

Thermodynamic Prescription of Local Equilibrium. A Revisit

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**Dedicated to Bjarne Andresen on completing 50 years at the University of Copenhagen,
Denmark**

Conventional Thermodynamic Prescription of Local Equilibrium

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The conceptual visualization of the local equilibrium at interior points of a spatially non-uniform system is depicted in Figure 1

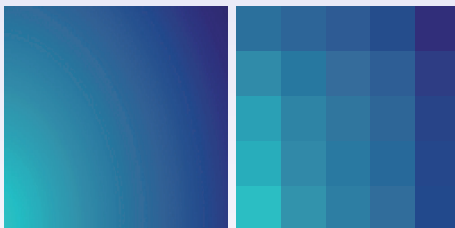


Figure 1: In the LTE (Local Thermodynamic Equilibrium) approximation a continuous gradient of say temperature in a system (left frame) is replaced by a number of small subsystems, each with a uniform temperature. Thus the full system with its continuous irreversibilities is represented by a collection of equilibrium systems with the irreversibilities located at their boundaries, i.e. endoreversible systems (right frame). This Figure is from the courtesy of Bjarne Andresen of the University of Copenhagen, Copenhagen, Denmark.

The traditional thermodynamic prescription of local equilibrium is:

$$s(\mathbf{r}, t) = s(u(\mathbf{r}, t), v(\mathbf{r}, t), x_k(\mathbf{r}, t)) \quad (1)$$

that permits to use the following Gibbs relation,

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_k \mu_k \frac{dx_k}{dt} \quad (2)$$

Let us combine it with the following internal energy balance equation,

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{q} - p\rho \frac{dv}{dt} + \boldsymbol{\Pi} : \nabla \mathbf{u} + \sum_k \mathbf{J}_k \cdot \mathbf{F}_k, \quad (3)$$

and the mass balance equation,

$$\rho \frac{dx_k}{dt} = -\nabla \cdot \mathbf{J}_k + \sum_{\alpha} \nu_k^{\alpha} M_k \frac{d\xi_{\alpha}}{dt} \quad (4)$$

That produces the following entropy balance equation:

$$\rho \frac{ds}{dt} + \nabla \cdot \mathbf{J}_s = \sigma_s \geq 0 \quad (5)$$

where σ_s is the entropy source strength that reads as,

$$\begin{aligned} \sigma_s = & \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) + \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{u} \\ & - \frac{1}{T} \sum_k \mathbf{J}_k \cdot \left(T \nabla \left(\frac{\mu_k}{T} \right) - \mathbf{F}_k \right) + \sum_{\alpha} \frac{\mathcal{A}_{\alpha}}{T} \frac{d\xi_{\alpha}}{dt} \geq 0 \end{aligned} \quad (6)$$

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

$$\mathbf{J}_s = \frac{\mathbf{q} - \sum_k \mu_k \mathbf{J}_k}{T} \quad (7)$$

where the chemical affinity has the following standard definition,

$$\mathcal{A}_\alpha = - \sum_k \nu_k^\alpha M_k \mu_k \quad (8)$$

where μ_k of eq. (8) is in per unit mass units.

The applicability of the Gibbs relation of eq. (2) does imply the accommodation of the existing physical fluxes in this thermodynamic framework. However, this claim of CIT is merely implicit one.

Now let us compare the outcomes in the De Donderian chemical thermodynamics and that in Gibbsian chemical thermodynamics. The De Donderian equation for spatially uniform closed system with irreversibility only due to chemical conversions at non-vanishing rates reads as (for the sake of demonstration we have assumed the occurrence of only one chemical reaction):

$$T \frac{dS}{dt} = \frac{dU}{dt} + p \frac{dV}{dt} + \mathcal{A} \frac{d\xi}{dt} \quad (9)$$

that implies the operation of the following functional dependence,

$$S = S(U, V, \xi) \quad (10)$$

Herein the mass balance equation reads as,

$$dn_k = \nu_k d\xi \quad (11)$$

Thus we obtain the following definition of the chemical affinity,

$$\mathcal{A} = - \sum_k \nu_k \mu_k \quad (12)$$

where μ_k are the respective chemical potentials defined as,

$$\mu_k = \left(\frac{\partial G}{\partial n_k} \right)_{T, p, n_{j \neq k}} \quad (13)$$

Whereas in the Gibbsian approach for a closed system carried along a reversible path the thermodynamic description is,

$$TdS = dU + pdV \quad (14)$$

with the following functional dependence,

$$S = S(U, V) \quad (15)$$

However, on a reversible path by definition we have $\mathcal{A} = 0$ hence eq. (9) reduces to eq. (14), that is on a reversible path the following functional dependence,

$$\xi = \xi(U, V) \quad (16)$$

is followed in the case of a chemically reacting closed system.

