



APPLICATIONS OF EXTENDED IRREVERSIBLE THERMODYNAMICS TO POLYMER SOLUTIONS- A REVIEW

Megha Sawangikar^a, Chandrakant Burande^b, Bharati Burande^{a,b,*}

^a“Department of Chemistry, Datta Meghe Institute of Engineering, Technology and Research”,
Wardha, India

^b“Department of Chemistry Priyadarshini Indira Gandhi College of Engineering”, Nagpur, India

ABSTRACT

In this review, we outline recent progress towards the use of Extended Irreversible Thermodynamics to describe polymer solutions and blends under shear flow. The basic idea is that, EIT is particularly well suited to describe process characterized by situations where the product of relaxation time and the rate of variation of the fluxes is important, or when the mean free path multiplied by the gradient of the fluxes is high; these situations may be found when either the relaxation times or the mean free paths are long, or when the rates of change in time and space are high.

EIT has proved to be of use in obtaining the relevant constitutive equations as the polymer solutions exhibit rather long relaxation times for the viscous pressure tensor, and, in that respect, it confirms in several cases the equations provided by other approaches.

Keywords: Extended Irreversible Thermodynamics, relaxation time, constitutive equations

1. Introduction

Extended irreversible thermodynamics (EIT), together with classical irreversible thermodynamics (CIT) and rational thermodynamics (RT) has been among the mainstream of research in non-equilibrium thermodynamics. EIT crosses the borders of the local-equilibrium hypothesis and explores new grounds. Since the early 1960s, several hundred papers have been published on EIT. Recently, two books (Jou et al 1993b, 1996a, Muller and Ruggeri 1993)1,2 have appeared wherein a

systematic analysis of EIT can be found. Other books closely related to EIT but with different aims and scopes have also been written by Sieniutycz and Salomon (1992)3, Eu (1992)4,5, Tzou (1997)6, Wilmanski (1998)7. In 1998, two review articles (Jou et al 1988a, Garcia-Colin 1988)1,8,9 opened a wider perspective on EIT. Because of the intense activity developed since the publication of first review, D. Jou, Casas – Vazquez and G. Lebon1 updated the vision and provide an overview of the progress with the basic ideas underlying the theory and its wide range of applications achieved during the last decade

The study of high frequency, short-wavelength phenomena and (or) large amplitude perturbations has known an extraordinary impetus due to the progress in material science and technology in general. During the 1960s, experiments on light and neutron scattering opened new perspectives and contributed to the developments of the so-called generalized hydrodynamics, where the usual transport laws are generalized to include memory and non-local effects. In the last two decades, the increasing miniaturization of physical devices (mainly in microelectronics) has directed attention to a regime where transport is no longer dominated by collisions amongst the particles, but rather by ballistic effects. All these features have motivated the formulation of a mesoscopic description, intermediate between the macroscopic and the microscopic ones. The main idea behind a statistical formalism is to eliminate the excess of information resulting from a purely microscopic description. An alternative, complementary attitude consists of starting from a macroscopic

description and adding relevant information to take into account peculiar features of the mesoscopic regime. The aim of EIT is precisely the latter one, i.e, to propose an extension of classical thermodynamics towards mesoscopic regimes. Obviously, the relevance of the theory should be checked by comparing it with experiment and the results derived from microscopic models.

By EIT are understood the thermodynamic theories which used as independent variables the dissipative fluxes in addition to the classical variables such as internal energy, density, mass concentrations, deformation tensor etc. In the first versions of EIT, the extra variables were selected to be the usual thermo-hydrodynamic fluxes as the heat flux, the viscous pressure tensor, the electric flux, and the diffusion flux. Later, higher-order fluxes, such as the flux of the heat flux, were included. Other keystones in the construction of EIT are the formulation of evolution equations for the fluxes and the establishment of a generalized Gibbs equation expressing the dependence of the non-equilibrium entropy with respect to the basic variables. These lines of thought define a general framework, in which coexist several different methods of approach, with either physical or mathematical emphasis and have fostered efforts towards a unified view. Many problems remains open in non-equilibrium thermodynamics in general and in EIT in particular. It is, however, expected that

the combination of an EIT approach and microscopic theories will emerge into a suitable framework for the description of mesoscopic phenomena¹⁰ out of equilibrium.

1.1 General Structure of EIT

In its original formulation, EIT included the usual dissipative fluxes-heat flux, diffusion flux, electric flux, viscous pressure-among the set of independent variables. The main motivation was the need to describe phenomena with timescales comparable to the relaxation times of these fluxes. Such situations are met when the phenomena are very fast or very steep (as ultrasound propagation, light scattering in gases, neutron scattering in liquids, heat propagation at low temperature, shock waves etc) or when the relaxation times of the fluxes become very long, as in polymeric solutions, suspensions, super fluids or superconductors.

