

On the nonequilibrium thermodynamic roots of the additional facets of chemical interaction

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Abstract

Keeping in view the limits of universe of operations of thermodynamics as stated by Bridgman [1] and experimentally verified by Evans et al [3] the Generalized Phenomenological Irreversible Thermodynamic Theory (GPITT) [2, 6, 8] has been developed. This reveals that thermodynamic irreversibility is all about the imbalances in corresponding chemical interaction. Even the physical fluxes like heat and momentum and the nonequilibrium population in internal configurational states of macromolecules are the manifestation of imbalances in corresponding chemical interaction. At the same time we have seen the need to modify the statements by Eddington [4] about the entropy and time's arrow. Actually it is the rate of entropy production and time's arrow that go hand in hand.

1 INTRODUCTION

Bridgman [1] in his 1953 and 1969 writings has conjectured about the universe of operations of thermodynamics both in terms of the size of the system and the duration of measurements. Thus there is a lower limit to the size of the system as well as for the duration of an experimental measurement below that one enters into the domain of natural fluctuations. Therefore, the laws of thermodynamics hold good above these limits. The shortest size limit on a thermodynamic system is well documented and hence is well known. However, hardly an attention is paid to know the lowest time scales that are amenable in thermodynamics, particularly that are permitted by the second law of thermodynamics. For example, the following well known thermodynamic inequality concerning the heat transfer between two rigid bodies, namely:

$$\frac{dQ}{dt} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) > 0 \quad (1)$$

where dQ is the amount of heat exchanged by the system 1 with system 2 and T 's are their temperatures, holds good for time duration $dt \geq \tau_{therm}$, where τ_{therm} is the minimum time needed to sense the temperature of a body by an other body in diathermal contact with it. Hence, dQ is the amount of heat exchanged by the system 1 with its surroundings of temperature T_2 during the time period $dt \geq \tau_{therm}$. The τ_{therm} can be as small as one or two orders lower than a nano-second [2] provided the lowest size limit has not been crossed. Therefore, equation 1 is a mathematical description of unidirectionality of the heat transfers. As all unidirectional processes are irreversible in time the shorter time duration of observations than τ_{therm} cannot sense the unidirectionality of a process or in other words the irreversibility of a process gets manifested only if the above condition of the time duration of observation is not flouted¹. Therefore, the same restriction holds for Clausius' inequality in the cyclic form, namely:

$$\oint_{irr} \frac{dQ}{T_R} < 0 \quad (2)$$

¹Recently, it has been experimentally demonstrated that there does exist the lowest limit to the system size as well as to the time duration of observation made [3]. It has been also demonstrated by the same experiment that at the colloidal particle size scale the not obeying of the second law of thermodynamics is observed even if the time duration of observations extends well beyond several seconds.

irr stands for the irreversibility involved in the cyclic operation of the device and T_R is the temperature of the heat reservoir at which the device exchanges dQ amount of heat, obviously during the time duration $\tau \geq \tau_{therm}$. At the same time in 1931 Eddington [4] has made a good number of assertion about the entropy function and irreversibility. As irreversibility by its nature is unidirectional in time it has to have an in-built index of time. The beauty of time is that it simply goes on and on. This index of time has been termed by Eddington [4] as *time's arrow*. Indeed there is no limit on the minimum length of time's arrow, however, the unidirectionality of processes as described by the inequality say of equation 1, determines the minimum length of its time's arrow as τ_{therm} . In this context we recall here the assertions of Eddington [4]. Various statements of Eddington's assertion (he says they are the secondary laws) [4] are:

1. "Time's arrow is the sole property of entropy".
2. "Nothing in the statistics of an assemblage can distinguish a direction of time when entropy fails to distinguish one".
3. "Other statistical characters besides entropy might perhaps be used to discriminate time's arrow, they can only succeed when it succeeds and they fail when it fails".

Thus time's arrow implied in above statements pertains to the time duration of observations $\tau (\geq \tau_{therm})$. Notice that an undercurrent in the above statements is that Eddington [4] is actually referring to the entropy function in nonequilibrium of entire universe. The importance of these assertions have also been reiterated by Katchalsky and Curran [5] for testing the consistency of nonequilibrium thermodynamic frameworks either proposed or developed.

