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Self-diffusion in remodelling and growth

by

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Abstract

Self-diffusion, or the flux of mass of a single species within itself, is viewed as an independent phenomenon amenable to treatment by the introduction of an auxiliary field of diffusion velocities. The theory is shown to be heuristically derivable as a limiting case of that of an ordinary binary mixture.

Keywords: Mixture theory, remodelling, mass flux, second-grade elasticity.

1 Introduction

Mass flux is the conveyance of mass through a material surface. This phenomenon is commonly associated with the diffusion of one species within another, like the proverbial drop of milk in a cup of coffee. Here we consider the more seemingly paradoxical issue of mass flux of a single species, or self-diffusion. That is, we consider the relative flux of a species with respect to itself. This concept raises certain epistemological questions, such as the following: Is self-diffusion possible or even meaningful? In partial answer to this question one may argue that if, for example, in a process of growth and remodelling a

body tends to render its mass density uniform (driven, say, by the gradient of the density itself), then the vehicle to express this phenomenon constitutively must surely be, at the continuum level, the flow of mass. Whatever one's position may be on this issue, it is certainly wise to formulate the field equations of continuous growth (balance of mass, linear momentum, angular momentum and energy and an entropy inequality) including the mass flux terms and study their mutual compatibility and physical interpretation.

To the best of our knowledge, the first treatment of mass flux within the context of a theory of growth is given in [3]. The treatment of the flux term therein, however, leads to a form of the balance equations that is not invariant under the action of the Galilean group. This is due to the fact that the balance of angular momentum contains an explicit dependence on the velocity. In other words, the theory is not inertial-observer independent. The same remark applies to the treatment presented in [6]. In [5], on the other hand, growth and remodelling are placed within the context of mixture theory involving at least two species and mass flux is used only in the context of diffusion of nutrients in the underlying tissue. Mass fluxes are, therefore, determined by relative velocities between the species, thus circumventing the invariance violation. Ultimately, the approach suggested herein can be regarded as a limit whereby the two species collapse into one while a new variable is introduced to represent the relative motion of the mass flow. In some sense, the situation is reminiscent of the representation of internal structure (in, say, a granular medium) by a process of homogenization leading eventually to a Cosserat medium (so that, for example, the high frequency 'optical' modes of vibration are not lost).

2 Mechanical balance laws

2.1 Gross motion and fluctuation

Inspired by statistical mechanics, we will assume that the material particles, moving as they do with velocity \mathbf{v} according to the underlying gross motion of the medium, carry nevertheless an extra amount of momentum due to fluctuations around the gross motion. In a mixture theory, the extra momentum of one species is expressed in terms of the difference between the specific velocity and an average local velocity of all the species. In our case, however, whereby only one species is present, we characterize the extra momentum by means of an extra diffusive momentum field \mathbf{p}_d per unit spatial volume, which may eventually be connected constitutively with the gross motion, whose velocity field is \mathbf{v} . Clearly, dividing the diffusive momentum by the local spatial density ρ one obtains a diffusive velocity field \mathbf{w}_d . We note that this diffusion velocity (as it represents

a relative velocity) behaves as an objective vector under a change of inertial observer. We also remark that the diffusion velocity should be understood only as a vehicle to express the extra momentum due to fluctuations. There is no implication that the sum $\mathbf{v} + \mathbf{w}_d$ represents the velocity field of another medium at play.

The gross motion will be described in the standard way. Cartesian coordinate systems X^I ($I = 1, 2, 3$) and x^i ($i = 1, 2, 3$) are used, respectively, in a fixed reference configuration and in space. The gross motion is represented by smooth functions:

$$x^i = x^i(X^1, X^2, X^3, t) \quad (i = 1, 2, 3), \quad (2.1)$$

and the deformation gradient \mathbf{F} at a body point \mathbf{X} is the tensor with components

$$F_I^i = \frac{\partial x^i}{\partial X^I}. \quad (2.2)$$

The gross velocity is given by:

$$v^i = \frac{\partial x^i}{\partial t}. \quad (2.3)$$

2.2 Balance of mass

In contradistinction with the traditional equation of mass conservation, in the case of growth one speaks of mass balance. Following the standard continuum mechanics paradigm for balance equations, we assume that the rate of change of the mass is balanced by the combination of a production (volumetric) term π and a flux (surface) contribution m . By Cauchy's theorem, the latter is expressible in terms of a mass flux vector \mathbf{m} (analogous to the heat flux vector) as:

$$m = -\mathbf{m} \cdot \mathbf{n}, \quad (2.4)$$

where \mathbf{n} is the unit normal to the surface. The global Eulerian version of the balance of mass reads

$$\frac{D}{Dt} \int_{\omega} \rho \, d\omega = \int_{\omega} \pi \, d\omega - \int_{\partial\omega} \mathbf{m} \cdot \mathbf{n} \, da. \quad (2.5)$$

In this equation ω denotes a sub-body with boundary $\partial\omega$, ρ is the spatial mass density, $d\omega$ is a generic spatial volume element, π is the mass production per unit time and per

unit spatial volume, and da is the generic spatial area with unit normal \mathbf{n} . Under the usual smoothness assumptions, the local Eulerian form of the balance of mass is obtained as:

$$\frac{D\rho}{Dt} = \pi - \rho \operatorname{div} \mathbf{v} - \operatorname{div} \mathbf{m}, \quad (2.6)$$

where div is the spatial divergence operator and D/Dt is the material time derivative (following the gross motion).

2.3 Balance of linear momentum

For clarity, we will express the various contributions in components on the spatial Cartesian coordinate system x^i . Unless otherwise specified, the summation convention for diagonally repeated indices is in force. In addition to the standard terms of momentum supply, we need to consider now the momentum contribution of the incoming mass, which we lump into a volumetric part p^i and a surface part ϕ^i . Denoting the body force per unit mass by b^i and the surface traction per unit spatial area by t^i , the integral Eulerian form of the balance of momentum reads:

$$\frac{D}{Dt} \int_{\omega} (\rho v^i + p_d^i) d\omega = \int_{\omega} (\rho b^i + p^i) d\omega + \int_{\partial\omega} (t^i + \phi^i) da. \quad (2.7)$$

As anticipated, note here the inclusion of an extra diffusive momentum term p_d^i carried independently of the momentum density ρv^i associated with the gross motion. The traction t^i can be expressed by means of the action of the Cauchy stress tensor t^{ij} on the unit normal n_i to a surface element, namely

$$t^i = t^{ij} n_j, \quad (2.8)$$

By Cauchy's tetrahedron argument, we conclude that the momentum flux vector with components ϕ^i is expressible via a momentum flux tensor ϕ^{ij} as:

$$\phi^i = \phi^{ij} n_j. \quad (2.9)$$

Localizing (2.7) while exploiting Equation (2.6) yields:

$$\rho \frac{Dv^i}{Dt} + \frac{Dp_d^i}{Dt} = \rho b^i + t^{ij}_{,j} + \phi^{ij}_{,j} + m^j_{,j} v^i - p_d^i v^j_{,j} + p^i - \pi v^i. \quad (2.10)$$

