Geno-nonequilibrium thermodynamics. I. Background and preparative aspects

Anil A. Bhalekar[1]

[1] Shanti Niketan Colony, Pallavi Apartments, Rana Pratap Nagar, NAGPUR - 440 022, India.; Department of Chemistry, R. T. M. Nagpur University, Amravati Road Campus, NAGPUR - 440 033, India, and Thunder Fusion Corporation, 150 Rainville Road, Tarpon Springs, FL 34689, U. S. A., and Institute for Theoretical Physics and Advanced Mathematics (IFM) Einstein-Galilei, via Santa Gonda 14 - 59100 PRATO, Italy

⋆ *Corresponding Author*. E-mail: anabha@hotmail.com

Abstract. Following decades of research, R. M. Santilli [1-5] has achieved a genotopic (that is, axiom inducing) lifting of 20th century mathematics with a Lie algebra structure as used for reversible systems into a covering Lie-admissible form which is irreversible beginning with basic multiplications and related units, today is known as *Santilli genomathematics*. However, its advantage has not been imparted, so far, to the field of thermodynamics of irreversible processes. Therefore, it is express to base thermodynamics of irreversible processes on genomathematics. The problems in the time reversal symmetry of the relevant dynamical mathematical equations has been discussed in support of the need to use genotopic branch of Santilli's new mathematics. We already have a host of nonequilibrium thermodynamic frameworks but they have certain basic shortcomings. The main point that we have discussed is the misconception in the postulation of *local equilibrium assumption* (LEA) in the sense it has been used in classical irreversible thermodynamics. In order to strengthen our claim we have described the thermodynamic meaning of equilibrium and reversibility vis-à-vis the traditional Gibbs relation. This shows that the traditional prescription of LEA is not a physical reality. For the sake of self-sufficiency we have availed this opportunity to describe in brief the basic structure of the new mathematics namely, iso-, geno-, hyper- and their isodual-mathematics.

1 Introduction

Following decades of research, R. M. Santilli [1] has achieved a genotopic (that is, axiom inducing) lifting of 20th century mathematics with a Lie algebra structure as used for reversible systems into a

covering Lie-admissible form which is irreversible beginning with basic multiplications and related units, known as *Santilli genomathematics,* which is particularly suited for quantitative treatment of thermodynamical processes of matter due to their irreversibility. Santilli has also identified an important subclass of genomathematics, also used for the description of thermodynamical processes of matter, which is an isotopic (that is, axiom-preserving) lifting of 20th century Lie mathematics with a Lie-isotopic structure, today known as *Santilli's isomathematics.* Finally, Santilli has discovered an anti-Hermitean map, called isoduality, for the description of antimatter, resulting in the novel *isodual genomathematics* and *isodual isomathematics,* that have permitted the first known initiation of thermodynamical studies for antimatter. To avoid a prohibitive length, we assume a technical knowledge of geno- and iso-mathematics for matter and their isoduals for antimatter as presented in Refs. [1-5]. Also Santilli proved the following basic theorem, namely:

NO REDUCTION THEOREM:

A classical system that is irreversible over time cannot be consistently reduced to a finite number of elementary particles all reversible over time and, vice-versa, a finite number of elementary particles all in reversible conditions cannot yield a macroscopic irreversible event under the correspondence or other principles.

The above theorem has far reaching implications on bridging macroscopic and microscopic domains of physical descriptions.

On the other hand, it is also a fact that while developing nonequilibrium thermodynamic frameworks no attempts were made to perform the vital test of the time reversal symmetry, instead the positive definiteness of the source of entropy was taken as conforming to the observed unidirectionality of time's arrow during irreversible processes. In view of this shortcoming it has now become express to reframe thermodynamics of irreversible processes using geno-mathematics. The present author has already responded to this demand by initiating the corresponding investigations. A short description of our preliminary attempts have been discussed recently [6] and a more detailed matter on this subject was presented [7] at the Seminar Course on Hadronic Mechanics held as a part of ICNAAM-2012 during September 19-25, 2012 at KOS, Greece. In this sequel the details of our further investigations are presented in two articles. The present one describes the background and some preparative aspects of developing geno-nonequilibrium thermodynamics and the following paper [8] describes the ab initio development of geno- version of generalized phenomenological irreversible thermodynamic theory (GPITT) [9-12].

In order not to fell pray, while developing a geno-nonequilibrium thermodynamic framework, to the trap in which the existing nonequilibrium thermodynamic frameworks got trapped we are discussing some what in details the relevant basic thermodynamic and dynamical aspects. That is, the present article dwells over on some of the relevant fundamental aspects i) of equilibrium thermodynamics including that of open systems, ii) of the nonequilibrium thermodynamic frameworks so far developed and iii) of the Newtonian mechanics and fluid dynamics including that of time reversal symmetry. This exercise clearly surfaces out to what extent and level the ambiguities exist in nonequilibrium thermodynamic literature and also insufficiency of traditional Newtonian mechanics and fluid dynamics gets once again revealed in conformity with Santilli's assertions.

Thus the sequence of the subject matter of this paper is as follows. In Section 2 we have highlighted the mess in time reversal symmetry of relevant mathematical dynamical descriptions, Section 3 discusses the shortcomings and advances of existing nonequilibrium thermodynamic formulisms particularly the misconception in the proposal of LEA, the relevant aspects of equilibrium thermody-

namics are discussed in Section 4, Section 5 contains a brief exposition of Santilli's new mathematics for the sake of ready reference and the concluding remarks constitutes Section 6. There is an appendix devoted to a brief and relevant discussion of CIT and the additional examples of the contradictions in the existing nonequilibrium thermodynamic frameworks including the so-called kinetic theory justification of LEA.

2 The Relevant Aspects of Time Reversal Symmetry

We first briefly describe the thermodynamic meaning of reversibility in the following subsection and then we will proceed to the aspects of time reversal symmetry.

2.1 Thermodynamic Reversibility

The *thermodynamic reversibility* gets mathematically described as follows.

$$dS = \frac{dQ}{T} \implies (-dS) = \frac{(-dQ)}{T} \implies dS = \frac{dQ}{T}$$
$$dU = dQ - p\,dV \implies (-dU) = (-dQ) - p\,(-dV)$$
$$\implies dU = dQ - p\,dV$$
$$dU = T\,dS - p\,dV \implies (-dU) = T\,(-dS) - p\,(-dV)$$
$$\implies dU = T\,dS - p\,dV \tag{2.1}$$

Notice that dQ is the amount of heat exchanged by the system in the forward direction and $(-dQ)$ is that in the reverse direction, but dQ is not the state function. Thus an equilibrium state of a closed system is described by any two state functions out of the four offered by $dU = T\,dS - p\,dV$, namely U, S, V, T, p but in this list obviously dQ doesn't appear.

This is an amazing outcome that demonstrates the *tight hold of the laws of thermodynamics on a state of the given system in equilibrium*. Indeed, this result is well tested in laboratory (see for example [13, 14]).

Thus a *thermodynamic reversible path* is the one on which a system can be equally carried along forward and reverse directions that guarantees the system to assume the identically same equilibrium states but in reverse order on reversing the transition. Hence on reversing the transition the magnitudes of heat and work exchanged by the system simply change their signs without altering their magnitudes. *Notice that this thermodynamic reversibility is not a result of the act of time reversal as there is no time parameter involved.*

2.2 Time Reversal Symmetry of Dynamical Systems

As stated above, one of the the serious shortcomings of thermodynamic equations as applied to the irreversible processes pertains to the time reversal symmetry test. On the other hand one uses Newtonian dynamics for the molecular motion to arrive at the irreversibility in the form of Boltzmann H-theorem [15-18], which is the well documented paradox. That is, the fundamental equations of motion of any conservative dynamical system, e.g. a monatomic gas, are Newton's, Lagrange's or Hamilton's equations. These equations are invariant to the substitution of $-t$ for t; or in other words, they are symmetric to time reversal but the H-theorem and the Boltzmann equation [15-18] violate

this symmetry. Hence let us discuss this vital aspect to understand why Newton's, Lagrange's or Hamilton's equations based descriptions are not suitable for developing a nonequilibrium thermodynamic framework. In doing so it also gets revealed that in good number of dynamical descriptions the time reversal symmetry remains ambiguous because they contain terms originating from the existing irreversibility.

The physical meaning of time reversal symmetry gets explained by the following simple experiment. Let us throw a stone vertically up. It goes up, becomes momentarily stationary at a certain height and then comes down. This motion is described by the Newtonian dynamics. If we had taken the movie of this motion of the stone and run the movie in reverse direction then we find that this reverse motion too is described by the same Newtonian dynamics. Hence we say that the corresponding dynamical equations are time reversal symmetric. Instead of taking movie of a motion the time reversal invariance test is performed by replacing t by $-t$ at a fixed position coordinate ($\mathbf{r} \to \mathbf{r}$). As a result the velocity vector also changes sign ($\mathbf{u} \to -\mathbf{u}$). Now let us denote the time reversal operation by $\overset{T}{\Longrightarrow}$ and operate on the velocity vector. How the sign of velocity vector changes is shown below,

$$\frac{d\mathbf{r}}{dt} = \mathbf{u} \overset{T}{\Longrightarrow} \frac{d\mathbf{r}}{d(-t)} = -\frac{d\mathbf{r}}{dt} = -\mathbf{u}$$

Thus the time reversal operation means $(\mathbf{r}, \mathbf{u}, t) \Rightarrow (\mathbf{r}, -\mathbf{u}, -t)$ and we denote it by $\overset{T}{\Longrightarrow}$.

On the other hand, the time reversal operation $\overset{T}{\Longrightarrow}$ can be executed at any stage of the motion and its result would be the reversal of motion both in space and in time. However, this is a paper and pencil operation because for the observer time is still increasing. At the same time the velocity vector has changed sign hence the dynamical states of the so-called reversed motion are not identically same as the ones of the actual forward motion. Hence, the two trajectories are not obtained as identically the same once when viewed in space-time space. Thus *the time reversed motion is an imaginary motion*. That is, *the time reversal operation is not a physical reality*. However, it seemingly appears that the time reversal operation gives an opportunity to *visualize past situations* without actually going into the past as going into the past is impossible.

Moreover, we will see below that there are *a large number of dynamic situations whose traditional mathematical descriptions when subjected to the time reversal operation produces ambiguous results*. This then further questions the *very basis of time reversal operation from its physical utility point of view*.

Below we consider the basic and some derived fluid dynamical equations and perform on them the time reversal operation to see whether they are symmetric or not to this operation.

2.3 Time Reversal Invariant Equations

1. **Basic Equations**:
   a) Relation between convective and local time derivatives:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \overset{T}{\Longrightarrow} \frac{d}{d(-t)} = \frac{\partial}{\partial(-t)} + (-\mathbf{u}) \cdot \nabla$$

$$\Rightarrow \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla$$

   b) Relation between convective and local time derivatives of mass density, ρ:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \mathbf{u}\cdot\nabla\rho \xRightarrow{T} \frac{d\rho}{d(-t)} = \frac{\partial\rho}{\partial(-t)} + (-\mathbf{u})\cdot\nabla\rho$$

$$\Rightarrow \frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \mathbf{u}\cdot\nabla\rho$$

c) Relation between convective and local time derivatives of velocity vector, $\mathbf{u}$:

$$\frac{d\mathbf{u}}{dt} = \frac{\partial\mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u} \xRightarrow{T} \frac{d(-\mathbf{u})}{d(-t)} = \frac{\partial(-\mathbf{u})}{\partial(-t)} + (-\mathbf{u})\cdot\nabla(-\mathbf{u})$$

$$\Rightarrow \frac{d\mathbf{u}}{dt} = \frac{\partial\mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u}$$

d) Relation between Lagrangian and Eulerian dynamics of a property, say z, a per unit mass quantity:

$$\rho\frac{dz}{dt} = \frac{\partial\rho z}{\partial t} + \nabla\cdot(\rho z\mathbf{u}) \xRightarrow{T} \rho\frac{dz}{d(-t)} = \frac{\partial\rho z}{\partial(-t)} + \nabla\cdot(\rho z(-\mathbf{u}))$$

$$\Rightarrow \rho\frac{dz}{dt} = \frac{\partial\rho z}{\partial t} + \nabla\cdot(\rho z\mathbf{u})$$

2. **Equations of Continuity**:
   a) Eulerian equation:

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\mathbf{u}) \xRightarrow{T} \frac{\partial\rho}{\partial(-t)} = -\nabla\cdot(\rho(-\mathbf{u}))$$

$$\Rightarrow \frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\mathbf{u})$$

   b) Lagrangian equation:

$$\frac{d\rho}{dt} = -\rho\nabla\cdot\mathbf{u} \xRightarrow{T} \frac{d\rho}{d(-t)} = -\rho\nabla\cdot(-\mathbf{u})$$

$$\Rightarrow \frac{d\rho}{dt} = -\rho\nabla\cdot\mathbf{u}$$

   c) Lagrangian equation in terms of specific volume, $v = \rho^{-1}$:

$$\rho\frac{dv}{dt} = \nabla\cdot\mathbf{u} \xRightarrow{T} \rho\frac{dv}{d(-t)} = \nabla\cdot(-\mathbf{u})$$

$$\Rightarrow \rho\frac{dv}{dt} = \nabla\cdot\mathbf{u}$$

3. **Rigid Body Motion**:
   Now assume that only the conservative body forces act upon a rigid body in motion, that means:

$$\mathbf{F} = -\nabla\psi, \quad \frac{\partial\psi}{\partial t} = 0, \quad \frac{\partial\mathbf{F}}{\partial t} = 0$$

   a) Equation of motion in Eulerian form:

$$\frac{\partial\rho\mathbf{u}}{\partial t} = -\nabla\cdot(\rho\mathbf{u}\mathbf{u}) + \rho\mathbf{F}$$

$$\xRightarrow{T} \frac{\partial\rho(-\mathbf{u})}{\partial(-t)} = -\nabla\cdot(\rho(-\mathbf{u})(-\mathbf{u})) + \rho\mathbf{F}$$

$$\Rightarrow \frac{\partial\rho\mathbf{u}}{\partial t} = -\nabla\cdot(\rho\mathbf{u}\mathbf{u}) + \rho\mathbf{F}$$

b) Equation of motion in Lagrangian form:

$$\rho \frac{d\mathbf{u}}{dt} = \rho \mathbf{F} \overset{T}{\Longrightarrow} \rho \frac{d(-\mathbf{u})}{d(-t)} = \rho \mathbf{F}$$

$$\Rightarrow \rho \frac{d\mathbf{u}}{dt} = \rho \mathbf{F}$$

c) Kinetic energy balance equation in Eulerian form:

$$\frac{\partial \frac{1}{2}\rho \mathbf{u}^2}{\partial t} = -\nabla \cdot \left(\frac{1}{2}\rho \mathbf{u}^2 \mathbf{u} \right) + \rho \mathbf{F} \cdot \mathbf{u}$$

$$\overset{T}{\Longrightarrow} \frac{\partial \frac{1}{2}\rho \mathbf{u}^2}{\partial (-t)} = -\nabla \cdot \left(\frac{1}{2}\rho \mathbf{u}^2(-\mathbf{u}) \right) + \rho \mathbf{F} \cdot (-\mathbf{u})$$

$$\Rightarrow \frac{\partial \frac{1}{2}\rho \mathbf{u}^2}{\partial t} = -\nabla \cdot \left(\frac{1}{2}\rho \mathbf{u}^2 \mathbf{u} \right) + \rho \mathbf{F} \cdot \mathbf{u}$$

d) Kinetic energy in Lagrangian form:

$$\rho \frac{d\frac{1}{2}\mathbf{u}^2}{dt} = \rho \mathbf{F} \cdot \mathbf{u} \overset{T}{\Longrightarrow} \rho \frac{d\frac{1}{2}\mathbf{u}^2}{d(-t)} = \rho \mathbf{F} \cdot (-\mathbf{u})$$

$$\Rightarrow \rho \frac{d\frac{1}{2}\mathbf{u}^2}{dt} = \rho \mathbf{F} \cdot \mathbf{u}$$

e) Potential energy in Eulerian form:

$$\frac{\partial \rho \psi}{\partial t} = -\nabla \cdot (\rho \psi \mathbf{u}) - \rho \mathbf{F} \cdot \mathbf{u}$$

$$\overset{T}{\Longrightarrow} \frac{\partial \rho \psi}{\partial (-t)} = -\nabla \cdot (\rho \psi(-\mathbf{u})) - \rho \mathbf{F} \cdot (-\mathbf{u})$$

$$\Rightarrow \frac{\partial \rho \psi}{\partial t} = -\nabla \cdot (\rho \psi \mathbf{u}) - \rho \mathbf{F} \cdot \mathbf{u}$$

f) Potential energy in Lagrangian form:

$$\rho \frac{d\psi}{dt} = -\rho \mathbf{F} \cdot \mathbf{u} \overset{T}{\Longrightarrow} \rho \frac{d\psi}{d(-t)} = -\rho \mathbf{F} \cdot (-\mathbf{u})$$

$$\Rightarrow \rho \frac{d\psi}{dt} = -\rho \mathbf{F} \cdot \mathbf{u}$$

g) Total mechanical energy in Eulerian form:

$$\frac{\partial \rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right)}{\partial t} = -\nabla \cdot \left[\rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right) \mathbf{u} \right]$$

$$\overset{T}{\Longrightarrow} \frac{\partial \rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right)}{\partial (-t)} = -\nabla \cdot \left[\rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right) (-\mathbf{u}) \right]$$

$$\Rightarrow \frac{\partial \rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right)}{\partial t} = -\nabla \cdot \left[\rho \left(\frac{1}{2}\mathbf{u}^2 + \psi \right) \mathbf{u} \right]$$

h) Total mechanical energy in Lagrangian form:

$$\rho\frac{d\left(\frac{1}{2}\mathbf{u}^2+\psi\right)}{dt}=0$$

i) Total energy, e (per unit mass), in Eulerian form:

$$\frac{\partial\rho e}{\partial t}=-\nabla\cdot(\rho e\mathbf{u})-\nabla\cdot\mathbf{J}_e$$

$$\overset{T}{\Longrightarrow}\frac{\partial\rho e}{\partial(-t)}=-\nabla\cdot(\rho e(-\mathbf{u}))-\nabla\cdot(-\mathbf{J}_e)$$

$$\Rightarrow\frac{\partial\rho e}{\partial t}=-\nabla\cdot(\rho e\mathbf{u})-\nabla\cdot\mathbf{J}_e$$

Notice that the the conductive flux, $\mathbf{J}_e$, has been assumed to reverse its sign on time reversal as it is a flux. However, we will see below while discussing corresponding internal energy balance equation that the time reversal antisymmetry for the heat flux density is not an unambiguous choice and hence same remains true of $\mathbf{J}_e$ as it is none else than the heat flux density.

j) Total energy in Lagrangian form:

$$\rho\frac{de}{dt}=-\nabla\cdot\mathbf{J}_e\overset{T}{\Longrightarrow}\rho\frac{de}{d(-t)}=-\nabla\cdot(-\mathbf{J}_e)$$

$$\Rightarrow\rho\frac{de}{dt}=-\nabla\cdot\mathbf{J}_e$$

k) The internal energy, u (per unit mass), is given by:

$$u=e-\left(\frac{1}{2}\mathbf{u}^2+\psi\right)$$

Hence, internal energy in Eulerian form reads as:

$$\frac{\partial\rho u}{\partial t}=\frac{\partial\rho\left(e-\left(\frac{1}{2}\mathbf{u}^2+\psi\right)\right)}{\partial t}=-\nabla\cdot(\rho u\mathbf{u}+\mathbf{J}_u)$$

where the convective flux of internal energy gets quantified as: $\rho u\mathbf{u}=\rho\left(e-\left(\frac{1}{2}\mathbf{u}^2+\psi\right)\right)\mathbf{u}$ whereas in the present case there is no conductive flux of mechanical energy hence $\mathbf{J}_e=\mathbf{J}_u$.