In view of the above conjectures and assertions we below describe an ab initio development of a thermodynamic framework for irreversible processes which turns out to be an yet another route of Generalized Phenomenological Irreversible Thermodynamic Theory (GPITT) [2, 6]. The steps that we have followed in the development of a thermodynamic framework surfaces out the existence of the additional facets of chemical interaction and it further reveals that the thermodynamic irreversibility is all about the imbalance in chemical interactions.

2 NONEQUILIBRIUM THERMODYNAMICS

When a system is spatially non-uniform that is,

$$\nabla T \neq 0, \nabla p \neq 0, \nabla \mu_k \neq 0, \nabla \mathbf{u} \neq 0 \quad (3)$$

and hence we have

$$\mathbf{q} \neq 0, \mathbf{\Pi} \neq 0, \mathbf{J}_k \neq 0. \quad (4)$$

The processes that take place are:

1. Chemical conversions at finite rate.
2. Matter diffusion.
3. Heat transfer.
4. Momentum transfer.

Hence there is a need to go for a local level description. The local level quantities are defined as,

$$U = \int_V \rho u dV, \quad G = \int_V \rho \mathcal{G} dV, \quad \text{etc.} \quad (5)$$

where ρ is the mass density and u , \mathcal{G} , etc. are the per unit mass quantities at a given position and time t . Before proceeding further we also need to keep in mind that the only valid versions of Clausius' inequality are:

$$\oint_{\text{irr}} \frac{dQ}{T_R(t)} < 0 \quad (6)$$

and

$$S_B - S_A = \Delta S > \int_A^B \frac{dQ}{T_R(t)} \quad (7)$$

whereas the following form of it, namely:

$$dS > \frac{dQ}{T} \quad (8)$$

is not simply a differential form of equation 7, the fact is that Clausius himself did not derive but simply stated this inequality [7]. In fact, in equation 8 S has to be primarily that for a nonequilibrium state through which the system evolves whereas in equation 7 S is that for the end equilibrium states. In the backdrop of above discussion, recently Eu, García-Colín and Bhalekar [2, 6, 8, 9, 10, 11] have used equation 6 and on following the steps adopted by Clausius himself arrived at the entropy function in nonequilibrium.

3 GPITT

Firstly, Clausius' uncompensation function, N is defined from equation 2 as [2, 6, 8, 10, 11],

$$N = - \oint_{\text{irr}} \frac{dQ}{T_R(t)} = - \oint_{\text{irr}} \frac{1}{T_R(t)} \frac{dQ}{dt} dt > 0 \quad (9)$$

then N is treated as an independent quantity to express as,

$$N = \oint_{\text{irr}} \frac{dN}{dt} dt \quad (10)$$

From equation 10 we have

$$dN > 0 \quad \text{as} \quad N > 0 \quad (11)$$

The positive definiteness of dN uniquely retains the unidirectionality of time's arrow during the irreversible evolution of the system.

On combining equations 9 and 10 we obtain

$$\oint_{\text{irr}} \left[\frac{1}{T_R(t)} \frac{dQ}{dt} + \frac{dN}{dt} \right] dt = 0 \quad (12)$$

As cyclic integral of equation 12 vanishes we obtain

$$\frac{dS}{dt} = \frac{1}{T_R(t)} \frac{dQ}{dt} + \frac{dN}{dt} \quad (13)$$

Thus S is the entropy of a nonequilibrium state. In the limit of $dN \rightarrow 0$ we have S (in nonequilibrium) $\rightarrow S$ (in equilibrium). Notice that equation 11 is the dictate provided by the second law of thermodynamics, namely $dN/dt > 0$, hence from equation 13 we obtain:

$$\frac{dS}{dt} > \frac{1}{T_R(t)} \frac{dQ}{dt} \quad (14)$$

which is nothing else but equation 8. However, equation 13 contains $T_R(t)$ hence the first term on its right hand side cannot be transformed as such to a local level description for a spatially non-uniform systems. For that purpose let us express the said term as [2, 8],

$$\frac{1}{T_R(t)} \frac{dQ}{dt} \equiv \oint_{\mathbf{A}} -\frac{\mathbf{Q}(\mathbf{A}, t)}{T(\mathbf{A}, t)} \cdot d\mathbf{A} \quad (15)$$

where $\mathbf{Q}(\mathbf{A}, t)$ is the heat flux density at the surface coordinate \mathbf{A} and at time t , $d\mathbf{A}$ is the differential area vector on the surface of the system and $T(\mathbf{A}, t)$ is temperature at \mathbf{A} and t [2, 8]. Now on applying Gauss theorem we obtain,

