

# A Unified Extended Thermodynamic Description of Diffusion, Thermo-Diffusion, Suspensions, and Porous Media

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*It is shown that extended irreversible thermodynamics (EIT) provides a unified description of a great variety of processes, including matter diffusion, thermo-diffusion, suspensions, and fluid flows in porous media. This is achieved by enlarging the set of classical variables, as mass, momentum and temperature by the corresponding fluxes of mass, momentum and heat. For simplicity, we consider only Newtonian fluids and restrict ourselves to a linear analysis: quadratic and higher order terms in the fluxes are neglected. In the case of diffusion in a binary mixture, the extra flux variable is the diffusion flux of one the constituents, say the solute. In thermo-diffusion, one adds the heat flux to the set of variables. The main result of the present approach is that the traditional equations of Fick, Fourier, Soret, and Dufour are replaced by time-evolution equations for the matter and heat fluxes, such generalizations are useful in high-frequency processes. It is also shown that the analysis can be easily extended to the study of particle suspensions in fluids and to flows in porous media, when such systems can be viewed as binary mixtures with a solid and a fluid component. [DOI: 10.1115/1.2131087]*

## 1 Introduction

Nonequilibrium thermodynamics presents several faces; even though thermostatics, the science of equilibrium, is a unique and universal theory, this is not so with thermodynamics, whose purpose is the study of nonequilibrium processes. Actually, one can distinguish at least four main schools in thermodynamics: classical irreversible thermodynamics (CIT), rational thermodynamics (RT), extended irreversible thermodynamics (EIT), and GENERIC (general equation for nonequilibrium reversible irreversible coupling). Rational thermodynamics is a rather formal and sophisticated theory; it has known some success in the past, but now it is practically forgotten if one excepts a cluster of irreducible adherents. GENERIC is a rather recent formalism based on a Hamiltonian formulation of continuum thermomechanics, there remain indiscretions of youth still to be solved, and this is why we shall not examine it further in the present paper.

Our purpose is to present a unified description of several processes, including diffusion, thermo-diffusion, suspensions, and porous media in the framework of EIT. However, for pedagogical reasons, we shall preliminarily recall the main ingredients of CIT and apply it to the problem of thermo-diffusion in binary mixtures. Although CIT has been applied with success to a wide variety of phenomena, it suffers from some shortcomings that will be analyzed in the forthcoming. These deficiencies have been eliminated in EIT, which is a formalism that has met a growing interest during the last two decades and which will constitute the main part of this work.

The paper will run as follows: after briefly recalling the basic tenets of CIT in Sec. 2, we discuss in Sec. 3.1 the foundations underlying EIT. Applications to successive problems as thermo-

diffusion, suspensions, and porous media are treated in Secs. 3.2–3.4. Since diffusion is a particular case of thermo-diffusion, we shall not devote special attention to this kind of process. General conclusions and an evaluation of the respective merits of CIT and EIT are found in Sec. 4.

## 2 Classical Irreversible Thermodynamics

**2.1 General Considerations.** Thermostatics is the science describing homogeneous systems at equilibrium. To cover more general and more realistic situations as nonhomogeneous systems undergoing dissipation, one needs new formalisms, presently known under the name of thermodynamic theories of irreversible processes. The first and simplest approach of nonequilibrium is provided by CIT, which has been developed by Onsager (Nobel Prize in chemistry 1968) [1], Prigogine (Nobel Prize in chemistry 1977) [2], Meixner [3], DeGroot and Mazur [4], among others. The basic assumption of CIT is the *local equilibrium hypothesis*. Accordingly, the local and instantaneous relations between thermal and mechanical properties of a material system are the same as for a uniform body in equilibrium. As a consequence the set of state variables are the same as in equilibrium at the condition to express them locally, which means that they depend explicitly on time  $t$  and position in space  $\mathbf{x}$ . Another consequence is that all the relations established in thermostatics, such Gibbs, Gibbs-Duhem, etc., relations remain valid when formulated locally. This is important as it allows us to calculate explicitly the rate of entropy production  $\sigma$ , defined through the time evolution equation of entropy

$$\rho \dot{s} = -\nabla \cdot \mathbf{J}^s + \sigma. \quad (1)$$

In virtue of the second principle of thermodynamics,  $\sigma$  is a positive definite quantity. The other quantities introduced in (1) are: the mass density  $\rho$ , the specific entropy  $s$ , and the entropy flux vector  $\mathbf{J}$ , the entropy production term  $\sigma$  is referred per unit volume while an upper dot denotes the material time derivative  $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ . It is shown [1–4] that  $\sigma$  takes the form of a bilinear relation in so-called thermodynamic fluxes  $\mathbf{J}^\alpha$  and forces  $\mathbf{X}^\alpha$ :

