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Extended non-equilibrium thermodynamics, scope and limitations

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Abstract. In the past twenty years a number of efforts have been undertaken to broaden the scope of linear irreversible thermodynamics (LIT). These efforts have stemed from the fact that there are a number of phenomena ocurring in non-equilibrium states lying clearly beyond the linear regime. Here we present a review of one of such efforts whose underlying conceptualization is based more on physical ideas closely connected with LIT. The framework of ideas behind this method as well as both its comparison with experiment and its derivation from mesoscopic and microscopic physics is exhaustively dealt with. Unsolved problems and an outlook are offered at the end of the paper.

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1. Introduction

The study of time dependent thermal phenomena ocurring in several types of macroscopic systems dates back to the mid ninteenth century with the discovery of the thermoelectric effects known as the Peltier heat conduction and the Seebeck effect. The first theoretical explanation was provided in 1854 by W. Thomson (later Lord Kelvin) on the grounds of the still not well developed science of thermodynamics. By the end of the century a large number of what we now clasify as irreversible processes, were well known but no formal theory, neither macroscopic nor microscopic had been developed to cope with them. We shall not dwell here at all in the historic aspects of non-equilibrium processes but refer the reader to the appropriate sources in the literature [1, 3].

The first, and so far unique macroscopic theory that has been set forth to extend the concepts of equilibrium thermodynamics (thermostatics) to non-equilibrium

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states is hardly sixty years old. Based on the ideas introduced by de Donder [4] around the early twenties and Onsager's reciprocity theorem proved in 1931 [5], Prigogine, Meixner and Casimir in the mid forties developed what is now known as linear non-equilibrium thermodynamics [2, 6]. In 1953 Onsager and Machlup [7] reformulated the original version of Onsager's proposal, mainly dealing with the decay of spontaneous fluctuations around an equilibrium state. This theory, although having several things in common with the Prigogine-Casimir-Meixner version should really be taken as an independen treatment of non-equilibrium processes. We shall come back to this point later.

Thus, linear irreversible or non-equilibrium thermodynamics (LIT) is a well established theory. Based on four postulates, it has been able to describe a wealth of phenomena in complete agreement with experiment [8, 9]. These phenomena encompass many fields in science, from physics and physical chemistry, to biochemistry, biophysics and many branches of engineering. In the past ten years we have also learned that LIT has severe limitations [10, 11]. A large number of phenomena ocurring under well defined conditions, or others by their own intrinsic nature, do not comply with one or several of the basic postulates of LIT. One is therefore posed with the challenge of either trying to derive a theory from first principles which is capable of explaining them, or constructing a phenomenological framework extending the scope of LIT in order to provide an adequate description for them. Efforts in both directions have been made in various ways giving rise to what may now be termed extended irreversible (non-equilibrium) thermodynamics (EIT). This implies that up to now there is no unique theory coping with these systems. But the non-negligible amount of situations that have been adequately handled by one of these efforts as well as the fact that it has been also rooted in more mesoscopic and even microscopic concepts justify a systematic presentation including its scope and limitations. This is precisely the reason for the title and for the paper itself. In the past seven years a small group of people has developed a method to handle systems whose states lie beyond the reach of LIT [12, 13]. In this paper, I would like to summarize in a systematic way the underlying ideas behind such method, the nature of the results drawn from its connection with the basic principles of statistical mechanics and which are, at present, its limitations. Technical details will be avoided but an extensive literature will be cited where the reader may find all the pertinent information.

To keep the paper self contained, section 2 is devoted to a brief summary of LIT. In section 3 some of the many systems which are beyond the scope of LIT are discussed, thus serving as a justsification for a broader thermodynamic framework. In section 4 we discuss the main ideas behind EIT; in section 5 we ennumerate the most relevant accomplishments of the theory; in section 6 we discuss how its basic equations are related to fundamental microscopic laws of physics and finally, in section 7 the present limitations will be mentioned which will serve as an outlook for the future.

2. Linear non-equilibrium thermodynamics

Linear irreversible or non-equilibrium thermodynamics (LIT) is based on four fundamental assumptions which will be briefly sketched here for the sake of convenience. For a broader treatment of the subject we urge the reader to consult the references listed at the end of this paper [2, 6, 8, 9].

The first assumption known as the local equilibrium assumption starts from the basic idea that the states of the system may be described by locally conserved densities such as mass, charge, momentum, energy, etc. Furthermore, it establishes that a local entropy density exists which depends on the position and time only through a funtional relationship with these densities. In the case of a simple fluid this relation is expressed as

$$s(\mathbf{r},t) = s[e(\mathbf{r},t), \rho(\mathbf{r},t)], \tag{1}$$

where $\rho(\mathbf{r},t)$ and $e(\mathbf{r},t)$ are the local mass and energy densities, respectively. It may also depend on the concentrations of the different components which form the various phases in an open system. Notice that equation (1) is formally identical to the thermostatic result expressing the entropy S as a function of E, the energy, and V, the volume. If one uses equation (1) to compute ds/dt and restores to the conservation equations which are satisfied by the locally conserved densities, one arrives at the well known equation, [2, 6, 9]

$$\rho\frac{ds}{dt} + \nabla\cdot\mathbf{J}_s = \sigma, \tag{2}$$

where $\mathbf{J}_s = \mathbf{J}_q/T$, $\mathbf{J}_q$ being the heat flux vector in the case of closed systems $d/dt = \partial/\partial t + \mathbf{u}\cdot\nabla$, where $\mathbf{u}(\mathbf{r},t)$ is the hydrodynamic velocity and σ a quantity known as the entropy production defined as:

$$\sigma = -\frac{\mathbf{J}_q}{T^2}\cdot\nabla T - \frac{\mathring{\boldsymbol{\mathcal{T}}}}{T} : (\mathring{\nabla}\mathbf{u})^s - \frac{\mathcal{T}}{T}\nabla\cdot\mathbf{u}. \tag{3}$$

Here, the momentum flux or stress tensor $\boldsymbol{\mathcal{T}}$ has been decomposed into its non-viscous part, $p(\mathbf{r},t)$ the local hydrostatic pressure and a viscous part whose traceless part is $\mathring{\boldsymbol{\mathcal{T}}}$ and $\mathcal{T}$ its trace. Also $(\mathring{\boldsymbol{\mathcal{A}}})^s$ denotes the symmetric traceless part of any arbitrary tensor $\mathcal{A}$.