$$\frac{1}{T_R(t)} \frac{dQ}{dt} \equiv \oint_{\mathbf{V}} \left[-\text{div} \left(\frac{\mathbf{q}(\mathbf{r}, t)}{T(\mathbf{r}, t)} \right) + \mathbf{q}(\mathbf{r}, t) \cdot \nabla \left(\frac{1}{T(\mathbf{r}, t)} \right) \right] dV \quad (16)$$

that reduces to,

$$\frac{1}{T_R(t)} \frac{dQ}{dt} \equiv \int_{\mathbf{V}} -\frac{1}{T} \text{div} \mathbf{q} dV \quad (17)$$

Other two terms of equation 13 get easily transformed to

$$\frac{dS}{dt} = \int_{\mathbf{V}} \rho \frac{ds}{dt} dV \quad (18)$$

$$\frac{dN}{dt} = \int_{\mathbf{V}} \rho \frac{dN}{dt} dV \quad (19)$$

On substituting equations 17-19 into equation 13 we obtain at the local level,

$$\rho \frac{ds}{dt} = -\frac{1}{T} \text{div} \mathbf{q} + \rho \frac{dN}{dt} \quad (20)$$

Notice that $dN/dt \leq 0$.

Now we use the simple fluid dynamical internal energy balance equation, namely:

$$\rho \frac{du}{dt} = -\text{div} \mathbf{q} - p\rho \frac{dv}{dt} + \mathbf{\Pi} : \nabla \mathbf{u} \quad (21)$$

On combining equations 20 and 21 we obtain

$$\rho \frac{ds}{dt} = \frac{1}{T} \left[\rho \frac{du}{dt} + p\rho \frac{dv}{dt} - \mathbf{\Pi} : \nabla \mathbf{u} \right] + \rho \frac{dN}{dt} \quad (22)$$

The steps involved in quantifying dN [2, 8, 9] first requires rearranging equation 22 as,

$$\begin{aligned} \rho \frac{dN}{dt} &= \rho \left[\frac{ds}{dt} - \frac{1}{T} \frac{du}{dt} - \frac{p}{T} \frac{dv}{dt} \right] + \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{u} \\ &= \frac{\rho}{T} \left[\frac{d(sT - u - pv)}{dt} - s \frac{dT}{dt} + v \frac{dp}{dt} \right] \\ &\quad + \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{u} \end{aligned} \quad (23)$$

as $sT - u - pv = -\mathcal{G}$ (the Gibbs function), equation 23 reads as,

$$\rho \frac{dN}{dt} = \frac{\rho}{T} \left[-\frac{d\mathcal{G}}{dt} - s \frac{dT}{dt} + v \frac{dp}{dt} + \rho^{-1} \mathbf{\Pi} : \nabla \mathbf{u} \right] \quad (24)$$

3.1 Chemical Interactions

3.1.1 Spatially uniform systems

Notice that the Gibbs function, \mathcal{G} , appearing in equation 24 basically determines the chemical interaction. This then means that the quantification of irreversibility, that is to find an expression for dN/dt , has to be made via identifying a proper expression of \mathcal{G} . Let us now reexamine what is revealed by thermodynamics about the chemical interaction in simple cases.

In the case of a spatially uniform closed system having irreversibility only due to the occurrence of chemical conversion at finite rates within it, there is no need to use the local level description. For such systems, the equilibrium thermodynamic expression of the Gibbs function, G , still remains valid, namely:

$$G = \sum_k n_k \mu_k \quad (\text{at given } T \text{ and } p) \quad (25)$$

Notice that G measures the existing chemical interaction. The time derivative of G reads as,

$$\frac{dG}{dt} = \sum_k n_k \frac{d\mu_k}{dt} + \sum_k \mu_k \frac{d_i n_k}{dt} \quad (26)$$

Recall that being a closed system the $d_e n_k$ containing term, namely, $\sum_k d_e n_k/dt$, remains effectively equal to zero. On substitution of equation 26 into the global level version of equation 24 we obtain,

$$\frac{dN}{dt} = \frac{1}{T} \sum_k \mu_k \frac{d_i n_k}{dt} > 0 \quad (27)$$

on simultaneous extraction of the corresponding Gibbs-Duhem equation, namely:

$$\sum_k n_k \frac{d\mu_k}{dt} + S \frac{dT}{dt} - V \frac{dp}{dt} = 0 \quad (28)$$

