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THE NATURE OF SPONTANEITY-DRIVEN PROCESSES

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ABSTRACT

There is a preferred direction for spontaneous changes in nature leading to decay and destruction, in accordance with the entropy law. Notwithstanding this assertion, the law does not prohibit changes opposite to spontaneity, only that such change cannot happen by itself. In this paper, I show that the second law points out the possibilities of constructive changes against spontaneity, as well as sets the limit to those possibilities. The actualization of those changes necessitates the concepts of useful work and reversible-like processes. Although all macroscopic processes in nature are spontaneity-driven, machines and machine operation can only be comprehended – not as spontaneous processes, but – as reversible-like processes, which are *designed* to be spontaneity-driven. Machines (and life) are the outcomes of constructive forces in nature, which derive their efficacy from the destruction of spontaneity; destruction and construction are two faces of the entropy law.

Keywords: causality, causation and design, destruction and construction, reversibility, reversible-like processes, spontaneity, spontaneous processes, the entropy law, useful work.

1 THERMODYNAMICS – A THEORY OF CHANGE

The second law of thermodynamics asserts the inexorable production of entropy – thus the inevitable collapse of things into chaos [1], leading to the perception of destruction, disintegration, and decay in the macroscopic world. I shall argue a different understanding of the second law, i.e. the destruction of spontaneity may be viewed in some instances also as the construction by spontaneity [1]; as a result of the destruction of spontaneity, constructions can be, and are *made* possible. This paper presents an analysis of this spontaneity–construction connection and the key role of *reversibility* in this connection as well as a general discourse on spontaneity-driven processes.

Thermodynamics is a theory of change. As a theory of change it unifies many scientific disciplines: disciplines of macroscopic physics involving mechanical, thermal, electrical, magnetic, radiative phenomena; physical chemistry; bioenergetics. Thermodynamic questions are also important questions in cosmology and evolution, both of which are historical sciences.

Change or process – ever since Heraclitus and Parmenides (and Zeno) – has persistently escaped our full comprehension, and thermodynamics, as a theory of change, proves to be no exception in its inability to provide precise definitions of its basic processes. The evidence of that inability can be seen in the following excerpts from the literature:

> The concept of *reversible processes*, which plays an essential role in many expositions of thermodynamics, is not required in the present approach. Many authors take reversible processes and quasi-static processes to be synonymous terms. Others use both terms with slightly different shades of meaning, and there does not seem to be unanimity on the precise difference between them.
>
> Landsberg ([2], p. 94)

> Whether this atypical (and infamous) ‘continuous free expansion’ process should be considered as quasi-static is a delicate point. On the positive side is the observation that the terminal states of the infinitesimal expansions can be spaced as closely as one wishes along the locus. On the negative side is the realization that the system necessarily passes through

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> nonequilibrium states during each expansion; the irreversibility of the microexpansions is essential and irreducible. The fact that $dS > 0$ whereas $dQ = 0$ is inconsistent with the presumptive applicability of the relation $dQ = TdS$ to all quasi-static processes. We *define* (by somewhat circular logic!) the continuous free expansion process as being 'essentially irreversible' and *non-quasi-static*.
>
> Callen ([3], p. 99)

> The work done during a process depends on the path followed as well as on the properties at the end states. Recall that reversible (quasi-equilibrium [i.e. quasi-static]) moving boundary work associated with closed systems is expressed in terms of the fluid properties as
>
> $$W_b = \int P\, dV$$
>
> We mentioned that the quasi-equilibrium work interactions lead to the maximum work output for work-producing devices and the minimum work input for work-consuming devices.
>
> Cengel and Boles ([4], p. 362)

What these excerpts reveal is extraordinary. Are reversible process and quasi-static process synonymous or not? Is the condition of applicability of the relations $\delta Q = TdS$ and $\delta W = PdV$ that a process is quasi-static? Or, a process is reversible? Cengel and Boles also wrote:

> Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property *entropy*. It is designated *S* and is defined as
>
> $$dS = (\delta Q / T)_{\text{int rev}} (\text{kJ/K})$$
>
> Cengel and Boles ([4], p. 333)

Is, then, the applicability condition for the relations $\delta Q = TdS$ and $\delta W = PdV$ that a process is internally reversible?

Quasi-static, or internally reversible, or reversible? Which one is it? Are they different? Are they synonymous? Does it matter?