1.2. Generalized Entropy in a One-Component Fluid

As in CIT, EIT assigns a central role to entropy. It is assumed that the entropy of a one-component fluid depends locally not only the classical conserved variables, such as internal energy u , specific volume v . but also on the fluxes, namely q (heat flux), p^v (bulk viscous pressure) and P^v (deviatoric part of the viscous pressure tensor).

In differential form, the entropy can be written as

$$ds = \frac{1}{\theta} du + \frac{1}{\theta} \pi v dv - \frac{1}{\theta} v \alpha_0 dp^v - \frac{1}{\theta} v \alpha_1 dq - \frac{1}{\theta} v \alpha_2 : dP^v \tag{1.1}$$

where all the extensive quantities s , u , v are measured per unit mass.

A general expression of the entropy flux J for isotropic systems is, up to second order in the fluxes,

$$J^s = \theta^{-1} q + \beta^i p^v q + \beta^{\prime\prime} P^v \cdot q \tag{1.2}$$

where the coefficients β and β are functions of u and v . In the linear approximation in the fluxes, the second and third terms in the right-hand side are negligible and θ can be identified with the local-equilibrium temperature, so the (6.15) reduces to the expression of the classical theory of irreversible processes, namely $J^s = T^{-1} q$. The

non-classical terms of J^s have been the subject of recent studies, both from a macroscopic point of view, by analyzing their connection with the non-local terms in the evolution equations of the fluxes, as well as from the viewpoint of information and kinetic theories by Jou et al (1995)¹, Lebon et al (1994)¹⁶, Nettleton

(1992)17.

1.3 Entropy Production and Evolution of Fluxes

This expression has the structure of a bilinear form

$$\sigma^s = q \cdot X_1 + p^v X_0 + \overset{\circ}{P}^v : X_2 \tag{1.3}$$

Consisting of a sum products of the fluxes q, p^v and $\overset{\circ}{P}^v$ and their conjugate generalized forces X_1, X_0 and $\overset{\circ}{X}_2$. The latter follow from direct comparison of (5.17) with (5.16). They are similar to the expressions obtained in CIT but contain additional terms depending on the time and space derivatives of the fluxes.

Upon defining the proper form of the forces X_1, X_0 and $\overset{\circ}{X}_2$, it can be noted that there exists a class of transformations of the time derivatives of q and $\overset{\circ}{P}^v$ which leave the entropy production

$$X_1 = \mu_1 q, \quad X_0 = \mu_0 p^v, \quad \overset{\circ}{X}_2 = \mu_2 \overset{\circ}{P}^v \tag{1.4}$$

where the coefficients μ_i may depend on u and v but not on the fluxes. When expressions (5.18) are introduced into (5.17), it led to,

$$\sigma^s = \mu_1 q \cdot q + \mu_0 p^v p^v + \mu_2 \overset{\circ}{P}^v : \overset{\circ}{P}^v \tag{1.5}$$

Within the linear approximation, the generalized Gibbs equation (5.11) has the form

$$ds = T^{-1} du + p T^{-1} dv - \frac{\tau_1}{\rho \lambda T^2} q \cdot dq - \frac{\tau_0}{\rho \zeta T} p^v dp^v - \frac{\tau_2}{2 \rho \eta T} \overset{\circ}{P}^v : d \overset{\circ}{P}^v \tag{1.6}$$

For pure heat conduction, the entropy is given by,

$$ds = T^{-1} du - \frac{\tau_1}{\rho \lambda T^2} q \cdot dq \tag{1.7}$$

After integration, (5.38) can be cast in the form

$$\rho s(u, q) = \rho s_{eq}(u) - \frac{\tau_1}{2 \lambda T^2} q \cdot q \tag{1.8}$$

Where $\rho s_{eq}(u)$ is the local-equilibrium entropy depending only on u . The corresponding entropy production is

$$\sigma^s = \frac{1}{\lambda T^2} q \cdot q \tag{1.9}$$

1.4 Non-equilibrium Equations of State

The existence of generalized entropy compatible with some classes of evolution equations for the fluxes is already discuss in previous section. This formalism aims to describe processes which are compatible with the existence of non-equilibrium entropy whose rate of production is non-negative. Once the expression of the entropy is known, there is no difficulty in deriving the corresponding equations of state which are directly obtained as the first derivatives of the

The entropy production is directly derived from the entropy balance equation

invariant. They allow us to introduce frame-indifferent time derivatives, for instance the corotational derivative, which is necessary in the analysis of rheological equations and in the discussion of the invariance of the properties of the equations of the fluxes1,18.