The volumetric momentum source p^i can be resolved into two additive components. The first, or *compliant*, component is given precisely by:

$$p_{comp}^i = \pi v^i. \quad (2.11)$$

Physically, it represents the contribution of the mass per unit volume (arising, for example, from externally driven chemical reactions) entering the system while carrying a specific momentum equal to that of the underlying medium. Any excess momentum source (arising, for example, from a differential velocity of the entering mass) will be encompassed in a non-compliant term that we denote by \bar{p}^i . Similarly, the momentum flux is given by:

$$\phi^i = m v^i. \quad (2.12)$$

Comparison with Equations (2.4) and (2.17) yields:

$$\phi^{ij} = -m^j v^i. \quad (2.13)$$

Substituting (2.11) and (2.13) into (2.10), we obtain the following local equation of linear momentum balance:

$$\rho \frac{Dv^i}{Dt} + \frac{Dp_d^i}{Dt} = \rho b^i + t^{ij}_{,j} - m^j v_{,j}^i - p_d^i v_{,j}^j + \bar{p}^i. \quad (2.14)$$

2.4 Balance of angular momentum

Assuming no other contributions but the moment of forces and of linear momenta, on the basis of Equation (2.7) we write:

$$\frac{D}{Dt} \int_{\omega} \epsilon_{kji} x^j (\rho v^i + p_d^i) d\omega = \int_{\omega} \epsilon_{kji} x^j (\rho b^i + p^i) d\omega + \int_{\partial\omega} \epsilon_{kji} x^j (t^i + \phi^i) da, \quad (2.15)$$

where ϵ_{kji} is the permutation symbol. The crucial point in exploiting this equation is that:

$$\frac{Dx^i}{Dt} = v^i, \quad (2.16)$$

in a manner consistent with our assumption that the diffusive momentum is independent of the gross motion. Following the standard procedure and making use of balance of mass and linear momentum, the localized version of Equation (2.16) is obtained as:

$$\epsilon_{kji} v^j p_d^i = \epsilon_{kji} (t^{ij} - m^j v^i). \quad (2.17)$$

2.5 Inertiality

In a properly formulated classical mechanical theory, the balance laws should be invariant under the action of the Galilean group. In physical terms, the balance laws should have the same form in all inertial frames. Clearly, as formulated so far, certain restrictions should be placed on various terms so that the resulting equations satisfy this criterion. Since the flux vector \mathbf{m} , the volumetric mass supply π and the density ρ are invariant, it follows that the mass balance equation (2.6) is invariant. Similarly, assuming the objectivity of the body force b^i , the Cauchy stress t^{ij} and the non-compliant momentum source \bar{p}^i , the equation of balance of linear momentum is invariant under a change of observer.

It remains to check whether or not the equation of balance of angular momentum is observer independent.* Applying a translational velocity c^i to Equation (2.17), we obtain the following identity:

$$\epsilon_{kji} (v^j + c^j) p_d^i = \epsilon_{kji} (t^{ij} - m^j (v^i + c^i)). \quad (2.18)$$

Since c^i is arbitrary, we can set $c^i = -v^i$, whence

$$\epsilon_{kji} t^{ij} = 0. \quad (2.19)$$

In other words, we recover the classical symmetry of the Cauchy stress. Introducing this result back into Equation (2.17), we conclude that:

$$\epsilon_{kji} v^j p_d^i = -\epsilon_{kji} m^j v^i. \quad (2.20)$$

Since we want this to be true for all velocities v^i , we must have:

$$\mathbf{p}_d = \mathbf{m}. \quad (2.21)$$

*We note that in previous treatments it was precisely the balance of angular momentum that violated the invariance.

We have arrived at the conclusion that, for the equation of balance of angular momentum to be observer independent, the diffusive momentum per unit volume (\mathbf{p}_d) must be numerically equal to the mass flux (\mathbf{m}) per unit area and per unit time. This coincidence is less surprising when expressed in terms of the putative diffusive velocity \mathbf{w}_d mentioned in Section 2.1. Indeed, the mass flux m can be readily expressed as $\rho \mathbf{w} \cdot \mathbf{n}$. On the other hand, the momentum per unit volume is measured by $\rho \mathbf{w}$. Note that, since \mathbf{w}_d can be interpreted as a relative velocity, the vector \mathbf{m} transforms in the right way under the action of the Galilean group. All the non-invariant terms have cancelled out.

Using the fundamental result embodied in Equation (2.21), the balance of momentum (2.14) can be cast in the final form:

$$\rho \frac{Dv^i}{Dt} + \frac{Dm^i}{Dt} = \rho b^i + t^{ij}_{,j} - m^j v^i_{,j} - m^i v^j_{,j} + \bar{p}^i. \quad (2.22)$$

It is remarkable that, although the theory started from the assumption that there are both mass flux and diffusive momentum, the latter has been effectively absorbed by the former and does not appear in the balance equations.

3 A posteriori justification of the theory

The introduction of the diffusive momentum \mathbf{p}_d may appear to be unsubstantiated since, unlike the case of the kinetic energy arising from oscillations around an equilibrium position, say, the momentum of the average position of a particle is exactly equal to the average momentum. To interpret physically what mass flux and self-diffusion actually mean, therefore, one needs to recognize the relation between the artefacts of a continuum theory and the underlying atomic phenomena. In a continuum theory, the very notion of ‘material particle’ is of dubious nature, lending itself to sundry interpretations. Consider, for example, the case of volumetric growth (without necessarily involving mass flux). We have a case of ‘the same’ particles acquiring new mass. In the ‘physical reality’, on the other hand, it is likely that growth at the molecular level occurs because of the addition of new molecules. A somewhat similar situation can be recognized in the case of mass flux. Indeed, as the self-diffusion process occurs, there is no need to identify any particles travelling from one place to the next (like a drop of milk would in a cup of coffee). Indeed, in the case of a single species, the diffusion can be interpreted as a ‘motion’ of the density from one particle to the next in a continuous manner, without necessarily moving the particles themselves. Nevertheless, it is remarkable, though not unexpected, that the theory just presented can be reproduced in many of its details by arbitrarily and artificially dividing at each time the single species into two parts of spatial densities ρ_1 and ρ_2 ,

adding up to the total density ρ . We can now attribute different velocity fields to each part, say $\mathbf{v}_1 = \mathbf{v}$ and \mathbf{v}_2 , respectively. In mixture theory it is customary to consider the relative motions of each of the species with respect to some averaged velocity. But, given the motivation that we have in mind, we are interested in adopting the point of view that the first component of the mixture is in some way the main one, to which we want to refer the motion of the second component. An observer moving with the first component with velocity $\mathbf{v}_1 = \mathbf{v}$ and intent upon measuring the vicissitudes of a small material volume (dragged by the particles of the first component) would then see a strange phenomenon: the particles of the second component of the ‘mixture’ enter and/or exit the material volume, as shown schematically in Figure 1. In other words, as far as this observer is concerned, there is mass flux even though there may not be any mass production at all (i.e., for each component mass conservation holds without sources or fluxes)! The crucial and convincing part of this argument is that, after enforcing the balance of mass of this artificially split mixture, the final result is, in a precise sense, independent of the partition of the density as long as one parameter is kept invariant (not surprisingly, this parameter represents what we have called in the previous treatment the diffusive momentum \mathbf{p}_d). This is exactly what we propose to do, by using the conventional theory of binary mixtures [1] (without mass fluxes) and then referring the results to the first component of the mixture.