The positive definiteness of equation 27 is guaranteed by the second law of thermodynamics c.f. equation 11. We have also kept in mind that there is no irreversibility on account of temperature non-uniformity even across the boundary of the system hence we rigorously have $T_R = T$. Next on substitution of equation 27 into equation 13 we are led to the following Gibbs relation, namely:

$$\frac{dS}{dt} = \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \sum_k \mu_k \frac{d_i n_k}{dt} \quad (29)$$

Further, Dalton's law for chemical reactions [12] gives us,

$$\frac{d_i n_k}{dt} = \sum_l \nu_k^l \frac{d\xi^l}{dt} \quad (30)$$

where ν_k^l is the stoichiometric coefficient of the component k in the l -th chemical reaction and ξ^l is the extent of advancement of l -th chemical reaction. Next on substitution of equation 30 into equation 29 produces the well known De Donderian equation [12], namely:

$$\frac{dS}{dt} = \frac{1}{T} \frac{dU}{dt} + \frac{p}{T} \frac{dV}{dt} + \frac{1}{T} \sum_l \mathcal{A}^l \frac{d\xi^l}{dt} \quad (31)$$

where the chemical affinity, \mathcal{A}^l , of l -th chemical reaction reads as [12],

$$\mathcal{A}^l = - \sum_k \nu_k^l \mu_k > 0 \quad (32)$$

now at equilibrium we rigorously have $dN = 0$ it then demands $\mathcal{A}^l = 0$ ($l = 1, 2, \dots$) at chemical equilibrium. Now as G measures the existing chemical interaction the chemical affinities \mathcal{A}^l ($l = 1, 2, \dots$) determines the existing extent of imbalance in chemical interaction. That is at chemical equilibrium the chemical interaction remains completely balanced, which is described by $\mathcal{A}^l = 0$ ($l = 1, 2, \dots$). In other words, the existence of imbalance in chemical interaction gets manifested by the non-zero value of chemical affinities and this forces chemical conversions to proceed at finite rates (of course, if chemical conversions take place the observed rates, broadly speaking, depends on how high or low is the energy of activation of the individual chemical reactions).

In nonequilibrium other processes that occur are,

1. Matter diffusion (\mathbf{J}_k)
2. Heat conduction (\mathbf{q})
3. Momentum transfer ($\mathbf{\Pi}$)

which is the case when system happens to be spatially non-uniform.

3.1.2 Spatially Non-uniform Systems

From kinetic theory of non-uniform gases [13] we learn that the population in translational quantum states in presence of heat and/or momentum fluxes is different from that given by Maxwellian distribution function, the latter corresponds to equilibrium. And when such a system is detached from the source of temperature gradient and/or velocity gradient the fluxes die fast and the population in translational quantum states becomes Maxwellian. On the same lines as we have seen in the preceding subsection the above observation means that when the distribution in translational energy states remains Maxwellian there is no imbalance in the corresponding chemical interaction whereas in nonequilibrium there exist imbalance in the corresponding chemical interaction. Therefore, we infer that in nonequilibrium the chemical potentials in various translational quantum states are not equal whereas in absence of these fluxes they have identical values. For the sake of simplicity, herein we consider an ideal monatomic gas in a spatially non-uniform system **having irreversibility only on account of heat transfer**. In kinetic theory the heat flux density, \mathbf{q} , is given by

$$\mathbf{q} = \int \frac{1}{2} m \mathbf{C}^2 \mathbf{C} f d\mathbf{c} \quad (33)$$

where m is the mass of the monatomic gas molecule, \mathbf{C} is the chaotic or peculiar velocity given by

$$\mathbf{C} = \mathbf{c} - \mathbf{u} \quad (34)$$

where \mathbf{c} is the velocity of a molecule and \mathbf{u} is the barycentric velocity at that position, and f is the distribution function.