To obtain evolution equations for the fluxes compatible with the positiveness of σ , we express the forces X_1, X_0 and $\overset{\circ}{X}_2$ as linear functions of the fluxes. As a consequence, we write

entropy with respect to the basic variables. In classical thermodynamics, it is known that the derivative of the entropy with respect to the internal energy (by keeping fixed the volume and the composition of the system) is the absolute temperature: the derivatives with respect to the volume and to the number of moles yield the equilibrium pressure and the chemical potentials (divided by the absolute temperature), respectively. It may then be asked whether the derivatives of the generalized entropy introduced

in EIT still allow one to define an absolute non-equilibrium temperature, as well as a non-equilibrium pressure and non-equilibrium chemical potentials. This is a very subtle and not completely solved problem which has, however, received partial answer in recent years, in that some specific gedanken experiments reflecting, in particular, the difference between the generalized temperature and the local-equilibrium temperature were proposed by Jou and Casas-Vazquez (1992) and a real experiment was interpreted by Luzzi^{23,24}. Since this is a fundamental question, it deserves detailed attention. With this objective in mind, let us try to better apprehend the physical meaning of the generalized entropy defined by eq.(5.37).

1.5 Physical Interpretation of Non-equilibrium Entropy

$$dN = -T^{-1}V\alpha_1 \cdot dq - T^{-1}V\alpha_2 : d\mathbf{P}^v \quad (1.10)$$

Indeed, the extra terms in the non-equilibrium entropy may be related to the uncompensated heat generated during the relaxation to equilibrium: it is logical that they are related to dN. It should be stressed that Eu’s presentation is general and rather abstract but does not help in selecting the variables. The choice of the relevant variables must always be, motivated by experimental and (or) microscopic considerations, as in EIT wherein the choice of \mathbf{q} and \mathbf{P}^v is determined from the dynamical equations (5.34)-(5.36) which have found

$$ds = \frac{1}{\theta} du + \frac{1}{\theta} \pi dv - \frac{v\tau_1}{\lambda T^2} \mathbf{q} \cdot d\mathbf{q} - \frac{v\tau_0}{\zeta T} p^v dp^v - \frac{v\tau_2}{2\eta T} \mathbf{P}^v : d\mathbf{P}^v \quad (1.11)$$

where, in contrast to (5.37), we have re-introduced in the first two terms the generalized absolute temperature θ and the thermodynamic pressure π instead of their respective local-equilibrium approximations T and p.

Another consequence of the non-equilibrium temperature is that even in steady situations the relation between heat flux and temperature gradient should be written as $\mathbf{q} = -\lambda \nabla \theta$ instead of $\mathbf{q} = -\lambda \nabla T$. This result can be used as the starting point of a better understanding of θ .

An analogous phenomenon should appear when the non-equilibrium situation is produced by

experimental confirmation. Another difficulty with respect to Eu’s argument is that it supposes the existence of an irreversible cycle. This is clearly not guaranteed as it implies the selection of a complete set of relevant variables. If the set is not complete, a cycle in the space of these variables would not correspond to a true cycle of the system, i.e. the final state could be different from the initial state despite the fact that the set of chosen variables take the same values in the initial and final states.

5.6 Non-equilibrium Temperature

Extended irreversible thermodynamics fosters the idea of nonequilibrium temperature mainly influenced by the one that is used in kinetic theory. However, it is being claimed as distinctly different in its physical contents as the one given by the traditional zeroth law of thermodynamics. Muschik^{25,26} proposes an idea of contact temperature in nonequilibrium which requires the use of a hypothetical heat reservoir (by its definition it is devoid of a heat flux) and making heat flux between it and the system (!) zero but they are silent about the possible existence of heat flux in the system before making of the diathermal contact. Bhalekar²⁷ proposes a generalized zeroth law of thermodynamics has been framed that takes care of the necessity of thermal equilibration for sensing the temperature. The Gibbs equation (5.11) may writer as

other fluxes (as a shear viscous pressure or an electrical) instead of a heat flux in the system. Indeed, recent computer simulations have shown that in the presence of a shear viscous pressure, heat flows between regions which, nevertheless, are at the same local-equilibrium temperature (Todd and Evans 1997)²⁸. Furthermore, there is some experimental evidence from spectroscopic analyses in photo excited plasma in semiconductors submitted to an external electric field, that indeed the temperature appearing in the non-equilibrium distribution function should depend not only on the local-equilibrium variables but also on the electrical current and heat flux (Luzzi et al 1997a)^{23,24}.

