

ENTROPY, ENTROPY FLUX, TEMPERATURE, AND SECOND LAW IN EXTENDED IRREVERSIBLE THERMODYNAMICS

David Jou

Grup de Física Estadística, Universitat Autònoma de Barcelona,
08193 Bellaterra, Catalonia, Spain
David.Jou@uab.cat

ABSTRACT

The formulation of the second law out of equilibrium implies several basic thermodynamic questions: a) the form of the entropy; b) the form of the entropy flux; c) the absolute temperature, and d) the concrete statement of the second law. Here, we illustrate these questions in the framework of extended irreversible thermodynamics, where fluxes are used as independent thermodynamic variables besides the classical variables. In this theory, the entropy and entropy flux depend on the several fluxes and are more general than their respective classical versions. This wider generality allows to explore for generalized transport equations including memory terms and non-local terms, which are not compatible with the local-equilibrium version of the second law, but whose consequences are experimentally observed.

INTRODUCTION

The second law was initially formulated by Clausius (1850) and Thomson (1851), in terms of impossibility of existence of some kind of engines or processes. Such reference to impossibility has been useful to extend the domain of applicability of thermodynamics to such surprising topics as black hole thermodynamics or quantum thermodynamics. The latter theories have been formulated by stating the impossibility of processes reducing the total area of black holes, in the first case, or increasing global quantum entanglement by means of local operations in the second one.

This way of formulating the second law is global in space and time: it refers to the globality of the system and to a whole process. Thus, it does not yield strong restrictions on specific parts of a process. For instance, it states that it is impossible to build a cyclic heat engine fully converting heat into work, but one may have full conversion of heat into work along an isothermal expansion of an ideal gas. Of course, in the total cyclic process this partial process is compensated by other parts, in such a way that, as a whole, only a part of heat may be converted into work.

In 1865, Clausius devised another way to formulate the second law, based on the definition of a new state quantity, called the entropy, defined in terms of the integral of heat reversibly exchanged over the absolute temperature. According to his formulation, in isolated systems processes increasing the total entropy are impossible (in other words, only those processes reducing or keeping constant the entropy are possible). Clausius entropy is defined only for equilibrium states, and his statement establishes whether it is possible in principle a process leading from an equilibrium state A to an equilibrium state B.

In 1872, Boltzmann related the entropy, a macroscopic quantity, to molecular disorder, a microscopic concept. In some occasions, attention to only a part of the system may be misleading. For instance, in a well-stirred solution of oil into water there are initially many oil droplets into water, but all these droplets aggregate in a single oil phase separated from the water phase. Apparently, this process goes from a more disordered state to a more ordered state. However, in fact this is not so, because the water molecules, not directly visible, have increased their global disorder, in such a way that the total disorder has indeed increased in the aggregation and separation process.

Thus, we see that the formulation of the second law in equilibrium has a global meaning, refers to equilibrium states, and must include all the relevant variables of the system. Going to non-equilibrium states leads to new challenges. One of the main aims of non-equilibrium thermodynamics is to analyze which transport equations are admissible according to the second law. This leads to restrictions on the sign of the transport coefficients, to relations between the several transport coefficients in coupled transport equations, and so on. Besides these restrictions coming from the second principle, one must add other restrictions arising from microscopic time reversibility, leading to the Onsager-Casimir reciprocity relations between linear coupled transport equations, established in 1931.

In general terms, going from equilibrium to non-equilibrium implies new problems: a) one is not dealing with equilibrium states, but with non-equilibrium states, which are not homogeneous and are, in general, time-dependent. This makes that a global description is not very illuminating, as we are precisely interested in the transfer of heat, mass, momentum and so on between different regions of the

system, in such a way that local features are needed, b) in non-equilibrium, many additional variables which do not play any role at equilibrium arise, and the choice of the variables necessary to describe the system is not clear a priori.

Thus, the formulation of the second principle in continuum non-equilibrium thermodynamics implies, at least, five basic questions [1-3]: a) the choice of variables; b) the form of the entropy; c) the form of the entropy flux; d) the meaning and form of absolute temperature [4,5]; and e) the concrete statement of the second law. Here we will discuss these topics.

