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Relationships between rational extended thermodynamics and extended irreversible thermodynamics

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We consider a few conceptual questions on extended thermodynamics, with the aim to contribute to a higher contact between rational extended thermodynamics and extended irreversible thermodynamics. Both theories take a number of fluxes as independent variables, but they differ in the formalism being used to deal with the exploitation of the second principle (rational thermodynamics in the first one and classical irreversible thermodynamics in the second one). Rational extended thermodynamics is more restricted in the range of systems to be analysed, but it is able to obtain a wider number of restrictions and deeper specifications from the second law. By contrast, extended irreversible thermodynamics is more phenomenological, its mathematical formalism is more elementary, but it may deal with a wider diversity of systems although with less detail. Further comparison and dialogue between both branches of extended thermodynamics would be useful for a fuller deployment and deepening of extended thermodynamics. Besides these two approaches, one should also consider the Hamiltonian approach, formalisms with internal variables, and more microscopic approaches, based on kinetic theory or on non-equilibrium ensemble formalisms.

This article is part of the theme issue 'Fundamental aspects of nonequilibrium thermodynamics'.

1. Introduction

Extended thermodynamics is a general denomination covering several thermodynamic theories having three

common points: (1) the incorporation of fluxes as independent variables of the formalism, (2) an extended entropy and an extended entropy flux depending on the classical thermodynamic variables and on the mentioned fluxes, and (3) the search for generalized transport equations for fast and steep phenomena, compatible with the second law formulated on the grounds of the extended entropy and the extended entropy flux. The motivations of the theory are especially clear if one begins with the third point we have mentioned: the practical need for formulating generalized transport equations for small systems and for fast processes is especially compelling at a time of interest in miniaturization of devices and of fast operation. Computers could be a good example of this: they are based on miniaturized, fast devices, dissipating much heat; thus, heat, speed and miniaturization appear in an intimate combination, asking for conceptual thermodynamic grounds to explore their attainable limits.

From the three basic ideas mentioned in the first paragraph, the several developments of extended thermodynamics may differ in: (a) the concrete fluxes taken into account; (b) the techniques being used in the exploitation of the second law; (c) the connections with the microscopic level of description; (d) the range of systems being analysed. In fact, the bibliography related to extended thermodynamics is considerably wide: it includes at least 18 monographs [1–18] and 17 review papers [18–35] but the diversity of approaches makes it difficult to give them a wide well-recognizable form beyond their mutual differences. The aim of this paper is to foster the contact between them.

Let us note that the central role given to the fluxes in extended thermodynamics, in contrast to local-equilibrium versions of non-equilibrium thermodynamics (in which the fluxes are determined by the gradients of the thermodynamic conjugates of the classical equilibrium variables) fits especially well to the spirit of our globalization epoch. Indeed, the fluxes are nowadays central concepts of our society: fluxes of capital, of matter (fuel, goods), of information and of people (migrations, tourism). In fact, they have become some of the critical parameters for the stability of our model of civilization. Thus, the application of ideas from physics to social sciences [36] is expected to find in extended thermodynamics a possible source of inspiration for the treatment of those fluxes.

We will conceptually examine, with a minimum number of equations, three main aspects: (1) transport equations, corresponding to the evolution equations for the fluxes and providing non-local and nonlinear transport equations with relaxation effects, applicable for instance to nanosystems, to fast processes or to slowly relaxing systems; (2) non-equilibrium equations of state for temperature, pressure and chemical potential, obtained as derivatives of a generalized entropy, incorporating a non-equilibrium contribution due to the presence of the corresponding fluxes; and (3) fluctuations around non-equilibrium steady states, with their second moments obtained from a generalized free-energy, leading to flux-fluctuation expressions yielding an asymmetric probability to fluctuate in the same direction or in the opposite direction to the steady-state flux.

2. Transport equations

Transport equations (which, together with the thermodynamic equations of state, define a material) are essential in the analysis of non-equilibrium systems. Usually, they express the fluxes in terms of gradients of some physical quantities (for instance, the thermodynamic conjugates to conserved variables). Indeed, in classical transport equations (Fourier Law, Fick Law, Ohm Law, Seebeck Law, Peltier Law, Soret Law, Dufour Law, etc.) the heat flux, the mass flux and the electric flux are expressed in terms of the gradients of temperature, chemical potentials and electrical potential, denoted as thermodynamic forces (with forces understood not as mechanical forces, but in a more general sense, in an analogous way to which one may speak of social forces or economical forces, as causes producing some effects) [15]. In fact, each flux may depend on several different forces, though a number of different couplings.

