

An extended thermodynamics modeling of non-Fickian diffusion

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Abstract

The problem of non-Fickian diffusion in a two-component mixture at uniform temperature is studied in the framework of extended irreversible thermodynamics (EIT). The basic idea underlying this formalism is to complement the space of classical variables (here the mass density, mass concentration and barycentric velocity) by dissipative fluxes (here the diffusion flux). The evolution equation for this extra variable is derived by using the Lagrange multipliers method of Liu. After solving the problem in the case of the linear regime, we extend our analysis to a non-linear situation. In the linear case, one recovers the classical Fick's law and the Cattaneo–Maxwell equation for the diffusion flux. In the non-linear case, our results are comparable with those obtained by using a Hamiltonian formalism. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of heat and mass transfers is of primary importance not only at the fundamental level but also in applied sciences. It is crucial in problems concerned with diffusion of polymers, flows through porous media and the description of liquid helium. In these situations, the classical diffusion laws of Fick and Fourier, relating linearly the mass (temperature) gradient to the mass (heat) flux, are generally not applicable. Although these laws hold under normal circumstances, they lead to some unacceptable results such as the propagation of perturbations at infinite velocity. Moreover, they are generally not useful for describing processes at high frequencies and diffusion in polymer solutions. Therefore, there is a need for finding a better formulation. In the past, several models have been proposed, but they are rather disperse, without sensitive links between them and only applicable in rather limited ranges. More recently and independently, two general formalisms have been proposed with the aim to go beyond the classical description: these are essentially the extended irreversible thermodynamics (EIT) [1–3] and the general equation for the non-equilibrium reversible–irreversible coupling (GENERIC) [4,5], a recent revisited

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version of the so-called Hamiltonian non-equilibrium description advocated some years ago by Grmela and his collaborators [6–8].

In the present work, we propose an EIT formulation of the problem of matter diffusion in a binary mixture of ideal fluids; by ideal fluids are understood a class of fluids chemically inert, characterized by absence of heat and viscous effects. Our results will be compared with those obtained recently by using the GENERIC formalism. The coupling of matter flow and thermal transport will be investigated in a future work.

A natural set of state variables allowing to describe a two-component fluid mixture is constituted by

$$\rho_1, \rho_2, \mathbf{v}_1, \mathbf{v}_2, \quad (1)$$

wherein ρ_i and \mathbf{v}_i designate the mass density and velocity of constituent i , respectively ($i=1, 2$); ρ_1 represents for instance the mass density of polymer molecules and ρ_2 the mass density of the solvent. However, instead of set (1), it is equivalent to work with

$$\rho, c, \mathbf{v}, \mathbf{J}, \quad (2)$$

wherein ρ , c , \mathbf{v} , and \mathbf{J} are the total mass density, the concentration of component 1, the barycentric velocity and the mass diffusion flux of constituent 1, respectively. These quantities are defined by

$$\rho = \rho_1 + \rho_2, \quad (3)$$

$$c = \frac{\rho_1}{\rho}, \quad (4)$$

$$\rho \mathbf{v} = \rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2, \quad (5)$$

$$\mathbf{J} = \rho_1 (\mathbf{v}_1 - \mathbf{v}). \quad (6)$$

It is interesting to observe that the variable \mathbf{J} is typical of an EIT description. Indeed, in EIT, the set of variables is formed by the union of the classical, slow and conserved variables (here ρ , c , \mathbf{v}) and flux variables (here \mathbf{J}) which, in contrast to the classical ones, are usually fast and non-conserved. It is therefore clear that set (2) enters naturally within an EIT description.

Having in a first step defined the set of variables, it is necessary in a second step to establish the corresponding evolution equations. Concerning the classical ones, they are given by the usual balances of mass, concentration and momentum, namely

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}, \quad (7)$$

$$\rho \frac{dc}{dt} = -\nabla \cdot \mathbf{J}, \quad (8)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla p - \nabla \cdot \left(\frac{\mathbf{J}\mathbf{J}}{\rho c(1-c)} \right), \quad (9)$$

wherein d/dt denotes the material time derivative, p is the pressure, and where $\mathbf{J}\mathbf{J}$ is the dyadic product of the vectors \mathbf{J} and \mathbf{J} . The last term in (9) arises as a consequence of diffusion [9,10] and will of course be neglected in a linear approach. It remains to determine the evolution equation for the diffusion flux \mathbf{J} and this represents the main original contribution of the present work.