The presence of a generalized temperature is not exclusive to extended irreversible thermodynamics. In his entropy-free formulation of non-equilibrium thermodynamics, Meixner (1973)^{29,30} postulated the existence of a dynamical temperature depending on the interactions of the system with the outside. Muller³¹ introduced a ‘coldness’ function assumed to depend on the empirical temperature and its time derivative: in a steady state, the ‘coldness’ reduces to the local-equilibrium temperature, in contrast with the generalized temperature appearing in EIT. More recently, Muschik introduced the notion of contact temperature is not identical to the local-equilibrium temperature. Finally, Keizer³² proposed a non-equilibrium temperature defined as the derivative with respect to the internal energy of a generalized entropy derived from statistical considerations about molecular fluctuation; this temperature depends not only on

the classical variables but also on the second moments of functions. It is worth stressing that the EIT generalized temperature may also be expressed in terms of the second moments of the energy fluctuation, in analogy with Keizer’s approach.

The problems have been posed by the definition and measurement of a non-equilibrium temperature have been contested in recent papers by Hoover³³, Nettleton¹⁷, Garcia-Colin¹⁹, Bhalekar and Garcia-Colin²⁷. Apart from notation (one could use T and T_{eq} instead of θ and T), a question under discussion is the nature of the variables to be kept constant during the differentiation of the entropy. With v and q fixed, one recovers the equation of state. If, instead, one keeps constant v and the quantity $(\tau/\lambda T^2)^{1/2} q$ the derivatives of the generalized entropy and of the local-equilibrium entropy coincide. Indeed, since

$$s(u, v, q) = s_{eq}(u, v) - \frac{\tau v}{2\lambda T^2} q \cdot q \tag{1.12}$$

then, of course,

$$\left(\frac{\partial s}{\partial u} \right)_{v, \sqrt{\tau/(\lambda T^2)} q} = \left(\frac{\partial s_{eq}}{\partial u} \right)_v \tag{1.13}$$

Still another possibility is to maintain fixed the temperature gradient and, since eq.(5.52) implies that for steady situations

$$s = s_{eq} - \frac{\tau v \lambda}{2T^2} \nabla T \cdot \nabla T \tag{1.14}$$

one is led to

$$\left(\frac{\partial s}{\partial u} \right)_{v, \nabla T} = T^{-1} + (1 + 2b) \left(\tau \lambda / 2\rho c_v T^3 \right) \nabla T \cdot \nabla T \tag{1.15}$$

where b is the exponent which characterizes the dependence of τ with T according to $\tau \approx T^{-b}$ (i.e. $b = 0$ for Maxwell molecules and $b = \frac{1}{2}$ for hard spheres). In fact, it can be argued that not all these definition may be valid: recall, indeed, that in equilibrium thermodynamics $(\partial s/\partial u)_v = T^{-1}$ but if one keeps constant the pressure instead of the volume during the differentiation, $(\partial s/\partial u)_p$ is different from T^{-1} ; clearly

$$\left(\frac{\partial s}{\partial u} \right)_p = T^{-1} \left[1 - (p v \alpha / c_p) \right]^{-1}$$

with α the coefficient of thermal expansion and c_p the specific heat at constant pressure. At the

present time, it is not clear which among the above restrictions is the most suitable to define appropriately the non-equilibrium temperature.

1.6 Applications

Having reviewed and discussed the foundations of EIT, it may be asked which kind of problems will specifically be solved by using the methods and results of EIT. Among the applications, several subjects of special practical interest, such as non-classical heat transport, polymer physics, non-Fickian diffusion, transport in submicronic devices, and dielectric relaxation, as well as some other topics like super fluids, nuclear collisions, and cosmological models, have been selected which are appealing from a more theoretical point

of view.

• **Non-classical Heat Transport**

It was shown that Cattaneo’s model is particularly well suited for analyzing short-time or high-frequency heat transport beyond Fourier’s law. These situations are found, for instance, in explosions, the heating of metals by short laser pulses, or the fast compression of solid hydrogen pellets by means of laser pulses to achieve nuclear fusion. However, the Cattaneo equation (5.4) remains silent about the spatial microstructure, which may play a role at the scale of very short wavelengths, in miniaturized devices, or in materials with microstructure whose transport properties depend, in general, on the ratio of the mean free path of the

• **Onsager Relations**

In classical irreversible thermodynamics, the evolution equations of the state variables a^α can be given the general form

$$\frac{\partial a^\alpha}{\partial t} = - \sum L^{\alpha\beta} \frac{\partial f}{\partial a^\beta} \tag{1.16}$$

where $\partial a^\alpha / \partial t$ is the thermodynamic flux, f is the free energy, $\partial f / \partial a^\beta$ the thermodynamic force, and $L^{\alpha\beta}$ the phenomenological coefficients. The latter obey the well known Onsager-Casimir relations

$$L^{\alpha\beta} = \pm L^{\beta\alpha} \tag{1.17}$$

wherein the sign + (respectively -) refers to state variables a^α and a^β with the same (respectively different) parity under time reversal. These equations may formally be cast in the form