That is though on a reversible path a chemical conversion takes place but ξ no more remain independent thermodynamic variable.

However, when the functional dependence of eq. (1) accommodates the existence of the physical fluxes then does it mean that there follows the following

$$\mathbf{q} = \mathbf{q}(u, v, x_k \text{'s}), \quad \mathbf{\Pi} = \mathbf{\Pi}(u, v, x_k \text{'s}) \quad (17)$$

and for all $\mathbf{J}_k = \mathbf{J}_k(u, v, x_l \text{'s})$

functional dependencies within the local equilibrium domain? The answer to it indeed has to be **affirmative**. However, it needs to be demonstrated.

The Amended Thermodynamic Proposal of Local Equilibrium

Whenever, there exists heat, momentum and diffusion fluxes or any one of them in a system then the corresponding distribution function, f , of chaotic velocity C is different than that in the corresponding equilibrium state, f^{eq} . Hence, when these fluxes vary with time, f too varies. That is,

$$\frac{df}{dt} \neq 0 \quad (18)$$

turns out as the internal irreversible process hence constitutes an additional source of scalar mechanism of irreversibility. So far this mechanism of irreversibility has not been recognized for developing corresponding NET.

Herein it is relevant to recall that eqs. (3) and eq. (4) take care of irreversible processes originating in spatial non-uniformity and by default only one scalar internal mechanism due to non-vanishing rates of chemical reactions contained in the mass balance equation also gets taken care of. Thus there is no scope at all to recognise the internal irreversible process described by eq. (18). Because of the non-recognition of this internal source of irreversibility the conventional classical irreversible thermodynamics turns out as an incomplete NET description for LTE domain.

Let us recall the following kinetic theory definitions,

$$\mathbf{q} = \frac{1}{2}\rho\overline{\mathbf{C}^2\mathbf{C}} \quad \text{and} \quad \mathbf{\Pi} = \rho\overline{\mathbf{C}\mathbf{C}} \quad (19)$$

where \mathbf{C} is the molecular chaotic or peculiar velocity and 'overbar' denotes the weighted average over all velocities as evaluated in kinetic theory.

It further indicates that the additional sources of irreversibility originate in the **nonequilibrium population of the internal quantum states**

- translational,
- rotational,
- vibrational,
- electronic and
- nuclear

of molecules.

The relative energies of the molecular quantum levels are depicted in Figure 2

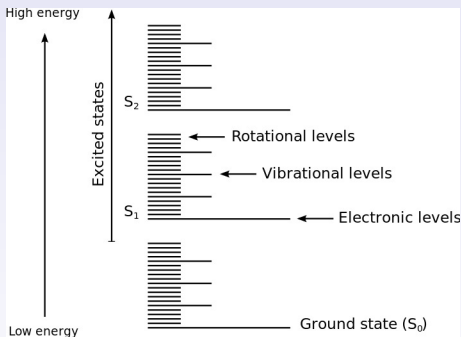


Figure 2: A schematic representation of the relative molecular quantum energy levels.

Electronic excitation produces *fluorescence and phosphorescence* phenomena and these constitute the *photo-physical processes*.

A schematic representation of the photo-physical processes is commonly represented by Jablonski diagram as depicted in Figure 3 for an organic molecule.

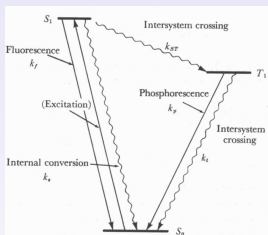


Figure 3: A schematic representation of the photo-physical processes, the Jablonski diagram for an organic molecule. It is a convention to represent the radiative transitions by straight arrows, \longrightarrow , and the non-radiative ones by \rightsquigarrow . k_{ST} is the rate constant for the non-radiative intersystem crossing between the excited singlet (S_1) and the triplet state (T_1), k_f is the rate constant of fluorescence emission from the singlet state (S_1), k_s is the rate constant for internal conversion between singlet states (herein shown between S_1 and S_0) and k_t is the rate constant for the non-radiative intersystem crossing from triplet (T_1) to ground singlet state S_0

Thus, in the following approach we choose to express the mass of the tiny cell δm as,

$$\delta m = \sum_j \delta m_j \quad (20)$$

where δm_j is the average mass of molecules in the j -th quantum state. In the absence of physical fluxes (i.e. the equilibrium population of translational quantum states) and equilibrium population of other molecular degrees of freedom we have,

$$\frac{d\delta m}{dt} = 0 \quad \text{and} \quad \frac{d\delta m_j}{dt} = 0. \quad (21)$$

