

ON THE GENERALIZED PHENOMENOLOGICAL IRREVERSIBLE THERMODYNAMIC THEORY (GPITT)

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Dedicated to Professor G.V. Bakore on his 66th birthday

Abstract

An outline of a new mathematical theory is presented, namely, the generalized phenomenological irreversible thermodynamic theory (GPITT) evolved by the author. This theory involves the identification of a new mathematical quantity designated as the thermodynamic heat (which is different from Born's mechanically definable one) and the adoption of a Universal Inaccessibility Principle (UIP) which yields the simplest extended Gibbs relation (EGR). The second law inequalities are thereby generalized and provide appropriate constraints on open systems. The potentiality of GPITT has been discussed with reference to Boltzmann's H -function and the thermodynamic entropy concept, and also in regard to the development of the abstract thermodynamic description, in particular with reference to the extended Gibbsian space (EGS) provided by the EGR as against the currently used Gibbsian space (GS).

This communication deals with the presentation of an outline of a new mathematical theory developed in the realm of irreversible thermodynamics, namely, the generalized phenomenological irreversible thermodynamic theory (GPITT). In a sense, this communication serves to establish our GPITT.

In the domain of the local equilibrium assumption (LEA), one assumes [1–5] the validity of Gibbs' relation (GR) in the local form:

$$\frac{d\hat{U}}{dt} = T \frac{d\hat{S}}{dt} - p \frac{dv}{dt} + \sum_k \mu_k \frac{dc_k}{dt}, \quad (1)$$

where U is the internal energy, S the entropy, v the specific volume, c_k are the mass fractions of the components, T is the thermodynamic temperature, p the thermodynamic pressure, and μ_k are the chemical potentials. The cap (^) over the symbols represents the corresponding specific quantities and t is time. The standard fluid-dynamical internal energy balance equation, e.g. for systems with no electromagnetic polarization effects but with conservative body forces, in the local form reads:

$$\frac{d\hat{U}}{dt} = -\rho^{-1}\nabla \cdot \mathbf{J}_q + \rho^{-1}\mathbf{T} : \nabla\vec{v} + \rho^{-1}\sum_k \mathbf{J}_k \cdot \mathbf{F}_k, \quad (2)$$

where ρ is the local material density, \mathbf{T} the stress tensor, \vec{v} the barycentric velocity, \mathbf{J}_k are the diffusion flux densities, \mathbf{F}_k are the conservative body forces per unit mass of the respective components, and \mathbf{J}_q is the so-called heat flux density.

The transformation of eq. (2) into eq. (1) is tantamount to the adoption of the condition:

$$\mathbf{T} = -p\delta + \Pi, \quad (3)$$

where Π is obtained as the dissipative stress tensor, δ is the unit tensor, and p is obtained as the thermodynamic pressure, not necessarily equal to $-(1/3)\text{Tr}\mathbf{T}$. The second condition gives the thermodynamic heat as:

$$\rho \frac{dq}{dt} = -\nabla \cdot \mathbf{J}_q + \Pi : \nabla\vec{v} + \sum_k \mathbf{J}_k \cdot \mathbf{F}_k - \sum_k \mu_k \rho \frac{dc_k}{dt}. \quad (4)$$

In eq. (4), the first three terms on the right-hand side quantify the calorimetrically measurable heat effects and are contained in the fluid-dynamical internal energy balance equation (2). The first term precisely measures the conduction-in of heat and matter taken together, the second one measures the dissipation of work into heat due to the contact forces, and the third one is the diffusive source of work against the body forces. Although the diffusion at nonvanishing rate is inherently dissipative, the diffusive source of work, as it appears in the internal energy balance equation, does not quantify the corresponding dissipation of energy. This then reveals that the mechanically definable heat, which we hereby designate as Born's heat and identify with the subscript B, contained in eq. (2) is given as:

$$\rho \frac{dq_B}{dt} = -\nabla \cdot \mathbf{J}_q + \Pi : \nabla\vec{v} + \sum_k \mathbf{J}_k \cdot \mathbf{F}_k. \quad (5)$$

