Article

The Non-equilibrium Thermodynamics of Natural Selection: From Molecules to the Biosphere

Karo Michaelian *

Posted Date: 17 May 2023

doi: 10.20944/preprints202305.1176.v1

Keywords: origin of life; evolution; disspative structuring; prebiotic chemistry; abiogenisis; adenine; biosphere; natural selection

doi:10.20944/preprints202305.1176.v1

Article

The Non-Equilibrium Thermodynamics of Natural Selection: From Molecules to the Biosphere

Karo Michaelian

Department of Nuclear Physics and Application of Radiation, Instituto de Física, Universidad Nacional Autónoma de México, Circuito Interior de la Investigación Científica, Cuidad Universitaria, Cuidad de México, C.P. 04510.; karo@fisica.unam.mx

Abstract: Evolutionary theory suggests that the origin, persistence, and evolution of biology is driven by the "natural selection" of characteristics improving the differential reproductive success of the organism in the given environment. The theory, however, lacks physical foundation, and, therefore, at best, can only be considered a heuristic narrative, of some utility for assimilating the biological and paleontological data at the level of the organism. On deeper analysis, it becomes apparent that this narrative is plagued with problems and paradoxes. Alternatively, non-equilibrium thermodynamic theory, derived from physical law, provides a physical foundation for describing material interaction with its environment at all scales. Here we describe a "natural thermodynamic selection" of characteristics of structures (or processes), based stochastically on increases in the global rate of dissipation of the prevailing solar spectrum. The different mechanisms of thermodynamic selection are delineated for the different biotic-abiotic levels, from the molecular level at the origin of life, up to the level of the present biosphere with non-linear coupling of biotic and abiotic processes. At the levels of the organism and the biosphere, the non-equilibrium thermodynamic description of evolution resembles, respectively, Darwinian and Gaia descriptions, although the underlying mechanisms and the objective function of selection are fundamentally very different.

Keywords: origin of life; evolution; disspative structuring; prebiotic chemistry; abiogenisis; adenine; biosphere; natural selection

MSC: 92-10; 92C05; 92C15; 92C40; 92C45; 80Axx; 82Cxx

1. Introduction

The *Modern Synthesis*, combining Mendelian genetic theory with Darwinian evolutionary theory incorporating reproduction with mutation, random genetic drift, gene flow, and natural selection, provides a contemporary framework for assimilation of much of the biological and paleontological empirical data concerning biological evolution at the level of the organism. However, fierce criticism (although not always scientific) has been leveled at the theory. The first serious scientific challenge concerned the theory's lack of physical foundation. In the 1957 book "The Poverty of Historicism", philosopher of science Karl Popper argued, "There are neither laws of succession nor laws of evolution." [1]). Popper conceded that there were historical trends in nature, but argued that trends cannot be characterized as universal generalizations and, therefore, are not laws.

In "The Myth of the Framework" Popper sharpened his criticism of evolutionary theory, arguing that if the common statistical definition of fitness (differential reproductive success of individuals within populations) were accepted "then the concept of the survival of the fittest becomes tautological, and irrefutable". Since Popper insisted that a "scientific" theory be refutable [2], this left him with no other choice other than to refer to Darwinian theory as a non-scientific "metaphysical research program".

Contrary to what is often claimed in the literature, Popper did not recant on this position latter in life. He did, however, concede that Darwinian theory could, nevertheless, be useful as "a possible framework for testable scientific theories" [3]. To Popper, Darwinian theory was not pseudoscience, but simply lacked a foundation based on fundamental empirical law which would make the theory testable [4]. The lack of physical foundation of evolutionary theory has rarely been addressed since Popper's criticism. This appears to be due, in part, to the inherent complexities of the issues, but also to a vigorous suppression of criticism of the theory, probably as an over-reaction to the aggressive non-scientific skepticism of the theory expressed by religious adherents.

The lack of foundation, however, manifests itself in the many unresolved problems and paradoxes afflicting the theory. Examples include; its inability to shed light on the origin of life, the tautology in a "natural selection" based on differential reproductive success, the problem of separating the environment from the organism (e.g., whether the environment is selecting the organism or vice-versa, and sexual selection wherein the selective environment experienced by one sex is created by properties of the other), explaining the paleontological evidence for punctuated equilibrium (long periods of stasis interrupted by rapid change [5]), the "paradox of the first tier" (failure to find the expected progress among organisms in competition, e.g. simple prokaryotes never surrendering their vast kingdom to more "evolved" organisms [5]), complex apparently "directed" mechanisms of change distinct from mutation (e.g. horizontal gene transfer - viral vectors, Lamarckian evolution - epigenetics, genetic drift - trans-splicing, cultural evolution), selection apparently operating at different levels from the gene to the biosphere (e.g. Dawkin's "selfish gene" [6]), and the concept of "reproductive success" losing interpretation at the higher biotic levels (e.g., ecosystem and biosphere) known as the "paradox of the evolution of a system of population one" [7].

Although these problems have not been ignored, they have usually been addressed only from "within the box", i.e., through attempts at keeping traditional evolutionary theory intact while allowing judicial extensions. These, however, have resulted in little further elucidation and have often created new paradoxes. For example, Richard Dawkins in his book "The Selfish Gene" [6] implores us to question the level at which natural selection was really operating, suggesting that it might be at the gene level, demoting the organism itself to the gene's "survival machine" [6]. Others have considered natural selection at the species level [8] and macroevolution at still higher levels. James Lovelock emphasized the empirical data pointing to mutual evolution of the entire biosphere, and thus argued for a collective, rather than individual, fitness function, related to biological control of planetary processes assuring "suitability for all life". In his most enthusiastic presentation of this idea, Lovelock considered the Earth itself as a homeostatic living organism and gave it the name Gaia, after the Greek goddess of Earth [9]. Steven Gould criticized this "strong Gaia hypothesis", suggesting it was only a metaphor, rather than a mechanistic theory [5]. Neo-Darwinism itself, however, has not escaped this same criticism [10]. Gould realized that selection was occurring simultaneously on many levels (living system hierarchies) and tiers (defined as distinct time periods, e.g. relevant to ecological processes, speciation and punctuated equilibrium, or extinctions) but his inability to find a satisfactory resolution of these issues from within the Darwinian paradigm led him to the same conclusion as Popper, that evolutionary theory was, at the very least, incomplete [5].

Perhaps the most conspicuous indication of the incompleteness of evolutionary theory is that it sheds no light on the origin of life. Here too, attempts have been made to stretch the fabric of traditional evolutionary theory to cover selection of individual molecules, for example, based on chemical stability, or on the ability of molecules to sequester molecular precursors through chemical affinity. Neither of these two lines of research have, however, proven fruitful.

Alternatively, non-equilibrium thermodynamic theory in the non-linear regime, as developed by Onsager, Machlup, Prigogine, Nicolis, Glansdorff [11–13], and others, provides a physical/chemical description of the complex dynamics of material interacting with its environment. Under this framework, processes, known as *dissipative structures* (flows) [14,15] arise "spontaneously" under an imposed external thermodynamic potential (force) to dissipate this potential. Under constant external conditions, multiple, locally stable *stationary states* exist for non-linear systems and this means that, under perturbation, the material system may evolve over these states, directed by both stochastic fluctuations and deterministic thermodynamic law.

The advantage of this thermodynamic framework over traditional evolutionary theory is that it is based on established fundamental law; the conservation laws, the second law of thermodynamics, and the existence of various solutions to, and instabilities in, non-linear systems, and furthermore applies simultaneously to all hierarchal levels, from the molecules at origin of life, to the present biosphere. Stubborn problems and paradoxes find resolution under this non-equilibrium thermodynamic framework, and a physical/chemical explanation of the origin, persistence, and evolution of life can be provided.

2. A Non-equilibrium Thermodynamic Framework

Dynamics involving material or energy (i.e., processes) are driven by what are known as *generalized thermodynamic potentials*. Examples include the electric potential which promotes the movement of charged material (a current), temperature potentials which promote a flow of energy (heat flow), concentration potentials which promote the flow of matter (diffusion), chemical and photochemical potentials which promote molecular transformations (chemical and photochemical reactions), etc. The gradients of these potentials with respect to space or concentrations (e.g. temperature and spatial concentration gradients or chemical and photochemical affinities, respectively) divided by the average temperature, are known as *generalized thermodynamic forces* because the size of this quantity determines the strength of the corresponding flow (e.g. heat flow or reaction rate), which are known as *generalized thermodynamic flows*.

When thermodynamic forces are sufficiently large, the relation between force and flow is not necessarily linear because the production of internal flows can lead to new internal forces, and so on, giving rise to a set of coupled processes and non-linear behavior. It is precisely this non-linearity between forces and flows that leads to many solutions and thus the exuberant diversity of dynamics seen in the interaction of material with its environment, especially for carbon based material when subjected to a strong photochemical potential (i.e., life). In the following sections we explore the possibility that the origin of life was a particular scenario of the dissipative structuring of carbon based material under the UV-C light potential of the Archean, and that the subsequent evolution of life corresponded to the continuation (evolution) of this dissipative structuring into the visible wavelengths and over the entire surface of Earth, so as to increase global photon dissipation in accordance with non-linear, non-equilibrium thermodynamic directives.

2.1. Origin of the Second Law and Irreversible Thermodynamic Theory

All generalized thermodynamic forces are ultimately manifestations of the *second law of thermodynamics*. This law captures the empirical fact that the conserved quantities of nature (e.g. energy, momentum, angular momentum, charge, etc.) "spontaneously" become, over time, globally (system plus environment) distributed over ever more microscopic degrees of freedom (e.g. vibrational, rotational, translational, and electronic degrees of freedom of the molecules or atoms of the material), and that this evolution is irreversible in time. This is considered to be a fundamental law of nature, valid macroscopically rather than microscopically, and obeyed statistically rather than deterministically.

Why the second law of thermodynamics (irreversibility) is part of nature, but not envisaged in our strictly reversible descriptions of both classical and quantum mechanics, has been debated for more than 150 years. A favored perspective is that it arises from quantum decoherence [16,17] related to the practical impossibility of completely isolating any macroscopic system from its environment [18]. Others believe that it arises from the non-linearity in nature, or the expansion of the universe. Still others (e.g. Einstein) believed that irreversibility is only an illusion, since time itself is an illusion. A proposal by Ilya Prigogine [16], which the author finds most appealing, is the realization that individual and integrable trajectories of elementary particles, for which classical physics, quantum mechanics, and equilibrium thermodynamics were developed, is only an idealization. Instead, real systems, even such simple systems as three bodies interacting gravitationally (the three-body problem), are non-integrable because there exists persistent interaction between particles, or, non-local (in space and time) resonances giving rise to infinities on integration. In this case, a probabilistic representation of the fundamental laws is required to properly describe the dynamics (i.e. the correct classical and quantum mechanics is not, in fact, reversible for real particles), and this necessitates the introduction of the second law of thermodynamics, with its signature of global entropy increase over time, when we employ traditional classical and quantum mechanics to describe nature.

Irrespective of the controversy, however, most scientists are content to consider the second law of thermodynamics as fundamental, since no macroscopic violations have yet been observed. It is the second law that we also adopt here as being fundamental to an understanding of evolution of material interacting with its environment from a physical-chemical perspective. Furthermore, we also accept as valid the results of Classical Irreversible Thermodynamic (CIT) theory developed by Onsager, Prigogine, and co-workers [11–13] which follows from the second law and the conservation laws under specific environmental conditions. CIT theory in the non-linear regime establishes the existence of multiple, locally stable, dissipative stationary states, consisting of processes which can break space and time symmetry (dissipative structuring), for a system interacting with its environment. CIT theory has been empirically validated for situations in which a macroscopic *local thermodynamic equilibrium* in space and time can be established, a restriction observed for most terrestrial, sufficiently dense, material systems [12], including "fast" systems involving, for example, photon-induced quantum electronic excitations [19].

2.2. Multiple Stationary States

For material systems under an imposed constant generalized thermodynamic potential from the environment, the material in the system will develop the corresponding internal flow (of mass, energy, charge, reaction rate, etc.) and induced secondary internal forces, but will eventually come to what is known as a *thermodynamic stationary state* in which the generalized thermodynamic flows and forces, and the entropy production, arrive at constant values at any given point within the system (although being potentially different throughout the system - see Figure 1). The total entropy of the material within the system could either increase or decrease [12], while the entropy of the system plus its environment necessarily increases, in observance of the second law of thermodynamics.