Therefore, in presence of a heat flux we have,

$$\mu_{\mathbf{C}} \neq \mu_{\mathbf{C}'} \neq \mu_{\mathbf{C}''} = \dots$$

whereas in equilibrium (in absence of heat flux) we rigorously have,

$$\mu_{\mathbf{C}} = \mu_{\mathbf{C}'} = \mu_{\mathbf{C}''} = \dots$$

With this background we define the required Gibbs function, \mathcal{G} , as,

$$\mathcal{G} = \frac{1}{m} \int \mu_{\mathbf{C}} x_{\mathbf{C}} d\mathbf{c} \quad (35)$$

and the mass fraction $x_{\mathbf{C}}$ as,

$$x_{\mathbf{C}} = \frac{f}{n} \quad (36)$$

when n is the local level number density of molecules. Notice that we have adopted $\mu_{\mathbf{C}}$ as a per molecule quantity and hence to have \mathcal{G} as a per unit mass quantity we have the factor $1/m$ on the right hand side of equation 35. On combining equations 35 and 36 we obtain:

$$\mathcal{G} = \frac{1}{mn} \int \mu_{\mathbf{C}} f d\mathbf{c} = \frac{n \langle \mu \rangle}{mn} = \frac{\langle \mu \rangle}{m} \quad (37)$$

where $\langle \mu \rangle$ is the average value of Gibbs function per molecule. Now in kinetic theory to obtain an expression of f (distribution function) in nonequilibrium one solves the Boltzmann integro-differential equation [13], namely:

$$\frac{\partial f}{\partial t} + \mathbf{C} \cdot \frac{\partial f}{\partial \mathbf{r}} = J(f|f) \quad (38)$$

where \mathbf{r} is the position vector and $J(f|f)$ is the Boltzmann collisional integral given by,

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

Here as usual, $\sigma(g, \Omega)$ 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. There are two standard methods namely: Chapman-Enskog [13] and Grad [14] methods. In both of them f is solved around local Maxwellian, $f^{(0)}$, which by definition is a function of u and ρ , the per unit mass local internal energy and local mass density respectively. On using such solutions one obviously incorporates the corresponding kinetic theory tenets into the thermodynamic description. **To have our thermodynamic expressions free of such incoherencies one needs to find out a direct method to measure $x_{\mathbf{C}}$.** However, the non-availability of such a method forces us to use Grad's solution of Boltzmann integro-differential equation. In Grad's 13-moment solution we have,

$$f = f^{(0)}(1 + \Phi) \quad (39)$$

where $f^{(0)}$ is the local Maxwellian distribution function, and on ignoring viscous effects we have to the first approximation,

$$\Phi = \frac{2m}{5pk_B^2 T^2} \left(\frac{1}{2} m C^2 - \frac{5}{2} k_B T \right) \mathbf{C} \cdot \mathbf{q} \quad (40)$$

On using the same assumption as that is involved in equation 39 we propose the following expression for $\mu_{\mathbf{C}}$, namely:

$$\mu_{\mathbf{C}} = \mu^{(0)} + k_B T \ln(1 + \Phi) \quad (41)$$

In this way $\mu^{(0)}$, the chemical potential, corresponds to the state of no heat flux. Now we substitute equation 41 into equation 35 that produces,

$$\begin{aligned} \mathcal{G} &= \frac{1}{mn} \int \mu^{(0)} f d\mathbf{c} + \frac{k_B T}{mn} \int f \ln(1 + \Phi) d\mathbf{c} \\ &= \frac{\mu^{(0)}}{mn} \int f d\mathbf{c} + \frac{k_B T}{mn} \int f \ln(1 + \Phi) d\mathbf{c} \\ &= \frac{\mu^{(0)}}{m} + \frac{k_B T}{mn} \int f \ln(1 + \Phi) d\mathbf{c} \end{aligned} \quad (42)$$

To solve equation 42 we expand $\ln(1 + \Phi)$ in a Taylor series,

$$\ln(1 + \Phi) = \Phi - \frac{\Phi^2}{2} + \dots \quad (43)$$

Now assume that the system is not far away from equilibrium that gives, the following approximation, namely:

$$\ln(1 + \Phi) \approx \Phi \quad (44)$$

Hence on substituting equation 44 into equation 42 we obtain,

$$\mathcal{G} \simeq \frac{\mu^{(0)}}{m} + \frac{k_B T}{mn} \int f \Phi d\mathbf{c} \quad (45)$$

and on using expression of equation 40 for Φ in equation 45 we get;

$$\begin{aligned} \mathcal{G} = & \frac{\mu^{(0)}}{m} + \frac{k_B T}{mn} \left(\frac{2m}{5pk_B^2 T^2} \right) \left(\int \frac{1}{2} m \mathbf{C}^2 \mathbf{C} f d\mathbf{c} \right) \cdot \mathbf{q} \\ & - \frac{k_B T}{mn} \left(\frac{m}{pk_B T} \right) \left(\int \mathbf{C} f d\mathbf{c} \right) \cdot \mathbf{q} \end{aligned} \quad (46)$$

