2}$, owing to their different masses. In a sealed blackbody cavity, in order to balance thermal flux densities in and out of the 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 $\frac{kT}{q}$ and gradients of order $\nabla V \sim \frac{V_{pl}}{\lambda_D}$. Sheath electrostatic gradients of the order of 10^3 V/m are common.

Chemical (Chapter 7; [4, 5, 6]) 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 (Chapter 6; [7, 8]) 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 (Chapter 9; [9]) When n- and p-doped semiconductors are joined (forming a standard p-n diode) the requirement for uniform chemical potential (Fermi level) throughout the diode, and the thermal diffusion of electrons and holes down concentration gradients between the two regions, gives rise to an electrostatic potential difference (built-in potential, V_{bi}) between the two regions, across the so-called *depletion region* (thickness x_{dr}). One can say that, in the depletion region, a balance is struck between electrostatic and chemical potentials. The equilibrium electrostatic potential gradient scales as $\nabla V \sim \frac{V_{bi}}{x_{dr}}$, which for typical p-n diodes is on the order of $\frac{1V}{10^{-6}m} = 10^6 V/m$. (The similarities between the plasma and solid state systems is not coincidental.)

The above *equilibrium* MPGs and their working fluids possess *all* of the required physical characteristics by which standard *nonequilibrium*, free-energy-driven MPGs are known to perform work in traditional thermodynamic cycles. The equilibrium MPGs are well understood and experimentally verified; all are macroscopic structures. They possess potential gradients of sufficient magnitude and directionality to overcome thermal fluctuations and to perform macroscopic work. They differ from their nonequilibrium counterparts only in that they are generated and maintained under equilibrium conditions.

If MPGs are so common, it is natural to ask why their aptitudes for challenging the second law were not discovered earlier. First, the thermodynamic regimes in which they thrive are extreme (*e.g.*, high-temperatures and low-pressure for chemical and plasma systems) or else their operational scale lengths are either too large (planetary for gravitator) or too small (sub-micron for p-n diode) to be easily studied. Furthermore, the paradoxical effects are usually secondary in magnitude to other system effects and must be carefully isolated.

Several of the MPG systems are thermodynamically non-extensive in the sense described by D.H.E. Gross [11, 12]; that is, they are “finite systems of size comparable to the range of the forces between their constituents,” and they are “thermodynamically unstable.” Their energies and entropies do not scale linearly with size — the hallmark of non-extensivity. This is most apparent in the plasma, solid state, and gravitational systems, whose electric and gravitational fields energies scale quadratically with field strength. (Recall, electrostatic energy density scales as $\rho \propto E^2$.)

Boundaries are critical to these systems; without them they would either not possess usable MPGs or could not utilize them, in which case they would not pose second law challenges. And, because of boundaries, these systems should properly be evaluated outside the usual thermodynamic limit assumptions of infinite particle number and volume. Microcanonical approaches like those championed by Gross might be more fruitful [11, 12].

10.1.2 Zhang-Zhang Flows

In 1992, Kechen Zhang and Kezhao Zhang (hereafter Zhang-Zhang) [10] demonstrated a number of new aspects to Maxwell demons within the framework of classical mechanics. These were developed in the context of what they termed *spontaneous momentum flows* (SMF). A SMF is a *sustaining and robust momentum flow inside an isolated mechanical system*. All qualifiers must be simultaneously satisfied. The momentum flow must arise spontaneously within the system without resort to internal exhaustible free energy sources or to external sources of free energy. It must be *robust* in the sense that minor perturbations do not destroy it and it must be able to restore itself if it is interrupted. It must be *sustaining* in the sense that the long-term average of the momentum flow is non-vanishing.

Zhang-Zhang show the second law can be formulated in terms of the nonexistence of SMF. They begin by arguing that [10]

- (i) the existence of a perpetual motion machine of the second kind implies the existence of SMF; and the existence of SMF implies the existence of a perpetual motion machine.

They demonstrate that “the Kelvin-Planck statement of the second law is equivalent to the statement *in any isolated system, no spontaneous momentum flow exists.*”

From here, Zhang-Zhang prove a nonexistence theorem for SMF for classical systems of N interacting point particles, defined through the force equation:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N; \dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N), \quad (10.1)$$

where \mathbf{r}_i and $\dot{\mathbf{r}}_i$ are the position and velocity of the i^{th} mass m_i . The Zhang-Zhang theorem shows that a system of N interacting point particles cannot harbor a SMF under two conditions:

- (i) Its energy function E is symmetric under momentum reversal, *i.e.*, $E(q_i, p_i) = E(q_i, -p_i)$, where q_i and p_i are generalized coordinates and momenta; and
- (ii) Its phase space volume $d\Omega = dq_1 \dots dq_N dp_1 \dots dp_N$ is temporally invariant.

The theorem does not require system ergodicity, although it applies equally well to the ergodic case. It is valid for classical systems; its demonstration in the quantum realm has not been pursued.

Using the Zhang-Zhang theorem, one can immediately discount challenges which demonstrate symmetric and invariant measure on their phase space energy surfaces. Zhang-Zhang develop an example of a purported Maxwell demon governed by the Lorentz force

$$m\ddot{\mathbf{r}} = q(\dot{\mathbf{r}} \times \mathbf{B}(\mathbf{r})) - q\nabla\phi(\mathbf{r}) \quad (10.2)$$

and show that, since the phase space volume of this system is preserved by its dynamics, it cannot support a SMF — therefore, cannot violate the second law — regardless of its complexity and intricacy of construction.

The Zhang-Zhang theorem demonstrates the deep relationship between the second law and phase space volume invariance of classical systems. They state:

... the validity of the second law relies on the dynamics in the underlying mechanical system, [but] this validity cannot be justified by the laws of classical mechanics alone. Invariance of phase volume appears as an additional factor which is responsible for this validity. ... Looking from another angle, if the second law is taken as a fundamental assumption, then the invariance of phase volume may be considered as a constraint imposed by the second law on the allowable dynamics of the mechanical systems.

Independently of Zhang-Zhang, in 1998 Sheehan [13] explained the necessary and sufficient conditions for the several USD challenges in terms of *asymmetric momentum fluxes*. He noted that each challenge relies on two broken symmetries — one thermodynamic and one geometric — in the physical design of the system. The broken thermodynamic symmetry creates an internal, steady-state asymmetric momentum flux and the geometric asymmetry converts this flux into work at the expense of the heat bath. Sheehan's asymmetric momentum fluxes are equivalent to the Zhang-Zhang spontaneous momentum flows. More recently, it has been recognized that the asymmetric momentum fluxes common to the USD systems arise due to macroscopic potential gradients (MPG), as discussed above (§10.1.1).

In their article, Zhang-Zhang assert “the concept of SMF is an imaginary one since no known physical systems exhibit it.” The several challenges in this volume stand as counterexamples to this claim. As derived, the Zhang-Zhang theorem is descriptive of all classical challenges to date, but rather than refuting them, it gives insight into their common basis. We suspect that deeper physics will be eventually uncovered linking them further. Attempts to fathom this *deeper* physics behind the second law have begun [14].

10.2 Thermosynthetic Life

10.2.1 Introduction

In this section the hypothesis is explored that life might exploit second law violating processes. All evidence will be theoretical and circumstantial since there is no experimental evidence that life violates the second law in the least, either macroscopically or microscopically. Quite the contrary, life is often considered to be a strong ally of the second law since biotic chemicals typically generate far more entropy in the world than they would otherwise create in an abiotic state.

It is estimated that since the emergence of life on Earth roughly 3.8 - 4 billion years ago, on the order of a billion species have existed and that, of these, roughly

10 million currently exist. Of this extant 1% of total species, perhaps only about 20% have been identified by name. Of those identified, few have been studied well enough to make general claims about their thermodynamics; however, those that have been studied carefully have shown compliance with the second law. In highly studied species — for instance, *E. coli*, *C. elegans*, mice, monkey, men — only a small fraction of proteins and biochemical pathways have been thoroughly studied. (Human are estimated to contain roughly 32,000 genes and about 10^6 proteins of which less than 10% have been positively identified.) Despite this apparent dearth of biochemical knowledge, there is significant biochemical commonality among species such that close study of a few should give an overview of the many. Nonetheless, current understanding of biology and biochemistry across all species is insufficient to rule conclusively that *all* biological processes, structures, and systems comply with the second law.

Several theoretical proposals for second law challenges have been inspired by biological systems. Modern work in this area dates back 25 years to the seminal proposals of L.G.M. Gordon (§5.2). The Crosignani-Di Porto mesoscopic adiabatic piston (§5.4) suggests that the second law might fail at scale lengths characteristic of living cells. There are suspicions by many that if the second law is violable, life would have exploited it.

The exigency of natural selection — *whatever survives to reproduce survives* — suggests that if subverting the second law confers a reproductive evolutionary advantage on organisms and if the second law can, in fact, be subverted, then the soaring cleverness, diversity and resourcefulness of Nature would, with high probability, achieve this end. Since there are several imaginable scenarios in which *thermosynthetic life* (TL) [15] would compete well with or even outcompete ordinary *free-energy life* (FEL) by subverting the second law, it is reasonable to seek biological violation. Standard FEL is divided into *chemosynthetic* and *photosynthetic* forms; the former derives its primary energy from chemical processes, while the latter relies on electromagnetic radiation (photosynthesis). Thermosynthetic life, which would derive its energy from heat, would constitute a third distinct type of life.

Basic characteristics of TL are suggested by thermodynamic considerations. Multicellular life is less likely to exploit thermal energy than unicellular life because it has an intrinsically lower surface-to-volume ratio and, thus, has access to less thermal energy per cell than unicellular life. Therefore, thermosynthetic life, if it exists, is most likely to be small and unicellular. The lower limits to the size of organisms (viruses, viroids, and prions aside) is a subject of debate. Recent studies suggest that it may be as small as 20 nm [16].

If TL must compete against FEL for material resources, then it will likely be outcompeted under everyday circumstances where rich free-energy sources are abundant, *e.g.*, sunlight, plant and animal tissue, or raw energetic chemicals spewing from hydrothermal vents. Pure TL would eschew these and so would be at a severe energetic and evolutionary disadvantage. Thermosynthetic life might best compete against FEL in free-energy poor environments; thus, it is also likely to be anaerobic and isolated geologically and hydrologically from chemosynthetic and photosynthetic life. This suggests TL might be best suited to life deep inside

the earth. (In recent years it has become apparent that deep-rock microbes enjoy significant diversity and might actually represent greater biomass than surface dwelling life [17].) These environments can also be quite stable so as to allow TL to evolve and thrive without direct competition from FEL for long periods of time.

Thermosynthetic life might have an edge in high-temperature environments. First, higher temperatures imply higher thermal power densities to drive biochemical reactions. Second, for reasons to be discussed shortly, high temperatures favor some second law violating mechanisms. Again, deep subsurface environments fit the bill. Temperatures rise with increasing depth in the Earth at a rate of roughly $1.5 - 3 \times 10^{-2} \text{K/m}$. At depths of 5 km rock temperatures approach 400 K. If it exists in deep rock, TL is likely superthermophilic and hyperbarophilic. In deep-sea hydrothermal vent environments, the high pressures augment thermophilic tendencies by raising the boiling point of water and by compressing molecular structures that might otherwise thermally disintegrate. In the laboratory, microbes have survived exposure to pressures of 1.6 GPa ($1.9 \times 10^4 \text{atm}$). Microbes have been discovered in continental rocks down to depths of 5.2 km [18]. The limit to the depth of life is likely set not only by temperature and pressure, but also by the pore sizes between rock grains, which are reduced at high pressures. It is expected that pressure, temperature and pore size would disallow carbon-based life below about 10 km.