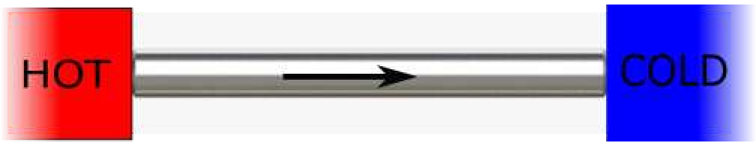

Figure 1. An example of a thermodynamic stationary state corresponding to a constant flow of heat from an infinite hot reservoir to an infinite colder one along a metal bar. Before the bar is connected to the heat reservoirs, local temperatures along the entire bar are the same, and we say the metal bar is in *thermodynamic equilibrium* with its environment. Connecting the bar to the heat reservoirs takes the system out-of-equilibrium, and the temperatures at each point along the bar begin to change, but eventually reach fixed values at which point the flow of heat and the entropy production come to constant values. In this situation, we say that the non-equilibrium system has arrived at a stable "stationary state". The generalized thermodynamic "force" is the spatial gradient of the temperature across the bar over the average temperature, and this is linearly proportional to the corresponding "flow" of heat (Fourier's law). The linearity of the flow to the force implies that, in this case, the stationary state is unique and globally stable. Each macroscopic, but small, region along the bar will be in local equilibrium and so will have a local temperature. CIT theory is therefore applicable and we can use the same variables, and the same Gibb´s relation among them, as we use in equilibrium thermodynamics, but now the variables become both space (position along the bar) and time dependent.

For systems in which flows are non-linearly related to the forces, there can be more than one stationary state available to the system for the same boundary and initial conditions (because non-linear equations have multiple solutions). Such stationary states are, therefore, only locally stable and large enough perturbations, particularly near *critical points*, can cause the system to evolve from one stationary state to another. For particular stationary states with non-linear positive feedback (for example, an auto-catalytic chemical reaction set dissipating an imposed chemical potential), it can be imagined that such a state will be more stable locally than other states (e.g., non-catalytic set of reactions) because statistical microscopic fluctuations would be less likely to alter the reaction route since the catalyzed route dissipates a greater amount of the free energy entering the system, free energy which could potentially alter the route. That is, the basin of attraction in a generalized phase space will be larger for the auto-catalyzed route (stationary state) and there will be a natural greater statistical probability of evolution, on stochastic perturbation, towards those stationary states with greater dissipation of the imposed potential. This will be demonstrated explicitly below with an example of the photochemical dissipative structuring of adenine, one of the fundamental molecules of life (those earliest molecules found in all three domains of life), from common precursor molecules in water solution under an imposed constant UV-C photochemical potential.

2.3. The Dynamics of Material-Environment Interaction

In summary, the elements of non-linear CIT theory which describe the dynamics of a material system interacting with its environment are, therefore:

1. The existence of at least one applied external generalized thermodynamic potential defining the environment, and the gradients of these (over the average temperature), which are the applied thermodynamic forces.
2. The spontaneous generation of internal generalized thermodynamic flows derived from the applied external generalized forces and the new internal forces that these flows themselves may generate.
3. The existence (in the asymptotic time limit) of various sets of these internal (to the system) forces and flows for non-linear systems for the same initial and boundary conditions, (i.e. multiple, locally stable, dissipative structures, or processes, at stationary states), which can have different rates of dissipation of the applied external potential (entropy production).
4. External stochastic perturbations, or internal microscopic fluctuations, which could cause the non-linear system to leave the local attraction basin of one stationary state and evolve to another, particularly near a critical point.
5. The statistical (non-deterministic) tendency for evolution on perturbation to stationary states (dissipative structures) of greater dissipation (entropy production) having positive feed-back, giving them a larger “attraction basin” in a generalized phase space.

This list of elements characterizing non-linear CIT theory, based only the conservation laws and the second law of thermodynamics, and assuming the establishment of local equilibrium, is sufficient to provide a physical and chemical explanation of the origin and evolution of life [20–24]. Using these elements of the theory, we will now show how the macroscopic concentration profiles of UV-C pigments (which we claim became the *fundamental molecules of life*; i.e. nucleic acids, amino acids, sugars, fatty acids, cofactors and pigments) arise through dissipative structuring from concentrations of simpler and common precursor molecules under UV-C light, in order to dissipate this light efficiently into heat. In order to understand this process on a microscopic mechanistic level, and therefore avoid the usual criticism of metaphoric speakeasy, it is first necessary to review the basics of molecular photochemistry.

3. The Photochemistry of Organic Molecules

The fact that the sun deity usually reigned supreme in past cultures suggests that humans have, consciously or subconsciously, always understood that the sun was at the foundation of life. This commemorated intuition turns out to be a good starting point for building a modern framework from within which to understand life. The “thermodynamic dissipation theory for the origin and evolution of life" considers life as a non-equilibrium thermodynamic process arising out of the imposed force or potential from the environment giving rise to the dissipative structuring and flow of the material within the system; in particular, the incident solar light flux at Earth's surface, and the dissipative structuring of pigments from common carbon based precursor molecules in water solvent.

Analogous to heat flow, or a convection cell, arising "spontaneously" under a temperature gradient to dissipate this gradient, the thermodynamic dissipation theory for the origin of life suggest that the fundamental molecules of life (nucleic acids, amino acids, sugars, fatty acids, cofactors, and their complexes) arose "spontaneously" as UV-C pigments, dissipatively structured on the ocean surface from common precursor molecules such as hydrogen cyanide HCN, cyanogen $(CN)_2$, carbon dioxide CO_2 and water under the soft UV-C photon flux (between approximately 205 and 285 nm, Figure 2 arriving at Earth's surface throughout the Archean [20–24]. This wavelength region has sufficient energy per photon to transform carbon covalent bonds (single and double), but generally not enough energy to ionize these molecules and thereby disassociate them.

The best geochemical evidence presently available suggests that this light would have been present on Earth's surface from before the origin of life (at $\sim$3.9 Ga) and for at least 1000 (perhaps even for 1500 [25]) million years until organisms evolved oxygenic photosynthesis which saturated available oxygen sinks [25–27], leading to a protective ozone layer in the stratosphere. Additionally, cyanobacteria (and today's plants) emit volatile organic compounds (VOCs) which, together with atmospheric oxides of nitrogen, are the precursors for photochemical production of ozone in the troposphere [28,29]. Oxygen and ozone are thus considered here as biology-procured pigments dissipating the UV-C region in the upper atmosphere, thereby allowing the present dissipative structuring of the more delicate (i.e. prone to UV-C disassociation) complex biosynthetic pathways producing visible pigments using multiple visible photons of lower energy but of much higher intensity.

A comprehensive description of the thermodynamic dissipation theory for the origin of life, including dissipative molecular structuring, the origin of homochirality, enzymeless nucleic acid replication, early information encoding, and protocell formation, has been given elsewhere [20–24, 30–34]). The purpose of this paper is to analyze in detail the mechanism of thermodynamic selection, operating at the molecular level at the origin of life, and subsequently at higher biotic levels, up to the present biosphere. Life's evolutionary history will be shown to be driven by a natural thermodynamic selection based on efficacy of photon dissipation of the biosphere. The paleontological evidence indeed indicates greater photon dissipative pigment concentration profiles over life's history [35,36].

The following subsection describes how UV-C light interacting with carbon-based precursor molecules structures these into complex UV-C pigments (the fundamental molecules of life, Figure 2) with conical intersections to internal conversion providing efficient photon dissipation.

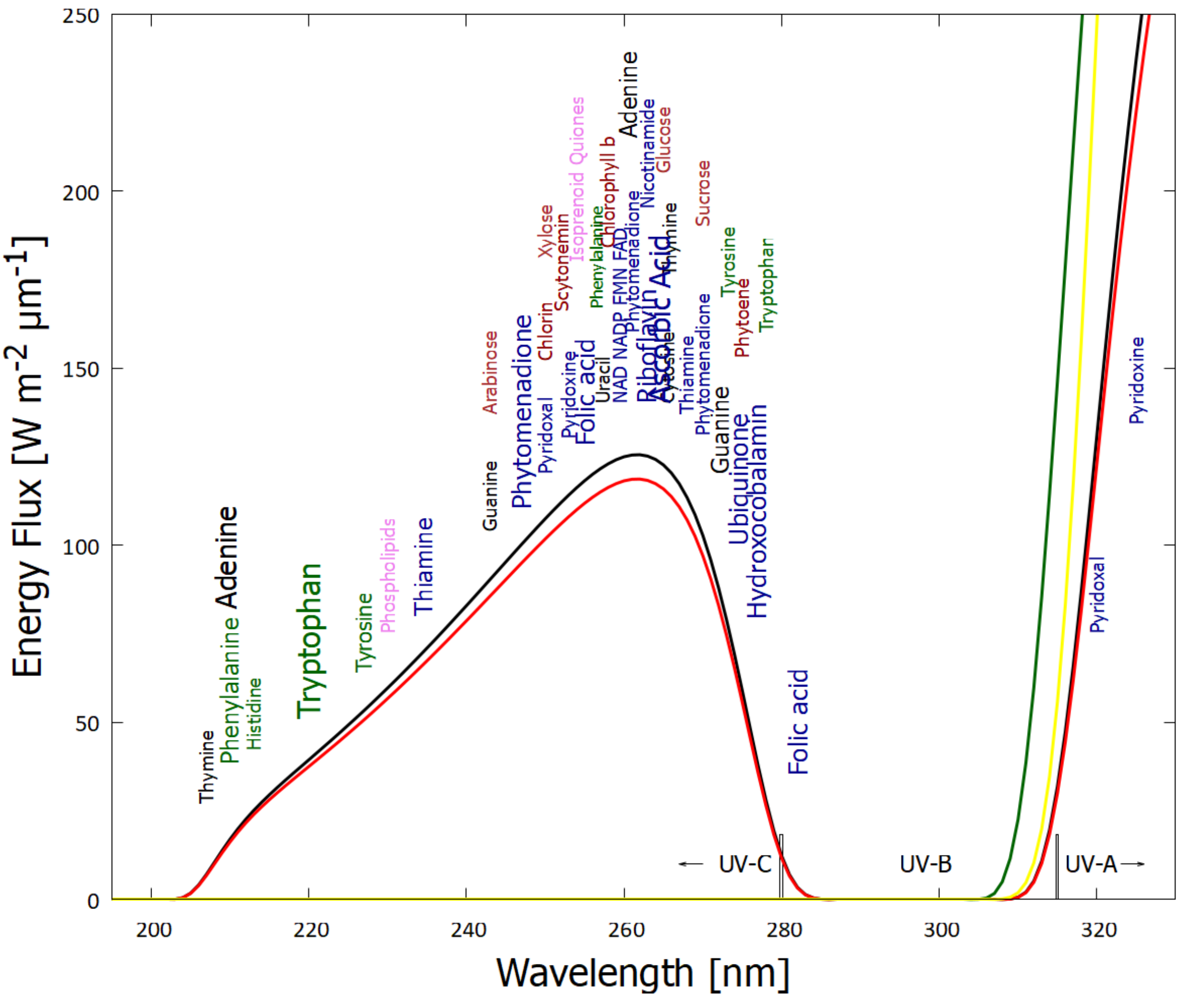

Figure 2. The spectrum of UV light available at Earth's surface before the origin of life at approximately 3.9 Ga and until at least 2.9 Ga (curves black and red respectively) (perhaps even extending throughout the entire Archean until 2.5 Ga [25])). Atmospheric CO_2 and probably some H_2S were responsible for absorption at wavelengths shorter than ∼205 nm, and atmospheric gas aldehydes (e.g. formaldehyde and acetaldehyde, common photochemical products of CO_2 and water) absorbed between about 280 and 310 nm [26]), approximately corresponding to the UV-B region. By around 2.2 Ga (green curve), UV-C light at Earth's surface was completely extinguished by the UV-C pigments oxygen and ozone resulting from organisms performing oxygenic photosynthesis. The yellow curve corresponds to the present surface spectrum. Energy fluxes are for the sun at the zenith. The fundamental molecules of life, suggested to have been dissipatively structured under this light as UV-C pigments, are plotted at their wavelengths of maximum absorption; nucleic acids (black), amino acids (green), fatty acids (violet), sugars (brown), vitamins, co-enzymes and cofactors (blue), and pigments (red) (the font size is roughly proportional to the relative size of the respective molar extinction coefficient). Adapted from [35].

3.1. Absorption of Light and its Dissipation through Internal Conversion

The absorption of UV-vis light in organic molecules is a phenomenon involving collective electron excitation requiring conjugation of carbon bonds (alternation of double and single carbon-carbon bonds - Figure 3). Conjugation, implies removing hydrogen atoms from saturated hydrocarbons to form carbon-carbon double bonds (C=C) thereby freeing electrons from their atomic orbitals. This provides a new set of collective electronic excited states involving a number of atomic nuclei now sharing their valence electrons. Atomic electronic orbitals thus become molecular orbitals which can be either *bonding* or *anti-bonding* between atoms. The greater the conjugation number, the greater the

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 17 May 2023 doi:10.20944/preprints202305.1176.v1

wavelength of peak absorption of the molecule (Figure 3). The energy difference between the ground state and first excited state for doubly and triply conjugated carbon based molecules corresponds to the range of energies of the soft UV-C photon region arriving at Earth's surface during the Archean (Figure 2).

