

Re-Thinking Biology—I. Maxwell's Demon and the Spontaneous Origin of Life

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Abstract

A hypothesis is advanced in which life began from a Darwinian selection among a diversification of molecular species containing the phosphate moiety which broke the constraints implicit in the Second Law of Thermodynamics, discussed famously by Schrodinger, by obtaining energy from specific infrared frequencies located in the phosphorus-oxygen vibration at a frequency around 1000 cm^{-1} . We propose the source of this energy was from the internal conversion of solar broadband energy by the phosphate mineral Apatite, present at the bottom of a primitive biogenesis pond. In this scenario, life is re-defined as being hotter than its environment and as using its excess energy, supplied by infra-red conversion, to react with its molecular environment and pump itself up the “entropy slope” thereby; replication is through breakages of increasingly large phosphate containing biopolymers. The idea has implications for modern explanations of living systems.

Keywords

Abiogenesis, Evolution, Infra-Red, Radiation, Thermodynamics, 2nd Law, Maxwell's Demon, Phosphate

1. An Insoluble Problem

The history of Natural Philosophy teaches us that if a problem seems insoluble, it is usually because the wrong questions are being asked. We propose re-addressing the commonly held scientific description of the mechanism of life, but will begin by presenting a novel approach to explaining abiogenesis—the spontaneous development of life from inorganic matter. In Part II we will turn to the description of living systems and examining evidence for our hypothesis. In both contributions, we will suggest experiments which may be carried out to support or

refute the description.

The nature of the spontaneous origin of life on Earth is one of the big questions remaining unsolved by Science. The Urey-Miller experiments [1] and similar synthetic chemistry approaches demonstrate that most of the individual building blocks found in living systems would have existed on the early earth, as suggested by the Oparin-Haldane primordial soup theory [2]. A number of interesting but basically implausible schemes take the problem forward from there and differently assemble these small molecules into polymers which, in order to get us to the present day, have to explain the development of systems of reproduction and also systems of metabolism. A favourite later intermediate scenario for the reproduction part of this is the “RNA world”, where somehow or another a primitive version of the nucleoside polymer RNA appears and gets to work replicating itself from surrounding necessary chemical substrate units [3]. Apart from the vanishingly remote probability aspect of this, no-one has resolved the metabolic part of this RNA world which is left in the air. For somehow, not only does the RNA precursor molecule have to appear, but it must do so together with a system of energy abstraction which enables it to maintain an energy advantage over its surroundings. The main schemes to take us from the simple molecules to the RNA world or similar complex life chemistry include hydrothermal vents [4], Iron-Sulfur world [5], Zinc world [6], clay hypothesis [7], deep hot biosphere [8], radioactive beach [9], lipid world [10] among others, and panspermia, the appearance of life from other worlds, which latter we may ignore as it merely transfers the problem elsewhere.

Indeed, for the purpose of this contribution, listing these explanations is unnecessary. There are a number of useful reviews [1]. The current favourite theory is one where life began in hydrothermal vents [3]. But though the many theories are remarkably interesting, there is a very large elephant in the room, the issue raised by Schrodinger in 1944 [11]. This problem, which is fatal for all of the theories of life so far, was raised recently by Moore [12] who basically dismissed all the theories but made an important contribution when he wrote:

I do not believe that the definition of life is an enormous problem: We have been merely looking in the wrong place.

2. Thermodynamics

This thermodynamic question, which was presented in 1944 by Schrodinger, is about the difference between life and other physical processes in the Universe. It has so far evaded resolution. Schrodinger pointed out that living creatures avoid the entropy requirements of spontaneous physical processes and thus appear to evade the constraints of the Second Law of Thermodynamics. A few attempts have been made to deal with this problem by attempting to deny its existence by encapsulating it. Thus, Pross dismissed it by postulating some kind of chemical kinetic anomaly where thermodynamic demands could be kept at bay for a period of time, a kind of kinetic vortex [13]. A similar “infinite improbability drive” [14] argument was developed as long ago as 1952 by Alan Turing [15]. These

approaches highlight the impossibility of life, rather than answering the thermodynamic problem. A more interesting and possible approach was that of Michaelian, [16] who argued that entropy could be supplied by what was termed a “dissipative process” involving organic pigments (like perhaps precursors of chlorophyll). This approach came at the problem head-on, and in some ways, is a similar argument to the one we present here.