In summary, if thermosynthetic life exists, it is likely to be small, unicellular, anaerobic, hyperbarophilic, superthermophiles confined to free-energy poor environments, well isolated from FEL in long-term stable locations. Deep rock microbes (Archaea) seem to be the best candidates, situated at and beyond the fringes of where FEL is known to survive.

Archaea are among the most ancient life forms; current molecular evidence based on RNA analysis places them near the base of the tree of life. (At present, three domains are generally recognized: eukaryotes (cells with nuclei), bacteria and archaea (cells without nuclei); the latter two display superthermophilicity.) Among the most ancient archaea are hyper- and superthermophiles, suggesting — but certainly not proving — that life may have originated in high temperature environments, like deep-sea marine vents or in the earth's crust.

The current high temperature record for culturable microbes is $T = 394\text{K}$, set by *Strain 121*, an Fe(III)-reducing archaea recovered from an active “black smoker” hydrothermal vent in the Northeast Pacific Ocean [19]. It grows between 85° and 121°C — temperatures typically used in autoclaves to sterilize laboratory equipment and samples. The upper temperature limit for microbes has been estimated to be roughly 425K (150°C) [20-26].

Archaea and bacteria have many special adaptations for survival at high temperatures. Unlike bacteria and eukaryotes which have lipid bilayer membranes, archaea have monolayer lipid membranes (ester cross-linked lipids) that resist thermal separation. Thermophiles also employ stiff, long-chain carotenoids that span their membranes, thereby reinforcing them against thermal separation. Carotenoids are highly conjugated organics also known for good electrical conductivity via long-range, delocalized molecular orbitals. They can mediate direct charge transport across membranes.

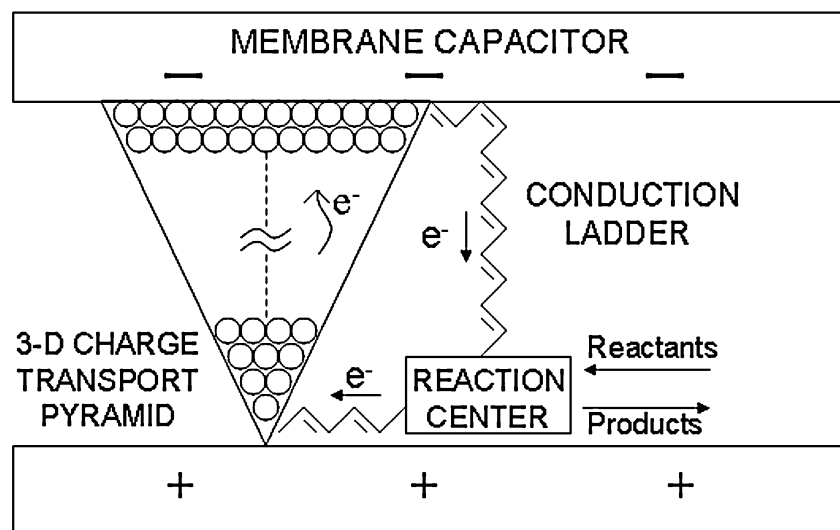


Figure 10.1: Schematic of proposed biochemical machinery for thermosynthetic life. Charge cycles clockwise: diffusively up through the pyramid and ballistically down the conduction ladder through the reaction center, where high-energy chemical products are formed.

Another possibility is that standard FEL life may harvest thermal energy as a supplement to standard free energy sources, or might resort to it under dire circumstances when its traditional free energy sources are cut off. This suggests that long-entombed and dormant microbes might be good candidates for TL. For example, bacteria have been found to remain viable for millions of years trapped in ancient salt crystals essentially absent of free energy sources and nutrients [27].

Thermosynthetic organisms would not necessarily be expected to arise *ex nihilo* from abiotic chemicals, but one can envision strong evolutionary forces by which they might evolve from standard FEL. Free energy life, wherever it first evolved — deep-ocean vents, surface, or deep rock — would naturally spread to all possible habitable regions. Where conditions were not initially favorable, in time, evolutionary forces would reshape the organism as far as possible. FEL would extend deeply into subsurface environments — as has been discovered [17, 18, 25] — down to the biochemical limits of heat and pressure, and to the lower limits of material and free energy resources. One can imagine conditions at the limits of free energy resources where FEL would face an evolutionary imperative to convert some (or all) of its cellular machinery over to the reclamation of heat — if this is possible — such as to push into regions uninhabitable by its competitors. As will be discussed below, variants of standard cellular machinery (membranes, carotenoids, enzymes) might be conducive to this enterprise.

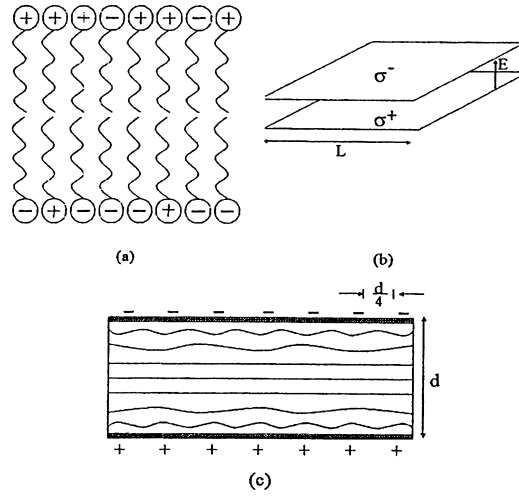


Figure 10.2: Charged biomembrane as a capacitor: a) Schematic of biomembrane lipid bilayer; b) Lipid bilayer as parallel plate capacitor; c) Equipotentials in biomembrane with finite point charges separated by $\frac{d}{4}$.

10.2.2 Theory

Here we consider the possibility that *macroscopic potential gradients* (§10.1.1, [15]) might be exploited by life to circumvent the second law. Consider a biochemical system consisting of five parts, depicted in Figure 10.1: 1) membrane capacitor; 2) 3-D pyramidal array of charge transport molecules; 3) electrically conducting molecular ladder spanning the membrane from pyramidal base to vertex; 4) chemical reaction center for utilization of superthermal charge; 5) small number of mobile charges (electrons or protons) that can circulate through the system.

One of life's most basic biological structures is capable of supporting a MPG and is also quite exposed to the thermal field: the cellular membrane. Particulars of cell membrane vary considerably across life forms so we will consider archetypical membranes consisting of ambipolar lipid layers. Simple polar lipids have a charged functional group on one end of a long organic skeleton. These can self-assemble electrostatically end-to-end to form a bilayer as shown in Figure 10.2a. Polar molecules (*e.g.*, water) outside the hydrophilic ends can stabilize the membrane, trapping the hydrophobic, non-polar organic skeleton within. In principle, opposite sides of the membrane can support permanent opposite surface charge densities.

Consider a planar section of membrane (Figure 10.2b) with fixed surface charge density σ . (These charges might be anions or cations fixed on the polar ends of the phospholipids.) In the infinite plane approximation ($l \gg d$) the membrane acts like a charged capacitor (Figure 10.2b). For biomembranes, typical scale lengths are $d \sim 10^{-8}$ m and $l \sim 10^{-6}$ m. For our model membrane, let $l = 2 \times 10^{-6}$ m and $d = 10^{-7}$ m. This structure (or multiple copies) could be sequestered within the cell rather than be exposed on its outer surface.

The maximum charge density and steady-state voltage drop supportable by

a biomembrane can be estimated from the dielectric strengths and compressive strengths of typical organics. If the electrostatic pressure due to σ exceeds the material compressive strength, the membrane will collapse; if the electric field exceeds its dielectric strength, it will arc through. Taking the dielectric strength of the membrane to be $E_{max} = 10^7$ V/m, dielectric constant $\kappa = 3$, and compressive strength to be 10^7 N/m², one finds that the maximum charge density supportable on the membrane surface to be roughly $\sigma_{max} = \kappa\epsilon_o E_{max} = 2.5 \times 10^4$ C/m² = 1.5×10^3 e⁻/μm². (Estimates from compressive strength yields larger σ_{max} .) This σ implies that the distance between excess charges is roughly $\frac{1}{\sqrt{\sigma}} \simeq 2.5 \times 10^{-8}$ m $\simeq \frac{1}{4}d$; thus, the majority of the molecules comprising the membrane need not contribute to the net surface charge. The electrostatic equipotentials are fairly parallel near the midplane of the membrane and are undulatory near the surfaces; likewise the electric field vectors are parallel in the interior and less so near the surfaces (Figure 10.2c). (Note that archaean cross-linked monolayer membranes would be relatively good at retaining capacitive charge separation since membrane molecules would be less likely to invert than standard bilayer lipids in bacteria and eukaryotes. Cross-linking also adds structural strength.)

The maximum potential drop across the model membrane surfaces will be on the order of $V_m \simeq E_{max}d = \frac{\sigma_{max}d}{\kappa\epsilon_o} = 1$ V; for this model, let $V_m = 0.8$ V. (This agrees quantitatively with common membrane potentials, scaled to membrane thickness $d = 10^{-7}$ m.) An electronic charge falling through this potential would have roughly the energy required to drive typical chemical reactions: $qV_m = \Delta\mathcal{E} \sim 0.5 - 4$ eV. Electrons and protons should be the most convenient mobile charges for this system; they are standard currency in biochemical reactions. Low-energy chemical reactions have been exploited by life. For instance, forms of bacterial chlorophyll have spectral absorption in the near IR, corresponding to energies of roughly 1 eV. The hydrolysis of ATP (adenosine triphosphate) into ADP (adenosine diphosphate) releases roughly 0.56 eV of free energy. ATP is the primary energy releasing molecule in most cells.

In principle, multiple membranes might be stacked in electrical series and self-triggered sequentially — the high energy charge from a previous step triggering the subsequent one — so as to create a series-capacitive discharge with resultant energy in multiples of a single membrane energy¹, $\Delta\mathcal{E}$. Or, each discharge could create low-energy chemical intermediates that could be brought together to drive a single, more energetic chemical reaction, similarly to how ATP is utilized in cells. In this way, the energy necessary to drive even high-energy chemical reactions might obtain.

It is biologically requisite that $\Delta\mathcal{E} \gg kT$ for at least some biochemical reactions because if they could all be thermally driven, none would be irreversible and the organism would find itself essentially at thermal equilibrium — and dead. (Also, unless $\Delta\mathcal{E} \gg kT$, molecules tend to thermally disintegrate.) A 0.8 eV potential energy drop across the membrane far exceeds the typical thermal energy associated with life ($kT(300\text{K}) \sim \frac{1}{40}$ eV $\sim \frac{1}{30}V_m$). At first glance, it seems improbable that

¹Many species are known to utilize series-capacitive discharge, *e.g.*, electric eels, rays, and catfish, achieving up to hundreds of volts in total potential.