Obviously, the average of peculiar velocity, \mathbf{C} , is zero, hence the last term on the right hand side of equation 46 vanishes leaving,

$$\mathcal{G} = \frac{\mu^{(0)}}{m} + \frac{2}{5npk_B T} \mathbf{q} \cdot \mathbf{q} \quad (47)$$

where we have used the kinetic theory definition of heat flux, namely equation 33. In the derivation of corresponding Gibbs relation we need to substitute an expression of $d\mathcal{G}/dt$ in equation 24. This expression is obtained from equation 47 as,

$$\begin{aligned} \frac{d\mathcal{G}}{dt} = & \frac{d(\mu^{(0)}/m)}{dt} - \frac{2}{5npk_B T^2} q^2 \frac{dT}{dt} \\ & - \frac{2}{5nk_B T p^2} q^2 \frac{dp}{dt} + \frac{4}{5npk_B T} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} \end{aligned} \quad (48)$$

Next we substitute equation 48 into equation 24, and extract the corresponding Gibbs-Duhem equation, namely:

$$\frac{d(\mu^{(0)}/m)}{dt} + \left(s - \frac{2}{5npk_B T^2} q^2 \right) \frac{dT}{dt} - \left(v + \frac{2}{5nk_B T p^2} q^2 \right) \frac{dp}{dt} = 0 \quad (49)$$

that produces the effective expression of rate of uncompensation function as,

$$\rho \frac{d\mathcal{N}}{dt} = - \frac{4\rho}{5npk_B T^2} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt}. \quad (50)$$

Next we substitute equation 50 into equation 22 that yields,

$$\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{p}{T} \frac{dv}{dt} - \frac{4}{5npk_B T^2} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} \quad (51)$$

which is nothing else but the extended Gibbs relation of extended irreversible thermodynamics (EIT) [15]. Only difference between the two is in the numerator of coefficient of the last term on the right hand side of equation 51 instead of the numeral 4 there in EIT they have the numeral 2 [15].

Now recall the Clausius-Duhem inequality [16], namely:

$$\rho \frac{ds}{dt} + \text{div} \mathbf{J}_s = \sigma_s \geq 0 \quad (52)$$

where \mathbf{J}_s is the entropy flux density and σ_s is the positive definite entropy source strength (or rate of entropy production per unit volume).

In the present case, on combining the corresponding version of equation 21 (that is by dropping the term describing viscous dissipation) with equation 51 gives,

$$\rho \frac{ds}{dt} = -\text{div} \left(\frac{\mathbf{q}}{T} \right) + \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) - \frac{4 \rho}{5npk_B T^2} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} \quad (53)$$

Hence on comparing equation 53 with equation 52 we obtain,

$$\mathbf{J}_s = \frac{\mathbf{q}}{T} \quad (54)$$

$$\sigma_s = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) - \frac{4 \rho}{5npk_B T^2} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} > 0. \quad (55)$$

Equation 55 clearly reveals that there are two mechanisms of entropy production one originates from the heat transfer across the boundaries of the system and the other operates by an internal mechanism, which is controlled internally by the collisions amongst the molecules within the tiny volume element.

In a stationary nonequilibrium state as the heat flux and other system properties are time invariant the last term in equation 55 describing collisional mechanism of entropy production drops out (as $d\mathbf{q}/dt = 0$) hence the expression for σ_s simplifies to

$$\sigma_s = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) > 0 \quad (56)$$

which is the well known traditional expression of entropy production. It is amusing to note that when the heat flux varies according to the Maxwell-Cattaneo-Vernotte (MCV) [17] equation, namely,

$$\tau \frac{d\mathbf{q}}{dt} = -\mathbf{q} - \lambda \nabla T \quad (57)$$

where τ is the relaxation time and λ is the thermal conductivity, then equation 55 simplifies as,

$$\begin{aligned} \sigma_s &= \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) + \frac{4 \rho}{5n\tau p k_B T^2} \mathbf{q} \cdot (\mathbf{q} + \lambda \nabla T) \\ &= -\frac{1}{T^2} \mathbf{q} \cdot \nabla T + \frac{4 \rho}{5n\tau p k_B T^2} \mathbf{q}^2 + \frac{4 \rho \lambda}{5n\tau p k_B T^2} \mathbf{q} \cdot \nabla T \end{aligned} \quad (58)$$

Thus if,

$$\frac{4 \rho \lambda}{5n\tau p k_B} = 1 \quad (59)$$

equation 58 reduces to the expression given by EIT, namely,

$$\sigma_s = \frac{4 \rho}{5n\tau p k_B T^2} \mathbf{q}^2 = \frac{1}{\lambda T^2} \mathbf{q}^2 > 0 \quad (60)$$

This means that the relaxation time τ in this case is given by,

$$\tau = \frac{4m\lambda}{5pk_B} \quad (61)$$

where $\rho = mn$ has been used.