The second assumption of LIT is that

$$\sigma \geq 0 \tag{4}$$

which as it is shown in the literature [2, 9] may be regarded as the extension of the second law of thermodynamics to non-equilibrium phenomena. It is worthwhile stressing that equations (2) and (3), which are not unique as far as the several ways that $\mathbf{J}_s$ and σ may be expressed, although preserving always the structure of equation (2), are in any case a direct consequence of the conservation equations and the validity of the local equilibrium assumption.

The third assumption of LIT is related to the fact that the conservation equations, five in total for a simple fluid, contain fourteen unknowns. To supply the necessary additional information one restores to experiment to find a way of relating the unknown quantities, the heat flux $\mathbf{J}_q$ and the momentum flux $\boldsymbol{\mathcal{T}}$ to the state variables $\rho, \mathbf{u}$ and T, the local temperature. The outcome of this search is that within a certain range of the thermodynamic forces, given by the gradients of the state variables, this relationship is a linear one. LIT thus adopts this fact as a postulate requiring that if g is a column vector whose components are the fluxes and $\mathcal{F}$ another one defined by the forces.

$$g = \mathbf{A}\mathcal{F}, \tag{5}$$

where $\mathbf{A}$ is a matrix whose elements do not depend on $\mathcal{F}$ but only on the equilibrium state variables of the system. For a simple fluid,

$$\begin{pmatrix} \mathbf{J}_q \\ \mathring{\boldsymbol{\mathcal{T}}} \\ \mathcal{T} \end{pmatrix} = \begin{pmatrix} \kappa & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \xi \end{pmatrix} \begin{pmatrix} \boldsymbol{\nabla} T^{-1} \\ -T^{-1}(\mathring{\boldsymbol{\nabla}}\mathbf{u})^s \\ -T^{-1}\boldsymbol{\nabla}\cdot\mathbf{u} \end{pmatrix}, \tag{6}$$

where κ, η and ξ are the thermal conductivity, the shear viscosity and the bulk viscosity of the fluid respectively, and are functions of the equilibrium density and temperature only.

If one substitutes equation (6) into equation (3) a quadratic form for σ is obtained,

$$\sigma = \kappa\Big(\frac{\boldsymbol{\nabla} T}{T}\Big)^2 + \eta\Big(\frac{\mathring{\boldsymbol{\nabla}}\mathbf{u}^s}{T}\Big)^2 + \xi\Big(\frac{\boldsymbol{\nabla}\cdot\mathbf{u}}{T}\Big)^2 \tag{7}$$

which according to equation (4) can hold true only and only if $\kappa > 0$, $\eta > 0$ and $\xi > 0$, a set of results well confirmed by experiment.

In more complicated systems where $\mathbf{A}$ has non-zero off diagonal elements, it is assumed that $\mathbf{A} = \mathbf{A}^{\top}$, its transposed, meaning that the matrix is symmetric. The proof of this statement from the microscopic equations of motion was Onsager's great achievement now known as the reciprocity principle [2]. Introducing this requirement into the framework of LIT leads to a complete set of partial differential equations, usually non-linear, whose solution depends on the information available for the initial state and the boundary conditions.

At present, it has been possible to determine experimentally [8, 9] the conditions under which this linear formalism describes non equilibrium phenomena in a wide variety of systems. But on the other hand, we are also aware of many non-equilibrium states for which this theory is uncapable of providing a satisfactory account of phenomena ocurring among them. They will be qualitatively described in the next section.

3. Non-equilibrium states beyond LIT

One of the first objections that was raised against LIT is that some of the differential equations describing the time evolution of the disturbances propagating in a medium predict their propagation with an infinite velocity. Such is the case of the heat conduction equation in a rigid heat conductor ($\rho =$ const., $\mathbf{u}(\mathbf{r},t) = 0$, $\boldsymbol{\mathcal{T}} = 0$) for which the energy conservation reads as

$$\rho\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{J}_q = 0. \tag{8}$$

Using the local equilibrium assumption to set $\partial e/\partial t = C_v \partial\rho/\partial t$ and the linear law [Eq. (6)] so that $\mathbf{J}_q = -\kappa\boldsymbol{\nabla}T$, one readily arrives at the heat conduction equation, namely

$$\frac{\partial T}{\partial t} = D\nabla^2 T, \tag{9}$$

where D is the thermal diffusivity defined as $D = \kappa/\rho C_v$. Clearly the absence of a term $c^{-2}\partial^2 T/\partial t^2$ in this last equation can be accounted for only if $c = \infty$. In order to overcome this difficulty Vernotte [14] and Cattaneo [15] independently, proposed to substitute Fourier's equation by a relaxation equation for $\mathbf{J}_q$ namely,

$$-\mathcal{T}_q\frac{\partial \mathbf{J}_q}{\partial t} = \mathbf{J}_q + \kappa\boldsymbol{\nabla}T, \tag{10}$$

where $\mathcal{T}_q$ is a relaxation time assumed to be finite. When equation (10) is substituted into equation (8) one obtains that

$$\mathcal{T}_q\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = D\nabla^2 T, \tag{11}$$

where $c^{-2} = \mathcal{T}_q$ so that the temperature disturbance propagates with the certainly large but not infinite velocity $\mathcal{T}_q^{-1/2}$. Equation (11) belongs to a class of equations that were known since the mid term of the last century. In fact, it was Kohlrausch [16] who first arrived at an equation of that type when examining the behaviour of glass fibres and later, in 1867 Maxwell [17] argued that in a viscous body the state of stress will tend to disappear at a rate which depends on the value of the state of stress and the nature of the body. Thus the class of equations of the type (10) which assign a finite relaxation time to the rate of disappearance of a flux are now referred to as Maxwell-Cattaneo-Vernotte equations. They served as a basic idea in the formulation of one version of extended thermodynamics known as the wave approach [18].