LOCAL VERSUS GLOBAL, INSTANTANEOUS VERSUS HISTORICAL FORMULATIONS

In classical non-equilibrium thermodynamics, the first four questions are answered by taking for the mentioned quantities their corresponding usual form in equilibrium thermodynamics, but with a local –instead of a global– meaning, and the fifth question is stated as the positive definite character of the entropy production. Note, however, that this formulation of the second law is more restrictive than the classical formulation, which only refers to entropy in equilibrium states, and imposes that the entropy of the final equilibrium state is higher or equal than the entropy of the initial equilibrium state which, after a number of constraints acting on it have been removed, evolves to the final equilibrium state. In contrast, the idea that the local entropy production per unit time must be always positive or zero implies that between the initial and the final equilibrium states the entropy must increase at any time and in any region. This is a sufficient but not a necessary condition for the classical statement of the second law to be fulfilled. Some authors, as Meixner, tried thus to avoid the use of an entropy in the intermediate non-equilibrium states and tried to have less restrictive conditions for the second law.

In fact, there are several physical phenomena, as for instance thermal oscillations (in discrete systems) or thermal waves (in continuous systems) which are compatible with the classical form of the second law (as the total entropy of the final equilibrium state in a relaxation process towards equilibrium is higher than that of the initial state), but they are not compatible with the local-equilibrium version of the second law (as the total local-equilibrium entropy integrated over the whole system does not increase in a monotonic way, but it exhibits an undulatory approach, with alternating increasing and decreasing behaviours of the entropy).

Thus, several basic questions arise: 1) must these phenomena be forbidden, although they are allowed by the classical version of the second law? This is not so, of course, because they are observed. 2) If they are actually observed, must one abandon the idea of a local instantaneous statement of the second law? 3) Must one drop the idea of generalizing the concept of entropy to non-equilibrium states? 4) Does this imply that a thermodynamic theory of non-equilibrium steady states (where the concept of non-equilibrium state cannot be avoided) should be abandoned? Or, in contrast, should one abandon the local-equilibrium hypothesis, although it has been so useful and successful in so many physical situations? Probably, there is not a single set of reasonable answers to these several questions. Here, in particular, we propose to go beyond the local-equilibrium hypothesis by looking for more general versions of entropy for non-equilibrium states.

The local-equilibrium hypothesis is valid as far as the rate of change of the local variables is slow enough to reach local equilibrium. If the fluxes are too high, for instance, the energy arriving to the system will leave from it without having had time enough to distribute amongst the several degrees of freedom and the several particles according to the equilibrium distribution. Analogously, if the rate of change of variables of the system (for instance, the cooling rate, the reaction rate of the speed of a solidification front) is too high, the system has no time enough to reach internal thermal equilibrium. In this case, the local-equilibrium distribution will no longer be valid and some generalizations of it must be explored.

CHOICE OF STATE VARIABLES IN NON-EQUILIBRIUM STATES

Of course, many possibilities of additional variables arise when the system is in non-equilibrium. For instance, one can consider the rates of change of the classical variables, or the fluxes of the classical variables, or higher-order variables as for instance higher-order time derivatives or higher-order fluxes, or some internal variables related to the microstructure of the system, as for instance the configuration tensor or the polarization of polymeric molecules in polymer solutions. These variables vanish at equilibrium and therefore an entropy incorporating them should in principle reduce to the usual equilibrium entropy in equilibrium states. One of the possibilities of describing the system is to take into account the fluxes as additional variables, in such a way that higher values for the fluxes will imply a higher departure from local equilibrium.

The choice of variables is a relevant matter in non-equilibrium systems, and it depends on the relative values of the rates or frequencies of external perturbations and the reciprocal of the relaxation times of the several internal degrees of freedom of the system. The variables much faster than the external perturbation may be considered at equilibrium; the variables much slower will be frozen in values dependent on the initial conditions; and the interest of the researcher will be focused on the dynamics of those variables whose typical relaxation times are of the order of the rate of the external perturbations [6-8].