Therefore, the time reversal operation produces,

$$\frac{\partial\rho u}{\partial t}=-\nabla\cdot(\rho u\mathbf{u}+\mathbf{J}_u)\overset{T}{\Longrightarrow}\frac{\partial\rho u}{\partial(-t)}=-\nabla\cdot(\rho u(-\mathbf{u})+(-\mathbf{J}_u))$$

$$\Rightarrow\frac{\partial\rho u}{\partial t}=-\nabla\cdot(\rho u\mathbf{u}+\mathbf{J}_u)$$

Notice that $\mathbf{J}_u$ also has been assumed to changes its sign on time reversal as it is none else but the $\mathbf{J}_e$ in the present case.

l) The Lagrangian form of internal energy balance equation in the present case reads as:

$$\rho\frac{du}{dt}=-\nabla\cdot\mathbf{J}_u=-\nabla\cdot\mathbf{q}$$

Thus $\mathbf{J}_u$ is nothing else but the heat flux density, $\mathbf{q}$.

i. Now we have,

$$\rho\frac{du}{dt} \overset{T}{\Longrightarrow} \rho\frac{du}{d(-t)} = -\rho\frac{du}{dt}$$

it implies that: $-\nabla \cdot \mathbf{q} \overset{T}{\Longrightarrow} -(-\nabla \cdot \mathbf{q})$

this can happen only when: $\mathbf{q} \overset{T}{\Longrightarrow} -\mathbf{q}$.

ii. However, one may have another argument, viz. *the empirical Fourier law*, $\mathbf{q} = -\lambda\nabla T$, *would allow the change of the sign of* $\mathbf{q}$ *only if* ∇T *changes sign. But the time reversal operation leaves the sign of* ∇T *unchanged, therefore,* $\mathbf{q}$ *will remain invariant on time reversal.*

iii. In view of the above two options let us consider Maxwell-Cattaneo-Vernotte (MCV) equation [19, 20], namely:

$$\tau\frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda\nabla T$$

where τ is the relaxation time and λ is the thermal conductivity. However, in both the above options for heat flux density the MCV equation is obtained as not time invariant, as shown below:

$$\tau\frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda\nabla T \overset{T}{\Longrightarrow} \tau\frac{d(-\mathbf{q})}{d(-t)} + (-\mathbf{q}) = -\lambda\nabla T$$

$$\Rightarrow \tau\frac{d\mathbf{q}}{dt} - \mathbf{q} = -\lambda\nabla T$$

or

$$\tau\frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda\nabla T \overset{T}{\Longrightarrow} \tau\frac{d\mathbf{q}}{d(-t)} + \mathbf{q} = -\lambda\nabla T$$

$$\Rightarrow -\tau\frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda\nabla T$$

However, the MCV equation, with positive t, may be considered as a description that describes approach to corresponding NSS and hence at NSS $\left(\frac{d\mathbf{q}}{dt} = 0\right)$ MCV equation correctly produces the Fourier law. While on the time reversed path we see from above that the Fourier law is not recovered if $\mathbf{q}$ has changed its sign. Therefore, *does it indicate that* $\mathbf{q}$ *is time reversal invariant?*

iv. Moreover, in kinetic theory [15-18] the expression of heat flux is $\mathbf{q} = \overline{\rho\frac{1}{2}C^2\mathbf{C}}$ for a non-uniform monatomic gas, where $\mathbf{C}(= \mathbf{c} - \mathbf{u})$ is the chaotic velocity of a molecule and $\mathbf{c}$ is the molecular velocity. In view of this definition $\mathbf{C}$ would change its sign on time reversal as the sign of both $\mathbf{c}$ and $\mathbf{u}$ changes on time reversal. Therefore, $\mathbf{q} = \overline{\rho\frac{1}{2}C^2\mathbf{C}}$ would change it sign on time reversal.

v. Furthermore, in classical irreversible thermodynamics (CIT) [21-33] the entropy source strength, σ_s, due to heat transfer is quantified as $\sigma_s = \mathbf{q} \cdot \nabla T^{-1} > 0$. Thus if on time reversal $\mathbf{q}$ changes its sign then the second law of thermodynamics appears to stand violated on

the time reversed path. Whereas, in extended irreversible thermodynamics (EIT) [34-49] we have $\sigma_s = \beta_{\mathbf{q}}\mathbf{q}^2 > 0$ hence even if $\mathbf{q}$ changes sign on time reversed path the second law is not violated.

vi. We need to recall at this juncture that when a system is evolving with time at every stage of it the second law of thermodynamics guarantees positive definite value of entropy source strength. Hence in past too, of the evolution, the entropy source strength was positive. Therefore, if the time reversal leads us to a past situation the entropy source strength should remain positive definite but this condition is not met by the CIT given expression of entropy source strength. *This then indicates that CIT has erred in accommodating spatial non-uniformity in the thermodynamic prescription of local equilibrium via the traditional Gibbs relation but in time rate form.* This is yet another demonstration that establishes the non-compatibility [12, 50] of the traditional Gibbs relation even in time rate form [21],

$$\frac{du}{dt} = T\frac{ds}{dt} - p\frac{dv}{dt} + \sum_k \mu_k \frac{dx_k}{dt}$$

with the internal energy balance equation given by fluid dynamics [51], for example:

$$\rho\frac{du}{dt} = -\nabla \cdot \mathbf{q} - p\rho\frac{dv}{dt} + \Pi : \nabla\mathbf{u}$$

where in preceding two equations u, s and v are the per unit mass quantities namely internal energy, entropy and volume respectively, μ_k is the chemical potential per unit mass of the component k, x_k is the mass fraction of the component k, p is the local pressure, ρ is the local mass density, ■ is the viscous stress tensor and $\mathbf{u}$ is the barycentric velocity. This aspect has been further illustrated in Section 3.1.

vii. The preceding argument when applied to the entropy source strength given by EIT we find that even on the time reversed path second law is not flouted. However, it does'nt mean that the time reversal operation in this case yields the entropy source strength that of the past situations. This is so because the sign of the heat flux even in the past was same as that when the time reversal is effected. This simply means that the act of time reversal produces entirely different trajectory on which the system gets carried that too only on paper. The reason for this can be traced on the one hand due to the existence of thermodynamic irreversibility and as stated above because the direction of heat flux gets reversed meaning thereby that the dynamical states have also changed.

From the above elaboration there emerges a strong indication that *in general $\mathbf{q}$ is not time reversal symmetric and hence the MCV equation is not time reversal symmetric*. But this is not the unambiguous option because *the Fourier law, $\mathbf{q} = -\lambda\nabla T$, and the CIT based expression of the second law of thermodynamics, $\sigma_s = \mathbf{q} \cdot \nabla T^{-1} > 0$, do suggest that $\mathbf{q}$ is time reversal symmetric* (though the Fourier law is a description at a nonequilibrium stationary state but in CIT it is freely used also for the systems evolving in time!!) and on using this conclusion the MCV equation would not be time reversal invariant.

2.4 Time Reversal Non-invariant Equations

A Viscous Fluid in Motion:

- In this case the Eulerian form of momentum balance equation is:

$$\frac{\partial}{\partial t}(\rho\mathbf{u}) = -\nabla\cdot(\rho\mathbf{uu}-\mathbf{T})+\rho\mathbf{F} \tag{2.2}$$

where $\mathbf{T}$ is the stress tensor, which measures the non-convective momentum flux density and alternately measures the normal and tangential forces per unit area. To be specific, the component, T_{ij}, of the stress tensor quantify the following:

$$\begin{aligned}T_{ij} = &\ (i-\text{component of force per unit area}\\ &\ \text{across a surface perpendicular to }\mathbf{e}_j)\\ = &\ (i-\text{component of momentum that crosses}\\ &\ \text{a unit area which is perpendicular to }\mathbf{e}_j, \text{per unit}\\ &\ \text{time, with the crossing being from}-x^j\text{ to }+x^j)\end{aligned}$$

- The corresponding equation in Lagrangian form reads as:

$$\rho\frac{d}{dt}(\mathbf{u}) = \nabla\cdot\mathbf{T}+\rho\mathbf{F} \tag{2.3}$$

With the above physical explanations of $\mathbf{T}$ we are led to the following conclusions about its time reversal symmetry.

1. Now as the components of $\mathbf{T}$ represent forces then on time reversal it should not change sign. Whereas the meaning as momentum flux suggests that it should change its sign on time reversal.
2. To the first approximation $\mathbf{T}$ is linearly related to gradient of velocity, $\nabla\mathbf{u}$, therefore on time reversal $\mathbf{u}$ changes its sign, its gradient would also change its sign and hence $\mathbf{T}$ would change its sign on time reversal.
3. In kinetic theory [15-18] we have $\mathbf{T}=\overline{\rho\mathbf{CC}}$ hence as $\mathbf{C}$ changes its sign on time reversal the sign of $\mathbf{T}$ would not change.
4. In CIT the entropy source strength from viscous dissipation reads as $\sigma_s = \blacksquare:\nabla\mathbf{u}>0$, where $\blacksquare$ is the viscous part of the stress tensor. Therefore, if $\blacksquare$ does not change its sign on time reversal then the second law is not followed on the reverse path. Whereas in EIT to the first approximation we have $\sigma_s = \beta_{\blacksquare}\blacksquare:\Pi>0$ and hence even if $\blacksquare$ changes its sign on the reverse path the second law of thermodynamics is obeyed.

Thus herein too *there is no unambiguous way to decide the symmetry property of* $\mathbf{T}$ *on time reversal operation*. In view of this revelation there is no need to consider other equations containing $\mathbf{T}$. Because their time reversal symmetry would also turn out as ambiguous. But as our premise is that of thermodynamics and the fluid dynamical version of the first law of thermodynamics that we will be using in this paper is,

$$\rho\frac{du}{dt} = -\nabla\cdot\mathbf{q}-p\rho\frac{dv}{dt}+\Pi:\nabla\mathbf{u}+\sum_k\mathbf{J}_k\cdot\mathbf{F}_k$$

where $\mathbf{J}_k$ is the diffusion flux density of the component k and $\mathbf{F}_k$ is the body force per unit mass exerted on the chemical component k. As there are terms $\mathbf{q}$ and $\blacksquare$ in it, in view of the above discussion, its time reversal symmetry remains ambiguous. On the other hand, the first law of thermodynamics for spatially uniform systems in nonequilibrium reads as,

$$\frac{dU}{dt} = \frac{dQ}{dt}-p\frac{dV}{dt}$$

and it is seen that this equation is symmetric to time reversal (as $dU, dQ, dV, \overset{T}{\Longrightarrow}, -dU, -dQ, -dV$ and $t, \overset{T}{\Longrightarrow}, -t$).

Thus in nonequilibrium thermodynamics one would then use the two different types of equations representing the first law of thermodynamics one symmetric to time reversal and the other ambiguous on this count.

2.5 Time Reversal Symmetry of Boltzmann Equation and Boltzmann's H-theorem

The Boltzmann integro-differential equation for monatomic gas on neglecting body forces reads as [52],

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} = J(f|f) \tag{2.4}$$

where f is the distribution function corresponding to the molecular velocity $\mathbf{c}$, $\mathbf{r}$ is the position vector and $J(f|f)$ is the Boltzmann collisional integral given by:

$$J(f|f) = \int \int (f_1' f' - f_1 f) g\sigma(g, \Omega) d\Omega d\mathbf{c}_1 \tag{2.5}$$

where $\sigma(g, \Omega)$ is the collision cross section that depends on the relative velocity $g = |\mathbf{c}_1 - \mathbf{c}|$ and the scattering solid angle Ω. The primes and indices in the distribution function have the usual meaning, namely, $f_1' = f(\mathbf{c}_1', \mathbf{r}, t)$ is the distribution function of particle 1 after collision, etc.

As stated above eq.(2.4) is not a time symmetric invariant that gets demonstrated as follows. The left hand side of eq.(2.4) changes sign on time reversal operation, namely:

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} \overset{T}{\Longrightarrow} \frac{\partial f}{\partial (-t)} + (-\mathbf{c}) \cdot \frac{\partial f}{\partial \mathbf{r}} \Rightarrow -\left(\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} \right)$$

but the right hand side of eq.(2.4) is obtained as time reversal invariant, namely:

$$J(f|f) = \int \int (f_1' f' - f_1 f) g\sigma(g, \Omega) d\Omega d\mathbf{c}_1 \overset{T}{\Longrightarrow}$$

$$J(f|f) = \int \int (f_1' f' - f_1 f) g\sigma(g, \Omega) d\Omega d\mathbf{c}_1$$

because it does not contain t explicitly.

So far so good but let us analyze it further. On instantaneous time reversal all molecules would reverse their motion then the distribution functions before collision should become those of after collision and vice versa. Then we would have $(f_1' f' - f_1 f) \overset{T}{\Longrightarrow} (f_1 f - f_1' f') \Rightarrow -(f_1' f' - f_1 f)$. However, the effecting of this time reversal operation does imply $f(\mathbf{c}, \mathbf{r}, t) = f(-\mathbf{c}, \mathbf{r}, -t)$. With this insight eq.(2.4) is obtained as time reversal invariant. But in essence the time reversal operation means the substitution of $-t$ for t without any alteration in the equation. Thus we see that both the options of time reversal operation have their shortcomings.

With these two options for time reversal symmetry of Boltzmann integro-differential equation, eq.(2.4), let us examine the famous Boltzmann's H-theorem. Boltzmann defined kinetic theory based H function whose negative is the kinetic theory definition of entropy function[1]. It reads as,

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[1] Actually the H-function has been defined [15, 52] as,

$$H = \int f \ln f d\mathbf{c}$$

which was later found to relate with the entropy function given in the text above.

$$\rho s = -k_B \int f(\ln f - 1) d\mathbf{c}$$

where k_B is the Boltzmann constant. On differentiation of above equation with respect to time and further effecting the standard mathematical manipulations produces,

$$\frac{\partial \rho s}{\partial t} = -div(\rho s \mathbf{u} + \mathbf{J}_s) + \sigma_s$$

where the entropy flux density, $\mathbf{J}_s$, is given by,

$$\mathbf{J}_s = -k_B \int \mathbf{C} f(\ln f - 1) d\mathbf{c}$$

where $\mathbf{C}$ is the molecular peculiar or chaotic velocity, and the entropy source strength, σ_s, is given by,

$$\sigma_s = -k_B \int J(f|f) \ln f d\mathbf{c}$$

The entropy source strength, σ_s, is further mathematically manipulated to produce,

$$\sigma_s = \frac{1}{4} k_B \int \int \int \left(\ln \frac{f' f_1'}{f f_1} \right) (f_1' f' - f_1 f) g^3 \sigma(g, \Omega) d\Omega d\Omega' dg d\mathbf{c}_{(1)} \geq 0$$

where $\mathbf{c}_{(1)}$ is the center of mass velocity of the colliding molecular pair. The positive definiteness shown in the preceding equation stems from the fact that if $\ln \frac{f' f_1'}{f f_1} > 0$ then we have $(f_1' f' - f_1 f) > 0$ and if the former is < 0 then the latter is also < 0 the rest of the terms of the integrands are positive numbers by definition. This is the Boltzmann's H-theorem [21].

Now we see that the positive definiteness of the preceding equation is time reversal invariant in both the above stated options of change or no change of the roles of the distribution functions on time reversal operation. This is a paradoxical situation because irrespective of the Boltzmann equation is taken time reversal invariant or variant the H-theorem that results from it is obtained as time reversal invariant.

2.6 Circumvention of the Problem

Let us first summarize the outcomes of the preceding elaborations.

1. The first observation is that the time reversal symmetric equations of motion produce two solutions namely $\mathbf{r}(t)$ and $\mathbf{r}(-t)$, which has been interpreted as motions in future and in past respectively. That is the same equation is also capable of describing a motion from present to past that seemingly ensures that the same dynamic states would be encountered but in the reverse order. But what is the physical reality of this result? For example, follow a motion with time for a certain time duration with simultaneously taking its movie. Now what one can do of it? One of the options is to run the movie in reverse direction but in doing so the clock doesn't get reversed, that is this reverse motion is only on the paper it is not a reality. Thus those equations having time reversal symmetry provide us a physical and a non-physical solutions, but the latter is merely an illusion giving one a feel that it describes a corresponding real reverse motion. Perhaps one can say that the time reversal invariant equations are capable of giving us an information about what happened in the past and when. But it doesn't mean that we have reversed the motion or clock.

2. An another query is about the velocities and fluxes. The state of a spatially non-uniform system is also determined by fluxes (their magnitude and direction) [29, 35, 36]. If suppose on time reversal the fluxes reverse their direction that will ensure the assuming of the same magnitudes, say of internal energy, in reverse order. But then those states will have all fluxes reversed and hence they are not the identically same states that were traversed in forward direction. For rigid bodies in motion the dynamic states are determined also by velocity vector. Thus on time reversal velocity changes its sign and hence during the so-called time reversed trajectory there would be different dynamic states though spatially the states appear to be the same.

3. We have also seen above that it is hardly possible to unambiguously decide the time reversal symmetry of equations containing fluxes and gradients of vectorial and tensorial quantities because there is no unambiguous way to decide the time reversal symmetry of vectorial and tensorial fluxes. Thus the dynamical irreversibility of such equations cannot be decided unambiguously.

4. The Boltzmann H-theorem is obtained as time reversal invariant but it is a paradoxical situation because this theorem is generated by using Boltzmann integro-differential equation whose time reversal symmetry is not uniquely determined.

5. A comment on the thermodynamic reversibility is also needed. As described above in Subsection 2.1 the thermodynamic reversible path is the one on which a system can be equally carried along forward and reverse directions that guarantees the system to assume the identically same equilibrium states but in reverse order on reversing the transition. Thus on reversing the transition the magnitudes of heat and work exchanged by the system simply change their signs without altering their magnitudes. Notice that this thermodynamic reversibility is not as a result of the act of time reversal as there is no time parameter involved. Notice that dQ in eq. (2.1) is the amount of heat exchanged by the system in the forward direction and $(-dQ)$ is that in the reverse direction, but dQ is not the state function. On the other hand, in the case of nonequilibrium $\nabla \cdot \mathbf{q}$ determines the heat exchanged but as we will see below $\mathbf{q}$ is a state function describing a nonequilibrium state the same has been revealed by EIT too [34-42, 44-49]. Thus an equilibrium state of a closed system is described by any two state functions out of the four offered by the last equation of eq.(2.1), namely U, S, V, T, p but in this list dQ does not appear.

The purpose of this detailed description on the time reversal symmetry of the mathematical descriptions of dynamical systems was to highlight the ambiguities in which we are driven to in large number of cases. Therefore, it becomes clear that we need to remedy it at the very fundamental level. The rational solution of this problem has been already given by Santilli via his no reduction theorem stated in the introduction of this paper. And in the sequel he formulated *Santilli-Newtonian mechanics* [1, 4, 5, 53] particularly the geno-mathematics. The latter seems to be appropriate for developing nonequilibrium thermodynamics. In geno-space there is no need to test time reversal symmetry of equations as in this setup all equations are generated as unidirectional in conformity with time's arrow associated with irreversible processes. As stated in the introduction a preliminary attempt on these lines has recently been described recently [6].

3 Advancement and Shortcomings of the Existing Nonequilibrium Thermodynamic Frameworks

Thermodynamics of irreversible processes is still a developing science. Although, till now two Nobel Prizes (Onsager, 1968 and Prigogine, 1977, both in Chemistry) have been earned by this subject

but its foundational aspects are not as sound as that of equilibrium thermodynamics. Of course, the soundness of the latter description lies in the fact that – it uses the laws of thermodynamics to build its structure and in doing so it does not need inputs from the molecular level considerations and/or statistical support. In other words, it stands on its own with no crutches at all of other scientific disciplines. On the other hand, the equilibrium statistical thermodynamics requires finishing touches from the equilibrium thermodynamics. To be specific – the physical meaning to Lagrange's undetermined multiplier, say β, in terms of the reciprocal of thermodynamic temperature is imparted by equilibrium thermodynamics. If equilibrium thermodynamics were not existed then it would have remained only a mathematical entity having roots in thermal interactions but then what its exact physical meaning would have remained submerged till the establishment of equilibrium thermodynamics. Thus the equilibrium statistical thermodynamics got established as an important discipline with the help of equilibrium thermodynamics and not vice versa. This basic fact is well known and is now a text book matter.