We shall organize our work as follows. In Section 2, we first examine the linear problem; this is motivated by pedagogical reasons and to make clear our methodology. Afterwards, in Section 3, we propose a non-linear extension and compare the results with a similar description performed by using GENERIC.

2. Linear analysis

The central idea in EIT is to assume that the flux variable — here the mass flux — obeys an evolution equation of the same type as the classical variables, i.e.

$$\rho \frac{d\mathbf{J}}{dt} = -\nabla \cdot \mathbf{J}^J + \boldsymbol{\sigma}^J, \quad (10)$$

with \mathbf{J}^J being the flux of the diffusion flux, a tensor of rank 2, and $\boldsymbol{\sigma}^J$, a source term, being a vectorial quantity. At this stage of the analysis, neither \mathbf{J}^J nor $\boldsymbol{\sigma}^J$ are known and they must therefore be expressed in terms of the state variables (2) through appropriate constitutive equations. Within the linear approximation, these are simply given by

$$\mathbf{J}^J = A(\rho, c)\mathbf{I}, \quad (11)$$

$$\boldsymbol{\sigma}^J = -\frac{\rho}{\tau(\rho, c)}\mathbf{J}, \quad (12)$$

wherein \mathbf{I} is the identity tensor while A and τ are unspecified functions of ρ and c ; the minus sign and the factor ρ in the r.h.s. of (12) have been introduced for convenience. Substituting (11) and (12) in (10) results in

$$\rho \frac{d\mathbf{J}}{dt} = -\nabla A - \frac{\rho}{\tau}\mathbf{J}. \quad (13)$$

An important point is that the above results must comply with the second principle of thermodynamics which can be written as

$$\sigma^s = \rho \frac{ds}{dt} + \nabla \cdot \mathbf{J}^s \geq 0, \quad (14)$$

where s is the entropy per unit mass, \mathbf{J}^s the entropy flux and where σ^s is the entropy production per unit volume. The entropy s as well as \mathbf{J}^s must be expressed by means of constitutive equations:

$$s = s(\rho, c, \mathbf{J}), \quad \mathbf{J}^s = \mathbf{J}^s(\rho, c, \mathbf{J}), \quad (15)$$

wherein the velocity field does not appear explicitly since s and \mathbf{J}^s are typically thermodynamical variables. At the first order in \mathbf{J} , we will write for \mathbf{J}^s

$$\mathbf{J}^s = \alpha(\rho, c)\mathbf{J}, \quad (16)$$

where $\alpha(\rho, c)$ is an undetermined coefficient.

Since the temperature is fixed, it is convenient to work with the Helmholtz free energy f rather than s ; both quantities are related by

$$f = u - T_0 s, \quad (17)$$

with u being the internal energy density and T_0 being the uniform temperature. In terms of f , entropy inequality (14) takes on the form

$$\sigma^s \equiv -\rho \frac{df}{dt} - p \nabla \cdot \mathbf{v} + T_0 \nabla \cdot \mathbf{J}^s \geq 0, \quad (18)$$

wherein use has been made of the internal energy balance law

$$\rho \frac{du}{dt} = -p \nabla \cdot \mathbf{v}. \quad (19)$$

Before exploiting inequality (18), it must be observed that the latter will not hold for all of the set of variables ρ , c , \mathbf{v} and \mathbf{J} but only for the solutions of the balance laws of mass, concentration, momentum and diffusion flux. That means that we can consider the balance laws as constraints for the entropy inequality to hold. To take these constraints into account is a difficult task and will lead to rather intricate calculations. An elegant way to circumvent this difficulty was proposed by Liu [11]: he was able to show that the entropy inequality becomes completely arbitrary at the condition to complement inequality ((14) or (18)) with a linear combination of the balance laws. The factors multiplying the balance equations are called Lagrange multipliers by analogy with the extremization problem with constraints, although the present situation is not strictly a problem of extremals.