However, from the above analysis it is evident that the thermodynamic definition of entropy follows from eq. (4) and not from eq. (5), i.e. we obtain:

$$\frac{dq}{dt} = T \frac{d\hat{S}}{dt} \neq \frac{dq_B}{dt}. \quad (6)$$

The failure of Born's heat in generating the thermodynamic thermal parameters, even in the realm of LEA, is thereby established. On the other hand, from eqs. (2), (3) and (4) we obtain:

$$\rho \frac{dq_B}{dt} = \rho \frac{d\hat{H}}{dt} - \frac{dp}{dt}, \quad (7)$$

on adopting the following obvious definition of the specific enthalpy \hat{H} :

$$\hat{H} = \hat{U} + pv. \quad (8)$$

Note that eq. (7) is the local form analogue of the relation:

$$dQ = dH - Vdp, \quad (9)$$

which is well known in classical thermodynamics for closed systems with no mechanical irreversibility therein.

Thus, the parallelism between eqs. (7) and (9) demonstrates that Born's heat has an enthalpomechanical character, while the equality in eq. (6) leads us to identify and establish the thermodynamic heat as distinctly different from the calorimetric heat. The former appears to assume a statistical character (an intuitive assertion). Now eq. (4) involves a methodology of converting Born's heat into the corresponding thermodynamic heat by adding to the former a nonconventional (nc) heat term. The latter, in the domain of LEA, is obtained as:

$$\rho \frac{dq_{nc}}{dt} = - \sum_k \mu_k \rho \frac{dc_k}{dt}. \quad (10)$$

Hence, we identify in the nonconventional heat term an index of enthalpo-mechanical-statistical compensation in nonequilibrium situations. However, this index vanishes only in the case of closed systems in the limit of thermodynamic reversibility (TR). Equation (4) may be more compactly expressed as:

$$\frac{dq}{dt} = \frac{dq_B}{dt} + \frac{dq_{nc}}{dt}. \quad (11)$$

An obvious need for working through the concept of heat is strongly indicated by the above analysis. Hence, below we present the ab initio development of the GPITT via the new mathematical quantity, the thermodynamic heat. Indeed, it is an irony of the situation that at the thermodynamic level one does not favour the use of the heat concept except at the very elementary level, whereas in all kinetic theory discussions [6,7] the heat concept, such as heat flux density, continues to occupy a definite place.

Since the fluid-dynamical internal energy balance equation (2) can provide only eq. (5) as the mechanically definable heat (irrespective of whether the system happens to be within or outside the domain of LEA), it is hereby proposed to adopt eq. (11) as the generalized definition of thermodynamic heat valid for the entire range of non-equilibrium situations. Thus, from eqs. (6), (7) and (11) we obtain:

$$- \frac{dq_{nc}}{dt} = \frac{d\hat{G}}{dt} - v \frac{dp}{dt} + \hat{S} \frac{dT}{dt} \quad (12)$$

as the generalized expression for the nonconventional heat, where \hat{G} is the specific Gibbs function:

$$\hat{G} = \hat{U} + p\nu - T\hat{S}. \quad (13)$$

On incorporating eqs. (3)–(6), (11) and (12) into eq. (2), we obtain the extended Gibbs relation (EGR):

$$\frac{d\hat{U}}{dt} = T \frac{d\hat{S}}{dt} - p \frac{d\nu}{dt} + \frac{d\hat{G}}{dt} - \nu \frac{dp}{dt} + \hat{S} \frac{dT}{dt}. \quad (14)$$

Amusingly, the operation of the dynamic local version of the Gibbs–Duhem equation (GDE),

$$\sum_k c_k \frac{d\mu_k}{dt} - \nu \frac{dp}{dt} + \hat{S} \frac{dT}{dt} = 0, \quad (15)$$

reduces the EGR to GR. This establishes that the primary criterion of the operation of LEA is the GDE, and the GR is obtained as the working one. The type of equilibrium required for the operation of LEA is thus the mutual control among the intensities within the continuum particles. Over and above this, if similar control is also established with the neighbouring continuum particles, we approach an overall thermodynamic equilibrium situation.