$$\frac{\partial a^\alpha}{\partial t} = - \sum_\beta L^{\alpha\beta} \frac{\partial f}{\partial a^\beta} - \sum_\beta M^{\alpha\beta} \nabla \cdot \left(\frac{\partial f}{\partial a^\beta} \right) + \dots \tag{1.18}$$

where a^α stands for q_i , $Q_{(ij)}$ and Q , respectively and

$$M^{qQ} = M^{Qq} = \frac{\lambda \eta T}{\tau_1 \tau_2} \tag{1.19}$$

$$M^{qQ} = M^{Qq} = \frac{\lambda \zeta T}{\tau_1 \tau_3} \tag{1.20}$$

or more generally $M_{\alpha\beta} = M_{\beta\alpha}$. These reciprocity relations, which are derived on purely macroscopic grounds, may be considered as generalizations of the Onsager-Casimir relations. It is worth noticing that the argument leading to the symmetry of the coefficients $M_{\alpha\beta}$ parallels the demonstration given by Onsager himself, who postulated that the fluxes are the time derivatives of the state variables while the forces are the derivatives of a thermodynamic potential with respect to the state variables. There is, however, one important difference to the Onsager-Casimir

quasiparticles (e.g. phonons) and the characteristic length describing the microstructure as, for instance, the width of the layers in a layered structure. A well known model including some non-local effects are that of Guyer and Krumhansl (1964)³⁸ which gives a satisfactory description of heat pulse propagation in dielectric crystals at very low temperature. However, even this model presents some limitations: it is a linearized equation; further, when coupled to the classical energy equation, it predicts infinite speed of propagation at very large frequencies: and therefore it is unable to describe ballistic propagation. An important question is then to ask how far EIT is able to describe not only high-frequency but also short-wavelength phenomena.

results it concerns the change of sign. Therefore, one should expect skew symmetry according to the Onsager-Casimir rules. But instead it is seen that relations (5.76) exhibit symmetry properties. The above observations seem to indicate that, under time reversal, microscopic reversibility requires not only that the sign of the time be reversed but also that of operator ∇ : $\nabla \rightarrow -\nabla$.

1.7 Critical Study

First of all, EIT clearly emphasizes the strong correlation between the transport equations and

thermodynamics. One cannot formulate transport equations independently of their thermodynamic background. For instance, it follows from the present work that introducing relaxation terms in the transport equations results in a modification of the expression of entropy whereas the presence of non-local terms leads to a generalization of the expression of the entropy flux. In that respect, EIT suggests that in the future more attention should be dedicated to this unifying aspect, which is usually forgotten, because of the almost exclusive focus on transport equations for themselves.

From a fundamental point of view, EIT has raised more challenging problems during the last decade than in the initial stage of its formulation. D. Jou, Casas Vazquez and G. Lebon has pointed out that rather than invalidating the basic concepts of the theory, EIT has raised important and fundamental questions in non-equilibrium thermodynamics and statistical mechanics. Among the open questions are the meaning of temperature and entropy in non-equilibrium states, and the relation between the H theorem and the formulation of the second law in non-equilibrium processes (Lebon et al 1992, 1996, Garcha-Colin 1995). Another important problem is the formulation of non-equilibrium equations of state and, in particular, the definitions of temperature and pressure outside equilibrium. Definite answers are undoubtedly beyond the scope of EIT, but the latter may be helpful in proposing some ways out and in formulating them in explicit terms. It should also be recalled that in classical irreversible thermodynamics such fundamental questions do not arise as they are eluded by appealing to the local – equilibrium postulate.

Concerning the selection of variables, it is shown that the use of the ‘equilibrium’ slow variables complemented by fast variables taking the form of fluxes of mass, momentum and energy is generally sufficient to solve a great variety of problems. The time-evolution equations of these variables generalize the classical transport equations of Fourier, Fick, and Newton: they display memory effects and may contain nonlinear and non-local contributions; they guarantee, in addition, that the causality principle demanding that effect comes after the cause is satisfied. It is evident that an increasing number

of variables is necessary to describe high-frequency responses of systems: Muller³¹ has computed the density correlation function by including in it more and more higher-order fluxes, and have compared them with the experimental results obtained from light scattering in gases. They show that after taking 230 moments, the results are no longer affected by the addition of more moments. Thus, depending on the details that one wants to reproduce, it appears that one should include an increasing number of variables. On the other hand the problem soon becomes intractable when too large a number of variables are involved. In this context, let us mention the work of Dedeurwaerdere³⁵ which, starting from an infinite number of fluxes, introduces a method based on an asymptotic continued-fraction expansion of the frequency- and wavelength-dependent variables and to include the effects of all the others in some effective relaxation times. This topic has also been examined from the microscopic point of view (Ichiyanagi 1995b, 1996, Luzzi et al 1998)^{41,24}. Instead of the common strategy that consists of eliminating all the fast variables, in order to describe the most prominent features of high-frequency response they include a few relevant fast variables and eliminate the others by a procedure similar to the renormalization scheme used in the analysis of critical phenomena.