To be explicit, the entropy inequality will be formulated in such a way that the constraints imposed by the balance equations (7)–(9) and (13) are explicitly introduced via the so-called Lagrange multipliers λ_1 , λ_2 , λ_3 , λ_4 : instead of (18), we will therefore write the following inequality:

$$\begin{aligned} & -\rho \frac{df}{dt} - p \nabla \cdot \mathbf{v} + T_0 \nabla \cdot \mathbf{J}^s + \lambda_1 \left(\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} \right) + \lambda_2 \left(\rho \frac{dc}{dt} + \nabla \cdot \mathbf{J} \right) \\ & + \lambda_3 \cdot \left(\rho \frac{d\mathbf{J}}{dt} + \nabla A + \frac{\rho}{\tau} \mathbf{J} \right) + \lambda_4 \cdot \left(\rho \frac{d\mathbf{v}}{dt} + \nabla p \right) \geq 0, \end{aligned} \quad (20)$$

which must hold for all field variables. The Lagrange multipliers λ_1 , λ_2 , λ_3 , λ_4 are unknown quantities that may depend on all the variables. Relation (20) can still be expressed as

$$\begin{aligned} & \frac{d\rho}{dt} (\lambda_1 - \rho f_\rho) + \rho \frac{dc}{dt} (\lambda_2 - f_c) + \rho \frac{d\mathbf{J}}{dt} \cdot (\lambda_3 - \mathbf{f}_J) + \frac{d\mathbf{v}}{dt} \cdot (\rho \lambda_4) + \nabla \rho \cdot (A_\rho \lambda_3 + T_0 \alpha_\rho \mathbf{J}) \\ & + \nabla c \cdot (A_c \lambda_3 + T_0 \alpha_c \mathbf{J}) + \nabla \cdot \mathbf{J} (\lambda_2 + T_0 \alpha) + \nabla \cdot \mathbf{v} (\rho \lambda_1 - p) + \frac{\rho}{\tau} \lambda_3 \cdot \mathbf{J} + \lambda_4 \cdot \nabla p \geq 0, \end{aligned} \quad (21)$$

wherein the notation $X_y = \partial X / \partial y$ ($y = \rho, c, \mathbf{J}$) has been used. Observe that inequality (21) is linear in the time and space derivatives of the basic variables. Since it must be satisfied for all fields ρ , c , \mathbf{v} , \mathbf{J} , it must in particular hold for arbitrary values of their derivatives. This means that positiveness of (21) could be violated unless we impose that all factors of the derivatives vanish identically. This leads to the conditions

$$\lambda_1 = \rho f_\rho = \frac{p}{\rho}, \quad (22)$$

$$\lambda_2 = f_c = \mu^0, \quad (23)$$

$$\lambda_3 = \mathbf{f}_J, \quad (24)$$

$$\lambda_4 = 0, \quad (25)$$

$$A_\rho \boldsymbol{\lambda}_3 + T_0 \alpha_\rho \mathbf{J} = 0, \quad (26)$$

$$A_c \boldsymbol{\lambda}_3 + T_0 \alpha_c \mathbf{J} = 0, \quad (27)$$

$$\alpha = -\frac{\lambda_2}{T_0}, \quad (28)$$

while the remaining term left in (21) is

$$\sigma^s \equiv \frac{\rho}{\tau} \boldsymbol{\lambda}_3 \cdot \mathbf{J} \geq 0. \quad (29)$$

As usual, we have defined the mixture chemical potential by $\mu^0 = f_c$, where μ^0 stands for the difference $(\mu^0)_1 - (\mu^0)_2$ of the chemical potentials of both constituents.

The relations (22)–(25) allow to identify the Lagrange multipliers. From (23) and (28), one obtains for the entropy flux

$$\mathbf{J}^s = -\frac{\mu^0}{T_0} \mathbf{J}, \quad (30)$$

which is the well-known result of classical irreversible thermodynamics [12]. Moreover, by using (26)–(28), we can reformulate the evolution (13) for the diffusion flux \mathbf{J} . Indeed, by introducing expression (28) in the relations (26) and (27), and identifying the two expressions for $\boldsymbol{\lambda}_3$, it is found that

$$\frac{1}{A_\rho} \mu_\rho^0 = \frac{1}{A_c} \mu_c^0. \quad (31)$$

Moreover, omitting non-linear terms in \mathbf{J} , μ^0 will only depend on ρ and c from which it follows that

$$\nabla \mu^0 = \mu_\rho^0 \nabla \rho + \mu_c^0 \nabla c; \quad (32)$$

multiplying this relation by A_c/μ_c^0 , one obtains

$$\frac{A_c}{\mu_c^0} \nabla \mu^0 = A_\rho \nabla \rho + A_c \nabla c \equiv \nabla A \quad (33)$$

after use is made of (31). Substituting this result in (13) yields for \mathbf{J} an evolution equation of the Cattaneo–Maxwell type, i.e.

$$\tau \frac{d\mathbf{J}}{dt} = -D \nabla \mu^0 - \mathbf{J}, \quad (34)$$

where D is given by

$$D = \frac{\tau}{\rho} \frac{A_c}{\mu_c^0}. \quad (35)$$

For τ tending to 0 and D finite, relation (34) reduces to

$$\mathbf{J} = -D \nabla \mu^0, \quad (36)$$

which is equivalent to Fick's classical law

$$\mathbf{J} = -D' \nabla c, \quad (37)$$

when ρ is constant and D' is given by

$$D' = \mu_c^0 D, \quad (38)$$

showing that the coefficient D is directly related to the diffusion coefficient D' .