2 THE PROBLEM OF CAUSALITY

That Landsberg, Callen, and Cengel and Boles all get lost on these same points suggests that a common source – the way that science has been practiced – is the root of their difficulty.

Science presupposes that (1) nature is not entirely arbitrary or whimsical; there are relations manifest in the world of phenomena; and (2) the relations between phenomena are, at least in part, capable of being perceived and grasped by the human mind, i.e. by the cognitive self. These *presuppositions of science* are named Natural Law by Rosen [5].

Presuppositions of science are the necessary conditions of possibility of empirical science according to Kant. Presuppositions are not scientific propositions. The distinction between truth and falsehood applies to propositions, but that distinction does not apply to presuppositions. The 'truth' of a presupposition formulated on its own cannot be independently established. Nonetheless, presuppositions are *objective* 'organizing conceptions', and a *successful* presupposition choice produces a plausible explanatory body of knowledge. That is, the objectivity of presuppositions is judged by their *pragmatic truth* [6].

Rosen further argued that

> the central concept of Newtonian mechanics, from which all others flow as corollaries or collaterals, is the concept of state, and with it, the effective introduction of recursion as the basic underpinning of science itself. Natural Law [presuppositions of science] does not in itself say anything about recursion, or about states, or even about systems. … Thus, in my view, the *Principia* ultimately mandated thereby the most profound changes in the concept of Natural Law itself; in some ways a sharpening, but in deeper ways, by imposing the most severe restrictions and limitations upon it. …
>
> If indeed analytic atomism is correct, … all of reality is necessarily embedded in the Newtonian synthetic theory. In this way, the synthetic theory *becomes* Natural Law, and that, in a nutshell, is precisely where we are, even today. The Newtonian synthetic theory has of course been extensively generalized, modified, and extended, as we have seen, but only in essentially technical directions; the heart of it [the Newtonian presupposition of science] has not changed. And the heart of it is recursion ([5], pp. 89–90).

The Newtonian presupposition of science is often referred to in physics as the *principle of causality* [7]. ‘This principle has a very definite significance independent of the popular ideas about cause and effect’ ([7], p. 19). Lindsay and Margenau (p. 517) quoted Laplace’s statement, which is considered by many scientists to be the essence of causality,

> An intelligence knowing, at a given instant of time, all forces acting in nature, as well as the momentary positions of all things of which the universe consists, would be able to comprehend the motions of the largest bodies of the world and those of the smallest atoms on one single formula, provided it were sufficiently powerful to subject all data to analysis; to it, nothing would be uncertain, both future and past would be present before its eyes..

They then sought a more precise statement of causality ([7], p. 522):

> Nature is consistent in the sense that she does not alter her ways; her reactions are independent of the time in an absolute manner. We shall refer to this property, which we wish to regard as the most adequate expression of the causality principle, as *consistency of nature*: *the differential equations in terms of which nature is described do not contain explicit functions of the time*.

In their interpretation of causality as consistency of nature Lindsay and Margenau introduced the concept of a *closed system*: ‘We often encounter such equations [which do not satisfy the *consistency of nature* requirement] when a problem is not completely analyzed, for example, in the case of forced oscillations. But here, as well as in all similar instances, the explicit time dependence could be eliminated by including in the analysis those parts of the system which produce the varying force, i.e., by “closing” the system. In fact, a closed system is simply one to which causal analysis can be applied’ ([7], p. 523). That is, a closed system is a physical system stripped off (closed from) any external causation; a closed system is not designed or design-like. ‘By its definition, a closed system is a causal one’ ([7], p. 525).

Lindsay and Margenau equated causality to consistency of nature. By restricting physics and science to ‘closed’ or independent physical systems and presupposing that the whole nature can be treated as such a *closed system* ([7], pp. 523–525), Lindsay and Margenau viewed science as the description of a deterministic nature. Nature is deterministic in the broad sense (i.e. strict determinism of states, but not necessarily of measurements); in this interpretation, deterministic phenomena include radioactivity, quantum phenomena, statistical mechanical phenomena, and even (reproducible) bifurcation phenomena leading to dissipative structures [8].

The way that science has been practiced is thus based on the characterization of a system in terms of its states, and the recursive chronicle of states (the trajectory) as solutions to differential equations. The causal laws of physics in the form of differential equations describe natural phenomena in terms of *constant conjunction* and *invariable succession* (in accordance with the Hume characterization of natural phenomena), not real *causation*.