3.1 The Classical Irreversible Thermodynamics (CIT)

The developmental story of thermodynamics of irreversible processes right from its very beginning starts with the formidable challenges to overcome. The foremost hurdle being that of establishing of a thermodynamic entropy function for nonequilibrium states [11]. Let us recall that Clausius and other stalwarts of high calibre for example Lord Kelvin, Maxwell, Gibbs, Boltzmann, Ehrenfest and others could never generate a thermodynamic entropy function for nonequilibrium states or the one directly based on the second law of thermodynamics that would be valid during the time evolution of a given system. Indeed, Boltzmann had formulated the statistically defined entropy function that is valid both for equilibrium and nonequilibrium states under respective appropriate conditions.

Local Equilibrium Assumption of CIT

However, instead of directly addressing to this formidable hurdle, an alternative but a round about way of approach was adopted. This route has been adopted because there seemed to be no other sound way within the sight. This route involved the adopting of a *local equilibrium assumption* (LEA) and imparting it a thermodynamic status. Its physical meaning is generally described in words as — *"although the total system is not in equilibrium but there exists within small mass elements of the system a state of "local" equilibrium for which the local entropy s has the same function of u, v and x_k as in real equilibrium"*. Thus it is a matter of a belief that under the dictates of the so-called LEA one can legitimately use the Gibbs relation of equilibrium thermodynamics in time rate form, namely:

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} - T^{-1}\sum_k \mu_k \frac{dx_k}{dt} \tag{3.1}$$

at local level of a given spatially non-uniform system, that seemingly is in accordance with the dictates of laws of thermodynamics (particularly the second law of thermodynamics) [21-29, 32]. Where in eq.(3.1) $s(\mathbf{r}, t)$ and $u(\mathbf{r}, t)$ are the per unit mass entropy and internal energy respectively, $v(\mathbf{r}, t)$ is the specific volume, p is the pressure, T is the temperature, $\mathbf{r}$ is the position vector, $\mu_k(\mathbf{r}, t)$ is the chemical potential per unit mass of the component k, $x_1(\mathbf{r}, t), x_2(\mathbf{r}, t), \ldots$ are the mass fractions of the components 1,2,..., and t is time. In this way one remains under impression that the entropy function that is being used in the time rate form of Gibbs relation has a sound base of second law

of thermodynamics. Of course, the adoption of this approach yielded rich dividends in which the Onsager reciprocity relations (a milestone in the history of science) [54-56], namely:
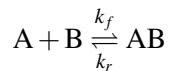
$$L_{ij} = L_{ji} \tag{3.2}$$

played an all important rôle. The phenomenological coefficients, L_{ij}, of eq.(3.2) relate generalized fluxes, J_i's, with generalized forces, X_j's, as,

$$J_i = \sum_j L_{ij} X_j, \qquad L_{ij} = \frac{\partial J_i}{\partial X_j}. \tag{3.3}$$

For example, the CIT has produced an unified thermodynamic description of coupled processes that were experimentally established much before the formal development even of equilibrium thermodynamics. It included electro-mechanical, thermo-mechanical, thermo-molecular, biochemical, etc. phenomena and the empirical linear relations like Ohm's law of electrical conduction, Fick's law of diffusion, Fourier law of heat conduction, Newton-Stokes relations of viscous forces, etc. [21-33]. At the same time, it was also realized that this description should hold good only for close to equilibrium situations and most probably in the domain of linear flux-force relationships, c.f. eq.(3.3). Therefore, this *classical irreversible thermodynamics* (CIT) has been also referred to as the *linear irreversible thermodynamics* (LIT). But contrary to the above claim the chemical reactions proceeding at finite rates say in spatially uniform systems (a scalar phenomena) constitute striking exceptions. Wherein for such evolutions right from the farthest away from equilibrium situations up to very close to equilibrium the time rate version of Gibbs relation or more appropriately the De Donderian equation [57], namely:

$$\frac{dU(t)}{dt} = T(t)\frac{dS(t)}{dt} - p(t)\frac{dV(t)}{dt} - \sum_\gamma \mathcal{A}^\gamma \frac{d\xi^\gamma}{dt} \tag{3.4}$$

has been found as adequate [22, 23, 26, 27, 30, 31]. Where in eq.(3.4) U is the internal energy, S is the entropy, p is the pressure, V is the volume, $\mathcal{A}^\gamma$ is the chemical affinity of γ-th chemical reaction, T is the temperature and ξ^γ is the extent of advancement of γ-th chemical reaction. Moreover, the thermodynamic description of chemical oscillations, chemical chaos, etc. the above thermodynamic description of eqs. (3.1) and (3.4) remain adequate. But in a no stretch of imagination these chemical processes including chemical reactions right from farthest away from equilibrium can be included in the linear region of flux-force relationships. For example, chemical kinetics [58] say for a bimolecular chemical reaction, namely:

$$\text{A} + \text{B} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{AB}$$

gives the following expression of rate of reaction, namely:

$$\frac{d\xi}{dt} = k_f[A][B] - k_r[AB] = \mathcal{R}_f - \mathcal{R}_r \tag{3.5}$$

where $\mathcal{R}_r = k_r[AB]$ is rate of reverse reaction, $\mathcal{R}_f = k_f[A][B]$ is the rate of forward reaction, k_f and k_r are the forward and reverse rate constants and [A], [B] and [AB] are the respective concentrations in appropriate units. The rate of entropy production, $\mathcal{P}$, in CIT for this chemical reaction reads as,

$$\mathcal{P} = \frac{\mathcal{A}}{T}\frac{d\xi}{dt} > 0 \tag{3.6}$$

Now on mathematical manipulations eq.(3.5) reads as,

$$\frac{d\xi}{dt} = \mathcal{R}_f \left[1 - \exp\left(-\frac{\mathcal{A}}{RT} \right) \right] \tag{3.7}$$

where we have the following De Donderian expression for the chemical affinity, $\mathcal{A}$, from eq.(3.4) and the following traditional expressions for the quotient Q and the equilibrium constant K,

$$\mathcal{A} = RT \ln \left(\frac{K}{Q} \right), \quad Q = \frac{[AB]}{[A][B]}, \quad K = \frac{[AB]^{eq}}{[A]^{eq}[B]^{eq}} \tag{3.8}$$

where R is the universal gas constant. Notice that eq.(3.7) is not a linear relation between the thermodynamic flux, $d\xi/dt$, and corresponding thermodynamic force, $\mathcal{A}/T$ but can be linearized by the condition of close to chemical equilibrium that reads as,

$$\frac{d\xi}{dt} = \frac{\mathcal{R}_f^{eq}}{R} \frac{\mathcal{A}}{T} \tag{3.9}$$

But the De Donderian eq.(3.4) and equivalently the Gibbs relation, eq.(3.1), and hence eq.(3.5) remains valid right from the initiation of chemical reaction till the chemical equilibrium is reached. Therefore, to relegate the validity of Gibbs relation, eq.(3.1), to not far away from equilibrium regime is simply an un-just act.

Therefore, the physical meaning of LEA remains ambiguous. To overcome this ambiguity there are other attempts to justify LEA and one of them is an attempt to explain LEA in terms of two time scales (see for example [29]). As an example we quote a passage from the monograph entitled "Understanding Nonequilibrium Thermodynamics" [29] that reads as follows.

"*In each individual cell (the small mass element stated above) the equilibrium state is not frozen but changes in the course of time. A better description of this situation is achieved in terms of two timescales: the first, τ_m, denotes the equilibration time inside one cell and it is of the order of the time interval between two successive collisions between particles, i.e. 10^{-12} s, at normal pressure and temperature. The second characteristic time τ_M is a macroscopic one whose order of magnitude is related to the duration of an experiment, say about 1 s. The ratio between both reference times is called the Deborah number $D_e = \tau_m/\tau_M$. For $D_e \ll 1$, the local equilibrium hypothesis is fully justified because the relevant variables evolve on a large timescale τ_M and do practically not change over the time τ_m, but the hypothesis is not appropriate to describe situations characterized by $D_e \gg 1$. Large values of D_e are typical of systems with long relaxation times, like polymers, for which τ_m may be of the order of 100 s, or of high-frequency or very fast phenomena, such as ultrasound propagation, shock waves, nuclear collisions, for which τ_M is very short, say between 10^{-5} and 10^{-10} s*".

The preceding justification of LEA tries to impress upon that — say the intensive parameters of equilibrium thermodynamics or rather those appearing in eq.(3.1) needs longer time duration of measurement and hence the use of Gibbs relation of eq.(3.1) implies the operation of LEA. However, thanks to the scientific advancements now we can, for example, measure T-jump (temperature jump) in nano-seconds [59], which implies that the efficiency of time required to measure T has increased to the same order or even less. Then does it mean that the diffusion controlled chemical reactions, exothermic and/or endothermic, whose half-lives are of the order of 10^{-9} s or less fall outside of the LEA domain? The answer to this question is no because the Gibbs relation or De Donderian equation based thermodynamic considerations of all such chemical reactions have been found adequate. There are no evidences to suggest that the additional intensive and extensive parameters over and above those appearing in eq.(3.4) are required.

Thus we see that the above two time scales based explanation of LEA is superfluous.

Notwithstanding the above ambiguities there are two major claims in CIT/LIT. The first one is the *principle of minimum production of entropy* [21-32] for *nonequilibrium stationary states* (NSS) that reads as,

$$\frac{d\mathcal{P}}{dt} \leq 0 \qquad (3.10)$$

where the total rate of entropy production, $\mathcal{P}$, in the linear region is given by,

$$\mathcal{P} = \int_V \sum_{a,b} L_{ab} X_a X_b dV. \qquad (3.11)$$

However, its generalized basis has been questioned by Lavenda [24], Lampinen [60], Müller [34] and the present author [11], though in a good number of cases this principle apparently seems to be valid. The second assertion is about the stability (asymptotic) of the envisaged local equilibrium states (in fact, these states in reality are the nonequilibrium states but identified as the so-called of special class) put forward by Glansdorff and Prigogine [26]. The proposed mathematical statement of this asymptotic thermodynamic stability of local equilibrium states reads as,

$$\delta^2 S < 0 \qquad \text{and} \qquad \frac{d}{dt}\frac{1}{2}(\delta^2 S) \geq 0 \qquad (3.12)$$

At a first glance as stated by Landsberg [61] perhaps it is the fourth law of thermodynamics. However, this proposal of stability of local equilibrium state was questioned by Keizer and co-workers [62]. They argued that it is devoid of the sanction of the second law of thermodynamics. This objection was answered by Glansdorff at al [63] asserting that their criteria of stability follows from the second law of thermodynamics but, in fact, was termed by Landsberg [61] as an extra-thermodynamic proposal. Indirectly meaning thereby that these mathematical statements do not follow from the second law of thermodynamics but Landsberg did hope that the proposed stability conditions may turned out to be the fourth law of thermodynamics. However, till date it never got proved or established. In the opinion of the present author it would never get established because LEA is a non-physical proposal how so ever it may be sound looking or attractive one. The LEA has been justified also from the kinetic theory consideration.

On the Kinetic Theory Justification of LEA

As there is no direct way to justify LEA, as stated above, an indirect justification seems to be given by the Boltzmann integro-differential equation [21], the latter for example reads as,

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} = J(f|f) \qquad (3.13)$$

where f is the distribution function corresponding to the molecular velocity $\mathbf{c}$, $\mathbf{r}$ is the position vector and $J(f|f)$ is the Boltzmann collisional integral that reads as,

$$J(f|f) = \int \int (f_1' f' - f_1 f) g \sigma(g, \Omega) d\Omega d\mathbf{c}_1$$

where $\sigma(g, \Omega)$ is the collision cross section that depends on the relative velocity $g = |\mathbf{c}_1 - \mathbf{c}|$ and the scattering solid angle Ω. The primes and indices in the distribution function have the usual meaning, namely, $f_1' = f(\mathbf{c}_1', \mathbf{r}, t)$ is the distribution function of particle 1 after collision, etc.

Now eq.(3.13) on applying to a monatomic gas and using $J(f|f) = 0$ produces the Maxwellian distribution, namely:

$$f^{(0)} = \frac{n}{(2\pi k_B T/m)^{3/2}} e^{-m\mathbf{C}^2/2k_B T} \tag{3.14}$$

where $f^{(0)}$ is the Maxwell distribution function, n is the number density of molecules, $\mathbf{C}(= \mathbf{c} - \mathbf{u})$ is the chaotic (peculiar) velocity of the molecule and k_B is the Boltzmann constant.

Now $J(f|f) = 0$ indeed implies equilibrium and hence the left hand terms of eq.(3.13) individually equals to zero, namely:

$$\frac{\partial f}{\partial t} = 0, \qquad \frac{\partial f}{\partial \mathbf{r}} = 0 \tag{3.15}$$

that is the system needs to be spatially uniform and all system properties are time invariant. That is it is a state of equilibrium[2].

Now recall that the kinetic theory based justification of the adoption of LEA is based on the Enskog iteration method of solution of Boltzmann equation, eq.(3.13) [21]. In this approach the distribution function is expressed as,

$$f = f^{(0)}(1 + \phi) \tag{3.16}$$

where ϕ is the "perturbation" function, that measures the deviation of the actual distribution function, f, from the local Maxwellian, $f^{(0)}$. By iteration one obtains the Enskog series solution of Boltzmnn equation, namely:

$$f = f^{(0)}\left(1 + \phi^{(1)} + \phi^{(2)} + \phi^{(3)} + \cdots\right) \tag{3.17}$$

thus $\phi^{(1)}$, $\phi^{(2)}$, $\phi^{(3)}, \cdots$ are the first, second, third, etc. level of approximations of the perturbation function ϕ.

Now the first approximation solution of the Boltzmann equation is obtained by substituting the Maxwellian , the zero order function $f^{(0)}$, on the left hand side of eq.(3.13) and linearizing the right hand side with respect to the perturbations ϕ's. Hence, eq.(3.13) to the first approximation of the perturbation function, reads as,

$$\frac{\partial f^{(0)}}{\partial t} + \mathbf{c} \cdot \frac{\partial f^{(0)}}{\partial \mathbf{r}}$$
$$= \int\int f^{(0)} f_1^{(0)}\left(\phi_1^{(1)'} + \phi^{(1)'} - \phi_1^{(1)} - \phi^{(1)}\right) g\sigma(g,\Omega) d\Omega d\mathbf{c}_1 \tag{3.18}$$

Notice that the use of eq.(3.18) means that *one is determining the space and time behaviour of $f^{(0)}$ on account of irreversibility at the first level of approximation*, that is by using $\phi^{(1)}$'s on the right hand side of eq.(3.18).

Next we recall that $f^{(0)}$ *is a function of* T, μ and $\mathbf{u}$ and hence it is *no wonder* that ϕ^1 is obtained as a function of T, μ and $\mathbf{u}$. And specifically we obtain $\phi^{(1)} = \phi^{(1)}(\nabla T, \nabla\mu, \nabla\mathbf{u})$. However, the Maxwellian distribution function produces the equilibrium thermodynamic relation $s = T^{-1}(u + pv - \mu)$ and hence it is believed that $\phi^{(1)} = \phi^{(1)}(\nabla T, \nabla\mu, \nabla\mathbf{u})$ *is obtained as commensurate* with the preceding relation.

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[2] One may argue that $J(f|f) = 0$ not necessarily imply $\frac{\partial f}{\partial t} = 0$, $\frac{\partial f}{\partial \mathbf{r}} = 0$. But if we assume $\frac{\partial f}{\partial t} = -\frac{\partial f}{\partial \mathbf{r}}$ it then prescribes the existence of spatial non-uniformity and that too time varying. However, $J(f|f) = 0$ would make entropy source strength to vanish according to the kinetic theory definition $\sigma_s = -k_B \int J(f|f)\ln f d\mathbf{c}$. This then would imply although there exists nonequilibrium due to spatial non-uniformity but no entropy is produced. This goes against the second law of thermodynamics. Hence, the assertion of eq.(3.15) is the only permitted physical choice

The question that we should raise, at this stage of arguments, is with this first order Enskog solution which distribution function would remain valid for the tiny volume element? Obviously the answer is $f = f^{(0)}\left(1 + \phi^{(1)}\right)$. But then it would not produce the equilibrium relation for s, namely $s = T^{-1}(u + pv - \mu)$ that CIT uses.[3]

But the above iteration method bound to produce $\phi^{(1)}$'s as a function of T, μ and $\mathbf{u}$. *Therefore, the basic question that arises is whether the above first order solution of Boltzmann equation corresponds to any sort of equilibrium? The answer is definitely not an affirmative one.*

This answer gets further confirmed when one solves Boltzmann equation using, say the Grad 13-moment method [16, 17]. On restricting to the first order approximation in EIT they obtain,

$$s = s_{\text{eq}}(u, v) - \frac{1}{2}\beta_{\mathbf{q}}\mathbf{q}\cdot\mathbf{q} - \frac{1}{2}\beta_{\blacksquare}\Pi : \Pi \tag{3.19}$$

where

$$\beta_{\mathbf{q}} = \frac{4}{5npk_BT^2} \quad \text{and} \quad \beta_{\Pi} = \frac{4}{mnpT}$$

We stress that both the methods, Enskog's and Grad's, are the first order approximations, that is pertaining to not far away from equilibrium situations, but then why respective solutions should virtually differ from one another, particularly in the final expression of s they produce. In the Grad solution s is obtained dependent also on $\mathbf{q}$ and Π and hence the solution pertains to a nonequilibrium situation is evident. Whereas in Enskog method it is argued that s is obtained as dependent only on the same independent variables that are given by equilibrium thermodynamics. But notice that it is an artifact of the methodology itself. Hence, to term it — a case of local equilibrium becomes an act of a haste. This point gets elaborated as follows as well as additionally it gets proved by our reanalysis presented in the Appendix of Enskog method based entropy, entropy source strength and entropy flux density expressions that it produces.

In Enskog method one is seemingly led to the following Gibbs relation, namely:

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[3] The kinetic theory definition of entropy is

$$\rho s = -k_B \int f\left(\ln f - 1\right) d\mathbf{c}$$

When the system is in equilibrium we have Maxwellian distribution function, namely:

$$f^{(0)} = \frac{n}{\left(2\pi k_BT/m\right)^{3/2}} e^{-m\mathbf{C}^2/2k_BT} = e^{\mu m/k_BT} e^{-m\mathbf{C}^2/2k_BT}$$

which on substitution in the preceding entropy equation elegantly produces,

$$\rho s = -\frac{\mu m}{T} \int f^{(0)} d\mathbf{c} + \frac{1}{T} \int \left(\frac{1}{2}m\mathbf{C}^2\right) d\mathbf{c} + k_B \int f^{(0)} d\mathbf{c}$$

$$= -\frac{\rho\mu}{T} + \frac{\rho u}{T} + \frac{p}{T}$$

But when we use $f = f^{(0)}\left(1 + \phi^{(1)}\right)$ we have,

$$\rho s = -k_B \int f^{(0)}\left(1 + \phi^{(1)}\right)\left[\ln f^{(0)}\left(1 + \phi^{(1)}\right) - 1\right] d\mathbf{c}$$

in which only one of the integrals would be, $-k_B \int f^{(0)}\left(\ln f^{(0)} - 1\right) d\mathbf{c}$ that would produce the said equilibrium entropy relation and the other integrals would quantify the nonequilibrium contribution to entropy. Then how one can use the equilibrium Gibbs relation in time rate form? This argument is strongly substantiated by our reanalysis of the Enskog method of kinetic theory based expressions of σ_s, s and $\mathbf{J}_s$ that has been described in the Appendix.