Hitherto, we have no information about the signs of τ and D . There is no difficulty in expressing the Lagrange multiplier λ_3 in terms of the coefficient D : from (23), (27), (28) and (35), it is checked that

$$\lambda_3 = \frac{\tau}{\rho D} \mathbf{J}, \quad (39)$$

so that the residual dissipation inequality (29) reads as

$$\frac{J^2}{D} \geq 0, \quad (40)$$

with, as a direct consequence, the positiveness of the parameter D . Moreover, since f must be minimum at equilibrium at constant ρ and c , its expansion around equilibrium (i.e. $\mathbf{J}=0$) will result in

$$\Delta f = f(\rho, c, \mathbf{J}) - f_{\text{eq}}(\rho, c) = \frac{1}{2} \left(\frac{\partial^2 f}{\partial \mathbf{J} \cdot \partial \mathbf{J}} \right)_{\text{eq}} \mathbf{J} \cdot \mathbf{J} > 0, \quad (41)$$

with, as a consequence of (24),

$$\frac{\partial^2 f}{\partial \mathbf{J} \cdot \partial \mathbf{J}} = \frac{\tau}{\rho D}. \quad (42)$$

In view of this result, it is inferred from (41) that τ is a positive quantity:

$$\tau > 0, \quad (43)$$

so that we are allowed to identify τ with the positive relaxation time.

Collecting the above results, we are able to formulate the generalized Gibbs' equation in the form

$$df = f_c dc + f_\rho d\rho + f_J \cdot d\mathbf{J} = \mu^0 dc - \frac{p}{\rho^2} d\rho + \frac{\tau}{\rho D} \mathbf{J} \cdot d\mathbf{J}, \quad (44)$$

wherein the equality of the mixed derivatives $\partial^2 f / \partial c \partial \mathbf{J}$ shows that, within the linear order of approximation, the coefficient $\tau / \rho D$ is constant. Compared to classical irreversible thermodynamics [12], the Gibbs' equation (44) contains a supplementary term in $d\mathbf{J}$ which vanishes as τ tends to 0.

Under the following conditions: τ tending to infinity, absence of global motion ($\mathbf{v}=0$), ρ and D'/τ constant, one obtains, after elimination of \mathbf{J} between (8) and (34), an evolution equation for the conserved variable c , namely

$$\frac{\partial^2 c}{\partial t^2} - \frac{D'}{\rho \tau} \nabla^2 c = 0, \quad (45)$$

which is a wave equation with a propagation velocity given by

$$v^2 = \frac{D'}{\rho \tau}. \quad (46)$$

This result is interesting as it exhibits the wave-like property of Eq. (34).

In conclusion, we have established an evolution equation (34) for the diffusion flux which reduces to Fick's law when the positive relaxation time τ tends to 0; we have also proved that the ratio $\tau/\rho D$ is independent of the concentration of the mixture and that τ and D are positive. It must be realized that expressions for τ and D cannot be derived from the above phenomenological formalism: they should either be determined from microscopic theories or experimental observations. In the next section, we will generalize the above technique to the non-linear regime.

3. Non-linear analysis

We extend the formulation developed in the previous section by allowing in the constitutive equations for \mathbf{J}^J , $\boldsymbol{\sigma}^J$ and \mathbf{J}^s for the presence of non-linear terms in the diffusion flux \mathbf{J} . Instead of the linear expressions (11), (12), (16), we will, respectively, write the following constitutive equations:

$$\mathbf{J}^J = A(\rho, c)\mathbf{I} + B(\rho, c)J^2\mathbf{I} - E(\rho, c)\mathbf{J}\mathbf{J}, \quad (47)$$

$$\boldsymbol{\sigma}^J = -\frac{\rho}{\tau}\mathbf{J}, \quad (48)$$

$$\mathbf{J}^s = \alpha(\rho, c)\mathbf{J} + \beta(\rho, c)J^2\mathbf{J}. \quad (49)$$

We have introduced a minus sign in the r.h.s. of (47) for convenience and omitted higher order terms in the expression of $\boldsymbol{\sigma}^J$ as they would contribute to terms, at least of order J^3 , in the evolution equation for \mathbf{J} ; for simplicity, we keep only quadratic terms in the fluxes in the evolution equations.