3 SPONTANEOUS PROCESS, QUASI-EQUILIBRIUM PROCESS, AND REVERSIBILITY IN SCIENCE

This is then how thermodynamic processes – as well as reversible processes – are understood in science. In another paper, I call this understanding 'reversibility in science' [9] (to differentiate it from the understanding of 'reversibility in engineering', as discussed in Section 4; also see Table 1 for the definition of this term and some other terms). Reversibility in science understands reversibility as the condition that prevails at equilibrium states; a reversible change is the limit of a quasi-equilibrium process, defined as a sequence of equilibrium states, when each of the quasi-static steps becomes infinitesimally small [9]. Approaching reversibility in science is understood to be a 'simple limiting process': as a simple limiting process, it is necessary to presume that the limit is well defined and it is also universally presumed that the system in approaching the limit becomes at all times infinitesimally near a state of thermodynamic equilibrium. The trajectory of equilibrium states, therefore, becomes the *fundamental constructs* (see the first edition of [3], p. viii, 1960), which fully characterize the reversible change. Both the presumptions and their inference that states are sole fundamental constructs turn out to be not always true. (See Section 6 for further discussion.)

This kind of (mis)-understanding is widely held because it is consistent with the Newtonian view of a deterministic nature. Spontaneity in nature is inevitably dissipated and all systems will eventually approach equilibrium either as spontaneous processes or, in the idealized depiction of which, as quasi-equilibrium processes. But, the first law and the second law of thermodynamics are not causal laws; their full meaning cannot be captured within the context of causality or deterministic physics. This insight was realized long ago by Poincaré ([10], pp. 122–123):

> [These thermodynamic laws] can have only one significance, which is that there is a property common to all possibilities; but in the deterministic hypothesis there is only a single possibility, and the laws no longer have any meaning. In the indeterministic hypothesis, on the other hand, they would have meaning, even if they were taken in an absolute sense; they would appear as a limitation imposed upon freedom. But these words remind me that I am digressing and am on the point of leaving the domains of mathematics and physics.

The change of a Lindsay and Margenau closed system has only a single possibility, a single possible nomic natural change (again, in the aforementioned broad sense). The system does eventually collapse into chaos. In that case, thermodynamic laws and the differential equations of physics governing the system must be consistent with each other, and thermodynamic laws add no new dimension to our view of nature (or no new 'meaning'). The real meaning of the laws lies in pointing out the existence of other possibilities: besides spontaneous processes there are other kinds of spontaneity-driven processes.

Reversibility in science views reversibility as a quasi-equilibrium change. But, a quasi-equilibrium change is merely the idealization of a spontaneous change – which has nothing in common with the reversibility that Carnot introduced, which I shall call 'reversibility in engineering' [9].

Table 1: Glossary of selected terms.

Spontaneity	The *active* condition of the macroscopic physical world exhibiting a natural tendency to change. Such changes are unidirectional and are said to be in the direction of spontaneity. Spontaneity exists in a nature endowed with *free energy*, which may be used as its metrics.
Spontaneous process	Natural process in the direction of spontaneity.
Quasi-staticity	A dense succession of equilibrium states (see [3], p. 96): this has been mistakenly considered to be the definition of *quasi-static process* (see below).
Quasi-static/quasi-equilibrium process	A 'quasi-equilibrium process' is made up of the set of a dense succession of equilibrium states *and* the second set of transient states between every pair of succeeding equilibrium states. A quasi-equilibrium process is the idealization of a spontaneous process.
Reversibility in science	'Reversibility in science' [9] is understood to be the condition of *microscopic reversibility* which prevails for systems at *equilibrium*. 'Reversibility', in this sense, prevails at each equilibrium state of the first set above; whether there is reversibility, or 'internal reversibility', for the second set is an entirely different question (see Section 6). Overlooking these details, 'reversibility in science' defines a reversible process to be a quasi-equilibrium process and mistakenly concludes that such a process always meet the true reversibility condition.
Useful work	System work is a way or mechanism of transferring energy (heat transfer is another way) between a system and its surroundings; 'useful work' is an energy transfer produced in such a way that a weight could be raised in the surroundings as a result. In general, *useful work = system work – system expanding work against the surroundings*. Both 'work' and 'useful work' are clearly anthropomorphic terms; devices that produce or consume useful work are designed.
Maximum useful work (MUW)	The useful work produced by a system which undergoes a reversible change (in the sense of *reversibility in engineering*, see below). The MUW of a system defined in terms of its final end state at equilibrium with the surroundings is known as the *free energy* of the system.
Reversible process ('reversibility in engineering')	A process that is performed in such a way that, at the conclusion of the process, both the system and the surroundings may be restored to their initial states; this is possible if the process produces MUW. See the sixth paragraph in Section 6 for further details of the reversibility requirements.
Irreversible processes	A process that does not fulfill the stringent requirements of reversibility (in engineering) is said to be irreversible; since no real process does, all real processes, including natural processes, *are* irreversible.

