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IS ENTROPY FAR FROM EQUILIBRIUM A STATE FUNCTION?

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ABSTRACT

This paper is an attempt to develop the new discipline of ecodynamics as a quest for evolutionary physics. Particular attention is devoted to goal functions, to relations of conceptualizations surrounding matter, energy, space and time, and to the interdisciplinary approach connecting thermodynamics and biology. Entropy is discussed as a fundamental goal function in the far from equilibrium framework. The relationship between entropy, as a non-state function, and the state function energy is stressed and discussed, in the light of the role of information. The evolutionary dynamics of complex systems, ranging from open physical and chemical systems (strange attractors, oscillating reactions, dissipative structures) to ecosystems have been investigated in terms of far from equilibrium thermodynamics (Prigogine). The theory of probability is also discussed in the light of new theoretical findings related to the role of events, and also in terms of entropy and evolutionary thermodynamics.
Keywords: ecodynamics, entropy, evolutionary thermodynamics, probability.

1 THE TIME PARADOX

The basic laws of physics from Newton to the present day have been time reversible; on the contrary, reality is constituted by phenomenological aspects: macromolecular organization, cellular differentiation, life processes, characterized by irreversibility of time. The reason for this lies in the dynamic interactions that take place in complex systems. The analysis of reality requires major modification of current physical chemistry equations and theories. What is now clear is that complex systems and their behaviour can only be analysed by means of relations including time as a directional factor.

On the one hand, the use of time-reversible classical and quantum physical chemistry approaches for studying matter at the molecular level and the behaviour of simple molecular systems has greatly improved man's understanding. On the other hand, we need new approaches and new time-irreversible theories to be able to describe the behaviour of complex systems.

The recognition that time is 'real' and plays a fundamental 'constructive' role in nature leads to Prigogine's [1] time paradox:

> How is this possible that on one hand the basic equations of dynamics, classical or quantum, are time reversible and that on the macroscopic level, on the other hand, the arrow of time plays a fundamental role? How can 'time' come from 'non-time'?

Prigogine [1] adds:

> I believe that we are therefore indeed at the beginning of a 'New Physics' which incorporates both dynamics and irreversibility. Until now, our view of nature was dominated by the theory of integrable systems, both in classical and quantum mechanics. This corresponds to an undue simplification. The world around us involves instabilities and chaos, and this requires a drastic revision of some of the basic concepts of physics.

As Khun [2] remarks, the passing of time often brings anomalies which existing theories are no longer able to explain. The divergence between theory and reality may become enormous and consequently a source of serious problems. This is exactly what is happening today between current scientific theories and the natural situation of the planet. In Khun's terms this means a shift toward a new paradigm. As Palomar in Italo Calvino's novel observed: 'if the model does not succeed in transforming reality, reality must succeed in transforming the model.'

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Based on the assumption that the interaction between biophysical constraints and evolution is not satisfactorily described by current scientific theories, this paper is an attempt to present a new model to be used in ecological physical chemistry with regard to entropy, energy and time fluctuations in biological and ecological systems.

The epistemology of the model derives from interdisciplinary cross-fertilization between physical chemistry, mainly thermodynamics, and ecology, mainly systems ecology. The logical consequence is a complete change of the point of view or a 'gestalt' shift in modelling the relationship between biophysico-chemical parameters and the global environment.

The starting point is Boltzmann's statement that the struggle for life is not a struggle for elements or energy, but rather a struggle for entropy available from solar energy [3].

2 STEPS TOWARDS ECODYNAMICS

In the framework of evolutionary physics we deal with goal functions instead of state functions; the ecodynamic models have to be based on relations evolving in time; 'far from equilibrium thermodynamics' (Prigogine) assumes upon itself the role of foundation of a new description of nature. Table 1 summarizes the main concepts related to this paradigm shift.

In his autobiography, Nobel Prize winner Ilya Prigogine recounts his first studies on far from equilibrium phenomena:

> It is difficult today to give an account of the hostility that such an approach was to meet. For example, I remember that towards the end of 1946, at the Brussels IUPAP meeting, after a presentation of the thermodynamics of irreversible processes, a specialist of great repute said to me, in substance: 'I am surprised that you give more attention to irreversible phenomena, which are essentially transitory, than to the final result of their evolution, equilibrium.'

Table 1: Comparison of ecodynamics, classical physics and ecology.