For maybe 40 years we have been concerned about the chemical basis of biological descriptions of life and have been developing a separate explanation. It is through this top-down approach that we have come to an explanation for the spontaneous origin of life. This explanation may stand alone, but if it is correct, it can be brought back to the present where it has significant importance for current descriptions of living systems. These will be developed in Part II.

Our explanation involves redefining life as self-sustaining reactivity. This enables us to take the argument back to the molecular level. If we redefine life as reactivity, then a highly reactive molecule like diazomethane, for example, is very alive, but has a very short lifespan. Unless the product of its reaction with its molecular surroundings is also reactive, it dies in one suicide move. What if there were a way to regenerate the molecule? Then it would react again and form another product. It is thus replicating, in a sense, although the product may not be the same. If energy is available to dissociate the product and regenerate the diazomethane molecule, all that has to be replicated is the ability to replicate. It has to have, in its environment, some energy source which can regenerate it so it can continue to react with elements of its environment, which are at a lower reactivity level.

The point is: there has to be energy separation between the living molecule and its dead surroundings, in other words the energetic molecule and its non-energetic surroundings. In all of the models listed above, there is no difference between the energies of the various components that make up the molecular soups in the regions where life is supposed to start. True, they are all regions where there is excess heat, or excess voltage, or excess radioactivity, but all the molecules in the region of interest are similarly affected. There is no obvious mechanism for selecting the living system from its surroundings. This is the important point. For example, in the geothermal vent scenarios, all molecules near the heat source, the hot water, will be equivalently heated up. They will then move away to cooler parts, and whatever reactions that occurred in the hot parts will just cease and cold, unreactive (dead) products will float off and dilute. What is required here is some universal process (like photosynthesis) where energy from some source continually pumps certain (reactive, living) molecular entities to a high energy state, selecting them over the other (unreactive, dead) lower energy surroundings, which these live molecules can continue to exploit (feed on) and thus grow and increase in number (replicate). The problem is selection. We have to find an energy source that is molecularly selective and continuous.

3. Maxwell's Demon

If life is alternatively considered as a heat engine, as such it needs an energy source and a sink. Chemical reactions are driven by energy. And reactivity also is a function of energy. Descriptions of molecular reaction kinetics give heat as causing the formation of activated complexes which then decay to products, given favourable energy differences between reactants and products [17]. In all cases excess energy required to form the intermediates derives from the molecular environment. If the mean energy of the molecular environment is everywhere the same, all molecular species have the same effective energy, and reaction successes are determined by strict classical thermodynamic considerations. There are no favoured molecules and reactions will take place until all the molecular species have moved to products described by the lowest energy state for the system. The flow of energy will be controlled by thermodynamic laws.

The thermodynamic process of life is compared with that of non-life in **Figure 1**. In chemical terms, the energy of the heat engine may also be described, as we have above, in terms of chemical reactivity. Thus, living systems may be seen as reacting with their environment, just like reactive chemicals such as diazomethane react with their environment. The difference is the product of the chemical reaction remains an inert product. The living system continues to react by acquiring more energy from its environment.

In order to avoid what we will term the *entropy catastrophe*, living systems have to somehow extract energy continuously from their surroundings. The principal sources of energy on the early planet are easily specified. They are:

- 1) Geothermal
- 2) Electrical (lightning, electric fields, electrochemical)
- 3) Physical (potential, kinetic, gravitational)