Another aspect of the choice of variables is between rates, fluxes, gradients, or internal variables. If one is interested in thermodynamics of non-equilibrium steady states, fluxes will be more useful than rates of change. Indeed, the latter vanish at steady states, whereas the fluxes indicate the rate of energy, matter, momentum and so on with the external world. Therefore, the fluxes provide essential information for non-equilibrium steady states. On the other side, if one is interested in a macroscopic description, where the fluxes are controlled parameters, the use of the fluxes will be more suitable than the use of internal variables which, instead, may be more useful if microscopic descriptions are sought for. The choice of variables will depend thus both on the time scales as on the particular interests and abilities of the observer.

In particular, the non-equilibrium thermodynamic theories taking the fluxes as independent variables are known as “extended thermodynamics” [9-14]. In extended thermodynamics, the questions mentioned in the introduction are given the following answers.

ENTROPY

The extended entropy is the local-equilibrium entropy plus a negative contribution proportional to the square of the fluxes; the corresponding coefficient is proportional to the relation time of the corresponding flux and inversely proportional to the respective transport coefficient; thus, the non-equilibrium contributions to the entropy are related to relaxational contributions to generalized transport equations. Two typical examples are: heat transport with non-vanishing relaxation time, in which the transport equation takes the form of the so-called Maxwell-Cattaneo equation

$$\tau \frac{dq}{dt} + q = -\lambda \nabla T \quad (1)$$

where λ is the thermal conductivity and τ the relaxation time of the heat flux. When the relaxation time is negligible, this equation reduces to the classical Fourier's equation. The corresponding extended entropy is

$$\mathfrak{S}(u, \mathbf{q}) = s_{\text{eq}}(u) - \frac{\tau}{2\lambda T^2} \mathbf{q} \cdot \mathbf{q} \quad (2)$$

with s_{eq} the local-equilibrium entropy.

Another typical situation is viscoelasticity, where a relaxational equation for the viscous pressure tensor is used, in the form

$$\tau \frac{d\mathbf{P}^v}{dt} + \mathbf{P}^v = -2\eta \mathbf{V} \quad (3)$$

or more general forms, taking more sophisticated kinds of time derivatives, as the corotational or the upper Maxwell convected ones. Here, η is the shear viscosity and \mathbf{V} is the symmetric part of the velocity gradient. When the perturbation of the flow is slow with respect to the time scale set by the relaxation time, the material behaves as a viscous fluid, and when they are fast it behaves as an elastic solid. The corresponding extended entropy has the form

$$\mathfrak{S}(u, c, \mathbf{P}^v) = s_{\text{eq}}(u, c) - \frac{\tau}{4\eta T} \mathbf{P}^v : \mathbf{P}^v \quad (4)$$

Note, in particular, that in both cases the transport equations as well as the entropy reduce to their classical forms when the relaxation times go to zero. Furthermore, as it will be commented below in more detail, the local production of the generalized entropy is always positive, whereas the production of the local-equilibrium entropy may be negative in some cases.

Eventually, note that when these expressions for the entropy are introduced into the Einstein equation for the probability of fluctuations, this extended entropy describes not only the second moments of the fluctuations of the classical variables but also the fluctuations of the corresponding fluxes [9-10]. This is a check of the physical interpretation of the non-equilibrium terms, and it shows that incorporating the fluxes in the description gives additional information on the system even in equilibrium situations, where the average value of the fluxes is zero but their fluctuations may be different from zero. In fact, the most

general versions of the fluctuation-dissipation theorem express the memory kernel of generalized transport equations in terms of the time-correlation function of the fluctuations of the corresponding dissipative fluxes (i.e the thermal conductivity in terms of the heat flux fluctuations; the shear viscosity in terms of the viscous pressure fluctuations, and so on). Thus, the interest on the dynamics of the fluxes is not something special of extended thermodynamics, but it is a general feature in modern non-equilibrium statistical physics.