Besides this objection, it is known that there are many other systems which can be driven into non-equilibrium states whose description lies beyond the scope of LIT. Perhaps the oldest example of this fact was pointed out by Osborne Reynolds in 1885 [19, 20] when he filled a leather bag with marbles toped it with water and then twisted it, thereby inducing a shear. The water level drops because the close packing of the marbles is disrupted as layers of them slide past each other, as a result the marbles are further apart on the average creating spaces that the water has to fill. This of course implies that the marble density N/V decreases when the system is subject to shear at constant pressure and temperature. Therefore the local equilibrium assumption is violated since the density is no longer a function of the pressure and temperature, it depends also on the rate of shear (twisting). The fact that $\rho(T,p;\gamma) < \rho(T,p;0)$ where γ is the shearing rate is called shear dilation. A similar phenomena pointed out by D. Burnett in 1934 whereby the viscosity of fluids decreases with γ is known as shear thinning. Other examples of systems that appear to be in contradiction with this one or another of the basic postulates of LIT will be discussed briefly.

Consider first the case of sound absorption and dispersion by monoatomic fluids [21–27]. The dispersion relation computed from the linearized version of the Navier-Stokes-Fourier equations of hydrodynamics is in agreement with experimental data only in the region of low frequencies. Although the discrepancy is partially improved by including in the calculation the corrections that come from the linear terms which are of higher order in the gradients, the so called linear Burnett and super Burnett terms [28], there is a complete disagreement between theory and experiment at high frequencies [13, 21]. Care should be taken in assessing these results since the non linear terms inherent in both the Navier-Stokes and Burnett regimes have never been included in the analysis. Nevertheless, since they represent corrections of higher order in the wave number $\kappa \sim \lambda^{-1}$ it is doubtful that they represent a potential improvement of the theory.

The formation of shock wave structures in matter has been extensively studied both theoretically and experimentally [30, 28]. For the case of weak shocks the Mach number $M = u/v_0$, v_0 being the velocity of the medium before the shock wave and u the velocity of the shock wave, is of the order of one, so that one can attempt a solution of the linearized equations of hydrodynamics to get the values of relevant quantities such as the density profile, and the thickness of the wave, in powers of $(M-1)$ [29]. Comparison of this type of calculations with the rather precise set of measurements performed by Alsmeyer in 1975 [30], clearly shows that beyond Mach numbers of the order of 1.75 neither the Navier-Stokes equations nor the corrections due to Burnett terms agree with experiment [31].

A much more drastic failure of LIT is observed in viscoelastic media and polymeric fluids [10]. For these systems, the ordinary linear constitutive laws of the Navier-Newton-Fourier hydrodynamics as written in equation (6) are uncapable of describing the flow of liquids containing polymers. Here, one is dealing of course with fluids composed of very large molecules, macro-molecules whose typical molecular weights range from 10^5 to 10^9. A similar comment is valid for viscoelastic fluids or materials such as rubber. A rather elaborated treatment of the flow of polymeric fluids has been developed in the past ten years [32–34] both from the phenomenological and the kinetic point of view as well. The ensuing hydrodynamic equations fail to belong to LIT scheme.

The subject now known as generalized hydrodynamics, understood as the effort to extend ordinary linear hydrodynamics which is valid in the low frequency, long wave length limit, to include higher frequencies and smaller wave lengths [10, 35] is also known to be at odds with LIT. In fact, the shape of the dynamic structure factor for simple liquids such as Ne and Ar obtained with neutron scattering techniques cannot be accounted for in such high frequency small wave length regime using the Navier-Newton-Fourier equations of hydrodynamics [35, 36]. The structure shown by the Rayleigh peak under these conditions can be accounted for by arbitrarily proposing that the transport coefficients appearing in these equations become both frequency and wave length dependent. From the thermodynamic point of view this is in contraposition with the local equilibrium assumption.

The last and also the oldest example I want to quote in this paper to exemplify the need to extend LIT, is provided by chemical kinetics. The introduction of the degree of advancement variable in a homogeneous chemical reaction as a "displacement" variable and the chemical affinity as the thermodynamic force necessarily requires of an extension of the thermodynamic space of state variables, even in the context of thermostatics [37]. And furthermore it has been known for many years that the mass action law as formulated by C.M. Guldberg and P. Waage over one hundred and twenty years ago [38–40] which holds true for elementary reactions ocurring in gaseous phase or ideal solutions lies beyond the scope of LIT [41–42]. Understood as a constitutive equation relating the chemical flux with the affinity (force), it is a highly non linear equation whose macroscopic status is beginning to manifest itself in a more transparent way [42–44]. The failure of LIT to account for all of these phenomena and other such as supercooled liquids [45–47], the glass transition [46–49], fluids driven far away from equilibrium into steady states [50–53] and so on, raises the obvious question as to how can one extend such a formalism with the hope of incorporating into it some, or all if possible, of these phenomena. This is the main subject to be dealt within the following sections.