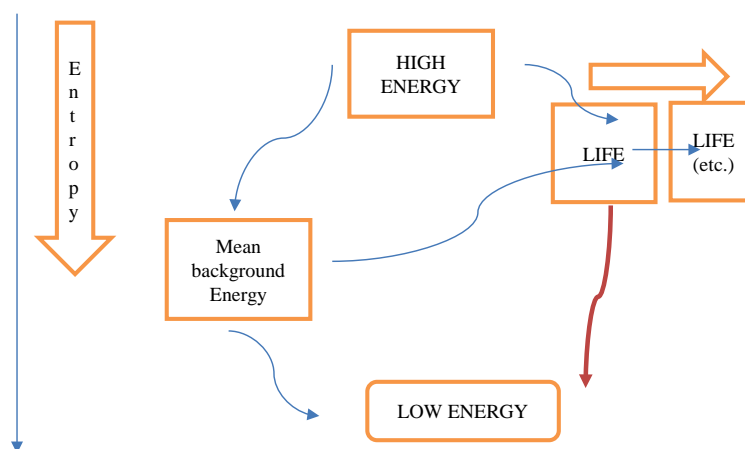


Figure 1. Life differs from non-life in the Universe. Energy flow in the equilibrium universe is always to increase entropy and disorganization. The orange arrow represents death of the individual. But reproduction (Green Arrow) keeps the living system repeating its trick and surviving in some form above the “energy well”, down which all physical and chemical equilibrium phenomena trend, according to the 2nd Law of Thermodynamics.

- 4) Solar Photonic electromagnetic: electronic, vibrational and rotational and
- 5) Ionizing radiation.

Other energy sources are, in terms of magnitude, second order.

The extremely narrow temperature window that life occupies within the overall temperature range of the universe is associated with statistical energy kT which is in the far infra-red. This immediately highlights a possible energy flow situation which a heat engine could exploit to do the work necessary to separate the living system from its dead surroundings. None of the energy sources listed apart from vibrational electromagnetic are specific enough to select certain molecules for energy enhancement processes. The higher energy electromagnetic vibrational-electronic absorption processes (eventually to be exploited by photosynthesis) are far too broadband and non-specific. Let us follow this up.

When the 2nd Law of Thermodynamics was first presented and its predictions discussed, a thought experiment was devised by Maxwell to illustrate the ideas. Maxwell created a hypothetical molecular scale entity, later called Maxwell's Demon by Lord Rayleigh. The Demon sat beside a doorway between two separate containers of a perfect gas and selectively operated a shutter to allow energetic gas molecules to enter a high energy (hot) container from a low energy (cold) container. Thus, the energy (measurable as temperature) of a hot assembly could be made higher (hotter) at the expense of a low energy (colder) one. Entropy of the high energy container (indeed of the entire assembly) would decrease. Note that the Demon is, of course, alive. However, the Maxwell Demon scenario was developed before Quantum theory. A new hypothetical Quantum Demon (which is not alive, and which really exists) can be invoked.

Maxwell's Demon argument (an illustration of Clausius's articulation of the Second Law) was that heat cannot be transferred to a hot body from a cold body. But this does not hold for quantized exchanges, since molecular species can be separated in energy terms through specific vibrational exchanges which have resonant absorption for certain molecular structures but not others. Thus, irradiating a mixture with infra-red radiation at a specific frequency which is absorbed by one molecule but not others immediately allows the resonant molecule to obtain extra energy and become hotter than its surroundings.

In the way described above, this excess energy may be used by the chosen molecules to react with other "cold" molecules in their environment and thus to grow, extend themselves, polymerise etc. They can be considered alive, as eating their environment, obtaining energy to do this from the specific infra-red radiation which energises them rather like a plant is energised with sunlight through the mediation of chlorophyll and various phosphate containing intermediates. As such, a molecule grows, the larger molecular entities produced will be favoured by acquisition of more molecular units containing the specific bond (or bonds with the same vibrational frequency) which are resonant with the incident infra-red feed.

We have here re-defined life to the molecular level: life now is any molecule

which can obtain energy from infra-red radiation and employ it to react with molecules in its surroundings which cannot obtain such infrared energy because they do not contain the correct resonant vibrational frequencies. This solves the metabolism problem if we can find a suitable specific source for the infrared radiation. The reproduction issue comes later in this scheme.

