Irreversible Thermodynamics: A Review

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Abstract- Lot of efforts were undertaken in the development of theories dealing with non-equilibrium thermodynamics. The theories of non-equilibrium thermodynamics are sequentially reviewed in this paper.

Keywords-Non equilibrium thermodynamics

I. INTRODUCTION

Equilibrium thermodynamics is based on two important statements:
1. The energy of the universe is constant (first law).
2. The entropy of the universe never decreases (second law).

Only in the first half of the twentieth century, it was felt necessary to go beyond the equilibrium approach. The first and so far unique macroscopic theory that has been set forth to extend the concepts of equilibrium thermodynamics (thermostatics) to non equilibrium states is around eighty five years old. Based on the ideas introduced by de Donder¹³ around the early twenties and Onsager’s reciprocity[4][5] theorem proved in 1931. Prigogine[6]-[9]Meixner[10] and Casimir[11] in the mid forties developed the theory of linear non-equilibrium thermodynamics. Nonequilibrium thermodynamics is a well-established classical discipline built on the grounds of two main hypotheses [6]-[9],[12],[15]

- First, the local equilibrium hypothesis assumes that the thermodynamic variables defined in each subsystem of a conveniently partitioned system admit the same interpretation as in equilibrium.
- Second, the entropy production of any isolated system is always nonnegative.

The theory attributes the deviations from equilibrium to the presence of unbalanced forces, such as electric fields or gradients, which give rise to fluxes, such as electric or heat currents. Forces and fluxes are in a relationship that is cause-effect compatible with the second law of thermodynamics and with the inherent symmetries, either macroscopic or microscopic. The dynamics follows from the local conservation laws for the thermodynamic field quantities, in which the fluxes are linear functions of the forces whose coefficients, the Onsager coefficients, satisfy reciprocity relations. The scheme of nonequilibrium thermodynamics has been used successfully to analyze irreversible processes in different systems.

II. LITERATURE REVIEW

In the following sections, the theories of non-equilibrium thermodynamics are reviewed. Non-equilibrium thermodynamics presents several faces: the most popular theory, is the Classical Irreversible Thermodynamics (CIT). Besides Classical Irreversible Thermodynamics, other theories are the Linear Irreversible Thermodynamics (LIT), Extended Irreversible Thermodynamics (EIT) and the rational thermodynamic (RT).

Energy dissipation and entropy production extremal principles are ideas developed within non-equilibrium thermodynamics that attempt to predict the likely steady states and dynamical structures that a physical system might show. According to Kondepudi (2008) [9] and to Grandy (2008)[25], there is no general rule that provides an extremum principle that governs the evolution of a far-from-equilibrium system to a steady state. According to Glansdorff and Prigogine (1971)[7] irreversible
effects are said to be coupled. Rayleigh's dissipation gradient.

This implies that all the relationships of classical thermodynamics between variables remain valid outside equilibrium. This means that all the variables of equilibrium thermodynamics remain significant and that all the physical properties of a physical system are the same as for uniform system at equilibrium. Therefore, the relaxation to equilibrium in such a system is monotone if it is sufficiently close to the equilibrium. The hypothesis postulates that the local and instantaneous relations between the thermal variables themselves that the dissipation of kinetic energy by friction is minimum. He wrote about electric current in an electrolyte solution with a concentration gradient. This work shows a non-equilibrium coupling between electric effects and concentration-driven diffusion. He also found a reciprocal relation, and this was another idea that tempted Onsager for the development of his theory of microscopic reversibility.

Hermann von Helmholtz [30] developed a principle of least viscous dissipation of kinetic energy subjected to a certain kind of boundary condition, namely; for a steady flow in a viscous liquid, with the speeds of flow on the boundaries of the fluid being given steady, in the limit of small speeds, the currents in the liquid so distribute themselves that the dissipation of kinetic energy by friction is minimum. He wrote about electric current in an electrolyte solution with a concentration gradient. This work shows a non-equilibrium coupling between electric effects and concentration-driven diffusion. He also found a reciprocal relation, and this was another idea that tempted Onsager for the development of his theory of microscopic reversibility.