The next task consists of reformulating the entropy inequality. Introducing the relations (47)–(49) in the dissipation inequality (18), one obtains after making use of the so-called Lagrange multipliers technique of Liu

$$\begin{aligned} \sigma^s \equiv & \frac{d\rho}{dt}(\lambda_1 - \rho f_\rho) + \rho \frac{dc}{dt}(\lambda_2 - f_c) + \rho \frac{d\mathbf{J}}{dt} \cdot (\boldsymbol{\lambda}_3 - \mathbf{f}_J) + \rho \frac{d\mathbf{v}}{dt} \cdot (\boldsymbol{\lambda}_4) \\ & + \nabla \mathbf{J} : [2T_0\beta\mathbf{J}\mathbf{J} + (2B - E)\boldsymbol{\lambda}_3\mathbf{J}] + \boldsymbol{\lambda}_4 \cdot \left[\nabla p + \nabla \cdot \left(\frac{\mathbf{J}\mathbf{J}}{\rho c(1-c)} \right) \right] \\ & + \nabla \rho \cdot [(A_\rho + B_\rho J^2)\boldsymbol{\lambda}_3 + T_0(\alpha_\rho + \beta_\rho J^2)\mathbf{J} - E_\rho\boldsymbol{\lambda}_3 \cdot \mathbf{J}\mathbf{J}] + \nabla c \cdot [(A_c + B_c J^2)\boldsymbol{\lambda}_3 \\ & + T_0(\alpha_c + \beta_c J^2)\mathbf{J} - E_c\boldsymbol{\lambda}_3 \cdot \mathbf{J}\mathbf{J}] + \nabla \cdot \mathbf{J}[\lambda_2 + T_0(\alpha + \beta J^2) - E\boldsymbol{\lambda}_3 \cdot \mathbf{J}] \\ & + \nabla \cdot \mathbf{v}(\rho\lambda_1 - p) + \frac{\rho}{\tau}\boldsymbol{\lambda}_3 \cdot \mathbf{J} \geq 0. \end{aligned} \quad (50)$$

Since this expression is linear in $d\rho/dt$, dc/dt , $d\mathbf{J}/dt$ and $d\mathbf{v}/dt$, the Lagrange multipliers λ_1 , λ_2 , $\boldsymbol{\lambda}_3$, $\boldsymbol{\lambda}_4$ can directly be identified and given by

$$\lambda_1 = \rho f_\rho = \frac{p}{\rho}, \quad \lambda_2 = f_c, \quad \boldsymbol{\lambda}_3 = \mathbf{f}_J, \quad \boldsymbol{\lambda}_4 = 0. \quad (51)$$

In addition, as inequality (50) is linear in $\nabla \rho$, ∇c , $\nabla \cdot \mathbf{J}$ and $\nabla \mathbf{J}$, their coefficient should vanish identically, which results in

$$(A_\rho + B_\rho J^2)\boldsymbol{\lambda}_3 + T_0(\alpha_\rho + \beta_\rho J^2)\mathbf{J} - E_\rho\boldsymbol{\lambda}_3 \cdot \mathbf{J}\mathbf{J} = 0, \quad (52)$$

$$(A_c + B_c J^2)\boldsymbol{\lambda}_3 + T_0(\alpha_c + \beta_c J^2)\mathbf{J} - E_c\boldsymbol{\lambda}_3 \cdot \mathbf{J}\mathbf{J} = 0, \quad (53)$$

$$\lambda_2 + T_0(\alpha + \beta J^2) - E\lambda_3 \cdot \mathbf{J} = 0, \quad (54)$$

$$2T_0\beta\mathbf{J}\mathbf{J} + (2B - E)\lambda_3\mathbf{J} = 0. \quad (55)$$

The remaining term left in (50) is simply

$$\sigma^s \equiv \frac{\rho}{\tau}\lambda_3 \cdot \mathbf{J} \geq 0. \quad (56)$$