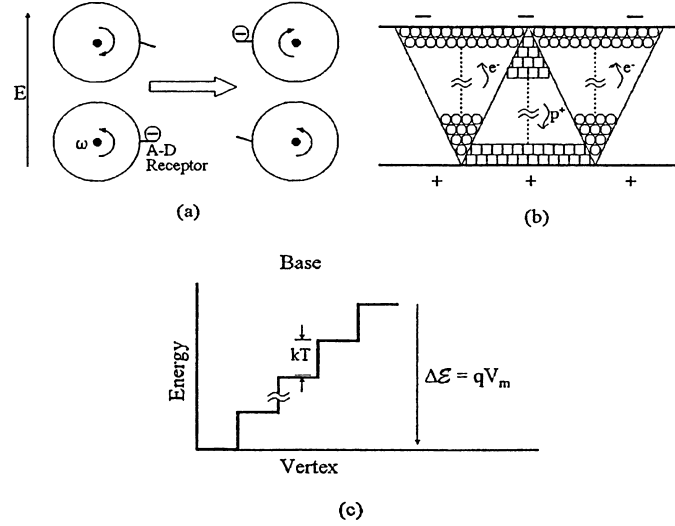


Figure 10.3: Proposed charge transport in a biomembrane: a) Rotary molecules transferring charge; b) Diffusive transport of electrons and protons between membrane faces by A-D molecules, up electrostatic potential gradients; c) Energy diagram for charge thermal transport and quantum transition in biomembrane.

thermal energy alone could drive charges up such a large electrostatic potential at room temperature, but if accomplished in steps it is less daunting.

Let the model membrane be embedded with charge transporting molecules arranged in a 3-D pyramidal structure, as depicted in Figure 10.3a. The actual molecular structure is unspecified — it could be simply a conductive-diffusive molecular matrix — but for this model consider it to be composed of rotary molecules, each with charge acceptor-donor (A-D) sites. The transport molecules spin freely, driven by thermal energy. When two A-D sites meet a charge can be transferred between them, with minimal energy of activation. This is taken to be a random process. Once charged, the electric force within the membrane will tend to constrain the rotor against charge movement up the potential gradient, but if the step sizes are small ($kT \simeq q\Delta V$) and if the transfer probability favors diffusion up the potential gradient either by favorable multiplicity of states, or in this case, by a favorable multiplicity of transfer molecules in the direction up the gradient (Figure 10.3b), then one can expect appreciable transport by diffusion alone.

Charge transport via diffusion can be placed on more realistic footing. Let the membrane have area $l^2 \sim 4 \times 10^{-12} \text{m}^2$ and let the area of an individual A-D molecule be $\delta^2 = (2 \times 10^{-9} \text{m})^2$. In the membrane depicted in Figure 10.2c, the base of the molecular pyramid accommodates roughly $\frac{l^2}{\delta^2} \sim 10^6$ molecules, the vertex accommodates one; the pyramid consists of roughly 50 molecular layers. At $T = 400\text{K}$, the electrostatic potential energy increase per level in the pyramid

is roughly $0.6kT$, thus allowing charges to rise comfortably upward against the gradient by thermal diffusion.

Applying Boltzmann statistics, the relative charge occupation probability (p_{rel}) for the base versus the vertex should be on the order of

$$p_{rel} \simeq \frac{g_{base}}{g_{vertex}} \exp \left[-\frac{\Delta\mathcal{E}}{kT} \right] \quad (10.3)$$

Here $\frac{g_{base}}{g_{vertex}}$, the ratio of multiplicity of states, is assumed to be the simple ratio of A-D molecules at each site: $\frac{g_{base}}{g_{vertex}} = \frac{l^2}{\delta^2} \simeq 10^6$. The energy difference $\Delta\mathcal{E} = qV_m \simeq 0.8\text{eV}$. Let the temperature be that survivable by the superthermophile *Strain 121*: 400K. These parameters render $p_{rel} \sim 10^{-3}$. (p_{rel} can be increased by further grading the quantum multiplicity of states in molecules toward the pyramid's base, for instance, by having more A-D sites per molecule at the base than at the vertex, or by simply packing more A-D molecules in the array.) For comparison, dropping the temperature by just 25% ($T = 300\text{K}$) reduces p_{rel} by over three orders of magnitude: $p_{rel} \simeq 4 \times 10^{-8}$. In all, despite a sizable potential difference ($V_m \gg \frac{kT}{q}$), charges have reasonable probability of traversing the membrane by purely thermal diffusive processes. The molecular pyramid creates a natural mechanism for charge transport and also offsets the deleterious Boltzmann exponential.

Once a charge has climbed the electrostatic potential via multiple small, diffusive sub- kT steps (Figure 10.3c), it can fall through the entire potential (base to vertex) in a single, nearly-lossless quantum transition ($qV_m = \Delta\mathcal{E}$) which, in principle, could drive a chemical reaction at the reaction center (*e.g.*, formation of ATP). Quantum transitions that require large and specific energies cannot be triggered prematurely (*i.e.*, by thermal energy steps); furthermore, the reactions can be triggered and mediated by structure dependencies, for instance, those that might occur only at the membrane boundaries. Or, they could require the participation of the reactants in the reaction center to complete the circuit. Thus, the multiple low-energy thermal transitions up the pyramid can be insulated from the single high-energy transition down the ladder.

Charge transfer from the pyramid's base back to its vertex can be plausibly executed across the thickness of the membrane ($d = 10^{-7}\text{m}$) along electrically conducting polymers. Aromatic and highly conjugated organics that span the entire membrane are the most promising candidates. Carotenoids are highly conjugated linear organics that are known to be electrically conducting and are also found in the membranes of thermophilic archaea, presumably to give structural strength against thermal disruption. Individual conducting organic molecules have demonstrated electron transport rates of roughly $10^{11}/\text{sec}$ and current densities far in excess of the best metallic conductors [28]. The directionality of the current might also be promoted by fashioning the conduction ladder as a molecular electronic diode [28, 29, 30]. These have been engineered [28] by attaching electron-donating and electron-withdrawing subgroups to a conducting carbon skeleton. Biological counterparts are conceivable.

Electrons falling down the conducting ladder to the reaction center in Figure 10.1 could drive useful biochemical reactions since their energy is far greater

than kT ; in this model, $\Delta\mathcal{E} = 0.8\text{eV} \simeq 23kT$. Reactants, diffusing in from other parts of the cell, could adsorb preferentially to specific locations (enzymes) at the reaction center, undergo reaction, and their products could preferentially desorb and diffuse back into the cell. Like pieces of metal laid together on an anvil and artfully struck to join them, reactants could be enzymatically forged using the energy of superthermal electrons delivered down the conducting ladder, perhaps in ways akin to ATP synthase. ATP synthase is a protein complex that resides in the membranes of chloroplasts and mitochondria. It catalyses the production of ATP using proton current through the membrane [31]. A proton gradient is established across the membrane by catabolic processes and the leakage current back across the membrane, down the gradient, through a channel in the ATP synthase catalyses the formation of ATP via phosphorylation of ADP. It is conceivable that thermosynthetic life could utilize similar intermolecular protein complexes as their reaction centers.

Specificity in the reaction direction could be further enhanced if the binding sites in the reaction center were chemically tuned to strongly adsorb reactants and quickly desorb products. In other words, reactants would be tightly bound on the reaction template until a high energy electron falls through the membrane potential and drives the reaction forward, at which time the product is loosely bound and, therefore, quickly desorbs and diffuses away, thereby suppressing the reverse reaction. This type of specificity in adsorption and desorption are hallmarks of enzymes.

The reactants, coupled with reactant-induced conformational changes in the binding enzyme, could act as an electronic switch in the reaction center; that is, electrons in the base of the pyramid would discharge through the reaction center when (and only when) the reactants are present in the reaction center. This description closely resembles the plasma (Chapter 8) and solid state (Chapter 9) thermal capacitive discharges. An electrical circuit is similar to that of the plasma paradox (Figure 8.8b, §8.4) is easily envisioned.

Thus, between the large potential energy rise upward through the carbon conduction ladder, the possibly diodic nature of the ladder, the reactant-product binding specificity of the reaction center, and its possible switching action, it appears that a unidirectional current is favored for this circuit. At first glance, this seems to violate the principle of detailed balance — which would demand no net current flow in the circuit — but since this system involves an inherently nonequilibrium process (a 0.8eV electrons driving a chemical reaction), detailed balance need not — and in this case, does not — apply. This chemical activity bears strong resemblance to those proposed by Gordon (§5.2.2) and Čápek (§3.6.4).

The power \mathcal{P}_m delivered by the thermosynthetic membrane should scale as $\mathcal{P}_m \sim \frac{p_{rel} N_q \Delta\mathcal{E}}{\tau_{vb}}$, where N_q is the number of charges in play in the membrane and τ_{vb} is the average transit time for charges from the vertex to the base. N_q must be substantially less than σl^2 in order to not significantly distort the membrane's electric fields; for this model, let $N_q = 10 \ll l^2 \sigma$. τ_{vb} depends critically on the mechanism of charge transport; as a measure we take it to be the diffusion time of a simple molecule (H_2) through water the thickness of the membrane; that is, $\tau_{vb} \sim \tau_{diff} \sim \frac{x_{rms}^2}{2D} \simeq 10^{-6}\text{sec}$. For the model membrane, one has $\mathcal{P}_m \sim \frac{p_{rel} N_q \Delta\mathcal{E}}{\tau_{diff}} \simeq$

2×10^{-16} W. This is orders of magnitude less than what would be allowed for radiative or conductive heat transfer into a cell, in principle. It is also on the order of 0.1% of the resting power requirement for mammalian cells; thus, from the viewpoint of these energetics, this TL would probably not compete well against FEL. On the other hand, many FEL organisms have far lower power requirements than mammalian cells. For instance, some deep rock microbes are believed to have infinitesimal metabolisms; by some estimates they grow and reproduce on time scales approaching centuries, whereas surface dwelling bacteria can run through a generation in minutes. Based on the availability of free energy sources and nutrients and on the amount of carbon dioxide produced from the oxidation of organic matter, it is estimated that many deep rock microbes have metabolisms that are more than a billion times slower than surface free-energy microbes, thereby possibly putting them below TL in energy utilization. If so, then whereas its low metabolic rates makes it unlikely to compete successfully with FEL on the surface, thermosynthetic life might compete quite well with free energy life in the deep subsurface.

The above diodic biochemical circuit should, of course, be considered critically in light of the failure of solid state diodes to rectify their own currents, thereby failing as second law challenges. Superficially, this biochemical diode bears resemblance to the solid state diode considered by Brillouin [32], Van Kampen [33], McFee [34] and others. This one, however, relies on quantum molecular processes, rather than on more classical solid state processes, and so cannot be directly compared. More detailed physical chemical analysis is currently being undertaken.

Thermosynthetic life would seem to enjoy several evolutionary advantages over free energy life. Most obvious is freedom from reliance on free energy sources since it simply harvests energy from its own thermal field. It is unclear whether this would allow it to economize on its metabolic machinery, but insofar as it does not require large bursts of energy, one can imagine that TL would not be so dependent on energy storage mechanisms (*e.g.*, fats) as FEL. Once grown, TL could, in principle, operate as a closed thermodynamic cycle, neither taking in nutrients nor expelling wastes as FEL must. Its material needs would be satisfied by those required for reproduction. This economy would confer evolutionary advantage both in reducing the necessary conditions for survival but also in reducing local bio-pollution which is known to be deleterious or even fatal to many species in closed environments. Third, supposing TL competed with FEL at the spatial margins of energy resources, TL could more easily strike off, explore, and inhabit niches unavailable to FEL. For instance, were superthermophiles to push more deeply into the subsurface, according to the discussion above, the temperature rise could further favor TL's heat-driven biochemistry.