However, when physical fluxes exist and/or the population in other molecular degrees of freedom is that of nonequilibrium we have,

$$\frac{d\delta m}{dt} = 0 \quad \text{and} \quad \frac{d\widetilde{\delta m}_j}{dt} \neq 0 \quad (22)$$

Herein, we have to distinguish between $\widetilde{\delta m}_j$ and δm_j since the population of energy levels in two cases are different that is why in the former case there appear physical fluxes and/or other molecular sources of irreversibility. However, there we have $\sum_j \widetilde{\delta m}_j = \widetilde{\delta m} = \sum_j \delta m_j = \delta m$.

In this way instead of the Gibbs relation of eq. (2) there results the following Gibbs relation.

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_{k,j} \tilde{\mu}_{k,j} \frac{d\tilde{x}_{k,j}}{dt} \quad (23)$$

where the mass fractions $\tilde{x}_{k,j}$ take into account the nonequilibrium population in all the internal degrees of freedom including translational ones. The companion Gibbs-Duhem equation reads as,

$$\sum_{k,j} \tilde{x}_{k,j} \frac{d\tilde{\mu}_{k,j}}{dt} + s \frac{dT}{dt} - v \frac{dp}{dt} = 0 \quad (24)$$

The above two equations and the following expressions are that from the Generalized Phenomenological Irreversible Thermodynamic Theory (GPITT).

Where $\tilde{\mu}_{k,j}$ are the respective chemical potentials per unit mass of the component. The mass balance reads as,

$$\rho \frac{d\tilde{x}_{k,j}}{dt} = -\nabla \cdot \tilde{\mathbf{J}}_{k,j} + \nu_{k,j} \frac{d\omega}{dt} + \sum_{\alpha} \nu_k^{\alpha} M_k \tilde{\gamma}_{k,j} \frac{d\xi_{\alpha}}{dt}, \quad (25)$$

The expression of entropy source strength and entropy flux density from the Gibbs relation eq. (23) reads as,

$$\begin{aligned}
\sigma_s = & \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) + \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{u} \\
& - \frac{1}{T} \sum_k \mathbf{J}_k \cdot \left(T \nabla \left(\frac{\tilde{\mu}_k}{T} \right) - \mathbf{F}_k \right) \\
& + \sum_\alpha \frac{\tilde{A}_\alpha}{T} \frac{d\xi_\alpha}{dt} \\
& + \frac{1}{T} \sum_{k,j} \tilde{\mu}_{k,j} \mathbf{J}_k \cdot \nabla (\tilde{\gamma}_{k,j}) + \frac{\tilde{B}}{T} \frac{d\omega}{dt} > 0
\end{aligned} \tag{26}$$

and

$$\mathbf{J}_s = \frac{\mathbf{q} - \sum_k \tilde{\mu}_k \mathbf{J}_k}{T} \geq 0 \quad (27)$$

wherein we have used the following defining relations,

$$\tilde{\mathbf{J}}_{k,j} = \tilde{\gamma}_{k,j} \mathbf{J}_k, \quad \tilde{\mu}_k = \sum_j \tilde{\gamma}_{k,j} \tilde{\mu}_{k,j} \quad (28)$$

and

$$\tilde{\mathbf{x}}_{k,j} = \mathbf{x}_k \times \tilde{\gamma}_{k,j} \implies d\tilde{\mathbf{x}}_{k,j} = \mathbf{x}_k d\tilde{\gamma}_{k,j} + \tilde{\gamma}_{k,j} d\mathbf{x}_k \quad (29)$$

the mass fractions $\tilde{\gamma}_{k,j}$ are defined as

$$\tilde{\gamma}_{k,j} = \tilde{\rho}_{k,j} / \rho_k \quad (30)$$

The expression of $\tilde{\mathcal{B}}$, the *internal population equilibration affinity* through the collisional mechanism reads as,

$$\tilde{\mathcal{B}} = - \sum_{k,j} \tilde{\mu}_{k,j} \nu_{k,j} \quad (31)$$

and that of the chemical affinity of the α -th chemical reaction gets defined as,

$$\tilde{\mathcal{A}}_{\alpha} = - \sum_{k,j} \nu_k^{\alpha} M_k \tilde{\gamma}_{k,j} \tilde{\mu}_{k,j} = - \sum_k \nu_k^{\alpha} M_k \tilde{\mu}_k, \quad (32)$$

Notice that the quantification of \mathcal{B} is done on the lines of a chemical reaction. That is, all $\nu_{k,j} = +1$ are treated as if they are the products and $\nu_{k,j} = -1$ as if they are the reactants of the scalar equilibration process.