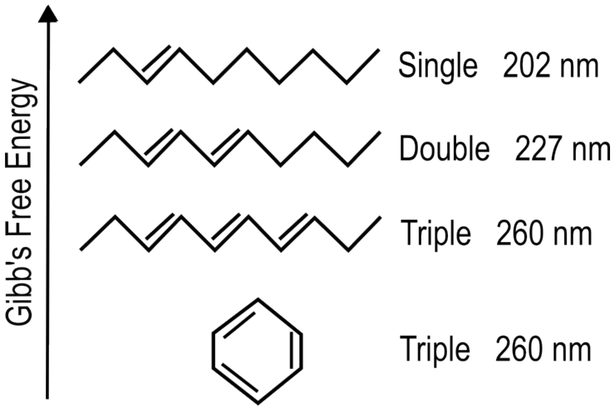

Figure 3. Conjugated carbon molecules are more stable (lower Gibb's free energy in the ground state) but more importantly provide new collective electron orbitals giving rise to excited states at energies adequate for the absorption of soft UV-C photons arriving at the Archean surface. The greater the conjugation, the greater the wavelength of maximum absorption. Conjugation is also important for giving the molecule a conical intersection allowing rapid dissipation of the excited state energy into heat (internal conversion).

The facility to form, and stability of, these UV-C light absorbing conjugations in carbon based molecules are probably the principle reasons that Earth's life is based on carbon. The other chemical properties of carbon-based molecules important to life [37] are probably only secondary. Elements with similar outer-shell electronic structure, like silicon, also support 4 covalent bonds, but silicon molecules only rarely present conjugation because Si-O bonds are significantly stronger than Si-Si bonds. In fact, double Si=Si bonds are unstable in aqueous solution [37]. Under the particular UV-C light environment at Earth's late Hadean and early Archean ocean surface, it may thus be safe to assume that only carbon based molecules, and complexes of these, could be dissipatively structured into stable and efficient UV-C pigments.

Empirical evidence supports our UV-C dissipative structuring conjecture for the fundamental molecules of life. First, the wavelength of maximum absorption of many of these molecules coincide with the predicted window in the Archean atmosphere (Figure 2). Secondly, many of the fundamental molecules of life are endowed with *peaked conical intersections* [23] giving them broad band absorption and high quantum yield for internal conversion, i.e. extremely rapid (sub-picosecond) dissipation of the photon-induced electronic excitation energy into vibrational energy of molecular atomic coordinates, and finally into the surrounding water solvent [22,38] (see Figure 4). Thirdly, many photochemical routes from common and simple precursor molecules to the synthesis of nucleic acids [39], amino acids [40], fatty acids [32], sugars [41], and other pigments [35] have been identified at these UV-C wavelengths, and the rate of photon dissipation within the Archean UV-C window generally increases after each incremental transformation on route to synthesis of the fundamental molecule, a behavior strongly suggestive of dissipative structuring in the non-linear non-equilibrium thermodynamic regime [22,23,32]. Finally, even minor transmutations (e.g. tautomerizations or methylations) of the fundamental molecules, which often, in fact, endows them with lower Gibb's free energy, eliminates or significantly reduces their special photon absorption and dissipation properties [42].

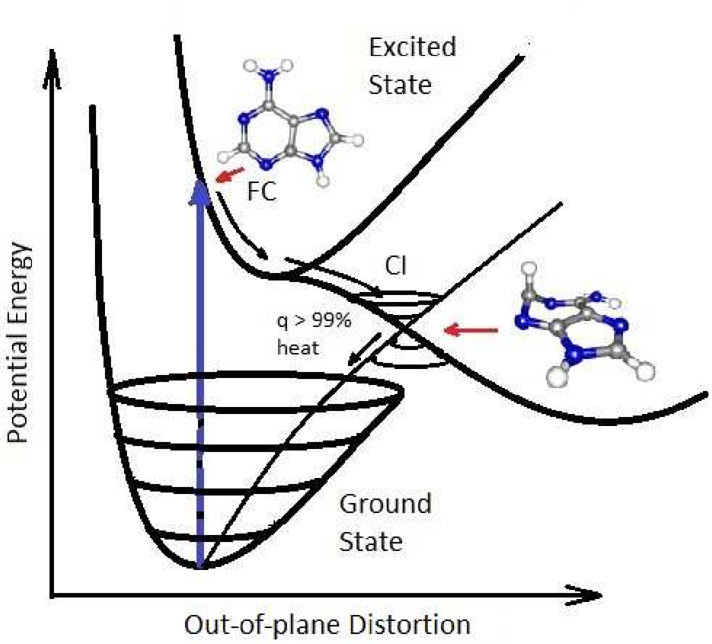

Figure 4. Conical Intersection (CI) for excited adenine showing a degeneracy of the electronic excited state with the electronic ground state after a UV-C photon absorption event (blue arrow) which induces a nuclear coordinate deformation, either activation of an N9–H stretch or a ring-puckering motion known as *pyramidalization* (shown in diagram). The most probable deformation from its original structure in the Franck-Condon (FC) region depends on the incident photon energy and protonation state. Conical intersections provide rapid (sub-picosecond) dissipation of the electronic excitation energy into vibrational energy (heat). The quantum efficiency, q, for this dissipative route is very large (> 99%) for the fundamental molecules of life, making them photochemically stable and, more importantly for our theory, very efficient at UV-C photon dissipation. Another common form of coordinate transformation mediated through conical intersections are proton transfers within the molecule or with the solvent environment. Based on data from Andrew Orr-Ewing [43], Roberts et al. [44], Kleinermanns et al. [45], and Barbatti et al. [46]).

Conical intersection seams on the excited potential energy surface, in multi-dimensional atomic coordinate space, determine the photoisomerization or photoreaction products that can be reached after a photon absorption event. Since conical intersections are located energetically down-hill from the Franck-Condon region (Figure 4), the direction and velocities of approach of the nuclear coordinates to a conical intersection are important in defining the outcome [38]). For example, it is known that for the molecule retinal in rhodopsin, the photoexcited molecule reaches the conical intersection extremely fast (75 femtoseconds) implying that the conical intersection must be peaked (inverted cone-like on the excited state potential energy surface) and, overwhelmingly, only one reaction product is reached, which for the case of retinal, as well as for the fundamental molecules of life, is the original ground state configuration [47]). A more extended seam with different minima can lead to different reaction products [48]) such as those intermediate molecules on route to the photochemical synthesis of the nucleobase adenine (Figure 5). The final products of the photochemical dissipative structuring (the fundamental molecules of life) have a *peaked* conical intersection to internal conversion so that they dissipate extremely rapidly the excitation energy to the ground state and thus become the *final* and *photo-stable* product of dissipative structuring in the relevant region of the solar spectrum.

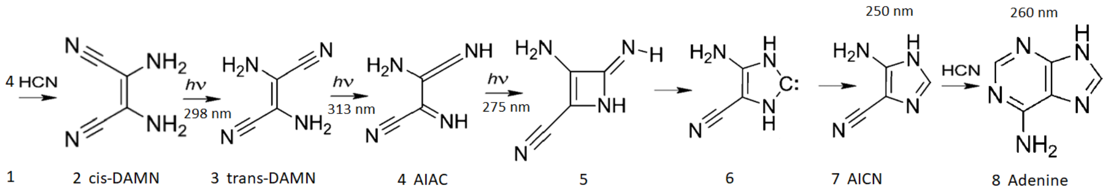

Figure 5. The photochemical dissipative synthesis of adenine from 5 molecules of hydrogen cyanide (HCN) in water, as discovered by Ferris and Orgel (1966) [39,49]). Four molecules of HCN (1) are transformed into the smallest stable oligomer (tetramer) of HCN, known as cis-2,3-diaminomaleonitrile (cis-DAMN) (2), which, under a constant UV-C photon flux isomerizes into trans-DAMN (3) (diaminofumaronitrile, also known as DAFN) which may be further converted on absorbing two more UV-C photons into an imidazole intermediate, 4-amino-1H-imidazole-5-carbonitrile (AICN) (7). Hot ground state thermal reactions with another HCN molecule or its hydrolysis product formamide (or ammonium formate) leads to the purine adenine (8). This is a microscopic dissipative structuring process which ends in adenine [22,23]), a UV-C pigment with a large molar extinction coefficient at maximum intensity of the UV-C Archean solar spectrum (at 260 nm) and a peaked conical intersection which promotes the dissipation of photons at these wavelengths (Figure 2). Adapted from Ferris and Orgel [39]).

It has been a recurrent theme in the literature that the rapid (sub-picosecond) deexcitation of the excited nucleobases due to their conical intersections had evolutionary utility in providing stability under the high flux of UV photons that penetrated the Archean atmosphere [26,50]) since a peaked conical intersection reduces the lifetime of the excited state to such a degree that further chemical transformations are improbable. Although this is true, photo-stability is never perfect for photon absorbing molecules, and photochemical reactions under UV-C light still occur for the fundamental molecules of life, particularly after excitation to the long-lived triplet state (examples are the UV induced cyclobutane pyrimidine dimers, 6-4, and other photo-products, in RNA and DNA [51])). An apparently more optimal and simpler solution for avoiding radiation damage with its concomitant degradation in biological function, therefore, would have been the synthesis of molecules transparent to, or reflective to, the offending UV light (for example, saturated hydrocarbons or molecules made from silicon atoms lacking the conjugation needed for photon absorption - see above). From the perspective of the thermodynamic dissipation theory for the origin of life, however, a large antenna for maximum UV-C photon absorption and a peaked conical intersection for its rapid dissipation into heat are, in fact, precisely the thermodynamic “design goals” of dissipative structuring.

4. Natural Thermodynamic Selection at the Origin of Life

Given the probable existence of common carbon based molecular precursors during the Archean, such as hydrogen cyanide (HCN), cyanogen $(CN)_2$, and carbon dioxide (CO_2) [23,24]), in a water solvent, under soft UV-C light between approximately 205 and 285 nm (Figure 2), photochemical and chemical (thermal) reactions will occur “spontaneously” to dissipate the respective photochemical and chemical potentials. Product molecules resulting from these reactions which absorb less well the incident soft UV-C spectrum will become less susceptible to further photochemical transformation, although still subject to further chemical reactions. Chemical reactions at Earth surface temperatures, however, result in much less product variety as compared to photochemical reactions in which the deposited photon energy is sufficient overcome high activation energies [23]). On the other hand, those product molecules which become progressively more photon absorptive in the soft UV-C spectrum will tend to continue to transform until the quantum efficiency for dissipation of the photon-induced excited state energy directly to the ground state (internal conversion) out-competes the quantum efficiencies for further transformation (i.e. they develop conical intersections to rapid internal conversion - Figure 4).

This makes the product molecules photochemically stable, but, more importantly from our perspective of the thermodynamic dissipation theory for the origin of life, they become strongly photon dissipative.

This mechanistic description of microscopic dissipative structuring of carbon based pigments under a soft UV-C light flux is analogous to the mechanistic description of the dissipative structuring of convection cells in a liquid held under gravity and a temperature gradient. In the latter case, at a particular "critical point" in the applied temperature gradient, buoyant forces acting on the less dense hot fluid overcome the opposing force of gravity and the liquid viscous forces, resulting in the "spontaneous" appearance of convection cells under the temperature gradient, which act to increase dissipation of this temperature gradient in comparison to conduction alone. In the pigment dissipative structuring case, for particular incident photon wavelengths shorter than some critical value allowing excitation to the first collective electronic excited state, the concentration profiles of the molecules in the system will gradually transform from the original poorly absorptive profiles of the precursor molecules towards the strongly absorbing concentration profiles of the product molecules, which have increased photon dissipation efficacy of the imposed external photon potential.

Figure 6 describes in detail how the initial precursor molecular concentration profile will gradually transform (evolve) towards a concentration profile with greater photon dissipative efficacy under the impressed soft UV-C photon spectrum of the Archean. Even though the product molecules can (but not necessarily do) have a lower Gibb's free energy than that of the precursor molecules from which they evolved, in thermal systems (chemical reactions) the evolution to the lower free energy state is not spontaneous if there are large energy barriers between configurations. However, coupling of the reactions to the impressed UV-C photon potential (photochemical reactions), allows the transformation to proceed over the barriers, and even to higher Gibb's free energy configurations, at a rate dependent on, i) photon intensities at the different wavelengths, $I(\lambda)$, ii) the absorption as a function of wavelength $A(\lambda)$, and iii) on the widths of the phase-space paths leading to the particular conical intersection on the electronic excited state potential energy surface (Section 3) (i.e., the quantum efficiencies q_i^j) leading to the molecular transformation $i \to j$. Backward transformations q_j^i, or transformations to other possible products (e.g. q_i^k), under the UV light are less probable if the quantum efficiencies are smaller (smaller phase-space path on the excited potential energy surface) as compared to its quantum efficiency for internal conversion to the ground state q_j^{IC}.