Continued

Table 1: *Continued*

Reversible-like process	A process that is designed to produce or to consume useful work is said to be reversible-like. A reversible-like process [9] may converge toward – but never reach – reversibility when the corresponding useful work approaches MUW. Real reversible-like processes, like real natural processes, are irreversible. The term is introduced to differentiate real reversible-like processes from natural spontaneous processes (which may thus be referred to as non-reversible processes as a contrast term).
Spontaneity-driven processes	All changes in macroscopic nature are driven by spontaneity. There are two types of changes: natural spontaneous changes and reversible-like changes designed to be spontaneity-driven. The former are in the direction of spontaneity only and the latter can be in either direction.

4 REVERSIBILITY IN ENGINEERING, USEFUL WORK, AND REVERSIBLE-LIKE PROCESSES

The second law of thermodynamics asserts that nature is unidirectional: there is a preferred direction in the natural change of a macroscopic system (i.e. a spontaneous change) between two known end states. The law does not prohibit the possibility of changes in the opposite direction, only that such changes against spontaneity cannot take place by themselves.

Such changes need to be made to happen. As Carnot realized from the very beginning – and Poincaré [10] reminded us later – the second law is a law that points out the limit or the constraint of such possibilities as well as suggests the *existence* of these very possibilities. Deterministic hypothesis [10], however, will not produce these new possibilities; *causation*, which is different from causality or determination, is a necessary concept here. In the present context, *useful work* (see Table 1 for definition) is the required efficacy for making things happen. The second law does not say that change against spontaneity cannot take place; only such change requires an input of useful work. (Unlike microscopic processes, which are reversible, all real macroscopic processes are irreversible or dissipative. Hence, changes corresponding to zero-spontaneity also require input of useful work to overcome dissipation.)

From the consequences of the second law and the first law comes a prediction, known as the Maximum Useful Work Theorem. It states that the useful work produced during a reversible change from an initial state to a final state is the maximum possible value among all possible changes between the given end states. The implication is that this maximum value is also the minimum required value to bring about the change when the process is reversed. A reversible change of a system, by producing maximum useful work, can, by the efficacy of this useful work as the required minimum amount, be reversed with the system going back to its initial end state and no change to its surroundings.

Useful work is, therefore, the essence of reversible (in engineering) processes [9] *and reversible-like processes* [9]. The identification of reversible-like processes with useful work production (or consumption) means that reversible-like processes are designed. They do not come into existence spontaneously; they are processes designed to be spontaneity-driven. Approaching reversibility in science is understood to be a simple limiting process; approaching reversibility in engineering, on the other hand, is understood to be an endless process of continuous improvements in design and advances in available materials [9]. Reversibility in science as quasi-equilibrium processes is the idealization of spontaneous changes; reversibility in engineering is the perfection of thermodynamic changes designed to be spontaneity-driven, which succeed in producing maximum useful work.

Useful work is the necessary linkage between spontaneity-driven reversible-like processes and reversible-like processes in the opposite direction of spontaneity. We may view these latter changes as constructive changes. The occurrence of these *constructive* changes is made possible as a result of their being connected through *useful work coupling* to the spontaneity-driven reversible-like processes. Examples of this kind of change include exergonic–endergonic coupling [1, 11] in biological cells. I shall consider two more examples in the next section.