	Classical physics	Ecology	Ecodynamics
Basic world view	Mechanistic Dynamic Molecular	Evolutionary Molecular	Evolutionary Systemic
Time	Reversible	Evolutionary	Irreversible Evolutionary
Focus	Object Subject Quantity Nature	Object Subject Quality Quantity Nature	Relations between quantity–quality and between subject–object
Viewpoint	Reductionist	Reductionist Holistic	Holistic
Goal	Knowledge	Survival of species	Sustainable development
Modelling	Deterministic	Evolutionary	Evolutionary Systemic Irreversible

He adds:

> As we started from specific problems, such as the thermodynamic signification of non-equilibrium stationary states, or of transport phenomena in dense systems, we have been faced, almost against our will, with problems of great generality and complexity, which call for reconsideration of the relation of physico-chemical structures to biological ones, while they express the limits of Hamiltonian description in physics. Indeed, all these problems have a common element: time.

Professor of physical chemistry at the University of Brussels, Ilya Prigogine was awarded the Nobel Prize in chemistry in 1977. His studies opened a window to nature. For the first time in the history of physical chemistry, tools, methods, equations and models were developed to describe the essence of the evolutionary properties of nature. This was a true change of paradigm. This change in paradigm: (i) implies that the intrinsic irreversibility of time has erupted in the basic equations of chemistry and physics; (ii) sustains Pascal's view that the whole is greater than the sum of its parts and hence negates the statement of Descartes that the world should be divided into the smallest possible parts in order to understand it; (iii) suggests that form and aesthetics (and hence quality as well as quantity) play a role in the evolution of nature. Nature is therefore conceived as $\varphi\upsilon\sigma\iota\sigma$ (*physis*, the word from which physics is derived) in the original Greek sense, a nature in which time, relations and aesthetics play a fundamental role.

The epistemological and historical foundations of this concept (iii) are explained by Bateson [4, 5] (I) and in relation to Archimedes in Plutarch's *Parallel Lives* [6] (II):

(I) Modern science takes the antiaesthetic assumption attributed to Bacon, Locke and Newton to an extreme. This assumption was that all phenomena can and must be studied and evaluated only in quantitative terms. However, the role of form, colour, flavour, sound, scent and beauty was fundamental for biological evolution, and is still fundamental today for a scientific view of complexity. Nature is threatened by the linear, mechanistic, crude approach of science at the service of a society that 'knows the price of everything and the value of nothing'.

(II) Archimedes is known for certain useful discoveries: his famous principle based on the concept of density led to the imprisonment of merchants doping gold with other metals, and he used solar energy to burn the sails of Roman ships. When asked to write these useful things or to invent others, he replied that he only concerned himself with 'fine and beautiful' things.

Pascal's concept (ii) brings thermodynamics and evolutionary biology to the centre of research on nature, relegating particle physics, molecular chemistry and molecular biology to the background. Obviously they still have a central role in the study of non-living matter and mechanics. This type of approach was proposed many years ago by Alfonso Maria Liquori [7], professor of physical chemistry at Rome's 'La Sapienza' University and often nominated for the Nobel Prize in chemistry.

Liquori wrote:

> In the case of proteins, molecules owe their stability to the same intermolecular forces that stabilise crystals: Van der Waals forces and weak electromagnetic interactions. In living organisms, very weak forces hold DNA molecules together, as well as proteins and membranes. *Because they are weak, they allow these structures to change conformation in order to change function*.

He adds:

> The path chosen by many physicists, not Schrödinger [8] of course, was to try to use quantum mechanics, which is a mistake (except for the phenomenon of sight) because among other things, the maths of quantum mechanics is unwieldy.

Erwin Schrödinger, winner of a Nobel Prize in physics and one of the fathers of quantum mechanics, introduced the concept of negentropy into his lessons in Dublin in the 1950s:

> How would we express in terms of the statistical theory the marvelous faculty of a living organism, by which it delays decay into thermodynamical equilibrium (death)? We said before that it feeds on negative entropy, attracting, as it were, a stream of negative entropy upon itself, to compensate the entropy increase it produces by living and thus to maintain itself on a stationary and fairly low entropy level.