Lord Rayleigh[31] introduced the dissipation function for the description of dissipative processes involving viscosity. More general versions of this function have been used by many subsequent investigators of the nature of dissipative processes and dynamical structures. Rayleigh's dissipation function was conceived from a mechanical viewpoint, and it did not refer in its definition to temperature, and it needed to be generalized to make a dissipation function suitable for use in non-equilibrium thermodynamics.

Lars Onsager[4]-[5] developed the theory of microscopic reversibility that is the symmetry of kinetic coefficients, called reciprocal relations. The reciprocal relations were discovered in the 19th century by Thomson and Helmholtz for some selected phenomena but the general theory was proposed by Lars Onsager in 1931. He found the connection between the reciprocal relations and detailed balance. For the equations of the law of mass action the reciprocal relations appear in the linear approximation near equilibrium as a consequence of the detailed balance conditions. According to the reciprocal relations, the damped oscillations in homogeneous closed systems near thermodynamic equilibrium are impossible because the spectrum of symmetric operators is real. Therefore, the relaxation to equilibrium in such a system is monotone if it is sufficiently close to the equilibrium.

I. Prigogine[6]-[9] proposed the classical irreversible thermodynamics (CIT) based on the local equilibrium assumption (LEA). The fundamental hypothesis assumes that the system can be split mentally into cells which are sufficiently large to be treated as macroscopic thermodynamic subsystems but, at the same time, sufficiently small that equilibrium is very close to being realized in each cell. The hypothesis postulates that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for uniform system at equilibrium. This implies that all the variables of equilibrium thermodynamics remain significant and that all the relationships of classical thermodynamics between variables remain valid outside equilibrium.
provided that they are stated locally at each instant of time. This means particularly that entropy outside equilibrium depends on the same variables as at equilibrium. He stressed that the irreversible processes usually are not governed by global extremal principles because description of their evolution requires differential equations which are not self-adjoint, but local extremal principles can be used for local solutions. He proved that the non-equilibrium steady states are the states with minimum production of entropy at local level. He developed stability theory for these state and extensively worked on self-organization of processes far from equilibrium through dissipation.

C.E.Shannon [16] published his famous paper a Mathematical Theory of Communication, in which he devoted a section to on choice, uncertainty, and entropy in signal coding, which present day is called as Information theory. Shannon's information entropy is a much more general concept than statistical thermodynamic entropy.

I. Gyarmati [32] gives a systematic presentation, and extends Onsager's principle of least dissipation of energy, to give a more symmetric form known as Gyarmati’s principle. He explains that the Onsager reciprocal relations concern variables which are even functions of the velocities of the molecules, and notes that Casimir went on to derive anti-symmetric relations concerning variables which are odd functions of the velocities of the molecules.

J.M.Ziman [33] gave very readable account on the general principle of the thermodynamics of irreversible processes: "Consider all distributions of currents such that the intrinsic entropy production equals the extrinsic entropy production for the given set of forces. Then, of all current distributions satisfying this condition, the steady state distribution makes the entropy production a maximum." He claimed that this was a general principle, discovered by Onsager, but was "not quoted in any of the books on the subject". He notes the difference between this principle and Prigogene's theorem, which states, that if not all the forces acting on a system are fixed the free forces will take such values as to make the entropy production a minimum.

E.T.Jaynes [17], [19] explained the principle of maximum entropy where he emphasized a natural correspondence between statistical mechanics and information theory. Jaynes offered a new and very general rationale why the Gibbsian method of statistical mechanics works. He argued that the entropy of statistical mechanics and the information entropy of information theory are principally the same thing. Consequently, statistical mechanics should be seen just as a particular application of a general tool of logical inference and information theory.

J. Keizer [20], [21] proposed the fluctuations for the formulations for a definition of entropy outside equilibrium. Keizer combines the molecular picture of Boltzmann and the stochastic picture of Onsager and lays the foundations of statistical thermodynamics of equilibrium and non-equilibrium steady states. Keizer’s theory has been the subject of numerous applications as ion transport through biological membranes, isomerization reactions, fluctuations caused by electrochemical reactions, light scattering under thermal gradients, laser heated dimerization etc.