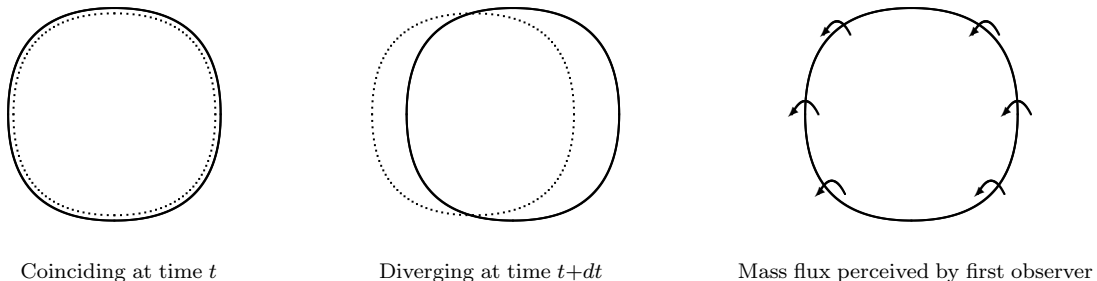


Figure 1: Two material volumes moving with different velocities

3.1 Mass balance

The mass balances of the two species are given by the usual continuity equation with volumetric sources π_1 and π_2 (but without mass flux) as:

$$\frac{\partial \rho_1}{\partial t} + (\rho_1 v_1^i)_{,i} = \pi_1, \quad (3.1)$$

and

$$\frac{\partial \rho_2}{\partial t} + (\rho_2 v_2^i)_{,i} = \pi_2. \quad (3.2)$$

Adding these two equations, the result can be written in the form:

$$\frac{\partial \rho}{\partial t} + (\rho v^i)_{,i} = -(\rho_2 w^i)_{,i} + \pi, \quad (3.3)$$

with

$$\rho = \rho_1 + \rho_2, \quad w^i = v_2^i - v_1^i, \quad \pi = \pi_1 + \pi_2. \quad (3.4)$$

Comparing this result with Equation (2.6) we conclude that both are identical provided that the following further identification is made:

$$\mathbf{m} = \rho_2 \mathbf{w}. \quad (3.5)$$

In other words, seen from the point of view of the first, arbitrarily selected, portion of the binary mixture of two identical materials, there is a mass flux given explicitly by (3.5). If Equation (3.3) alone is used as the balance of mass (of the restored one-species body), clearly the mass flux \mathbf{m} will have to be specified constitutively. Notice that neither the density ρ_2 nor the velocity \mathbf{v}_2 appear elsewhere in this field equation. So, the choice of decomposition into two components is, in fact, immaterial as long as a constitutive equation is specified for the particular combination (3.5).

3.2 Mixture theory revisited

While the handling of mass balance for the mixture and its reinterpretation as the equation of mass balance of the proposed theory of self-diffusion have been straightforward, this is not necessarily the case for the remaining mechanical and thermodynamical balance equations. One of the reasons for the expected difficulties is rooted in mixture theory itself. To understand this point it is convenient to consult the seminal article by Truesdell [7] and the treatise by Truesdell and Toupin [8]. In these works, as well as in all subsequent research in this field, one of the fundamental guiding criteria has been to postulate that, although the balance equations for each individual component of the mixture might

include extra interaction terms, the balance equations for the mixture itself should look exactly like the corresponding balance equations for an ordinary material. To fulfill the requirements of this postulate, it was noticed that the mere addition of the properties of the various species (such as stresses, heat fluxes, internal energies, and so on) was not enough to obtain the correct form of the equations for the mixture as a whole. Moreover, certain additional conditions had to be imposed on the interactions between the various species.

As the first instance of the application of these requirements, let us consider the stress tensor \mathbf{t} of a binary mixture. Denoting by \mathbf{t}_1 and \mathbf{t}_2 , respectively, the *partial stresses* of the first and second species, the unexpected result $\mathbf{t} \neq \mathbf{t}_1 + \mathbf{t}_2$ arises. Instead, the *inner part* of the total stress is defined as:

$$\mathbf{t}_I = \mathbf{t}_1 + \mathbf{t}_2, \quad (3.6)$$

while the total stress necessitates the introduction of a correction term incorporating the *diffusive velocities* \mathbf{u}_1 and \mathbf{u}_2 of the components, as one would expect from, say, the kinetic theory of gases. The diffusive velocities are defined as deviations from the average, namely:

$$\mathbf{u}_1 = \mathbf{v}_1 - \mathbf{v}_0, \quad \mathbf{u}_2 = \mathbf{v}_2 - \mathbf{v}_0, \quad (3.7)$$

where the (barycentric) velocity of the mixture is defined as the weighted average:

$$\mathbf{v}_0 = \frac{1}{\rho} (\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2). \quad (3.8)$$

In terms of these quantities, the total stress is given by:

$$\mathbf{t} = \mathbf{t}_I - \rho_1 \mathbf{u}_1 \otimes \mathbf{u}_1 - \rho_2 \mathbf{u}_2 \otimes \mathbf{u}_2. \quad (3.9)$$

From the physical point of view, this total stress is affected by the relative velocities of the components with respect to an observer travelling with the local average velocity \mathbf{v} of the mixture. This observer, indeed, must account for the momentum fluxes corresponding to the diffusive velocities. For the interpretation required to fulfill our purposes, however, we should place this observer at the biased position of the first species and thus measure the diffusive velocities with respect to it. Clearly, the first diffusive velocity vanishes by construction and the second diffusive velocity is precisely equal to \mathbf{w} , already defined. In this spirit, we now define the total stress *as seen by the first species* as:

$$\mathbf{t} = \mathbf{t}_I - \rho_2 \mathbf{w} \otimes \mathbf{w}. \quad (3.10)$$

It is this total stress that will replace the standard total stress (3.9) of the mixture in our formulation.

The second kind of requirement imposed by the above mentioned postulate is illustrated by the fact that, although each component of the mixture functions as an open system in terms of inputs of mass, the total mass input must add up to zero, namely:

$$\pi_1 + \pi_2 = 0. \quad (3.11)$$

On the other hand, if the mixture itself is open to mass input (such as is the case in theories of biological growth), Equation (3.11) has to be replaced by:

$$\pi_1 + \pi_2 = \pi, \quad (3.12)$$

as, in fact, we have already done in the equation of mass balance for the mixture. These observations are sufficient to proceed to the formulation of the balance of momentum, while further redefinitions will be introduced later, when dealing with thermodynamical balance.