The thermodynamic equations of state for the intensities from the Gibbs relation of eq. (23) read as,

$$\left(\frac{\partial s}{\partial u}\right)_{v, \tilde{x}} = \frac{1}{T}, \quad \left(\frac{\partial s}{\partial v}\right)_{u, \tilde{x}} = \frac{p}{T}, \quad \left(\frac{\partial s}{\partial \tilde{x}_{k,j}}\right)_{u, v, \tilde{x}'} = \frac{\tilde{\mu}_{k,j}}{T} \quad (33)$$

where the subscript \tilde{x} denotes all composition variables kept constant and the subscript \tilde{x}' denotes except $\tilde{x}_{k,j}$ all the composition variables kept constant.

In the above development we have used the following expression of the local Gibbs function, \mathcal{G} ,

$$\mathcal{G} = \sum_{k,j} \tilde{x}_{k,j} \tilde{\mu}_{k,j} \quad (34)$$

The Gibbs relation of eq. (23) on using the first equality of eq. (29) and the second definition of eq. (28) gets transformed to,

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_k \tilde{\mu}_k \frac{dx_k}{dt} \quad (35)$$

However, the corresponding expression of entropy source strength reads as,

$$\begin{aligned} \sigma_s = & \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) + \frac{1}{T} \mathbf{\Pi} : \nabla \mathbf{u} + \sum_{\alpha} \frac{\tilde{A}_{\alpha}}{T} \frac{d\xi_{\alpha}}{dt} \\ & - \frac{1}{T} \sum_k \mathbf{J}_k \cdot \left(T \nabla \left(\frac{\tilde{\mu}_k}{T} \right) - \mathbf{F}_k \right) > 0 \end{aligned} \quad (36)$$

and the expression of entropy flux density still reads as that given in eq. (27).

The companion Gibbs-Duhem equation of eq. (35) reads as,

$$\sum_k \tilde{x}_k \frac{d\tilde{\mu}_k}{dt} + s \frac{dT}{dt} - v \frac{dp}{dt} = 0 \quad (37)$$

The comparison of the expressions of source strength of eqs. (26) and (36) we learn that though $\tilde{\mu}_k$ takes care of the nonequilibrium population of internal molecular quantum states still in the latter equation there are missing two mechanisms of irreversibility quantified by the last two terms on the r.h.s. of the former equation.

That is the use of the expression

$$\mathcal{G} = \sum_k x_k \tilde{\mu}_k \quad (38)$$

submerges **two equilibration mechanisms** quantified by

$$+ \frac{1}{T} \sum_{k,j} \tilde{\mu}_{k,j} \mathbf{J}_k \cdot \nabla (\tilde{\gamma}_{k,j}) + \frac{\tilde{\mathcal{B}}}{T} \frac{d\omega}{dt} > 0$$

which gets explained by the differentiation of eq. (38) w.r.t. time t ,

$$\frac{d\mathcal{G}}{dt} = \sum_k \tilde{\mu}_k \frac{dx_k}{dt} + \sum_k x_k \frac{d\tilde{\mu}_k}{dt} \quad (39)$$

Notice that in eq. (39) there we have dx_k/dt which is incapable to incorporate the internal equilibration process of the j -th quantum state expressed by

$$\nu_{k,j} \frac{d\omega}{dt}$$

whose origin lies in the collisional equilibration of the population of the molecular internal quantum states.

From the definition of eqs. (34) and (24) the following functional dependence is obtained,

$$\mathcal{G} = \mathcal{G}(T, p, \tilde{x}_{k,j}'\text{'s}) \quad (40)$$

whereas from eqs. (35) and (38) there results,

$$\mathcal{G} = \mathcal{G}(T, p, x_k'\text{'s}) \quad (41)$$

What effectively one does in going from the functional dependence of eq. (40) to that in eq. (41) is to eliminate the consideration of the internal irreversible processes originating in the nonequilibrium population of molecular quantum states. This lacunae needs to be eliminated that too by identifying the corresponding macroscopic variables.