4. Extended irreversible thermodynamics

Starting from the assumption that any reader is convinced by now that there exists a legitimate task of enlargening the scope of LIT to include the wide variety of phenomena sketched in the previous section, we now devote ourselves to the discussion of one possible way of doing so. A word of caution is required since extended irreversible thermodynamics (EIT) is far from implying a unique framework to undertake such a program. There exist in the literature under the same or a similar heading, a wide variety of proposals which claim extensions of conventional thermodynamics in one or other direction [12, 18, 53, 92]. The one to be presented here originated in some ideas set forth by Meixner around twenty years ago and that were more or less put into the form of a theory by I. Mueller in 1967 [54]. Later on Lebon [12] in Belgium and Casas-Vázquez, Jou, Rubí [12, 55, 56, 57, 58] and others in Spain shaped them into a more thermodynamic-like context and attempted to relate them with kinetic theory. Mention should be made that from an entirely different point of view and without pinning any name to the results, H. Grad had actually derived this version of EIT from kinetic theory already in 1949 [59, 60]. But his work had another objectives and its content, in this context, passed completely unnoticed. The present version of the theory has been developed in Mexico by the author of this paper and a small group of collaborators. It has many features in common to the views of the originators but its physical conceptualization is somewhat different. I will avoid a critical comparison of the different versions of the theory as well as its comparison with others because of space reasons. The interested reader may find these aspects dealt at length in many different sources [13, 61, 62].

For strictly pedagogical reasons the discussion of the underlying principles behind this theory will be set forth using as a prototype system a rigid infinite conductor which being at rest, has a zero velocity $\mathbf{u}(\mathbf{r}, t) = 0$ and a constant density $\rho(\mathbf{r}, t) = \text{const}$. Therefore, it requires only of the energy density $e(\mathbf{r}, t)$ as the single conserved variable necessary to describe its thermodynamic states, according to LIT. The transcription of the results here obtained to her complicated systems such as fluids [63–64] binary mixtures [65–66], porous media [67], suspensions [70], dielectric relaxation in complex materials [68–69], chemical reactions [41, 44, 71] and others [72–73a] have been dealt with in detail and as the reader may easily convince himself it is more a question of semantics and laborious algebra and not of the basic physics involved in the process.

According to our previous discussions the main stumbling block in LIT hampering its extension to a wider class of phenomena lies in the local equilibrium assumption. This assumption states that only the locally conserved densities which are even under time reflections are required to appear as independent variables in the local entoropy which is further assumed to be a time and space independent functional of these variables. Therefore, what we are seeking for is to enlarge this space in a way which is at least asymptotically consistent with this condition. As H. Grad pointed out in 1949, the best candidates to be raised to the status of independent variables in the case of fluids are the fluxes themselves, $\mathbf{J}_q, \mathring{\boldsymbol{\mathcal{T}}}$, and $\mathcal{T}$, where we follow the notation used in earlier sections. And this is precisely the content of Mueller's assumption, to postulate the existence of a "generalized entropy function" which will depend not only on the locally conserved densities but also on a set of fast or non-conserved quantities which he chose to be the fluxes. In the case or our rigid conductor the only flux is $\mathbf{J}_q$, the heat flux, so that we would have that

$$\eta = \eta(e, \mathbf{J}_q), \tag{12}$$

where η is by assumption, a continuous and at least twice differentiable function. But we shall altogether avoid referring to it as an entropy or any other similar names. Then,

$$d\eta = \left(\frac{\partial \eta}{\partial e}\right)_{\mathbf{J}_q} de + \left(\frac{\partial \eta}{\partial \mathbf{J}_q}\right)_e d\mathbf{J}_q. \tag{13}$$

Here, the two differential coefficients appearing in equation (13), a scalar and a vector respectively, can be functions of all the scalar invariants and vectors which may be defined in the space of state variables [123]. These are e, J_q^2, J_q^4, eJ_q^2, …, etc. and the vector $\mathbf{J}_q$.

Therefore,

$$\left(\frac{\partial \eta}{\partial e}\right)_{\mathbf{J}_q} = f(e, J_q^2, \ldots); \qquad \left(\frac{\partial \eta}{\partial \mathbf{J}_q}\right)_e = g(e, J_q^2, \ldots)\mathbf{J}_q.$$

If we manipulate equation (13) with the full information contained in these coefficients we immediately arrive at higly non-linear equations whose full significance is still obscure. We therefore introduce the approximation consisting in expanding functions, such as f and g above, in power series of the non-conserved variables around the local equilibrium state. Keeping the lowest order (first term) in these expansions and remembering that $(\partial\eta/\partial e)_{\text{loc.eq.}} = (\partial s/\partial e) = T^{-1}$, where T is the local equilibrium temperature, the first equality following from the fact that for local equilibrium $\mathbf{J}_q = 0$ and η reduces to the local entropy s, we may rewrite equation (13) after dividing by dt as,

$$\frac{d\eta}{dt} = \frac{1}{T}\frac{de}{dt} + g(e)\mathbf{J}_q \cdot \frac{d\mathbf{J}_q}{dt} \tag{14}$$

which is clearly the first order generalization of the Gibbs equation in LIT [2, 6, 9]. Here $g(e)$ is of course an undetermined function of the local energy density $e(\mathbf{r}, t)$

The objective of any thermodynamic theory is to provide for a complete set of equations for the variables describing the states of the system. In this simple example this means we are required to determine the time evolution equations for $e(\mathbf{r}, t)$ and $\mathbf{J}_q(\mathbf{r}, t)$.

But the former one is known, it is the balance equation for the energy density, namely

$$\rho\frac{de}{dt}+\boldsymbol{\nabla}\cdot\mathbf{J}_q=0. \tag{15}$$

The question is how to obtain the time evolution equation for $\mathbf{J}_q$. For this purpose we introduce the second assumption of this theory, namely, that η satisfies a balance type equation, necessarily of the form

$$\rho\frac{d\eta}{dt}+\boldsymbol{\nabla}\cdot\mathbf{J}_\eta=\sigma_\eta, \tag{16}$$

where $\mathbf{J}_\eta$ is a vector and σ_η a scalar both defined in the space of state variables. Following the steps leading to equation (14) this clearly implies that

$$\mathbf{J}_\eta=\beta(e,J_q^2,\ldots)\mathbf{J}_q\simeq\beta(e)\mathbf{J}_q, \tag{17}$$

where $\beta(e)$ depends only on $e(\mathbf{r},t)$. On the other hand σ_η is the most general scalar that may be constructed in the space of state variables therefore implying that the operations indicated in the left hand side of (16) must lead to quantities necessarily defined in such a space. Thus equation (16) may be interpreted as a closure assumption whose full potentiality has been discussed and exploited in more complex systems [72, 73]. Mathematically, this means that

$$\sigma_\eta=\mathbf{X}_q\cdot\mathbf{J}_q=\mu(e,J_q^2,\ldots)\mathbf{J}_q\cdot\mathbf{J}_q\simeq\mu(e)\mathbf{J}_q\cdot\mathbf{J}_q. \tag{18}$$