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} \tag{3.20}$$

whereas the Grad method based approach of EIT produces the following Gibbs relation, namely:

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} - \beta_{\mathbf{q}}\mathbf{q}\cdot\frac{d\mathbf{q}}{dt} - \beta_{\Pi}\Pi:\frac{d\Pi}{dt} \tag{3.21}$$

where it is termed as an *extended Gibbs relation* in *extended irreversible thermodynamics* (EIT) [44].

Notice now — that the latter equation, eq.(3.21), superfluously reduces to eq.(3.20), on substituting $\frac{d\mathbf{q}}{dt} = 0$ and $\frac{d\Pi}{dt} = 0$. But these vanishing rates would also imply $\frac{du}{dt} = 0$ and $\frac{dv}{dt} = 0$ hence one ends up into a nonequilibrium stationary state (NSS). In spite of it, still we have $s = s(u, v, \mathbf{q}, \Pi)$, that is the magnitude of s changes from one NSS to another on changing the magnitudes of $\mathbf{q}$ and/or Π.

On the other hand, the Enskog method seemingly generates eq.(3.20) under the functional dependence $s = s(u, v)$ or equivalently $s = s(T, v)$ hence s is not dependent on $\mathbf{q}$ and/or Π. The same then remains true of a NSS. We are led to this unrealistic description because the Enskog method seeks nonequilibrium contribution to distribution function under the T, μ and $\mathbf{u}$ dependencies of the Maxwellian.

Therefore, does it mean that there are two different classes of NSS in one they depend only on u, v and in another class they depend on $u, v, \mathbf{q}, \Pi$. Even if one is inclined to accept it then how one can physically differentiate one from the another class of NSS? Unfortunately, it is simply not possible to make such a differentiation physically. This clearly suggest that there is no physical basis of LEA and hence of beyond LEA.

Hence the proposal of local equilibrium in the sense it has been prescribed in CIT is a case of *a wrong foot put forward*.[4]

We recall that under the condition of NSS the extended Gibbs relation, eq.(3.21), produces the same expression of entropy production that the classical irreversible thermodynamics (CIT) [21] uses. Hence, all successful applications of CIT follow herein too but now with no ambiguities at all. For example, recall the assertion that *the physical justification of LEA follows from the successful applications of the thermodynamic expressions it generates* [21]. Thus we see that such a round about approach is not needed at all if Grad's solution is used.

3.2 Thermodynamics Beyond CIT

In spite of, the above stated ambiguities about LEA that sheds light on the status of CIT/LIT and the additional elaborations on it given in the appendix of this paper, a further development of the subject of nonequilibrium thermodynamics did follow with an enquiry whether the thermodynamics beyond LEA can be formulated. The investigations on these lines led to the development of a thermodynamic framework which is now termed as *extended irreversible thermodynamics* (EIT). Unfortunately, EIT has several versions and none appears to converge into the other one [34-49]. However, all of them claim that their formulism is the legitimate extension of CIT/LIT beyond LEA. But these so-called beyond LEA efforts have also added to the debate on basic thermodynamic aspects. For example, the physical quality of entropy, temperature and pressure in EIT is claimed as different than that in CIT and equilibrium thermodynamics. That is $T \neq T^{LEA} = T^{eq}, p \neq p^{LEA} = p^{eq}, \mu_k \neq \mu_k^{LEA} = \mu_k^{eq}$ where

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[4] EIT has never challenged LEA instead they opted to treat $\mathbf{q}$, Π as fast variables and then argue that when the magnitudes of say $\frac{d\mathbf{q}}{dt}$ and $\frac{d\Pi}{dt}$ become insignificant compared to that of $\frac{du}{dt}$ and $\frac{dv}{dt}$ the system enters into the regime where LEA operates. Thus it is a simple case of falling prey to the unsound LEA proposal.

T, p, μ_k are the temperature, pressure and chemical potentials as given by extended Gibbs relation of EIT. This is a non-thermodynamic non-physical outcome, which has been shown by the present author is the artifact of not considering the conditions provided by the corresponding Gibbs-Duhem equation [64, 65].

The fact is that the development of EIT remains strongly guided also by i) the kinetic theory of non-uniform gases, ii) the non-linearity of the constitutive theories of the processes and iii) whether the constitutive description is of parabolic or hyperbolic character. The details of these ambiguities have been recently described in reference [11] and for the sake of self sufficiency we have described them in the appendix of this paper. Thus the general scenario is that the EIT needs the help of non-thermodynamic crutches for its existence. On the success side herein too one finds very large number of processes getting for the first time the so-called thermodynamic description. The notable examples are the wave propagation of heat, momentum and matter diffusion and high frequency phenomena. What the present author feels about the existing ambiguities is that a little attention is paid in these later thermodynamic developments to have a direct base of the second law of thermodynamics.

3.3 Other Nonequilibrium Thermodynamic Frameworks

Indeed, besides the CIT and EIT there are other nonequilibrium thermodynamic frameworks too. For example, they are – finite-time thermodynamics [29, 66, 67], Keizer's statistical thermodynamics that is developed based on the fluctuations about the NSS [29, 68], rational thermodynamics [29, 69], thermodynamics of driven systems [70], GENERIC formulation [29, 71], meso-scopic nonequilibrium thermodynamics [29, 72, 73], thermodynamics with internal variables [29,74-78], axiomatic nonequilibrium thermodynamics [79] and the present author's generalized phenomenological irreversible thermodynamic theory (GPITT) [9-12, 50, 65, 80-83]. Out of the above list the finite-time thermodynamics is different in approach. It is based on the concept of endoreversibility of a real device that in principle pose no problem like LEA. The other thermodynamic frameworks some way or other are connected with LEA or beyond it or some similar postulations. On the other hand, as per the thermodynamic requirements GPITT first generates entropy function directly from Clausius' inequality valid during irreversible evolution of the system. Then by using fluid dynamical internal energy balance equation the thermodynamic structure gets developed, which is termed as GPITT. Strikingly, in doing so no question arises therein either of local equilibrium or that of beyond it. This last named aspect of GPITT makes it free from the shortcomings involved in CIT/LIT and EIT.

Although the development of GPITT is in itself an achievement as stated above but it fails the vital test of time reversal symmetry as is the case with all nonequilibrium thermodynamic frameworks for example those listed above. In fact so far no one has attempted to subject any one of the nonequilibrium thermodynamic frameworks to this crucial test. Therefore, this and the following paper is an attempt to remove all the above shortcomings by using geno-mathematics. In order not to leave any iota of ambiguity we start from where equilibrium thermodynamics has left us. In this endeavour the next section reconsiders the Gibbs relations of closed and open system carried reversibly.

4 Relevant Aspects of Equilibrium Thermodynamics

For the sake of self-sufficiency of the present discussion we describe the following basic steps that build equilibrium thermodynamics and spell out what meaning and description is there about the thermodynamic equilibrium and reversibility, which unfortunately has not been rigourously taken note of

particularly while developing nonequilibrium thermodynamics. Thus not to again get trap into the ambiguities described in the preceding section we need to keep in mind the vital contents of equilibrium thermodynamics described below while developing genononequilibrium thermodynamics.

4.1 Closed Systems

The second law of thermodynamics rigourously provides [13, 84] the Clausius entropy, S, say by using a reversible Carnot device, as:

$$dS = \frac{dQ}{T} \qquad \text{(A closed system carried reversibly)} \qquad (4.1)$$

and then it is coupled with the mathematical description of the first law of thermodynamics, say the following one:

$$dU = dQ - p\,dV \qquad \text{(A closed system carried reversibly)} \qquad (4.2)$$

that produces,

$$dU = T\,dS - p\,dV \qquad \text{(A closed system carried reversibly)} \qquad (4.3)$$

where in the preceding three equations dQ is the differential amount of heat exchanged reversibly by the system at temperature T with its thermally interacting surroundings, p is the equilibrium pressure of the system, U is the internal energy of the system and V is its volume.

The relevant inherent features of the above equations are:

1. Eq.(4.1) is the necessary and sufficient condition of thermodynamic reversibility and hence it considers only the equilibrium states. That is the description remains in the domain of thermodynamic reversibility. The use of eq.(4.1) in any mathematical development ensures that the resulting equations can only be used for thermodynamic reversible transitions. Therefore, though all the terms of eq.(4.3) are the state functions, that is their values do not depend on the history of achieving a given equilibrium state, it is a description only on reversible paths. The reversible paths are those which do not allow thermodynamic irreversibility (thermal, mechanical and chemical) to exist within and across the boundaries of a system. Thus no heat, matter and momentum fluxes and chemical reactions at finite rates are accommodated by eq.(4.3) nor one should attempt otherwise as it is not at all permitted.
2. In view of 1 above one simply cannot use eq.(4.3) in a time rate form for some irreversible evolution of a system.
3. In deriving eq.(4.3) no specifications are made about the composition of the system. This implies that the system may be composed of several components and phases and the components may be chemically reactive. Still eq.(4.3) remains a complete description on a reversible path, even if the the composition changes of the phases may accompany due to chemical conversion and transport of matter amongst the phases within the given system.

4.2 Open Systems

There are a good number of thermodynamic approaches dealing open systems [13, 23, 33, 57, 84, 85]. One of the innovative approaches is that described by Lewis and Randall [13] that involves first to use the defining relation of Gibbs function, $G(= U + pV + TS)$ in eq.(4.3) that yields:

$$dG = -S\,dT + V\,dp \qquad \text{(A closed system carried reversibly)} \qquad (4.4)$$

As G is an extensive function its magnitude will also depend on the amount of matter contained in a system. Now in an experiment described by them, which any one can carry out in a laboratory, one takes a solution of sodium thiosulfate say 25 ml in a beaker and fill the same solution in a burette. The solution contained in the beaker and in the burette are at ambient temperature and atmospheric pressure and have same concentration. Now let us add say 5 ml of solution from burette to beaker. In doing so p and T remains constant but the amount in burette and that in beaker changes and hence G of beaker would increase and that of burette decrease. This produces the following definition of chemical potential, μ, namely:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} \neq 0 \tag{4.5}$$

Therefore, in the case of a multicomponent system eq.(4.5) gets transformed to produce the following definition of chemical potential, μ_k,

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,p,n_{j\neq k}} \neq 0 \tag{4.6}$$

of the component k. Of course, the maintenance of reversibility in increase and decrease of the amounts of components is not evident in the above described Lewis and Randall experiment. However, the above development demonstrate that instead of eq.(4.4) we have for an open system, the following relation, namely:

$$dG = -S\,dT + V\,dp + \sum_k \mu_k\,dn_k \qquad \text{(for open systems)} \tag{4.7}$$

Now on using $G(=U+pV+TS)$ eq.(4.7) transforms to the Gibbs relation, namely:

$$dU = T\,dS - p\,dV + \sum_k \mu_k\,dn_k \qquad \text{(for open systems)} \tag{4.8}$$

instead of eq.(4.3).

However, still it would be a haste to consider eq.(4.8), as it is, an equilibrium description. Let us elaborate it. If an open system under scrutiny is composed of several phases and its components are chemically reactive then in general the net mole number changes of each phase, dn_k^α, are given by,

$$dn_k^\alpha = d_e n_k^\alpha + \sum_\gamma d_i n_k^{\alpha(\gamma)} \tag{4.9}$$

where $\alpha(\gamma)$ refers to the γ-th chemical reaction in α-th phase, d_e refers to the differential change computed for matter exchange and d_i refers to the differential change due to internal chemical conversion. For such an open system eq.(4.8) reads as,

$$dU = T\,dS - p\,dV + \sum_\alpha \sum_k \mu_k^\alpha\,dn_k^\alpha \qquad \text{(for open systems)} \tag{4.10}$$

Further, by Dalton's law of constant proportions [57] the mole number changes say of k-th component for γ-th chemical reaction in α-th phase is given by,

$$d_i n_k^{\alpha(\gamma)} = \nu_k^{\alpha(\gamma)}\,d\xi^{\alpha(\gamma)} \tag{4.11}$$

where $v_k^{\alpha(\gamma)}$ is the stoichiometric coefficient of the k-th component in γ-th chemical reaction of α-th phase and $\xi^{\alpha(\gamma)}$ is the extent of advancement of γ-th chemical reaction in α-th phase. Thus on substitution of eqs.(4.9) and (4.11) into eq.(4.10) yields,

$$dU = TdS - pdV + \sum_\alpha \sum_k \mu_k^\alpha d_e n_k^\alpha + \sum_\alpha \sum_\gamma \sum_k \mu_k^\alpha v_k^{\alpha(\gamma)} d\xi^{\alpha(\gamma)} \tag{4.12}$$

Now as usual use the following definition of chemical affinity, $\mathcal{A}^{\alpha(\gamma)}$, namely:

$$\mathcal{A}^{\alpha(\gamma)} = -\sum_k \mu_k^\alpha v_k^{\alpha(\gamma)} \tag{4.13}$$

for the γ-th chemical reaction of α-th phase, which transforms eq.(4.12) to,

$$dU = TdS - pdV + \sum_\alpha \sum_k \mu_k^\alpha d_e n_k^\alpha - \sum_\alpha \sum_\gamma \mathcal{A}^{\alpha(\gamma)} d\xi^{\alpha(\gamma)} \tag{4.14}$$

However, if the above development is that for a reversible transformation of an open system and is self-consistent then by imposing the condition of closed system ($d_e n_k^\alpha = 0$) on eq.(4.14) it should get transformed to eq.(4.3). But we notice that this can only happen if on a reversible path each $\mathcal{A}^{\alpha(\gamma)}$ identically vanishes (notice that no concomitant vanishing of $d\xi^{\alpha(\gamma)}$ is demanded). This then reveals that on a reversible path chemical equilibrium is maintained, though in general chemical conversion would take place within the system as the open system is carried on a reversible path. Thus it produces the standard thermodynamic description of chemical equilibrium, namely:

$$\mathcal{A}^{\alpha(\gamma)} = 0 \qquad \text{(chemical equilibrium)} \tag{4.15}$$

Therefore, the *operative Gibbs relation* describing the reversible transformation of an open system seems to read as,

$$dU = TdS - pdV + \sum_\alpha \sum_k \mu_k^\alpha d_e n_k^\alpha \tag{4.16}$$

Thus eq.(4.16) does not allow the existence of irreversibility on account of chemical conversions. Now we need to check if eq.(4.16) is free of irreversibility on account of matter exchange too. This check we perform as follows.

Notice that each $d_e n_k^\alpha$ gets split into two contributions. The first one is the exchange of matter with the exterior surroundings, $d_{ee} n_k^\alpha$, and the second one is the internal exchange of matter amongst the phases of the system, $d_{ei} n_k^\alpha$. Hence we have,

$$d_e n_k^\alpha = d_{ee} n_k^\alpha + d_{ei} n_k^\alpha \tag{4.17}$$

Thence, eq.(4.16) gets expressed as,

$$dU = TdS - pdV + \sum_\alpha \sum_k \mu_k^\alpha d_{ee} n_k^\alpha + \sum_\alpha \sum_k \mu_k^\alpha d_{ei} n_k^\alpha \tag{4.18}$$

But the mass conservation in internal matter exchange demands,

$$\sum_\alpha d_{ei} n_k^\alpha = 0 \tag{4.19}$$

that gives,

$$d_{ei}n_k^\alpha = -\sum_\ell d_{ei}n_k^\ell \tag{4.20}$$

where ℓ sums only $(\alpha - 1)$ terms. Therefore, on incorporation of eq.(4.20) into eq.(4.18) produces,

$$dU = TdS - pdV + \sum_\alpha \sum_k \mu_k^\alpha d_{ee}n_k^\alpha + \sum_\ell \sum_k \left(\mu_k^\ell - \mu_k^\alpha\right) d_{ei}n_k^\ell \tag{4.21}$$

Once again on imposing the condition of closed system ($d_{ee}n_k^\alpha = 0$) on eq.(4.21) it should get reduced to eq.(4.3). However, it is seen that this can happen only if the spatial uniformity of chemical potentials for each component exists, namely:

$$\mu_k^1 = \mu_k^2 = \mu_k^3 = \cdots\cdots\cdots = \mu_k^{\alpha-1} = \mu_k^\alpha = \mu_k \tag{4.22}$$

which is the standard thermodynamic description of attainment of equilibrium against the diffusive matter transfer. Thus it clearly reveals that the reversible diffusive mass transfers amongst the internal phases do not contribute to the *equilibrium Gibbs relation* that reads as,

$$dU = TdS - pdV + \sum_k \mu_k d_e n_k \quad \text{(open systems carried reversibly)} \tag{4.23}$$

where we have used,

$$d_e n_k = \sum_\alpha d_{ee}n_k^\alpha \tag{4.24}$$

4.3 The Relevant Revelations

The elaborations of the preceding two subsections clearly reveal that:

1. The equilibrium thermodynamic relation namely eq.(4.3) does not debar the occurrence of *reversible chemical conversion within the system* as well as the reversible matter exchanges amongst the phases within a closed system though the corresponding extensive variables do not appear as independent variables. Whereas the equilibrium thermodynamic relation eq.(4.23) does not debar the reversible chemical conversion within the system and reversible matter exchanges within and across the boundaries of an open system.

2. The equilibrium thermodynamic relations namely eqs.(4.3) and (4.23) do not allow the existence of irreversibility on account of heat, matter and momentum transfers and also on account of chemical conversions.

3. In view of the 1 and 2 above *it is not clear at all* how one can adopt the time rate forms of eqs.(4.3) and (4.23) to describe the so-called local equilibrium that would allow the occurrence of chemical reactions at finite rates and also the existence of heat, momentum and matter diffusion fluxes. In answering this query one may say that actually one is not using eq.(4.23) but eq.(4.8) is being used in CIT. But then eq.(4.8) is not an equilibrium description. However, the latter equation is definitely capable of accommodating irreversibility only on account of chemical conversions and internal matter exchanges but does not allow the existence of heat and momentum fluxes. But then how one can attach the adjective equilibrium (in the form of local equilibrium) to it or its local level version does not get clarified. In view of these revelations it is clear that there is no legitimacy to call eq.(3.1) a description of local equilibrium.

4. Therefore, if one wishes to use a local equilibrium description it should be the time rate form of eq.(4.23) and not that of eq.(4.8). But then by simply re-expressing eq.(4.23) in the time rate form doesn't imbibe thermodynamic irreversibility on account of heat and momentum transfers. On the other hand, from the steps of arriving at eq.(4.8) it is clear that no irreversibility on account of heat and momentum exchanges are permitted in this equation too. But it does accommodate a description of chemical conversions and matter exchanges and hence expressing it in the time rate form only permits the irreversibility description of chemical reactions at finite rates and matter diffusion. Therefore, eq.(3.1) is not a local equilibrium description but it accommodates the irreversibility only on accont of chemical reactions at finite rates and matter diffusion. But then no restriction of close to equilibrium gets attached to it. Even if one accepts it as a description of the said irreversibility the basic question that still remains unanswered is about the legitimacy of entropy function contained in it as that of a nonequilibrium state. Because we have not derived the entropy function appearing in it directly from the Clausius inequality that takes care of existing irreversibility.

Thus the concept of LEA of nonequilibrium thermodynamics has been demonstrated as a misconception having neither the thermodynamic sanction nor a sound physical meaning. We assert that — what has been confused is the following. For experimentally measuring a property there is a requirement of adequate equilibration of the measuring device with the local pocket of the system. Moreover, the efficiency of measurements is getting refined day by day and hence one is able to make measurements in shorter time durations than earlier without significantly disturbing the local nonequilibrium state or even local and global equilibrium state of a system. Thus by the act of measurement the state of the system whether it is in equilibrium or in nonequilibrium remains absolutely unaffected. *This requirement — of reliable experimental measurements — therefore, cannot be translated into the prescription of local equilibrium in the sense of the so-called* LEA of CIT. Moreover, to make the fluid dynamical theories or for that matter any dynamical theory a physically useful one the requirement of reliable measurements of the involved quantities is demanded and not the postulation of equilibrium or local equilibrium has been imposed upon. Then why in thermodynamics of irreversible processes one should go for LEA and beyond LEA is a million dollar question. The answer to this question lies in the inability (in those days) of arriving at the entropy function for a nonequilibrium state directly from the second law of thermodynamics. Therefore, it was believed that by postulating LEA we impart the thermodynamic sanction to the entropy function of eq.(3.1). But the above illustration clearly demonstrates that the reality is not so.