The condition for evolution of the macroscopic molecular concentration profile in the forward direction (Figures. 5 and 6), towards an increasing concentration of molecule j (assuming, for simplicity, only two possible molecular configurations, i and j) is thus;

$$\int_0^\infty I(\lambda) \cdot A_i(\lambda) \cdot \frac{q_i^j(\lambda)}{(q_i^{IC}(\lambda) + q_i^j(\lambda))} d\lambda > \int_0^\infty I(\lambda) \cdot A_j(\lambda) \cdot \frac{q_j^i(\lambda)}{(q_j^{IC}(\lambda) + q_j^i(\lambda))} d\lambda \tag{1}$$

where $q_i^{IC}(\lambda)$ is the quantum efficiency for internal conversion to the ground state for molecule i at wavelength λ.

Since (for our simplified model of only two molecular configurations),

$$q_i^{IC}(\lambda) + q_i^j(\lambda) = 1 \text{ and } q_j^{IC}(\lambda) + q_j^i(\lambda) = 1, \tag{2}$$

equation (1) for the condition for evolution of the macroscopic concentration profile in the forward direction can be written as;

$$R_{i\to j} \equiv \int_0^\infty I(\lambda)[A_i(\lambda) \cdot q_i^j(\lambda) - A_j(\lambda) \cdot q_j^i(\lambda)] d\lambda > 0, \tag{3}$$

where $R_{i\to j}$ is the molar rate of conversion of species i to species j, $A_i(\lambda) = \epsilon_i(\lambda)c_i l$ with $\epsilon_i(\lambda)$ the molar absorption coefficient of species i, c_i the concentration of species i, and l the path-length of the light. Using equations (2) in equation (3), the condition for evolution in the forward direction is,

$$R_{i\to j} = \int_0^\infty I(\lambda)[A_i(\lambda)\cdot(1-q_i^{IC}(\lambda)) - A_j(\lambda)\cdot(1-q_j^{IC}(\lambda))]d\lambda > 0. \tag{4}$$

This condition will be satisfied if, 1) molecule j absorbs less photons than molecule i (i.e., that $\int I(\lambda)\epsilon_j(\lambda)d\lambda < \int I(\lambda)\epsilon_i(\lambda)d\lambda$), and/or, 2) the quantum efficiency for dissipation through the conical intersection to the ground state is greater in general for molecule j than it is for molecule i, i.e. $\int q_j^{IC}(\lambda)d\lambda > \int q_i^{IC}(\lambda)d\lambda$.

Therefore, the molecular profile could either 1) evolve towards a concentration profile with little absorption of light, or 2) towards a profile strongly absorbing light, but with large quantum efficiency for the rapid dissipation of this light through a conical intersection to the ground state. Assuming, for simplicity for the moment, no other coupled dissipative process, and ignoring small changes in the structural entropy of the molecules (compared to the entropy production of UV photon dissipation), evolution of a macroscopic concentration profile of molecules towards a less absorptive profile under a constant light flux would be a violation of the second law of thermodynamics which demands that, in any macroscopic process, the entropy of the system plus environment increases. The only possibility, therefore, is that the evolution must be towards a stronger absorbing concentration profile with a large quantum efficiency for the rapid dissipation of the excitation energy to the ground state through a conical intersection.

These two characteristics, i.e., strongly absorbing over a greater wavelength region and rapid dissipation, are, in fact, complementary since rapid dexcitation to the ground state implies a large wavelength bandwidth for absorption by the Heisenberg uncertainty relation $\Delta t\Delta E \geq \hbar/2$. The lowest possible rate of entropy production for any macroscopic process (the thermodynamic limit) carried out at constant volume V and particle number N in a time interval Δt would thus be,

$$\left.\frac{\Delta S}{\Delta t}\right|_{V,N} = \left.\frac{\Delta E}{T\Delta t}\right|_{V,N} \geq \frac{\hbar}{2T\cdot(\Delta t)^2} \tag{5}$$

indicating that short period Δt processes (e.g. internal conversion through a conical intersection) at lower temperatures T lead to greater minimal entropy production.

This example shows how the Heisenberg uncertainty principle arises from the second law of thermodynamics (or vice versa), because equation (5) indicates that entropy production $\Delta S/\Delta t$ in any finite time process at any finite temperature must be positive definite since the right hand side of equation (5) is positive definite. That the Heisenberg uncertainty relation is related to the second law is something already known for a few years now [52]) but this simple example makes this relation obvious and shows the inherent discreteness of the second law and that there exists a minimum possible increment in the entropy for a real process. Note also that equation (5) implies that entropy production increases quadratically with shorter time processes and is always a positive definite quantity, even for time reversed macroscopic processes (i.e. $\Delta t < 0$).

As noted above, the Heisenberg uncertainty principle does not apply to one process of two coupled irreversible processes. For example, if the quantum efficiency for de-excitation through an additional conical intersection to photon-induced ionization and subsequent molecular disassociation is included in equation (1), then this would be a coupled irreversible process that could occur macroscopically provided that the final disassociated molecular components have higher entropy than the original precursors. However, given the myriad of photochemical reactions available for carbon based molecules under soft UV-C light, such a local stationary state, if it were visited by the system would be unstable and of little dissipation (only due to photon reflection into a greater solid angle without changing wavelength).

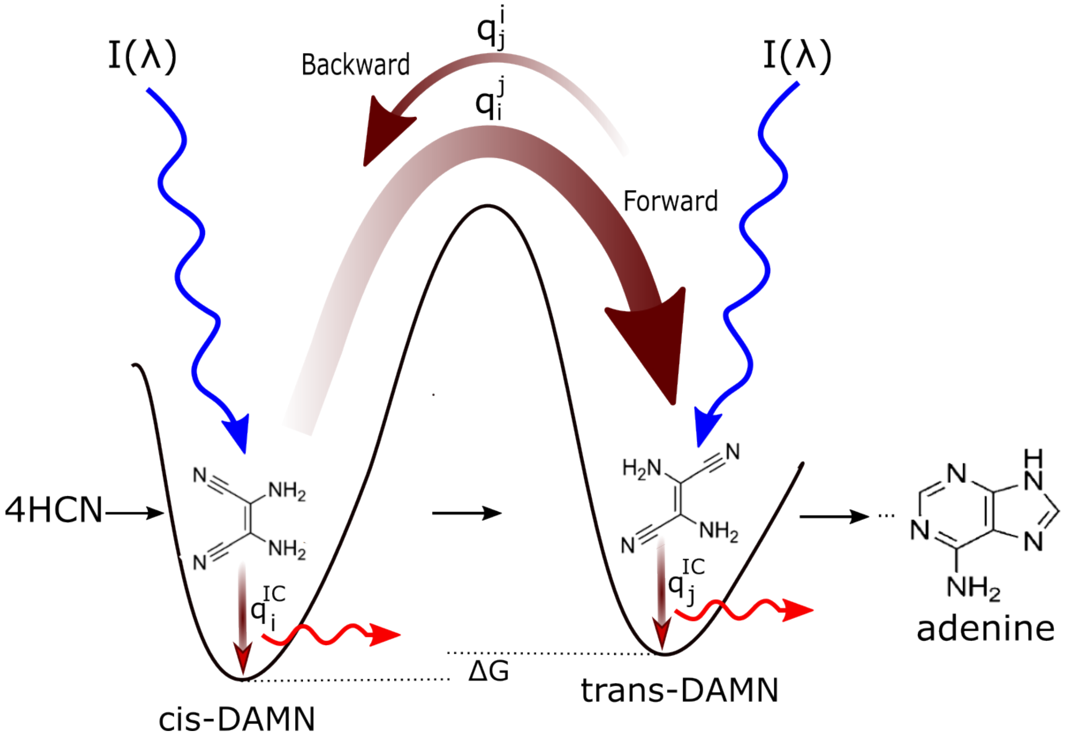

Figure 6. Mechanism for the evolution of molecular structures towards ever greater photon dissipative efficacy (microscopic dissipative structuring) on route to the fundamental molecules (in this case adenine, see Figure 5). The high activation barriers between configurations mean that reactions will not proceed spontaneously but only through coupling to photon absorption events. Forward and backward rates depend on photon intensities I(λ) at the different wavelengths of maximum absorption for the two structures, and on the phase-space widths of paths on their excited potential energy surface leading to the conical intersection giving rise to the particular transformation, implying different quantum efficiencies for the forward (q_i^j) and backward (q_j^i) reactions. Assuming that the intensity of the incident spectrum is constant, and since $q_i^j + \cdots q_i^{IC} = 1$ and $q_j^i + \cdots q_j^{IC} = 1$ (where the “$\cdots$” represents quantum efficiencies for other possible molecular transformations), those stationary states (corresponding macroscopically to concentration profiles) with greater photon dissipative efficacy (higher quantum efficiency for internal conversion q_j^{IC}) will therefore gradually become more predominant under a continuously impressed UV-C photon flux, independently of the sign or size of the difference in the Gibb’s free energies ΔG of the molecules. This process, of evolution towards the right in the diagram, leading to molecular concentration profiles of ever greater photon dissipative efficacy, we call *natural thermodynamic selection*.

In general, the rate of dissipation of the system in its most probable stationary states will depend on the incident spectrum, the quantum efficiencies for molecular dissociation and the quantum efficiency for dissipation to the ground state through a conical intersection, q_j^{IC}. For example, if hard, dissociating, UV-C photons ($\lambda < 220$ nm) were copiously available at Earth’s surface, then evolution may be towards concentration profiles of molecular dissociation products and not molecular dissipative structuring products (Figure 7), as probably occurred at some epoch on the surface of Mars. The dissociation energy of hydrogen cyanide (HCN) in gas phase is 129 kcal/mole, corresponding to a photon wavelength of 222 nm, while that of cyanogen (NCCN) is 145 kcal/mole, corresponding to a photon wavelength of 197 nm [53].

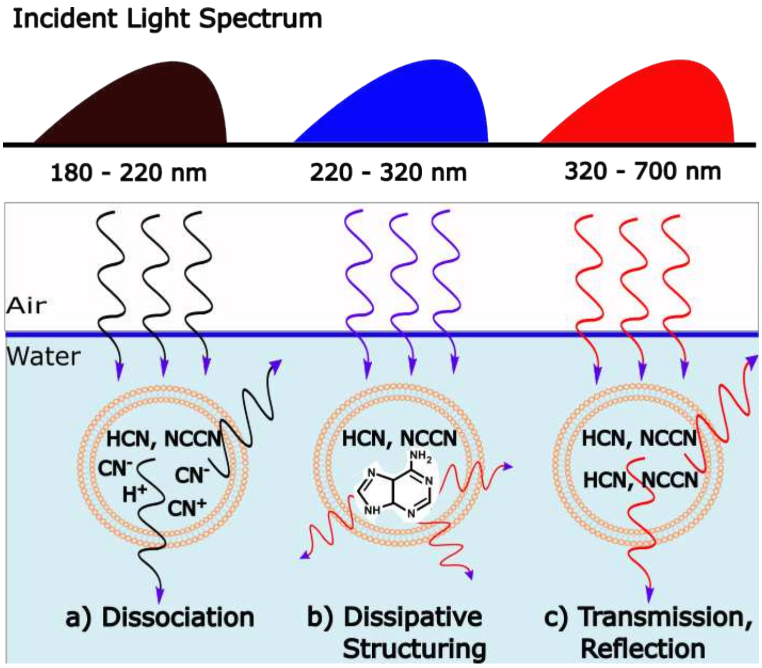

Figure 7. Different wavelength regimes led to different irreversible processes at the origin of life. a) Hard UV-C wavelengths (< 220 nm) lead to dissociation of the precursors hydrogen cyanide (HCN) and cyanogen (NCCN). Entropy production here results from the increase in structural entropy of the disassociated fragments in water and some reflection and transmission of the incident photons into a greater solid angle [54]. b) Soft UV-C wavelengths ($220 < \lambda < 280$) and UV-B ($280 < \lambda < 320$), with energies of the order of carbon covalent bonding, lead to dissipative structuring of the fundamental molecules of life (e.g. adenine). Entropy production here results from the dissipation of most of the strongly absorbed incident photons into heat through the conical intersection of the dissipatively structured molecules. c) UV-A and visible wavelengths do not have enough energy to reconfigure carbon covalent bonds, so the precursors remain intact. Here, the production of entropy is a result of the transmission and scattering of the incident photons into a greater solid angle [54]. Considering the historical evolution of life on Earth, with continued dissipative structuring in the soft UV-C regime b) came more complex biosyntheic pathways allowing carbon covalent bonds to be reconfigured with the lower energy photons of regime c) by combining the energy of two or more photons (e.g., ATP and its role in visible photosynthesis). This began to occur some hundreds of millions of years after the origin of life in regime b).