ENTROPY FLUX

The entropy flux is the classical entropy flux plus a non-equilibrium contribution proportional to the product of the fluxes times their corresponding higher-order fluxes; thus, the non-equilibrium contribution is related to the non-local contributions appearing in generalized transport equations. A typical example is, for instance, the heat transport equation with relaxation terms and non-local terms, also known as Guyer-Krumhansl equation,

$$\tau \frac{dq}{dt} + q = -\lambda \nabla T + \ell^2 \nabla^2 q \quad (5)$$

with ℓ the mean free path. The entropy is still (2) but the entropy flux has the form

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} - \frac{\ell^2}{\lambda T^2} (\nabla q) \cdot \mathbf{q} \quad (6)$$

Another typical example is the equation for dilute gases as obtained from Grad's approach in the second-order approximation

$$\tau \frac{dq}{dt} + q = -\lambda \nabla T + \beta \nabla \cdot \mathbf{P}^v \quad (7)$$

$$\tau \frac{d\mathbf{P}^v}{dt} + \mathbf{P}^v = -2\eta \mathbf{V} + \beta \nabla q \quad (8)$$

In general, the relaxation times will be different for the different variables. The corresponding entropy is a combination of (2) and (4), namely,

$$\mathfrak{S}(u, c, \mathbf{P}^v) = s_{\text{eq}}(u, c) - \frac{\tau_1}{2\lambda T^2} \mathbf{q} \cdot \mathbf{q} - \frac{\tau_2}{4\eta T} \mathbf{P}^v : \mathbf{P}^v \quad (9)$$

and the entropy flux is

$$\mathbf{J}^s = \frac{\mathbf{q}}{T} + \beta \mathbf{P}^v \cdot \mathbf{q} \quad (10)$$

It is seen in Eqs. (6) and (10) that non-local terms, related to the gradients or divergences of other fluxes, are related to extra contributions of the generalized entropy flux.

TEMPERATURE

Absolute temperature, was defined by the first time by

Thomson in 1848, and set the basis for a universal material-independent foundations for thermodynamics. Absolute temperature is given by the reciprocal of the derivative of the entropy with respect to the internal energy (at constant values of the other extensive variables). When the extended entropy (2) is used instead of the local-equilibrium entropy, the resulting absolute temperature θ

$$\frac{1}{\theta} = \left(\frac{\partial s}{\partial u} \right)_{\mathbf{v}, \mathbf{q}} = \frac{1}{T} - \frac{1}{2} \left(\frac{\partial \alpha}{\partial u} \right) \mathbf{q} \cdot \mathbf{q} \quad (11)$$

with $\alpha = \tau/\lambda T^2$. It differs from the local-equilibrium temperature T and depends on the fluxes;. Several comments about (11) are in order. A) Relation (11) is purely formal unless a process of measuring it is specified. In equilibrium, all the many possible operational definitions of temperature lead to the same value, and all the thermometers will indicate it. However, this is not so out of equilibrium, where different kinds of thermometers yield different values for the temperature. In particular, the temperature defined in (1) may be related to the average kinetic energy of the particles in the plane perpendicular to the fluxes, and it is in general different from the “temperatures” of the other degrees of freedom, which may have different values [4, 9]. B) The fact that θ depends on T and \mathbf{q} may be checked by considering a heat conducting bar introduced between two systems at the same T , but one of them at equilibrium and the other one submitted to a steady heat flux. According to the classical irreversible thermodynamics, where

$$\mathbf{q} = -\lambda \nabla T, \quad (12a)$$

heat should not flow; however, in extended irreversible thermodynamics, where

$$\mathbf{q} = -\lambda \nabla \theta, \quad (12b)$$

heat should flow between them. For ideal gases it may be shown that $\theta < T$ and heat would flow from the system at equilibrium to the system in non-equilibrium steady state. C) In the kinetic theory of ideal gases, the absolute temperature is defined through the caloric equation of state relating the average kinetic energy to the absolute temperature

$$\frac{3}{2} k_B T = \langle \frac{1}{2} m \mathbf{C}^2 \rangle \quad (13)$$

where m is the mass of the particles and \mathbf{C} their peculiar velocity with respect to the barycentric mass. However, in the presence of a heat flow along the z direction, and up to the second order in the heat flux, it may be seen, from maximum-entropy arguments, that

$$\langle \frac{1}{2} m \mathbf{C}_x^2 \rangle = \langle \frac{1}{2} m \mathbf{C}_y^2 \rangle = \frac{1}{2} k_B \theta < \frac{1}{2} k_B T \quad (14a)$$

and

$$\langle \frac{1}{2} m \mathbf{C}_z^2 \rangle = \frac{1}{2} k_B (3\theta - 2T) > \frac{1}{2} k_B T \quad (14b)$$

in such a way that the usual definition of T is satisfied, but there is also a place for a non-equilibrium temperature.