Our GPITT is based on the following crucial postulates:

- (a) It is possible to identify the thermodynamic work coefficients (e.g. the negative of the thermodynamic pressure) $L^{(\alpha)}$ in nonequilibrium situations such that $L^{(\alpha)}dI^{(\alpha)}$ (where $I^{(\alpha)}$ are the conjugate work coordinates [4,8]) measures the respective nondissipative components of the work associated with the nondiffusive works (e.g. due to the contact forces and electromagnetic polarization).
- (b) Thermodynamic heat is distinctly different from Born's heat except in the limit of TR for closed systems.
- (c) Thermodynamic thermal parameters for the nonequilibrium states are guaranteed by the equality in eq. (6), which is the explicit result of adopting a Universal Inaccessibility Principle (UIP) and applying it to the thermodynamic heat element. The UIP reads as follows:

In every neighbourhood of every equilibrium or nonequilibrium state of a thermodynamic system, there exist states which are unattainable from it by any reversible or (totally) spontaneous path.

This principle is based on the fact that through every nonequilibrium state of a thermodynamic system, one and only one real trajectory passes. The exceptions are the nonequilibrium stationary states through which none (real trajectory) exists.

In the event of component-wise inhomogeneity within the continuum particles, instead of eq. (6) UIP provides that:

$$\frac{dq}{dt} = \sum_k T_k \frac{d\hat{S}_k}{dt}, \tag{16}$$

and hence accordingly the GR, EGR and GDE become modified. Also, if the work due to electromagnetic polarization is included, the corresponding nondissipative terms would appear in EGR, GDE and GR. In this event, the generalized EGR takes the form:

$$\begin{aligned} \frac{d\hat{U}}{dt} &= \sum_k T_k \frac{d\hat{S}_k}{dt} + \sum_\alpha L^{(\alpha)} \frac{d\hat{l}^{(\alpha)}}{dt} + \frac{d\hat{G}}{dt} \\ &+ \sum_\alpha \hat{l}^{(\alpha)} \frac{dL^{(\alpha)}}{dt} + \sum_k \hat{S}_k \frac{dT_k}{dt}. \end{aligned} \tag{17}$$

Thus, $L^{(\alpha)}$ are the nonequilibrium thermodynamic work coefficients and $l^{(\alpha)}$ are the respective conjugate work coordinates.

Moreover, to conform with the requirement of the generalized entropy law,

$$\rho \frac{d\hat{S}}{dt} = -\nabla \cdot \mathbf{J}_S + \sigma_S, \tag{18}$$

$$\nabla \cdot \mathbf{J}_S \geq 0, \tag{19}$$

$$\sigma_S \geq 0, \tag{20}$$

where \mathbf{J}_S is the conductive flux density of entropy and σ_S is the rate of entropy production per unit volume, the nonconventional heat in its source term must have a dissipative component. For example, in eq. (12) we have:

$$\begin{aligned} \rho \left(\frac{dq_{nc, source}}{dt} \right)_{diss} &= -\sum_k \mu_k m_k \\ &- \left[\sum_k \left(\rho_k \frac{d\mu_k}{dt} \right) - \frac{dp}{dt} + \hat{S} \rho \frac{dT}{dt} \right]_{diss} \geq 0, \end{aligned} \tag{21}$$

where we have used the standard fluid-dynamical relation [1,2]:

$$\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k + m_k, \tag{22}$$

where the m_k are the mass fraction source densities of the components due to their participation in chemical reactions.