As in the previous section, we define the chemical potential by $\mu = f_c$ but we allow μ to depend quadratically on \mathbf{J} so that

$$\mu = \mu^0(\rho, c) + \mu^1(\rho, c)J^2, \quad (57)$$

with μ^0 and μ^1 being arbitrary coefficients depending on ρ and c ; we can thus express the Lagrange multiplier λ_2 in the form

$$\lambda_2 = \mu^0 + \mu^1 J^2. \quad (58)$$

Omitting third-order contributions in \mathbf{J} , the Lagrange multiplier λ_3 will be written as

$$\lambda_3 = a(\rho, c)\mathbf{J}, \quad (59)$$

so that (56) becomes

$$\sigma^s \equiv \frac{\rho}{\tau}aJ^2 \geq 0. \quad (60)$$

with $a(\rho, c)$ being an undetermined coefficient.

The generalized Gibbs' equation

$$df = f_\rho d\rho + f_c dc + f_J \cdot d\mathbf{J}$$

can now be cast in the explicit form

$$df = \frac{p}{\rho^2} d\rho + (\mu^0 + \mu^1 J^2) dc + a\mathbf{J} \cdot d\mathbf{J}. \quad (61)$$

Let us exploit this equation. In virtue of the equality of the mixed derivatives $\partial^2 f / \partial c \partial \mathbf{J}$, μ^1 is related to a_c by

$$\mu^1 = \frac{a_c}{2}. \quad (62)$$

Moreover, stability of equilibrium demands that the Helmholtz potential f is minimum at equilibrium, i.e. around $\mathbf{J}=0$, from which it follows that

$$\Delta f = \frac{1}{2} \left(\frac{\partial^2 f}{\partial J^2} \right)_{\text{eq}} J^2 = \frac{1}{2} a J^2 > 0, \quad (63)$$

and, as a direct consequence,

$$a > 0. \quad (64)$$

It should also be noticed that the above result could as well have been drawn from the property that the entropy s is a convex function of the state variables; as shown elsewhere [9], the convexity property is

equivalent to require that the field equations are hyperbolic. Combining the result (64) with the property of positiveness of entropy (60), it is found that

$$\tau > 0, \quad (65)$$

which allows to identify the parameter τ with the positive relaxation time as in the previous section.

Let us now make use of the identities (54) and (55) in order to reformulate the constitutive equation for the entropy flux (49). Taking the trace of the tensor (55), one obtains

$$2T_0\beta J^2 = (E - 2B)\lambda_3 \cdot \mathbf{J}, \quad (66)$$

while relation (54) can be written as

$$\alpha = -\frac{\lambda_2}{T_0} + \frac{E + 2B}{2T_0}\lambda_3 \cdot \mathbf{J}. \quad (67)$$

Using the expressions (58) and (59) of the Lagrange multipliers λ_2 and λ_3 , we obtain the next results for the coefficients α and β :

$$\beta = \frac{a}{2T_0}(E - 2B), \quad (68)$$

$$\alpha = -\frac{\mu^0}{T_0} + \frac{1}{2T_0}[(E + 2B)a - 2\mu^1]J^2. \quad (69)$$

As $\alpha(\rho, c)$ is by definition independent of \mathbf{J} , the term between brackets in (69) must vanish, from which follows a relation between B and E , namely

$$2B = -E + 2\frac{\mu^1}{a}, \quad (70)$$

while α is simply given by

$$\alpha = -\frac{\mu^0}{T_0}. \quad (71)$$

Substituting (70) in (68) allows us to write the parameter β as

$$\beta = \frac{a}{T_0} \left(E - \frac{\mu^1}{a} \right). \quad (72)$$

Having determined expressions (71) and (72) for α and β , the entropy flux will take the final form

$$\mathbf{J}^s = -\frac{\mu}{T_0}\mathbf{J} + \frac{a}{T_0}EJ^2\mathbf{J}, \quad (73)$$

which reduces to the classical expression $-(\mu^0/T_0)\mathbf{J}$ by omitting the non-linear contribution in \mathbf{J} .