But we have another independent way of computing σ_η using equation (14) and the divergence of $\mathbf{J}_\eta$ computed from equation (17). When we compare the two terms for σ_η we come to the result that

$$\begin{aligned}\rho g(e)\mathbf{J}_q\cdot\frac{d\mathbf{J}_q}{dt}-\frac{1}{T}\boldsymbol{\nabla}\cdot\mathbf{J}_q+\beta(e)\boldsymbol{\nabla}\cdot\mathbf{J}_q&\\+\mathbf{J}_q\cdot\boldsymbol{\nabla}\beta(e)=\mu(e)\mathbf{J}_q\cdot\mathbf{J}_q.&\end{aligned} \tag{19}$$

Now we impose the obvious restriction that when the subspace spanned by the fast variables is the void space, equation (16) must reduce to equation (2), the true entropy balance of LIT with σ given by equation (3). This immediately imposes the requirement that $\beta(e)=1/T$ and equation (19) reduces to

$$\frac{\rho g(e)}{\mu(e)}\frac{d\mathbf{J}_q}{dt}=-\frac{1}{\mu(e)}\boldsymbol{\nabla}T^{-1}+\mathbf{J}_q. \tag{20}$$

Furthermore, if the left hand side of (20) is such that it is very small compared with the terms in the r.h.s., what may be called the stationary value of $\mathbf{J}_q$ is reached, then

$$\mathbf{J}_q = -\frac{1}{\mu(e)T^2}\boldsymbol{\nabla}T,$$

which is precisely Fourier's equation if $\mu(e) = (\kappa T^2)^{-1}$. Calling now $-\mathcal{T}_q = \rho g(e)\kappa T^2$ the relaxation time for the heat flux $\mathbf{J}_q$ we get that

$$-\mathcal{T}_q\frac{d\mathbf{J}_q}{dt} = \kappa\boldsymbol{\nabla}T + \mathbf{J}_q. \tag{10}$$

This is precisely equation (10), the equation proposed by Vernotte and Cattaneo to remove the inconvenient infinite velocity that arises from the LIT formalism. But some other rather pertinent comments are somewhat useful. The first one is addressed to the nature of equation (10), in the sense that it is by no means representative of the generality behind the postulates of EIT. It actually stands for a first approximation of the theory arising from the fact that we have kept only the first term in the power series expansions in terms of the fast variables of the coefficients appearing in equations (13), (17) and (18). When this restriction is partially removed, one is lead to much broader results [74, 75], including the possibility of obtaining non-linear time evolution equations whose full physical meaning is still unclear. A second comment is concerned with the possibility of deriving the ordinary constitutive equation required for instance in hydrodynamics. When the relaxation equations for the fast variables are projected onto the subspace spanned by the locally conserved quantities by formally setting the relaxation times such as $\mathcal{T}_q$ equal to zero then, as seen above, one recovers Fourier's equation for heat conduction and so on. In the general case of a simple fluid the Burnett and higher order equations of hydrodynamics may be derived [27, 63, 76], and similar situations are found in viscoelastic media [73], dielectric solids [69] and so on. From this point of view, the enlargening of the space of state variable by including fast variables may very well serve as a basis to search for a more concrete definition of the up to now somewhat fantasmagoric concept of "far away from equilibrium". The third pertinent comment deals with the nature of the phenomenological coefficients μ, g, etc. which appear in the theory. One must keep in mind that they are quantities which are still space and time dependent through the locally conserved densities. In many applications, in order to simplify the solution of the resulting differential equations, they are taken as constants but this is an additional approximation. And moreover in equations such as equation (10), $\mathbf{J}_q$ may be determined from the microscopic information contained in the time space correlation functions of the fluctuations in the fast variables, the heat flux in the case just mentioned [77–81]. Also one is able to show that $g(e) < 0$ as equation (10) demands. This provides a contact between the macroscopic theory and microscopic dynamics. We will come back to this question later on.

Summarizing the results of this section, we may conclude by stating that the EIT in the version here offered, represents an improvement on LIT in that it permits us to include in the formalism information capable in principle to cope with phenomena beyond the scope of LIT. This statement will be clarified further in the following section dealing with applications.

5. Applications of EIT

Although many of the applications of EIT have dwelt with the questions mentioned in section 3 of this paper that lead to the formulation of the theory, not all of them have been studied so far, like shock waves, whereas many others have. Therefore, to keep track of facts, the applications mentioned here are taken in a more or less chronological order, and furthermore the list is to be understood as being indicative and not as an exhaustive one. For the more complete aspects of the theory as well as other views of extensions of thermodynamics, we refer the reader to some review articles that have appeared recently [12, 13, 53, 75].