Moreover, in the foreword of *The Essence of Time* Prigogine [9] wrote:

> The first part of this book deals with the passage 'from a space to a time culture'. This is indeed an essential part of the scientific revolution we are witnessing at the end of the 20th century. Science is a dialogue with nature. In the past this dialogue has taken many forms. We feel that we are at the end of the period which started with Galileo, Copernicus and Newton and culminated with the discovery of quantum mechanics and relativity. This was a glorious period but in spite of all its marvelous achievements it led to an oversimplified picture of nature, a picture which neglected essential aspects. Classical science emphasized stability, order and equilibrium. Today we discover instabilities and fluctuations everywhere. Our view of nature is changing dramatically. At all levels we observe events associated with the creative power of nature. I like to say that *at equilibrium matter is blind, far from equilibrium it begins to 'see'.*
>
> Although quantum mechanics and general relativity are revolutionary, as far as the concept of time is concerned, they are direct descendants of classical dynamics and carry a radical negation of the irreversibility of time.
>
> Irreversibility is not related to Newtonian time or its Einsteinian generalization, but to an 'internal time' expressed in terms of the relations between the various units of which the system is composed, as are relations between particles.

This simply means that we no longer deal with state functions, but rather with evolving ecodynamic functions.

Faced with the evolutionary character of nature and life, classical science (physics and chemistry) encounters three paradoxes:

- Prigogine's time paradox;
- the paradox of negentropy that cannot be calculated on the basis of conservative, deterministic and purely quantitative terms (energy and classical entropy) but which must consider information, forms and quality;
- the probability paradox (probability is an aseptic, atemporal mechanistic concept) which has to account for events, emerging phenomena, choices made by plants, animals and ecosystems, random fluctuations of evolutionary biology and the phenomena of far from equilibrium systems.

The second and third paradoxes will be discussed in the following paragraphs.

3 ENTROPY EXISTS

The role of thermodynamics in scientific thought boils down to defining relations and identifying constraints; thermodynamics is the science of what is possible and is to physics as logic is to philosophy. Entropy is the enigma of thermodynamics because it has the intrinsic properties of time irreversibility, quality and information that other thermodynamic functions lack. This is why entropy is a central concept in biology and ecology: entropy is the basis of *ecodynamics*.

The Second Law of Thermodynamics states that the universe, or each isolated section of it, tends towards maximum entropy. Statistical mechanics and kinetic theory tell us that maximum entropy implies maximum disorder within the framework of the constraints of the system. Hence when we think about evolution in this context (Boltzmann's H theorem) [10], we think of evolution towards increasingly disordered states of the system.

This idea is strikingly at variance with our knowledge of biology. Clearly the trend of living organisms is towards the creation of order where previously there was disorder: it is the trend to organize and self-organize. Life seems to contradict the Second Law of Thermodynamics. The solution to this apparent contradiction between biological and physical theory, according to Morowitz [11], lies in the realization that the Second Law of Thermodynamics applies to systems close to equilibrium, whereas the surface of the Earth, the matrix of biological evolution, belongs to a different class of physical systems. The biosphere is a far from equilibrium system, as all the living systems are (open systems far from the thermodynamic equilibrium).

Prigogine [1] gives a clear and simple description of the ecodynamic peculiarities of the biosphere: the biosphere is far from equilibrium because it is characterized by instability, bifurcations and dissipative chaos; time is therefore real and plays a fundamental constructive role.

Prigogine introduces the concept of the arrow of time to describe irreversible changes. The main issue derived from the theory of dissipative structures is that the evolution and maintenance of open systems far from equilibrium are possible only if irreversible thermodynamic processes occur. Such processes dissipate energy and matter, increasing entropy in the environment.

The evolutionary process is such that systems become more and more complex and organized. Biological diversity is the product of long-term interactions at a genealogical and ecological level: the genealogical interactions consider the dissipation of entropy by irreversible biological processes; the ecological interactions consider entropy gradients in the environment.

There are also chemical systems that show phenomena of self-organization such as the formation of stationary spatial structures or periodic oscillatory states. We performed a large number of experiments by studying the Belousov–Zhabotinsky (BZ) oscillating reaction. Figure 1 shows the dissipative

Figure 1: Spiral waves, stationary Turing-like patterns and other exotic structures formed by the BZ reaction in a Petri dish.

structures that emerged during the evolution of the BZ system performed in a Petri dish. It is clear that the genesis of the shapes in such a medium is deeply connected with the self-organizing capacity of this chemical system mediated by the peculiarities of the water medium in which is performed [12]. The phenomenon is clearly related to the role of entropy in dissipative structures and to the input–output entropy flows. In his 1994 MOA lecture Prigogine underlined the following statements, which explain this behaviour:

Classic laws of nature are *deterministic* and *reversible*

Thermodynamics and entropy describe an *evolutionary* view of nature

Entropy means evolution

Irreversible processes, which *create* entropy, distinguish between past and future

We cannot describe nature without making a distinction between past and future

Many years before 1972 Landsberg [13] reviewed a book by Glansdorff and Prigogine [14] and reached the following conclusion:

> Zeroth law—empirical temperature exists. First law—internal energy exists. Second law—entropy and absolute temperature exist. Third law—states that T = 0 do not exist. Fourth law—for a class of non-equilibrium states, and for equilibrium states, extensive and intensive variables exist.