5 Santilli's New Mathematics

For the sake of self-sufficiency we are presenting in this section the rudiments of Santilli's new mathematics in brief. For details the reader may consult the profusely cited references in this paper.

5.1 Brief Outline of Iso-, Isodual- and Geno- Mathematics

The 20th century mathematics' first generalization (lifting) is known as *Santilli-isomathematics* and then it is further lifted into single-valued structurally irreversible generalization known as *Santilli-genomathematics*. The former is designed to take into account also the interior dynamical features. For example, consider the special relativity of particle physics. Recall that the classical point-like

particles do not exist, such as the electrons do not have "point-like wavepackets" and hence they have contact effects of nonlocal-integral type and zero-range nonpotential forces. Thus the *Santilli-isomathematics* treats both the exterior and interior dynamical aspects of a system. They include gravitational, quantum mechanical, nuclear physical, astrophysical, quantum chemical, etc. problems.

Whereas *Santilli-genomathematics* is an invariant formulation of irreversibility. This is characterized by two real-valued, non-singular, non-symmetric, generalized units, interconnected by hermitian conjugates, one of which is assumed to characterize motion forward in time and the other, motion backward in time. The differences between the basic units for the two directions of time guarantee irreversibility for all possible reversible Hamiltonians. Since all potential interactions are reversible, these non-symmetric, generalized units represent the interactions responsible for irreversibility namely, Lagranges and Hamiltons external terms. This second set of methods is intended for an invariant representation of open irreversible processes, such as chemical reactions, and is part of the so-called genotopic branch of hadronic mechanics and chemistry.

To resolve the problems related to antimatter , it was found necessary to introduce additional new mathematics. The form of these additional mathematics are *antiisomorphic* to the proposed iso- and geno-mathematics, have their own channel of quantization, and the operator images are indeed antiparticles, defined as charge conjugates of conventional particles on a Hilbert space.

It is possible to see that, despite their generality, the invariant irreversible genoformulations referred to above are insufficient for in depth treatments of biological systems. In fact, the studies conducted by Illert [86] have pointed out that the shape of sea shells can certainly be represented via conventional mathematics, such as the Euclidean geometry. However, the latter conventional geometries are inapplicable for a representation of the growth over time of sea shells. Computer simulations have shown that the imposition to sea shell growth of conventional geometric axioms causes the lack of proper growth, such as deformations and cracks, as expected, because said geometries are strictly reversible over time, while the growth of sea shells is strictly irreversible.

At the same time the studies by Illert [86] have indicated the need of a mathematics that is not only structurally irreversible, but also multi-dimensional. As an example, Illert achieved a satisfactory representation of sea shells growth via the doubling of the Euclidean reference axes, namely, via a geometry appearing to be sixdimensional. A basic problem in accepting such a view is the lack of compatibility with our sensory perception. When holding sea shells in our hands, we can fully perceive their shape as well as their growth with our three Eustachian tubes. Hence, any representation of sea shells growth with more than three dimensions is incompatible with our perception of reality.

Similarly, our sensory perception can indeed detect curvature. Thus, any representation of sea shell growth with the Riemannian geometry would equally be incompatible with our sensory perception. At any rate, any attempt at the use of the Riemannian geometry for sea shell growth would be faced with fatal inconsistencies, such as the inability to represent bifurcations and other aspects since such representations would be prohibited by curvature.

These occurrences pose a rather challenging problem, the construction of yet another new mathematics that is

1. Structurally irreversible over time (as that of the genomathematics);
2. Capable to represent deformations;
3. Invariant under the time evolution in the sense of predicting the same number under the same conditions but at different times;
4. Multi-dimensional; and, last but not least,
5. Compatible with our sensory perception.

The solution that Santilli proposed requires the building an irreversible multivalued (rather than multi-dimensional) new mathematics, in the sense that the basic axioms of the space representation can remain three-dimensional to achieve compatibility with our sensory perception, but each axis can have more than one value, thus being multi-valued.

A search in the mathematical literature soon revealed that a mathematics verifying all the above requirements did not exist and had to be constructed. After a number of trials and errors, a yet broader mathematics verifying the above five conditions was identified by Santilli in a monographs [1] of 1995 and in his works [87, 88], and subsequently he and the mathematician T. Vougiouklis published their study in a paper [89] of 1996 (see also mathematical study [90]). These studies resulted in a formulation today known as Santilli's hypermathematics.

The above described development of new mathematics by Santilli has been applied to the field of thermodynamics. The first initiation of this work is by Dunning-Davies [91, 92]. He has formulated iso-, geno- and isodual- thermodynamics. He demonstrated that the basic thermodynamic relations, such as $TdS = dU - dW$, $TdS = dU + pdV - \mu dN$, etc. are *isoselfdual*. That is these relations are equally valid for antimatter systems too [91-95]. A more detailed account of this thermodynamic development is reproduced in the following paper in this series.

In tune with the above stated background the following six subsections of the present subsection have been devoted to describe in brief the basic features of the above four new branches of the mathematics and their implications.

Lie-Santilli Isotheory

The main idea [96] is the lifting the conventional, trivial, n-dimensional unit $I = diag.(1,1,...,1)$ of Lie's theory into a real-values, nowhere singular and positive-definite $n \times n$-dimensional matrix, $\hat{I}$, called *isounit* (where the prefix "iso-" means "axiom-preserving"), with an unrestricted functional dependence on time t, coordinates $r = (r^k)$, momenta $p = (p^k), k = 1, 2, 3$, wavefunctions ψ, and any other needed variable,

$$I = diag.(1, 1, ..., 1) \rightarrow \hat{I}(t, r, p, \psi, ...) = \frac{1}{\hat{T}} \neq I. \tag{5.1}$$

The applicable mathematics, called *isomathematics*, is the lifting of the *totality* of conventional mathematics (with a well defined unit), without any exception known in literature, into a new form admitting $\hat{I}$, rather than I, as the correct left and right unit. This calls for:

1. The lifting of the associative product $A \times B$ among generic quantities A, B (such as numbers, vector-fields, operators, etc.) into the form, called *isoassociative product*, for which $\hat{I}$ is indeed the left and right unit,

$$A \times B \rightarrow A \hat{\times} B = A \times \hat{T} \times B, \hat{I} \hat{\times} A = A \hat{\times} \hat{I} = A; \tag{5.2}$$

2. The lifting of fields $F = F(a, +, \times)$ into the *isofields* $\hat{F} = \hat{F}(\hat{a}, \hat{+}, \hat{\times})$ of *isonumbers* $\hat{a} = a \times \hat{I}$ (isoreal, isocomplex and isooctonionic numbers) with *isosum* $\hat{a} \hat{+} \hat{b} = (a + b) \times \hat{I}$, *isoproduct* $\hat{a} \hat{\times} \hat{b} = (a \times b) \times \hat{I}$, *isoquotient* $\hat{a} \hat{/} \hat{b} = (\hat{a}/\hat{b}) \times \hat{I} = (a/b) \times \hat{I}$, etc. (see [97] for details) ;
3. The lifting of functions $f(r)$ on F into *isofunctions* $\hat{f}(\hat{r})$ on $\hat{F}$, such as the *isoexponentiation* $\hat{e}^{\hat{A}} = \hat{I} + \hat{A}/\hat{1}! + \hat{A} \hat{\times} \hat{A}/\hat{2}! + ... = \left(e^{\hat{A} \times \hat{T}}\right) \times \hat{I} = \hat{I} \times \left(e^{\hat{A} \times \hat{T}}\right)$, and related lifting of transforms into *isotransforms* (see [90] and references cited therein for details);

4. The lifting of the ordinary differential calculus into the *isodifferential calculus*, with basic rules $\hat{d}\hat{r}^k = \hat{I}_i^k \times d\hat{r}^i$, $\hat{d}\hat{p}_k = \hat{T}_i^k \times d\hat{p}_i$ (because r^k and p^k are defined on *isospaces* with isometrics inverse of each other), *isoderivatives* $\hat{\partial}/\hat{\partial}\hat{r}^i = \hat{T}_i^j \times \partial/\partial r^j$, $\hat{\partial}/\hat{\partial}\hat{p}_k = \hat{I}_k^i \times \partial/\partial \hat{p}_i$, $\hat{\partial}\hat{r}^i/\hat{\partial}\hat{r}^j = \hat{\delta}_j^i = \delta_j^i \times \hat{I}$, etc.(see [90] and references cited therein for details);

5. The lifting of conventional vector, metric and Hilbert spaces into their isotopic images, e.g., the lifting of the Euclidean space $E(r, \delta, R)$ with local coordinates $r = (r^k)$ and metric $\delta = Diag.(1,1,1)$ into the *isoeuclidean spaces* $E(\hat{r}, \hat{\delta}, \hat{R})$ with *isocoordinates* $\hat{r} = r \times \hat{I}$ and *isometric* $\hat{\delta} = \hat{T} \times \delta$ over the *isoreals* $\hat{R}$, or the lifting of the Hilbert space $\mathcal{H}$ with inner product $< | \times | > \times I$ over the complex field C into the *isohilbert space* $\hat{\mathcal{H}}$ with *isoinner product* $< |\hat{\times}| > \times \hat{I}$ over the *isocomplex field* $\hat{C}$; etc. (see [90] and references cited therein for details).

6. The lifting of geometries and topologies into their corresponding isotopic images (see [98] for details);

The main operator formulation of the Lie-Santilli isotheory can be written as,

$$
\begin{aligned}
\hat{A}(\hat{w}) &= \hat{e}^{i\hat{X}\hat{\times}\hat{w}} \hat{\times} \hat{A}(\hat{0}) \hat{\times} \hat{e}^{-i\hat{w}\hat{\times}\hat{X}} \\
&= \left[e^{iw \times \hat{X} \times \hat{T}} \times A(0) \times e^{-iw \times \hat{T} \times \hat{X}} \right] \times \hat{I}, \hat{X} = \hat{X}^{\hat{\dagger}}, \hat{T} = \hat{T}^{\hat{\dagger}},
\end{aligned}
\tag{5.3}
$$

$$
i\hat{d}\hat{A}/\hat{d}\hat{w} = \hat{A}\hat{\times}\hat{X} - \hat{X}\hat{\times}\hat{A} = \hat{A} \times \hat{T} \times \hat{X} - \hat{X} \times \hat{T} \times \hat{A} = [\hat{A}\hat{,}\hat{X}]_{\text{operator}},
\tag{5.4}
$$

$$
\hat{e}^{i\hat{X}\hat{\times}\hat{w}} = \left(\hat{e}^{-i\hat{w}\hat{\times}\hat{X}} \right)^{\hat{\dagger}},
\tag{5.5}
$$

with classical counterpart

$$
\hat{A}(\hat{w}) = \hat{e}^{-w \times (\partial\hat{X}/\partial\hat{r}^k)\hat{\times}(\hat{\partial}/\hat{\partial}\hat{p}_k)} \hat{\times} \hat{A}(\hat{0}) \hat{\times} \hat{e}^{w \times (\partial/\partial\hat{r}^k)\hat{\times}(\partial\hat{X}/\partial\hat{p}_k)},
\tag{5.6}
$$

$$
\begin{aligned}
\frac{\hat{d}\hat{A}}{\hat{d}\hat{w}} &= \frac{\hat{\partial}\hat{A}}{\hat{\partial}\hat{r}^k} \hat{\times} \frac{\hat{\partial}\hat{X}}{\hat{\partial}\hat{p}_k} - \frac{\hat{\partial}\hat{X}}{\hat{\partial}\hat{r}^k} \hat{\times} \frac{\hat{\partial}\hat{A}}{\hat{\partial}\hat{p}_k} \\
&= \left[\frac{\partial A}{\partial r^k} \times \frac{\partial X}{\partial p_k} - \frac{\partial X}{\partial r^k} \frac{\partial A}{\partial p_k} \right] \times \hat{I} = [A\hat{,}X]_{\text{classical}},
\end{aligned}
\tag{5.7}
$$

and unique interconnecting map called *isosymplectic quantization* [1].

A most salient feature of the Lie-Santilli isotheory is that it is *form invariant under all possible nonunitary transforms*, thus achieving the fundamental physical objective indicated earlier. In fact, an arbitrary nonunitary transform on $\mathcal{H}$ over F can always be uniquely written as the *isounitary transform* on $\hat{\mathcal{H}}$ over $\hat{F}$,

$$
V \times V^\dagger = \hat{I} \neq I, V = \hat{V} \times \hat{T}^{1/2}, V \times V^\dagger = \hat{V}\hat{\times}\hat{V}^{\hat{\dagger}} = \hat{V}^{\hat{\dagger}}\hat{\times}\hat{V} = \hat{I},
\tag{5.8}
$$

under which we have the isoinvariance laws

$$
\hat{I} \to \hat{V} \times \hat{I} \times \hat{V}^{\hat{\dagger}} = \hat{I}' = \hat{I},
\tag{5.9}
$$

$$
\hat{A}\hat{\times}\hat{B} \to \hat{V}\hat{\times}(\hat{A}\hat{\times}\hat{B})\hat{\times}\hat{V}^{\hat{\dagger}} = (\hat{V}\hat{\times}\hat{A}\hat{\times}\hat{V}^{\hat{\dagger}})\hat{\times}(\hat{V}\hat{\times}\hat{A}\hat{\times}\hat{V}^{\hat{\dagger}}) = \hat{A}'\hat{\times}\hat{B}'
\tag{5.10}
$$

$$\hat{H} \hat{\times} |\hat{\psi}> = \hat{E} \hat{\times} |\hat{\psi}> \rightarrow \hat{V} \hat{\times} \hat{H} \hat{\times} |\hat{\psi}> = \hat{V} \hat{\times} \hat{H} \hat{\times} \hat{V}^{\hat{\dagger}} \hat{\times} \hat{V} \hat{\times} |\hat{\psi}>$$
$$= \hat{H}' \hat{\times} |\hat{\psi}'> = \hat{V} \hat{\times} \hat{E} \hat{\times} |\hat{\psi}> = \hat{E}' \hat{\times} |\hat{\psi}'>, \hat{E}' = \hat{E}, \qquad (5.11)$$

with corresponding isoinvariances for the classical counterpart.

As one can see, isomathematics achieves the invariance of the numerical values of the isounit, isoproduct and isoeigenvalues, thus regaining the necessary conditions for physical applications.

It is easy to prove that isohermiticity coincides with the conventional Hermiticity. As a result, all conventional observable of unitary theories remain observable under isotopies. The preservation of Hermiticity-observa-bility in time is then ensured by the above isoinvariances. Detailed studies conducted earlier (see [90, 99] and references cited therein) established the resolution of all inconsistencies of nonunitary theories.

The physical implications of the Lie-Santilli isotheory are far reaching. By recalling that Lie's theory is at the foundation of all of physics, Eqs. (5.3) to (5.7) have permitted a structural generalization of the fundamental dynamical equations of classical and quantum mechanics, superconductivity and chemistry into new disciplines called isomechanics, isosuperconductivity, and isochemistry (see [90, 99] and references cited therein). These new disciplines essentially preserve the physical content of the old theories, including the preservation identically of the total conserved quantities, but add internal non-Hamiltonian effects represented by the *isounit* that are outside any hope of representation via Lie's theory.

In turn, these novel effects have permitted momentous advances in various scientific fields, such as the first axiomatically consistent unification of electroweak and gravitational interactions [90, 100].

An illustrative classical application of the Lie-Santilli isotheory is the representation of the structure of Jupiter when considered isolated from the rest of the Solar system, with action-at-a-distance gravitational and other interactions represented with the potential ψ in the Hamiltonian H and additional, internal contact-non-Hamiltonian interactions represented via the isounit $\hat{I}$.

An illustrative operator application is given by novel structure models of the strongly interacting particles (called *hadrons*) for which the theory was constructed [101]. In turn, the latter application has far reaching implications, including the prediction of novel, clean *subnuclear* energies.

Lie-Santilli Genotheory

The main insufficiency of the *Lie-Santilli isotheory* is that it preserves the totally antisymmetric character of the classical and operators Lie brackets, thus being unsuited for a representation of open-nonconservative systems. In particular, despite the broadening of unitary-canonical theories into nonunitary-noncanonical extensions, the fundamental problem of the *origin of the irreversibility* of our macroscopic reality does not admit quantitative treatment via the Lie-Santilli isotheory because the latter theory is also is structurally reversible (that is, the theory coincides with its time reversal image for reversible Hamiltonians and isounits).

The resolution of this insufficiency required the broadening of the Lie- Santilli isotheory into a form whose brackets are neither totally antisymmetric nor totally symmetric. In turn, the achievement of an invariant formulation of the latter theory required the construction of a new mathematics that Professor Santilli formulated way back in 1978 [96] under the name of *genomathematics* (where the prefix geno now stands for axiom-inducing).

The main idea of genomathematics is the selection of *two different generalized units* called *genounits*, the first $\hat{I}^{>}$ for the *ordered multiplication to the right $A > B$*, called *forward genoproduct*, and the second $^{<}\hat{I}$ for the *ordered multiplication to the left $A < B$*, called *backward genoproduct*, according to the general rules [90, 96, 99]:

$$\hat{I}^{>} = 1/\hat{S}, A > B = A \times \hat{S} \times B, \hat{I}^{>} > A = A > \hat{I}^{>} = A, \tag{5.12}$$

$$^{<}\hat{I} = 1/\hat{R}, A < B = A \times \hat{R} \times B, {}^{<}\hat{I} < A = A <^{<} \hat{I} = A, \tag{5.13}$$

$$A = A^{\dagger}, B = B^{\dagger}, \hat{R} = \hat{S}^{\dagger} \tag{5.14}$$

where $\hat{S}$ and $\hat{R}$ are the respective *genotopic elements*, that is for the forward and the backward products respectively.

The broader genomathematics is then given by:

1. The lifting of isofields $\hat{F}(\hat{a}, \hat{+}, \hat{x})$ into the *forward and backward geno-fields* $\hat{F}^{>}(\hat{a}^{>}, \hat{+}^{>}, >)$ and ${}^{<}\hat{F}({}^{<}\hat{c}, {}^{<}\hat{+}, <)$ with *forward and backward genonumbers* $\hat{a}^{>} = a \times \hat{I}^{>}$ and ${}^{<}\hat{a} = {}^{<}\hat{I} \times a$, and related operations [97];

2. The lifting of isofunctions $\hat{f}(\hat{r})$ on $\hat{F}$ into the *forward and backward genofunctions* $\hat{f}^{>}(\hat{r}^{>})$ and ${}^{<}\hat{f}({}^{<}\hat{r})$ on $\hat{F}^{>}$ and ${}^{<}\hat{F}$, respectively, such as $(\hat{e}^{>})^{\hat{X}^{>}} = \left(e^{\hat{X}^{>} \times \hat{R}}\right) \times \hat{I}^{>}$ and ${}^{<}\hat{e}^{<\hat{X}} = {}^{<}\hat{I} \times e^{\hat{S} \times {}^{<}\hat{X}}$, with consequential genotopies of transforms and functional analysis at large (see ref. [90] and references cited therein);

3. The lifting of the isodifferential calculus into the *forward and backward genodifferential calculus* with main forward rules $\hat{d}^{>}\hat{r}^{>k} = \hat{I}_{i}^{>k} \times d\hat{r}^{>i}, \hat{d}^{>}\hat{p}_{k}^{>} = \hat{S}_{k}^{>i} \times d\hat{p}_{i}^{>}, \hat{\partial}^{>}(/^{>})\hat{\partial}^{>}\hat{r}^{>i} = \hat{S}_{i}^{>j} \times \partial/\partial\hat{r}^{>j}, \hat{\partial}^{>}(/^{>})\hat{\partial}^{>}\hat{p}_{k}^{>} = \hat{S}_{k}^{>i} \times \partial/\partial\hat{p}_{i}^{>}, \hat{\partial}^{>}\hat{r}^{>i}(/^{>})\hat{\partial}^{>}\hat{r}^{>j} = \hat{\delta}_{j}^{>i} = \delta_{j}^{i} \times \hat{I}^{>}$, etc., and corresponding backward rules easily obtainable via conjugation (see ref. [90] and references cited therein);

4. The lifting of isotopologies, isogeometries, etc. into the dual forward and backward genotopic forms; and

5. The lifting of the Lie-Santilli isotheory into the genotheory, including the genotopies of the various aspects, such as universal enveloping associative algebras for ordered product to the right and to the left, etc. (see ref. [90] and references cited therein).