One of the achievements of the GPITT is that no new thermodynamic parameters need be identified which are strange to equilibrium thermodynamics, even for situations far from equilibrium. Of course, these thermodynamic intensities now have been defined for nonequilibrium situations. All the Maxwell relations tenable in nonequilibrium situations simply follow from the EGR on applying Euler's reciprocity criteria of exactness. In comparison with the EGR developed in extended irreversible thermodynamics (EIT) [9–21], and those in the statistical theories of Eu [22–25] and Keizer [26,27], ours appears to be simplest. The self-consistency of the GPITT may be appreciated in several ways. For example, the generalized expression for the entropy production σ_S , e.g. corresponding to the EGR (14):

$$\begin{aligned} \sigma_S = & \sum_k \left[(J_{q_k} - \mu_k J_k) : \nabla \left(\frac{1}{T_k} \right) + \frac{1}{T_k} \left(\Pi_k + J_k \vec{v}_k \right) : \nabla \vec{v} \right. \\ & - (J_k / T_k) \cdot \nabla (\psi_k + \mu_k) - \frac{\mu_k m_k}{T_k} \\ & \left. - \left\{ \frac{\rho_k}{T_k} \left(\frac{d\mu_k}{dt} - v_k \frac{dp_k}{dt} + S_k \frac{dT_k}{dt} \right) \right\}_{\text{diss}} \right] \geq 0, \end{aligned} \quad (23)$$

reduces to the conventional entropy production expression corresponding to the LEA domain [1] on guaranteeing the validity of GDE.

Moreover, the GPITT offers an opportunity to revisit Clausius' second law inequalities. Thus, the generalized Clausius second law inequality in the local form is obtained as:

$$\rho \frac{d\hat{S}}{dt} \geq \sum_k \frac{1}{T_k} \left(-\nabla \cdot J_{q_k} + \rho \frac{dq_{\text{nc},k,\text{cond}}}{dt} \right), \quad (24)$$

and in the global form (open systems) as:

$$\frac{dS}{dt} = \int_V \rho \frac{d\hat{S}}{dt} \delta V \geq \int_V \sum_k \frac{1}{T_k} \left(-\nabla \cdot J_{q_k} + \rho \frac{dq_{\text{nc},k,\text{cond}}}{dt} \right) \delta V, \quad (25)$$

which, for the closed systems with no component-wise inhomogeneity, reduces to the conventional one:

$$\frac{dS}{dt} \geq \frac{1}{T} \left(\frac{dQ}{dt} \right). \quad (26)$$

In eq. (25), V denotes the volume of the entire system. The above inequalities seem to pose a practical difficulty, for, instead of nonequilibrium thermodynamic system temperatures T (T_k), one precisely measures the surrounding temperature T_0 . However, this ambiguity is superfluous. For example, consider the inequality (26), in which the adopted definition of temperature gives:

$$\begin{aligned} T < T_0, \quad dQ > 0, \\ T > T_0, \quad dQ < 0. \end{aligned} \quad (27)$$

In both situations we have precisely

$$\frac{dQ}{T} > \frac{dQ}{T_0}. \quad (28)$$

Hence, instead of (26) we have the more practical expression:

$$\frac{dS}{dt} \geq \frac{1}{T_0} \frac{dQ}{dt}. \quad (29)$$

The thermodynamic description in the framework of GPITT is basically for spontaneous transitions and hence for those occurring between nonequilibrium states. However, it can be easily truncated for those spontaneous paths whose end states are the equilibrium states, which in turn can be further truncated for the reversible paths under the constraint of TR. With the advent of the GPITT, the nonequilibrium states have been more convincingly established as key ones among the range of thermodynamic states. The generalized thermodynamic equation of state in the local form (per unit mass version) is obtained as:

$$\hat{U} = \sum_k T_k \hat{S}_k + \sum_\alpha L^{(\alpha)} \hat{I}^{(\alpha)} + \hat{G}, \quad (30)$$

which, we note, is entirely determined by the system's thermodynamic extensities and the conjugate intensities. This results from the ab initio consideration of the nonequilibrium states in the development of the GPITT.