Another difference between EIT and the classical theories is the formulation of non-equilibrium equations of state: as a matter of fact, the latter are now flux dependent. A typical example is the caloric equation of state wherein the internal energy does not only depend on the local-equilibrium temperature but, in addition, on the fluxes. This dependence is supported by experimental results on the decay of photo excited plasma in semiconductors in the presence of an electric current, or by computer simulations. Moreover, such a generalized equation of state is a consequence of the existence of a non-equilibrium temperature different from the classical local-equilibrium temperature introduced is most formalism. Kinetic theory developments indicate that the non-equilibrium temperature is directly related to the translational kinetic energy of the particles in the plane normal

to the heat flux. More generally, it is also expected that different degrees of freedom may have different 'temperatures', in such a way that thermometers sensible to different degrees of freedom will indicate different temperature. Similar conclusions hold for the non-equilibrium pressure and non-equilibrium chemical potential which are also allowed to be flux dependent

The relation between the Boltzmann and the macroscopic entropy was clarified where the link between the H theorem and the second law of thermodynamics. Indeed, the H theorem refers to the evolution of the microscopic Boltzmann entropy, defined in terms of the one-particle distribution function which is the exact solution of the Boltzmann equation, whereas the second law of thermodynamics is formulated in terms of macroscopic entropy, defined from a reduced number of macroscopic variables.

The debate about such fundamental questions as the definitions of non-equilibrium temperature, pressure, entropy and the H theorem has been given a new impetus mainly due to the recent development of EIT. Thus, it was shown that the latter can be described in terms of a generalized Hamiltonian structure in the light of formulation of GENERIC (General Equations of Non-equilibrium Reversible and Irreversible coupling) developed recently by Grmela et al (1998)42-44. It is well recognized that a macroscopic theory is not fully self-consistent as it contains unknown phenomenological coefficient which cannot be determined and interpreted without referring to experiments or microscopic model theories.

Second-sound propagation was evidenced experimentally during the 1960s and explained theoretically within the framework of EIT. Second sound was first discovered in liquid helium II, and the peculiar properties of He are usually investigated by means of Landau's classical two-fluid model. The problem has been revisited recently by several authors who proposed a more general description based on EIT.

Radiation hydrodynamics is another example of non-classical heat transport. This is not surprising as radiation has a well-defined maximum speed, and therefore the need of a hyperbolic equation for the description of energy transport is widely recognized. A particularly interesting result

arising from EIT is that it imposes that a signal such as the heat flux, cannot reach an unbounded value but is 'saturated' by a limiting value equal to the energy density times a maximum speed, say the speed of light in radiative heat transfer. This saturation effect cannot be described by the classical Fourier law.

Another privileged domain of application of EIT is that of polymer solutions, as they exhibit rather long relaxation times for the viscous pressure tensor. EIT has proved to be of use in obtaining the relevant constitutive equations and, in that respect, it confirms in several cases the equations provided by other approaches. In contrast to the formalisms based on internal variables, EIT identifies from the start the viscous pressure as an additional variable. This allows one to unify the description of very large classes of material systems, passing from ideal gases to viscoelastic materials, the fundamental differences being the value of the relaxation time and the microscopic form of the pressure tensor. Another more exclusive advantage of EIT is that it predicts generalized equations of state which are particularly well suited to study phase transitions in polymer solutions. It is well known that two effects, a pure thermodynamically one and a dynamical one, may contribute to such phase changes. Since both effects are naturally incorporated in the description of EIT, it is not surprising that one obtains a better agreement with experiments concerning the shift of the critical temperature or the spindle curve than with more classical approaches. In parallel with non-Fourier heat transport, non-Fickian mass diffusion finds a natural place in EIT. Non-standard diffusion is of practical importance mainly in polymer diffusion, like sorption or permeation of a solvent in a film. As shown in section, EIT is also well suited for the description of Taylor's diffusion which plays an important role in many practical applications.

In analogy with the classical theory, an absolute temperature θ and a generalized pressure π as partial derivatives of the entropy with respect to the internal energy and the volume, were defined respectively. These quantities contain non-equilibrium contribution.

1.8 Conclusion

The variety of subjects covered by the present review demonstrates that the domain of applications of EIT has been considerably enlarged during the last decade. EIT has been shown to be the specific corpus wherein a wide variety of problems find a natural accommodation. A more thorough treatment of these topics is a typical challenge of EIT at the level of applications.