In summary, it is conceivable that thermosynthetic life could utilize macroscopic electrostatic potential gradients in biomembranes and other standard biochemical machinery to rectify thermal energy into chemical reactions so as to compete well with free energy life in some environments.

10.2.3 Experimental Search

An experimental search for thermosynthetic life would probably prove problematic at present. First, in most terrestrial environments FEL would dominate over TL, rendering TL a trace population, at best. In more extreme environments where FEL is crippled, perhaps in hot, deep, subsurface deposits, a search might prove fruitful. It has been estimated that the depth-integrated biomass of subsurface microbes might be equivalent to a meter or more thick of surface biomass over the entire planetary surface [17, 25]. Most of these organisms have not been cataloged or studied. Second, the vast majority of *all* microbes — surface or subsurface dwelling — are either difficult or impossible to culture in the laboratory; it is estimated that perhaps less than 10% of microbes from *any* random natural setting can be cultured with present techniques. Since, in principle, full-fledged TL might ingest little or no chemical fuel (aside from that required for reproduction) and might expel little or no chemical waste, many standard tests for life should fail.

The above profile for TL — small, unicellular, anaerobic, hyperbarophilic superthermophiles, geologically and hydrologically isolated from FEL in long-term, stable, free-energy poor environments — suggests how and where TL might be discovered. For pure TL, a search might be conducted in deep, geologically stable rock that is nearly biochemically barren both of material and energy resources; that is, look where there is little hope of finding anything alive. Rock samples with organisms, but lacking appropriate levels of biological wastes would be signposts for TL. Thermosynthetic life might be physically subsumed into the cells of standard free energy life, perhaps in a role similar to that of mitochondria which are believed to have once been free living cells before being captured and incorporated as the energy-producing cellular machinery of parent cells. Hybrid FEL-TL might display the advantages of both types of life.

Recovery of deep subsurface microbes has been carried out to depths of 5.2km in igneous rock aquifers. Boreholes (without microbe recovery) have been conducted to depths of 9.1 km, so searches for proposed thermosynthetic life appear feasible. Culturing would probably be more problematic. One might suppose that TL can be discriminated experimentally from FEL by isolating a mixed culture from all free energy sources for sufficiently long to starve FEL, thereby isolating only TL. Unfortunately, *sufficiently long* can be *very long*. Microbes can place themselves in low-energy, sporulating, static modes for years, decades, and perhaps centuries or millenia awaiting favorable conditions. With microbes, sometimes there seems to be no clear distinction between *fully alive* and *truly dead*.

Ancient samples might offer good candidates for TL. Recently, viable cultures have been made of a halotolerant bacterium believed to have been entombed in salt crystals for 2.5×10^8 years [27]. It is unclear how such organisms remain viable for millenia against the ravages of natural radioactivity and thermal degradation. There are a number of biochemical and genetic repair processes that contribute but, presumably, all require free energy. A reliable energy source like thermosynthesis would be convenient for such ongoing repair.

DNA/RNA analysis might eventually help identify TL. Currently, it can be used to identify species, but it cannot yet be used to predict the function, structure, or viability of an organism. Presumably, genomics will eventually advance to the

point where cellular structure and biochemical function can be predicted from DNA/RNA analysis alone such that thermosynthetic life forms could be identified solely from their genetic maps. This type of search, however, is still years or decades away.

In summary, given the exigencies of natural selection and the plausibility of second law violation by biologically-inspired systems, we predict that thermosynthetic life will be discovered in the deep subsurface realm, and that perhaps some forms of free energy life will be found to resort to it under suitable circumstances in less extreme environments.

10.3 Physical Eschatology

10.3.1 Introduction

The history and future of the universe are inextricably tied to the second law. That the cosmos began in a low gravitational entropy state destined its subsequent thermodynamic evolution into the present. And, to a fundamental degree, its fate is defined by its inexorable march toward equilibrium. Although *heat death* in the Victorian sense has been commuted into merely *heat coma* by modern cosmology, the prognosis is still rather bleak.

Study of the far future and the end of the universe has become a popular scientific pastime, in many ways replacing religious myths with scientific ones [35-47]. The number of books and articles on the subject are almost beyond reckoning. In this section, we explore the *physical eschatology* for a universe in which the second law is violable.

Future projections are almost certainly seriously off the mark (if not entirely wrong) — just as are ancient myths, considered in the light of modern science — since even the most basic eschatological questions have no definitive answers. Is the universe open or closed? Will it continue to expand or will it eventually collapse? Is space flat? Is the proton stable? What is the nature of dark matter and dark energy? What is the composition of 99% of the universe? What is the nature and energy of the vacuum state? Is there a theory of everything and if so, what is it? What is time and *when* did it begin? What is the role of intelligent life in the universe?

For gaining a true understanding about the future universe, eschatological studies are probably futile because they assume that our knowledge of physical laws is both *accurate* and *complete*. Historically, this assumption has always failed; therefore, there is little reason to believe it will not fail again [48, 49]. Nonetheless, as pointed out by Dyson [35], the value of eschatology may not lie so much in predicting the future, but in raising germane questions that might eventually lead to better understanding.

We stand with Dyson in asserting that scientific inquiry need not be divorced from issues of human purpose and values. Science finds fruition as and where it touches the human condition. We are bound by the second law and to it are tied the deepest human aspirations, fears, sufferings and joys. We would be remiss not

to acknowledge this central truth. We hope one of the legacies of this volume will be to help illumine our future both in light of the second law and in its probable violation.

Most eschatologies ignore intelligent action as a factor in the development of the universe. This is partially attributable to the scientific habit of ‘ignoring the observer,’ but it is also largely in recognition of mankind’s relative impotence within the cosmic order. The latter might not always be the case. Consider, for example, that humans are now the primary movers of soil on Earth, outstripping natural processes; we have significantly altered between 1/4 and 1/3 of the Earth’s surface. Over the last several thousand years we have modified the composition of the atmosphere sufficiently to change the climate measurably. We now extract fish from the world’s oceans at rates equaling or exceeding their rates of replenishment. As a species, we are both “the prince of creation” [50] and a principal instrument of mass extinction. If the last 100 years are any indication of the dominance humans can wield over their home planet, then extrapolating this last 10^{-7} fraction of Earth’s history out to cosmological time scales, one cannot rule out the possibility that intelligent action — though almost certainly not *genetically human* and, hopefully, more than *humanly wise* — could have a significant effect on the cosmic order. Dyson alludes to this [35]:

Supposing that we discover the universe to be naturally closed and doomed to collapse, is it conceivable that by intelligent intervention, converting matter to radiation and causing energy to flow purposefully on a cosmic scale, we could break open a closed universe and change the topology of space-time so that only a part of it would collapse and another part of it would expand forever?

(Actually, the reverse is now considered more likely.)

We wish to explore another scenario — that the second law is violable — and speculate how this might affect humanity and the universe in the distant future. This discussion will be relatively brief and general, in keeping with its speculative nature. We adopt the logarithmic unit of time η , introduced by Adams and Laughlin [36], defined by $\eta \equiv \text{Log}_{10}(\tau)$, where τ is years since the Big Bang. In this notation, the present is $\eta \simeq 10$.

The fate of the universe for ($\eta \leq 100$) depends on many unknowns, some of which are listed above. Chief among these are whether the universe will expand forever and whether the proton is stable. Under the assumptions of continuing expansion and proton decay, the various cosmic ages proposed by Adams and Laughlin [36] are summarized as follows:

Radiation-Dominated Era ($-\infty < \eta < 4$): Big Bang, expansion, particles and light elements created. Energy primarily in radiation form.
Stelliferous Era ($6 < \eta < 14$): Energy and entropy production dominated by stellar nuclear processes. Energy primarily in matter form.
Degenerate Era ($15 < \eta < 37$): Most baryonic matter found in stellar endpoints: brown dwarfs, white dwarfs, neutron stars. Proton decay and particle annihilation.

Black Hole Era ($38 < \eta < 100$): Black holes, the dominate stellar objects, evaporate via Hawking process.

Dark Era ($\eta > 100$): Baryonic matter, black holes largely evaporated. Detritus remains: photons, neutrinos, positrons, electrons.

This grim analysis ignores issues of dark matter and dark energy.

Classical heat death, discovered shortly after the discovery of the second law [51, 52, 53] is a process by which the universe moves toward thermodynamic equilibrium as it exhausts its available free energy sources. At its terminus, the universe becomes uniform in temperature, chemical potential, and entropy. It is lifeless. In the latter half of the 19th and through the early 20th centuries, before cosmological expansion was discovered, the general sentiment surrounding heat death was perhaps most famously expressed by Bertrand Russell [54]:

All the labours of the ages, all the devotion, all the inspiration, all the noonday brightness of human genius are destined to extinction in the vast death of the solar system, and ... the whole temple of man's achievement must inevitably be buried beneath the debris of a universe in ruins.

Hope for temporary reprieve is offered by Bernal [55]:

The second law of thermodynamics which ... will bring this universe to an inglorious close, may perhaps always remain the final factor. But by intelligent organizations the life of the Universe could probably be prolonged to many millions of millions of times what it would be without organization.

Even after the modifications wrought by cosmological expansion, the fateful effects of the second law remain, as pointed out more recently by Atkins [56]:

We have looked through the window on to the world provided by the Second Law, and have seen the naked purposelessness of nature. The deep structure of change is decay; the spring of change in all its forms is the corruption of the quality of energy as it spreads chaotically, irreversibly and purposelessly in time. All change and time's arrow, point in the direction of corruption. The experience of time is the gearing of the electrochemical processes in our brains to this purposeless drift into chaos as we sink into equilibrium and the grave.

This depressing vision — as inescapable as the second law itself — has penetrated so deeply into Western culture and consciousness as to be almost invisible. Arguably, the second law is no longer simply a scientific principle; it has become a sociological neurosis of Western civilization.

10.3.2 Cosmic Entropy Production

For this discussion we assume an ever-expanding universe since, in the last decade, strong evidence for it has accumulated. This includes observations of distant supernovae, cosmic microwave background (CMB) anisotropies, and inadequate gravitating matter inventories to cause collapse [57]. There are, of course, many eschatologies that assume collapse [44, 58, 59]. Since the apparent discovery of dark energy with its negative pressure [60, 61], the traditional topological terms *open* ($\Omega > 1$) and *closed* ($\Omega < 1$) are no longer adequate to describe cosmological evolution. Even a topologically closed universe can undergo continuous expansion given a positive cosmological constant (negative pressure), as is associated with dark energy.

In the standard cosmological model, the universe begins with exceptionally low gravitational entropy. That it does not immediately achieve something akin to thermal equilibrium — for instance, during the recombination era ($z \sim 1500$) when it moved from a fairly spatially uniform plasma state to a neutral atom state — is due primarily to the gravitational clumping and, to a lesser degree, to the cosmic expansion itself which continually creates more configuration states for matter. As large and small scale structures emerged (stars, galaxies, super-clusters), thermodynamic entropy production gave way to gravitational entropy production. This, in turn, allowed further thermodynamic entropy production, *e.g.*, in the form of stellar nucleosynthesis, planetary formation, geochemistry, and life.