Peter Landsberg [34]-[37] suggested that the temperature of a moving body should remain unchanged. He pointed out that the apparent temperature must depend on how the temperature is measured or defined. He suggested that when the heat source moves transversely relative to the observer, the temperature change would not involve Doppler’s effect, which can be determined only by considering how high-speed mobile objects reach thermal equilibrium. The relative velocities of the particles in different coordinate systems be offset relative to each other, the temperature would not change, it must be Lorentz invariant.

He reviewed the history of the relativistic transformation and its impact on the development of statistical thermodynamics. He derived entropy order/disorder formulas based on a combination of thermodynamics and information theory arguments. He argues that when constraints operate on a
system, such that it is prevented from entering one or more of its possible or permitted states, as contrasted with its forbidden states, the measure of the total amount of "disorder" in the system.

B. Lavenda [38] studied the basic formalism applicable to nonlinear thermodynamic processes at a mathematical level accessible to physicists and theoretically inclined chemists and biologists. He examined the approach to nonlinear thermodynamics based on a confluence of thermodynamic and kinetic concepts regarding evolution and stability. He discussed thermodynamics systems found in the immediate neighbourhood of a non-equilibrium state along with the discussion of non-equilibrium variational principles, including the principle of Le Chatelier, the principle of least dissipation of energy, and the kinetic formulation of thermodynamic variational principles. He developed the theory of the nonlinear thermodynamics of irreversible processes applicable to systems far from equilibrium. He studied the concept of dissipative structures.

de Groot and Mazur [8] presented a comprehensive and insightful survey of the foundations of the (CIT) in their text book. They provided a complete discussion of the linear theory of irreversible thermodynamics. The applications of this theory were found in diffusion, heat conduction, fluid dynamics, relaxation phenomena, and the behavior of systems in an electromagnetic field. They treated in detail the statistical foundations of non-equilibrium thermodynamics and classified the various irreversible phenomena according to their "tensorial character" that is: Scalar phenomena: which are related to chemical reactions. Vectorial phenomena: which are related to diffusion and heat conduction. Tensorial phenomena: which are related to the tensorial quantities occurring in the thermodynamics of fluid systems such as the pressure tensor and the velocity gradient.

Lebon, Jou and Vazquez [12],[13],[39]-[45] emphasized that the basic formula for the rate of entropy production have the characteristic sum of the products of thermodynamic fluxes and of conjugated generalized forces. The rate of production of entropy is the sum of products of each flux with the associated force. Evidently, all fluxes and forces vanish at equilibrium. The existence of a non-negative entropy production is one of the main points underlying CIT. They postulated that the fluxes and the generalized forces are related linearly and hence rate of entropy production becomes the quadratic in fluxes which are positive definite. They developed extended irreversible thermodynamics (EIT) provides a link between thermodynamics and dynamics of fluxes, and it is especially useful in describing systems with relatively long relaxation times, e.g. solids at low temperature, super fluids, some visco elastic fluids. They have chosen the fluxes rather than the gradients of the classical variables as new independent quantities because fluxes were associated with well defined microscopic operators and they are advantageous for slow and steady state phenomena. The formalization of EIT is the subject of some criticism, namely;

- every dissipative flux is considered as quantity characterized by a single evolution equation. However, this is not always the case in practice.
- There exist still other "additional" variables and variety of evolution equations for the fluxes as well.
- Entropy is regarded as an analytical function of the fluxes, but this is not an essential assumption and non-analytical developments have been proposed.

They studied the critical examination that in rational thermodynamics the physical fluxes are viewed as dependent quantities. In RT the temperature and entropy are introduced as primitive concepts of general validity without a sound physical interpretation. Also, in RT the second law of thermodynamics takes the form of the so-called Clausius-Duhem inequality, which locally in the absence of the heat supply.