The explicit realization of the Lie-Santilli genotheory can be expressed via the following finite and infinitesimal forms with related interconnection (at a fixed value of the parameter w, thus without its ordering) (see ref. [90] and references cited therein)

$$\hat{A}(\hat{w}) = (e^{>})^{i\hat{X}^{>}>\hat{w}} > \hat{A}(\hat{0}) < ({}^{<}e)^{-i\hat{w}<{}^{<}\hat{X}}$$
$$= \left[e^{i\hat{X} \times \hat{S} \times w} \times \hat{I}^{>}\right] \times \hat{S} \times \hat{A}(\hat{0}) \times \hat{R} \times \left[{}^{<}\hat{I} \times ({}^{<}e)^{-iw \times \hat{R} \times \hat{X}}\right], \tag{5.15}$$

$$i\frac{\hat{d}\hat{A}}{\hat{d}\hat{w}} = \hat{A} < \hat{X} - \hat{X} > \hat{A} = \hat{A} \times \hat{R} \times \hat{X} - \hat{X} \times \hat{S} \times \hat{A} = \left(\hat{A}\hat{;}\hat{X}\right)_{\text{operator}}, \tag{5.16}$$

$$^{<}\hat{X} = \left(\hat{X}^{>}\right)^{\hat{\dagger}}, \hat{R} = \hat{S}^{\dagger} \tag{5.17}$$

the classical counterpart (see ref. [90] and references cited therein),

$$\hat{A}(\hat{w}) = (\hat{e}^{>})^{-\hat{X}^{>}>\hat{w}} > \hat{A}(\hat{0}) < ({}^{<}\hat{e})^{\hat{w}<{}^{<}\hat{X}}$$
$$= \hat{e}^{-w \times (\hat{\partial}^{>}\hat{X}^{>}/\hat{\partial}^{>}\hat{r}^{>k}) > (\hat{\partial}^{>}/\hat{\partial}^{>}\hat{p}_{k}^{>})} > \hat{A}(\hat{0}) < \hat{e}^{w({}^{<}\hat{\partial}/{}^{<}\hat{\partial}^{<}\hat{r}^{k}) < ({}^{<}\hat{\partial}^{<}\hat{X}/{}^{<}\hat{\partial}^{<}\hat{p}_{k})},$$

$$\tag{5.18}$$

$$\frac{d\hat{A}}{d\hat{w}} = \frac{^<\hat{\partial}^{<}\hat{A}}{^<\hat{\partial}^{<}\hat{r}^k} {}^{<} \frac{^<\hat{\partial}^{<}\hat{X}}{^<\hat{\partial}^{<}\hat{p}_k} - \frac{\hat{\partial}^>\hat{X}^>}{\hat{\partial}^>\hat{r}^{>k}} {}^{>} \frac{\hat{\partial}^>\hat{A}^>}{\hat{\partial}^>\hat{p}_k^>}$$
$$= {}^{<}\hat{I} \times \left[\frac{\partial A}{\partial r^k} \times \frac{\partial X}{\partial p_k} \right] - \left[\frac{\partial X}{\partial r^k} \times \frac{\partial A}{\partial p_k} \right] \times \hat{I}^> = (A\hat{,}X)_{\text{classical}} \qquad (5.19)$$

with unique interconnecting map called *genosymplectic quantization* (see ref. [90] and references cited therein).

A most important feature of the Lie-Santilli genotheory is its *form invariance*. This can be seen by noting that a *pair* of nonunitary transforms on $\mathcal{H}$ over $\hat{C}$ can always be identically rewritten as the *genounitary transforms* on genohilbert spaces over genocomplex fields,

$$V \times V^\dagger \neq 1, V = {}^{<}\hat{V} \times \hat{R}^{1/2}, V \times V^\dagger = {}^{<}\hat{V} {}^{<} \hat{V}^\dagger = {}^{<}\hat{V}^\dagger {}^{<}\hat{V} = {}^{<}\hat{I}, \qquad (5.20)$$

$$W \times W^\dagger \neq 1, W = \hat{W}^> \times \hat{S}^{1/2},$$
$$W \times W^\dagger = \hat{W}^> > \hat{W}^{>\dagger} = \hat{W}^{>\dagger} > \hat{W}^> = \hat{I}^>, \qquad (5.21)$$

under which we have indeed the following forward genoinvariance laws [101],

$$\hat{I}^> \to \hat{I}'^> = \hat{W}^> > \hat{I}^> > \hat{W}^{>\dagger} = \hat{I}^>, \qquad (5.22)$$

$$\hat{A} > \hat{B} \to \hat{W}^> > (\hat{A} > \hat{B}) > \hat{W}^{>\dagger} = \hat{A}' > \hat{B}', \qquad (5.23)$$

$$\hat{H}^> > |> = \hat{E}^> > |> = E \times |> \to \hat{W}^> > \hat{H}^> > |>$$
$$= \hat{H}'^> > |>' = \hat{W}^> > \hat{E}^> > |> = E \times |>', \qquad (5.24)$$

with corresponding rules for the backward and classical counterparts.

The above rules confirm the achievement of the *invariance of the numerical values of genounits, genoproducts and genoeigenvalues*, thus permitting physically consistent applications.

By recalling again that Lies theory is at the foundation of all of contemporary science, the Lie-Santilli genotheory has permitted an additional structural generalization of classical and quantum isomechanics, isosuperconductivity and isochemistry into their genotopic coverings.

Intriguingly, the product $\hat{A} < \hat{B} - \hat{B} > \hat{A} = \hat{A} \times \hat{R} \times \hat{B} - \hat{B} \times \hat{S} \times \hat{A}, \hat{R} \neq \hat{S}$, is manifestly non-Lie on conventional spaces over conventional fields, yet it becomes fully antisymmetry and Lie when formulates on the bimodule of the respective envelopes to the left and to the right, $\{^<\hat{\mathcal{A}}, \hat{\mathcal{A}}^>\}$ (explicitly, the numerical values of $\hat{A} < \hat{B} = \hat{A} \times \hat{R} \times \hat{B}$ computed with respect to $^<\hat{I} = 1/\hat{R}$ is the same as that of $\hat{A} > \hat{B} = \hat{A} \times \hat{S} \times \hat{B}$ when computed with respect to $\hat{I}^> = 1/\hat{S}$) (see ref. [90] and references cited therein).

More importantly, genotheories have permitted a resolution of the historical problem of the origin of irreversibility via its reduction to the ultimate possible layers of nature, such as particles in the core of a star. The interested reader can find the invariant genotopic formulations of: Newtons equations, Hamiltons equations with external terms, quantization for open-irreversible systems, operator theory of open-irreversible systems in references cited in [90].

Lie-Santilli Hypertheory

By no means *genotheories* are sufficient to represent the entirely of nature, e.g., because they are unable to represent *biological structures* such as a cell or a sea shell. The latter systems are indeed open-nonconservative-irreversible, yet they possess a structure dramatically more complex than that of a nonconservative Newtonian system. A study of the issue has revealed that the limitation of genotheories is due to their single-valued character.

As an illustration, mathematical treatments complemented with computer visualization [86] have established that the shape of sea shells can be well described via the conventional single-valued three-dimensional Euclidean space and geometry according to the empirical perception of our three Eustachian tubes. However, the same space and geometry are basically insufficient to represent the growth in time of sea shells. In fact, computer visualization shows that, under the exact imposition of the Euclidean axioms, sea shells first grow in time in a distorted way and then crack.

Illert [86] showed that a minimally consistent representation of the sea shells growth in time requires six dimensions. But sea shells exist in our environment and can be observed via our three-dimensional perception. The solution of this apparent dichotomy was proposed [86] via multi-valued hypermathematics essentially characterized by the relaxation of the single-valued nature of the genounits while preserving their nonsymmetric character (as a necessary condition to represent irreversible events), according to the rules [90, 99]:

$$\hat{I}^> = \left\{ \hat{I}_1^>, \hat{I}_2^>, \hat{I}_3^>, ... \right\} = 1/\hat{S}, \tag{5.25}$$

$$A > B = \left\{ A \times \hat{S}_1 \times B, A \times \hat{S}_2 \times B, A \times \hat{S}_3 \times B, ... \right\},$$
$$\hat{I}^> > A = A > \hat{I}^> = A \times I, \tag{5.26}$$

$$^<\hat{I} = \left\{ {}^<\hat{I}_1, {}^<\hat{I}_2, {}^<\hat{I}_3, ... \right\} = 1/\hat{R}, \tag{5.27}$$

$$A < B = \left\{ A \times \hat{R}_1 \times B, A \times \hat{R}_2 \times B, A \times \hat{R}_3 \times B, ... \right\},$$
$$^<\hat{I} < A = A <^< \hat{I} = I \times A, \tag{5.28}$$

$$A = A^\dagger, B = B^\dagger, \hat{R} = \hat{S}^\dagger \tag{5.29}$$

All aspects of the bimodular genotheories admit a unique, and significant extension to the above hyperstructures and their explicit form is here omitted for brevity [90, 99]. The expression of the theory via *weak equalities and operations* was first studied by Santilli and Vougiouklis in Ref. [86].

Isodual Theories

Mathematicians appear to be unaware of the fact that, contrary to popular beliefs, *the totality of contemporary mathematics, including its isotopic, genotopic and hyperstructural liftings, cannot provide a consistent classical representation of antimatter*. In fact, all these mathematics admit only *one quantization channel*. As a result, the operator image of any classical treatment of antimatter via these

mathematics simply cannot yield the correct charge conjugate state, but it merely yields a particle with the wrong sign of the charge.

The occurrence should not be surprising because the study of antimatter constitutes one of the biggest scientific unbalances of this century. In fact, matter is treated at all possible mathematical and physical levels, from Newtons equations and underlying topology, all the way to second quantization and quantum field theories, while antimatter is solely treated at the level of *second quantization*. However, astrophysical evidence suggests quite strongly the existence of macroscopic amounts of antimatter in the universe, to the point that even entire galaxies and quasars could eventually result to be made up entirely of antimatter.

The only possible resolution of this historical unbalance is that via the construction of a *yet new mathematics*, specifically conceived for a consistent classical representation of antimatter whose operator counterpart yields indeed the correct charge conjugate states.

Recall that charge conjugation is anti-homomorphic, although solely applies at the operator level. It then follows that the new mathematics for antimatter should be, more generally, anti-isomorphic and applicable at all levels of study.

After a laborious research, Santilli proposed back in 1985 [102] the *isodual mathematics*, namely, mathematics constructed via the *isodual map* of numbers, fields, spaces, algebras, geometries, etc..

The *isodual conventional mathematics* is characterized by the simplest conceivable anti-isomorphic map of the unit into its *negative-definite form*,

$$I > 0 \rightarrow -I = I^d < 0, \tag{5.30}$$

under which we have the transformation law of a generic, scalar, real-valued quantity,

$$A(w) \rightarrow A^d(w^d) = -A(-w), \tag{5.31}$$

with reconstruction of numbers, fields, spaces, algebras, geometries, quantization, etc. in such a way to admit I^d, rather than I, as the correct left and right unit.

The isodual map characterizing the broader *isodual iso-, geno- and hyper-mathematics* is instead given by:

$$\hat{I}(\hat{t}, \hat{r}, \hat{p}, \hat{\psi}, ...) \rightarrow -\hat{I}^\dagger(-\hat{t}^\dagger, -\hat{r}^\dagger, -\hat{p}^\dagger, -\hat{\psi}^\dagger., ...) = \hat{I}^d(\hat{t}^d, \hat{r}^d, \hat{p}^d, \hat{\psi}^d, ...), \tag{5.32}$$

and consequential reconstruction of the entire formalism to admit $\hat{I}^d$ as the correct left and right new unit.

The above map is not trivial, e.g., because it implies the reversal of the sign of *all* physical characteristics of matter (and not only of the charge). As such, isodual theories provide a novel intriguing representation of antimatter which *begins* at the primitive classical Newtonian level, as desired, and then persists at all subsequent levels, including that of second quantization, in which case isoduality becomes equivalent to charge conjugation [103].

This is the most general mathematics described above is the *isoselfdual hypermathematics* [90], namely, a hypermathematics that coincides with its isodual, and is evidently given by hypermathematics multiplied by its isodual. The latter mathematics has been used for one of the most general known cosmologies [104] inclusive of antimatter as well as of biological structures (as any cosmology should be), in which the universe: has a multivalued structure perceived by our Eustachian tubes as a single-valued threedimensional structure; admits equal amounts of matter and antimatter; removes

any need for the "missing mass"; reduces considerably the currently believed dimension of the measured universe; possesses all *identically null* total characteristics of time, energy, linear and angular momentum, etc.; eliminates any singularity at the time of creation.

Classification of Hadronic Mechanics Based on the Basis Units Used

Thus, Hadronic mechanics can be classified into sixteen different branches, including: four branches of classical treatment of particles with corresponding four branches of operator treatment also of particles, and eight corresponding (classical and operator) treatments of antiparticles [104, 105]. This classification is based on the topological features of the assumed basis units and is listed below:

1. $I = 1 > 0$:
   Hamiltonian and Quantum Mechanics:
   Used for description of closed and reversible systems of point-like *particles* in exterior conditions in vacuum;

2. $I^d = -1 < 0$:
   Isodual Hamiltonian and Isodual Quantum Mechanics:
   Used for the description of closed and reversible systems of point-like *antiparticles* in exterior conditions in vacuum;

3. $\hat{I}(r, v, ...) = \hat{I}^{\dagger} > 0$:
   Classical and Operator Isomechanics:
   Used for the description of closed and reversible systems of extended *particles* in interior conditiona;

4. $\hat{I}^d(r^d, v^d, ...) = (\hat{I}^d)^{\dagger} < 0$:
   Isodual Classical and Isodual Operator Isomechanics:
   Used for the description of closed and reversiblesystems of extended *antiparticles* in interior conditions;

5. $\hat{I}^>(r^>, v^>, ...) = (^<\hat{I})^{\dagger}$:
   Classical and Operator Genomechanics:
   Used for the description of open and irreversible systems of extended *particles* in interior conditions;

6. $\hat{I}^{d>}(r^{d>}, v^{d>}, ...) = (^<\hat{I}^d)^{\dagger}$:
   Isodual Classical and Isodual Operator Genomechanics:
   Used for the description of open and irreversible systems of extended *antiparticles* in interior conditions;

7. $\hat{I}^>(\hat{I}_1^>, \hat{I}_2^>, \hat{I}_3^>...) = (^<\hat{I})^{\dagger}$:
   Classical and Operator Hypermechanics:
   Used for description of multivalued open and irreversible systems of extended *particles* in interior conditions;

8. $\hat{I}^{d>}(\hat{I}_1^{d>}, \hat{I}_2^{d>}, \hat{I}_3^{d>}...) = (^<\hat{I}^d)^{\dagger}$:
   Isodual Classical and Isodual Operator Hypermechanics:
   Used for the description of multivalued open and irreversible systems of extended *antiparticles* in interior conditions.

Notice that an *antiparticle* is an anti-isomorphic image of the corresponding *particle*. And also the *antimatter is characterized by negative mass, negative energy and negative magnitudes of other physical quantities.*

Moreover, although the *isodualmechanics* has been formulated to deal with the *antimatter* but Santilli [99] has conjectured that it would also serve in describing the evolution of biological systems. Therefore, in the following we would try to comprehend it too.

Time's Four Arrows

From the above Lie-Santilli isotheory and its isodual it is evident that there are *four* directions of time. Recall that Eddington's arrow of time identifies only two directions of time, namely future and past [106]. The identification of two hither to unnoticed directions of time became possible on adopting *isoduality* by Professor Santilli. Notice that the traditional *time reversal* changes only the direction of time while keeping the underlying space and units *unchanged* whereas the *isoduality* changes the direction of time while mapping the underlying space and units into different forms. Therefor, in reality, *time has four different directions* depending on whether the motion is forward or backward and occurs in the future or in the past. Herein the forward and backward motions are referred to that of matter and antimatter respectively whereas while spelling out the time indicating the particular motion the matter and antimatter is not specified to assert that it is a more general classification of time's arrows.

- Thus we have the following four representations, namely [105]:
  1. Time $\hat{t}$ is taken to represent the *motion forward to future time*.
  2. Time $-\hat{t}$ is taken to represent the *motion backward in past time*.
  3. Time $\hat{t}^d$ is taken to represent the *motion forward in past time*.
  4. Time $-\hat{t}^d$ is taken to represent the *motion backward in future time*.

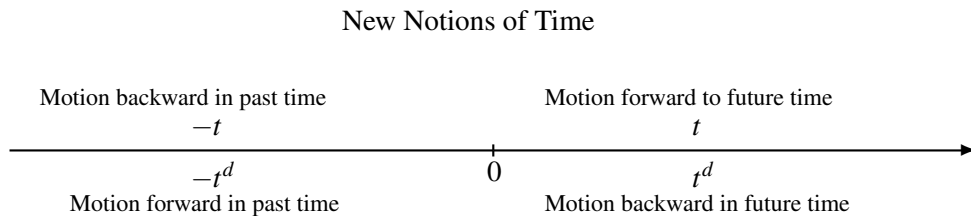 We depict the above stated directions of time in the following Figure 1

<div align="center">New Notions of Time</div>

Motion backward in past time		Motion forward to future time
$-t$		t

$$\longrightarrow$$

$-t^d$	0	t^d
Motion forward in past time		Motion backward in future time

Fig. 1 A schematic view of the four possible "time's directions".

- As noted by Santilli this classification based on iso- and isoduality lacks the irreversibility involved in natural processes and hence he formulated the genotheory. Thus the irreversible descriptions are inherent in genomechanics and in its isodual. The four explicit directions of time now get the following representations, namely [1, 4]:
  1. Time $\hat{t}^>$ is taken to represent the *motion forward in future time*.
  2. Time $^<\hat{t}$ is taken to represent the *motion backward in past time*.
  3. Time $^<\hat{t}^d$ is taken to represent the *motion backward in future time*.
  4. Time $\hat{t}^{d>}$ is taken to represent the *motion forward in past time*.