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Contributed by the Applied Mechanics Division of ASME for publication in the JOURNAL OF APPLIED MECHANICS. Manuscript received May 18, 2004; final manuscript received October 5, 2005. Review conducted by B. A. Younis. Discussion on the paper should be addressed to the Editor, Prof. Robert M. McMeeking, Journal of Applied Mechanics, Department of Mechanical and Environmental Engineering, University of California - Santa Barbara, Santa Barbara, CA 93106-5070, and will be accepted until four months after final publication in the paper itself in the ASME JOURNAL OF APPLIED MECHANICS.

$$\sigma = \sum_{\alpha} \mathbf{J}^{\alpha} \mathbf{X}^{\alpha}. \quad (2)$$

These fluxes and forces are related by linear laws

$$\mathbf{J}^{\alpha} = \sum_{\beta} L^{\alpha\beta} \mathbf{X}^{\beta}, \quad (3)$$

indifferently called phenomenological or constitutive equations,  $L^{\alpha\beta}$  are the phenomenological coefficients relating the processes  $\alpha$  and  $\beta$ . These coefficients satisfy the celebrated Onsager-Casimir reciprocity relations [1,4]

$$L^{\alpha\beta} = \pm L^{\beta\alpha}, \quad (4)$$

while the coefficients with the same indices are positive ( $L^{\alpha\alpha} > 0$ ) in order to satisfy the positiveness of  $\sigma$ . Let us now illustrate these general considerations with the example of thermo-diffusion.

**2.2 Thermo-Diffusion in a Binary Mixture.** For simplicity, the analysis is restricted to a binary mixture formed by a solute (1) and a solvent (2), both constituents are in motion and are assumed to be incompressible Newtonian fluids. In virtue of the local equilibrium hypothesis, the basic thermodynamic variables are the same as in equilibrium, i.e.,  $\rho$ , the total mass density  $\rho_1 + \rho_2$ ,  $c (= \rho_1/\rho)$  the mass concentration of one of the components, say the solute, and the specific internal energy  $u$  (or the temperature  $T$ ). Of course, this set of variables must be complemented by the kinetic variable, the barycentric velocity  $\mathbf{v}$  defined by  $\mathbf{v} = (\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2)/\rho$ . The thermodynamic variables obey the following Gibbs relation, written in rate form as

$$\dot{s} = T^{-1} \dot{u} + T^{-1} p(1/\rho)' - T^{-1} \mu \dot{c}, \quad (5)$$

wherein  $p$  designates the pressure and  $\mu = \mu_1 - \mu_2$  the difference of the chemical potentials. To calculate the rate of entropy production, we need the expressions of the evolution equations of the variables  $c$  and  $u$ , the mass density remains constant because of incompressibility ( $\nabla \cdot \mathbf{v} = 0$ ); they take the form

$$\rho \dot{c} = -\nabla \cdot \mathbf{J}, \quad (6)$$

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} + \tau : (\nabla \mathbf{v})^{\text{sym}}, \quad (7)$$

wherein  $\mathbf{J} = \rho_1(\mathbf{v}_1 - \mathbf{v})$  is the diffusion flux of the solute and  $\tau$  the viscous symmetric stress tensor, superscript *sym* means the symmetric part of the corresponding tensor. By introducing (6) and (7) in the Gibbs equation (5) and by comparing with the balance Eq. (1) for  $s$ , we are able to derive the explicit expressions for the entropy flux  $\mathbf{J}^s$  and the entropy production  $\sigma$ :

$$\mathbf{J}^s = (\mathbf{q} - \mu \mathbf{J})/T, \quad (8)$$

$$\sigma = \mathbf{q} \cdot \nabla T^{-1} - \mathbf{J} \cdot \nabla(\mu/T) + T^{-1} \tau : (\nabla \mathbf{v})^{\text{sym}}, \quad (9)$$