The fluxes are not necessarily simple physical quantities, but they may be constituted by a sum of several contributions. For instance, the heat flux may contain terms related to the transport of molecular kinetic energy, molecular potential energy, vibrational and rotational energies of the molecules, and so on [17]. Analogously, the mass flux will be a sum of the contributions of the mass fluxes of different kinds of chemical species in the system, and the momentum flux in macromolecular solutions or blends will contain the contributions of the several internal degrees of freedom of the macromolecular chains or networks [5,6,9–12,16,17].

The classical transport laws mentioned above have a broad and useful range of validity but they are found to break down for too-fast perturbations or too-steep gradients. Indeed, from a microscopic perspective, these equations imply a high number of collisions among heat carriers between the two opposite boundaries of the system. The average time between successive collisions of a particle is called the average collision time and the average length between two successive particles is called the mean free path. If the system becomes too rarefied, or too small, or if the external perturbations are too fast or too steep, the number of particles collisions involved during the experimental time is small and the classical equations are no longer valid.

Furthermore, for short times the system will not be ergodic, as it will not have time enough to visit a sufficiently wide region of the phase space, and the temporal average of the microscopic variables will not coincide in general with the usual ensemble averages [35]. Another reason for not being ergodic in relation to classical equilibrium ensembles, or in the case of steady states, is that if the system is submitted to strong fluxes the region accessible to the evolution of the system in the phase space will be more restricted than that accessible in equilibrium, so that the temporal average will not coincide with the equilibrium ensemble average, and other kinds of ensembles will be necessary [9,11,12], leading to the need for a different kind of thermodynamics.

Generalized transport equations are needed for the description of heat, mass, momentum and electric transport in systems comparable to or smaller than the mean-free path of the corresponding microscopic carriers. Furthermore, one would like such equations to be compatible with the second law of thermodynamics. These apparently simple statements constitute, in fact, a complicated and debated program [1–12]. Three main questions underlying it are:

- (1) Is it truly worth the effort of obtaining mesoscopic transport equations, or would it be better to go directly to the microscopic level and work on the basis of computer simulations of the systems?
- (2) In which circumstances is the existence of mesoscopic transport equations conceptually consistent, meaningful and practically useful?
- (3) What is the form of the second law of thermodynamics at mesoscopic levels?

Let us discuss briefly these three questions.

- (1) Since the computation speed and power are steadily increasing and detailed simulations are becoming more widely accessible, why should one be interested in getting less detailed mesoscopic transport equations instead of solving the microscopic equations of the system? There are two kinds of answers to this question. First, most of the measurements involve a relatively high number of particles and are interpreted in terms of thermodynamic variables, as for instance temperature. Thus, going from microscopic simulations to actual experiments requires some conceptual identifications that are far from trivial, and which may be better understood if one tries to go from microlevel to macrolevel in some detail, by incorporating intermediate levels. Second, from a practical perspective, having effective transport equations of relatively simple form leads to a much faster exploration of the system. This allows us to consider a wide range of different initial conditions, boundary conditions, system geometries and material compositions in a relatively short time. After having compared the solutions and identified the most promising situations, these could be simulated in greater detail. By contrast, a detailed

microscopic simulation of all the different possibilities would not be possible in a realistically manageable time.

- (2) It is not clear in which circumstances mesoscopic descriptions are truly possible and meaningful. They are clearly consistent when there are variables with some intermediate range of relaxation times and correlation lengths, but when such temporal and spatial intermediate ranges do not exist, and all the relaxation times except those of the macroscopic conserved variables are very short and of the same order of magnitude, it is not clear how to select a reduced but representative set of intermediate variables.
- (3) The form of the second law for short times and short lengths (small systems, for instance) is not known *a priori*, and therefore it is not clear how to formulate and apply the second law at intermediate levels. Neither the existence of an entropy in these situations, nor the explicit form of this entropy is well known. On the other side, the classical formulation of the second law of thermodynamics compares the entropy of a final equilibrium state with that of an initial equilibrium state, but does not contain information about the intermediate states of the system.

All these questions have been examined in extended thermodynamics, and particular answers to them in some situations have been proposed and examined in detail. To show a particular simple example, incorporating non-zero relaxation times and mean-free paths, we write generalized evolution equations for the several contributions q_i to heat flux $q = \sum_i q_i$, and for the respective fluxes of the heat flux Q_i (a second-order flux giving the flux of q_i) (see equations (2.1) and (2.2)) as well as forms of the extended entropy and the extended entropy flux (see equations (2.3) and (2.4)) making the evolution equations (2.1) and (2.2) consistent with the second law of thermodynamics. Indeed, although they are able to describe actual experimental observations, equations (2.1) and (2.2) are not compatible with the local-equilibrium form of the second principle. However, they may be made compatible with a more general form of it, expressed in terms of the positive character of the extended entropy (2.3) and considering the extended entropy flux (2.4).