4. Specific Infra-Red Conversion of Broad-Band Solar Energy

When a mineral is heated by sunlight, a broad band electromagnetic energy source, (or any other means, e.g. geothermally) to a higher temperature than its surroundings, it re-emits the excess energy at quite specific frequencies in the far infrared region of the electromagnetic spectrum. The origin of these infrared bands is chemical bond vibrations which are characteristic of the composition of the mineral [18]. The main primitive minerals present at the time of the origin of life, in terms of these infrared emissions, were silicates and phosphates [19]. Their sharp and strong infrared emission bands were in the region 800 cm^{-1} to about 1100 cm^{-1} or wavelengths between 9 and 12 microns. This is roughly the diameter of the living cell. The bandwidth of these vibrational energies is very small.

So a specific infra-red frequency would be generated through the solar (or geophysical) heating of a mineral situated at the bottom of a primitive Oparin-Huxley-Darwin pond. This energy source is continuous, and provides the energy necessary for the survival and growth and replication of the molecular species containing the resonant absorption characteristics. It might be seen as a primitive infrared photosynthesis, in which the analogue of chlorophyll is the resonant chemical bond vibration. Whilst all of the primitive minerals will emit infrared radiation at their specific frequencies when heated by the sun, it is of interest in searching for a most likely candidate to move forward in time and look for clues in current living system biochemistry.

5. The Identity of the Quantum Demon

If the hypothesis were correct, then we are looking for a common mineral which was present on the early earth and which has a very strong specific infra-red absorption/emission frequency. It would be an advantage for this mineral to be slightly soluble and also to favour, in solution, the build-up through reactions involving the energised key vibrating excited state bond, of polymeric compounds that could retain the ability to resonate with the converted solar energy at the specific frequency.

There are two approaches to any attempt to find the minerals that might have supplied the energy necessary to separate out the living from the dead molecules. One is to look at what minerals there are that would probably have been around on an early earth. The other is to look at living creatures and see what they are made of. Because if the model has any basis in reality, we could reasonably assume that whatever it was that supplied the key vibrational energy band to set up

the life system is likely to be part of the life system that exists today. So we can work back from current living forms to the early earth and its prebiotic soups and ask what there is in common.

Such approaches have been part of the search-for-life enthusiasts' armoury already. So of course, there had to be questions asked about the early possibilities of creating the known building block chemicals. Let's list these.

Starting with the primary constituents we have:

Carbon, Hydrogen, Nitrogen, Oxygen, Phosphorus. These elements are in living system at proportions greater than a few percent. Then there are secondary constituents which are present below about 1%. These include Sodium, Magnesium, Calcium, Sulphur, Chlorine and Potassium. We can ignore, for the purpose of biogenesis, the trace elements. Those in search of the first molecules always concentrate on the organic compounds. They need to populate the warm pool with amino acids, the purine and pyrimidine bases, constituents of DNA and RNA, and they include these nucleotides and nucleosides. Then we need the lipids and their precursors, the fatty acids and alcohols, the sugars and the energy molecules in the various energy cycles. There are vitamins and coenzymes, proteins. And finally, we have to have water, carbon dioxide, ammonia and the oxides and oxy-acids of phosphorus.

If we are interested in minerals that might have been the original Demon we do not find silicates, and we do not find sulphates in living systems. It is possible that we find carbonates, but not as organo-carbonates as they are too unstable. Following the geothermal vent scenarios we may be interested in sulphides, but there are not any sulphides in living systems either. What there is in living systems in very large amounts is phosphates. Indeed the DNA and RNA "aperiodic crystal" is a polyphosphate. The fundamental energy transfer molecules in the cell are phosphates. And if we are seeking to identify our primal mineral at the base of the soup pool it is most likely that we have found it.

6. Phosphorus and the P = O Frequency [20] [21]

Phosphorus always occurred combined, it is a common element on Earth, and the average percentage in the lithosphere is 0.157 and in ordinary soil 0.1%. The primary minerals are Apatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ and chlorapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ which are hard and practically insoluble even in dilute acids. From them, soft phosphate deposits occur of $\text{Ca}_3(\text{PO}_4)_2$, calcium metaphosphate and hydroxyapatites. Phosphates are ubiquitous in living systems. Compounds occur in vegetable and animal tissues, especially in seeds in which it is concentrated in the germ. Cereal grains contain 0.4% of Phosphorus. Egg yolks, nerves and brain and bone marrow contain the fatty esters of phosphoric acid, lecithins or glycerophosphates. In order to repair tissues and provide phosphate for bones, phosphorus compounds are essential in foods. Plants take this from the soil as calcium phosphate. Fresh bones contain about 58% of calcium phosphate. The natural mineral phosphates contain salts of ortho-phosphoric acid H_3PO_3 . This is tribasic and forms three series of salts, primary e.g. KH_2PO_4 , secondary, Na_2HPO_4 and