This simple example shows that beyond local equilibrium, energy equipartition should not be expected in general, so

that different degrees of freedom may have different values of the temperature. One of the aims of a non-equilibrium thermodynamics of steady states should be to relate the temperatures for the different degrees of freedom when the total energy and energy flux are specified. It is not sufficient to formally define a non-equilibrium temperature through a relation like (11), but one must also identify under which physical conditions this temperature may be measured, and which is its relation with other temperatures of other degrees of freedom. Furthermore, since different kinds of thermometers have different sensitivities to different degrees of freedom, it is also important to be able to relate the temperatures measured by different kinds of thermometers. Thus, thermodynamics beyond local equilibrium is indeed a demanding task.

STATEMENT OF THE SECOND LAW

The second law is usually stated as the positive definite character of the entropy production. Depending on the kind of entropy being considered, the entropy production will have different forms and will yield different restrictions on the transport equations. In particular, this statement expressed in terms of the extended entropy allows several surprising features which are forbidden by the classical form of the second law: at short time scales and short spatial scales, for instance, heat may flow from lower to higher temperature [5]. Some of these features have been checked through thermal waves, or could be checked in systems with relatively long mean-free paths. For instance, in a heat transport equation with a relaxation term, the heat exchange between two small subsystems in thermal contact take the form of a damped oscillation. During some time intervals, heat is flowing from lower to higher temperature. This is against the local-equilibrium version of the second law but not against the classical version of the second law, because during the total equilibration process the net heat exchange from higher to lower temperature is higher than in the opposite direction [9-14].

An analogous situation of heat flowing in the opposite direction as allowed by the second law is found in phonon backscattering in rough-walled silicon nanowires, in a thin layer (the so-called Knudsen layer) close to the walls. From a microscopic perspective this may be understood, as phonons collide against the roughness peaks and they recede backwards. This reduces very much the effective thermal conductivity of the nanowire. This feature violates the local-equilibrium version of the second law, but not the classical version, because the net heat flux is against the temperature gradient, as it should be. A similar situation may be found in radial heat transport at short scales [15].

In both cases, the local-entropy production of the EIT entropy is positive everywhere, in contrast with the production of the local-equilibrium entropy. Thus, at small lengths and short times the formulation of a local and instantaneous version of the second law need a generalization of the entropy. Note that these situations seem, in principle, out of the reach of thermodynamic descriptions, because the number of collisions is very small. However, in steady states one may make many different measurements and a statistical description is possible. Particular situations could violate the positive definite character of the extended entropy production but, on the average, they are expected not to violate it. However, the average value could violate the positive character of the local-equilibrium entropy production.

Furthermore, one may use information theoretical arguments to obtain the expression for the entropy, subject to constraints on the average values of the classical variables and the fluxes [6, 9]. Such arguments also imply a statistical meaning. However, one could explore the ideas of algorithmic information theory, where information does not require a statistical description, but the minimum amount of information to describe a given physical situation. In this case, one could use thermodynamic concepts in situations beyond the usual ones.

CONCLUDING REMARKS

In this final section we briefly comment on some questions arising in non-linear and in non-Markovian situations and concerning the relation between the entropy and the Boltzmann H-function in non-equilibrium situations.

Non-linear transport equations

A problem of the application of the second law is its use for non-linear transport laws. In principle, the admissible laws are those yielding a positive entropy production. However, when this restriction is applied not to the full laws but to second or fourth-order approximation in the forces, the restrictions may be unsuitable, in the sense that they may require some coefficient to be zero although they are not truly zero. Indeed, the negative contribution of some second or fourth-order terms may be compensated by the positive contributions of higher-order terms. In this case of approximations to fully nonlinear laws, the second law may indicate, rather than a strict restriction on the coefficients, a bound on the domain of applicability of such approximations; thus, instead of setting restrictions on material properties (as it is usual in the linear domain) they may set limits on the processes to which such equations may be applicable.