Thus the above derivation appears to be a better justification of treating heat flux density as an additional thermodynamic variable. This result is not surprising because as in EIT herein too we have used the kinetic theory expressions. However, it would be interesting to see whether one would lead to the same results if alternative expressions for $x_{\mathbf{C}}$ and $\mu_{\mathbf{C}}$ become available that are not based on kinetic theory.

The above step by step derivation clearly reveals that **the existence of heat flux itself is a manifestation of existing imbalance in corresponding chemical interaction** within the system as the heat flux in equation 51 appears on quantifying \mathcal{G} function the latter basically describes the chemical interaction. The same remains true of the existence of the momentum flux, Π . Indeed, the existence of the diffusion flux, \mathbf{J}_k , is the well known pretty old example of imbalance in the corresponding chemical interaction.

3.2 Complex Systems in Nonequilibrium

The above described GPITT methodology of developing a nonequilibrium thermodynamic framework clearly demonstrates that the quantification of irreversibility in the last step demands an appropriate quantification of the Gibbs function, \mathcal{G} . Further, this exercise has to be done keeping in view the nature and complexity of the system. For example, in the natural evolution of a system in nonequilibrium consisting of macromolecules, e. g. enzymes, polymers, etc. the non-thermal effects do play a major role. Their physicochemical properties are governed by their internal configuration. Hence these internal configurational states have to be considered as different entities. Thus if ϵ is taken as the distinguishing parameter of various configurational states of a macromolecule then we need to first define \mathcal{G} as,

$$\mathcal{G} = \int \mu_{\epsilon} x_{\epsilon} d\epsilon \quad (62)$$

where the chemical potential, μ_{ϵ} , is identified as per unit mass quantity and x_{ϵ} are the mass fractions of the internal configurational states of the macromolecule.

The substitution of the preceding expression of \mathcal{G} in equation 24 produces the following expression of the local level uncompensation function, namely:

$$\rho \frac{d\mathcal{N}}{dt} = \frac{\rho}{T} \left[-\frac{d \int \mu_{\epsilon} x_{\epsilon} d\epsilon}{dt} - s \frac{dT}{dt} + v \frac{dp}{dt} + \rho^{-1} \Pi : \nabla \mathbf{u} \right] \quad (63)$$

Now on extracting the following Gibbs-Duhem equation from equation 63, namely:

$$s \frac{dT}{dt} - v \frac{dp}{dt} + \int \frac{d\mu_{\epsilon}}{dt} x_{\epsilon} d\epsilon = 0 \quad (64)$$

reduces equation 63 to,

$$\rho \frac{d\mathcal{N}}{dt} = T^{-1} \Pi : \nabla \mathbf{u} - \frac{\rho}{T} \int \mu_{\epsilon} \frac{dx_{\epsilon}}{dt} d\epsilon \quad (65)$$

Next on substituting equation 65 into equation 22 produces the following Gibbs relation, namely:

$$\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{p}{T} \frac{dv}{dt} - \frac{1}{T} \int \mu_{\epsilon} \frac{dx_{\epsilon}}{dt} d\epsilon \quad (66)$$

The finer aspects of the Gibbs relation, equation 66, can only be obtained after finding out the expression of μ_{ϵ} and x_{ϵ} in terms of ϵ , the internal configurational parameter, and further on the functional dependences of μ_{ϵ} and x_{ϵ} on other system parameters, such as, p , ρ , Π , relaxation time of physical fluxes, conductivity, coefficient of viscosity, etc. Or in other words, by using the constitutive equations of x_{ϵ} and an expression for μ_{ϵ} rationally proposed say via x_{ϵ} . Again notice that on the right hand side of equation 66 the last summational term appears because of the existence of imbalance in corresponding chemical interaction.