We decompose the heat flux in various contributions because in phonon heat transfer (for instance) the phonons corresponding to the different modes (corresponding to different frequencies) have different relaxation times and different mean-free paths. Therefore, it is of interest, when possible, to keep an explicit trace of such difference. In many occasions, one simplifies these equations assuming that all the relaxation times are equal, in which case equation (2.1), with $Q_i = 0$, leads to the Maxwell–Cattaneo equation. Another motivation to decompose the heat flux in several contributions arises in heat transport in dense gases or in non-monomeric gases, where the heat flux contains a contribution from the molecular kinetic energy and other contributions from internal degrees of the molecule (for instance, rotational and vibrational).

The mentioned equations are

$$\tau_{1i} \left(\frac{dq_i}{dt} \right) + q_i = -\lambda_i \text{grad } T - \text{div } Q_i, \quad (2.1)$$

$$\tau_{2i} \frac{dQ_i}{dt} + Q_i = -\lambda_{2i} \text{grad } q_i, \quad (2.2)$$

$$ds = T^{-1} du - \sum_i \left(\frac{\tau_i}{\lambda_i T^2} \right) q_i \cdot dq_i - \sum_i \left(\frac{\tau_{2i}}{\lambda_{2i} T} \right) Q_i : dQ_i \quad (2.3)$$

and
$$J_i^s = T^{-1} \sum_i q_i + T^{-1} \sum_i \beta_i Q_i \cdot q_i. \quad (2.4)$$

Here, T is temperature, λ_i the contribution of i th mode to the thermal conductivity, τ_{1i} the relaxation time of q_i , τ_{2i} the relaxation flux of Q_i , λ_{2i} a generalized transport coefficient relating the steady-state value of Q_i to the gradient of q_i , s the extended entropy per unit volume, u the internal energy per unit volume, J_i^s the contribution of i th mode to the entropy flux, and β_i a coefficient describing the contribution of Q_i to the entropy flux. The dot between two quantities stands for their mutual contraction in one index, namely, $q_i \cdot q_i = q_{ij} q_{ij}$, with summation over j

(recall that j corresponds to the coordinate, $j = 1, 2, 3$, whereas i stands for the number of the mode), and $\mathbf{Q}_i \cdot \mathbf{q}_i = Q_{ijk} q_k$, with summation over k (from 1 to 3); thus $\mathbf{q}_i \cdot \mathbf{q}_i$ is the scalar product of the two vectors, whereas $\mathbf{Q}_i \cdot \mathbf{q}_i$ is a vector, corresponding to the contraction of the tensor \mathbf{Q}_i times the vector \mathbf{q}_i .

Equations (2.1) and (2.2) lead to a finite speed for heat pulses of i th mode given by $U_i^2 = (\rho c)^{-1} [(\lambda_i/\tau_{1i}) + (\lambda_{2i}/\tau_{2i})]$, with ρ mass density and c specific heat [6]. This is in contrast to classical theory, where the speed of pulses (namely, the high-frequency limit of the speed of waves) diverges. Furthermore, these equations describe a transition from a reversible behaviour at times shorter than the relaxation times to an irreversible behaviour at times longer than the relaxation time [6]. This agrees with the views of the theory of deterministic chaos, where behaviour is reversible for times much shorter than the characteristic times set by the reciprocal of the Lyapunov exponents, and irreversible for longer times [37]. Eventually, equations (2.1) and (2.2) describe a transition from diffusive behaviour to ballistic behaviour for an increasing Knudsen number, such number being the ratio of the heat carriers' mean-free path to the characteristic size of the system. For a small Knudsen number, the behaviour is diffusive (collisions among particles are dominant), whereas for high values of the Knudsen number the behaviour is ballistic (collisions with the walls dominate collisions among particles) [18,38–40]. Thus, the effects considered by equations (2.1) and (2.2) are not minor quantitative corrections to the classical equations, but imply far-reaching qualitative modifications of the conceptual framework.

Concerning the thermodynamic implications of such equations, note that when the relaxation times τ_{1i} and τ_{2i} are different from zero, the entropy s contains non-classical contributions related to the fluxes; furthermore, the presence of non-local effects in equations (2.1) and (2.2) is related to the presence of non-classical effects in the entropy flux (2.4), where the coefficients β_i are proportional to the coefficient λ_{2i} . Without the modifications (2.3) in the entropy and (2.4) in the entropy flux, equations (2.1) and (2.2) are not compatible with the second law of thermodynamics. More general equations than (2.1) and (2.2), incorporating higher-order fluxes, nonlinear terms, and higher-order couplings for instance, could also be considered [6,7,14,15].