Since for non-linear systems under soft UV-C photons, many stationary states with different pigment concentration profiles, and therefore dissipative efficacy, could exist, given fluctuations, the system would be free to roam over the stationary states, being most probably found at those molecular concentration profiles representing molecules with the largest conical intersections for rapid internal conversion to their ground states [23].

The photochemical and chemical reactions involved in the dissipative structuring of the nucleobase adenine from the precursors HCN and water have been given in detail in reference [23] and, similarly, for the dissipative structuring of guanine from HCN and NCCN in reference [24]. Evolution towards a concentration profile of more of these greater photon dissipating molecules of lower entropy (complexes of molecules) can only occur for systems over which a soft UV-C photon potential is impressed. There is no possibility of evolution towards molecular concentration profiles of lower entropy if only thermal reactions occur within an isolated system, i.e. with no contact with its external environment, since an isolated system is obligated by the second law to increase its entropy. The origin of life, therefore, was completely contingent upon the Archean soft UV-C photon potential from the external environment. Subsequent evolution of biology to even greater complexity and dissipation, similarly depended upon the external photon potential, but now with displacement of absorption towards the region of higher intensity, but less energetic, UV-A and visible wavelengths (see caption of figure 7), requiring new mechanisms of thermodynamic selection giving rise to more complex dissipative structuring, which is described in the following section.

5. Natural Thermodynamic Selection at Higher Levels

Biotic levels higher than the molecular level also display historical evolutionary trends towards seemingly greater complexity and greater photon dissipation. Examples include the, nucleic acid - amino acid association (codons and the stereochemical era [55]), endosymbiosis, nervous system with sensory perception and intelligence, symbiosis and mutualism among species, ecosystem succession, the general increase in species diversity over time [56], human societal and technological evolution, the coupling of life to abiotic processes such as the water, carbon, and nitrogen cycles, as well as life-induced changes to Earth's atmosphere and surface [57].

Traditional evolutionary theory tacitly assumes that this evolutionary dynamics observed at these higher levels is simply the emergent result of natural selection acting on reproductive success operating at the organismal level. Global trends enumerated in the Gaia hypothesis, such as surface temperature control (to the liquid water regime in spite of increasing solar output), atmospheric transparency to visible wavelengths, limitation of atmospheric oxygen and ocean pH levels and salt concentration, would have to be considered as mere peculiarities.

Furthermore, if selection was only acting at the level of the organism, other global phenomena would also need explanation. For example, why would pigments continually arise over time to cover ever more of the solar spectrum given that a large part of the spectrum is not used for photosynthesis (or for any other physiological process of utility to the organism) but is simply dissipated directly into heat [35]? Why would organisms expend resources to make and exude pigments into their environment without apparent benefit to the organism [35]? Why would the organism level be the "chosen" level for selection, rather than, for example, Dawkin's suggestion of selection at the gene level [6]? What could be the physical-chemical explanation for the "selfishness" of the genes in the Dawkin's perspective, or the physical-chemical explanation of the innate "will to survive and reproduce" of the individual in the neo-Darwinian perspective?

If, on the other hand, it is argued that evolution at the higher levels is not a strictly emergent phenomena, but that a type of Darwinian natural selection is also acting at higher levels, this would implore us to identify a plausible fitness function for selection at these higher levels. However, even if efforts were successful in delineating a viable fitness function leading to the differential success of these higher order entities, the competing population numbers dwindle going up the biological hierarchy, until, at the highest level of the biosphere, a paradox arises which can be paraphrased as "the evolution of a system of population one" [7]. There is little doubt that the biosphere has grown, become more complex, and diversified over the history of life on Earth, but Darwinian natural selection as the driver of evolution at this level, looses all interpretation because the biosphere is not in competition with another. The traditional evolutionary paradigm is also plagued with problems and paradoxes at these higher levels.

The non-equilibrium thermodynamic paradigm, instead, suggests that evolutionary process occurring in nature at all hierarchal levels , including molecular structuring, replication, complexation, endosymbiosis, societies, biotic-abiotic coupling, are all examples of dissipative structuring and are all contingent on increasing dissipation. The greater the rate of dissipation of the imposed solar photon potential, the greater the stability, or probability, of the processes (see section 4). Such irreversible processes "spontaneously" arise as dissipative structures in nature driven by the entropic forces of dissipation of an externally imposed generalized thermodynamic potential and lead to internal flows which, themselves, give rise to new internal forces. For example, the impressed photon potential gives rise to chemical potentials in plants, which then becomes relevant to herbivores, and the chemical potential of the herbivores relevant to carnivores. It will be shown in the following sections how each of these components of the biosphere couples in a catalytic way to increase global photon dissipation.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 17 May 2023 doi:10.20944/preprints202305.1176.v1

The dynamics of the evolution of the biosphere can also be described in non-equilibrium thermodynamic terms. For non-linear systems under an impressed thermodynamic force or potential, various stationary states with different rates of photon dissipation, with only local stability, are available to the system for the same initial and boundary conditions. Fluctuations near critical points cause the system to evolve over such states, generally towards those of greater dissipation, as explained in the example of the dissipative structuring of adenine given in Section 4. In the following section, this mechanics of natural thermodynamic selection is generalized to the higher biotic-abiotic levels.

5.1. Generalization of Natural Thermodynamic Selection

Dissipative structuring at thermodynamic stationary states in the form of molecular concentration profiles of UV-C pigments, and natural thermodynamic selection of these profiles occurred “spontaneously' at the origin of life', driven by the thermodynamic imperative of increasing the dissipation of the soft UV-C photons arriving at Earth's surface during the Archean. In this section the concept of natural thermodynamic selection is generalized to higher biotic levels, evolving continuously from the molecular level at the origin of life under the soft UV-C photons, to the level of the present biosphere under the visible photons of today.

Thermodynamic selection is contingent upon stationary state stability, and this, in turn, is contingent upon photon dissipation. Those internal or external fluctuations, macroscopic or microscopic, of any of the components of the biosphere which lead the biosphere to stationary states of greater global entropy production, will most likely be amplified (e.g. auto-catalytic or positive feedback processes), most often leading the biosphere to a new stationary state of greater entropy production. In terms of thermodynamic forces and flows, a fluctuation in the biosphere may cause new thermodynamic forces to arise at any hierarchal level, giving rise to new generalized flows and the elimination of others. In this way, particular molecular concentration profiles, complexes of molecules, individual organisms, communities, species, clades, ecosystems, biospheres, arise, wax and wane, or go extinct accordingly.

Since selection is contingent on the photon dissipation of the whole biosphere, at any particular hierarchal level, the biotic units do not compete with each other, or fight against their external environment, as imagined in the Darwinian perspective, but rather form part of a quasi-stable global stationary state which “competes”, on stochastic fluctuation, with other similar available stationary states of different photon dissipative efficacy in the neighborhood (of a generalized phase space, e.g. species population space at the level of the ecosystem). Those stationary states, under the specific environmental conditions (the solar photon potential arriving at Earth's upper atmosphere), which result in greater photon dissipation are generally more stable, with a larger attraction basin, and thus more likely to be occupied at any given period in Earth's history (Figure 8).

doi:10.20944/preprints202305.1176.v1

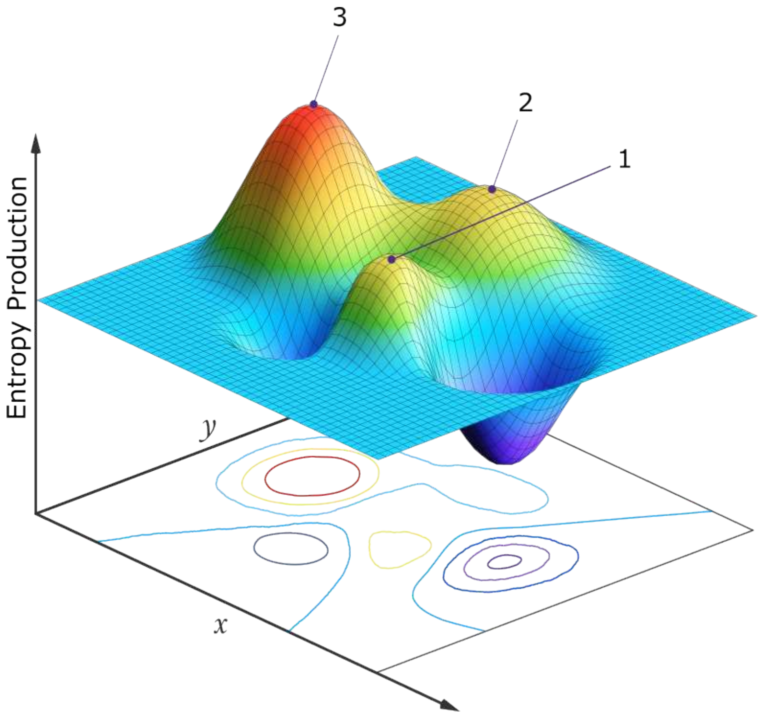

Figure 8. A simplified 2-dimensional schematic representation of the entropy production surface for a biosystem under a constant solar photon potential. The variables x and y at the origin of life may be, for example, the concentrations of different molecules, while for an ecosystem of today, the variables maybe the populations of different species. Three locally stable stationary states at a local maximum in entropy production are presented. On large enough external or internal perturbation, the system may evolve from the maximum of one stationary state to another. Although fluctuations are generally stochastic, the system will most often be found in those stationary states with a larger attraction basin and with a larger maximum in photon dissipation (the stationary state labeled "3"). For molecules, this corresponds to concentration profiles with greater quantum efficiency for dissipation to the ground state through a conical intersection. For an ecosystem, this corresponds to animal and plant population profiles giving greater total photon dissipation. If the system began in stationary state 1, its most probable future evolution would be 1→2→3, but any combination could be possible. For the biosphere, the x and y variables might be the number of species in two different clades and sub-peaks corresponding to different species populations would exist on the main peaks and evolution would usually be local among the sub-peaks but every once in a while a perturbation may be large enough (for example, an asteroid impact) to move the system from one main peak to another (e.g., 1 →3, mammals y becoming more prominent than dinosaurs x).

5.2. Selection of Fundamental Molecule Complexes

Since the origin of life, each new dissipating level of the biosphere was added incrementally to an existing one through, for example, a particular molecular complexation, endosymbiotic, symbiotic, parasitic, mutualistic, or abiotic coupling event, each event usually (but not always) adding to the systems overall photon dissipative efficacy. For example, at the molecular level, and at the origin of life, thermodynamic selection of the molecule was based on the rate of UV-C absorption and dissipation of the excited state energy to the ground state through a conical intersection (the quantum efficiency for internal conversion through a conical intersection q_i^{ic}), as presented in the previous section (Figure 6).

Going up the biological hierarchy, we postulate here that the addition of ribose (or deoxyribose) to the nucleobases to form the nucleosides was an example of dissipative complexation occurring "spontaneously" because this reduces the lifetimes for internal conversion to the ground state following UV-C excitation by about a factor of two for adenosine, cytidine and thymidine compared to the isolated bases [58]. The decrease in lifetime is mediated by an additional internal conversion pathway involving a proton transfer along a hydrogen bond from the sugar to base [58]. The attached sugar also changes the conical intersection most probable for internal conversion from the N9 stretch to the ring puckering [59] shown in figure 4 which puts the maximum of absorption of the complex closer to the peak in the Archean surface solar spectrum at $\sim$ 260 nm (Figure 2). Both these effects make the nucleoside more photon dissipative than the nucleobase and ribose as separate entities.

Phosphates and nucleosides in aqueous solution under UV-C light leads to UV-activated phosphorylated nucleotides [60]. Adding a phosphate group $H_2PO_4^-$ does not provide an additional route to internal conversion for adenine monophosphate (AMP), but it does provide additional absorption at 247 nm with a small oscillator strength of 0.0064 [59] allowing the phosphate group to act as an antenna chromophore, further increasing photon dissipation efficacy of the nucleotide complex in the soft UV-C region. Additionally, nucleotides are much more soluble in water (because they become more polar) than nucleosides, and considerably more so than the nucleobases, allowing them to spread throughout the volume and thereby absorb more photons (an effect similar to hyperchromism in which absorption increases by approximately 30% in going from stacked double- to unstacked single-strand DNA [33]).

Hydrogen bonding between the complimentary nucleotides (e.g., A-T, G-C) also further reduces the excited state lifetimes [58]. This again appears to be due to a proton transfer reaction between the complimentary bases, which can give rise to DNA or RNA denaturing (see below). A more photon dissipative complex would have been more likely to increase its concentration under the Archean surface UV-C light, as we have seen for the concentration profiles of the molecules on route to the synthesis of adenine (Figure 6) and as we will see for double strand RNA or DNA (Figure 9).