4 Concluding Remarks

Adhering to the dictates spelled out by Bridgman [1] and further experimentally proved by Evans et al [3] of the laws of thermodynamics we have described the development of GPITT based thermodynamic framework. This reveals that the thermodynamic irreversibility is all about the imbalances in chemical interaction. That is the existence of physical fluxes, e.g. heat flux and momentum flux, is because of the imbalance in the corresponding chemical interaction. Thus the present discussion has surfaced out the additional facets of chemical interaction, namely those lead to the existence of heat and momentum fluxes. In complex systems too the distribution in internal configurational states differing than that in equilibrium corresponds to the imbalance in corresponding chemical interaction. The already well known traditional examples of imbalance in corresponding chemical interaction are the ones that lead to the chemical conversion at finite rates and the matter diffusion or transport.

Moreover, it is evident from the above discussion that Eddington's assertions about the entropy function are needed to be modified. If entire universe is taken as the thermodynamic system then obviously its entropy change is entirely on account of entropy production and hence whether one states that time's arrow is the sole property of entropy or time's arrow is the sole property of entropy production remains equivalent. However, if a system is not isolated or adiabatically insulated then time's arrow and its entropy will not go hand in hand. Therefore, the safest statement would be that "Time's arrow is the sole property of rate of entropy production", this statement would remain valid for all systems in nonequilibrium as in the case of equilibrium time's arrow does not exist. In introduction of this paper we have stated two more statements of Eddington and they too have to be restated as,

1. "Nothing in the statistics of an assemblage can distinguish a direction of time when the entropy production function fails to distinguish one".
2. "Other statistical characters besides entropy production function might perhaps be used to discriminate time's arrow, they can only succeed when it succeeds and they fail when it fails".

For example, recall that in the domain of natural fluctuations various physical fluxes do exist but devoid of time's arrow and the same remains true of the entropy production function. The latter does not retain its positive definite sign in the domain of natural fluctuations, randomly it takes positive and negative values in quick succession.

Acknowledgements

This work has been financially supported by CSIR, New Delhi via the "Emeritus Scientist, CSIR" scheme to one of us (A. A. B.).

References

- [1] P. W. Bridgman, *Reflections on Thermodynamics*, *Proc. Amer. Acad. Arts Sci.*, **82** (1953) 301; *The Nature of Thermodynamics*, Peter Smith, Gloucester, MA, 1969.
- [2] A. A. Bhalekar, *Indian J. Phys.*, **76B** (2002) 715; **77B** (2003) 391.
- [3] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles and D. J. Evans, *Phys. Rev. Lett.*, **89** (2002) 050601-1.
- [4] A. S. Eddington, *The Nature of the Physical World*, Cambridge University Press, Cambridge, 1931.

- [5] A. Katchalsky and P. F. Curran, *Nonequilibrium Thermodynamics in Biophysics*, Harvard University Press, Cambridge, MA, 1965.
- [6] A. A. Bhalekar, *J. Math. Chem.*, **5** (1990) 187; *Asian J. Chem.*, **12** (2000) 417.
- [7] J. Meixner, *Rheol. Acta*, **12** (1973) 465.
- [8] A. A. Bhalekar, *Bull. Cal. Math. Soc.*, **94(3)** (2002) 209.
- [9] A. A. Bhalekar, *Ind. J. Phys.*, **74B** (2000) 153.
- [10] B. C. Eu, *Phys. Rev.*, **E51** (1995) 768.
- [11] B. C. Eu and L. S. García-Colín, *Phys. Rev.*, **E54** (1996) 2501.
- [12] I. Prigogine and R. Defay, *Chemical Thermodynamics*, (Translator) D. H. Everett, Longmans Green, London, 1954.
- [13] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, 1970.
- [14] H. Grad, *Commun. Pure Appl. Math.*, **2** (1949) 331; *Principles of the kinetic theory of gases*: In S. Flügge (Editor), *Thermodynamics of Gases*, Vol. XII in Encyclopedia of Physics, Springer, Berlin, 1958, p. 205.
- [15] D. Jou, J. Casas-Vázquez and G. Lebon, *Extended Irreversible Thermodynamics*, Springer-Verlag, Berlin, 1996.
- [16] W. Muschik, *J. Phys. Chem. Solids*, **49** (1988) 709.
- [17] D. D. Joseph and L. Preziosi, *Rev. Mod. Phys.*, **61** (1989) 41; **62** (1990) 375.