the latter expression appearing as a bilinear relation in the fluxes  $\mathbf{q}$ ,  $\mathbf{J}$ ,  $\tau$ , and their conjugated forces  $\nabla T^{-1}$ ,  $\nabla(\mu/T)$ ,  $(\nabla \mathbf{v})^{\text{sym}}$ . Introducing a new heat flux

$$\mathbf{q}' = \mathbf{q} - (h_1 - h_2) \mathbf{J}, \quad (10)$$

where  $h_k (= u_k + p/\rho_k)$  is the specific enthalpy of constituent  $k$  and making use of the result

$$T \nabla (T^{-1} \mu_k) = -h_k T^{-1} \nabla T + (\nabla \mu_k)_T, \quad (11)$$

where subscript  $T$  refers to a quantity evaluated at constant temperature, it is found that (9) takes the form

$$T \sigma = -\mathbf{q}' \cdot \frac{\nabla T}{T} - \mu_{11} \mathbf{J} \cdot \frac{\nabla c}{c} + \tau : (\nabla \mathbf{v})^{\text{sym}}, \quad (12)$$

with  $\mu_{11} = \partial \mu_1 / \partial c$ . Invoking *Curie's principle* [4], which forbids coupling between fluxes and forces of different tensorial orders, expression (12) suggests the following flux-force relations:

$$\mathbf{q}' = -\lambda \nabla T - \frac{\rho \mu_{11} T}{c} D_F \nabla c, \quad (13)$$

$$\mathbf{J} = -\rho D_T \nabla T - \rho D \nabla c, \quad (14)$$

$$\tau = \eta (\nabla \mathbf{v})^{\text{sym}}, \quad (15)$$

wherein we have introduced the usual transport coefficients; namely, the coefficient of diffusion  $D$ , the Dufour coefficient  $D_F$ , the thermal diffusion coefficient  $D_T$ , and the dynamic shear viscosity  $\eta$ . Positivity of  $\sigma$  implies that  $\lambda > 0$ ,  $D > 0$ ,  $\eta > 0$ , whereas from Onsager's reciprocity property, it is deduced that

$$D_F = D_T. \quad (16)$$

This equality was first established by Stefan at the end of the 19th century and widely confirmed theoretically and experimentally during the 20th century. The results (13) and (14) reflect the well-known properties of Dufour and Soret effects and can be directly generalized to the case of a  $n$ -component mixture. In absence of coupling, (13) and (14) reduce to the classical laws of Fourier and Fick respectively:

$$\mathbf{q} = -\lambda \nabla T \text{ (Fourier)}, \quad \mathbf{J} = -\rho D \nabla c \text{ (Fick)}. \quad (17)$$

**2.3 Shortcomings of CIT.** Despite its successes, CIT presents several shortcomings that are now briefly discussed. First of all, it should be realized that CIT is in contradiction with the principle of causality demanding that an effect be perceived after the application of a cause. In CIT, the field equations take the form of a set of parabolic partial differential equations with the consequence that any perturbation will be felt instantaneously and everywhere inside the system. Indeed going back to Fourier's (or Fick's) law, it is directly seen that any temperature (or concentration) gradient gives rise instantaneously to a heat (or mass) flux throughout the whole system, from which follows that cause and effect are simultaneous, in opposition with causality requirement.

Second, CIT is a linear theory in fluxes and forces. Therefore, it is only applicable in the close vicinity of equilibrium and cannot be generalized to nonlinear situations as polymers, non-Newtonian fluids, or shock waves. Third, the validity of the Onsager relations has been acridly contested mainly by the RT school, indeed there is no explicit demonstration of the validity of the reciprocity relations at the macroscopic level; the only pseudodemonstration that is available rests on pure microscopic considerations and has also been the subject of severe criticisms. These are the main reasons that have prompted people to propose other formalisms. EIT, which is one of them, will be presented in the next section.