Non-Markovian systems

Another topic of interest is the formulation of the second law for non-Markovian systems. In this case, the value of the variables of the system at time $t + \tau$ are a function not only of the values at time t , but also at time $t - \tau$ (and maybe other precedent times). Then, a description of the evolution of the system requires knowing not only the values at t but also at $t - \tau$, namely

$$X_i(t + \tau) = F[X_j(t), X_k(t - \tau)] \quad (15)$$

where X_i are the variables of the system, and $F[\dots]$, a suitable functional or differential equation. Therefore, the entropy should be expressed in terms not only of the variables at t but also at $t - \tau$, namely

$$S = S(X_j(t), X_k(t - \tau)) \quad (16)$$

When the difference between the values at time t and time $t - \tau$ is expanded up to the first order in τ , the fluxes or the rates of change arise in a natural way in the entropy. Higher-order fluxes or time derivatives appear if the expansion goes to second or higher orders in τ . The formalism of EIT has been also applied to some situations of this kind at a microscopic level, when the usual H function is not sufficient to account for the second law restrictions [9]. Non-Markovian transport

equations may also be expressed in terms of memory functions; the second-law restrictions on memory functions are an interesting topic in the so-called rational thermodynamics.

H-function and non-equilibrium entropy

Another topic of interest for our discussion is the relation between the microscopic H-function and the extended entropy. In equilibrium states, the H-function reduces to the thermodynamic entropy. Then, it is logical to ask what is the relation between both functions out of equilibrium. The H-function, described in terms of the microscopic distribution function, may be a functional of many variables, as for instance, of many moments of the distribution function, may higher-order fluxes, or many higher-order gradients of the hydrodynamic variables. But a thermodynamic description is deemed to use only a relatively small number of independent variables, having a macroscopic (or mesoscopic) limit. Thus, the H-function does not directly provide a truly thermodynamic entropy.

To have a thermodynamic entropy, one should project the entropy onto a space of a relatively small but sufficiently efficient and realistic set of variables. This may be done, but it is not sure that such a projected (or reduced) version of the entropy must have a positive entropy production. As a consequence, the H-theorem does not yield a deep basis to the formulations of the second law based on reduced entropies.

To be more explicit, consider that the non-equilibrium distribution function may be written as

$$f(\mathbf{r}, \mathbf{C}, t) = f_{eq}(\mathbf{r}, \mathbf{C}, t)[1 + \Phi] \quad (17)$$

with f_{eq} the equilibrium distribution function characterized by the local values of the thermodynamic parameters, and Φ a non-equilibrium contribution. Up to the second order in Φ , the "entropy" s obtained from the H-function has the form

$$s = s_{eq} - \frac{1}{2} k_B \int f_{eq} \Phi^2 d\mathbf{C} \quad (18)$$

It is seen that, in principle, s will differ from the local-equilibrium entropy s_{eq} . However, in view of (17) and (18), the practical success of the local-equilibrium version of the second law may be easily understood. Indeed, from a microscopic basis, the local-equilibrium hypothesis does not imply a local-equilibrium form for the microscopic distribution function, but a suitable non-equilibrium contribution Φ is needed; otherwise, because of symmetry reasons, the values of the fluxes (which are usually odd functions of the molecular velocity) would be zero. But, up to the first order in Φ , the entropy reduces to the local-equilibrium entropy, because the first-order contribution in Φ may be shown to vanish. Then, the use of a non-vanishing Φ in the calculation of the fluxes is compatible with the use of the local-equilibrium entropy. This consistency is lost when the equations for the fluxes, i.e. the transport equations, incorporate second-order terms, because in this case second-order terms should also be considered in the entropy.

When Grad's approach to the solution of the Boltzmann equation is used, i.e. when Φ is expressed in terms of the second or the third moments of the velocity distribution function for ideal gases, which are directly related to the

viscous pressure tensor or the heat flux, respectively, the expressions (4) and (2) for the entropy are obtained, and expression (10) for the entropy flux is also obtained, consistent with linear transport equations (7) and (8). However, the microscopic transport equations are in fact more general than (7) and (8), as they contain non-linear contributions.