Systems are driven forward thermodynamically — kept out of equilibrium — not by entropy *per se*, but by *entropy gradients*. This was recognized as far back as Poincaré. The Earth's biosphere, for instance, is driven by the solar-terrestrial entropy gradient more surely than it is driven by solar energy. This gradient has been conveniently expressed by Frautschi through photon counting [62]. For every fusion nucleon at the core of the Sun ($T \sim 1.5 \times 10^7 \text{K}$), at the Sun's surface (photosphere, $T = 5800 \text{K}$) roughly 5×10^6 photons are emitted. Each solar photon reaching Earth is converted, via photosynthesis, biochemical reactions, and thermalization, into roughly 20 photons ($\sim \frac{5800 \text{K}}{300 \text{K}} \simeq 20$). These are then mostly radiated back into space where they eventually equilibrate, each producing roughly another 100 CMB photons. Thus, a single, well-localized — and apparently entropy-reducing — fusion reaction in the Sun's core gives rise to $\sim 10^{10}$ photons and substantial entropy. Thus, it is fair to say that it is not the Sun's energy that drives the Earth's biosphere; rather, it is the solar-terrestrial entropy gradient. Were there not an entropy gradient between the two, then by definition they would be at mutual equilibrium and the nonequilibrium processes necessary for life would not be possible.

In the far future, the march toward equilibrium will step to a different beat: rather than being set by nuclear fusion, it will be set mainly by proton decay, black hole and positronium formation and evaporation. If the cosmos continues to expand, however, it can never reach constant temperature or equilibrium. Thus, while it may dodge classical heat death, it still dies in the sense that the entropy of comoving volumes asymptotically approach a constant value. This limiting value should be far below that set by the Bekenstein limit [62, 63]. Actually, in most

Entropy Source	$\Delta \eta$	$\text{Log}_{10} \left[\begin{array}{c} \text{Relative Entropy} \\ \text{Increase Over} \\ \text{CMB} \end{array} \right]$
Stellar Nucleosynthesis	11	-2
Black Hole Formation		
- <i>Stellar</i>	11	≤ 10
- <i>Galactic</i>	≤ 20	≤ 21
- <i>Galactic Supercluster</i>	≤ 20	≤ 24
Proton Decay	≥ 32	3
Black Hole Evaporation	≤ 106	≤ 24
Positron Formation and Decay	≥ 116	≥ 13

Table 10.2: Primary entropy production into the far-future ($\eta < 120$), after Frautschi [62]. Duration is expressed in $\Delta\eta$ and total entropy produced is compared to entropy of CMB.

cosmological scenarios, the entropy of a comoving frame falls further and further behind its theoretical maximum.

Entropy production is proposed to extend into the far-future ($\eta > 50$) [36, 62]. Several of the dominant sources are listed in Table 10.2. The predominant future entropy source should be black hole evaporation, whose total integrated entropy production should outpace stellar nucleosynthesis by roughly 26 orders of magnitude. Note, too, the entropy associated with Hubble expansion is negligible compared with it. This underscores the tremendously small initial entropy of the cosmos relative to its theoretical maximum.

The pinnacle of gravitational entropy is the black hole. The classical black hole is a thermodynamically simple object, specified entirely by three parameters: mass, angular momentum and electric charge. Particles falling into a black hole lose their individual identities and many of their normally conserved properties (*e.g.*, baryon number, lepton number). Since a hole's interior quantum states are not measurable, they are equally probable; thus, a black hole represents a real information sink and entropy source. The Bekenstein-Hawking entropy of a black hole of mass M_{BH} [64]

$$S_{\text{BH}} = \frac{4\pi kGM_{\text{BH}}^2}{\hbar c} \quad (10.4)$$

is enormous compared to standard thermodynamic sources. For instance, the gravitational entropy for a one solar mass black hole is $\frac{S_{\text{BH}}}{k} \simeq 10^{77}$, while the thermodynamic entropy of the Sun is $\frac{S_{\text{Sun}}}{k} \simeq 10^{58}$. As for other gravitational entropies, black hole entropy is nonextensive, scaling as M_{BH}^2 . Since M_{BH} is proportional to radius ($M_{\text{BH}} = \frac{R_{\text{BH}}c^2}{2G}$), a hole's entropy is proportional to its surface area A :

$$S_{\text{BH}} = \frac{kc^3}{4\hbar G} A \quad (10.5)$$

Since traditional black holes only accrete mass, thereby increasing their entropies and areas, a gravitational analog to the thermodynamic second law can be formulated. If S_m is defined as the entropy of mass-energy outside a hole, then a *generalized entropy* can be defined, $S_g \equiv S_m + S_{\text{BH}}$. The *generalized second law* states that S_g never decreases. (Each law of classical thermodynamics has a black hole equivalent.)

In 1974, Hawking proposed black hole evaporation via emission of thermal quantum particles [65, 66]. To it an effective temperature can be ascribed:

$$T_{\text{H}} = \frac{\hbar c^3}{8\pi G M_{\text{BH}} k} \simeq 6.2 \times 10^{-8} \left[\frac{M_{\odot}}{M_{\text{BH}}} \right] K. \quad (10.6)$$

The evaporation timescale for a hole ($\tau_{\text{H}}(\text{yr})$) should be roughly

$$\tau_{\text{H}} \simeq \frac{16\pi^2 G M_{\text{BH}}^3}{\hbar c^3} \simeq 10^{62} \left[\frac{M_{\text{BH}}}{M_{\odot}} \right]^3 (\text{yr}) \quad (10.7)$$

Clearly, for even the smallest black hole generated by standard astrophysical processes, the evaporation time is tens of orders of magnitude longer than the age of the universe: the far future. Evaporation is in the form of random thermal particles with the maximum entropy per unit mass.

The maximum value of entropy for a system of radius R and energy E is given by the Bekenstein limit [63]:

$$S \leq \frac{2\pi R E}{\hbar c}, \quad (10.8)$$

This limit can be attained by black holes.

The action of a black hole can be likened a bit to a home trash compactor: relatively low-entropy items like fruits and vegetables are thrown in, ground up and mixed into a high entropy state, compacted and then, as they rot, slowly evaporate back out as a diffuse, non-descript, high-entropy gas.

10.3.3 Life in the Far Future

Whether one subscribes to traditional thermodynamic heat death or to merely heat coma mediated by proton decay and black hole evaporation, the second law ($\frac{dS}{dt} \geq 0$) is a prime mover and the grim reaper. If the second law can be violated and applied on astrophysical scale lengths, however, then it would seem our eschatological fate might be altered. The basic requirement for survival is this: that the natural rate of entropy production be less than or equal to the entropy reduction rate achieved by second law violation. Too little is known about either process to claim a theoretical victor at this point. Nonetheless, we briefly introduce three scenarios by which life might at least be extended in a dying universe.

Matrix: Within our cosmological horizon ($R \sim 10^{26}$ m) it is estimated there are on the order of 10^{11} galaxies of average mass $10^{11}M_{\odot}$, giving for the entire universe a mass on the order of 10^{52} kg. The baryon number is about $N_b \sim 10^{79}$; there are roughly 10^9 photons per baryon, predominately in the CMB. (It is estimated the cosmic mass-energy is fractionated into roughly 73% dark energy (nature unknown), 23% dark matter (nature unknown), and 4% baryonic matter (only about 25% of which can be seen or inferred directly); thus, roughly 99% of the mass-energy of the universe remains mysterious.)

Let the mass and scale length of the universe be M and R , respectively. Let this mass be rolled into large sheets whose atomic scale length is r and whose thickness in number of atomic layers is n . The number of sheets of scale size R that can be constructed from M should be roughly $N_s \sim \frac{N_b r^2}{n R^2}$. For $n = 10$, $m = 10$ amu and $M = 10^{52}$ kg one has $N_s = 10^6$. In other words, the intrinsic mass of the universe could, in principle, be fashioned into a matrix of 10^6 partitions spanning the universe. Arranged uniformly, they would be spaced roughly every 10^4 ly. If these partitions were antennae and second law violators for CMB or other far-future particle fields (*e.g.*, neutrinos, e^+/e^-), then the universe's energy might be recycled many times and heat coma forestalled. This, of course, presupposes the harvested energy would be sufficient to repair the ravages of the natural entropic process like proton decay [62]. Since the energy intercept time for this matrix should be on the order of 10^4 yr, while primary decay processes like proton decay and black hole evaporation exceed 10^{32} yr, if the matrix were even only mildly efficient at entropy reduction, it should be able to keep pace. Easy calculations show that a matrix could, in principle, reverse the current entropy production by stellar nucleosynthesis [67]. Additionally, if the future civilization were able to *rearrange the furniture* on a cosmic level — see Dyson above — then perhaps spacetime topology could be modified either to avert continued expansion, so as to create a thermodynamically steady-state universe or sub-universe.

Outpost: On a more limited scale, the second law might be held at bay through construction of a finite outpost, perhaps the size of a solar system, surrounded by a well-insulated thermal shell. Like the matrix, it would harvest heat and particle from the exterior thermal background fields and concentrate it internally. Its success depends on it being well-insulated to heat and particle emission. Presumably, it would recycle its own interior heat into work. As the surrounding universal temperature falls and this is communicated to its interior, however, the outpost would have to rely on lower and lower temperature second law violation processes and lower power densities. Since negentropic processes have been proposed down to superconducting temperatures already (Chapter 4), it is plausible that lower temperature processes will be discovered. The primary requirement for sustainability is that the heat harvested from the exterior space at least match the heat (and mass-energy due to particle decay) that leaves through the insulating shell².

²For thermal insulation, one might guess that the optimum would be a hollow black hole (*e.g.*, a thin spherical shell: $R = 200$ AU, $M = 10^{10} M_{\odot}$, $T_H = 10^{-17}$ K, $\tau_H \sim 10^{92}$ yrs). Unfortunately, general relativity forbids this as a stable geometry, although naive calculations indicate it might be possible.

Thermal Life There has been considerable debate as to whether life, intelligence and consciousness (LIC) can survive indefinitely in a dying universe [35, 62]. We will assume that if life is possible, so too are intelligence and consciousness. A general condition assumed by Dyson invokes entropy: $\int \frac{dS}{dt} dt = \infty$; that is, since LIC rely on inherently nonequilibrium processes, the entropy growth in a comoving volume must continuously increase. If the second law is violable, however, this limitation is suspect.

The very definitions of and conditions for LIC are themselves a matter of longstanding debate and we will not be drawn into the fray. We note, however, that since thermosynthetic life appears possible in principle (§10.2), there may be hope that life could survive in the far future by directly tapping the thermal fields alone, even if an entropy gradient is absent. Hopefully, such life would be more subtle than Hoyle's black cloud [68] or Čapek's sentient computer [69], but as before, its energy budget would be limited to what it could harvest from its surroundings, which, if the universe becomes increasingly diffuse, would constitute a long, slow road into heat coma.