3.3 Momentum balance

Moving on now to the balances of linear momentum, we write:

$$\rho_1 \frac{D_1 v_1^i}{Dt} = t_1^{ij}{}_{,j} + \rho_1 b_1^i + \hat{p}_1^i, \quad (3.13)$$

and

$$\rho_2 \frac{D_2 v_2^i}{Dt} = t_2^{ij}{}_{,j} + \rho_2 b_2^i + \hat{p}_2^i, \quad (3.14)$$

where we have used the notation D_1 , D_2 to indicate material derivatives with respect to the velocity fields \mathbf{v} , \mathbf{v}_2 , respectively, and where the partial Cauchy stresses (t_1^{ij} , t_2^{ij}), body forces per unit mass (b_1^i , b_2^i) and momentum supplies per unit volume (\hat{p}_1^i , \hat{p}_2^i) are indicated in a similar way. Expressing the operator D_2 in terms of D_1 , Equation (3.14) can be rewritten as:

$$\rho_2 \frac{D_1 v_2^i}{Dt} + \rho_2 v_2^i{}_{,j} w^j = t_2^{ij}{}_{,j} + \rho_2 b_2^i + \hat{p}_2^i. \quad (3.15)$$

Adding Equations (3.13) and (3.15) and making use of Equations (3.2) and (3.10) and a few straightforward algebraic replacements we obtain:

$$\rho \frac{D_1 v^i}{Dt} + \frac{D_1(\rho_2 w^i)}{Dt} = \rho b^i + t^{ij}{}_{,j} - (\rho_2 w^j) v_{1,j}^i - (\rho_2 w^i) v_{1,j}^j + \hat{p}_1^i + \hat{p}_2^i + \pi_2 w^i, \quad (3.16)$$

where the total body force is defined as:

$$b^i = \frac{1}{\rho} (\rho_1 b_1^i + \rho_2 b_2^i). \quad (3.17)$$

In mixture theory, there is an extra requirement to be fulfilled for the equation of the mixture to be of the right form. This requirement is:[†]

$$\hat{p}_1^i + \hat{p}_2^i + \pi_1 u_1^i + \pi_2 u_2^i = 0. \quad (3.18)$$

There are two modifications to be made to this condition. The first one stems from replacing the diffusion velocities u_1^i and u_2^i by 0 and w^i , respectively, as already discussed in relation to Equation (3.10). The second modification has to do with the fact that Equation (3.18) applies for the case in which the total mass input vanishes. Thus, we will replace the right-hand side with \bar{p} , namely, a net momentum supply for the mixture. As a result of these remarks, we obtain the modified condition:

$$\hat{p}_1^i + \hat{p}_2^i + \pi_2 w^i = \bar{p}^i. \quad (3.19)$$

Introducing this result in Equation (3.16), we obtain the following equation for the balance of momentum of the binary mixture as seen by an observer carried along with the first species:

$$\rho \frac{D_1 v^i}{Dt} + \frac{D_1(\rho_2 w^i)}{Dt} = \rho b^i + t^{ij}{}_{,j} - (\rho_2 w^j) v_{1,j}^i - (\rho_2 w^i) v_{1,j}^j + \bar{p}^i. \quad (3.20)$$

On comparing Equation (3.20) with (2.22), they are seen to be identical term by term modulo the same identification (3.5) already made for the case of mass balance. In other words, our one-species model stands alone as distinct from a mixture theory, but it

[†]See [1], Equation (1.4.31).

reproduces the same results as would arise from arbitrarily partitioning the single species into two parts. The crucial point is that, in the last analysis, the final equations are independent of the partitioning itself. It is only the product $\rho_2 \mathbf{w}$ that manifests itself in the final equations as a new variable that we have called the diffusive momentum. The theory as it stands avoids any kind of extra assumptions as to any particular partition and differs from the mixture approach per se, with which it is in a physically meaningful relation only.

4 Thermodynamic balance

4.1 Balance of energy

So far we have obtained the purely mechanical equations of self-diffusion and we have shown how the introduction of the diffusive momentum as a new state variable is all one needs to be in agreement with classical mixture theory, with minor physically reasonable modifications. The situation with the thermodynamic aspects of the phenomenon, which cannot be neglected, is somewhat more complicated. In particular, in writing down the balance of energy, one should have a clear definition of what the extra (diffusive) kinetic energy should be to agree with the assumed diffusive momentum. At first sight, it would appear that the most reasonable assumption should be to resort to the notion of diffusive velocity \mathbf{w}_d , introduced in Section 2.1 but judiciously avoided in all derivations, and to write the total kinetic energy content as:

$$\begin{aligned}
 K &= \int_{\omega} \frac{1}{2} \rho (\mathbf{v} + \mathbf{w}_d) \cdot (\mathbf{v} + \mathbf{w}_d) d\omega \\
 &= \int_{\omega} \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + (\rho \mathbf{w}_d) \cdot \mathbf{v} + \frac{1}{2} \rho \mathbf{w}_d \cdot \mathbf{w}_d \right) d\omega.
 \end{aligned} \tag{4.1}$$

Upon some reflection, however, it is apparent that this expression cannot be in agreement with any derivation that can possibly be obtained from mixture theory in the same spirit as the mechanical equations. Indeed, let us write the kinetic energy content as would be provided by the binary mixture version of the arbitrarily partitioned single species:

$$\begin{aligned}
K_{mix} &= \int_{\omega} \left(\frac{1}{2} \rho_1 \mathbf{v}_1 \cdot \mathbf{v}_1 + \frac{1}{2} \rho_2 (\mathbf{v}_1 + \mathbf{w}) \cdot (\mathbf{v}_1 + \mathbf{w}) \right) d\omega \\
&= \int_{\omega} \left(\frac{1}{2} \rho \mathbf{v}_1 \cdot \mathbf{v}_1 + (\rho_2 \mathbf{w}) \cdot \mathbf{v}_1 + \frac{1}{2} \rho_2 \mathbf{w} \cdot \mathbf{w} \right) d\omega.
\end{aligned} \tag{4.2}$$

Comparing Equations (4.1) and (4.2), it is obvious that the third terms under the last integrals cannot be made compatible with the identification $\rho \mathbf{w}_d = \rho_2 \mathbf{w}$. Since the identification of both theories should be independent of the arbitrary partition of ρ into ρ_1 and ρ_2 , as ρ_2 becomes vanishingly small while keeping the product $\rho_2 \mathbf{w}$ constant, the last term in Equation (4.2) blows up without bound. This can be avoided only by excluding this term altogether. Namely, we must of necessity adopt the following expression for the kinetic energy content of the one-species self-diffusive model:

$$K = \int_{\omega} \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + (\rho \mathbf{w}_d) \cdot \mathbf{v} \right) d\omega = \int_{\omega} \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \mathbf{m} \cdot \mathbf{v} \right) d\omega. \tag{4.3}$$

We remark that it is not unusual in theories of diffusion to neglect quadratic terms in the diffusion velocities, which may be seen as a physical justification for the choice of Equation (4.3). On the other hand, it should be clear that (4.3) is not an approximation but just a definition in the theory being proposed. In fact, it will be eventually shown that the energy equation of a binary mixture, in which no such neglecting has been enforced, does coincide with that of the proposed theory under the appropriate identifications.