In the case when τ_{2i} is zero (or very small with respect to τ_{1i}), equation (2.2) leads to $\mathbf{Q}_i = -\lambda_{2i} \text{grad } \mathbf{q}_i$ and equations (2.1)–(2.4) reduce to

$$\tau_i \left(\frac{d\mathbf{q}_i}{dt} \right) + \mathbf{q}_i = -\lambda_i \text{grad } T + l_i^2 \text{div} \cdot \text{grad } \mathbf{q}_i, \quad (2.5)$$

$$ds = T^{-1} du - \sum_i \left(\frac{\tau_i}{\lambda_i T^2} \right) \mathbf{q}_i \cdot d\mathbf{q}_i \quad (2.6)$$

and
$$\mathcal{J}^s = T^{-1} \sum_i \mathbf{q}_i + T^{-1} \sum_i l_i^2 (\text{grad } \mathbf{q}_i) \cdot \mathbf{q}_i, \quad (2.7)$$

where the coefficient l_i (related to the mean-free of the i th mode) is given by $l_i^2 = l_{2i}/\tau_{1i}$. Of course, this system does not lead to a finite speed for heat pulse propagation, but it may be useful in practical applications if $\tau_{2i} \ll \tau_{1i}$, in the regime when the frequency of perturbation is higher than $1/\tau_{1i}$ but lower than $1/\tau_{2i}$. Combining (2.5) with the energy balance equation leads to an evolution equation for the temperature analogous to the equation obtained from a two-temperature model, namely, assuming the system is composed of two interpenetrating materials, each one with its own local temperature, and exchanging heat between them in a way proportional to the difference of their temperatures [6]. It is worth recalling this fact because it illustrates that some macroscopic equations may arise from very different microscopic models; indeed, equation (2.5) may follow from the kinetic theory of phonons (with a specially remarkable contribution of the momentum-conserving collisions) [6,7,41] and the kinetic theory of electrons, but its combination with the energy balance equation may be very similar to such a different model as a mixture of phonons and electrons, or of a light gas and a heavy gas, or of two interpenetrating solids.

Some of the differences between rational extended thermodynamics (RET) and extended irreversible thermodynamics (EIT), are, for instance, that RET requires the system of equations

to have the form of balance laws, local in space (i.e. the non-local effects are only related to the divergence of the corresponding flux), and to be symmetric hyperbolic, thus leading to finite speeds of propagation [7,17]. From a thermodynamic perspective, the interest of this restriction is that mathematical theorems on these kinds of systems allow one to prove in purely mathematical terms the existence of a supplementary balance law for a quantity whose production term has a definite (positive) sign, thus allowing us to identify it as an entropy related to the main fields [7]. This is especially interesting because beyond equilibrium the classical arguments for the existence of an entropy function become arguable and insufficient to provide firm grounds for the existence of entropy. Furthermore, it assumes that the equations must satisfy Galilean invariance and frame-indifference.

In EIT, it is also considered that, in principle, the speeds of propagation should be finite; however, it still admits equations like (2.5) as an approximation to actual experiments in which the frequency of perturbations is higher than $1/\tau_{1i}$ but lower than $1/\tau_{2i}$. Doing this implies that the equations are no longer local nor hyperbolic (in contrast to RET); thus, some mathematical advantages are lost. Note, however, that this contrast with RET is not as radical as it could seem, because equations (2.5) may be obtained from (2.1), which are of the local balance form required in RET. Note that in the case of (2.5), the extended entropy (2.6) does not include the contribution of the flux of the heat flux \mathbf{Q} , but \mathbf{Q} contributes to the entropy flux (2.7).

RET has devoted much attention to wave propagation, including acceleration waves, and to the shock waves, including singularities arising beyond some critical value of the Mach number (or the propagation speed). In these fields, the wealth of results of RET is very wide, beyond the results achieved in EIT; the effort devoted to the scrutiny of the mathematical aspects of the theory is also much more sophisticated than that in EIT. Another difference between RET and EIT is that the former has explored in much detail monatomic ideal gases, phonon gases, photon gases [7,17] and electron gases in metals or semiconductors [25,32], by considering the whole structure of nonlinear terms, searching for consistency with the approaches of the kinetic theory of gases. Recently, it has also considered polyatomic ideal gases [17,42] and dense gases [43], by loosening the too-tight original structure of the theory, excessively limited by the proximity to ideal monatomic gases, and becoming slightly more phenomenological, which gives it higher flexibility. By contrast, EIT has not paid so much attention to the detailed structure of the nonlinear terms, but it has considered ideal gases (monatomic or not, as well as photon gases, phonon gases and electron gases), dense gases (incorporating the transport of intermolecular potential energy) [6], superfluids [29,34], nuclear matter, fast solidification fronts in alloys and mixtures [35], and polymer solutions and blends [10,21–25,28] and ecological systems [16]. In such systems, the detailed structure of the evolution equations becomes unmanageable, and one tries to have some phenomenologically satisfactory expressions rather than exact expressions of the equations. A further advantage of the simplified expressions like (2.1)–(2.4) or (2.5)–(2.7) is that they allow the incorporation of an infinite number of higher-order fluxes, giving a continued-fraction expansion of the thermal conductivity in terms of the frequencies and wavevectors of the perturbations, or on the system size, which are useful for the computation of the effective thermal conductivity of nanosystems, or nanostructured systems (as superlattices, phononic crystals, thermal metamaterials, graduated systems, suspensions of nanoparticles in heat-conducting fluids) or of dilute systems, depending not only on the material but also on the size and geometry of the system.