Life is commonly considered antithetical to and distinguishable from thermodynamic equilibrium in at least two fundamental ways:

- 1) Biotic matter is physically arranged in a *non-random*, far from equilibrium configuration.
- 2) Biochemical reactions are superthermal and cannot be maintained at equilibrium.

Both assumptions should be re-examined in light of second law challenges. With regard to (1), there is no absolute, agreed upon definition of order, so conversely, there is no absolute definition of disorder. Furthermore, large-scale organized dynamic structures are not forbidden at equilibrium; Debye sheaths, for example, are dynamically-maintained large-scale structures that arise by thermal processes at the edges of plasmas within which highly non-equilibrium processes occur. Thus, it is not clear *a priori* that equilibrium could not support the sort of large scale energy-producing structures necessary for life.

Assumption (2) is undercut by the spectrum of second law challenges in this volume. In MPG systems (§10.1.1), superthermal nonequilibrium particle currents are maintained in equilibrium settings. Nikulov's persistent supercurrents arise out of purely quantum effects at low temperatures (§4.4). One cannot rule out that other contra-entropic effects will be discovered at even lower temperatures.

It is unclear what form life might take in the far future. Must it be solid-liquid like terrestrial life? Could it exist, for example, as complex, long-range, correlations in the electron-positron detritus predicted for the far future? It is not clear what the minimum requirements for life are, especially given that its definition is still a matter of debate.

Thermosynthetic life is predicted to be survivable in an equilibrium environment, but must it be at most an island in an equilibrium sea? Could it co-exist with thermal equilibrium; that is, might life assimilate itself directly into the thermal field? This is a modest extrapolation from J.A. Wheeler's mystic vision of the uni-

verse as “a self-synthesizing system of existences, built on observer-participancy” [70]. (Čápek’s phonon continuum model (§3.6.6) might also be mined for ideas on how this might play out.) Presumably, this *thermal life* would wind down with the rest of the universe. Since this would not be a struggle against nature, but rather an acquiescence to it, this could be considered an *if you can’t beat ’em, join ’em* strategy for the far future.

Although violation the second law appears useful for survival into the far future, one should be careful of what one wishes for. Entropy reduction, though useful, is an impoverishment of the universe’s phase space complexity. Moreover, if carried out on cosmic scales, it would amount to a ‘turning back’ of the thermodynamic clock. This reversal of thermodynamic time would not imply time reversal in the palindromic sense that physical processes would precisely reverse — that the universe would retrace its exact path in phase space — but it would entail returning the universe to a lower entropy state. The clock would be turned back to a new and different clock each time. It would be akin to erasing a chalkboard in preparation for writing something new — and getting the chalk stick back, to boot³. Presumably, the cosmic horizon would not be affected since the mass-energy would not be changed, but simply rearranged. However, if carried out to the extreme, converting and removing all heat, the universe could freeze and die just as surely as by standard heat death⁴. A little bit of disorder (heat) is a good thing.

In conclusion, we reiterate that the continuing uncertainties surrounding cosmological issues, basic physical laws, and definitions of life, intelligence and consciousness make eschatological studies largely moot. The second law, however, appears integral to most, such that its possible violation should be considered in future studies.

10.4 The Second Law Mystique

Perhaps more has been written about the second law across the breadth of human knowledge and endeavor than about any other physical law. Direct and indirect references to it can be found in all branches of science, engineering, economics, arts, literature, psychology, philosophy, and popular culture.

Quite aside from its profound physical, technological, social, philosophical and humanistic implications, the second law is *famous for being famous*. It has become the epitome of scientific truth, notorious for its absolute status, virtually unquestioned by the scientific community. Much of its mystique can be traced to the imprimaturs of scientists like Einstein, Planck, Eddington, Fermi, Poincaré, Clausius, and Maxwell. Their reputations are reciprocally burnished by association

³Earlier thinking on time and change can be found in the Rubáiyát of Omar Khayyám (ca. 1100 C.E.): “The moving finger writes and having writ moves on. And all your poetry and wit cannot erase half a line, nor all your tears one word of it.”

⁴“Some say the world will end in fire, some say ... that for destruction ice is also great, and would suffice.” Robert Frost, *Fire and Ice* (1920).

with this fundamental law; thus, a cycle of mystique is established.

The following are representative quotes from the sciences [71] and humanities dealing with the second law and its absolute status. Outside of theatre, rarely does one find such melodrama.

Einstein [72]

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

Eddington [73]

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

Fermi [74]

The second law of thermodynamics rules out the possibility of constructing a *perpetuum mobile* of the second kind ... The experimental evidence in support of this law consists mainly in the failure of all efforts that have been made to construct a *perpetuum mobile* of the second kind.

Clausius [75]

Everything we know concerning the interchange of heat between two bodies of different temperatures confirms this, for heat everywhere manifests a tendency to equalize existing differences of temperature ... Without further explanation, therefore, the truth of the principle [second law] will be granted.

Maxwell [76]

The second law of thermodynamics has the same degree of truth as the statement that if you throw a thimbleful of water into the sea, you cannot get the same thimbleful of water out again.

Çengel and Boles [77]

To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient evidence of its validity.

Horgan [78]

To Gell-Mann, science forms a hierarchy. At the top are those theories that apply everywhere in the known universe, such as the second law of thermodynamics and his own quark theory.

Maddox [79]

The issue is not whether the second law of thermodynamics is valid in the ordinary world; nobody doubts that.

Park [80]

Each failure, each fraud exposed, established the laws of thermodynamics more firmly. ... Extending mistrust of scientific claims to include mistrust of the underlying laws of physics, however, is a reckless game.

Maddox [81]

Maxwell's demon is therefore no longer regarded as a limitation of the second law.

Lieb and Yngvason [82]

No exception to the second law of thermodynamics has ever been found — not even a tiny one.

Brillouin [83]

Nobody can doubt the validity of the second principle, no more than he can the validity of the fundamental laws of mechanics.

In the humanities, explicit, implicit and interpretable references to the second law are uncountable. Many dwell on the futility of existence within its sphere, while others lament the heat death of the universe [54, 55, 56, 84]. The following are exemplars.

George Gordon (Lord Byron), from *Darkness* [85]

I had a dream, which was not a dream.
 The bright sun was extinguish'd, and the stars
 Did wander darkling in the eternal space,
 Rayless, and pathless, and the icy earth
 Swung blind and blackening in the moonless air;
 Morn came and went — and came, and brought no day...
 ... The world was void,
 The populous and the powerful was a lump
 Seasonless, herbless, treeless, manless, lifeless,
 A lump of death — a chaos of hard clay...
 The waves were dead; the tides were in their grave,
 The Moon, their mistress, had expired before;

The winds were wither'd in the stagnant air,
 And the clouds perish'd; Darkness had no need
 Of aid from them — She was the Universe.

D.P. Patrick, from *Helena Lost*

... Though Time must carve into our flesh his name,
 Erase the precious ledgers of our minds,
 Corrode our bones, corrupt our breaths and maim,
 And, thus, to us Oblivion consign ...

Robert Frost, *Fire and Ice* [85]

Some say the world will end in fire,
 Some say in ice.
 From what I've tasted of desire
 I hold with those who favor fire.
 But if it had to perish twice,
 I think I know enough of hate
 To say that for destruction ice
 Is also great
 And would suffice.

Archibald Macleish, from *The End of the World* [85]

... And there, there overhead, there, there, hung over
 Those thousands of white faces, those dazed eyes,
 There in the starless dark the poise, the hover,
 There with vast wings across the canceled skies,
 There in the sudden blackness the back pall
 Of nothing, nothing, nothing — nothing at all.

In the literary sphere, resignation to the second law and heat death seems almost a romantic death wish; however, it is firmly rooted in scientific faith. In the scientific sphere this resignation, though resting on broad experimental and theoretical support, ultimately, is also rooted in faith, especially as it pertains to second law inviolability. It has been a goal of this volume to shake this faith in the hope of attaining something more illuminating.

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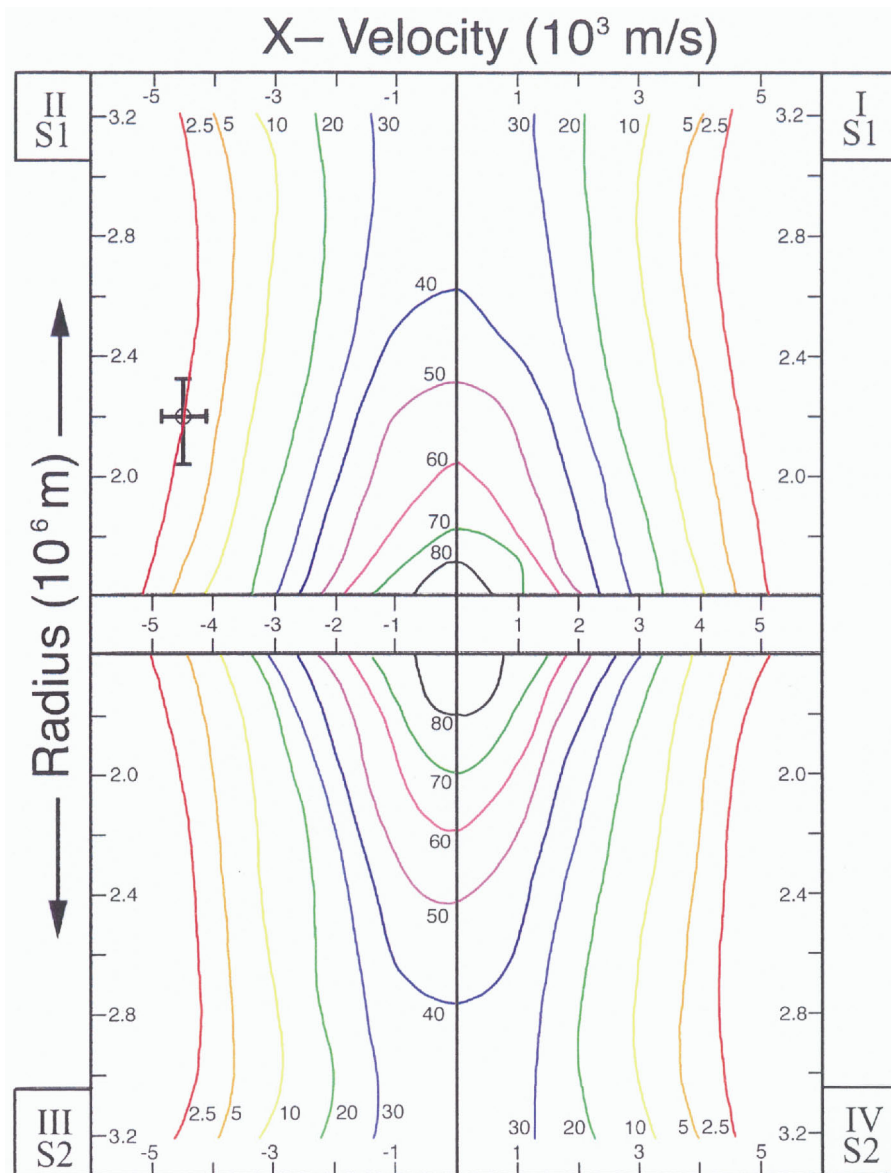


Plate I Phase space diagram v_x versus r for *standard gravitator*. (3000 patch crossings; 30° polar domes over S1 and S2); ($r_{patch} = 2.475 \times 10^6$ m).