The formation of phosphodiester bonds between the nucleotides (also UV-C induced) helps to improve the stability of the nucleobases (UV-C pigment) by providing enhanced stability against hydrolysis [61]), but more importantly, it provides a scaffold for the attachment of UV-C antenna molecules (e.g., codon - amino acid affinity, see Figure 9), allowing for still greater dissipation [34].

At the macro-molecular level of the nucleic acid (e.g., DNA and RNA), we have suggested, and experimentally measured [21,33], an Ultraviolet and Temperature Assisted Reproduction (UVTAR) process in which the enzymeless replication of DNA or RNA could occur through UV-C induced denaturing of double strand segments in the daylight hours and magnesium ion catalyzed extension during the night. Because of a small component ($\sim$ 5%) of circularly polarized light at the ocean surface (of opposite handedness in the morning and afternoon), UV-C induced denaturing could have given rise to, not only increased dissipation ($\sim$ 30% hyperchromic effect) but also the homochirality of the nucleic acids due to an increase in UV-C-induced denaturing with surface temperature [31]. We have shown experimentally that UV-C light indeed denatures DNA [33] and it has also been demonstrated by Jin et al. [62] that extension can be catalyzed with Mg^{+2} or Fe^{+2} ions at cooler overnight sea surface temperatures. Just as at the fundamental molecular level (e.g., the nucleobases), at the macro-molecular nucleic acid level, therefore, selection is also based on efficacy of photon dissipation, in this latter case through a dissipation-denaturing relation [33] operating through the UVTAR mechanism (see Figure 9).

For complexes of non-covalently bound fundamental molecules, thermodynamic selection would also be based on the same UVTAR dissipation-replication mechanism. For example, because of the chemical affinity of codons of nucleic acid to the amino acid tryptophan [55] (which abosrbs strongly in the UV-C - an antenna molecule) it can pass its excitation energy through resonant energy transfer to the nucleic acid for dissipation through the conical intersection of one of its bases, thereby increasing overall photon dissipation. Similarly, nucleic acid affinity to the amphipathic amino acids would make the nucleic acid - amino acid complex less susceptible to sedimentation and therefore more exposed to the surface UV-C light. Since greater dissipating nucleic acid complexes are more likely to denature and therefore replicate [33], the UVTAR process would thus lead to information concerning the affinity to antenna or amphiphilic molecules (i.e. codon-amino acid association) becoming programmed into the nucleic acid oligos [34] (Figure 9), leading to a stereochemical era, for which there appears to be ample evidence [55]. This could be considered an early example of thermodynamic molecular "group selection" (codon plus amino acids), again based on incrementing the efficacy of photon dissipation.

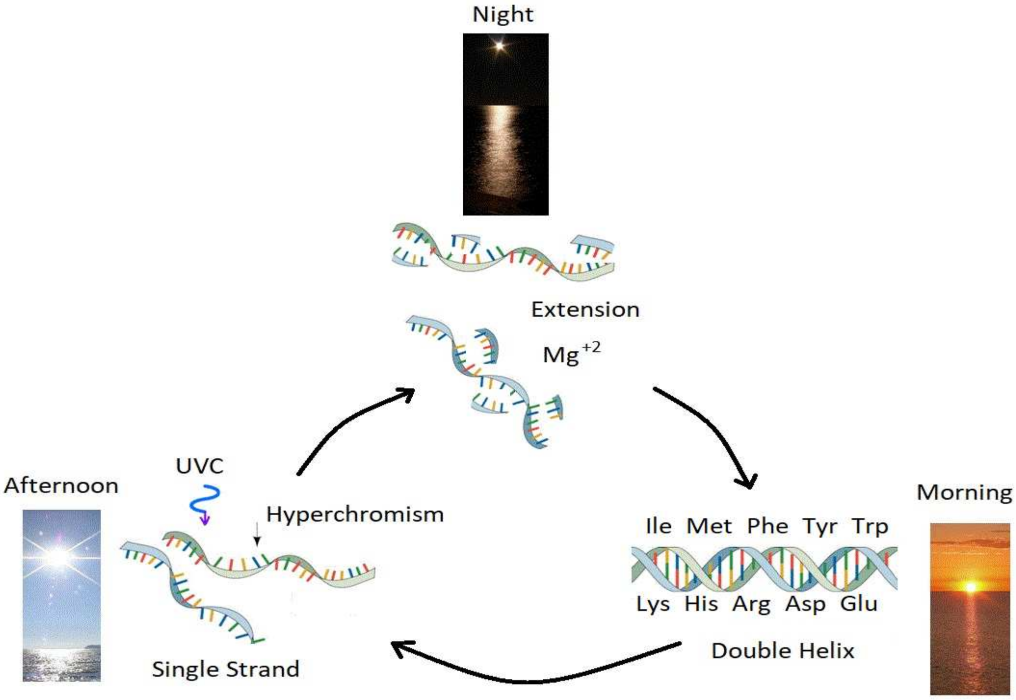

Figure 9. Ultraviolet and Temperature Assisted Reproduction (UVTAR) of RNA and DNA. A mechanism proposed for the enzyme-less replication of RNA and DNA assisted by the absorption and dissipation of the prevailing UV-C light flux and the high temperatures of the ocean surface during the late Hadean or early Archean, including a day/night diurnal warming and cooling cycle of the water surface due mostly to the absorption of solar infrared light. Most denaturing would occur in the late afternoon when ocean surface temperatures were highest (UV-C induced denaturing is temperature dependent [33]). Extension occurs overnight with the aid of Mg^{+2} ions, UV-C activated nucleotides, and colder surface temperatures [62]. "Hyperchromism" refers to an increase ($\sim$ 30%) in the absorption (and dissipation) of photons at UV-C wavelengths ($\sim$ 260 nm) once RNA or DNA are denatured into single strands. Oligos which had chemical affinity to the 10 amino acids listed in the figure (all of which have photon absorption and dissipation fomenting characteristics [34]), would have had a greater chance of denaturing during afternoon hours when the surface temperature was warmest, and could therefore be replicated overnight. This particular selection is only one of a number of mechanisms based on greater photon dissipation, that we have termed "natural thermodynamic selection" [20,21,23,30]. The important aspect of this auto-catalytic (template directed) mechanism is that replication is tied to photon dissipation, providing a thermodynamic imperative for reproduction and proliferation over all of Earth's surface. Taken with permission from [34].

We can also take this complexation another step further to the association, also stereochemical, of the dissipative nucleic acid - amino acid complex with dissipatively structured fatty acid vesicles [32]. Besides diurnal variations of the sea surface environment due to Earth's rotation, there would also be seasonal variations due to axial tilt of Earth and its elliptical orbit around the sun. The ocean surface was also cooling throughout the Archean epoch. Thus, depending upon the latitude, or the epoch, some regions of the ocean surface may have become too cold in winter to allow the UVTAR mechanism to be effective. In these regions, DNA or RNA oligos with affinity to fatty acid vesicles may have become favored since the vesicles provided an insulating enclosure where UV-C light could enter and be absorbed on the fundamental molecules, but the heat of dissipation would have remained trapped for some time (due to the low heat conductivity of the fatty acid hydrocarbon tails), raising the temperature within the vesicle enclosure sufficient to allow the UVTAR process to occur in the afternoon on colder seas.

Fatty acid vesicles therefore provided, i) an enclosure for concentration of the components, through differential permeability, facilitating further chemical and photochemical interactions [23], ii) continued UVTAR replication in colder seas through the trapping of the heat of photon dissipation within the vesicle (Figure 9), and iii) the shielding from hard (short wavelength) UV-C photons that could ionize or disassociate the molecular complexes [63]. The stereochemical information for this nucleic + amino + fatty acid association would thus also gradually become programmed into the DNA through the UVTAR mechanism in the same way as it was for the nucleic acid - amino acid association [34].

The protocell vesicle walls would have to be permeable to the small precursor molecules, but impermeable to large dissipatively structured fundamental molecules like nucleotides and RNA or DNA segments. The lipid membranes would also need to have the characteristic of growth and binary fission triggered finally on RNA or DNA replication. The facilitation of replication, and therefore greater dissipation (through the UVTAR mechanism) may have been the main thermodynamic reason for the origin of the lipid enclosure, leading to the first protocell [23,32].

5.3. Symbiotic, Parasitic and Mutualistic Association

Natural thermodynamic selection of evolutionary events leading to ever greater molecular complexity were thus contingent on greater photon dissipative efficacy. The symbiosis of different cellular organelles and the parasitic, symbiotic or mutualistic interaction among species from all three domains of life, and the coupling of biotic with abiotic dissipative processes, can all be associated with increasing the spread of the photon dissipative organic pigments over the whole of Earth's surface [35,57,64]. An example of this at the ecosystem level is the re-introduction of wolves into their historical homelands in Yellowstone National Park after uncontrolled hunting led to their extinction. On re-introduction, these top predators kept the deer and elk populations always on the move, thereby preventing them from overgrazing and helping to spread their excrement and dead carcases as plant nutrients over a wider area. This led to a general greening of the park [65], which, of course, means greater photon dissipation. This is an example of how natural thermodynamic selection operates at the ecosystem level, bringing it to climax states (stationary thermodynamic states) of ever greater photon dissipation (Figure 8). Similarly, fish and whales in the oceans bring nutrients from the depths and deposit them as excrement and dead carcases at the ocean surface, even far from shore where there are little nutrients, for fomenting the photon dissipating algae and cyanobacteria.

5.4. The Biosphere and Human Culture

This coupling of irreversible processes is repeated at each biological level, incorporating, as well, abiotic dissipative processes, creating the greatest dissipative process of all on Earth, the biosphere of today. For example, the water cycle is coupled through the heat of dissipation of photons in organic pigments in the leaves of plants or within cyanobacteria on the surfaces of the oceans, lakes, and wet soils. The coupling of the water cycle to photon dissipation is also autocatalytic (i.e., leading to still greater photon dissipation) since more water in the water cycle implies a greater greening of Earth [57,66]. The water cycle dissipates the infrared light of the heat of photon dissipation in the leaves even further towards the infrared, finally emitted into space by the cloud tops at an approximate black-body temperature of -14 °C (corresponding to emission peak at $\sim 11\ \mu$m).

An example of thermodynamic selection involving the human species, operational at the societal level, is the human-induced increase in atmospheric CO_2 since the industrial revolution, which, surprisingly, has also led to an important greening of Earth (e.g., increased growth rates of algae, cyanobacteria, and vegetation, and high albedo glaciers replaced by low albedo forests) [67]. Although one might expect that too much atmospheric CO_2 may lead to ecosystem collapse through, for example, a run away greenhouse effect, natural thermodynamic selection will eventually assert itself in no uncertain terms, as indeed seems to be happening, for example by limiting the activity of humans through drought associated with global warming, and thus, in the long run, Earth can be expected to arrive at a stationary state with an atmospheric concentration of CO_2 concordant with greater photon dissipation. This sounds much like the Gaia hypothesis [9], but the fitness function being optimized is not the suitability of Earth for all life, but rather photon dissipation over the entire planet.

Finally, since today's biosphere has both biotic and abiotic components coupled on many different levels and over different time scales, it is relevant to make a few remarks concerning the coupling of biotic and abiotic irreversible process. Both biotic organisms and abiotic processes have the ability to adapt to a changing impressed thermodynamic potential, implying that thermodynamic selection is a finite time process. Biotic organisms today adapt through their organismal plasticity (e.g., the ability to migrate, the ability to survive off different thermodynamic potentials - heterotrophy, or through their genetic apparatus and reproduction - plasticity at the species level). In contrast, abiotic processes have an inherent plasticity, for example, a change in size or direction of a hurricane in response to a change in the size or direction of the ocean surface temperature, fomented by cyanobacterial life [68].

Neo-Darwinian evolutionary theory suggests that life strives to survive against an imposing external environment, while Gaia theory speaks of "life shaping the environment for its own suitability". In our non-equilibrium thermodynamic perspective, processes are not "striving to survive", rather, they are instead thermodynamic flows that rise and fall in response to changes in internal thermodynamic forces as fluctuations take the global system to different stationary states, in the general direction of greater stability, which under the impressed photon flux, corresponds to increasing photon dissipation.

The thermodynamic dissipation theory speaks of life coupling at many different levels to other irreversible thermodynamic processes (both biotic and abiotic) which are together evolving to ever greater levels of biosphere photon dissipation (entropy production) under the prevailing solar photon potential. It is this impressed photon potential, together with non-equilibrium thermodynamic principles (in particular the second law and the conservation laws), that are the creators, transformers, and selectors of those irreversible dissipating processes at all levels that we associate with life.