In sum, there are two types of spontaneity-driven processes – non-reversible spontaneous processes and reversible-like processes – each of which can be further classified as follows

1. Non-reversible (spontaneous) processes (in the direction of spontaneity)
    1A. Spontaneous processes toward equilibrium (see Section 6)
    1B. Spontaneous changes from meta-stable equilibrium to equilibrium (see Section 7)
    1C. Spontaneous self-organization in far-from-equilibrium conditions (see Section 7)
    (By definition, all non-reversible processes involve no useful work.)
2. Reversible-like processes
    2A. Reversible-like processes (in the direction of spontaneity) designed to be spontaneity-driven
    2B. Reversible-like processes opposite to spontaneity, which is made possible by being coupled to spontaneity-driven reversible-like processes

Reversibility in engineering is the perfection limit of reversible-like processes. Important reversibility limits [9] are the Carnot limit for the conversion between thermal energy and mechanical energy, the Gibbs limit for the conversion between chemical energy and mechanical or electrical energy, and the Landsberg limit [12, 13] for the conversion of solar radiation energy into electrical or mechanical energy. It is interesting to note that in 1961 Landsberg [2] was mainly concerned with the question of reversibility in science when he wrote the lines quoted in Section 1, whereas in 1980 Landsberg [12] had a different perspective and was concerned with reversibility in engineering.

5 THE CONCEPT OF SPONTANEITY: COMMENT ON THE CLAUSIUS STATEMENT AND THE KELVIN–PLANCK STATEMENT

The classical Clausius statement and the classical Kelvin–Planck statement of the second law, the mathematical statement of the second law, and the law (commonly referred to as the principle) of the increase of entropy are all statements which suggest that *there are preferred directions in the natural processes of the macroscopic world*. Such natural processes are called spontaneous processes. In the Section 4 I have made the inference from the observation of spontaneous processes to the formation of the concept of spontaneity. In this section I shall add further argument toward the objective nature of the concept of spontaneity.

The objective nature of spontaneity rests on the '*equivalence* among the various statements of the second law' and the 'possibility of having a *quantitative measure* of "spontaneity" '. 'If we can disprove the Kelvin statement, the falsity of the Clausius statement is implied, and if we can disprove the Clausius, then farewell Kelvin too' ([1], pp. 26–28). The two statements are famously equivalent to each other as the 'two faces of a single second law' ([1], p. 28). The same sort of equivalence can be demonstrated between any pair of two statements of the second law by constructing an appropriate thought-experiment. When each statement of the second law can be shown to be a 'paraphrase' of the single second law (of which there is perhaps no perfect statement), all of them are explicative nomic statements concerning a single concept – the concept of spontaneity.

The point can be further reinforced with the demonstration that for each 'paradigmatic example' of spontaneity, constructive process against the said spontaneity can be made to happen by being coupled to an appropriate 'spontaneity-driven reversible-like process' (derived from another source of spontaneity). Consider the Clausius statement: 'No process is possible in which the sole result is the transfer of energy from a cooler to a hotter body' ([1], p. 25). Heat (thermal energy) transfers spontaneously from a hot body to a cold body; the transmission of heat from a cooler to a hotter body is against spontaneity. However, the useful work output from a heat engine that is maintained, i.e. spontaneity-driven, by fuel and air can drive a heat pump to facilitate the transmission of heat from a cooler to a hotter body.

The Kelvin–Planck statement of the second law ([1], p. 24): 'No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.' Mechanical energy can be spontaneously converted through friction into thermal energy; the conversion of thermal energy into mechanical energy is against spontaneity. However, the complete conversion of heat into work can be done through the coupling of a heat bath with a gas–vacuum composite system. As depicted in Fig. 1, the spontaneity of the gas–vacuum composite system makes it possible for the gas subsystem within the composite system to expand against a piston absorbing heat from the heat bath as a result of expansion cooling. The absorbed heat maintains the isothermal condition for the gaseous expansion process (thus, the internal energy of the gas subsystem remains constant); the expanding gas absorbs heat from the heat bath and converts the absorbed heat completely into mechanical work.