To summarize, the motivations behind the formulation of EIT were the following:

- To go beyond the local equilibrium hypothesis
- To avoid the paradox of propagation of signals with an infinite velocity
- To generalize the Fourier, Fick, Stokes, and Newton laws by including:

- Memory effects (fast processes and polymers)
- Non-local effects (micro- and nano-devices)
- Non-linear effects (high powers)

The main innovations of the theory are:

- To raise the dissipative fluxes to the status of state variables
- To assign a central role to generalized entropy, assumed to be a given function of the whole set of variables, and whose rate of production is always positive definite

Extended irreversible thermodynamics provides a decisive step towards a general theory of non-equilibrium processes by proposing a unique formulation of seemingly such different systems as dilute and real gases, liquids, polymers, microelectronic devices, nano-systems, etc. EIT is particularly well suited to describe process characterized by situations where the product of relaxation time and the rate of variation of the fluxes is important, or when the mean free path multiplied by the gradient of the fluxes is high; these situations may be found when either the relaxation times or the mean free paths are long, or when the rates of change in time and space are high.

In summary, EIT offers new perspectives which must be carefully scrutinized, and henceforth enlarge the domain of applications of classical thermodynamics. The present time is rather exciting in relation with the development of EIT. The fundamental questions raised above are not

particular to EIT, but they are rather general and fundamental in non-equilibrium thermodynamics and statistical physics. Comparison between EIT and other approaches should be encouraged. It is also hoped that in the future more applications with industrial impact will be developed.

Acknowledgements:

This work has been supported by the discussions with many researchers Prof David Jou, Prof Ingo Muller, Prof Bhalekar and their research materials available on the website

https://www.researchgate.net/publication/258454098_Extended_Irreversible_Thermodynamics.

REFERENCES

1. Jou D., Casas-Vázquez J. and Lebon G. 2001. *Extended Irreversible Thermodynamics*, 3rd ed., Springer, Berlin Heidelberg New York, Muller I. and Ruggeri T., *Rational Extended Thermodynamics*, 2nd ed., Springer, Berlin Heidelberg New York, 1998.
2. Salamon P. and Sieniutycz S. (eds.), *Finite-Time Thermodynamics and Optimization*, Taylor and Francis, New York, 1991.
3. Eu B.C., *Kinetic Theory and Irreversible Thermodynamics*, Wiley, New York, 1992.
4. Eu B.C., *Nonequilibrium Statistical Mechanics: Ensemble Method*, Kluwer, Dordrecht, 1998.
5. Tzou D.Y., *Macro-to-Microscale Heat Transfer. The Lagging Behaviour*, Taylor and Francis, New York, 1997.
6. Wilmanski K., *Thermodynamics of Continua*, Springer, Berlin Heidelberg New York, 1998
7. D. Jou, J. Casas-Vázquez. and M. Criado-Sancho, "Thermodynamics of Fluids under Flow", Springer, Berlin, 2000.
8. L. S. Garcia Colin, "Selected Topics in Non-equilibrium Phenomena", *Monografias en Fisica I*, institute de Fisica, Brazil, 1984.
9. Rubi J.M., The non-equilibrium thermodynamics approach to the dynamics of mesoscopic systems, *J. Non-Equilib. Thermodyn.* 29 (2004) 315–325.