Generalized Phenomenological Irreversible Thermodynamic Theory in the Format of Extended Irreversible Thermodynamics

Thus equivalent functional dependence to that in eq. (40) is adopted as,

$$\mathcal{G} = \mathcal{G}(T, p, x_k's, \xi_{rv}, \mathbf{q}, \mathbf{\Pi}, \mathbf{J}_k's) \quad (42)$$

Which lead us to the following Gibbs relation and the companion Gibbs-Duhem equation,

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_k \tilde{\mu}_k \frac{dx_k}{dt} + \tilde{A}_{rv} \frac{d\xi_{rv}}{dt} - \beta_{\mathbf{q}} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} - \beta_{\mathbf{\Pi}} \mathbf{\Pi} : \frac{d\mathbf{\Pi}}{dt} - \sum_k \beta_{\mathbf{J}_k} \mathbf{J}_k \cdot \frac{d\mathbf{J}_k}{dt} \quad (43)$$

and

$$\sum_k x_k \frac{d\tilde{\mu}_k}{dt} + s \frac{dT}{dt} - v \frac{dp}{dt} + \sum_{k,j} \tilde{x}_{rv}^{k,j} \frac{d\tilde{\mu}_{rv}^{k,j}}{dt} + \frac{1}{2} \mathbf{q}^2 \frac{d\beta_{\mathbf{q}}}{dt} + \frac{1}{2} \mathbf{n}^2 \frac{d\beta_{\mathbf{n}}}{dt} + \frac{1}{2} \sum_k \mathbf{J}_k^2 \frac{d\beta_{\mathbf{J}_k}}{dt} = 0 \quad (44)$$

where we have used the following relations for the mass balance and the chemical affinity of the rotational-vibrational equilibration process,

$$\rho \frac{d\tilde{x}_{rv}^{k,j}}{dt} = \nu_{rv}^{k,j} \frac{d\xi_{rv}}{dt}, \quad \tilde{A}_{rv} = - \sum_{k,j} \nu_{rv}^{k,j} \tilde{\mu}_{rv}^{k,j} \quad (45)$$

However, on the lines of De Donderian approach for the chemical reactions we, without a loss of generality, modify the expression of \tilde{A}_{rv} to,

$$\tilde{A}_{rv} = \sum_k (\mu_{k,rv} - \tilde{\mu}_{k,rv}) \quad (46)$$

where

$$\begin{aligned} \tilde{\mu}_{k,rv} &= \sum_j \tilde{\mu}_{rv}^{k,j} \tilde{\gamma}_{rv}^{k,j}, \\ \mu_{k,rv} &= \sum_j \gamma_{rv}^{k,j} \mu_{rv}^{k,j} = \sum_j \gamma_{rv}^{k,j} \mu_{k,rv} = \mu_{k,rv} \end{aligned} \quad (47)$$

We would like to once again stress that the additional variables appearing in eq. (42) are not merely the case of raising them to independent thermodynamic variables. Indeed, they have their origin in the nonequilibrium population of quantum states. In following Section 4 we have discussed Fast and Slow variables wherein this contention gets further strengthened.

The thermodynamic equations of state for intensive parameters read from eq. (43) as follows,

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u} \right)_{v, x_k's, \mathbf{q}, \mathbf{\Pi}, \mathbf{J}_k's, \xi_{rv}} \quad (48)$$

$$\frac{p}{T} = \left(\frac{\partial s}{\partial v} \right)_{u, x_k's, \mathbf{q}, \mathbf{\Pi}, \mathbf{J}_k's, \xi_{rv}} \quad (49)$$

$$-\frac{\widetilde{\mu}_k}{T} = \left(\frac{\partial s}{\partial x_k} \right)_{u, v, x_{j \neq k}'s, \mathbf{q}, \mathbf{\Pi}, \mathbf{J}_k's, \xi_{rv}} \quad (50)$$

⋮

$$-\frac{\beta_{\mathbf{q}}}{T} \mathbf{q} = \left(\frac{\partial s}{\partial \mathbf{q}} \right)_{u, v, x_k's, \mathbf{\Pi}, \mathbf{J}_k's, \xi_{rv}} \quad (51)$$

⋮

Fast and Slow Thermodynamic Variables in Generalized Phenomenological Irreversible Thermodynamic Theory

Notice that the internal population redistribution in molecular quantum states are very fast processes (relaxation times are $\sim 10^{-8} - 10^{-14}$ s). However, we have introduced physical fluxes as independent thermodynamic variables in place of irreversibility originating in the nonequilibrium population of translational quantum levels. Hence in the time domain of fast population redistribution in the internal translational quantum energy states the functions u , v and x_k 's remain practically constant. Implying that the evolution in the *faster domain* is taking place as if it is taking place in isolation. Hence, the rate of entropy change is entirely the rate of entropy production. Thus, in this time domain and in the **absence of absorption of radiations** the rate of entropy change gets expressed by using eq. (43) as,