  Note that *the four possible "time arrows" are represented by the time genounits,* $\hat{I}_t^>$, $^<\hat{I}_t$, $\hat{I}_t^{d>}$, $^<\hat{I}_t^d$, *while time remains the ordinary real quantity*. Hence, the above four times are generated from the real time, t, as follows:

$$\hat{t}^> = t\hat{I}_t^>, \quad \hat{I}_t^> = (\hat{T}_t^>)^{-1} \neq (\hat{I}_t^>)^\dagger \quad \text{for motion forward to future times, } >$$

$$^<\hat{t} = {}^<\hat{I}_t t, \qquad {}^<\hat{I}_t = (\hat{I}_t^>)^\dagger \qquad \text{for motion backward in past times, } <$$

$$^<\hat{t}^d = {}^<\hat{I}_t^d t, \qquad {}^<\hat{I}_t^d = (\hat{I}_t^{d>})^\dagger \qquad \text{for motion backward in future times, } <$$

$$\hat{t}^{d>} = t\hat{I}_t^{d>}, \quad \hat{I}_t^{d>} = (\hat{T}_t^{d>})^{-1} \neq (\hat{I}_t^{d>})^\dagger \quad \text{for motion forward in past times, } >$$

The non-Hermiticity of Santilli genounits and its isodual is prescribed by

$$\hat{I}_t^> \neq {}^<\hat{I}_t, \quad \hat{I}_t^{d>} \neq {}^<\hat{I}_t^d$$

and the time in isodual genospace increases in reverse direction than that in the genospace is ensured by

$$\hat{t}^{d>} = -\hat{t}^>, \quad {}^<\hat{t}^d = -{}^<\hat{t} \quad \text{implying} \quad \hat{I}_t^{d>} = -\hat{I}_t^>, \quad {}^<\hat{I}_t^d = -{}^<\hat{I}_t$$

The genotopic directions of time have been depicted below in Figure 2

GENOTIMES

Motion backward in past time		Motion forward to future time
$^<\hat{t}$		$\hat{t}^>$

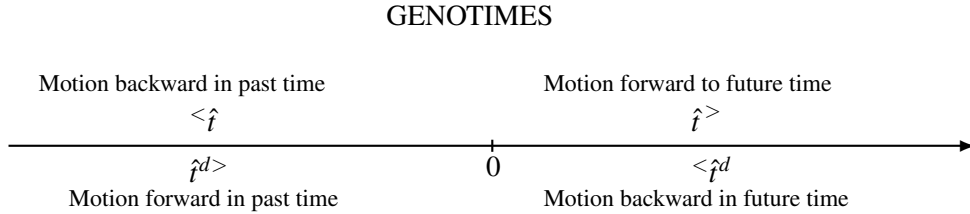| $\hat{t}^{d>}$ | 0 | $^<\hat{t}^d$ |
| Motion forward in past time | | Motion backward in future time |

Fig. 2 A schematic view of the four possible "Genotime's directions". It coincides with that of Figurer 1 when forward and backward genounits coincide.

- Whenever, one is required to use a complex number then its isodual is generated by keeping in view that imaginary unit i is *isoselfdual*, viz. $i^d = -i^\dagger = -\bar{i} = -(-i) = i$, the isodual of an isonumber is obtained as $\hat{n}^d = -\hat{n}$ and $\hat{\times}^d = (\times\hat{T}\times)^d = \times\hat{T}^d\times = \times(-\hat{T})\times = -\hat{\times}$. Now let $\hat{c} = (\hat{a} + i\hat{\times}\hat{b})$ be a complex function whose complex conjugate reads as $\bar{\hat{c}} = (\hat{a} - i\hat{\times}\hat{b})$. Then the steps to compute isodual of $\hat{c}$ are

$$\hat{c}^d = (\hat{a} + i\hat{\times}\hat{b})^d = \hat{a}^d + i^d\hat{\times}^d\hat{b}^d = -\hat{a} + i(-\times)(-\hat{b}) = -(\hat{a} - i\hat{\times}\hat{b}) = -\bar{\hat{c}}$$

- A very important outcome of Santilli's iso-mathematics demonstrated by Santilli himself is the *isotopic law of numerical values of functions* [1, 94, 107, 108]. That is the numerical values of a function $f(r)$ and isotopically lifted isofunction, $\hat{f}(\hat{r})$, remain identically same. The difference appears when $\hat{f}(\hat{r})$ is projected on the original space that gives $f(r \times \hat{T})$.
- Thus when $f(r)$ is time t the correspondingly the isotopic law of numerical values get expressed as,

$$t_{ext} = t_{ext} \times 1 = \hat{t}_{intr} = t_{intr} \times \hat{I}_{\hat{t}}$$

From the preceding equation it is clear that the pace of t_{intr} is not the same as that of t of our universe, t_{ext}. That is when $\hat{I}_{\hat{t}} > 1$ there we have a slower pace of t_{intr} than t_{ext} ($t_{intr} < t_{ext}$) and when $\hat{I}_{\hat{t}} < 1$ there we have faster pace of t_{intr} than t_{ext} ($t_{intr} > t_{ext}$).

- Moreover, the *anti-isomorphic map* of the *isotopic law of numerical values for time* then reads as [1, 94, 107, 108],

$$t_{ext} = t_{ext} \times 1 = -\hat{t}^d_{intr} = -t_{intr} \times \hat{I}^d_{t_{intr}}$$

Thus we see that if $\hat{I}^d_{t_{intr}} > -1$ we have $t_{ext} < \ |t_{intr}|$ and if $\hat{I}^d_{t_{intr}} < -1$ we have $t_{ext} > \ |t_{intr}|$. Therefore, the pace of time in isodual space would be either higher or less than that in our time space.

- Similarly, we have *Genotopic Law of Numerical Values of Genotopic Functions*. That for geno-times gets expressed as,

$$t_{ext} = t_{ext} \times 1 = \hat{t}^>_{intr} = t_{intr} \times \hat{I}^>_{\hat{t}}$$

Thus the pace of t_{intr} would be faster for $\hat{I}^>_{\hat{t}} < 1$ and it would be slower for $\hat{I}^>_{\hat{t}} > 1$ as compared to our time t_{ext}. The advantage of the genotopic description over the isotopic one is that the irreversibility of the involved processes gets clearly prescribed in the former.

- At the same time the following intriguing and far reaching aspect emerges in biology. In the above description we have strictly used isodual theories for the sole representation of antimatter. However, Illert [86] has shown that the representation of the bifurcations in seashells requires the use of all four directions of time. Hence in this context isodual theory is lifted to take care of additional directions needed in biology but thereby no features of antimatter would get involved. The latter aspect is an additional illustration of the complexity of biological system. In fact, the occurrence of the said complexity implies that the intrinsic time of a seashell, that is, the time perceived by a seashell as a living organism, is so complex that so far remained beyond our comprehension. Alternatively, we can say that the complexity of hypertimes is intended to reflect the complexity of biological systems [94]. In Santilli's words:

  When we look at a seashell in our hands, we perceive it as evolving according to our time, while in reality the seashell could evolve according to an intrinsic time arbitrarily in the future or the past with respect to our time, the differences depending on the value of the internal isounit of time. The compatibility of different internal times with our own time is assured by the isotopies because the numerical value of the properly formulated isotopic time (that on a time isospace over a time isofield) coincides with our own time. In different words, consider an external entity, such as a seashell, or external event in the universe, such as supernova explosion. Their view we perceive via reflected light, by no means, implies that the considered external entity or event evolves according to our own time, since it could evolve in four completely different, forward and backward, future and or past time. This is a reason for my believing that the raising of questions such as "the age of the universe" is an indication of our ignorance vis-á-vis the complexity of nature because, when we include antimatter, the total time of the universe could well be identically null as a condition to avoid discontinuity at creation.

As we aim to develop a comprehensive thermodynamic theory of irreversible processes of systems consisting of matter to begin with the formalism must be smoothly extendable to the biological system. But the constitutive theory of biological systems using new mathematics has not been accomplished to the desired level. Our attempts at thermodynamic level perhaps may show a path to accomplish it.

6 Concluding Remarks

The 20th century science of irreversible processes is based on the time reversal symmetric mathematical equations. This is the basic contradiction that led to inadequacies almost in all scientific fields. However, the advent of the genotopic branch of Santilli's new mathematics offered to successfully remove this drawback by using two different genounits for right and left multiplication. Accordingly, Santilli genotopically lifted all mathematical descriptions of irreversible processes (see for example [5] and references cited therein).

The first attempt to frame thermodynamics using these branches of new mathematics is that of Dunning-Davies [91, 92]. He developed iso-, geno-, and isodual- thermodynamics that established the validity of traditional basic thermodynamic equations in these new settings too and they are iso-selfdual. However, so far the field of nonequilibrium thermodynamics has not been benefited by geno-mathematics. In view of this the present author has recently initiated work on these lines and two short papers of the present author have appeared recently [6, 7]. The present series of papers is an attempt to develop systematically and in ab initio steps the geno-nonequilibrium thermodynamics.

In this paper we have described in adequate details the background and preparative aspects of developing genononequilibrium thermodynamics. The aspects those we have described are — the mess in the 20th century relevant mathematical descriptions from the point of view of time reversal symmetry, the shortcomings (other than that of time reversal symmetry) at the basic level in the existing nonequilibrium thermodynamic formulisms, the thermodynamic meaning of equilibrium and reversibility vis-à-vis the traditional Gibbs relation and a brief account of Santilli's new mathematics, namely, iso-, geno-, hyper- and their isoduals, and time's four arrows identified by Santilli.

The subject matter discussed in this paper forms the basis of systematic development of the genononequilibrium thermodynamics that we are describing in the following paper [8] of this series. One of the notable outcomes of our effort is the identification of four thermodynamic time's arrows based on the dictates of the second law of thermodynamics.

A Appendices

Below we have elaborated the problems other than those described in the main text of this paper that get inherited on using LEA and then looking beyond LEA.

A.1 Classical Irreversible Thermodynamics (CIT)

We recall that the CIT [21 - 25] for the first time attempted to legitimize nonequilibrium states and seemingly brought them into the fold of thermodynamics that appears to have helped in removing the apprehensions about the thermodynamic status of nonequilibrium states. The backbone of CIT is the *Local Equilibrium Assumption* (LEA), which for a spatially non-uniform system envisages the existence of a local equilibrium at every point within the system. In other words, *when LEA operates within a system, which is globally in nonequilibrium, its every interior tiny volume element may be approximated as if they are in equilibrium*. It is then believed that this assumption allows one to use,

- an entropy function for such nonequilibrium states.
- a temperature function for such nonequilibrium states.
- the same functional dependencies of the so accepted entropy function on the system quantities as that has been established in equilibrium thermodynamics.

- all state functions of such nonequilibrium states have the time and position dependencies whereas when the system happens to be in a nonequilibrium stationary state (NSS) thermodynamic quantities are only position dependent.

Traditionally, LEA gets mathematically expressed as [21 - 28],

$$s(\mathbf{r}, t) = s(u(\mathbf{r}, t), v(\mathbf{r}, t), x_1(\mathbf{r}, t), x_2(\mathbf{r}, t), ...) \tag{A.1}$$

where $s(\mathbf{r}, t)$ and $u(\mathbf{r}, t)$ are the per unit mass entropy and internal energy respectively, $v(\mathbf{r}, t)$ is the specific volume, $\mathbf{r}$ is the position vector, $x_1(\mathbf{r}, t), x_2(\mathbf{r}, t), ...$ are the mass fractions of the components 1, 2, ..., and t is time. This then seemingly opens for us a gateway to use as such the Gibbs relation at the local level and in the time rate form, namely:

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} - T^{-1}\sum_k \mu_k \frac{dx_k}{dt} \tag{A.2}$$

where μ_k is the chemical potential per unit mass of the component k. However, one seems to be unaware that the adoption of eq.(A.2) as a description of *local equilibrium* has following ambiguities, namely:

1. Recall that the equilibrium Gibbs relation is eq.(4.23) of the main text of this paper that reads as,

$$dU = TdS - pdV + \sum_k \mu_k d_e n_k$$

whose local time rate form would be,

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} - T^{-1}\sum_k \mu_k \frac{d_e x_k}{dt}$$

but not eq.(A.2). Then what sort of equilibrium one is envisaging by using eq.(A.2) ?

2. Actually by adopting eq.(A.2) one explicitly contain in it the following nonequilibrium terms, namely:

$$-T^{-1}\sum_k \mu_k \frac{d_e x_k}{dt}$$

that takes care of the irreversibility on account of matter diffusion as it is in time rate form and another term, viz.:

$$-T^{-1}\sum_k \mu_k \frac{d_i x_k}{dt} \geq 0$$

but the sum appearing in the preceding expression equals to zero in equilibrium.

3. Thus next question is how one gets assured that eq.(A.2) takes care of irreversibility originating from the existence of say heat and momentum fluxes !

In spite of the above ambiguities let us continue our short discussion of CIT.

For the sake of simplicity the explicit position and time dependencies have not been shown but is implied from here onwards. Next, one uses the fluid dynamical internal energy balance equation, which in a simple situation reads as,

$$\rho\frac{du}{dt} = -\nabla \cdot \mathbf{q} - \rho p\frac{dv}{dt} + \Pi : \nabla\mathbf{u} \tag{A.3}$$

where ρ is the local mass density, p is the local pressure, $\mathbf{q}$ is the heat flux density, Π is the dissipative stress tensor (the momentum flux density) and $\mathbf{u}$ is the barycentric velocity. Now on combining eq.(A.3) with eq.(A.2) the following entropy balance equation is obtained, namely:

$$\rho\frac{ds}{dt} + \nabla \cdot \mathbf{J}_s = \sigma_s \tag{A.4}$$

where $\mathbf{J}_s$ is the entropy flux density and σ_s is the entropy source strength and their expressions are obtained as,

$$\mathbf{J}_s = \frac{\mathbf{q}}{T} \tag{A.5}$$

$$\sigma_s = \mathbf{q} \cdot \nabla\left(\frac{1}{T}\right) + T^{-1}\Pi : \nabla\mathbf{u} + \sum_\gamma \frac{\mathcal{A}^\gamma}{T}\frac{d\xi^\gamma}{dt} \tag{A.6}$$

where the chemical affinity, $\mathcal{A}^\gamma$, of γ-th chemical reaction reads as,

$$\mathcal{A}^\gamma = -\sum_k \mu_k v_k^\gamma \tag{A.7}$$

and from Dalton's law [57] the advancement of the γ-th chemical reaction, ξ^γ, is given by,

$$dx_k = \sum_\gamma v_k^\gamma d\xi^\gamma \tag{A.8}$$

where v_k^γ is the stoichiometric coefficient of the component k in the γ-th chemical reaction and by convention it is taken positive for products and negative for the reactants and ξ^γ is the mass fraction based degree of advancement of the γ-th chemical reaction.

Further, each term on the right hand side of eq.(A.6) can be shown as a positive definite contribution and hence in the case under consideration eq.(A.4) is nothing else but the well known Clausius-Duhem inequality [109], namely:

$$\rho\frac{ds}{dt} + \nabla \cdot \mathbf{J}_s = \sigma_s \geq 0. \tag{A.9}$$

In CIT $\mathbf{q}$, Π and $d\xi^\gamma/dt$ are termed as thermodynamic fluxes (J_a's) and $\nabla(1/T)$, $\nabla\mathbf{u}$ and $\mathcal{A}^\gamma/T$ as thermodynamic forces (X_a's). In general σ_s is composed of three kinds of terms namely scalar, vectorial and tensorial ones and each kind is composed of more than one term depending upon the existing sources of irreversibility. However, it is obvious that the fluxes may depend on the magnitudes of the forces of their kind. This in general is expressed in a Taylor expansion as,

$$J_a = \sum_b \frac{\partial J_a}{\partial X_b}X_b + \frac{1}{2}\sum_{b,c}\frac{\partial^2 J_a}{\partial X_b \partial X_c}X_b X_c + \cdots\cdots \tag{A.10}$$

Now *as LEA has been supposed to operate it is obvious to conjecture that it can be realized only when the given system happens to be close to equilibrium.* Therefore, the second and higher order terms in eq.(A.10) would contribute a little to the sum and hence are customarily ignored. Therefore, the following linear relations oprtate, namely:

$$J_a = \sum_b L_{ab}X_b, \qquad L_{ab} = \frac{\partial J_a}{\partial X_b}. \tag{A.11}$$

In the view of operation of these linear relationships CIT is also termed as *linear irreversible thermodynamics* (LIT). Thus the expression of entropy source strength, σ_s, gets simplified to a quadratic bilinear form, namely:

$$\sigma_s = \sum_{a,b} L_{ab} X_a X_b \geq 0. \tag{A.12}$$

A further simplification is obtained as it has been shown that the Onsager reciprocal relations, namely:

$$L_{ab} = L_{ba} \tag{A.13}$$

are followed too [54, 56] and hence eq.(A.12) further simplifies to,

$$\sigma_s = \sum_a L_{aa} X_a^2 + 2 \sum_{\substack{b,c \\ b \neq c}} L_{bc} X_b X_c \geqslant 0. \tag{A.14}$$

Indeed, we are not required to describe herein the entire development of CIT the interested reader is advised to read the corresponding references cited in the bibliography.

However, the reader might have noticed that by combining eqs.(A.2) and (A.3) one has imported in the above so called thermodynamic description the irreversibility on account of temperature and velocity gradients, though eq.(A.2) on its own has absolutely no clue about how to accommodate it. Therefore, it turns out that the adoption of LEA is indeed a smart trick!

Perhaps to avoid handling of such unwelcome basic queries one tries to stress that — *the hypothesis of "local" equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it* [21].

A.2 LEA = Close to Equilibrium !

Now we pose a question. Is it true that LEA operates only when system happens to be close to equilibrium? This is a valid question because to allow the use of a linear flux-force relation we have ignored the second and higher order terms in eq.(A.10) that means that only those nonequilibrium situations have been permitted in our description that meet this requirement. This definitely does'nt mean that the corresponding constitutive equations and overall thermodynamic descriptions too should be linear ones [21, 110, 111]. However, on going through the literature we observe that:

1. In the case of a spatially non-uniform system in nonequilibrium stationary state the above CIT/LIT description fits very well and it has been successfully subjected to experimental verifications. Amongst such examples are thermodiffusion, thermoelectric effects, thermo-mechanical effects and the Saxen's relations. In such phenomena validity of eq.(A.14) has been verified [21 - 28].
2. However, the irreversibility on account of chemical reactions at finite rates has a different story to tell. This has been spelled out by De Groot and Mazur by stating that the close to equilibrium is too restrictive in the case of chemical reactions [21, 110, 111]. This aspect we have already elaborated in the main text.

A.3 Parabolicity/Hyperbolicity and Infinite/Finite Speed of Propagation Arguments

In the beginning of sixties of the preceding century a new thermodynamic framework got developed which is termed as Extended Irreversible Thermodynamics (EIT) [29, 35]. In EIT it is claimed that this framework is the legitimate extension of CIT to describe beyond LEA situations. Let us compare the following two Gibbs relations:

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} \tag{A.15}$$

$$\frac{ds}{dt} = T^{-1}\frac{du}{dt} + T^{-1}p\frac{dv}{dt} - \beta\mathbf{q}\cdot\frac{d\mathbf{q}}{dt}. \tag{A.16}$$

In the preceding two equations the latter one is termed as an extended Gibbs relation of EIT and the former one is the Gibbs relation wherein LEA is believed to be obeyed. In eq.(A.15) the heat flux density, $\mathbf{q}$, is not an explicit thermodynamic variable but the entropy production due to the existence of heat flux is given by,

$$\sigma_s = \mathbf{q}\cdot\nabla\left(\frac{1}{T}\right) \geq 0. \tag{A.17}$$

Whereas, in EIT, the heat flux density, $\mathbf{q}$, is an additional thermodynamic variable and the entropy production due to the existence of heat flux to the lowest order approximation reads as,

$$\sigma_s = \frac{1}{\lambda T^2}\mathbf{q}\cdot\mathbf{q} \geq 0 \tag{A.18}$$

where λ is the heat conductivity. The question that obviously arises is — what is the physical difference between close to equilibrium prescribed by LEA and the lowest order approximation involved in equation (A.18)?