The biosphere or ecosystem can thus be described by a matrix of coefficients representing the interaction between between different biotic and abiotic dissipative processes, associated, for the most part, with photon dissipation. These interaction coefficients evolve not to optimize the survival of the individual irreversible process (the gene, individual, species, ecosystem, or the biosphere) but instead to optimize the photon dissipation of the entire biosphere [69]. Natural thermodynamic selection still acts at the molecular level today by selecting pigments in the leaves of the plants and cyanobacteria that are most efficient at absorbing and dissipating the photon flux into heat, and new pigments will arise in the future, pushing dissipation even further towards the infrared.

The information required for building the entire biosphere, including its abiotic components (such as the water cycle, the transparency of the atmosphere, oxygen levels, sea levels, ocean currents, winds, surface temperature, etc.), becomes, in this way, encoded into the collective genomes of all biotic organisms. Complex biotic dissipative structures, such as animals, trees, or societies, having evolved through this process of genome information accumulation related to photon dissipation, can store information about the generalized chemical potentials existing in their present and past environments. This information endows them with a plasticity to "adapt" to different chemical potentials by building on existing structures (e.g., the Archean UV-C dissipative nucleobase pigments used today as a code letter to store information in the nucleic acid), or to rapidly return to dissipation of potentials that have come back to the environment after a certain absence, thus allowing them to evolve into ever more numerous, efficient, and adaptive dissipative structures.

6. Resolution of Problems and Paradoxes Inherent in Traditional Evolutionary Theory

The non-equilibrium thermodynamic paradigm provides resolution of some existential problems and paradoxes inherent in traditional evolutionary theory. First and foremost, the thermodynamic

doi:10.20944/preprints202305.1176.v1

paradigm provides a foundation for evolutionary theory based on well established physical law. The conservation laws and the second law of thermodynamics incorporated into classical irreversible thermodynamic theory in the non-linear regime is sufficient to describe the general dynamics of a material system interacting with its environment. Such a system evolves over a multi-dimensional generalized phase-space through perturbation near critical points, leading generally, particularly for positive feedback (autocatalytic) systems, to greater dissipation of the impressed environmental potential (e.g., the solar photon flux at the level of the biosphere).

Unlike traditional evolutionary theory, in which the origin of life remains an enigma, the dissipation paradigm provides a unified framework from within which both the origin of life and its subsequent evolution can be explained. First, the initial dissipative structuring of UV-C pigments to dissipate this region of the solar spectrum prevalent at Earth's surface throughout the Archean, and then greater molecular complexation to increase photon dissipation, and finally, after the invention of oxygenic photosynthesis responsible for exuding the UV-C pigments oxygen and ozone into the atmosphere, thereby shielding the surface from UV-C, the dissipative structuring of the visible pigments through more delicate, but complex, biosynthetic pathways to dissipate the visible wavelengths.

There is no "survival of the survivors" tautology in thermodynamic theory since there is an explicit fitness function that is being optimized over time, which is greater biosphere photon dissipation, because such stationary states are generally more stable to fluctuation.

There is no single level on which natural thermodynamic selection operates. It acts simultaneously on all levels, selecting, generally, but not always (through statistical fluctuation), stationary states of the biosphere of generally greater photon dissipation. At the highest level of the biosphere, the paradox of "the evolution of a system of one" is resolved since greater biosphere photon dissipation is a valid fitness function for selection and evolution at this level.

The paradox of the first tier is resolved since thermodynamic selection does not depende on competition between species leading towards a "better fit" species, but rather increases in photon dissipation and this is often obtained by building on previous dissipative structures and re-purposing, as we have seen for the fundamental molecules of life which began as UV-C pigments bu are now information carrying molecules. The archea and bacteria of the first tier are found today as the organelles and symbionts in higher level organisms like the eucaryots. They were not "out-competed" but instead incorporated into a new level of dissipation.

Punctuated equilibrium, a hallmark of biological evolution [5], without explanation in the traditional paradigm can be understood as the statistical evolution through different stationary states of the non-linear non-equilibrium system, promoted by fluctuations close to critical points. Selection, related to dissipative stability, is thermodynamic and involves both the system and its environment through the coupling of biotic with abiotic irreversible processes.

At the level of the organism, our thermodynamic theory appears somewhat analogous to Darwinian theory since the greater the number of dissipative organisms, usually (but not always) the greater the global photon dissipation. Reproductive success at this level is then usually correlated with photon dissipation. However, different species are coupled in non-linear ways to other species and to the abiotic irreversible processes (like the water cycle). Selection is thus not truly based on reproductive success of the individual, but on the global photon dissipation rate of the whole system, which are the greater peaks with wider attraction basins available to the system in the generalized phase space, as given schematically in Figure 8. At the level of the biosphere, our thermodynamic theory appears somewhat analogous to Gaia theory in that there is a coupling of biotic processes with abiotic processes, but selection of the abiotic characteristics is not based on "suitability for all life", but rather, again, on the global photon dissipation.

7. Conclusions

Traditional evolutionary theory can only be regarded as a heuristic narrative, useful for making some sense of the biological and paleontological data concerning evolution at the level of the organism.

The theory, however, lacks a chemical-physical foundation which leaves it with many problems and paradoxes. Even its most conscientious proponents consider the theory as, at the very least, "incomplete". Here I have presented a non-equilibrium thermodynamic framework for understanding material interaction with its environment based on Classical Irreversible Thermodynamic theory founded on the conservation laws and the second law of thermodynamics. In this paradigm, material under an impressed thermodynamic potential, organizes "spontaneously" in such a manner so as to dissipate more efficiently the imposed potential. The mechanisms of organization and selection leading to evolution are different at different biotic-abiotic levels, but all are based on increasing dissipation, and the process is thus known as "dissipative structuring".

The Archean soft UV-C photon potential is identified as the thermodynamic potential or impressed force giving rise to the resulting flow (photochemical reactions) corresponding to the dissipative structuring of the fundamental molecules (UV-C pigments) at the origin of life. The propensity of UV-C light to form conjugations in carbon based molecules, which promotes photon absorption and dissipation, is probably the most important reason why life is based on carbon, and not other similar outer electron shell elements like silicon. A specific example was given of the dissipative structuring of adenine. Each additional molecular complexation which occurred (e.g., nucleic acid - amino acid association) was selected since this led to greater photon dissipation and thus greater probability (stability) under the photon flux.

Many stationary states, consisting of different molecular concentration profiles, are available to such a non-linear system, and the number of these states grows as the size of the system grows with each new layer increasing the photon dissipation of the growing biosphere. Stationary states with greater photon dissipation are generally more stable since these are those most efficient at dissipating the free energy in the impressed photon potential available for change. Evolution to greater photon dissipative states is stochastic, dependent on fluctuations near a non-equilibrium thermodynamic critical point, but guided by thermodynamic law (the conservation laws and the second law of thermodynamics).

In today's biosphere, thermodynamic selection is still based on photon dissipation, as it was at the origin of life. Today, however, with no UV-C light arriving at Earth's surface, the possibility of direct, single photon, permutation of carbon covalent bonds to produce new dissipatively structured pigments no longer exists, and that is why life *de novo* has not appeared since the Archean. The biosynthetic pathways of today have evolved to be necessarily more complex in order to make use of the lower free energy, but higher intensity, available in visible photons. The pigments oxygen and ozone were necessary before this stage of life could begin since these blocked the UV-C light from the more delicate biosynthetic pathways now incorporating not only covalent bonding, but weaker Van der Waals and ionic bonding. Thermodynamic selection today, therefore, is still based principally on photon dissipation, with a much smaller part attributable to animal dissipation of chemical potentials. Animals, however, play a much greater thermodynamic role in spreading nutrients over the whole surface of Earth, thus fomenting the growth and propagation of the photon dissipating plants and cyanobacteria. Humans have recently, and unwittingly, played an important role by greening the planet through the dissipative structuring of a number of societal and cultural processes leading to a greater concentration of CO_2 in the atmosphere, and it appears not to be long before we begin to do the same on other planets of our solar system.

Funding: This research was funded by DGAPA-UNAM grant number IN104920.

Conflicts of Interest: The author declares no conflict of interest.

The following abbreviations are used in this manuscript:

AIAC	**2-amino-3-iminoacrylimidoyl cyanide**
AICN	**4-aminoimidazole-5-carbonitrile**
ATP	**adenine triphosphate**
CIT	**Classical Irreversible Thermodynamics**
DAMN	**diaminomaleonitrile**
DAFN	**diaminofumaronitrile**
HCN	**hydrogen cyanide**
NCCN	**cyanogen**
UV-A	**light in the region 360-400 nm**
UV-B	**light in the region 285-360 nm (only the region 310-360 nm is relevant here)**
UV-C	**light in the region 100-285 nm (only the region 210-285 nm is relevant here)**
UVTAR	**Ultraviolet and Temperature Assisted Replication**

References

1. Popper, K. *The Poverty of Historicism*; Routledge, 1957.
2. Popper, K.R. *The logic of scientific discovery*; Basic Books New York, 1959; p. 479 pages.
3. Popper, K.R. The Myth of the Framework. In *Rational Changes in Science. Essays on Scientific Reasoning: Boston Studies in the Philosophy of Science, vol. 98*; Pitt, J.C.; Pera, M., Eds.; 1987; pp. 35–62.
4. Elgin, M.; Elliot, S. POPPER'S SHIFTING APPRAISAL OF EVOLUTIONARY THEORY. *Journal of the International Society for the History of Philosophy of Science* **2017**, *7*, [2152-5188/2017/0701-0001].
5. Gould, S.J. *The structure of evolutionary theory / Stephen Jay Gould*; Belknap Press of Harvard University Press Cambridge, Mass, 2002; pp. xxii, 1433 p. :.
6. Dawkins, R. *The Selfish Gene*; Oxford University Press, Oxford, UK, 1976.
7. Swenson, R., The Cybernetics of Complex Systems: Self-organization, Evolution, and Social Change; Intersystems Publications, 1991; chapter End-directed physics and evolutionary ordering: Obviating the problem of the population of one, pp. 41–60.
8. Lande, R. Microevolution in Relation to Macroevolution - Macroevolution: Pattern and Process. Steven M. Stanley W. H. Freeman and Co.; San Francisco. 1979. xi 332 pp. *Paleobiology* **1980**, *6*, 233–238. doi:10.1017/S0094837300006771.
9. Lovelock, J.E. *The Ages of Gaia; A Biography of Our Living Earth*; W. W. Norton&Company, 1988.
10. Skipper, R.A.; Millstein, R.L. Thinking about evolutionary mechanisms: natural selection. *Studies in History and Philosophy of Science Part C: Studies in History and Philosophy of Biological and Biomedical Sciences* **2005**, *36*, 327–347. Mechanisms in biology, doi:https://doi.org/10.1016/j.shpsc.2005.03.006.
11. Onsager, L.; Machlup, S. Fluctuations and Irreversible Processes. *Phys. Rev.* **1953**, *91*, 1505–1512.
12. Prigogine, I. *Introduction to Thermodynamics Of Irreversible Processes*, third ed.; John Wiley & Sons, 1967.
13. Glansdorff, P.; Prigogine, I. *Thermodynamic Theory of Structure, Stability and Fluctuations*; Wiley - Interscience., 1971.
14. Prigogine, I.; Nicolis, G. On Symmetry-Breaking Instabilities in Dissipative Systems. *J. Chem. Phys.* **1967**, *46*, 3542.
15. Prigogine, I.; Nicolis, G. Biological order, structure and instabilities. *Quarterly Reviews of Biophysics* **1971**, *4*, 107–144.
16. Prigogine, I. *The End of Certainty: Time, Chaos, and the New Laws of Nature*; Free Press, 1997.
17. Gemmer, J.; Otte, A.; Mahler, G. Quantum Approach to a Derivation of the Second Law of Thermodynamics. *Phys. Rev. Lett.* **2001**, *86*, 1927–1930. doi:10.1103/PhysRevLett.86.1927.
18. Zurek, W.H.; Paz, J.P. Decoherence, chaos, and the second law. *Phys. Rev. Lett.* **1994**, *72*, 2508–2511. doi:10.1103/PhysRevLett.72.2508.
19. Tangde, V.M.; Bhalekar, A.A. How Flexible Is the Concept of Local Thermodynamic Equilibrium? *Entropy* **2023**, *25*. doi:10.3390/e25010145.
20. Michaelian, K. Thermodynamic origin of life. *ArXiv* **2009**, [arXiv:physics.gen-ph/0907.0042].
21. Michaelian, K. Thermodynamic dissipation theory for the origin of life. *Earth Syst. Dynam.* **2011**, *224*, 37–51, [https://esd.copernicus.org/articles/2/37/2011/esd-2-37-2011.html]. doi:10.5194/esd-2-37-2011.