tertiary, e.g. Na_3PO_4 . The alkali phosphates are soluble; generally the alkali earth phosphates are not or are, at most, very slightly soluble. The alkali primary phosphates are weakly acid, the secondary phosphates are practically neutral and the tertiary phosphates are alkaline. Thus ortho-phosphoric acid is an ideal molecule to act as a polybasic ion capable of a whole range of reactions in aqueous solution, and with a very strong $\text{P}=\text{O}$ absorption in the infrared [21]. The ion can combine with itself to form pyrophosphates and can polymerise to form long chain polyphosphates, or chains coupled as linked secondary esters, the most famous of which are the ribose esters RNA and DNA. It reacts with organic compounds to form such esters and indeed almost with any organic molecule with a functional group to give an enormous range of organo-phosphates.

It is Apatite, the hard, primeval mineral form of phosphate which is the most likely identity of the Quantum Demon. Its infra-red spectrum is shown in **Figure 2** and the mineral in **Figure 3**. If we are looking for our most likely substrate energy source mineral it is Apatite and the detector energy receiver antenna in the heat engine is the $\text{P}=\text{O}$ vibration. There are various apatite minerals but all are based on Calcium phosphate. And living systems incorporate very large amounts of phosphates. Indeed Schrodinger's "aperiodic crystal" the DNA and RNA, are based upon on a polymeric organo-phosphate. The fundamental energy transfer molecules in the cell, Adenosine triphosphate, the NADP of the plant version are phosphates, triphosphates and diphosphates. Skeletons are constructed of phosphates. Phospholipids make up the cell wall and other critical membrane structures (which would be clearly amenable to a control by localised energy at the key vibrational phosphate frequency). The phosphate-oxygen bond $\text{P}=\text{O}$ has its stretching frequency at about 1000 cm^{-1} or 10 microns wavelength, the mean diameter of the cell, perhaps not an accident, since this would represent a resonant cavity for the key energy source. It is one of the most powerful absorptions in the infra-red, and energy mediating molecule Adenosine Triphosphate (ATP) has three PO_4 moieties, a total of seven equivalent absorber/emitters for this frequency.

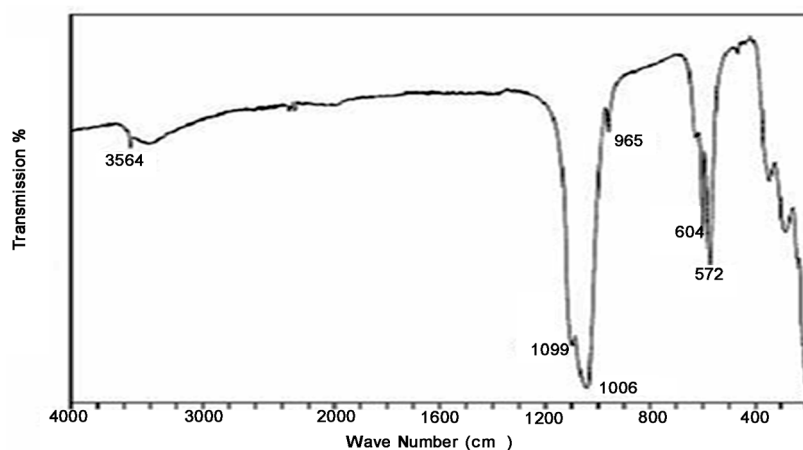


Figure 2. IR spectrum of Apatite.



Figure 3. The origin of life? A 8 cm polished specimen of Apatite from Madagascar.