They pointed out that (EIT) was originally born out to generalize the local equilibrium assumption and to extend the Fick, Fourier and Newton laws outside the linear and steady domain covered by (CIT). They summarized the (EIT) as follows:

the physical fluxes in EIT are considered as independent variables.
In EIT, a generalized Clausius-Duhem relation is used. This relation states that the entropy flux is not simply for all cases but may contain supplementary terms; moreover the entropy is not a function of the classical variables but depends on the physical fluxes. The temperature and entropy in EIT assigned a physical interpretation.

Netton and Sobolev[46],[47] proposed that classical irreversible thermodynamics of multi component systems is formulated upon the assumption of local equilibrium thermodynamics, which states that the entropy per unit mass of the mixture depends on the internal energy, the specific volume, and the mass fraction.

Liu [48] studied the restrictions of rational thermodynamics imposed on the processes by the balance equation of mass, momentum and energy by means of Lagrange multipliers. In case of heat conduction, he assumed that there exists an entropy that obeys a balance law with a non-negative production.

Trusedell [49]-[50], proposed rational thermodynamics (RT). He referred that the (RT) presents a very mathematical formalism and it abandons the hypothesis of local equilibrium. It's constitutive equations take the form of time –functional. Finally, he pointed out that the cornerstone of this theory was its assumption that the internal energy must depend on the physical fluxes in addition to its classical variables.

Bataille and Kestin [51] explained that the concept of local equilibrium in Rational thermodynamics(RT) was abandoned and for the characterization of a system the new concept of memory is introduced. The behavior of the system was thus determined not only by the present value of the variables but also by the whole history of their past value. The main objective of the RT was to provide a method for deriving constitutive equation which serves for a most faithful description of actual physical process.

Garcia-Colin and Selva [52]-[57]proposed that in EIT the additional macroscopic quantities (e.g., heat flux in conductive systems) play the role of independent variables. This means that the whole set of space variables describing the system is formed by the classical (conserved) variables plus the (non-conserved) fluxes presented in the system. They modified Gibbs equation.

Fort, Vazquez and Mendez [58] studied an incompressible, multi component fluid in which diffusion and other transport processes were absent and assuming for simplicity that the heat of reaction may be neglected. They found that the evolution equation for the specific entropy in non equilibrium processes.

A. Bhalekar [59]-[65] demonstrated that the temperature and pressure concept retains the same physical meaning whether the system is in equilibrium or non-equilibrium situations. He stressed that there is no need of non-equilibrium temperature. He pointed out in his several research papers the existing theories of irreversible thermodynamics violating the dictates of second law of thermodynamics. He proved that most of the existing theories are only applicable near to equilibrium. He independently developed comprehensive thermodynamic theory of stability of irreversible processes (CTTSIP).

J.M. Rubi [66],[67] developed mesoscopic thermodynamics. He shows that how to extend the use of thermodynamic concepts into the mesoscopic domain where fluctuations and nonlinearities play an important role and study the dynamics of single molecules, activated processes and nonlinear transport in confined systems. He shows that the probabilistic interpretation of thermodynamics together with probability conservation laws can be used to obtain Fokker-Planck equations for the relevant degrees of freedom. This approach provides a systematic method to obtain the stochastic dynamics of a system directly from its equilibrium properties.
Chandrakant Burande[68]-[72] had worked on thermodynamic stability of stress relaxation processes in viscoelastic fluids, complex chemical reactions, chemical and biological spatially uniform and nonuniform systems in reference to perturbation in fluxes and concentrations.

Vijay Tangde [73]-[75] had worked stability of industrial chemical reactions such as ammonia synthesis and oxidation of sulfurdioxide under temperature perturbation.

III. INFERENCES

- Most of the study in above referred survey centred on the local equilibrium assumption (LEA) proposed by Prigogine. LEA discriminately uses global equilibrium variables for case of local equilibrium.
- In most of the proposals thermodynamics fluxes are linearly related to thermodynamic forces. But in most of the cases they are not linearly related and only validate at equilibrium or closed to equilibrium.
- Not necessarily that the all non-equilibrium steady states are states of minimum entropy production.

Under these circumstances the thorough analysis of theories of irreversible thermodynamics is inevitable to find out a comprehensive formalism of theory of irreversible thermodynamics which encompass all non-equilibrium processes.

REFERENCES