For dilute gases, whose molecules can have only translational motion, the kinetic theory [6,7] generates expressions for each term of the internal energy balance equation using the peculiar velocity vector which, by definition, is the velocity of the hidden motion of the molecules. Recognition that the participation of matter in hidden motion explicitly leads to the internal energy balance equation (as mentioned above) can be exploited to develop a concealed-continuum model (CCM) on assigning every contribution in the internal energy to some sort of translational motion of matter. Considering the motion of matter in CCM provides an alternative and equivalent expression for the internal energy balance and also for Born's heat. On the other hand, for the thermo-

dynamic heat, we analogously propose a thermo-continuum model (TCM). Details of these aspects will be discussed in a following communication.

It is well known that there are implicit as well as explicit claims regarding the interpretation of the negative of Boltzmann's H -function as the entropy function. This, in view of the concept of thermodynamic heat generated in GPITT, requires the following correspondence at the continuum particle level:

$$-\sum_k \frac{1}{T_k} \frac{dq_k}{dt} \Leftrightarrow n (1 + \ln f) \frac{d \ln f}{dt}, \quad (31)$$

where f is the distribution function and n is the number density of molecules. On independently establishing the equivalence (31), in which our TCM and CCM will play an important role, the ambiguities between the thermodynamic and statistical entropies would be resolved. Accordingly, we have already undertaken the investigation of this aspect.

Yet another aspect of thermodynamic studies currently attracting much attention is the generation of abstract thermodynamic descriptions [28–36], namely, metric geometrical and network thermodynamic descriptions. In these studies, even descriptions for nonequilibrium situations have been attempted. In the metric geometrical approach, the loss of the availability function ΔA^u is exploited to generate the corresponding description. The inherent advantage in the use of this function lies in the fact that herein one simply need not bother about the identification of the system intensities, which anyway cannot be uniquely assigned to the entire global system in nonequilibrium situations (*vide supra*). Thus, a direct global description is promised; however, it is important to note that therein one works within the thermodynamic Gibbsian space (GS) determined solely by the system extensities. In GPITT we obtain an EGR which requires the construction of an extended Gibbsian space (EGS) for abstract thermodynamic purposes; this is generated by the system intensities and extensities taken as variables. However, the GS turns out to be a suitable projection space within the EGS. Further, from the GPITT there evolves a description at the continuum particle level, which in turn has to be integrated to generate the corresponding global description. Thus, an alternative but complementary metric geometrical description seems probable with the advent of the GPITT. Similarly, in the network thermodynamic description, the nonreciprocal networks are indicated for the spontaneous paths. This is because at present in network thermodynamics, one still continues to work within the GS; again, the EGS through the GPITT promises reciprocal networks for the spontaneous paths.

Our approach demands a search for the more abstract criteria for distinguishing between the real (spontaneous) and apparent paths through nonequilibrium states on the one hand, and that between the reversible and spontaneous paths on the other hand. The solution seems to lie, firstly, in arriving at a decision whether the EGS possesses Euclidean, Riemannian or Lobachevskian geometry and, secondly, on the role of the operation of Lyapunov functional-type criteria [37–39] for the spontaneous paths. Furthermore, the criteria to be evolved within the EGS have to reproduce those existing

essentially in GS on a simple but suitable projection within the EGS. Moreover, one is also tempted to enquire whether the existing dilemma of Andresen et al. [34] regarding the noncompatibility between the thermodynamic Gibbsian (Euclidean) geometry and the semi-Riemannian one (Weinhold's metric) is due to the non-recognition of the EGS.