Jørgensen and Svirezhev [15] refer to the maximum exergy hypothesis as the Fourth Law of Thermodynamics and underline, correctly, that this is consistent with the maximum power principles presented by Lotka [16] and Odum and Pinkerton [17]. Probably, add Jørgensen and Svirezhev, the unification of maximum power and maximum exergy is the Fourth Law of Thermodynamics and this statement is also consistent with Prigogine's theory and with the conclusions of this paper [15]. For a complete review of the consistency among goal functions refer to Fath *et al*. [18] and to Jørgensen and Svirezhev's book [15]. We may add that the Fourth Law of Thermodynamics is fundamental for 'far from equilibrium systems', either living systems or complex steady-state ecosystems. The second and fourth laws of thermodynamics trace an entropic and exergetic watershed between classical systems and far from equilibrium systems, whenever the last ones behave as evolutionary systems.

Along the same lines, analysing the input–output entropy flows, Aoki [19, 20] stated:

- The first law formulates the energy concept; the second law formulates the entropy concept.
- The first law deals with flows of the conservative quantities: energy and matter; the second law deals with flows of the *non-conservative quantity, entropy*.

It is possible to summarize this section by saying that entropy exists, it is a non-conservative function and is related to evolution.

4 THE ENTROPY PARADOX: ENERGY VS. ENTROPY

The last conclusion is a big step because it overcomes the old dilemma of whether entropy was the shadow of energy or vice versa, and does not reduce the ingenious invention of entropy to a purely energy dogma. The First Principle formulates the concept of energy in a conservation framework; the Second formulates that of entropy in an evolutionary framework. This is where evolutionary biology and mechanics meet. Schrödinger's introduction of the concept of negentropy was an inspired one: a living system absorbs negentropy from the external environment, structuring itself and evolving on the basis of this interaction. In other words, energy and entropy can be related, as is done in classical thermodynamics and statistical thermodynamics, but from the point of view of time, the two concepts are irreducible and different. In an evolutionary gestalt, entropy has an extra gear which is the key necessary for studying living systems and ecology. It is important to study flows of energy and matter, quantities that are intrinsically conserved; it is also important to study entropy flows, an intrinsically evolutionary and non-conserved quantity. The appearance of a term for entropy production, or 'source term' as Aoki [19, 20] calls it, is the watershed dividing the evolutionary world from the special case of conserved energy and mass. *But if energy and mass are intrinsically conserved and entropy is intrinsically evolutionary, how can entropy be calculated on the basis of energy and mass quantities (entropy paradox)?* This question is still unanswered [21] and all we can do is to note that the ecodynamic viewpoint is different from that of classical physics and classical ecology (see again Table 1).

Let us consider the different relations of energy and entropy vs. information. An energy flow can lead to destruction (increase in entropy, e.g. a cannon ball) or organization (decrease in entropy, e.g. photosynthesis). The same quantity of energy can destroy a wall or kill a man; obviously the loss of information and negentropy is much greater in the second case. Energy and information are never equivalent.

The classical example of the mixing of gases in an isolated system shows us that there can be an increase in entropy without energy input from outside. The point is that E and S are related functions, but energy is intrinsically reversible whereas entropy is not. Entropy has the broken time symmetry of which Prigogine speaks. In other words, entropy has an energy term plus a time term that energy does not have.

Entropy has an intrinsic temporal parameter. Energy obeys spatial and material constraints; entropy obeys spatial, material and temporal constraints.

If history and the succession of events are of scientific relevance, the concept of function of state should be revised at a higher level of complexity. The singularity of an event also becomes of particular importance: if a certain quantity of energy is spent to kill a caterpillar, we lose the information embodied in the caterpillar. But were this the last caterpillar, we would lose its unique genetic information forever. The last caterpillar is different from the *n*th caterpillar.

Stories take place in a setting, the details of which are not irrelevant to the story. What happens in the biosphere, the story of life, depends on the constraints of the biosphere itself. Hence it is important to have global models of the biosphere in terms of space, time, matter, energy, entropy, information and their respective relations.