### 3 Extended Irreversible Thermodynamics (EIT)

**3.1 Generalities.** The basic idea in EIT is to extend the space of state variables by including the dissipative fluxes among the set of variables. Denoting by  $\mathbf{C}$  the ensemble of classical variables and by  $\mathbf{F}$  the flux variables, the space of state variables will be formed by the union of  $\mathbf{C}$  and  $\mathbf{F}$ :

$$\mathbf{V} = \mathbf{C} \cup \mathbf{F}. \quad (18)$$

In addition, it is postulated that there exists a nonequilibrium entropy that is a function of the whole set of variables [i.e.,  $s = s(\mathbf{V})$ ], it is worthwhile to stress that by doing so, we go beyond the local equilibrium hypothesis of CIT which implied that  $s = s(\mathbf{C})$ . To fulfil the requirement placed by second law of thermodynamics, it is admitted that the rate of entropy production  $\sigma$  is never negative:  $\sigma \geq 0$ .

The behavior in the course of time and in space of the classical variables  $\mathbf{C}$  is well known as it is governed by the classical balance equations of mass, momentum and energy. The open problem in EIT is to derive the time evolution equations for the flux variables  $\mathbf{F}$ : several approaches have been proposed [5,6] that are

either inspired by the method followed in CIT to obtain the phenomenological relations or by more general and sophisticated procedures as utilized in rational thermodynamics. Here, for the sake of uniformity, we have decided in favor of the technique used in CIT. Of course, these evolution equations for the flux variables cannot take any arbitrary form as they are subject to the restrictions placed by the second law and the general axioms of thermomechanics.

**3.2 Thermo-diffusion in Binary Mixtures.** As in Sec. 2, we shall consider diffusion in a mixture of two incompressible Newtonian fluids subject to a temperature gradient. The space of basic variables is formed by the union of the space  $\mathbf{C}$  of classical variables (mass concentration  $c$  of one of the constituents, internal energy  $u$  (or temperature  $T$ ), plus eventually the barycentric velocity  $\mathbf{v}$ ) and the space  $\mathbf{F}$  of the flux variables, here the flux of diffusion  $\mathbf{J}$  and the heat flux  $\mathbf{q}'$ . The corresponding Gibbs equation will take the form

$$\dot{s} = T^{-1}\dot{u} - T^{-1}\mu\dot{c} + \frac{\alpha}{\rho T}\mathbf{J} \cdot \dot{\mathbf{J}} + \frac{\beta}{\rho T}\mathbf{q}' \cdot \dot{\mathbf{q}}' \quad (19)$$

wherein, for simplicity, it has been assumed that  $\partial s / \partial \mathbf{J} = (\alpha / \rho T)\mathbf{J}$ ,  $\partial s / \partial \mathbf{q}' = (\beta / \rho T)\mathbf{q}'$  where  $\alpha$  and  $\beta$  are unknown phenomenological coefficients allowed to depend on  $c$  and  $T$ , coupling and nonlinear terms in the fluxes are neglected. To calculate the entropy flux and the entropy production, we follow the same procedure as in Sec. 2. We substitute the evolution equations of  $c$  and  $u$  in the above Gibbs relation and compare with the general evolution equation (1) of  $s$ , it is then found that the entropy flux is still given by its classical expression (8), while the entropy production reads as

$$T\sigma = -\mathbf{J} \cdot \left( \frac{\mu_{11}}{c} \nabla c + \alpha \mathbf{J} \right) - \mathbf{q}' \cdot \left( \frac{\nabla T}{T} + \beta \mathbf{q}' \right) + \tau : (\nabla \mathbf{v})^{\text{sym}}. \quad (20)$$

It is interesting to observe that the above relation is a bilinear expression in generalized fluxes and forces, the latter being the quantities appearing between brackets. Assuming linear flux-forces relations, one recovers at once Newton's law (15) between the stress and the symmetric velocity gradient tensors plus the missing evolution equations of  $\mathbf{q}'$  and  $\mathbf{J}$ , that can be given the form

$$\dot{\mathbf{J}} + \frac{1}{\alpha \rho \Delta} \mathbf{J} = -\frac{\mu_{11}}{\alpha c} \nabla c + \frac{\xi}{\alpha} \mathbf{q}', \quad (21)$$

$$\dot{\mathbf{q}}' + \frac{1}{\beta T \Lambda} \mathbf{q}' = -\frac{1}{\beta T} \nabla T + \frac{\gamma}{\beta} \mathbf{J}, \quad (22)$$

wherein  $\Lambda$ ,  $\gamma$ ,  $\Delta$ , and  $\xi$  are four supplementary phenomenological coefficients. In the case of time-independent processes, expressions (21) and (22) reduce to Dufour and Soret relations (13) and (14). This comparison is interesting as it allows us to identify the supplementary unknown coefficients introduced in (21) and (22). It is easily found that

$$\Lambda = \lambda - \frac{\rho T \mu_{11}}{c} \frac{D_F D_T}{D}, \quad \gamma = \frac{\mu_{11}}{c \Lambda} \frac{D_F}{D}, \quad (23)$$

$$\Delta = \frac{c}{\mu_{11}} D - T \frac{D_F D_T}{\lambda}, \quad \xi = \frac{D_T}{\lambda \Delta}.$$