In some aspects, EIT is closely parallel to thermodynamic theories with internal variables [44], which take into account the independent character and the dynamics of a number of microscopic variables related to the composition or the structure of the system. Indeed, one could consider the heat flux and other fluxes (diffusion, electric, higher-order fluxes) as internal variables. The thermodynamic theories with internal variables are as flexible as EIT, and also try to make compatible the evolution equations for the system (including that of internal variables) with the second law of thermodynamics, via a generalized entropy incorporating the contributions of the internal variables. However, the fluxes play a special role in non-equilibrium thermodynamics, because in steady state they describe a central aspect of the interaction of the system with the

environment. Comparison between theories with internal variables and EIT, for some concrete systems, is very illustrative and stimulating. For instance, in the approach of [38] to heat transport, a vectorial and a tensorial quantity are considered as internal variables; in the case that these variables are identified with the heat flux and the flux of the heat flux, the resulting equations for the heat equation, the entropy and the entropy flux become very close to those of extended irreversible thermodynamics. The fact that the generalized entropy flux has been introduced in a very different form than in such theory makes the coincidence of the results of both approaches especially reassuring, as they are supporting each other.

Despite their restricted character, the answers provided by extended thermodynamics to the previously mentioned conceptual questions may be a useful guide to more general situations, and they are helpful to give to the mentioned answers some more precise and concrete forms. For instance, the reduction of the extended entropy with respect to the local-equilibrium entropy may be physically interpreted in two different but complementary and mutually consistent ways. On the one side, the reduction arises from the entropy produced by the relaxation of the fluxes during their decay towards their zero equilibrium value after the system (in fact, a small volume of the system) has been suddenly insulated. A second interpretation is in terms of the reduction of the number of accessible microscopic states when the system is submitted to a non-vanishing heat flux. These interpretations may take concrete explicit forms in the kinetic theory of gases [5,7,14,17] or in maximum-entropy approaches [7,9,11,12], where the non-equilibrium distribution function f is obtained, in terms of the local equilibrium quantities and of the fluxes acting on the system (or on the gradients present in the system), so that the calculation of the entropy in terms of the integral of $f \log f$ may be carried out, leading to the local equilibrium entropy plus some explicit corrections.

The generalized transport equations (corresponding to evolution equations for the fluxes, as (2.1) and (2.2)) are required to be compatible with a positive character of the generalized entropy production, obtained from the balance equation for the extended entropy (2.3) combined with expression (2.4) for the entropy flux. This positive character of such generalized entropy production is considered as the corresponding expression of the second law, more general than the requirement of positive production of the classical local-equilibrium entropy, but not completely universal. Unfortunately, much of the current efforts in providing generalized transport equations focus on the description of dynamical aspects of the system, but completely ignore the thermodynamic aspects.

Let us note that taking higher-order fluxes is a particular way of proposing a multilevel description of the system. Multilevel descriptions are of much interest when one is interested in going from microscopic to macroscopic descriptions, thus going through a wide number of possible mesoscopic descriptions. Searching for the common features to all such descriptions is one of the aims and merits of the so-called GENERIC formalism [45–47]. A further relevant merit of this formalism is the requirement of a Hamiltonian structure of the evolution equations at all levels of description. This is particularly interesting as it provides a rich and interesting mathematical structure to the reversible terms appearing in the evolution equations, for which the positive definite character of entropy production is unable to give any information.

3. Non-equilibrium equations of state

A natural question after having got a generalized entropy is what it is useful for. We have already mentioned that, in principle, such generalized entropies are introduced in order to explore the compatibility of generalized transport equations with the second law. Unfortunately, researchers interested in simulations focus their interest on the dynamical aspects of the system, without paying attention to the compatibility with the second law. This is logical because, on the one side, the form of the second law at this level is not well known and, on the other side, because it is reasonable to expect that if the equations successfully describe the observed dynamics of the system they should be compatible in some way with the unknown form of the second law. Thus,

at first sight, the knowledge of the precise form of the generalized entropy does not seem to be of much interest, except for a few specialized researchers.

Anyway, once the entropy is obtained, one may try to get more information from it, especially on equations of state for the intensive variables (temperature, pressure, chemical potentials) conjugated to the classical variables (internal energy, volume, number of moles), and on the fluctuations of the several intensive variables appearing in the entropy. Such information is expected to be valid at least in non-equilibrium steady states, where they will contain additional contributions of the non-vanishing fluxes, and are supposed to reduce to the classical results for equilibrium states, when the fluxes tend to zero [6,10,27]. These aspects have been considerably studied in EIT, but the number of studies from RET is scarce.