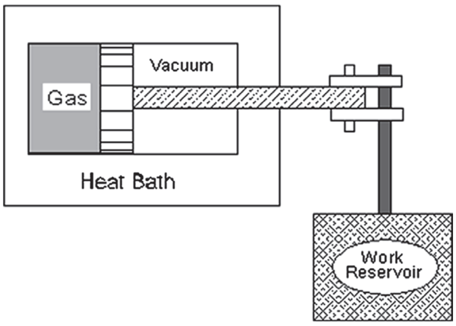

Figure 1: The depiction of a composite system consisting of a gas subsystem and a vacuum subsystem, where the two subsystems are separated by a piston linked to a work reservoir. The composite system is shown in its initial state. The spontaneity of the composite system in the initial state in the form of gas pressure over vacuum will lead to the gaseous expansion against the piston force. If the gaseous expansion is sufficiently slow, the expansion cooling in the gas will be compensated by the absorbed heat from the heat bath; thus, the gaseous expansion remains isothermal – which means that the internal energy of the gas remains constant. All the heat absorbed from the heat bath is converted completely into mechanical, or electrical, energy stored in the work reservoir. The 'impossible' process of the complete conversion of heat from a heat bath into work can be made to happen with the heat bath being coupled to a system – the composite gas–vacuum system – with spontaneity.

Now consider the following. If the initial end state of a system and its final *dead state* (when it is at equilibrium with its surroundings) are characterized by a positive maximum useful work, the system at its initial state is said to have spontaneity – the 'degree' or the 'extent' of the spontaneity is the value of maximum useful work. According to the second law, therefore, a quantitative measure of the spontaneity of a system may be represented by its maximum useful work defined in terms of its dead state, which is also known as the *free energy* of the system.

We may now state the second law in a new perspective as follows: *No spontaneity, no useful work; all macroscopic processes in nature* – including natural processes and reversible-like processes in the direction of spontaneity, and reversible-like processes against spontaneity – *are spontaneity-driven.*

With this understanding of causality, causation, reversibility in science, useful work, reversibility in engineering and reversible-like processes, and spontaneity and spontaneity-driven processes, we shall now provide precise definitions for quasi-staticity, internal reversibility, and reversibility (which henceforth will be understood as reversibility in engineering).

6 QUASI-STATICITY, INTERNAL REVERSIBILITY, AND REVERSIBILITY

Zeno of Elea maintains that motion is merely the collection of positions; there is no such thing as a *state* of motion. Likewise, the principle of causality maintains that change is merely the recursive chronicle of states of a system; there is no such thing as a *state* of change.

A quasi-static process is an idealization of type 1A (non-reversible spontaneous process). We have to step out of the principle of causality, however, and consider that in the quasi-static idealization of a process, a system – by making its process into small steps and representing the system at the end of each step in terms of its equilibrium states – passes through a series of equilibrium states (the first set) *and*, this is important, between each pair of equilibrium states, passes through transient states, which may be 'non-representable non-equilibrium states' [3, 14] (the second set).

One fact that contributes to the confusion is the issue of the *internal reversibility* (IR) condition. IR is not a process but a condition. IR is the condition that prevails *when, and only when*, the second set of transient states becomes 'at all times infinitesimally near' [14] the corresponding pair of equilibrium states of the first set. Note that while the equilibrium states of each pair can always made to be infinitesimally near each other, the merging of the second set into the first set is – surprisingly, in view of Zeno – not automatic.

The second set of a quasi-static process sometimes (e.g. thermal processes) merges into the first set, i.e. the transient states become infinitesimally near the equilibrium states, but in other instances – e.g. mechanical *free expansion* processes ([3], p. 99) and chemical processes – it does not merge into the first set and the transient states remain non-representable and in non-equilibrium.

Parmenides and Zeno hold that change is not real: change is merely the recursive chronicle of states of a system without ontological status. Bergson [15] maintains the opposite doctrine that there must be in the system some *internal state* of change and '*all change as being absolutely indivisible*' [15]. I shall not go so far as Bergson's position on all changes. But some thermodynamic reversible changes are shown to be characterized by their design or control (these attributes define the state, or the essence, of the changes) so that they are fundamentally different from other thermodynamic changes along identical paths [14]. In these cases, the system that is changing is intrinsically different, at each instant, from what it would be if it were in a thermodynamic equilibrium state, which is either unchanging or an equilibrium state of the first set of quasi-equilibrium states. In these cases, Zeno's argument loses its force; thermodynamic change and life processes in the macroscopic irreversible world are real.

It is useful to introduce the conditions of reversibility, IR, and quasi-staticity. Reversibility is synonymous with the reversible process, which is ensured by the condition of having all affinity differences balanced and all affinity gradients kept infinitesimally small. Reversibility means having this condition both within the system (internally reversible) and outside the system (externally reversible).