22. Michaelian, K. Microscopic Dissipative Structuring and Proliferation at the Origin of Life. *Heliyon* **2017**, *3*, e00424, [https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5647473/]. doi:10.1016/j.heliyon.2017.e00424.
23. Michaelian, K. The Dissipative Photochemical Origin of Life: UVC Abiogenesis of Adenine. *Entropy* **2021**, *23*, [https://www.mdpi.com/1099-4300/23/2/217]. doi:10.3390/e23020217.
24. Hernández, C.; Michaelian, K. Dissipative Photochemical Abiogenesis of the Purines. *Entropy* **2022**, *24*, 1027. doi:10.3390/e24081027.
25. Meixnerová, J.; Blum, J.D.; Johnson, M.W.; Stüeken, E.E.; Kipp, M.A.; Anbar, A.D.; Buick, R. Mercury abundance and isotopic composition indicate subaerial volcanism prior to the end-Archean “whiff” of oxygen. *Proceedings of the National Academy of Sciences* **2021**, *118*, e2107511118, [https://www.pnas.org/doi/pdf/10.1073/pnas.2107511118]. doi:10.1073/pnas.2107511118.
26. Sagan, C. Ultraviolet Selection Pressure on the Earliest Organisms. *J. Theor. Biol.* **1973**, *39*, 195–200.
27. French, K.L.; Hallmann, C.; Hope, J.M.; Schoon, P.L.; Zumberge, J.A.; Hoshino, Y.; Peters, C.A.; George, S.C.; Love, G.D.; Brocks, J.J.; Buick, R.; Summons, R.E. Reappraisal of hydrocarbon biomarkers in Archean rocks. *Proceedings of the National Academy of Sciences* **2015**, *112*, 5915–5920, [http://www.pnas.org/content/112/19/5915.full.pdf]. doi:10.1073/pnas.1419563112.
28. Zuo, Z. Emission of cyanobacterial volatile organic compounds and their roles in blooms. *Frontiers in Microbiology* **2023**, *14*. doi:10.3389/fmicb.2023.1097712.
29. Wedow, J.M.; Ainsworth, E.A.; Li, S. Plant biochemistry influences tropospheric ozone formation, destruction, deposition, and response. *Trends in Biochemical Sciences* **2021**, *46*, 992–1002. doi:https://doi.org/10.1016/j.tibs.2021.06.007.
30. Michaelian, K. *Thermodynamic Dissipation Theory of the Origina and Evolution of Life: Salient characteristics of RNA and DNA and other fundamental molecules suggest an origin of life driven by UV-C light*; Self-published. Printed by CreateSpace. Mexico City. ISBN:9781541317482., 2016.
31. Michaelian, K. Homochirality through Photon-Induced Denaturing of RNA/DNA at the Origin of Life. *Life* **2018**, *8*, [http://www.mdpi.com/2075-1729/8/2/21]. doi:10.3390/life8020021.
32. Michaelian, K.; Rodriguez, O. Prebiotic fatty acid vesicles through photochemical dissipative structuring. *Revista Cubana de Química* **2019**, *31*, 354–370.
33. Michaelian, K.; Santillan, N. UVC photon-induced denaturing of DNA: A possible dissipative route to Archean enzyme-less replication. *Heliyon* **2019**, *5*, e01902, [https://www.heliyon.com/article/e01902].
34. Mejía Morales, J.; Michaelian, K. Photon Dissipation as the Origin of Information Encoding in RNA and DNA. *Entropy* **2020**, *22*, [https://www.mdpi.com/1099-4300/22/9/940]. doi:10.3390/e22090940.
35. Michaelian, K.; Simeonov, A. Fundamental molecules of life are pigments which arose and co-evolved as a response to the thermodynamic imperative of dissipating the prevailing solar spectrum. *Biogeosciences* **2015**, *12*, 4913–4937, [https://bg.copernicus.org/articles/12/4913/2015/].
36. Simeonov, A.; Michaelian, K. Properties of cyanobacterial UV-absorbing pigments suggest their evolution was driven by optimizing photon dissipation rather than photoprotection. *ArXiv* **2017**, [arXiv:physics.bio-ph/1702.03588].
37. Petkowski, J.J.; Bains, W.; Seager, S. On the Potential of Silicon as a Building Block for Life. *Life* **2020**, *10*. doi:10.3390/life10060084.
38. Schuurman, M.S.; Stolow, A. Dynamics at Conical Intersections. *Annu. Rev. Phys. Chem.* **2018**, *69*, 427–450.
39. Ferris, J.P.; Orgel, L.E. An Unusual Photochemical Rearrangement in the Synthesis of Adenine from Hydrogen Cyanide. *J. Am. Chem. Soc.* **1966**, *88*, 1074–1074.
40. Sagan, C.; Khare, B.N. Long-Wavelength Ultraviolet Photoproduction of Amino Acids on the Primitive Earth. *Science* **1971**, *173*, 417–420, [https://science.sciencemag.org/content/173/3995/417.full.pdf]. doi:10.1126/science.173.3995.417.
41. Ruiz-Bermejo, M.; Zorzano, M.P.; Osuna-Esteban, S. Simple Organics and Biomonomers Identified in HCN Polymers: An Overview. *Life* **2013**, *3*, 421–448. doi:10.3390/life3030421.
42. Cohen, B.; Hare, P.M.; Kohler, B. Ultrafast Excited-State Dynamics of Adenine and Monomethylated Adenines in Solution: Implications for the Nonradiative Decay Mechanism. *Journal of the American Chemical Society* **2003**, *125*, 13594–13601, [https://doi.org/10.1021/ja035628z]. PMID: 14583057, doi:10.1021/ja035628z.
43. Orr-Ewing, A. Reaction Dynamics –Relaxation Pathways. *Lecture Notes* **2014**, pp. 1–36.

44. Roberts, G.M.; Marroux, H.J.B.; Grubb, M.P.; Ashfold, M.N.R.; Orr-Ewing, A.J. On the Participation of Photoinduced N–H Bond Fission in Aqueous Adenine at 266 and 220 nm: A Combined Ultrafast Transient Electronic and Vibrational Absorption Spectroscopy Study. *The Journal of Physical Chemistry A* **2014**, *118*, 11211–11225, [https://doi.org/10.1021/jp508501w]. PMID: 25296392, doi:10.1021/jp508501w.
45. Kleinermanns, K.; Nachtigallová, D.; de Vries, M.S. Excited state dynamics of DNA bases. *International Reviews in Physical Chemistry* **2013**, *32*, 308–342, [https://doi.org/10.1080/0144235X.2012.760884]. doi:10.1080/0144235X.2012.760884.
46. Barbatti, M.; Aquino, A.; Szymczak, J.; Nachtigallová, D.; Hobza, P.; Lischka, H. Relaxation mechanisms of UV-photoexcited DNA and RNA nucleobases. *Proc Natl Acad Sci U S A* **2010**, *107*, 21453–21458. doi:doi:10.1073/pnas.1014982107.
47. Polli, D.; Altoè, P.; Weingart, O.; Spillane, K.M.; Manzoni, C.; Brida, D.; Tomasello, G.; Orlandi, G.; Kukura, P.; Mathies, R.A.; Garavelli, M.; Cerullo, G. Conical intersection dynamics of the primary photoisomerization event in vision. *Nature* **2010**, *467*, 440–443. doi:10.1038/nature09346.
48. Serrano-Perez, J.J.; de Vleeschouwer, F.; de Proft, F.; Mendive-Tapia, D.; Bearpark, M.J.; Robb, M.A. How the Conical Intersection Seam Controls Chemical Selectivity in the Photocycloaddition of Ethylene and Benzene. *J. Org. Chem.* **2013**, *78*, 1874–1886.
49. Boulanger, E.; Anoop, A.; Nachtigallova, D.; Thiel, W.; Barbatti, M. Photochemical Steps in the Prebiotic Synthesis of Purine Precursors from HCN. *Angew. Chem. Int.* **2013**, *52*, 8000–8003.
50. Mulkidjanian, A.Y.; Cherepanov, D.A.; Galperin, M.Y. Survival of the fittest before the beginning of life: selection of the first oligonucleotide-like polymers by UV light. *BMC Evolutionary Biology* **2003**, *3*, 12. doi:10.1186/1471-2148-3-12.
51. Goto, N.; Bazar, G.; Kovacs, Z.; Kunisada, M.; Morita, H.; Kizaki, S.; Sugiyama, H.; Tsenkova, R.; Nishigori, C. Detection of UV-induced cyclobutane pyrimidine dimers by near-infrared spectroscopy and aquaphotomics. *Sci Rep* **2015**, *5*, 11808.
52. Hänggi, E.; Wehner, S. A violation of the uncertainty principle implies a violation of the second law of thermodynamics. *Nat Commun* **2013**, *4*, 1670–577.
53. Knight, H.T.; Rink, J.P. Dissociation Energy of Cyanogen and Related Quantities by X-Ray Densitometry of Shock Waves. *The Journal of Chemical Physics* **2004**, *35*, 199–208, [https://pubs.aip.org/aip/jcp/article-pdf/35/1/199/8125578/199_1_online.pdf]. doi:10.1063/1.1731891.
54. Michaelian, K.; Cano, R.E. A Photon Force and Flow for Dissipative Structuring: Application to Pigments, Plants and Ecosystems. *Entropy* **2022**, *24*, 76. doi:10.3390/e24010076.
55. Yarus, M.; Widmann, J.; Knight, R. RNA-Amino Acid Binding: A Stereochemical Era for the Genetic Code. *J Mol Evol* **2009**, *69*, 406–429. doi:10.1007/s00239-009-9270-1.
56. Rohde, R.; Muller, R. Cycles in fossil diversity. *Nature* **2005**, *434*, 208–210.
57. Michaelian, K. Biological catalysis of the hydrological cycle: lifeś thermodynamic function. *Hydrol. Earth Syst. Sci.* **2012**, *16*, 2629–2645, [www.hydrol-earth-syst-sci.net/16/2629/2012/]. doi:10.5194/hess-16-2629-2012.
58. Camillis, S.D.; Miles, J.; Alexander, G.; Ghafur, O.; Williams, I.D.; Townsend, D.; Greenwood, J.B. Ultrafast non-radiative decay of gas-phase nucleosides. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23643–23650. doi:10.1039/C5CP03806E.
59. Brøndsted Nielsen, S.; Sølling, T.I. Are Conical Intersections Responsible for the Ultrafast Processes of Adenine, Protonated Adenine, and the Corresponding Nucleosides? *ChemPhysChem* **2005**, *6*, 1276–1281, [https://chemistry-europe.onlinelibrary.wiley.com/doi/pdf/10.1002/cphc.200400644]. doi:https://doi.org/10.1002/cphc.200400644.
60. Simakov, M.; Kuzicheva, E. Abiogenic photochemical synthesis on surface of meteorites and other small space bodies. *Adv. Space Res.* **2005**, *36*, 190–194.
61. Saladino, R.; Crestini, C.; Ciciriello, F.; Di Mauro, E.; Costanzo, G. Origin of informational polymers: Differential stability of phosphoester bonds in ribomonomers and ribooligomers. *J. Biol. Chem.* **2006**, *281*, 5790–5796.
62. Jin, L.; Engelhart, A.E.; Zhang, W.; Adamala, K.; Szostak, J.W. Catalysis of Template-Directed Nonenzymatic RNA Copying by Iron(II). *Journal of the American Chemical Society* **2018**, *140*, 15016–15021, [https://doi.org/10.1021/jacs.8b09617]. PMID: 30335371, doi:10.1021/jacs.8b09617.
63. Lechuga, I.; Michaelian, K. Fatty Acid Vesicles as Hard UV-C Shields for Early Life. *Preprints* **2023**, p. 2023010011. doi:10.20944/preprints202301.0011.v1.

64. Michaelian, K. The Biosphere; INTECH: London, 2012; chapter The biosphere: A thermodynamic imperative, pp. 51–60.
65. Ripple, W.J.; Beschta, R.L. Trophic cascades in Yellowstone: The first 15years after wolf reintroduction. *Biological Conservation* **2012**, *145*, 205–213. doi:https://doi.org/10.1016/j.biocon.2011.11.005.
66. Kleidon, A.; Fraedrich, K.; Heimann, M.A. Green Planet Versus a Desert World: Estimating the Maximum Effect of Vegetation on the Land Surface Climate. *Climatic Change* **2000**, *44*, 471–493.
67. Zhu, Z.; Piao, S.; Myneni, R.; et al.. Greening of the Earth and its drivers. *Nature Clim Change* **2016**, p. 791–795.
68. Gnanadesikan, A.; Emanuel, K.; Vecchi, G.A.; Anderson, W.G.; Hallberg, R. How ocean color can steer Pacific tropical cyclones. *Geophysical Research Letters* **2010**, *37*, [https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2010GL044514]. doi:https://doi.org/10.1029/2010GL044514.
69. Michaelian, K. Thermodynamic stability of ecosystems. *Journal of Theoretical Biology* **2005**, *237*, 323 – 335, [https://www.sciencedirect.com/science/article/pii/S0022519305001839?via%3Dihub]. doi:https://doi.org/10.1016/j.jtbi.2005.04.019.