Denoting by ϵ the internal energy per unit mass, we can write the global Eulerian form of the energy balance as:

$$\begin{aligned}
&\frac{D}{Dt} \int_{\omega} \left(\rho \epsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \mathbf{m} \cdot \mathbf{v} \right) d\omega \\
&= \int_{\omega} (\mathbf{b} \cdot (\rho \mathbf{v} + \mathbf{m}) + \rho r) d\omega + \int_{\omega} \left(\pi (\epsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v}) + \bar{\epsilon} + \bar{\mathbf{p}} \cdot \mathbf{v} \right) d\omega \\
&+ \int_{\partial\omega} \left(\mathbf{t} \cdot \mathbf{v} + m (\epsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v}) + h \right) ds,
\end{aligned} \tag{4.4}$$

where $\bar{\epsilon}$ is the non-compliant volumetric contribution to the internal energy[‡] and where r and h represent, respectively, the rate of non-mechanical energy supply per unit mass

[‡]In principle, this term could have been absorbed into r , with the understanding that it may eventually be specified constitutively, rather than just externally.

(“radiation”) and per unit area (“conduction”). The latter can be expressed (again, through Cauchy’s tetrahedron argument) in terms of a heat flux vector \mathbf{q} :

$$h = -\mathbf{q} \cdot \mathbf{n}. \quad (4.5)$$

Some remarks are in order to explain the various power contributions to the right-hand side of Equation (4.4). Starting from the contribution of the body force \mathbf{b} , the reason that it has been multiplied by the sum of the gross and the diffusive momenta stems heuristically from looking at the power of the body forces in the binary mixture, which is given by $\rho_1 \mathbf{b}_1 \cdot \mathbf{v}_1 + \rho_2 \mathbf{b}_2 \cdot (\mathbf{v}_1 + \mathbf{w})$. In partitioning the one-species material, however, it makes sense to assume $\mathbf{b}_1 = \mathbf{b}_2$, since these are forces per unit mass (such as gravity). Thus, the power of the body force can be written exactly as $\mathbf{b} \cdot (\rho \mathbf{v}_1 + \rho_2 \mathbf{w})$. The power of the surface traction \mathbf{t} , on the other hand, is obtained via the gross motion alone, as results from a reasoning similar to that yielding the kinetic energy expression. Finally, the power of the incoming mass per unit volume π and per unit area m is obtained by considering only the compliant part, which includes only the kinetic energy of the gross motion. Using Equations (2.6) and (2.22), the local form of Equation (4.4) is obtained as:

$$\rho \frac{D\epsilon}{Dt} + m^i \frac{Dv_i}{Dt} = b_i m^i + \rho r + \bar{\epsilon} + t^{ij} v_{i,j} + m^j \epsilon_{,j} - q^j_{,j}. \quad (4.6)$$

4.2 Justification of the energy balance

Considering now the binary mixture perspective, we start by writing the energy balance for the individual components as:

$$\rho_1 \frac{D_1 \epsilon_1}{Dt} = t_1^{ij} v_{1i,j} - q_{1,i}^i + \rho_1 r_1 + \hat{\epsilon}_1, \quad (4.7)$$

and

$$\rho_2 \frac{D_2 \epsilon_2}{Dt} = t_2^{ij} v_{2i,j} - q_{2,i}^i + \rho_2 r_2 + \hat{\epsilon}_2, \quad (4.8)$$

with an obvious notation. The total radiation is defined as:

$$r = \frac{1}{\rho} (\rho_1 r_1 + \rho_2 r_2). \quad (4.9)$$

According to the tenets of mixture theory[§], the inner part of the total internal energy is defined by:

$$\rho \epsilon_I = \rho_1 \epsilon_1 + \rho_2 \epsilon_2, \quad (4.10)$$

while the total internal energy is given by:

$$\rho \epsilon = \rho \epsilon_I + \frac{1}{2} (\rho_1 \mathbf{u}_1 \cdot \mathbf{u}_1 + \rho_2 \mathbf{u}_2 \cdot \mathbf{u}_2). \quad (4.11)$$

Just as in the case of the total stress, we remark that this expression is defined with respect to the average velocity, whereas we are interested in defining quantities as perceived by the first component of the mixture. To this end, we systematically replace \mathbf{u}_1 and \mathbf{u}_2 by $\mathbf{0}$ and \mathbf{w} , respectively. Thus, we define the total internal energy as:

$$\rho \epsilon = \rho \epsilon_I + \frac{1}{2} \rho_2 \mathbf{w} \cdot \mathbf{w}, \quad (4.12)$$

instead of Equation (4.11). It is not our intention to justify this definition on any physical grounds, but to just proceed formally with the appropriate substitutions. Thus, the standard definition of the inner part of the heat flux, namely:

$$\mathbf{q}_I = \mathbf{q}_1 + \mathbf{q}_2 - \mathbf{t}_1^T \mathbf{u}_1 - \mathbf{t}_2^T \mathbf{u}_2 + \rho_1 \epsilon_1 \mathbf{u}_1 + \rho_2 \epsilon_2 \mathbf{u}_2, \quad (4.13)$$

will be replaced by:

$$\mathbf{q}_I = \mathbf{q}_1 + \mathbf{q}_2 - \mathbf{t}_2^T \mathbf{w} + \rho_2 \epsilon_2 \mathbf{w}. \quad (4.14)$$

Finally, the total heat flux vector for the mixture as seen from the first component is defined as:

$$\mathbf{q} = \mathbf{q}_I + \frac{1}{2} \rho_2 (\mathbf{w} \cdot \mathbf{w}) \mathbf{w}. \quad (4.15)$$

Adding Equations (4.7) and (4.8), implementing all the above definitions, using balance of mass and momentum and a considerable amount of algebra, yields the following result:

$$\begin{aligned} \rho \frac{D_1 \epsilon}{Dt} + (\rho_2 w_j) \frac{D_1 v_1^j}{Dt} &= t^{ij} v_{1i,j} - q^i_{,i} + \rho r + (\rho_2 w_j) b_2^j + \hat{\epsilon}_1 + \hat{\epsilon}_2 \\ &\quad + \hat{p}_2^j - \pi \epsilon + \pi_1 \epsilon_1 + \pi_2 \epsilon_2 + \frac{1}{2} \pi_2 w^j w_j. \end{aligned} \quad (4.16)$$

[§]See [1], pp 24–25.

At this point we still need to implement the consistency condition[¶] of standard mixture theory, which when translated to our terms reads:

$$\hat{\epsilon}_1 + \hat{\epsilon}_2 + w_j \hat{p}_2^j + \pi_1 \epsilon_1 + \pi_2 \left(\epsilon_2 + \frac{1}{2} w_j w^j \right) = \bar{\epsilon} + \pi \epsilon. \quad (4.17)$$

Substituting this condition into Equation (4.16), we obtain the energy balance equation of the mixture as:

$$\rho \frac{D_1 \epsilon}{Dt} + (\rho_2 w_j) \frac{D_1 v_1^j}{Dt} = t^{ij} v_{1i,j} - q^i_{,i} + \rho r + (\rho_2 w_j) b^j + (\rho_2 w^i)_{,i} \epsilon + \bar{\epsilon}, \quad (4.18)$$

where we have used $\mathbf{b}_2 = \mathbf{b}$. Comparing Equation (4.18) with (4.6), we observe that the two equations coincide term by term, except for the term $m^i \epsilon_{,i}$, which in the mixture version is replaced by $m^i_{,i} \epsilon$. We note that this discrepancy can be remedied by removing the last term of the definition of the inner part of the heat flux in Equation (4.13) and setting $\epsilon_2 = \epsilon$, as it is logical to assume. If that were done, the two versions would coincide in every detail. We remark that in mixture theory there is a certain degree of arbitrariness in defining the partial quantities of the species, a subject that has not been completely settled to this day.