The two remaining coefficients  $\alpha$  and  $\beta$  are related to the relaxation times  $\tau_J$  and  $\tau_q$  corresponding to the heat and mass fluxes respectively; indeed, referring to (21) and (22) these relaxation times are given, respectively, by

$$\tau_J = \alpha \rho \Delta, \quad \tau_q = \beta T \Lambda. \quad (24)$$

If these relaxation times can be determined either theoretically or experimentally, the above relations provide a direct means to evaluate  $\alpha$  and  $\beta$ .

It should also be observed that within a more general context, expressions (21) and (22) may contain extra contributions of the form  $\nabla \times \mathbf{J}$  and  $\nabla \times \mathbf{q}'$ , which do not contribute to the entropy production and represent so-called "gyroscopic" or "lift" forces.

In absence of coupling between thermal and matter transports, Eqs. (21) and (22) take the form of Cattaneo relations [7]:

$$\tau_J \dot{\mathbf{J}} + \mathbf{J} = -\rho D \nabla c, \quad (25)$$

$$\tau_q \dot{\mathbf{q}}' + \mathbf{q}' = -\lambda \nabla T, \quad (26)$$

which play an important role in high-frequency phenomena. It is true that the relaxation times  $\tau_J$  and  $\tau_q$  are generally very small in ordinary fluids and in homogeneous materials (of the order of the time between two successive collisions in gases) and are therefore negligible in a great majority of applications. For polymer solutions and nonhomogeneous materials as organic tissues they can be relatively large of the order of 1 to 100 sec. Equations of the form (21) and (22) or (25) and (26) are also useful in the description of suspensions and porous media, as briefly described in the forthcoming.

**3.3 Suspensions.** In the case of *suspensions* of solid rigid particles in a fluid at uniform temperature, a good choice for the extra flux variable is the particle diffusion flux  $\mathbf{J} = \rho c(1-c)(\mathbf{v}_p - \mathbf{v}_f)$  where  $c$  is the particle's mass fraction and indices  $p$  and  $f$  refer to the particles and the fluid, respectively. By following the same procedure as above, it has been shown that  $\mathbf{J}$  obeys a time-evolution equation of the form [8]

$$\dot{\mathbf{J}} + \frac{\mathbf{J}}{\tau_J} = -\omega \nabla \mu + \chi \nabla \cdot \boldsymbol{\tau} + \varsigma \nabla \cdot \boldsymbol{\tau}^* + O(\mathbf{J} \cdot \mathbf{J}), \quad (27)$$

where  $\omega$ ,  $\chi$ ,  $\varsigma$  are phenomenological coefficients, the second-order tensors  $\boldsymbol{\tau}$  and  $\boldsymbol{\tau}^*$  designate two viscous stress tensors; the first is related to the global convective motion and the second one to the relative motion of the particles and are given [8] by the following constitutive relations:

$$\boldsymbol{\tau} = \eta [\nabla(\mathbf{v} + \chi \mathbf{J})]^{\text{sym}}, \quad (28)$$

$$\boldsymbol{\tau}^* = \eta^* [\nabla(\varsigma \mathbf{J})]^{\text{sym}}, \quad (29)$$

with  $\eta$  and  $\eta^*$  two positive viscosity coefficients. Equation (28) is a generalization of Newton's law in presence of suspensions whereas (29) is typical of systems with suspensions. When nonlinear effects are taken into consideration, expression (27) becomes much more complicated [8] and the physical interpretation of the various phenomenological coefficients is a tedious task. To clarify their meaning, EIT is of no help and one must address to other theories like the kinetic theory or the internal variable theory [9]. In the case that coefficients  $\chi$  and  $\varsigma$  vanish, evolution equation (27) boils down to Cattaneo relation (25).