10. L. Onsager, *Phys Rev*, 37, 405, 1931.
11. L. Onsager and S. Machlup, *Phys. Rev.* 91, 1505-1512, 1953.
12. Cattaneo C., Sulla conduzione del calore, *Atti Seminario Mat. Fis. University Modena* 3 (1948) 83–101.
13. Joseph D.D. and Preziosi L., *Heat waves*, *Rev. Mod. Phys.* 61 (1989) 41–74; 62 (1990) 375–392.
14. Criado-Sancho M. and Llebot J.E., Behaviour of entropy in hyperbolic heat transport, *Phys. Rev. E* 47 (1993) 4104–4108.
15. Lebon G., Desai Th. and Dauby P.C., A unified extended thermodynamic description of diffusion, thermo-diffusion, suspensions, and porous media, *J. Appl. Mech*, 73 (2006a) 16–20.
16. Nettleton R.E. and Sobolev S.L., Applications of extended thermodynamics to chemical, rheological and transport processes: a special survey, *J. Non-Equilib. Thermodyn.* 20 (1995) 200–229, 297–331.
17. Lebon G. and Dauby P.C., Heat transport in dielectric crystals at low temperature: a variational formulation based on extended irreversible thermodynamics, *Phys. Rev. A* 42 (1990) 4710–4715.
18. Garcia-Colin L.S., Extended irreversible thermodynamics beyond the linear regime: a critical overview, *J. Non-Equilib. Thermodyn.* 16 (1991) 89–128.
19. Criado-Sancho M. and Llebot J.E., Behaviour of entropy in hyperbolic heat transport, *Phys. Rev. E* 47 (1993) 4104–4108.
20. Gyarmati I., *Non-equilibrium Thermodynamics*, Springer, Berlin Heidelberg New York, 1970.
21. L.S. Garcia Colin and R.M. Velasco *Phys. Rev. A* 16, 2187, 1982.
22. Luzzi R., Vasconcellos A.R. and Ramos J.G., *Statistical Foundations of Irreversible Thermodynamics*, Teubner, Leipzig, 2001.
23. Luzzi R., Vasconcellos A.R. and Ramos J.G., *Predictive Statistical Mechanics: A Non-equilibrium Ensemble Formalism*, Kluwer, Dordrecht, 2002.
24. Muschik W., Empirical foundation and axiomatic treatment of non-equilibrium temperature, *Arch. Rat. Mech. Anal.* 66 (1977) 379–401.
25. Muschik W., *Aspects of Non-Equilibrium Thermodynamics*, World Scientific, Singapore, 1990.
26. A. Bhalekar and L. S. Garcia Colin, *Pramana, J. Phys.*, 50(4), 281-294, 1998.
27. Evans D.J. and Morriss G.P., *Statistical Mechanics of Non-Equilibrium Liquids*, Academic, London, 1990.
28. Meixner J., The entropy problem in thermodynamics of processes, *Rheol. Acta* 12 (1973a) 272–283.
29. Meixner J., On the Foundations of Thermodynamics of Processes, in *A Critical Review of Thermodynamics* (Stuart E., Gal-Or B. and Brainard A., eds.), Mono Book Corp., Baltimore, 1973.
30. Muller I., On the frame dependence of stress and heat flux, *Arch. Rat. Mech. Anal.* 45 (1972) 241.
31. Keizer J., *Statistical Thermodynamics of Nonequilibrium Processes*, Springer, Berlin Heidelberg New York, 1987.
32. Hoover W., Moran B., More R. and Ladd A., Heat conduction in a rotating disk via non-equilibrium molecular dynamics, *Phys. Rev. A* 24 (1981) 2109–2115.
33. Grad H., Principles of the Kinetic Theory of Gases, in *Hd. der Physik*, vol. XII (Flugge S., ed.), Springer, Berlin Heidelberg New York, 1958.
34. Dedeurwaerdere T., Casas-Vázquez J., Jou D. and Lebon G., Foundations and applications of a mesoscopic thermodynamic theory of fast phenomena, *Phys. Rev. E* 53 (1996) 498–506.
35. Chapman S. and Cowling T.G., *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, Cambridge, 1970.
36. Braun D. and Libchaber A., *Phys. Rev. Lett.* 89 (2002) 188103.
37. Guyer R.A. and Krumhansl J.A., Solution of the linearized Boltzmann phonon equation, *Phys. Rev.* 148 (1966) 766–788.

38. S.R.de Groot and P.Mazur, "Non-equilibrium thermodynamics", Dover publications, New York, USA, 1984.
39. D. Kondepudi and I. Prigogine, "Modern Thermodynamics", John Wiley and Sons, New York, 1998.
40. Ichiyanagi M., Variational principles in irreversible processes, Phys. Rep. 243 (1994) 125–182.
41. Grmela M. and Lebon G., Hamiltonian extended thermodynamics, J. Phys. A: Math. Gen. 23 (1990) 3341–3351.
42. Grmela M. and Ottinger H.C., Dynamics and thermodynamics of complex fluids. I. Development of a generic formalism, Phys. Rev. E 56 (1997) 6620–6632.
43. Grmela M., Elafif A. and Lebon G., Isothermal non-standard diffusion in a twocomponent fluid mixture: a Hamiltonian approach, J. Non-Equilib. Thermodyn. 23 (1998) 312–327.
44. Van der Geer, J., Hanraads, J. A. J., & Lupton, R. A. (2000). The art of writing a scientific article. *Journal of Science Communication*, 163, 51–59.
45. Strunk, W., Jr., & White, E. B. (1979). *The elements of style* (3rd ed.). New York: MacMillan.
46. Mettam, G. R., & Adams, L. B. (1999). How to prepare an electronic version of your article. In B. S. Jones & R. Z. Smith (Eds.), *Introduction to the electronic age* (pp. 281–304). New York: E-Publishing Inc.
47. Fachinger, J., den Exter, M., Grambow, B., Holgerson, S., Landesmann, C., Titov, M., et al. (2004). Behavior of spent HTR fuel elements in aquatic phases of repository host rock formations, 2nd International Topical Meeting on High Temperature Reactor Technology. Beijing, China, paper #B08.
48. Fachinger, J. (2006). Behavior of HTR fuel elements in aquatic phases of repository host rock formations. *Nuclear Engineering & Design*, 236, 54.