4.3 The Clausius-Duhem inequality

What does the Second Law of Thermodynamics have to say when one has come to terms with the assumption that, at least for modelling purposes, matter is continuous? A possible answer to this question is the one embodied in the Clausius-Duhem inequality. It is not our intention to either contest or defend the validity of this, or any other, particular form of the Second Law. Suffice it to say that the introduction of the diffusive momentum field \mathbf{p}_d raises questions as to the need to introduce corresponding entropy sources in the formulation. Must the formulation of the Clausius-Duhem inequality be modified, perhaps augmented, in the presence of extra kinematic variables? Or must we recalcitrantly cling to the original form and live with the consequences? We proceed to the formulation of the Clausius-Duhem inequality adding terms that are consistent with the philosophy used for the balance equations formulated so far.

Defining the entropy content per unit mass, η , we write the Eulerian version of the global Clausius-Duhem inequality as follows:

[¶]See [1], Equation (1.5.46).

$$\frac{D}{Dt} \int_{\omega} \rho \eta \, d\omega \geq \int_{\omega} \left(\frac{\rho r + \bar{\epsilon} - \bar{h}}{\theta} + \pi \eta \right) d\omega + \int_{\partial\omega} \left(\frac{h + h_d}{\theta} + m \eta \right) ds, \quad (4.19)$$

θ being the absolute temperature. We note that we have added a further volumetric sink \bar{h} of non-compliant entropy, which should be specified constitutively.^{||} More importantly, we recognize that the thermal energy flux h must be augmented (as indeed done in mixture theories) to account for the diffusive phenomena. This idea is encompassed in the flux term $h_d = -\mathbf{q}_d \cdot \mathbf{n}$ to be defined later. The resulting local form is:

$$\rho \frac{D\eta}{Dt} \geq \frac{\rho r + \bar{\epsilon} - \bar{h}}{\theta} - m^i \eta_{,i} - \left(\frac{q^i + q_d^i}{\theta} \right)_{,i}. \quad (4.20)$$

The Clausius-Duhem inequality in the form (4.20) that we have just proposed within the context of the self-diffusion model can also be justified from the point of view of an arbitrarily partitioned binary mixture. We will not follow the same procedure as we have used in deriving the balance equations of the mixture starting from those of the components, since it is customary to formulate the entropy inequality only on the mixture and not on the individual species. Following [1], the Clausius-Duhem inequality for the mixture is given by:

$$\rho \dot{\eta} + \left(\frac{h^i}{\theta} \right)_{,i} - \frac{\rho r}{\theta} \geq 0, \quad (4.21)$$

where a superposed dot denotes the material derivative with respect to the average motion with velocity \mathbf{v}_0 defined in Equation (3.8), which can also be written as:

$$\mathbf{v}_0 = \mathbf{v}_1 + \frac{\rho_2}{\rho} \mathbf{w}. \quad (4.22)$$

The modified heat flux vector \mathbf{h} is defined as [1]:

$$\mathbf{h} = \mathbf{q}_1 + \mathbf{q}_2 + \rho_1 \theta \eta_1 \mathbf{u}_1 + \rho_2 \theta \eta_2 \mathbf{u}_2, \quad (4.23)$$

where the specific entropy densities η_1 and η_2 are related to the entropy density η of the mixture by:

$$\rho \eta = \rho_1 \eta_1 + \rho_2 \eta_2. \quad (4.24)$$

^{||}We follow here the idea of Cowin and Hegedus [2], with a slightly different notation.

From their definition and using Equation (4.22), it is not difficult to see that the material derivatives are related by:

$$\dot{\eta} = \frac{D_1\eta}{Dt} + \frac{\rho_2}{\rho}\eta_{,i}w^i. \quad (4.25)$$

Using Equations (4.21-4.25) and assuming $\eta_1 = \eta_2 = \eta$ (since these are entropies per unit mass), we obtain:

$$\rho \frac{D_1\eta}{Dt} + (\rho_2 w^i)\eta_{,i} + \left(\frac{q_1^i + q_2^i}{\theta} \right)_{,i} - \frac{\rho r}{\theta} \geq 0. \quad (4.26)$$

This inequality is similar to (4.21) except for two details. The first one has to do with the absence of non-compliant terms in (4.26). This could be attributed in part to our assumption that $\eta_2 = \eta$ and in part to the fact that, since we are dealing with a mass-wise open system additional terms could be expected. The second discrepancy is more subtle, as it has to do with the definition of the total heat flux vector \mathbf{q} of mixture theory [1]. In particular, we note that the modification entailed in Equation (4.23) is not applied to the heat flux vector, and not even to its inner part, but only to the sum of the partial heat fluxes. For consistency, therefore, our vector \mathbf{q}_d should reflect this important difference, as we will show later.

5 Recapitulation and assessment

The field equations of the proposed theory of self-diffusion can be summarized as follows:

- (1) Balance of Mass

$$\frac{D\rho}{Dt} = \pi - \rho v_{,i}^i - m_{,i}^i. \quad (5.1)$$

- (2) Balance of linear momentum

$$\rho \frac{Dv^i}{Dt} + \frac{Dm^i}{Dt} = \rho b^i + t^{ij}_{,j} - m^j v_{,j}^i - m^i v_{,j}^j + \bar{p}^i. \quad (5.2)$$

- (3) Balance of angular momentum

$$\epsilon_{kji} t^{ij} = 0. \quad (5.3)$$

- (4) Balance of energy

$$\rho \frac{D\epsilon}{Dt} + m^i \frac{Dv_i}{Dt} = b_i m^i + \rho r + \bar{\epsilon} + t^{ij} v_{i,j} + m^j \epsilon_{,j} - q^j_{,j}. \quad (5.4)$$

(5) Clausius-Duhem inequality

$$\rho \frac{D\eta}{Dt} \geq \frac{\rho r + \bar{\epsilon} - \bar{h}}{\theta} - m^i \eta_{,i} - \left(\frac{q^i + q_d^i}{\theta} \right)_{,i}. \quad (5.5)$$

It is important to stress that these equations have not been derived in any way from their mixture theory counterparts. Rather, they are the direct consequence of the introduction of an extra state variable \mathbf{m} into a conventional one-species continuum. On the other hand, we have shown how, by a precise interpretation of this extra variable, one may relate the proposed field equations to those of a binary mixture obtained by arbitrarily subdividing the continuum into two components. The two theories differ, however, in that to solve an initial-boundary value problem in the mixture case we have at our disposal the balance equations of each of the components individually and the corresponding component-wise constitutive equations. In the case of the proposed theory of self-diffusion, on the other hand, the number of equations is much smaller, as the second component has been absorbed into the first via the introduction of the extra field \mathbf{m} , for which constitutive equations should be specified.