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References

- [1] S.R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1969).
- [2] I. Gyarmati, *Non-Equilibrium Thermodynamics* (Springer-Verlag, Berlin, 1970).
- [3] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Wiley-Interscience, New York, 1967).
- [4] R. Haase, *Thermodynamics of Irreversible Processes* (Addison-Wesley, Reading, MA, 1969).
- [5] S. Wisniewski, B. Staniszewski and R. Szymanik, *Thermodynamics of Nonequilibrium Processes* (Reidel, Dordrecht, 1976).
- [6] S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1970).
- [7] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- [8] R. Haase, in: *Physical Chemistry, An Advanced Treatise*, Vol. 1, ed. W. Jost (Academic Press, London, 1971).
- [9] I. Müller, *Z. Phys.* 198(1967)329.
- [10] M.S. Boukary and G. Lebon, *J. Non-Equilib. Thermodyn.* 12(1987)95.
- [11] G. Lebon, D. Jou and J. Casas-Vazquez, *J. Phys. A (London)* 13(1980)25.
- [12] L.S. Garcia-Colin and M. Lopez de Haro, *J. Non-Equilib. Thermodyn.* 7(1982)95.
- [13] L.S. Garcia-Colin, M. Lopez de Haro, R.F. Rodriguez, J. Casas-Vazquez and D. Jou, *J. Stat. Phys.* 37(1984)465.
- [14] M. Lopez de Haro, R.F. Rodriguez and L.S. Garcia-Colin, *Physica* 128A(1984)535.
- [15] R.F. Rodriguez, L.S. Garcia-Colin and M. Lopez de Haro, *J. Chem. Phys.* 83(1985)4099.
- [16] D. Jou, J. Casas-Vazquez, J.A. Robles-Dominguez and L.S. Garcia-Colin, *Physica* 137A(1986)349.
- [17] M. Ferrer and D. Jou, *J. Chem. Phys.* 89(1988)1651.
- [18] G.M. Kremer and I. Müller, preprint.
- [19] G.M. Kremer, *Physica* 144A(1987)156.
- [20] R.E. Nettleton, *J. Phys. A: Math. Gen.* 21(1988)3939.
- [21] R.E. Nettleton, *Physica* 144A(1987)219.
- [22] B.C. Eu, *J. Chem. Phys.* 82(1985)4283.
- [23] B.C. Eu, *Acc. Chem. Res.* 19(1986)153.
- [24] B.C. Eu, *J. Non-Equilib. Thermodyn.* 11(1986)211.
- [25] B.C. Eu, *J. Phys. Chem.* 91(1987)1184.
- [26] J. Keizer, *J. Chem. Phys.* 82(1985)2751.
- [27] J. Keizer, *Phys. Rev. A* 30(1984)1115.
- [28] F. Weinhold, *J. Chem. Phys.* 63(1975)2479; 2484; 2488; 2496.

- [29] G. Ruppeiner, Phys. Rev. A27(1983)1116; A34(1986)4316.
- [30] R. Gilmore, Phys. Rev. A30(1984)1994.
- [31] J.D. Nulton and P. Salamon, Phys. Rev. A31(1985)2520.
- [32] B. Andresen, R.S. Berry, M.J. Ondrechen and P. Salamon, Acc. Chem. Res. 17(1984)266.
- [33] K.H. Hoffmann and P. Salamon, Phys. Rev. A35(1987)369.
- [34] B. Andresen, R.S. Berry, R. Gilmore, E. Ihrig and P. Salamon, Phys. Rev. A37(1988)845.
- [35] B. Andresen, R.S. Berry, E. Ihrig and P. Salamon, Phys. Rev. A37(1988)849.
- [36] L. Peusner, J. Chem. Phys. 83(1985)1276.
- [37] N.G. Chetayev, *The Stability of Motion* (Pergamon Press, New York, 1961).
- [38] J. La Salle and S. Lefschetz, *Stability by Liapunov's Direct Method* (Academic Press, New York, 1961).
- [39] I.Z. Shtokalo, *Linear Differential Equations with Variable Coefficients (Criteria of Stability and Instability of Their Solutions)* (Hindustan, Delhi, India, 1961).