The first two problems on which in the author's opinion, EIT has played a decisive role are in chemical kinetics and in generalized hydrodynamics. As it was briefly mentioned in section 3 the mass action law which governs the kinetics of elementary chemical reactions ocurring either in gaseous phase or in ideal solutions had not find its place in a thermodynamic theory until EIT was formulated. When written in a conveniente way [2–9] it clearly points out that the relationship between the chemical driving force, de Donder's affinity and the chemical flux (reaction velocity) is far from being a linear one, emphasizing that chemical reactions are highly non-linear processes. Only when the affinity is small compared with the thermal energy (RT) the linear relationship between the force and the flux holds as demanded by LIT. And this may be verified when we are close to equilibrium [44]. By raising the chemical flux to the status of an independent variable it was recently shown [41, 42] that, firstly the generalized mass action law which states that there is a general relationship among the affinity, the temperature and the concentrations of reactants and products, may be obtained without restoring to any specific model for the participant species. Furthermore, if one introduces an additional assumption of a mechanistic nature which in essence optimizes the nature of the reactive collisions, Guldberg and Waage's law is completely recovered. And moreover, if the diffusive fluxes and the heat flux are included as fast variables several rather interesting properties about the influence of these quantities in the reaction kinetics, are obtained. A preliminary report on this question was published four years ago [43] and further work is in progess. In short, EIT is the natural framework for the chemical processes empirically described by the mass action law.

In the case of generalized hydrodynamics [35], nicely surveyed three years ago by Alder and Alley [10, 82], the idea is to extend the linearized version of the Navier-

Stokes-Fourier version of ordinary hydrodynamics to include effects that occur as we go into the short wave length high frequency regime [35].

This effect is clearly seen in the computer simulations of the transverse components of the velocity autocorrelation function, the longitudinal velocity autocorrelation function and the dynamic structure factor of a fluid which may be obtained by neutron scattering experiments. When these quantities are calculated from first principles [35, 83–84], one finds that they obey a linear integral equation which in general is both non local in space and time. The kernel appearing in such equations, referred to as the "memory function"is therefore an expression for the corresponding generalized transport coefficient. This quantity still contains the information relevant to the N-body dynamics so that its explicit calculation has never been accomplished in a rigorous way. In order to compare the theoretical results either with computer simulations or with experiments, people have restored to *ad hoc* models for such functions, being the exponential and the gaussian functions the most popular ones [35, 36]. The success of EIT in this field is that it allows for a systematic way of actually deriving the memory functions from the full set of equations describing the dynamics of the state variables. Clearly the results so obtained will contain undetermined coefficients, like in all macroscopic formalisms, which are to be extracted from experiment. Nevertheless forms of such memory functions which many years ago were adopted *ad hoc* to describe the experimental results have been derived for the transverse and longitudinal velocity correlation function [85, 86], for the diffusion in an inert binary mixture [65], for viscoelastic fluids [73] for the structure factor of fluids with internal degrees of freedom [87–88] dielectric relaxation in complex materials [89] and so on.

There are a number of other interesting situations to which EIT has been applied with encouraging results such as the theory of fluctuations [71, 77–81], the constitutive equations of non-Newtonian fluids [73, 73a, 76], thermoelectric phenomena [89] the flow of fluids in porous media [67] suspensions of neutral brownian particles [70] resonance phenomena in solids [90] and the properties of fluids driven onto far from equilibrium stationary states by external gradients [50–53]. There is no space here to even superficially cover each one of these topics so that we refer the interested reader to the original sources.

6. Microscopic basis for EIT

One of the stumbling blocks that has hampered the study of non-equilibrium processes either micro or macroscopically is that contrary to what occurs in equilibrium where the concept of equilibrium state is unique, a great deal of laxitude exists as to how to characterize a non equilibrium state. Except for the case of the local equilibrium state concept basic to LIT, a theory which is well rooted from the microscopic point of view, we know very little as to how to go about in defining a non-equilibrium state and even less as to how to provide for a macroscopic basis for the phenomenological equations expected to describe its behaviour. EIT is not an exception to this situation. There are many conceivable ways of extending the local equilibrium state by adding extra variables [60, 91, 92].

In mostly all the work that we have referred to here, the fluxes have been raised to the status of independent variables and the reason for it comes from the work of H. Grad in 1949 [59]. The revival of his ideas to illustsrate that his work contains the essence of an extended thermodynamics were published four years ago [93], so we shall limit ourselves here to a brief discussion of them.

In his study of the possibility of finding general solutions to the full non linear Boltzmann equation, Grad designed the method now referred to as the moment method for solving that equation. The method is based essentially in expanding the single particle distribution function in terms of a complete set of orthonormal functions namely, n-dimensional Hermite tensor polynomials, around a local or a true equilibrium state. The coefficients in this expansion are taken to depend both on space coordinates and time. They therefore play the role of local macroscopic variables and include the conserved densities: number density, momentum and energy. Their time evolution is given through an infinite set of coupled differential equations whose solution requires some arbitrary way of truncating the system. This truncation happens to be direct for the case of Maxwellian molecules and it is such that if one keeps the first thirteen moments of the distribution function as independent variables, one raises the heat flux and the symmetric traceless part of the stress tensor to independent variables. This truncation is entirely arbitrary and, in principle, one may keep as many terms as desired. Furthermore the local equilibrium assumption is not involved nor the Boltzmann equation a priori linearized as it occurs in the Chapman-Enskog method for its solution [97]. Therefore, the broadening of the space of state variables is a consequence of the method itself.

One faces still two questions, the existence of an H-theorem which justifies the identification of the η function of EIT with an entropy, and the possibility of constructing an entropy balance equation. We recall the reader that the H function for the Boltzmann equation satisfying the well known inequality $dH/dt \leq 0$ is a global, general property of Boltzmann equation requiring only the existence of a solution for some arbitrary initial conditions and the convergence of some integrals in phase space. But the H function is proportional to the thermodynamic entropy S only and only if the distribution function is taken to be a Maxwellian, local or equilibrium [60, 94–97]. Therefore if we substitute into the definition of H an arbitrarilly truncated form of the exact solution of the Boltzmann equation we should not expect to have the H theorem satisfied nor the resulting form for H identifyable with a thermodynamic entropy. When the calculations are performed with the thirteen moment form for the solution one finds that [93]

$$T\,d\eta = T\,ds - \frac{1}{pRT^2}\mathring{\boldsymbol{T}} : d\mathring{\boldsymbol{T}} - \frac{4}{5}\frac{1}{(\rho RT)^2}\mathbf{J}_q \cdot d\mathbf{J}_q, \tag{21}$$

where $T\,ds$ stands for the local equilibrium entropy density of an ideal gas. This is precisely of the form of equation (13) had we included there $\mathring{\mathcal{T}}$ in the space of state variables. Notice however that in equation (21) the coefficients of the differentials of the fast variables are given as functions of the local equilibrium variables p, the pressure, ρ the density and T the temperature.