6 Consequences of the Clausius-Duhem inequality

6.1 Restatement of the inequality

Before proceeding to the exploitation of the constitutive restrictions imposed upon constitutive equation by the Second Law of Thermodynamics, we proceed to a few manipulations that will render the Clausius-Duhem inequality (4.20) more amenable to this purpose. Our first step in this direction is the introduction of the Helmholtz free energy per unit mass, defined as:

$$\psi = \epsilon - \theta\eta, \quad (6.1)$$

We can now use the balance of energy to rewrite Equation (4.20) in the form:

$$\rho \frac{D\psi}{Dt} + \rho \frac{D\theta}{Dt} \eta + m^i \left(\frac{Dv_i}{Dt} - b_i - \psi_{,i} - \eta\theta_{,i} \right) - \bar{h} - t^{ij} v_{i,j} + \frac{1}{\theta} q^i \theta_{,i} - \theta \left(\frac{q_d^i}{\theta} \right)_{,i} \leq 0. \quad (6.2)$$

This expression can be further transformed by exploiting the equation of balance of momentum. Indeed, using Equation (2.22) we obtain:

$$\rho \frac{D\psi}{Dt} + \rho \frac{D\theta}{Dt} \eta + m^i \left(\frac{1}{\rho} \left(-\frac{Dm_i}{Dt} + t_{i,j}^j - m^j v_{i,j} - m_i v_{,j}^j + \bar{p}_i \right) - \psi_{,i} - \eta \theta_{,i} \right) - \bar{h} - t^{ij} v_{i,j} + \frac{1}{\theta} q^i \theta_{,i} - \theta \left(\frac{q_d^i}{\theta} \right)_{,i} \leq 0. \quad (6.3)$$

This inequality can be considerably clarified by defining several new variables. The first one is the *inner part of the free energy*, defined as:

$$\psi_I = \psi - \frac{m_i m^i}{2\rho^2}. \quad (6.4)$$

Although this definition is clearly inspired by mixture theory, we emphasize that it is entirely within the purview of the proposed theory of self-diffusion. In particular, no extraneous quantities have been invoked beyond the free energy, the mass flux and the density. Similarly, we define, always within the self-diffusion context proper, the *inner part of the stress tensor* as:

$$\mathbf{t}_I = \mathbf{t} + \frac{\mathbf{m} \otimes \mathbf{m}}{\rho^2}. \quad (6.5)$$

Finally, at this juncture, and based on previous considerations, we adopt the following form for the diffusive part of the heat flux:

$$q_d^i = \frac{t^{ji} m_j}{\rho} - \frac{m^k m_k m^i}{\rho^2}. \quad (6.6)$$

Introducing these expressions in the inequality (4.21), yields:

$$\rho \frac{D\psi_I}{Dt} - \frac{\pi}{\rho^2} m_i m^i + \rho \frac{D\theta}{Dt} \eta + \frac{m^i}{\rho} \bar{p}_i - m^i (\psi_{I,i} + \eta \theta_{,i}) - \bar{h} - t_I^{ij} v_{i,j} + \frac{1}{\theta} (q^i + q_d^i) \theta_{,i} - \left(\frac{1}{\rho} \right)_{,i} t^{ji} m_j - \frac{1}{\rho} t^{ji} m_{j,i} \leq 0. \quad (6.7)$$

6.2 Is mass flux possible?

Properly speaking, the field equations we have presented are adequate for simple materials only. Had we wanted to include second-grade effects, we might have changed, for instance, the energy balance equation to include the power of the hyperstress. That said, we will proceed to assume that the second gradient of the deformation (that is, the gradient of

\mathbf{F}) is included in the list of arguments of the constitutive equations. By the principle of equipresence, we will include it in all constitutive equations and let the Clausius-Duhem inequality eliminate this argument wherever it is inconsistent with the principle of dissipation.

There are at least three conceptually different ways to treat the new variable \mathbf{m} . In the first approach, the mass flux \mathbf{m} is treated as an additional constitutive quantity, in the hope that the Clausius-Duhem inequality may allow the gradient of \mathbf{F} to stay as an independent variable of \mathbf{m} , much in the same way as it allows the gradient of θ to remain as an independent variable of \mathbf{q} . In the second approach, \mathbf{m} is treated as an internal state variable appearing as an argument in all constitutive equations and subject to a law of evolution such as an ordinary or partial differential equation

$$\dot{\mathbf{m}} = \mathbf{f}(\mathbf{m}, \mathbf{a}). \quad (6.8)$$

In this equation, \mathbf{f} is some constitutive function governing the evolution and \mathbf{a} is a list of arguments. In the third approach, the mass flux \mathbf{m} may be prescribed externally as a result of the evolution of parameters extraneous to the system at hand. Thus, for example, the mechanism of force production in skeletal muscle can be triggered voluntarily by the brain. Effectively, one has introduced entropy sinks that cannot arise automatically in the Clausius-Duhem inequality, thus possibly weakening its ability to place restrictions on constitutive equations by using it as an identity.

As an example of the use of the first approach, let us assume that the constitutive equations specify the constitutive quantities ψ_I , η , \mathbf{t}_I , \mathbf{q} , $\bar{\mathbf{p}}$, and \mathbf{m} as functions of the following arguments:

$$(F_I^i, F_{I,J}^i, \theta, \theta_I; X^I, t). \quad (6.9)$$

These independent variables represent a (second-grade) thermoelastic heat conductor. The volumetric mass source π and the non-compliant sources of internal energy \bar{u} and of entropy \bar{h} may be either given externally or constitutionally. Notice that we have left the possibility of an explicit dependence on the material coordinates X^I and on time t (elapsed from some defining event). The explicit dependence on X^I indicates that the reference configuration is not homogeneous (which can be the case even if the material itself is homogeneous). The time dependence is an indication of the fact that the material may be evolving in time as a result of processes of remodelling, growth and/or aging.** We indicate the corresponding partial derivatives with the subscript “e”, while the rest

**This explicit time dependence is usually mediated by internal state variables.

is handled by the chain rule of differentiation. Expanding first the time derivatives only, Equation (6.7) becomes:

$$\begin{aligned} & \rho \left(\left(\frac{\partial \psi_I}{\partial t} \right)_e + \frac{\partial \psi_I}{\partial F_K^k} \dot{F}_K^k + \frac{\partial \psi_I}{\partial F_{K,L}^k} \dot{F}_{K,L}^k + \frac{\partial \psi_I}{\partial \theta} \dot{\theta} + \frac{\partial \psi_I}{\partial \theta_{,K}} \dot{\theta}_{,K} \right) \\ & \quad - \frac{\pi}{\rho^2} m_i m^i + \rho \frac{D\theta}{Dt} \eta + \frac{m^i}{\rho} \bar{p}_i - m^i (\psi_{I,i} + \eta \theta_{,i}) \\ - \bar{h} - (t_I)_k^j \dot{F}_K^k F_j^{-K} + \frac{1}{\theta} (q^i + q_d^i) \theta_{,i} - \left(\frac{1}{\rho} \right)_{,i} t^{ji} m_j - \frac{1}{\rho} t^{ji} m_{j,i} & \leq 0. \end{aligned} \quad (6.10)$$