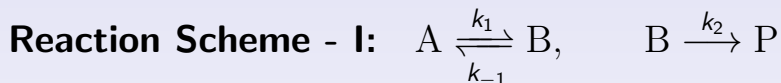
$$\begin{aligned}
 \rho \frac{ds}{dt} &= \sigma_s \\
 &= -\frac{\rho}{T} \beta_{\mathbf{q}} \mathbf{q} \cdot \frac{d\mathbf{q}}{dt} - \frac{\rho}{T} \beta_{\Pi} \Pi : \frac{d\Pi}{dt} \\
 &\quad - \frac{\rho}{T} \sum_k \beta_{\mathbf{J}_k} \mathbf{J}_k \cdot \frac{d\mathbf{J}_k}{dt} > 0
 \end{aligned} \tag{52}$$

On the other hand, in the *slower domain* the functional dependencies of physical fluxes read as, $\mathbf{q} = \mathbf{q}(u, v, x_k\text{'s})$, $\Pi = \Pi(u, v, x_k\text{'s})$ and for all $\mathbf{J}_k = \mathbf{J}_k(u, v, x_l\text{'s})$ as well as $d_t \xi_{rv} = d_t \xi_{rv}(u, v, x_k\text{'s})$. Therefore, the Gibbs relation of eq. (43) produces the following operative Gibbs relation,

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_k \tilde{\mu}_k \frac{dx_k}{dt} \quad (53)$$

which is none else than the Gibbs relation of eq. (35). Compare this relation with the Gibbs relation of eq. (2), the distinction is that instead of μ_k in the latter there we have $\tilde{\mu}_k$ in eq. (53), which means in the system there exist physical fluxes too. The expression of the entropy source strength in the *slower domain* reads as that given in eq. (6) except μ_k of it gets replaced by $\tilde{\mu}_k$.

The thermodynamic behaviour in the slower domain described by eq. (53) is akin to the chemical kinetics of two step chemical reaction say,



where A is the starting reactant, B is the reactive intermediate species, P is the final product, k_1 and k_{-1} are respectively the forward and reverse rate constants of the first step and k_2 is the rate constant of the conversion of B to P in the second step. Chemical kinetics illustrates that the first step would act as a pre-equilibrium step when $k_{-1} \gg k_2$. That is the first step is much faster than the second step.

Thus, in the *slower domain* the variation of the concentration of A is governed by $[B] = K[A]$ as the first step of the reaction maintains a dynamic chemical equilibrium (the dynamic equilibrium constant K is given by $K = k_1/k_{-1}$ throughout the course of reaction in the slower domain). Hence, the rate of production of P reads as,

$$\frac{d[P]}{dt} = k_2[B] = k_2K[A] = -\frac{d[A]}{dt} \quad (54)$$

It does imply that in the *slower domain* one has,

$$\frac{d[B]}{dt} \simeq 0 \quad (55)$$

because the rate of production of B in the first step practically equals the rate of consumption of it in the second step. Moreover, the *dynamic chemical equilibrium* does not demand,

$$\frac{d[A]}{dt} = 0 \quad (56)$$

As the first step of **Reaction Scheme-I** is assumed as very fast compared to the second step, therefore, the faster domain gets also described as a chemical relaxation. All chemical relaxation processes follow the following equation,

$$\tau \frac{dx_i}{dt} + x_i = x_i^{eq} \quad (57)$$

where $(x_i - x_i^{eq})$'s are the sufficiently small perturbation from equilibrium quantified with respect to some chosen time independent reference concentration, C_i^0 of the species, i , and τ is the relaxation time for the relaxation process. The mass conservation gets described as,

$$C_i = C_i^0 + x_i, \quad C_i^{eq} = C_i^0 + x_i^{eq} \implies C_i = C_i^{eq} + (x_i - x_i^{eq}) \quad (58)$$

That is, in the *slower domain* of time the rate of entropy change is determined by, eq. (53), even if the magnitude and directions of the physical fluxes changes with time. However, the details of this dependence gets appropriately expressed by the use of a chosen constitutive equation of the fluxes.

Thus we will have two levels of description i.e. in the *faster domain* and for its companion *slower domain* for each set of constitutive equations.