A non-equilibrium equation of state for the reciprocal of temperature is obtained from the partial derivative of the generalized entropy (containing the fluxes as additional variables) with respect to the internal energy. Such an equation of state leads to a temperature dependent on the classical conserved variables and on the fluxes. The conceptual meaning of such temperature has been discussed in detail in [8,9]. In fact, beyond local-equilibrium, the several definitions of temperature proposed by extrapolating expressions analogous to equilibrium ones lead to different values for the respective temperature when the system is in non-equilibrium steady states [27]. This is logical because, the system being out of equilibrium, equipartition is no longer obeyed and, therefore, different degrees of freedom may exhibit different values of their effective temperature. Also, different thermometers, sensitive to different degrees of freedom, will yield different values of temperature. Thus, in these situations, what is needed is to relate the different temperatures for a system submitted to given values of the fluxes. In particular, it raises the problem of how to measure the non-equilibrium 'absolute' temperature related to the derivative of the entropy with respect to the internal energy. It may be seen that, at least in ideal gases submitted to a heat flux, such absolute temperature coincides with the microscopic kinetic temperature measured perpendicularly to the heat flux, which is different (lower) than the microscopic kinetic temperature measured along the axis parallel to the heat flux [6,8]. Later we will refer to the consequences of the non-equilibrium chemical potential.

Note that the entropy is written in different forms in rational extended thermodynamics and in extended irreversible thermodynamics. In the case of heat flux as a single additional variable, in RET one writes

$$ds = \Lambda_1 du + \Lambda_2 \cdot dq, \quad (3.1)$$

where Λ_1 and Λ_2 are the respective Lagrange multipliers related to the evolution equations for u and q (or, equivalently, the Lagrange multipliers conjugated, respectively, to u and q in a theoretical-information approach). Instead, in EIT one writes

$$ds = T^{-1} du - \left(\frac{\tau}{\lambda T^2} \right) q \cdot dq. \quad (3.2)$$

Of course, the T in (3.2) is not the local-equilibrium temperature, but a more general, dynamical temperature depending not only on u but also on the heat flux q as

$$T^{-1} = T_{\text{eq}}^{-1} - \left(\frac{1}{2} \right) \left[\frac{d(\tau/\lambda T^2)}{du} \right] q \cdot q, \quad (3.3)$$

with T_{eq} being the local-equilibrium temperature of the system. Apparently, (3.1) is more general than (3.2), because it does not directly identify Λ_1 with the reciprocal of temperature. However, in practical terms, having an explicit expression for the difference between T and T_{eq} is useful in practice to interpret in physical terms the meaning of T and explore its applications. On the other side, having a physical interpretation for Λ_2 , as $\Lambda_2 = -(\tau / \lambda T^2) q$, is also clarifying with respect to the physical meaning of this coefficient, instead of having it as an abstract unidentified parameter. Recently, this difference between both approaches is being reduced, not only because in RET one considers the Lagrange multiplier conjugated to the internal energy as a non-equilibrium absolute

temperature, but also because the difference between such non-equilibrium temperature and the local-equilibrium temperature has been evaluated for some systems [48].

Explicit expressions for Λ_2 in terms of u and q (for instance) may be obtained in a very nonlinear form from maximum-entropy techniques, as Lagrange multipliers making compatible the distribution function with the physical conditions acting on the system. For instance, these conditions may refer to constraints on the average internal energy and on the average heat flux, in the usual view of the informational theoretic approach to statistical physics [9,11,12], or on the evolution equations of the internal energy and of the heat flux, according to the Liu interpretation [7,17], which is more general than the usual interpretation, as it covers dynamical aspects. These interpretations lead to the same result for dilute gases, but not necessarily so for dense gases.

From a practical perspective, the contribution of the fluxes to the non-equilibrium equations of state is particularly relevant when one considers, for instance, flowing polymer solutions or blends [10,21,28]. In this case, the important flux is the momentum flux, expressed by the stress tensor or the viscous pressure tensor \mathbf{P}^v , which influences the chemical potential of the several polymers. In this case, instead of equations (2.1)–(2–4) being expressed in terms of the heat flux, they must be expressed in term of the several contributions to the viscous pressure tensor. In this way, one gets equations describing viscoelastic behaviour, or more complex rheological behaviours. On the other side, the entropy becomes dependent on several contributions to the viscous pressure tensor. Thus, when computing the chemical potential, as minus the absolute temperature times the partial derivative of the generalized entropy with respect to the number of molecules of the polymer, it is found in a natural way that the chemical potential is modified by the viscous pressure (or by the shear rate). As a consequence, the phase diagram of polymer solutions is modified in a flowing system, because of a shear-induced shift of the critical temperature, the spinodal line and the coexistence line [10]. Thus, some solutions which are expected to be a one-phase fluid in the classical theory become two-phase systems, one phase rich in the polymer and the other one poor in the polymer. This has practical consequences in polymer processing.