One can also show that the η-balance equation is satisfied and that

$$\mathbf{J}_\eta = \frac{\mathbf{J}_q}{T} - \frac{4}{5}\frac{1}{pRT}\mathbf{J}_q \cdot \mathring{\mathcal{T}} \tag{22}$$

which corroborates the form for $\mathbf{J}_\eta$ given in equation (17) in the case of a rigid conductor; and that

$$\sigma_\eta = \mu_{10}\mathbf{J}_q \cdot \mathbf{J}_q + \mu_{01}\mathring{\mathcal{T}} : \mathring{\mathcal{T}}, \tag{23}$$

where the coefficients μ_{10} and μ_{01} are given in terms of complicated collision integrals that we shall not write down here. Also, the general proof that $\sigma_\eta \geq 0$ is not available, but this is a property not required by EIT although some of the adepts to this theory do insist in including this condition [58, 98].

It remains only to discuss the equations of motion for the state variables, in particular those associated to the heat flux $\mathbf{J}_q$ and the stress tensor $\mathring{\mathcal{T}}$. Their full form is too complicated to be reproduced here [60] but in the simplest approximation they are of the form of the Maxwell-Cattaneo-Vernotte equation as exemplified by equation (10) although they provide explicit expressiones for the corresponding relaxation times $\mathcal{T}_q$ and $\mathcal{T}_\tau$. Indeed, one finds that [60, 93]

$$\mathcal{T}_q = (\beta\rho)^{-1}, \qquad \mathcal{T}_\tau = \left(\frac{2}{3}\beta\rho\right)^{-1}$$

where $\beta = (3\pi/2)(2/mK)^{1/2}A_2(5)$, and K is the constant of the law of force, m the mass of a molecule and $A_2(5)$ an integral whose numerical value is given in the literature [97]. For chlorine, whose properties are well predicted by Maxwellian spheres at room temperature, and taking the experimental viscosity ($\eta = 1218 \times 10^7\,\mathrm{gm\,sec^{-1}cm^{-1}}$) to evaluate $2mK^{-1}$ one finds that these relaxation times are, as expected, of the order of magnitude of 10^{-10} sec. which coincides with a mean free time.

Nevertheless, Grad's method provides a solid basis for EIT. In a similar fashion, fluids with internal degrees of freedom may be dealt with macroscopically, using the methods of EIT [87] to derive the equations of motion of the appropriate macroscopic variables, which in turn may be obtained by applying Grad's method to solve the Wang Chang-de Boer-Uhlenbeck's equation [99], the generalization of the Boltzmann equation to polyatomic gases.

Once more, the comparison too much involved to be summarized here, shows that the postulates of EIT are fully contained in the framework of the kinetic theory of gases. Thus, just as the Chapman-Enskog method to solve the Boltzmann equation to first order in the gradients allows one to derive the basic postulates of LIT [2], the moment method of Grad yields a kinetic foundation for the basic postulates of EIT. This last statement has been recently reinforced with the derivation of the generalized hydrodynamic equations with explicit forms for the transport coefficients as outlined in section 5, using Grad's moment method of solution of the Boltzmann equation [100].

One can also wonder how is EIT related to the basic principles of statistical mechanics, as for instance LIT may be derived either from the ideas of linear response theory [101] or from the Onsagerian approach to the theory of spontaneous fluctuations [7, 102, 103]. Although a full answer to this question is still pending, a partial answer may be sought if one examines the microscopic formulation of the theory of irreversible processes set forth by Mori [101], and Zwanzig [105, 107] over twenty years ago. The gist of this method consists in selecting amongst the $2fN$ independent variables of a system composed of N particles, each with f degrees of freedom, those whose relaxation times are the longest in comparison, for instance with the time duration of a prototype measurement in the laboratory of a set of macroscopic properties. This means of course that amongst the chosen set, the constants and quasiconstants of the motion must be included. In classical statistical mechanics, each of these dynamical variables will depend on the coordinates Γ in phase space, and on time. We shall denote the set by $\{A_i(\Gamma)\}$ and emphasize on the fact that their time evolution is dictated by the laws of classical mechanics. But the quantities the observer is interested in are not the $A_i(\Gamma)'$s themselves but their numerical values a_i, which are those obtained through experiment. However, these quantities are not subject to the ordinary laws of mechanics. Thus one is forced to seek the time evolution of their distribution function for given initial conditions [107–110, 110a]. The differential equations obtained for such distributions are known as exact kinetic equations because they still contain the totality of information related to the N-body system. The next step is to learn how to device a method whereby we can extract the pertinent information which is directly related to the macroscopic observable properties of the system. Surprisingly enough, it turns out that such information may be shoveled into a set of variables which are, for a large class of initial conditions [103, 111, 112] identical to the so called regression variables introduced by Onsager in 1931 [5, 7]. However, the differential equations obeyed by these variables are far from being linear and moreover, they are non-local in time.