**3.4 Porous Media.** It is not unusual to model fluid motion through porous media as a binary system whose respective components are the fluid and the solid porous matrix, the latter being generally assumed to be rigid and at rest, so that its velocity  $\mathbf{v}_s = 0$ . As a flux variable, it is then rather natural to select the fluid diffusion flux  $\mathbf{J} = \rho_f(\mathbf{v}_f - \mathbf{v})$ . Following the same procedure as in the previous sections, it is easily shown [10] that  $\mathbf{J}$  obeys an evolution equation of the form

$$\dot{\mathbf{J}} = -\frac{\rho D}{\tau_J} \nabla c - \frac{1}{\tau_J} \mathbf{J}, \quad (30)$$

where  $D$  is a diffusion coefficient and  $\tau_J$  a relaxation time, nonlinear terms and thermal effects have been omitted. From the defi-

inition of  $\mathbf{J}$  and making use of the momentum equation

$$\rho \dot{\mathbf{v}} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{F}, \quad (31)$$

with  $\boldsymbol{\tau}$  the viscous stress tensor and  $\mathbf{F}$  the body force per unit mass, expression (30) will read as

$$\dot{\rho}_f(\mathbf{v}_f - \mathbf{v}_f) + \rho_f \dot{\mathbf{v}}_f - \frac{\rho_f}{\rho}(-\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{F}) = -\frac{\rho D}{\tau_J} \nabla c - \frac{\rho_f}{\tau_J}(\mathbf{v}_f - \mathbf{v}). \quad (32)$$

Introducing Newton's law and the result  $\mathbf{v}_f - \mathbf{v} = (\rho_s/\rho)\mathbf{v}_f$  in (32) leads to

$$\rho_f \dot{\mathbf{v}}_f = -\frac{\rho_f}{\rho} \nabla p - \frac{\rho_f}{\rho} \eta \nabla^2 \mathbf{v} + \rho_f \mathbf{F} - \frac{\rho_s \rho_f}{\rho \tau_J} \mathbf{v}_f, \quad (33)$$

where  $\eta$  is the dynamic viscosity of the fluid and where the term involving the diffusion coefficient has been omitted as it is generally negligible. Let us now introduce the permeability  $K$  of the porous medium and the effective viscosity  $\eta_{\text{eff}}$  defined respectively as

$$K = \frac{\tau_J \phi \eta}{\rho_s}, \quad \eta_{\text{eff}} = \frac{\rho_f \eta}{\rho \phi}, \quad (34)$$

where  $\phi$  designates the porosity of the medium; i.e., the ratio of the volume occupied by the fluid and the total volume. With this notation, Eq. (33) reads as

$$\rho \dot{\mathbf{v}}_f = -\nabla p - \frac{\eta}{K} \mathbf{u} + \eta_{\text{eff}} \nabla^2 \mathbf{u} + \rho \mathbf{F}, \quad (35)$$

wherein  $\mathbf{u} = \phi \mathbf{v}_f$  is the seepage velocity. In absence of body forces and under stationary conditions, one recovers the Brinkman relation

$$-\nabla p - \frac{\eta}{K} \mathbf{u} + \eta_{\text{eff}} \nabla^2 \mathbf{u} = 0. \quad (36)$$

It is clear that (36) reduces to Navier-Stokes equation for  $K \rightarrow \infty$  and to Darcy's relation

$$\nabla p = -\frac{\eta}{K} \mathbf{u} \quad (37)$$

for  $K/L^2 \ll 1$ , where  $L$  is a reference length scale. It follows from the above considerations that Darcy and Brinkman relations are particular cases of the evolution equation for the diffusion flux. Darcy's law is generally selected when the volume of the solid particles is larger than the volume occupied by the fluid; otherwise, Brinkman's law is preferred. It is also interesting to recall that  $\tau_J$  is of the order of the collision time between particles; i.e.,  $10^{-8}$  to  $10^{-13}$  s. Identification (34) indicates that the permeability  $K$  will be of the same order of magnitude, and this is indeed confirmed by experimental observations.

## 4 Conclusions

The aim of this paper is to convince the reader that extended irreversible thermodynamics (EIT) provides a valuable tool for studying a large variety of macroscopic processes. In the present work, four different situations have been analyzed: diffusion in binary systems, thermo-diffusion, suspensions, and flows through porous media. The central role played by the diffusion flux has been emphasized, it has in particular been shown that most of the relevant results in (thermo)diffusion, suspensions and porous media are derivable from one single relation: the time evolution equation of the mass flux. Such results attest of the simplicity and the universality of EIT.