Now, let us go back to the general expression (10) of the evolution equation for the diffusion flux \mathbf{J} . First, by using the constitutive equations (47) and (48), we can put this equation in the form

$$\rho \frac{d\mathbf{J}}{dt} = -\nabla A - J^2 \nabla B - 2B(\nabla \mathbf{J}) \cdot \mathbf{J} + (\nabla E) \cdot \mathbf{J}\mathbf{J} + E(\nabla \cdot \mathbf{J})\mathbf{J} + E(\nabla \mathbf{J})^T \cdot \mathbf{J} - \frac{\rho}{\tau}\mathbf{J}, \quad (74)$$

where an upper T means transposition. Next, by exploiting the identities (52) and (53), we can eliminate the parameter A . Indeed, in virtue of (59), (71) and (72), relations (52) and (53) can, respectively, be formulated as

$$aA_\rho - \mu_\rho^0 = -(T_0\beta_\rho + aB_\rho - aE_\rho)J^2 \quad (75)$$

and

$$aA_c - \mu_c^0 = -(T_0\beta_c + aB_c - aE_c)J^2. \quad (76)$$

Multiplying them, respectively, by $\nabla\rho$, ∇c and summing up, one obtains

$$a\nabla A - \nabla\mu^0 = -(T_0\nabla\beta + a\nabla B - a\nabla E)J^2. \quad (77)$$

As a , A and μ^0 are independent of \mathbf{J} , it follows that

$$\nabla A = \frac{\nabla\mu^0}{a} \quad (78)$$

and

$$T_0\nabla\beta + a\nabla B - a\nabla E = 0, \quad (79)$$

which, in virtue of (70) and (72), can be written as

$$\nabla\mu^1 = a \left(\nabla B + \frac{E}{E - 2B} \nabla E \right). \quad (80)$$

According to the definition (57) of μ and the results (70), (78) and (80), it is easily checked that

$$\nabla\mu = a(\nabla A + J^2\nabla B) + \frac{aE}{E - 2B} J^2\nabla E + a(2B + E)(\nabla\mathbf{J}) \cdot \mathbf{J}. \quad (81)$$

Elimination of ∇A between (74) and (81) will result in the final expression of the non-linear evolution equation for \mathbf{J} :

$$\rho \frac{d\mathbf{J}}{dt} = -\frac{\nabla\mu}{a} + E[\nabla\mathbf{J} + (\nabla\mathbf{J})^T + (\nabla \cdot \mathbf{J})\mathbf{I}] \cdot \mathbf{J} + \frac{E}{E - 2B} J^2\nabla E + \mathbf{J}\mathbf{J} \cdot \nabla E - \frac{\rho}{\tau} \mathbf{J}, \quad (82)$$

wherein an upper T indicates transposition. Of course, complete resolution of Eq. (82) implies to complete it with relevant initial and boundary conditions. The latter will either be provided by experiences or otherwise by thermodynamical techniques as those proposed by Waldman [13] and more recently by Struchtrup and Weiss [14]. Waldman considers the bounding surface as a material system and expresses the boundary conditions under the form of flux–force relations as in the classical theory of irreversible processes [12], while Struchtrup and Weiss start from the principle of minimum–maximum entropy. It is our goal to investigate this crucial problem in more detail in a future work.

Combining (82) with (8), it is no longer possible to establish an equation in c analogous to Eq. (45) obtained in the linear case. Nevertheless, the convexity of entropy guarantees hyperbolicity [9], i.e. the wave-like property of the set of field equations.

It is interesting to consider some simplified expressions of (82) in order to gain more physical information about the various undetermined coefficients a , E and B . By assuming that E is constant, one obtains

$$\rho \frac{d\mathbf{J}}{dt} = -\frac{\nabla\mu}{a} - \frac{\rho}{\tau}\mathbf{J} + E(\nabla\mathbf{J} + (\nabla\mathbf{J})^T + (\nabla\mathbf{J})\mathbf{I}) \cdot \mathbf{J}. \quad (83)$$

If E is set equal to 0, (83) reduces to

$$\tau \frac{d\mathbf{J}}{dt} = -D\nabla\mu - \mathbf{J}, \quad (84)$$

wherein the coefficient D is given by

$$D = \frac{\tau}{\rho a}, \quad (85)$$

a positive quantity according to (60). Eq. (84) is of Cattaneo's type and represents the simplest generalization of Fick's law. Another possible simplification of (82) is to put $B=0$, in which case (82) reduces to

$$\rho \frac{d\mathbf{J}}{dt} = -\frac{\nabla\mu}{a} + E[\nabla\mathbf{J} + (\nabla\mathbf{J})^T + (\nabla \cdot \mathbf{J})\mathbf{I}] \cdot \mathbf{J} + J^2\nabla E + \mathbf{J}\mathbf{J} \cdot \nabla E - \frac{\rho}{\tau}\mathbf{J}. \quad (86)$$