At this stage of the procedure one has to invoke some type of scheme in order to extract from such complicated equations, other simpler ones that may be compared with available macroscopic theories. One of such schemes, certainly not unique, is based on the existence of a slowness parameter in the system which governs the time rate of change of the dynamic $A_i(\Gamma)$ variables [104–110, 113]. When this parameter δ is known to be less than one $[\dot{A}_i(\Gamma, t) \sim \delta < 1]$, a systematic expansion may be performed in a power series in δ which allows one to transform the exact time evolution equations for the regression variables into one which resembles de Kramers-Moyal expansion for the "master equation' [115, 116, 114]. At this stage one is able to introduce several approximations, the most drastic one being removing the non local character of the equations as well as neglecting the non-linear terms in the a_s'. One winds up with linear equations for such variables which express the linear regression assumption introduce by Onsager also in 1931, and thus recovers the Onsagerian form of what is now referred to as the linear theory for spontaneous fluctuations [2, 5, 7]. The remarkable fact about this theory is that the nature of the $\{a\}$ variables is not forcefully specified so that one may chose among them non-conserved variables. In fact, in the strict Onsagerian form of the formulation of this theory [7] the conserved quantities, which are those whose relaxation times are the longest and therefore survive to become the equilibrium macroscopic variables, serve as a basis to describe the reference state, taken to be the equilibrium state around which the espsontaneous fluctuations take place. One may then easily prove that all those spontaneous fluctuations which occur among non-conserved variables and whose time evolution equations are linear regression equations, belong to a class of processes that are macroscopically included in EIT and characterized by Maxwell-Vernotte-Cattaneo type equations of the same structure as equation (10) without the inhomogeneous term. Typical among these are homogeneous chemical reactions ocurring very close to equilibrium so that the macroscopic fluctuations may be charactrerized by the degree of advancement of the reaction, which is well known to obey a linear law [2, 6, 9]. The chemical transport coefficient may then be computed from the microscopic equations of motion and shown to be given by a time correlation function of the chemical flux. This relationship was first derived by Yamamoto [177] in 1960 using linear response theory. Other relaxation processes may be shown to belong in the same category [118]. Thus a class of phenomena naturally beloging to the EIT framework can be extracted in a systematic way from first principle calculations. The macroscopic analogous of non linear and non-local regression type equations [103, 112–119] are still a subject of study.

Finally we shall also mention that the full form of the generalized Maxwell-Cattaneo-Vernotte relaxation type equations for fast or non-conserved quantities seem to follow from first principles calculations based in the projection operator method [81–110a] and on Zubarev's method known as the Non-equilibrium Statistical Operator Method [120]. Exhaustive studies on this latter approach which look very promising have ben recently carried out by several workers [121] and the connection with EIT seems to be on its way [122]. If this program is succesfully accomplished one will have also solved the perennial question concerning the statistical mechanical justification of EIT.

7. Summary and outlook

A close examination of the material presented in this paper cleary reflects the status of a theoretical framework that has been set forth to provide for an extension of LIT. Such an extension is further supported by a number of phenomena occurring in nature which are beyond the scope of the linear theory. The theory is based on two rather simple assumptions which describe the properties of a certain function, taken to be the extension of the local entropy density of LIT, which is defined in a space of state variables formed by the union of two subsets of variables, one given by the locally conserved densities and the other one by a set of fast or non conserved variables. With those assumptions one may derive a complete set of time evolution equations for the whole set of state variables. The formalism is developed in such a way that if the subset of the fast or non-conserved variables is the void set then the results reduce themselves to those of LIT. In general, the full content of the time evolution equations is difficult to analyze since they are highly nonlinear in the state variables and contain unknown coefficients which are also not constants. Therefore, in most of the work performed so far a number of approximations have been introduced, namely:

a) The coefficients are assumed to be expandable in power series of the non-conserved variables. In most of the systems dealt with so far only the first coefficient has been retained.
b) Under the approximation stated in (a), the coefficients appearing in the time evolution equations which now become linear coupled equations among the state variables, are still space and time dependent through the locally conserved quantities. Yet in practice they have been taken as constants.
c) The two approximations described in (a) and (b) lead to time relaxation equations of the Maxwell-Cattaneo-Vernotte type. That they are indeed relaxation equations which yield time decaying functions with positive relaxation times is borne out by kinetic theory [93].

In this context the theory incorporates into the time relaxation spectra, those times associated with the underlying fast variables. Emphasis should be laid on the fact that this feature results from the approximations (a) to (c). Nevertheless, it is precisely in this context in which the theory has been able to yield the successful explanation of all the systems that were discussed in the text. Furthermore, it is also in this context where it may be convincingly justified by the methods of the kinetic theory of gases and of non-equilibrium statistical mechanics. This is rewarding but far from being fully satisfactory. Some of the open questions that remain to be aswered to enhance the power of the formalism, are:

i) A study of at least a class of non-linear time evolution equations relevant to known phenomena is desirable. Lack of experimental results makes this task rather difficult.
ii) The analytical behaviour of the coefficients appearing in the time evolution equations is doubtful near points of instability, critical points, etc. Thus the validity of assumption (a) in these cases, is questionable.

iii) The relationship between EIT and the laws of microscopic physics beyond the realxation type equations satisfied by fast variables close to equilibrium is not yet known.

iv) The nature of the fast variables to be included as state variables has been a long debated issue. No definite agreement exists yet on the physical criteria one must use to select them.

v) The physical significance of the η-function is lacking, in spite of the fact that for some very particular cases it exhibits all the properties of the entropy function.

vi) The behaviour of truly complex systems such as glasses, supercooled liquids, polymer solutions, melts, etc. is stilll outside the reach of EIT.

vii) Its extension to include non local effects in space and time is not available.

Other aspects such as the uniqueness of the theory, its comparison with other versions of extended thermodynamics, the mathematical properties of the space of state variables, etc. may still be added to this list and when regarded altogether are clearly indicative of the enormous task that still remains for the future.

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Resumen. Desde hace veinte años se realizan esfuerzos por tener una visión más amplia de los procesos termodinámicos no lineales irreversibles. Dichos esfuerzos han surgido del hecho que existan fenómenos en estados que no están en equilibrio y que se encuentran fuera del caso lineal. Se presenta un resumen de un método cuyos conceptos descansan sobre principios físicos estrechamente relacionados con los procesos termodinámicos lineales irreversibles. Se tratan exhaustivamente el conjunto de ideas detrás del método, así como su comparación con el experimento y su derivación de la física mesoscópica y microscópica. Finalmente, se ofrecen problemas que no han sido resueltos.