The another limitation of LEA that is spelled out in EIT texts is that in CIT the linear Fourier law, namely:

$$\mathbf{q} = -\lambda\nabla T \tag{A.19}$$

operates that produces an infinite speed of spatial heat propagation. This is so because on using equation (A.19) and the internal energy balance equation appropriate in this case, the following *parabolic partial differential equation* for the propagation of temperature is obtained namely:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_v}\nabla^2 T \tag{A.20}$$

where ρ is the mass density and c_v is the specific heat capacity. On the other hand, one obtains a *hyperbolic equation of telegraphers type*, namely:

$$\tau\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_v}\nabla^2 T \tag{A.21}$$

on using the Maxwell-Cattaneo-Vernotte (MCV) equation [19, 20], for heat flux, namely:

$$\tau\frac{d\mathbf{q}}{dt} = -(\mathbf{q} + \lambda\nabla T) \tag{A.22}$$

and the internal energy balance equation expressed as,

$$\rho\frac{du}{dt} = \rho c_v\left(\frac{\partial T}{\partial t}\right)_v = -div\,\mathbf{q}. \tag{A.23}$$

Notice that the hyperbolic equation, eq.(A.21), produces temperature waves of finite speed.

Notice that, in deriving above parabolic equation, eq.(A.20), one uses the time dependent eq.(A.23) and assumes the validity of Fourier law, eq.(A.19), during time evolution of the system. But there is no experimental proof to support this assumption of validity of Fourier law during time evolution.

The clinching argument in favour of hyperbolic equations is customarily produced on the basis of finite/infinite speeds of wave propagation of the fluxes. But this then side tracks the basic question whether the Fourier law is at all valid during time evolution of a system in certain nonequilibrium situations.

Next consider eq.(A.20) whose one dimensional version reads as:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c_v} \frac{\partial^2 T}{\partial x^2} = \chi \frac{\partial^2 T}{\partial x^2} \tag{A.24}$$

where χ is the thermal diffusivity. Equation (A.24) is *parabolic* in nature. The implication of parabolicity of this equation is that the sudden application of a temperature difference would give rise to an instantaneous rise to the finite heat flux everywhere in the system. That is, it predicts heat propagation at infinite speed. Thus, it indicates that for the time evolving nonequilibrium states the Fourier law is not perhaps valid. In EIT, pains are taken to emphasize that the Maxwell-Cattaneo-Vernotte equation based derivation produces eq.(A.21), which is *hyperbolic* in nature and hence the problem of infinite speed does'nt arise. To appreciate how equation (A.21) produces finite speed of propagation of temperature waves let us consider the one dimensional version of it, namely:

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \chi \frac{\partial^2 T}{\partial x^2} \tag{A.25}$$

From eq.(A.25) the speed of the temperature wave, V, is obtained as:

$$V = (\chi/\tau)^{1/2} \qquad \text{where} \qquad \chi = (\lambda/c_v \rho) \tag{A.26}$$

Moreover, for monatomic dilute gas the Kinetic Theory provides us the following relationship [15], namely:

$$\lambda = (5 p k_B / 2m)\tau \tag{A.27}$$

therefore from equations (A.26) and (A.27) we notice that as $\lambda \to 0$, $\chi \to 0$ and $\tau \to 0$ and vice versa. Hence, V always remains finite. That is the problem of infinite velocity of temperature waves gets overcome. For $\tau = 0$ eq.(A.22) reduces to Fourier law that according to eq.(A.26) demands infinite speed of propagation of heat (temperature) waves.

In this way, the problem of infinite speed of second sound gets amicably solved as eq.(A.21) assigns a finite speed to heat waves. But we need to remind us that we have still used $u = u(T,v)$ in deriving eq.(A.21). Whereas, in EIT we have $s = s(u,v,\mathbf{q})$ and hence there we have $u = u(T,v,\mathbf{q})$.

In view of this crucial thermodynamic requirement of EIT one should have used $u = u(T,v,\mathbf{q})$ instead of $u = u(T,v)$ in deriving the corresponding temperature equation, but so far it has not been attempted. However, now we have undertaken this exercise in the case of rigid body heat conduction. In this exercise we have used MCV eq.(A.22), $u = u(T,\mathbf{q})$ and the corresponding internal energy balance equation. The steps of this exercise involves the manipulation of the internal energy balance equation as depicted below,

$$\rho \frac{du}{dt} = \rho c_v \left(\frac{\partial T}{\partial t} \right)_{v,\mathbf{q}} + \rho \left(\frac{\partial u}{\partial \mathbf{q}} \right)_{v,T} \cdot \left(\frac{d\mathbf{q}}{dt} \right) = -div\,\mathbf{q} \tag{A.28}$$

and then on combining it with MCV eq.(A.22) the result is the following *non-parabolic* complex equation, instead of eq.(A.21), for the heat propagation, namely:

$$\tau\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \frac{\lambda}{\rho c_v}\nabla^2 T + \frac{2\lambda\alpha}{\rho\tau c_v}\mathbf{q}\cdot\nabla T + \frac{\alpha}{\rho\tau c_v}\mathbf{q}^2$$

$$+ \frac{\lambda^2\alpha}{\rho\tau c_v}(\nabla T)^2 - \frac{\alpha\lambda}{\rho c_v}\mathbf{q}\cdot\frac{\partial\nabla T}{\partial t} = 0 \tag{A.29}$$

where we have used $\alpha\mathbf{q} = (\partial u/\partial\mathbf{q})_{T,v}$ as a first approximation. However, one also gets a *non-parabolic* equation of heat propagation on using $u = u(T,\mathbf{q})$, the Fourier law and the internal energy balance eq.(A.28), that reads as:

$$\frac{\partial T}{\partial t} - \frac{\lambda}{\rho c_v}\nabla^2 T + \frac{\alpha\lambda^2}{\tau c_v}\nabla T\cdot\frac{\partial(\nabla T)}{\partial t} = 0. \tag{A.30}$$

Thus from the above demonstration we see that if $\mathbf{q}$ is used as an additional thermodynamic variable then the use of both *linear* and *nonlinear equations* of heat conduction produce corresponding *non-parabolic* equations of temperature waves. Therefore, the hyperbolicity and/or the non-parabolicity of the constitutive equations is not a necessary and sufficient reason to consider that it is the case of breakdown of LEA.

In this way, the overall scenario that get painted is that — the appropriateness of the thermodynamic framework gets decided by the constitutive theory, which is not a welcome proposition.

A.4 Arguments Based on The Principle of Minimum Production of Entropy

Yet another celebrated aspect of CIT is the *principle of minimum production of entropy*. The basic description of this principle can be found in any one of the nonequilibrium thermodynamic texts cited in this paper. However, in the hope that the NSS corresponds to the minimum production of entropy Lampinen [60] used the Euler-Lagrange method of variational calculus [112] to minimize entropy production in one dimensional heat conduit using Fourier law of heat transfer and the expression of entropy production given by CIT (c.f. eq.(A.6)) [21], namely:

$$\sigma_s = \mathbf{q}\cdot\nabla\left(\frac{1}{T}\right) \geq 0. \tag{A.31}$$

On using the one dimensional version of eqs.(A.31) and (A.19) we obtain for the rate of entropy production, $\mathcal{P}$, for the whole heat conduit, the following expression,

$$\mathcal{P} = A\lambda\int_0^L \frac{1}{T^2}\left(\frac{\partial T}{\partial x}\right)^2 dx \geq 0 \tag{A.32}$$

where A is the uniform cross-sectional area of the heat conduit of length L. The minimum production of entropy, $\mathcal{P}$, is obtained by Euler-Lagrange method of variational calculus [112] by imposing:

$$\delta\left[\int_0^L \frac{1}{T^2}\left(\frac{\partial T}{\partial x}\right)^2 dx\right] = 0. \tag{A.33}$$

But on solving eq.(A.33) Lampinen obtained the following expression [60] of temperature profile at NSS; namely:

$$T(x) = T_0(T_1/T_0)^{x/L}. \tag{A.34}$$

It is not the same expression the one, that is obtained from equation (A.24) at NSS, namely:

$$T(x) = T_0 + (T_1 - T_0)(x/L) \tag{A.35}$$

where, T_1 and T_0 are the temperatures of heat reservoirs $(T_1 > T_0)$ between which the heat conduit of the length L is kept. We recall that eq.(A.35) exactly matches with the experimental temperature profile. Thus the result that is obtained on minimizing the rate of entropy production is eq.(A.34), which is entirely different then the experimental one, eq.(A.35), this then questions the correctness of the principle of minimum production of entropy or one may choose to say that a NSS does not correspond to the principle of minimum entropy production. Of course, the Fourier law is a description of a NSS.

The same analysis has been carried out by Müller [34] in that he assumed $\lambda = \lambda(T)$ that produces following relation from internal energy balance equation, namely:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial \ln \lambda}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2 = 0 \tag{A.36}$$

whereas on minimizing entropy production he gets,

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial \ln \sqrt{\frac{\lambda}{T^2}}}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2 = 0 \tag{A.37}$$

Müller then points out that eqs.(A.36) and (A.37) are not identical and further asserts that — unless $\lambda(T) \propto \dfrac{1}{T^2}$ holds good the two equations are not identical, which is not a realistic proposition for any material.

Thus along with Müller we conclude that there is a serious flaw in the so called principle of minimum production of entropy.

A.5 A Thermodynamic Argument

The CIT given expression of entropy source strength for heat conduction is eq.(A.31), namely:

$$\sigma_s = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) \geq 0$$

As argued above the Fourier law is not valid for nonequilibrium states other than the NSS, let us examine how good is the MCV equation to study the entropy evolution with time. Thus on substitution of eq.(A.22), the MCV equation, into eq.(A.31) we obtain,

$$\sigma_s = \frac{\lambda}{T^2} (\nabla T)^2 + \frac{\tau}{T^2} \frac{d\mathbf{q}}{dt} \cdot \nabla T. \tag{A.38}$$

Now, if we isolate the rigid body instantly from its environment, its entropy will vary with time as,

$$\frac{dS}{dt} = \int_V \sigma_s dV \tag{A.39}$$

The solution of one dimensional version of the preceding equation was obtained earlier [29] and the result is the non-monotonic increase of entropy depicted in the Figure 1 by dashed curve. However, this result is not in conformity with the second law of thermodynamics. This is taken as a demonstration of the *incompatibility* of MCV equation with CIT.
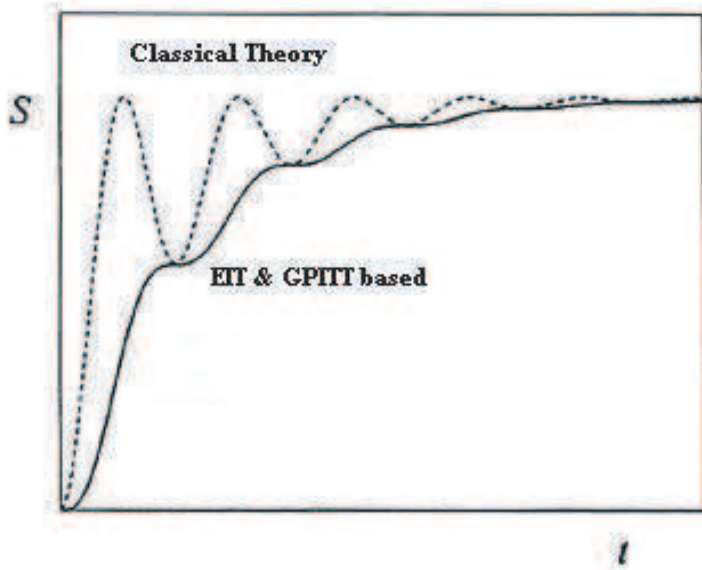
Fig. 3 Evolution of entropy based on the Classical Irreversible Thermodynamic Theory during the equilibration of an isolated system when use is made of Cattaneo's equation is given by the *dashed curve*. The evolution of entropy using EIT and GPITT descriptions is represented by the *solid curve*.

A.6 Some of the Kinetic Theory Based Considerations

Though we have tried in the preceding subsections to limit our discussion at the level of thermodynamics only but it would be profitable if we also consider kinetic theory description to shed additional light on the status of LEA and other aspects. Herein we consider additional aspects over and above those we have considered in the main text of this paper.

Some Basic Aspects of Kinetic Theory

In kinetic theory [15, 17, 21] the volume element $d\mathbf{r}$ is taken about the local position $\mathbf{r}$. Thus $d\mathbf{r} \approx dV$ of fluid dynamics which is the same as the tiny cell envisaged while prescribing a local equilibrium. The instantaneous values of mass density, ρ, hydrodynamic linear momentum density, $\rho\mathbf{u}$, and kinetic energy density, $\frac{1}{2}\rho\mathbf{u}^2$, for a non-uniform monatomic gas are given by,

$$\rho = m \int f d\mathbf{c} = m \int f^{(0)} d\mathbf{c} \tag{A.40}$$

$$\rho\mathbf{u} = m \int \mathbf{C} f d\mathbf{c} = m \int \mathbf{C} f^{(0)} d\mathbf{c} \tag{A.41}$$

$$\frac{1}{2}\rho\mathbf{u}^2 = m \int \frac{1}{2}\mathbf{C}^2 f d\mathbf{c} = m \int \frac{1}{2}\mathbf{C}^2 f^{(0)} d\mathbf{c} \tag{A.42}$$

where the rest of the quantities of above equations have same meaning that has been described in relevant sections of this paper and the integration is carried over all velocities $-\infty$ to $+\infty$, that is over all molecules contained in the volume element $d\mathbf{r}$ that number by definition is very large to justify it. Thus within the assumed volume element $d\mathbf{r}$ for example no temperature gradient can be assigned as the temperature is defined as,

$$\frac{3}{2}nk_BT = m\int\frac{1}{2}\mathbf{C}^2 f d\mathbf{c} = m\int\frac{1}{2}\mathbf{C}^2 f^{(0)}d\mathbf{c} = \rho u \tag{A.43}$$

where u is the internal energy per unit mass.

Notice that, while evaluating the above integrals no assumption of local equilibrium is involved. But if the so evaluated quantities are to coincide with the experimentally measured ones then almost all molecules of the tiny volume element $d\mathbf{r}$ must have collided at least once with the measuring gadget and this requires minimum time duration of interaction of the measuring gadget with the local pocket. The same fact remains true of all kinetic theory given macroscopic level equations including the internal energy balance equation that is identical to say of eq.(A.3). The same is true of all fluid dynamical equations. Therefore, within $d\mathbf{r}$ no gradients of intensive quantities can be assigned. The gradients in kinetic theory gets assigned between the adjacent volume elements. This doesn't mean that within the volume elements, $d\mathbf{r}$, some sort of equilibrium can be assigned when the system globally is in nonequilibrium. There are only two choices. If system is globally in equilibriun (nonequilibrium) the tiny volume element, $d\mathbf{r}$, would be in equilibriun (nonequilibrium).

Kinetic Theory Given Entropy Function Based Considerations

Suppose that the system at the local level needs to be described by the distribution function $f = f^{(0)}(1+\phi^{(1)})$, that is only the first approximation level is adequate. With this assumption as well as system is supposed to be not much away from equilibrium allows us to restrict upto second order terms in $\phi^{(1)}$'s. Therefore, the operative kinetic theory based thermodynamic expressions are the following,

$$\rho s = \rho s^{(0)} - k_B \int\frac{1}{2}f^{(0)}\left(\phi^{(1)}\right)^2 d\mathbf{c}, \tag{A.44}$$

$$\begin{aligned}
\sigma_s = &-k_B\int\int\int f_1^{(0)}f^{(0)}\phi^{(1)}\Delta\phi^{(1)}g\sigma(g,\Omega)d\Omega d\mathbf{c}_1\,d\mathbf{c}\\
&-k_B\int\int\int f_1^{(0)}f^{(0)}\phi^{(1)}\Delta(\phi^{(1)}\phi^{(1)})g\sigma(g,\Omega)d\Omega d\mathbf{c}_1\,d\mathbf{c}\\
&+\frac{1}{2}\int\int\int f_1^{(0)}f^{(0)}(\phi^{(1)})^2\Delta\phi^{(1)}g\sigma(g,\Omega)d\Omega d\mathbf{c}_1\,d\mathbf{c},
\end{aligned} \tag{A.45}$$

where
$\Delta\phi^{(1)} = \left(\phi_1^{(1)'}+\phi^{(1)'}-\phi_1^{(1)}-\phi^{(1)}\right)$ and $\Delta(\phi^{(1)}\phi^{(1)}) = \left(\phi_1^{(1)'}\phi^{(1)'}-\phi_1^{(1)}\phi^{(1)}\right)$,

$$\mathbf{J}_s = -k_B\int\mathbf{C}f^{(0)}\phi^{(1)}\ln f^{(0)}d\mathbf{c} - \frac{1}{2}k_B\int\mathbf{C}f^{(0)}(\phi^{(1)})^2 d\mathbf{c}. \tag{A.46}$$

From the above expressions it is clear that the respective nonequilibrium contributions are determined by the magnitudes of $\phi^{(1)}$'s . If $\phi^{(1)} < 1$ and $(\phi^{(1)})^2 \ll 1$ then the $(\phi^{(1)})^2$ containing term in eq.(A.44) may be ignored. That reduces eq.(A.44) to,

$$\rho s \approx \rho s^{(0)}, \tag{A.47}$$

That is we obtain $s = s(u,v)$, which is the functional dependence of equilibrium thermodynamics. Now let us examine eqs.(A.45) and (A.46). In eq.(A.45) we have in the integrand of the first integral the products $\phi^{(1)}\Delta\phi^{(1)}$ that is nothing but the difference between the squared terms of $\phi^{(1)}$'s pertaining

to before and after the collision. The second integral contains the product $\phi^{(1)}\Delta(\phi^{(1)}\phi^{(1)})$, which is the difference in the cubic terms in $\phi^{(1)}$'s pertaining to the before and after the collision. And the last integral contains the term $(\phi^{(1)})^2\Delta\phi^{(1)}$ that also is a difference in the cubic terms in $\phi^{(1)}$'s. Hence all the three integrals of eq.(A.45) are vanishingly small that makes $\sigma_s \to 0$.

Now in eq.(A.46) we have in one integral the squared term $(\phi^{(1)})^2$ and in another integral its integrand has $\phi^{(1)}\ln f^{(0)}$. As $\phi^{(1)}$ is a very small quantity and $\ln f^{(0)}$ being a logarithmic quantity it too would be very small. In view of this the right hand side of eq.(A.46) becomes vanishingly small that in turn makes $\mathbf{J}_s \to 0$.

Thus we see that both the nonequilibrium determining quantities vanish that means under the said restrictions on $\phi^{(1)}$'s no irreversibility can exist. That is commensurate with the outcome $s = s^{(0)} = s(u,v)$ and is not accompanied by any sort of spatial non-uniformity based irreversibility.

Therefore, if irreversibility is to exist in our description $(\phi^{(1)})^2$ and similar terms should exist in our description. Therefore, to the minimum level of irreversibility description under the Enskog method we must have the following description,

$$\rho s = \rho s^{(0)} - k_B \int \frac{1}{2} f^{(0)} \left(\phi^{(1)}\right)^2 d\mathbf{c},$$

$$\sigma_s = -k_B \int \int \int f_1^{(0)} f^{(0)} \phi^{(1)} \Delta\phi^{(1)} g\sigma(g,\Omega) d\Omega d\mathbf{c}_1 \, d\mathbf{c},$$

$$\mathbf{J}_s = -k_B \int \mathbf{C} f^{(0)} \phi^{(1)} \ln f^{(0)} d\mathbf{c}.$$

Therefore, even in the Enskog method $k_B \int \frac{1}{2} f^{(0)} \left(\phi^{(1)}\right)^2 d\mathbf{c}$ will add additional terms to $s = T^{-1}(u + pv - \mu)$ originating in irreversibility. Thus we have clearly established that there is absolutely no Enskog method based proof of the so-called LEA. Hence, now there is no contradiction between Grad's and Enskog solutions based nonequilibrium thermodynamics in the sense that both provide additional terms in Gibbs relation to describe irreversibility on account of spatial non-uniformity. In the former it is the physical fluxes that serve as additional thermodynamic variables whereas in the latter they are the physical gradients of intensive properties if we restrict only to the second order terms in $\phi^{(1)}$'s in the entropy expression. In reaching such a Gibbs relation neither we require the postulation of LEA nor the consideration of beyond LEA.

Acknowledgments

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