It must be realized that EIT does not allow to justify one or another of the above approximations. This is not surprising as EIT provides only a phenomenological macroscopic approach. The only way out is to compare with experimental data or other microscopic or macroscopic theories. In that spirit, we will compare our results with those derived recently by Grmela et al. [8] on the bases of a Hamiltonian formalism. In our notation, Grmela et al. obtained the following expression for the problem of non-Fickian diffusion of two ideal fluids, at constant temperature and total mass density:

$$\begin{aligned} \rho \frac{d\mathbf{J}}{dt} = & -\frac{\nabla\mu}{a} + E[\nabla\mathbf{J} + (\nabla\mathbf{J})^T + (\nabla \cdot \mathbf{J})\mathbf{I}] \cdot \mathbf{J} + J^2\nabla E + \mathbf{J}\mathbf{J} \cdot \nabla E - \frac{\rho}{\tau}\mathbf{J} \\ & - \frac{1}{c(1-c)}(\mathbf{J}\nabla c + (\mathbf{J}\nabla c)^T) \cdot \mathbf{J}, \end{aligned} \quad (87)$$

wherein a and E stand for

$$a = \frac{1}{\rho^2 c(1-c)}, \quad E = \frac{2c-1}{c(1-c)}. \quad (88)$$

Clearly, (87) is similar to (86) at the exception of the last term on the right-hand side. However, such a term could be recovered from an EIT description by introducing a non-local contribution of the form $(\nabla c) \cdot \mathbf{J}\mathbf{J}$ in expression (48) of the source term σ^J .

4. Conclusions

The main objective of this work is to propose a derivation of a non-linear and non-Fickian mass diffusion in the framework of EIT. The original idea consists of introducing the flux of diffusion \mathbf{J} as an independent variable. Following the procedure of EIT, we are then able to obtain an evolution equation for this extra variable. For pedagogical reasons and to make clear our methodology, we have started with

a simple linear description, before performing a weakly non-linear analysis. It should be noticed that, in the non-linear case, the space of state variables spans the same variables as in the linear description; no additional variable has been introduced. The relevant equation for the diffusion flux is obtained in a straightforward, systematic and elegant way. As in Cattaneo–Maxwell’s equations, both diffusion-like and wave-like propagations are present in the non-linear description.

The analysis has been restricted to a two-component fluid mixture composed of two miscible diffusing fluids chemically inert and characterized by constant and uniform temperature and negligible viscosity. The present work opens the way to more complicated situations involving for instance diffusion of polymers, thermal effects, phase change and multicomponent mixtures. Diffusion in polymers is particularly interesting and important because of the coupling between viscous stresses and diffusion and also because it allows to shed some light on the physical content of the coefficients τ , a , B and E appearing in the diffusion flux equation.

By comparing our results with a recent analysis based on GENERIC [8], one observes a qualitative agreement. At the exception of one term, we recover the result of GENERIC. At this point, it should be mentioned that, in GENERIC, there is no parameter left free. This is because the Hamiltonian structure imposes from the start more constraints on the evolution equations, namely a Poisson bracket structure which has no equivalent in EIT. However, in our opinion, EIT presents some advantages: the procedure is simple and systematic and is more easily generalized to more complicated situations like those involving the coupling between mass and heat transfer. In addition, EIT makes explicit the strong correlation between dynamics and thermodynamics; for instance, it is seen that the coefficients a and E appearing in the evolution equation (82) or (86) are the same as the coefficients present in the expressions of the entropy flux and Helmholtz function.

The present work parallels another article published in the present issue by Jou and Casas-Vázquez [15] and concerned with polymer solutions. This paper is however different from ours in several aspects. Indeed, Jou and Casas-Vázquez are mainly interested in shear-induced effects on polymer flows, while diffusion effects are assumed to be negligible. Here, viscous effects, and consequently, shear effects are not taken into consideration, but emphasis is put on mass diffusion effects. Another difference with [15] is that we are mainly interested in a non-linear situation, while Jou and Casas-Vázquez analysis is essentially devoted to the linear regime. In the future, it is our intention to couple both aspects, i.e. to consider that both the viscous pressure tensor \mathbf{P}^v and the diffusion flux \mathbf{J} are spanning the space of state variables. Clearly, the coupling between these two effects and its application to polymer flows would contribute to a better comprehension of the physics behind the above axiomatic formalism.

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