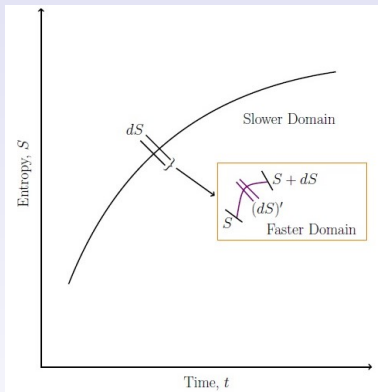


Figure 4: The main curve depicts the entropy, S , variation with time in the slower domain. On this curve we have arbitrarily depicted the infinitesimal change dS . Whereas the corresponding faster time scale change, is depicted in the box by a curve. The correspondingly infinitesimal change is expressed as $(dS)'$. Thus, we have $dS = \int (dS)'$. Hence, $S + dS$ includes the contribution from the entropy production of the corresponding *faster time scale*. That is why, there is no need to separately add a contribution from the rate of entropy production of the faster time scale in the entropy production expression corresponding to the slower time scale.

If one is not careful there may crop-in a question about the rate of entropy production in the *slower domain* expressed in eq. (36). That is, is it a complete description? In other words whether the change $d_i S$ on the *slower time scale* does accommodate the net entropy production in its *faster time scale measured by the integration of the expression of eq. (52)*? And if it is yes, then the latter part remains unaccounted for or not? The answer is no, there is no need to add additional term in eq. (36) that gets explained on using the Figure 4.

Expressions of Entropy Source Strength in Generalized Phenomenological Irreversible Thermodynamic Theory Using Constitutive Equations for Fluxes

For the sake of demonstration we are discussing the **case of heat conduction**. Let us recall following constitutive equations. (i) Maxwell-Cattaneo equation,

$$\tau_{\mathbf{q}} \frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda \nabla T, \quad (59)$$

(ii) the Guyer-Krumhansl's relation,

$$\tau_{\mathbf{q}} \frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda \nabla T + l^2 \nabla^2 \mathbf{q} + 2l^2 \nabla (\nabla \cdot \mathbf{q}) \quad (60)$$

and (iii) Jeffreys' type equation,

$$\tau_{\mathbf{q}} \frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda \nabla T - \tau_{\mathbf{q}} \mathbb{k} \frac{d\nabla T}{dt} \quad (61)$$

where \mathbb{k} is the effective thermal conductivity and where l is the mean free path of the phonons.

On using eq. (59) there we have,

$$\sigma_s = - \left(\frac{1}{T^2} - \frac{\rho\beta_{\mathbf{q}}\lambda}{\tau_{\mathbf{q}}T} \right) \mathbf{q} \cdot \nabla T + \frac{\rho\beta_{\mathbf{q}}}{\tau_{\mathbf{q}}T} \mathbf{q}^2 > 0 \quad (62)$$

Whereas on using eq. (60) we obtain,

$$\begin{aligned} \sigma_s = & - \left(\frac{1}{T^2} - \frac{\rho\beta_{\mathbf{q}}\lambda}{T\tau_{\mathbf{q}}} \right) \mathbf{q} \cdot \nabla T + \frac{\rho\beta_{\mathbf{q}}}{T\tau_{\mathbf{q}}} \mathbf{q}^2 \\ & - \frac{\rho\beta_{\mathbf{q}}l^2}{T\tau_{\mathbf{q}}} \mathbf{q} \cdot \nabla^2 \mathbf{q} - \frac{2\rho\beta_{\mathbf{q}}l^2}{T\tau_{\mathbf{q}}} \mathbf{q} \cdot \nabla(\nabla \cdot \mathbf{q}) > 0 \end{aligned} \quad (63)$$

and on using eq. (61) the expression that is obtained is,

$$\sigma_s = \frac{\rho\beta_{\mathbf{q}}}{T\tau_{\mathbf{q}}}\mathbf{q}^2 + \left(\frac{\rho\beta_{\mathbf{q}}\lambda}{\tau_{\mathbf{q}}T} - \frac{1}{T^2} \right) \mathbf{q} \cdot \nabla T$$

$$+ \frac{\rho\beta_{\mathbf{q}}\mathbb{k}}{T}\mathbf{q} \cdot \frac{d\nabla T}{dt} > 0 \quad (64)$$

Now on using the following expression of $\beta_{\mathbf{q}}$,

$$\beta_{\mathbf{q}} = \frac{\tau_{\mathbf{q}}}{\rho\lambda T} \quad (65)$$

we see that both equations eqs. (62) and (64) reduce to,

$$\sigma_s = \frac{1}{\lambda T^2}\mathbf{q}^2 > 0 \quad (66)$$

whereas eq. (63) produces,

$$\sigma_s = \frac{1}{\lambda T^2} (\mathbf{q} - l^2 \nabla^2 \mathbf{q} - 2l^2 \nabla(\nabla \cdot \mathbf{q})) \cdot \mathbf{q} > 0 \quad (67)$$

Notice that the preceding two equations are the flux representation of the first term on the r.h.s. of eq. (36)

$$\sigma_s = \mathbf{q} \cdot \nabla \left(\frac{1}{T} \right) > 0 \quad (68)$$

which is a description in the *slower domain*. Thus it does demonstrate that the expression of eq. (68) does not necessarily belong to the domain of a linear flux-force relationship.