The extended entropy production is positive for equations (7) and (8), but it may become negative when non-linear terms are taken into consideration. However, these negative contributions could be balanced by positive contributions arising from higher-order non-linear terms, but this would require a knowledge of all such terms. Eu [12] made an interesting proposal to deal with non-linear terms, which leads to a positive entropy production for relatively complex and useful generalizations of the transport equations (7) and (8). Otherwise, in Grad's approach –and also in Chapman-Cowling approach–, the positive character of the truncated entropy cannot be shown, in contrast to the positive character of the production of the H function.

ACKNOWLEDGMENTS

I acknowledge the support of the Spanish Ministry for Economía y Competitividad (MINECO) under grant FIS 2012-32099 and of Direcció General de Recerca of the Government of Catalonia, under grant 2009 SGR 164. Discussions with Profs G. Lebon and J. Casas-Vázquez along more than thirty years are warmly acknowledged.

NOMENCLATURE

k_B Boltzmann constant
 s entropy per unit mass
 \mathcal{J}^s entropy flux
 \mathbf{q} heat flux
 u internal energy per unit mass
 ρ mass density
 ℓ mean free path
 τ relaxation time
 η shear viscosity
 λ thermal conductivity
 \mathbf{X} variables of a system
 \mathbf{C} velocity of molecules
 \mathbf{V} velocity gradient
 \mathbf{P}^v viscous pressure tensor

REFERENCES

- [1] G. Lebon, D. Jou, J. Casas-Vázquez, Understanding non-equilibrium thermodynamics, Springer, Berlin, 2008.
- [2] S. Kjelstrup and D. Bedeaux, Non-equilibrium Thermodynamics of Heterogeneous Systems, World Scientific, Singapore, 2008.
- [3] H.C. Oettinger, Beyond Equilibrium Thermodynamics, Wiley, New York, 2005.
- [4] J. Casas-Vázquez and D. Jou, Temperature in non-equilibrium states: a review of open problems and current proposals, *Rep. Prog. Phys.* Vol 66, pp. 1937-2023, 2003.
- [5] W. Muschik, Aspects of Non-equilibrium Thermodynamics, World Scientific, Singapore, 1990.
- [6] R. Luzzi, A R Vasconcellos and J G. Ramos, Statistical foundations of irreversible thermodynamics, Teubner, Leipzig, 2001
- [7] D. Jou and L. Restuccia, Mesoscopic transport equations and contemporary thermodynamics, *Contemp Phys* vol. 52, pp. 465-474, 2011.
- [8] G. Lebon, D. Jou and J. Casas-Vázquez, Questions and answers about a thermo dynamic theory of the third type, *Contemp Phys* vol. 33, pp. 41- 51, (1992).
- [9] D. Jou, J. Casas-Vázquez and G. Lebon, Extended irreversible thermodynamics, Springer, Berlin, 2010, fourth edition.
- [10] D. Jou, J. Casas-Vázquez and M. Criado Sancho, Thermodynamics of Fluids under Flow, Springer Verlag, Berlin 2000.
- [11] I. Müller and T. Ruggeri, Rational extended thermodynamics, Springer, New York, 1997.
- [12] B. C. Eu, Kinetic theory and irreversible thermodynamics, Wiley, New York, 1992.
- [13] D.Y. Tzou, Macro to Micro-scale Transfer. The Lagging Behaviour, Taylor and Francis, New York, 1997.
- [14] M. S. Mongiovi and D. Jou, “Evolution equations in superfluid turbulence”, in *Condensed matter: new research*, M. P. Das, editor, Nova Publishers, Hauppauge, New York, 2006
- [15] A. Sellitto, V A Cimmelli and D Jou, Entropy flux and anomalous axial heat transport at the nanoscale, *Phys. Rev. B* Vol 87, 054302, 2013.
- [16] P. Galenko and D. Jou, “Diffuse-interface model for rapid phase transformation in nonequilibrium system”, *Phys. Rev. E* Vol. 71, 046125, 2005.