Analogous problems arise in fast solidification fronts, where hyperbolic equations for the diffusion flux, analogous to (2.1), are needed to describe the dynamics, and also the composition of the solid phase as related to that of the fluid phase is not the equilibrium one, but depends on the speed of the front [35].

4. Non-equilibrium fluctuations

The analysis of the dynamics of fluctuations has played a relevant role in non-equilibrium thermodynamics. Three results are especially well known and important. The Onsager–Casimir reciprocity relations, based on the hypothesis of temporal reversibility of the microscopic dynamics, from which emerges the well-known reciprocity relations between the phenomenological coefficients relating the several fluxes to the thermodynamic forces [6,11,15]. A second result is a fluctuation–dissipation theorem, relating fluctuations to dissipation, namely, linking the stochastic fluctuations of the velocity to the hydrodynamic friction coefficient (and so on for other dynamical variables). This relation, as well as its dynamical aspects, has been used as a starting point for some approaches to statistical thermodynamics of non-equilibrium processes [49]. The third one, closely related to the second one, is the Green–Kubo relations between the time correlation function of the fluctuations of the fluxes in an equilibrium state to the memory kernels relating the fluxes to the thermodynamic forces in the formalisms in which the relationship between fluxes and forces is not instantaneous, but the value of a flux at one time is a function of the history of the corresponding thermodynamic force [6,12]. The fluctuations are especially relevant in small systems, and therefore they must be considered in the thermodynamics at small spatial scales and short times [50].

Concerning fluctuations around the average value in a non-equilibrium steady state, one may use for the probability of fluctuations of the fluxes around equilibrium the Einstein relationship

between the probability Pr of fluctuations and the second differential $\delta^2 S$ of the extended form of entropy (2.3), namely,

$$Pr = A \exp\left(\frac{\delta^2 S}{2k_B}\right), \quad (4.1)$$

with k_B the Boltzmann constant and A a proportionality constant. In this way, one finds from (2.3) an expression for the second moments of fluctuations which is equivalent to that of Green–Kubo relations for the particular case of an exponential memory function. More general forms for the memory may be obtained from this procedure, using more general expressions for the entropy (2.3), as for instance by assuming that each flux is a sum of contributions which decay exponentially with their own relaxation time.

For fluctuations around non-equilibrium steady states, the situation is more complicated and much richer [51]. Equation (4.1) is no longer sufficient and one must use, for instance,

$$Pr = A \exp\left(\frac{\Delta G}{k_B}\right), \quad (4.2)$$

with G a Gibbs free energy dependent on the actual heat flux q and of the average heat flux q_0 . This leads to an analogy of the Green–Kubo relationships between fluctuations of the fluxes and the memory kernels of the corresponding transport equations, but incorporating the effect of the non-vanishing value of the average flux. Furthermore, it leads to a flux-fluctuation expression for the relative probability of a fluctuation of the flux along the average non-vanishing flux characterizing the steady state, and of a fluctuation of the flux in the opposite direction [6]. The result obtained from this mesoscopic entropy agrees with results derived from several microscopic approaches [6].

A further aspect related to fluctuations far from equilibrium is the description of turbulence. The methods of extended thermodynamics have been applied in [13] to turbulence in viscous fluids. In some aspects, the conceptual problems are close to those of extended thermodynamics of gases. In the latter case, the most direct relationship between extended thermodynamics and the kinetic theory of monatomic gases is through Grad's approach, describing the state of the gas in terms of the moments of the non-equilibrium distribution function [6,7], and finding from the Boltzmann equation the evolution equations for the higher-order moments. This procedure leads to a hierarchy of equations in which in the evolution equation for the moment of order n appears to be a contribution of the moment of order $n + 1$. Thus, the problem of closure of the hierarchy requires choosing for n some value N and expressing the moment of order $N + 1$ in terms of the moments of order less than or equal to N . In the theory of turbulence, the average value of the second moments of fluctuations appears in the equation for the time average of the density, the velocity and the temperature. If one searches for an evolution equation of the second moments (starting from the Navier–Stokes evolution equation, and so on) it is found that moments of third order in the turbulent fluctuations appear in the evolution equations for the second moments, and so on. In this way, one has a hierarchy of evolution equations for the higher-order moments of the turbulent fluctuations. On physical grounds, it is necessary that the truncations leading to a closure for such hierarchy satisfy the second law of thermodynamics. As in usually extended thermodynamics, in this approach one must use an extended entropy and entropy flux depending on the moments of the order less than or equal to N , being N the order of the highest moments being retained in the description. As shown in [13], the application of extended thermodynamics has led to some useful improvements of the closures existing up to now. A more systematic and exhaustive application of the thermodynamic theory should be carried out.