Note the very high absorbance of the P = O stretch, which has a much higher extinction than the O-H stretch of water at 3500 cm^{-1} . The oscillator strength (or infra-red cross section) is very large and if, as is the case in polyphosphates or polymeric esters where there are a number of $-\text{OPO}_3$ residues, Fermi Resonance will occur and make the intensity of the emission extremely significant. The PO band is so intense that it can be used to detect POCl_3 impurity in PCl_3 at 1 part per 10^4 or 0.01% [21].

7. Chirality

One further unsolved problem is that the amino acid components of contemporary living systems are all chiral molecules of the same L-rotation type. The emission of infrared radiation and its selection by specific molecular species would suggest surface polymerisation at or near an optically active substrate. The process we suggest here would also favour selection of chirality since it is essentially driven by optical exchanges in the infra-red scattered through a mineral surface which has been shown to have chiral properties [22].

8. From Excess Energy to Polymerization

Having energised selected molecules in the primeval aqueous mix, using the infrared conversion of sunlight (or geothermal heat), these molecules have to react with their low energy surroundings and provide a route for natural selection to operate and refine the efficiency with which they evolve. It is clear that polymerisation is the first step. Polymeric phosphate chains would be predicted to form since the phosphate absorption would be stronger per molecule in such polymers. Since these are generally insoluble, selection advantages would accrue by the binding of solubilisation agents like amines (which bind strongly to phosphate) or end chain carboxyl groups, any entity that created an ionic ter-

minal hydrophilic (detergent like) property. The accumulation of hydrophobic organic chains which led to surfactant activity would stabilise longer and longer chains which would be expected at some point to form micellar structures. This might lead to the kind of lipid world descriptions [10] but with the difference that there would be an energy source for the primitive assembly of molecules or proto-creatures. There is no advantage in rehearsing all the possible developments. At this point, we give way to Mr Darwin. We have provided a plausible energy source and plausible description for the development of life from non-life which resolves the main outstanding problem, the Schrodinger problem.

However, if this is the correct explanation, then it has significant implications for current descriptions of biology. It has been described elsewhere [Busby 2016] and we will discuss these issues in Part II.

9. Reproduction

In the scheme suggested, reproduction does not have to be perfect replication. *i.e.* exact copy. Nor is it, today. All that has to be reproduced is the ability to reproduce. The splitting of the long chain is assumed to be effected by sheer thermodynamic probability-based processes, longer and longer chains becoming increasingly likely to become cleaved somewhere in the middle. The molecule, at whatever stage of development (growth or partial polymerisation) changes its morphological or chemical structural identity (and molecular weight) but so long as it retains the energisable phosphate band growth centre, or more than one, it is still counting as “reproduction”. Of course, the phosphate polymers will have the most potential energy for such reproduction. Such a quality could be assessed by [Phosphate PO bonds]/[all bonds]. Efficiency of survival would also involve acquisition of solubility-enhancing components. The idea that a phospholipid micellar structure would have resonant absorption also due to an optimum cavity diameter is an attractive one. The existence of such favoured structures everywhere in contemporary life points to their stability.

10. Experimental and Supporting Investigation

The obvious set of experiments is to repeat the various Urey-Miller investigations in the presence of a bed of apatite heated by a broad band lamp source. It is of interest that Fox [23] carried out experiments in which heated minerals were used to accelerate the formation of proteinaceous material from amino acids but Fox’s temperatures were very high. One experiment might be to employ a control in which a primitive insoluble silicate mineral was employed and the end point was a measurement of polymer chain length where the equivalently heated substrate involved different minerals.

11. Conclusions

The conversion of solar broadband (black body) radiation (or alternatively geothermal heating) into specific phosphate P = O stretch vibrational energy at 1000 cm^{-1} by the mineral Apatite in some version of the primeval soup pond is post-

ulated to be the origin of a primitive molecular life. Such life remains energised continuously by a kind of infrared photosynthesis. Such molecular life exploits its environment, grows, divides and uses its acquired energy to avoid the entropy trap discussed by Schrodinger.

If life developed through infrared exchanges of energy it would seem plausible that such exchanges remain a significant part, or perhaps the main mechanism of living systems and that the dynamic of life is not fundamentally chemical but that the chemical components of living systems fulfill a different function to that which is currently understood. The evidence for this was outlined recently elsewhere [24] and will be the subject of a separate contribution in Part II.

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