When comparing EIT with CIT, the classical theory of irreversible processes [1–4], the following statements are worth pointing out.

- (i) The phenomenological relations obtained in CIT (for in-

stance, the Soret and Dufour expressions), are in EIT replaced by evolution equations for the mass and heat fluxes. EIT may be considered as a natural extension of CIT that is recovered when the relaxation times are going to zero.

- (ii) In CIT, the differential field equations are parabolic, whereas they are hyperbolic in EIT. The consequence is that the application of an arbitrary disturbance will result in a signal propagating at infinite velocity in CIT but at finite velocity in EIT. This is important because, in contrast with CIT, EIT is in full agreement with the principle of causality requiring that any effect will be felt after the application of the cause; in CIT, cause and effect are simultaneous.
- (iii) Because of the axiom of local equilibrium, the range of applications of CIT is restricted to linear and local processes, strictly speaking CIT is applicable to situations close to equilibrium. Such a constraint is not applicable to EIT, which encompasses nonlinear and nonlocal processes as it eliminates the local equilibrium hypothesis.
- (iv) It can be argued that one shortcoming of EIT is the presence of a rather large number of phenomenological coefficients. However as shown in Sec. 3.2, such a difficulty can be circumvented by comparing with experimental data and/or other theories, such as kinetic theory or statistical mechanics.

To summarize, it can be claimed that that main characteristics of EIT are simplicity and universality. The basic idea is to enlarge the space of variables by including the fluxes; the latter are well defined as they are the dissipative parts of the fluxes appearing in the classical balance equations. In some problems involving strong nonlocality, it may be necessary to introduce higher-order fluxes like the flux of the fluxes [5], but this does not generate fundamental difficulties. Universality of EIT has been proved though the large amount of applications treated during the two last decades and for which the present analysis provides only a restricted partial sample.

## Acknowledgment

Support from ESA through PRODEX VII and CIMEX II projects is acknowledged.

## Nomenclature

$D$	= diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$D_F$	= Dufour diffusion coefficient, $\text{m}^2 \text{s}^{-1} \text{K}^{-1}$
$D_T$	= Soret or thermal diffusion coefficient, $\text{m}^2 \text{s}^{-1} \text{K}^{-1}$
$\mathbf{J}$	= diffusion flux, $\text{kg m}^{-2} \text{s}^{-1}$
$\mathbf{J}^s$	= entropy flux, $\text{W m}^{-2} \text{s}^{-1}$
$K$	= permeability, $\text{m}^2$
$T$	= temperature, K
$c$	= mass concentration
$h$	= specific enthalpy, $\text{J kg}^{-1}$
$p$	= pressure, $\text{N m}^{-2}$
$\mathbf{q}$	= heat flux, $\text{W m}^{-2}$
$s$	= specific entropy, $\text{J kg}^{-1} \text{K}^{-1}$
$u$	= specific internal energy, $\text{J kg}^{-1}$
$\mathbf{u}$	= seepage velocity, $\text{m s}^{-1}$
$\mathbf{v}$	= velocity field, $\text{m s}^{-1}$

## Greek symbols

$\Lambda$	= phenomenological coefficient
$\alpha, \beta, \Delta, \gamma, \zeta$	= phenomenological coefficients
$\phi$	= porosity
$\eta$	= viscosity coefficient, $\text{N s m}^{-2}$
$\lambda$	= heat conductivity, $\text{W m}^{-1} \text{K}^{-1}$
$\mu$	= chemical potential, $\text{J kg}^{-1}$
$\xi$	= phenomenological coefficient



$\rho$  = mass density, kg m<sup>-3</sup>  
 $\varsigma$  = phenomenological coefficient  
 $\sigma$  = rate of entropy production per unit volume, W K<sup>-1</sup> m<sup>-3</sup>  
 $\tau$  = stress tensor, N m<sup>-2</sup>  
 $\tau_j, \tau_q$  = relaxation times, s  
 $\chi, \omega$  = phenomenological coefficients

#### Subscripts

eff = effective  
 f = fluid  
 s = solid

#### Superscripts

· (upper dot) = time derivative  
 sym = symmetric part of a tensor

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