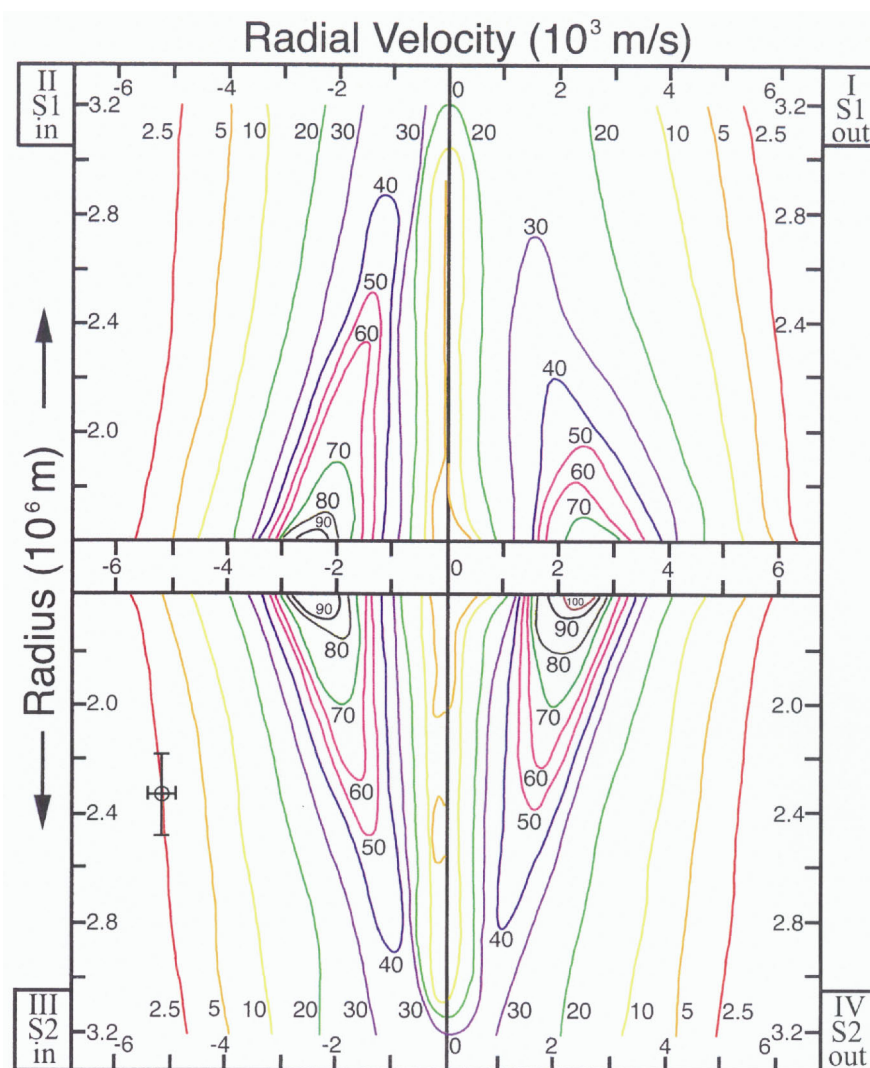


Plate II Phase space diagram v_r versus r for *standard gravitator*. (3000 patch crossings; 30° polar domes over S1 and S2; $r_G < r_{patch} < r_c$)

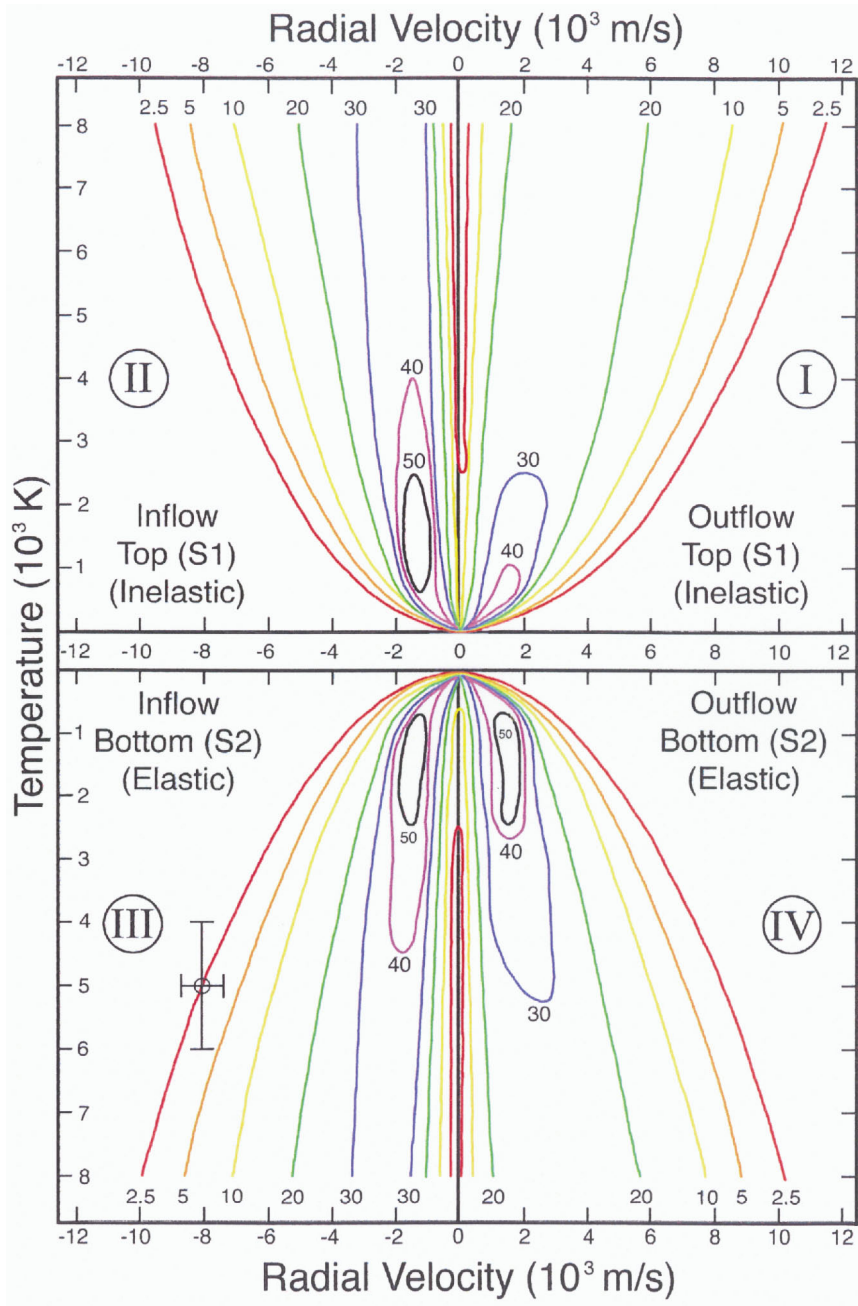


Plate III Phase space diagram v_r versus T for *standard gravitator*. (3000 patch crossings, 30° polar domes over S1 and S2, $r_{patch} = 2.405 \times 10^6$ m)

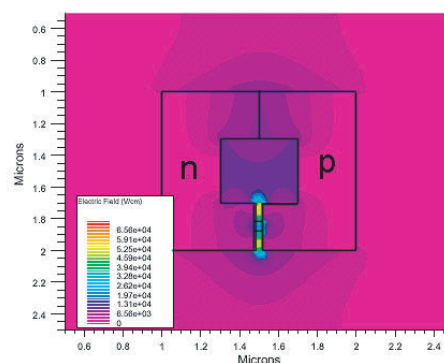
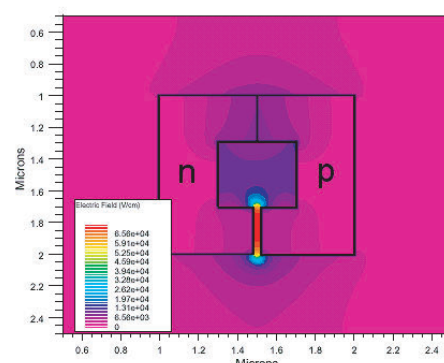
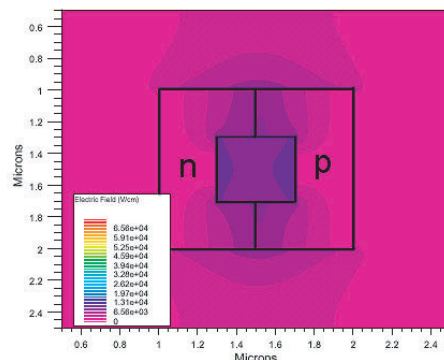


Plate IV Atlas 2-D numerical simulations of electric field for three related variations of the *standard device*. a) Case 1: *standard device* without J-II gap; b) Case 2: *standard device*; c) Case 3: *standard device* with $300\text{\AA} \times 600\text{\AA}$ undoped silicon piston at gap center.

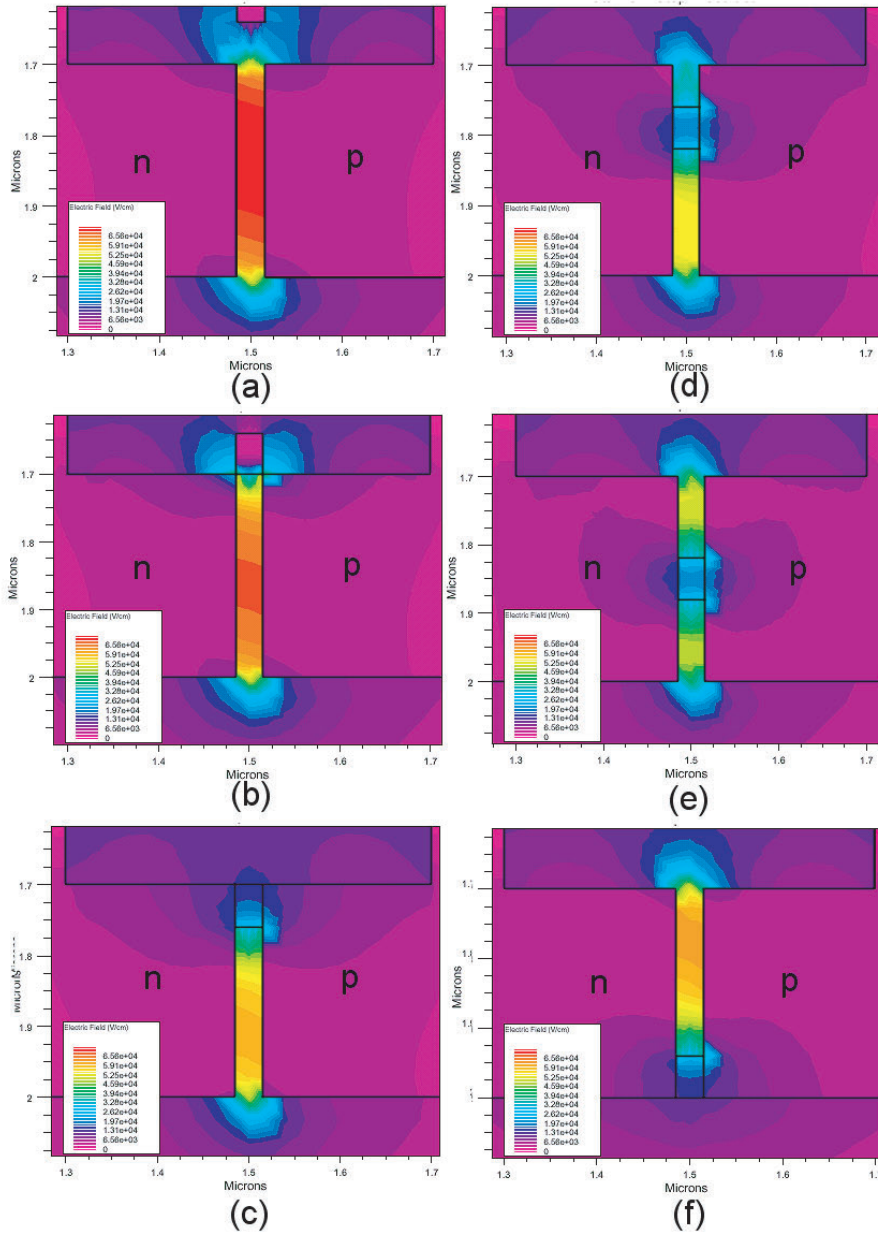


Plate V Sequence of 2-D Atlas simulations of electric field for *standard device* with static piston at various locations in J-II channel.