Reversibility, thus, is a subset of IR, which is defined above. Quasi-staticity is the condition that a system passes through a series of equilibrium states, i.e. the first set of states of a quasi-static process. (Quasi-staticity, therefore, is not synonymous with quasi-static process.) It is clear then that IR is a subset of quasi-staticity. The relationship of reversibility, IR, and quasi-staticity is illustrated by Fig. 2. We are reminded in Fig. 3 that reversible processes (and reversible-like processes, see Fig. 4) and quasi-static processes are different processes. The condition of IR is superimposed on the two distinctive processes in both figures to show that while a reversible process always meets the IR condition, some quasi-static processes do and others do not. Some reversible-like processes such as an ideal Rankine cycle meet IR as well (see Fig. 4). *Reversible-like processes (of both type 2A and 2B) are shown in Fig. 4 as an expanding domain to signify that reversible-like processes in nature are continuously constructed and created.*

IR is the necessary and sufficient condition [14] for the applicability of

$$\delta Q = TdS \quad \text{and} \quad \delta W = PdV.$$

The applicability of the two relations facilitates energy analyses of thermodynamic systems when the systems meet IR exactly or only approximately.

More important than making analyses tractable (and indeed prior to the possibility of such analyses), the condition of IR is essential in the development of thermodynamic theory to its logical completion. Thermal processes such as quasi-static heating from absolute zero kelvin to room temperature can be made to satisfy IR. This enables the determination of entropy values for most chemical species.

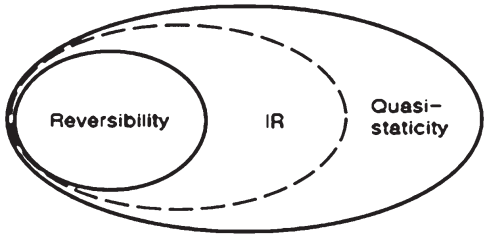

Figure 2: Venn diagram of reversibility, IR, and quasi-staticity.

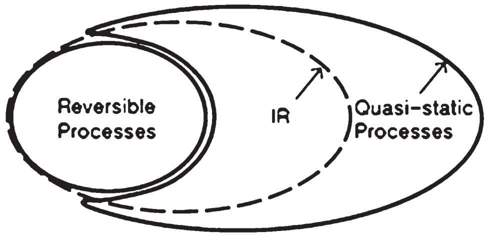

Figure 3: Venn diagram of reversible processes and quasi-static processes, with the condition of IR superimposed.

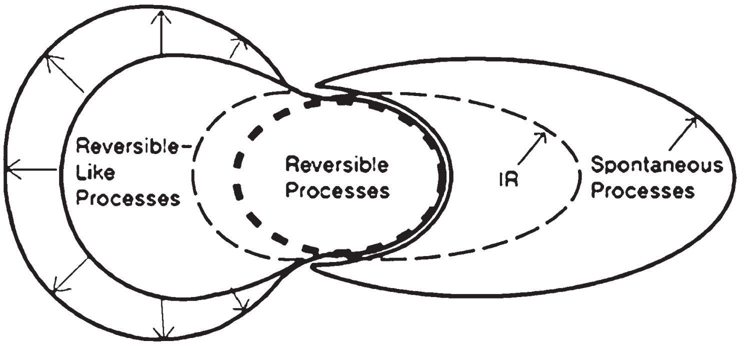

Figure 4: Venn diagram of reversible-like processes and non-reversible (spontaneous) processes. The domain of spontaneous processes here includes all three sub-types of spontaneous processes – 1A, 1B, and 1C. Reversible-like processes are shown to be an expanding domain, signifying that reversible-like processes are continuously created and constructed. IR is shown to overlap a part of reversible-like processes to represent idealized practical reversible-like processes such as an ideal Rankine cycle. Even an idealized 'air-standard' Otto cycle may be considered as an internally reversible reversible-like cycle in that overlapped domain.

7 THE PROBLEM OF PATTERN FORMATION

There are two other sub-types of spontaneous processes. Type 1B spontaneous processes are the fast state-transition processes from meta-stable equilibrium states to stable equilibrium phases (or, to equilibrium broken-symmetry states [16], or macromolecules of apparent complex structures [1]). These transitions are spontaneous phenomena of systems seeking lower energy (free energy) states, leading to new patterns.