Finally, if we consider the evolutionary transition from anaerobic to aerobic living systems, the ratio of energy to stored information is clearly different. The information that led to an evolution and organization of the two types of systems is not proportional to the flow of energy.

Thus entropy breaks the symmetry of time and can change irrespective of changes of energy, making energy a conservative and reversible property, whereas entropy is evolutionary and irreversible per se. The flow of a non-conservative quantity, negentropy, makes life go and the occurrence of a negentropic production term is just the point that differs from analysis based on merely conservative terms (energy and matter).

The situation is explained in Fig. 2 'The death of the deer': mass and energy do not change, whereas entropy does. There is an entropic *watershed* between far from equilibrium (living) systems and classical systems (the dead deer or any inorganic not living system).

We may conclude that in the far from thermodynamic equilibrium systems (biology and ecology) *entropy is not a state function, since it has intrinsic evolutionary properties*, strikingly at variance with classical thermodynamics.

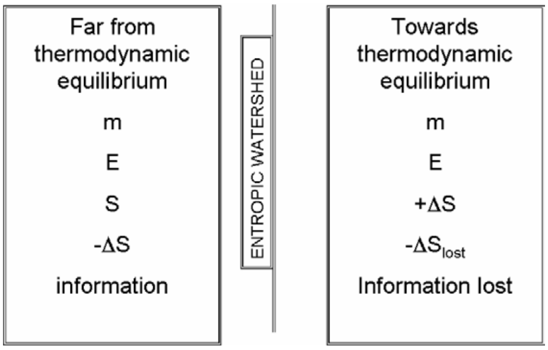

Figure 2: The death of the deer.

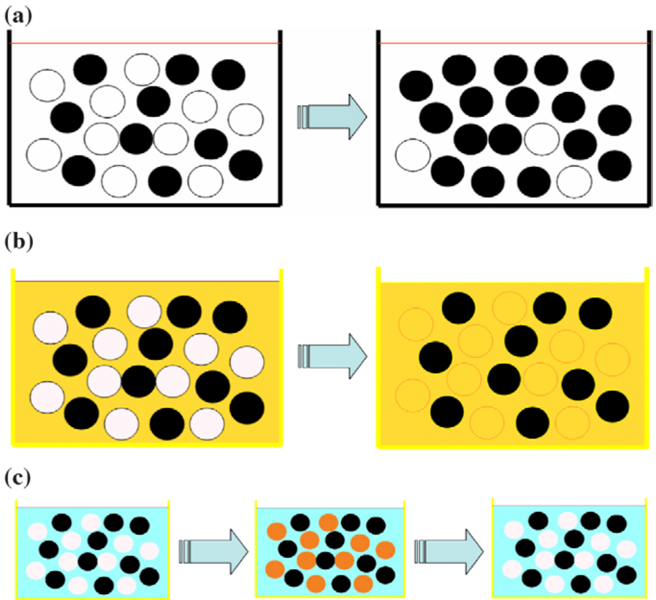

Figure 3: Unexpected events that may occur in living systems: (a) oxidation; (b) the chameleon effect; (c) an oscillating reaction.

5 THE PROBABILITY PARADOX

An event occurs in a stochastic manner because it is preceded by others. There are genetic and environmental constraints. Evolutionary events proceed in a manner that depends on time: they show a direction of time; they are irreversible.

Past time has determined the constraints; the future is largely unpredictable, and always has a stochastic or probable element. Previously unobserved events cannot be predictable; rare and extreme events may completely change the dynamics of complex systems.

Figure 3 shows the *emergence* of a probability paradox in the presence of events:

(a) Suppose that an oxidation (chemical event), unknown to the observer, arises in the classic 'white and black spheres' game: the probability of white/black is no more fifty-fifty (only if the oxidation is changing the white sphere to grey, I may know what happened).