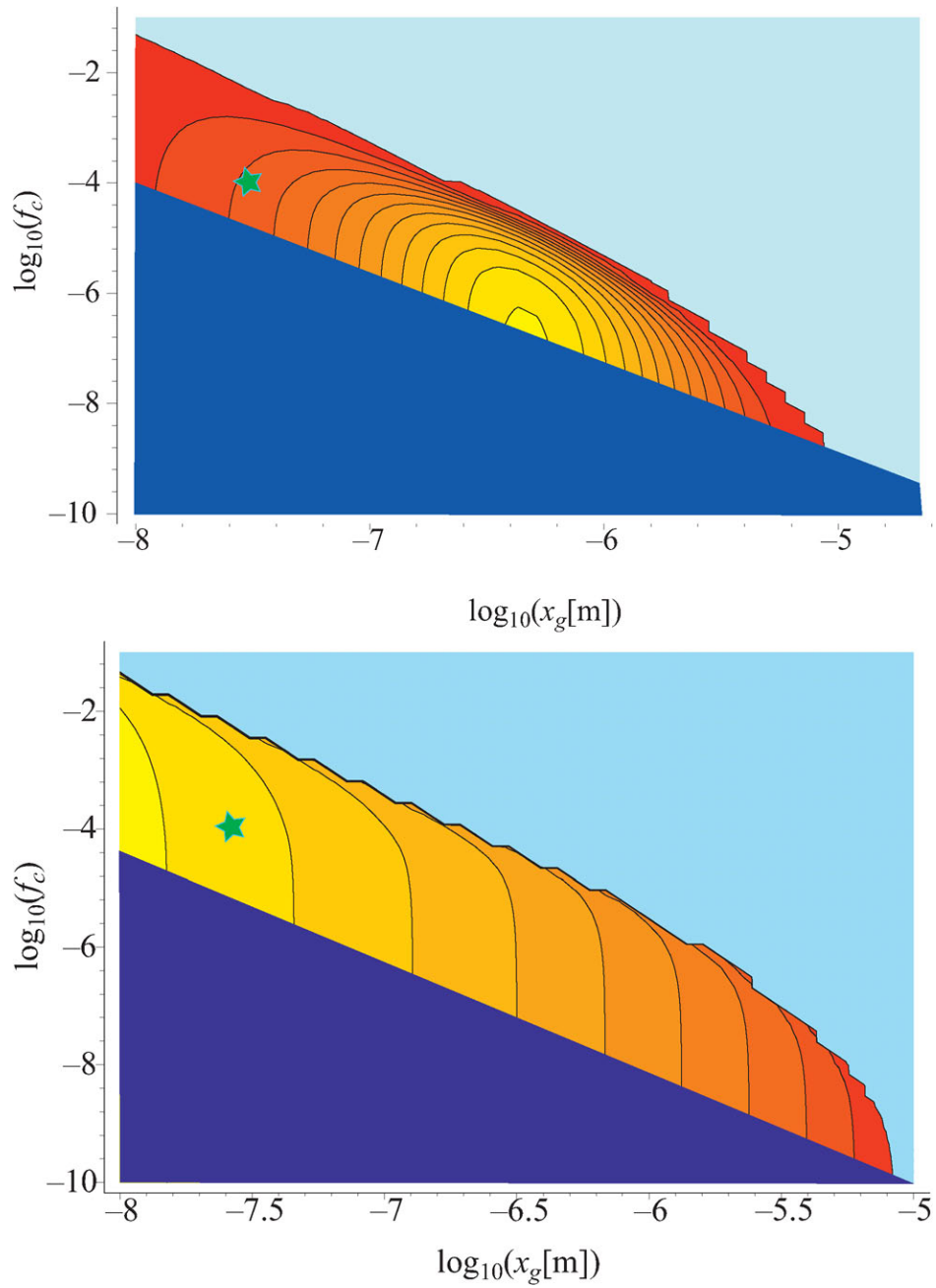


Plate VI Device power and power density over range of devices size-scaled to *standard device*.

(TOP): Maximum power output versus gap width (x_g) and contact fraction (f_c). Contours vary linearly from $10^{-9}\text{W}/\text{device}$ (red) to $1.2 \times 10^{-8}\text{W}/\text{device}$ (yellow).
 (BOTTOM): Power density (Wm^{-3}) versus x_g and f_c . Contours vary logarithmically from 10^1Wm^{-3} (red) to 10^{10}Wm^{-3} (yellow). Star indicates location of *standard device*.

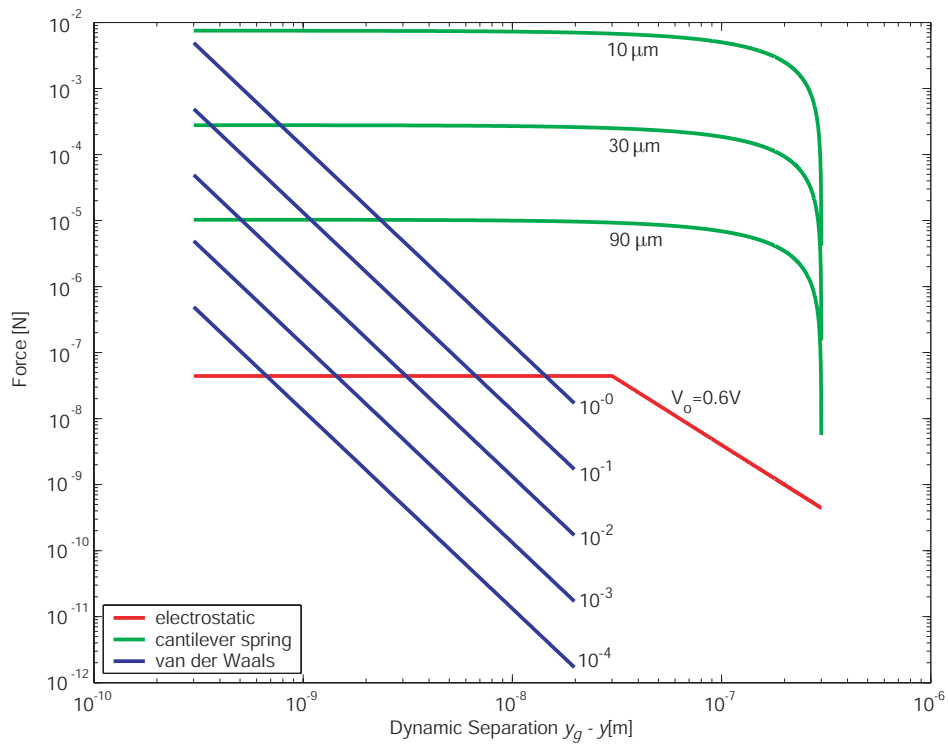


Plate VII Force (N) on hammer versus dynamic separation (m) with anvil (SUMMiTTM case). Spring force (green); van der Waals force (blue); Electrostatic force (red). Device parameters: $l_z = l_h = 5\mu\text{m}$, $t_c = 4.5\mu\text{m}$, $t_h = 6\mu\text{m}$, $l_c = 10, 30, 90\mu\text{m}$; $10^{-4} \leq \eta \leq 1$, $V_o = V_{bi} = 0.6V$.

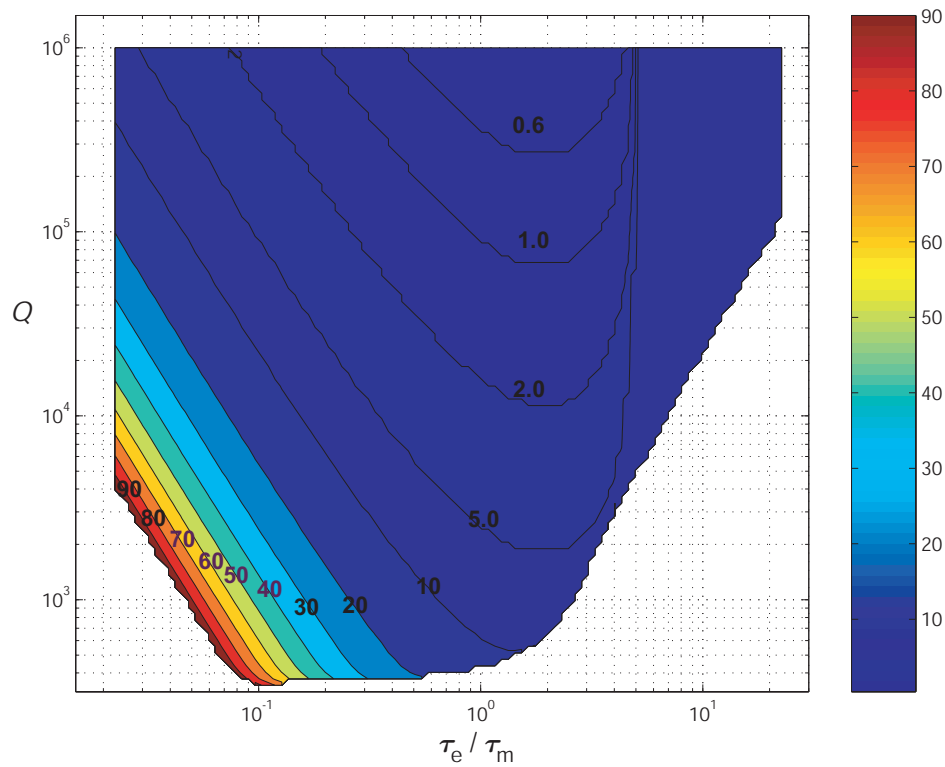


Plate VIII Minimum external bias voltage required for sustained oscillation for SUMMiTTM device (Figure 9.13b), plotted versus Q and $\frac{\tau_e}{\tau_m}$. In sweet spot ($0.25 \leq \frac{\tau_e}{\tau_m} \leq 4$) and ($2 \times 10^3 \leq Q \leq 10^5$), low dc-voltage ($1V \leq V \leq 5V$) drives oscillation.