In recent times, a third sub-type of spontaneous (nomic natural) processes (1C) – spontaneous self-organization processes in far-from-equilibrium conditions – has attracted intense interest. This interest grew out of constructing an explanatory framework of life processes as 'self-organized processes' or 'orderly events'. In 1944, Schrödinger ([17], p. 80) made the observation

> It appears that there are two different 'mechanisms' by which orderly events can be produced: the 'statistical mechanism' which produces 'order from disorder' and the new one, producing 'order from order'.

Genetic theory on the basis of molecular biology has answered the 'order from order' question posed by Schrödinger. Spontaneous self-organization has the potential of answering his other question of 'order from disorder'.

On this issue, I shall mention only two groups of researchers: the Brussels School [8, 18, 19], which introduces the phrase *dissipative structures*, and a group of researchers with strong interest in the Earth system [20–22], which links dissipative structures to the maximum entropy production (MEP) principle. 'Structural instability may progressively drive far-from-equilibrium systems to higher states of entropy production and higher states of order' [19]. According to MEP [20–22], self-organization processes in far-from-equilibrium conditions lead to *rate increase of entropy-production*. In this regard, type 1C similarly describes, as type 1B does, spontaneous pattern-formation phenomena of systems seeking lower system free energy states, and correspondingly, higher total entropy.

However, type 1C describes changes leading to not only higher total entropy but also to a higher rate of entropy production. Furthermore, these systems are in far-from-equilibrium conditions. 'Structural patterns' and 'far-from-equilibrium conditions': herein are the main attractions of the theories, since living systems are organizations with patterns and can only exist far from equilibrium. However, such theories face two issues.

Structures of living systems are stable and persistent. Anderson and Stein [23] have raised the question on the issue of structure, 'Is there a theory of *dissipative structures* comparable to that of equilibrium structures, explaining the existence of new, stable properties and entities in such systems? … We believe that there is *no such theory*, and it even may be that there are no such [stable and persistent, dissipative] structures as they are implied to exist by Prigogine, Haken, and their collaborators.' Atkins ([1], pp. 198–199) also wrote, 'the coherence is intrinsically transient, and crumbles into incoherence when the structure ceases to be driven by a flow of energy'.

The second issue is the rate change of entropy production. The rate change of entropy production is not the inevitable necessity of the entropy law, but the outcome of the types of macroscopic processes. While type 1C self-organization processes lead to higher and higher rate of entropy production, processes of type 2A coupled with type 2B hint at the possibility of a scenario of decreasing rate of entropy production, thus, enabling the creation of suitable conditions (of a free energy reservoir) for the Earth system – so that the Earth system endowed with suitable high free energy conditions may undergo the occasional spontaneous 'pattern formation' transitions toward the states of lower free energy. The possibilities of a different understanding of pattern formation should make it worthwhile to study the implication of this idea.

The suggestion made above may be expressed by paraphrasing Schrödinger with a key change

> It appears that there are two different 'mechanisms' by which orderly events can be produced: the '*reversible-like mechanism*' which produces 'order from disorder' and the 'genetic mechanism of molecular biology', producing 'order from order'.

8 THE TWO FACES OF THE ENTROPY LAW

There is spontaneity in the unidirectional nature. I have shown, in contrast to the unchanging 'block universe' of the microscopic world, the essential reality of change in the macroscopic irreversible world, and that all macroscopic changes are, directly or indirectly, spontaneity-driven. Although all macroscopic processes are spontaneity-driven, machines and machine operation are the kinds of macroscopic processes that can only be comprehended – not as (non-reversible) spontaneous processes, but – as reversible-like processes *designed* to be spontaneity-driven, the essence of which is the production and/or consumption of useful work. The entropy law does not prohibit change opposite to spontaneity, only that such change cannot happen by itself; in fact, the law points out the possibilities of constructive processes [1, 10, 11], which are coupled to reversible-like processes that are directly driven by spontaneity in nature. On Earth with the abundance of life, destruction precedes construction and destruction follows construction; destruction and construction are the manifestation of the two faces of the entropy law.

In closing, I offer the following two quotes (which together echo Poincaré's insight) from the Foreword of a wonderful little book *Engines, Energy, and Entropy* [24]:

> Poetry is about imaginary gardens with real toads in them. (Marianne Moore)
>
> Thermodynamics examines imaginary processes and thereby defines what is possible in our real physical world. (D. Herschbach, 1981)

Thermodynamic laws define the imaginary garden of possibilities; reversible-like processes make the possible into the actual.

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