5. Conclusion

In this text, we have tried to reflect on several conceptual questions posed by non-equilibrium thermodynamics beyond the local-equilibrium regime. In local equilibrium, the thermodynamic behaviour of the systems is described by the same variables and the same functional dependence

of the thermodynamic potentials as in equilibrium. However, when some additional variables have a long relaxation time or a long coherence length, these additional variables become independent variables of the system, and several essential thermodynamic topics must be re-examined. These topics are, for instance, the form of the entropy, the statement of the second principle of thermodynamics, and the form of the equations of state for temperature, pressure or chemical potential. They are not only deeply problematic fundamental issues, but they also provide practically helpful tools to deal with a wide diversity of applications.

As some paradigmatic current applications of such mesoscopic formalisms, and to refer only to heat transport, we could mention heat transport in nanosystems; and heat transport in laminar and turbulent superfluid helium. In nanosystems, the small size of the system, which becomes comparable to the mean free path of the heat carriers, means that classical transport equations, valid in the diffusive regime, are no longer valid, because heat transport takes place in a situation intermediate between diffusive and ballistic regime; it is well known this is a very active topic, very inspiring in the theory and applications of transport theory and thermodynamics. In superfluid helium, the macroscopically coherent quantum effects lead to a long relaxation time and a long coherence length for the heat flux and to a quantization of the circulation of vortices [10,11,29,34]; when the heat flux exceeds some threshold, related to a critical value (of the order of 100) of the quantum heat number $Re_q = qd(\rho T s \kappa)^{-1}$, with κ the quantum of vorticity, given by $\kappa = h/m$, with h Planck's constant and m the atomic mass of helium, and d the diameter of the tube where heat is flowing, quantized vortices appear. These vortices exert a friction force on the helium flow and contribute to the thermal resistance of the system. Thus, heat transfer in helium superfluid and in Bose–Einstein condensates exhibits an especially rich phenomenology which requires a sophisticated transport theory combined with an advanced thermodynamic framework.

Among the open problems of the theory, let us mention the following ones. (1) The characterization of the fundamental variables to be used in a variety of systems, and its relation to microscopic models [52]. (2) The clarification of the non-equilibrium equations of state depending on the fluxes (or on additional internal variables) and their consequences on the limits of stability of the states of the system [53]. (3) The clarification of the second law when it is applied to approximate models: does the requirement of a positive entropy production forbid some approximate equations, or, in contrast, does it allow them but indicate their limits of validity [54]? (4) To examine nonlinear generalizations of the theory, leading, for instance, to solitonic heat transport, and to breather solutions, and the application to such results, for instance, to thermal transmission of information (thermal bits), or to compare with genuinely nonlinear microscopic models of heat transport in nonlinear lattices. (5) To study in depth the boundary conditions of the equations; indeed, as the number of independent variables and of evolution equations increases, one should complement them with suitable boundary conditions; this is the case of equation (2.2) or (2.5) (also known as Guyer–Krumhansl equation), whose solution in nanowires and other kinds of nanosystems requires in many occasions a slip heat flow along the walls, described by an expression similar to that of the velocity slip condition along the walls for rarefied gases. (6) To compare the macroscopic theory not only with monatomic dilute gases, but also for rarefied gases and for dense gases and for liquids, in order to clarify the density dependence of the several evolution equations. (7) To explore the role of the slip flows along the walls in the fluctuations of fluxes in narrow channels, thus extending the flux-fluctuation expressions known up to now.

Besides these questions, arising in the purely thermodynamic context, other aspects may also have relevance in sociological, economic and political contexts. Of course, the concepts of energy and of entropy play an important role in these fields [47,55]. We are referring here to a more subtle point of view, going beyond equilibrium or local-equilibrium approaches, and referring to the energy distribution in the different microstates. Indeed, the non-equilibrium corrections when the fluxes are high arise because the energy (or the mass, or the electric charge) entering into the system in a given short period of time do not stay for a long enough time in the system to become sufficiently thermalized. Thus, the local state of the system will not correspond to the equilibrium situation, but will depend much on the value of the flux. Such situations also arise, for instance,

in migration fluxes. If the flux is sufficiently small in order that the place receiving the newcomers may accommodate to the new situation (in housing, care services, schools and so on) the social system stays in a relatively equilibrated state and there are no major problems. If the flux is too high in relation to the accommodation time of the system, the system will become sociologically unstable. Thus, the relationship between fluxes and accommodation times (or equilibration times, or relaxation times) is a feature of wider general interest than a particular thermodynamic model, and is certainly worth considering from a wider perspective [36].

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