Thus, the use of expression of eq. (66) relegates the description to the *slower domain* wherein heat flux no more act as an independent thermodynamic variable. It gets demonstrated that in the *slower domain* the last term on the r.h.s. of eq. (64) does not significantly contribute to the entropy source strength because $d\nabla T/dt$ too becomes insignificant when $d\mathbf{q}/dt$ becomes insignificant. This can be alternatively comprehended as follows.

Its one of the interpretation is as follows. The heat flux \mathbf{q} is expressed as the sum of two heat fluxes \mathbf{q}_F and \mathbf{q}_{MC} , where the subscripts F and MC denote Fourier and Maxwell-Cattaneo respectively.

The Maxwell-Cattaneo and Fourier laws are combined in the following steps.

$$\mathbf{q}_F = -\lambda_F \nabla T$$

$$\tau_{\mathbf{q}} \frac{d\mathbf{q}_{MC}}{dt} + \mathbf{q}_{MC} = -\lambda_{MC} \nabla T \quad (69)$$

$$\therefore \tau_{\mathbf{q}} \frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda \nabla T - \tau_{\mathbf{q}} \lambda_F \frac{d\nabla T}{dt}$$

where $\lambda = \lambda_F + \lambda_{MC}$. Thus when $d\mathbf{q}/dt$ becomes insignificant we have both $d\mathbf{q}_F/dt$ and $d\mathbf{q}_{MC}/dt$ insignificant hence $d\nabla T/dt$ too becomes insignificant simultaneously.

On the same lines we have demonstrated that as the use of the expression of eq. (65) relegates system to the *slower domain* the same is achieved on using the following expressions

$$\beta_{\mathbf{\Pi}} = \frac{\tau_{\mathbf{\Pi}}}{2\rho\eta}, \quad \beta_{\mathbf{J}_k} = \frac{RT\tau_{\mathbf{J}_k}}{\rho^2 D_k c_k} \quad (70)$$

This then implies that the following conditions,

$$\beta_{\mathbf{q}} \neq \frac{\tau_{\mathbf{q}}}{\rho\lambda T}, \quad \beta_{\mathbf{\Pi}} \neq \frac{\tau_{\mathbf{\Pi}}}{2\rho\eta}, \quad \beta_{\mathbf{J}_k} \neq \frac{RT\tau_{\mathbf{J}_k}}{\rho^2 D_k c_k} \quad (71)$$

operates in the *faster domain*, wherein \mathbf{q} , $\mathbf{\Pi}$ and \mathbf{J}_k 's act as the independent thermodynamic variables.

As eq. (62) is the description when the Maxwell-Cattaneo equation is used, we re-express it in the following form,

$$\sigma_s = \frac{\rho\beta_{\mathbf{q}}}{T\tau_{\mathbf{q}}}\mathbf{q}^2 + \Delta_{T,\mathbf{q}}\mathbf{q} \cdot \nabla T > 0 \quad (72)$$

with

$$\Delta_{T,\mathbf{q}} = \left(\frac{\rho\beta_{\mathbf{q}}\lambda}{\tau_{\mathbf{q}}T} - \frac{1}{T^2} \right) \neq 0 \quad (73)$$

Now we adopt the following simple functional dependence

$$\Delta_{T,\mathbf{q}} = f(\mathbf{q}^2) \quad (74)$$

and further to the first approximation use the following simple expression,

$$\Delta_{T,\mathbf{q}} = -a_{\mathbf{q}}\mathbf{q}^2 \quad (75)$$

that produces the following expression of $\beta_{\mathbf{q}}$,

$$\beta_{\mathbf{q}} = \frac{\tau_{\mathbf{q}}}{\rho\lambda T} (1 - a_{\mathbf{q}} T^2 \mathbf{q}^2) \quad (76)$$

with the following limiting condition,

$$\begin{aligned} \text{When } \mathbf{q} = \mathbf{q}(u, v, x_k \text{'s}), \\ \text{there we have } 1 \gg a_{\mathbf{q}} T^2 \mathbf{q}^2 \end{aligned} \quad (77)$$

Unless we identify a physical expression for $a_{\mathbf{q}}$ we are unable to work out within the *faster domain*.

Hence we are left to work only within the *slower domain*.

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