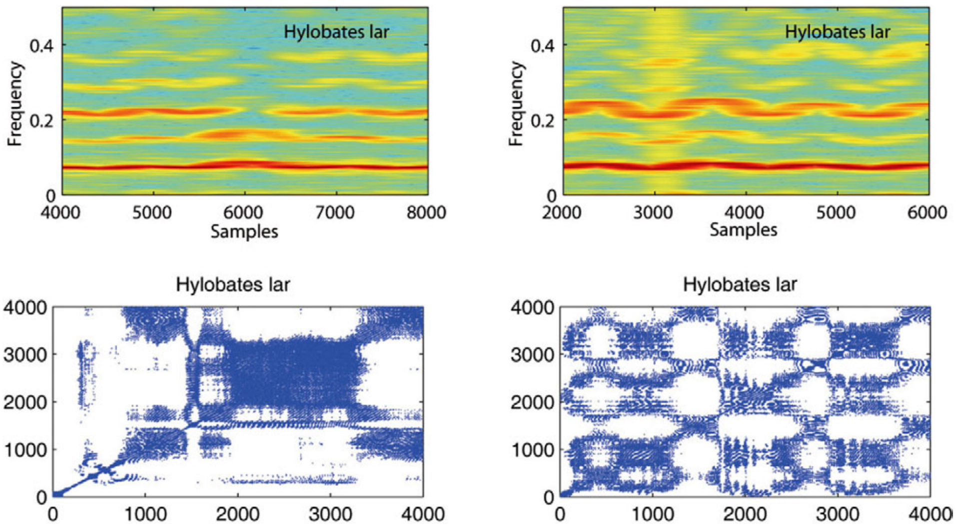

Figure 4: Recurrence plot analysis of the calls of two different *Hylobates lar* gibbons. The spectrograms show two very similar signals, characterized by a light frequency modulation. On the contrary, the recurrence plots show completely different patterns.

(b) Suppose that an evolutionary event also occurs, related to the 'chameleon' effect (sensible to the environment): again the probability is no more fifty-fifty. Moreover, the event's interval depends on the 'chameleon'.

(c) Suppose an oscillating event occurs, similar to the previously observed BZ reaction: the situation is more complex and depends on many parameters. Again the observer has no possibility to predict which sphere will be picked up from the container.

It is possible to conclude that in the far from equilibrium framework a classical probability approach does not apply and new models will probably have to be developed for the Boltzmann relation $S = k\ln W$.

6 STRANGE ATTRACTORS

Because open ecosystems are self-organizing, complex adaptive systems responding to current environmental conditions, we view the organizing principles as 'orientors' or 'attractors'. Again Prigogine underlines that the evolutionary dynamics of complex systems (strange attractors, oscillating reactions, dissipative structures) has to be investigated in terms of far from equilibrium thermodynamics.

Figure 4 shows an experiment performed on gibbon vocalizations [22]. The comparison between the two lower figures (*recurrence plots of strange attractors*) is a clear *evidence of biodiversity* marked by a *vocal fingerprint*. Similar experiments have been performed on bats' *vocal fingerprint* and on Sardinian deers [23]. Experiments on whales' songs are in progress. Again Prigogine's far from equilibrium thermodynamics is the theoretical basis for these calculations.

Biodiversity is strictly related to biological evolution and, also in this case, we have to refer to goal evolutionary functions: entropic change and flow are the key to understanding the experimental results of the recurrence plots, and these outcomes are a further incentive to develop new steps towards an evolutionary physics.

7 CONCLUDING REMARKS

In order to understand reality, let us divide it into parts, as many as possible

Cartesio

The whole is more than the sum of its parts

Pascal

We may conclude that in classical science:

– geometric rules and mechanistic laws apply;
– Newton's laws are reversible deterministic laws.

Prigogine adds and counterpoises the concept of 'events' to 'laws of nature' of this kind. We know that such laws are not true for living systems, ecosystems, and the events of biology and ecology.

Far from equilibrium we witness new states of matter having properties sharply at variance with those of equilibrium states. This suggests that irreversibility plays a fundamental role in nature. We must therefore introduce the foundations of irreversibility into our basic description of nature (evolutionary thermodynamics).

It is also important to underline that:

– *space is, by its structure, reversible;*
– *time is, by its structure, irreversible*.

In order to achieve an ecodynamic description we need to shift our attention from state functions to goal functions.

We may conclude also with the following two statements by Sven Jørgensen:

> The presence of irreducible systems is consistent with Gödel's theorem, according to which it will never be possible to give a detailed, comprehensive, complete and comprehensible description of the world. Most natural systems are irreducible, which places profound restrictions of the inherent reductionism of science.

> Many ordered systems have emergent properties defined as properties that a system possesses in addition to the sum of properties of the components—the system is more than the sum of its components. S. Wolfram [24, 25] calls these *irreducible systems* because their properties cannot be revealed by a reduction to some observations of the behaviour of the components.

and we may refer to Jørgensen's book [15] for a complete review of the 'Thermodynamic Theory for Ecosystems'.

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