It follows that:

$$(t_I)_k^j = \rho F_K^j \frac{\partial \psi_I}{\partial F_K^k}, \quad (6.11)$$

$$\frac{\partial \psi_I}{\partial F_{K,L}^k} = 0, \quad (6.12)$$

$$\eta = -\frac{\partial \psi_I}{\partial \theta}, \quad (6.13)$$

and

$$\frac{\partial \psi_I}{\partial \theta_{,K}} = 0. \quad (6.14)$$

According to Equations (6.12) and (6.14), the inner free-energy density is independent of the second gradient of the deformation and of the temperature gradient. Consequently, on account of Equations (6.11) and (6.13), so are the inner stress and the entropy density. Using these equations, we further obtain the following residual inequality:

$$\begin{aligned} & \rho \left(\frac{\partial \psi_I}{\partial t} \right)_e - \frac{\pi}{\rho^2} m_i m^i + \frac{m^i}{\rho} \bar{p}_i - m^i \left(\frac{1}{\rho} (t_I)_k^j F_j^{-K} F_i^{-J} F_{K,J}^k + \left(\frac{\partial \psi_I}{\partial X^K} \right)_e F_i^{-K} \right) \\ & \quad - \bar{h} + \frac{1}{\theta} (q^i + q_d^i) \theta_{,i} - \left(\frac{1}{\rho} \right)_{,i} t^{ji} m_j \\ - \frac{1}{\rho} t^{ji} F_j^{-K} \left(\left(\frac{\partial m_i}{\partial X^K} \right)_e + \frac{\partial m_i}{\partial F_L^k} F_{L,K}^k + \frac{\partial m_i}{\partial F_{H,L}^k} F_{H,LK}^k + \frac{\partial m_i}{\partial \theta} \theta_{,K} + \frac{\partial m_i}{\partial \theta_{,L}} \theta_{,LK} \right) & \leq 0. \end{aligned} \quad (6.15)$$

From the last line of this expression it follows that the Clausius-Duhem inequality would not allow for a dependence of the mass flux vector (and, hence, the diffusive momentum) on the second gradient of the deformation or the temperature gradient. The remaining terms would impose a severe restriction on its dependence on the deformation gradient and the temperature. A probable cause for these disappointing conclusions may be the inconsistency arising from not having assumed a second-grade theory *ab initio*. Moreover, a modified version of the inequality (including an explicit form for the non-compliant terms) may be claimed to apply for a theory that includes the new variable \mathbf{m} . Thus, the role of the Clausius-Duhem inequality in imposing restrictions on constitutive equations for self-diffusion rests on less secure grounds than it does in the conventional formulation. We also note that a strict application of the Clausius-Duhem inequality in the theory of mixtures presented in [5] leads to the same conclusion.

In the second approach, whereby the mass flux \mathbf{m} is considered as an internal state variable, some of the rather pessimistic conclusions of the previous derivation are avoided. Thus, the Clausius-Duhem inequality will not be violated, but Fick's law will not necessarily arise directly from this formulation either. Finally, the third approach remains to be studied on a case by case basis.

7 An example

In problems involving solids, it is convenient to restate the field equations in the Lagrangian formulation. The relation between the spatial densities and their referential counterparts is given by:

$$\rho = J^{-1}\rho_0, \tag{7.1}$$

$$\pi = J^{-1}\Pi, \tag{7.2}$$

$$\mathbf{m} = J^{-1}\mathbf{F}\mathbf{M}, \tag{7.3}$$

$$\mathbf{t} = J^{-1}\mathbf{T}\mathbf{F}^T, \tag{7.4}$$

$$p_d^i = J^{-1}P_d^i, \tag{7.5}$$

where J denotes the determinant of the deformation gradient \mathbf{F} . We confine our attention to the purely mechanical equations, namely:

(1) Balance of Mass

$$\frac{D\rho_0}{Dt} = \Pi - M_{,I}^I. \quad (7.6)$$

(2) Balance of linear momentum

$$\rho_0 \frac{Dv^i}{Dt} + F_I^i \frac{DM^I}{Dt} = \rho b^i + T^{iI}_{,I} - 2M^I v_{,I}^i + \bar{P}^i. \quad (7.7)$$

(3) Balance of angular momentum

$$\epsilon_{kji} T^{jI} F_I^i = 0. \quad (7.8)$$

In a one-dimensional setting, assuming the body aligned with the X -axis and the deformation to be given as:

$$x = x(X, t), \quad (7.9)$$

and indicating partial derivatives with respect to X and t by means of a prime and a dot, respectively, the balance of mass and of momentum can be written as:

$$\dot{\rho}_0 = -M' \quad (7.10)$$

and

$$\rho_0 \ddot{x} = T' - \dot{M}x' - 2\dot{x}'M, \quad (7.11)$$

where we have assumed the volumetric mass supply, the body force and the non-compliant volumetric source of momentum to vanish. At this point we must make some constitutive assumptions. In particular, it is important to bear in mind that, since the density in the reference configuration changes with time, the constitutive equation for the stress will be affected somehow. There are several possibilities to model this phenomenon, two of which are: the adaptive elasticity model and the inelastic evolution model.

7.1 Adaptive elasticity model

In the adaptive elasticity model, originally suggested in [2], the added material is assumed to find available space at the expense of the porosity in such a way that there are no additional residual stresses generated. In other words, if the reference configuration is

stress-free at the initial time t_0 (which we assume to be the case), it will remain free of stress at all subsequent times. A simple elastic constitutive law is:

$$T(X, t) = \frac{\rho_0(X, t)}{k} E(x' - 1), \quad (7.12)$$

where E is a constant positive modulus of elasticity and k is a reference density. For the mass flow, we assume the Fick-like law:

$$M = -D \rho'_0, \quad (7.13)$$

where D is a positive constant. Substituting this expression in Equation (7.11), we obtain the diffusion equation:

$$\dot{\rho}_0 = D \rho''_0. \quad (7.14)$$

Our severe simplifications have rendered the mass balance equation decoupled from the balance of momentum. Thus, given initial and boundary conditions and solving the diffusion equation, the referential density becomes a definite function $\rho_0(X, t)$ of X and t . Using the constitutive equation (7.12), the balance of momentum equation becomes:

$$\rho_0(X, t) \ddot{x} = \frac{\rho_0(X, t)E}{k} x'' + 2D \rho'_0(X, t) \dot{x}' + \frac{\rho'_0(X, t) E}{k} (x' - 1) - D \dot{\rho}_0 x'. \quad (7.15)$$

The discriminant of this linear equation (namely $\rho_0^2 E/k + \rho_0'^2 D^2$) is strictly positive, so that the equation is hyperbolic. This simple example shows that the equations of the theory lead to solutions in agreement with the physical interpretation of the Second Law. In fact, this example can be considered as an instance of the application of the third approach of those discussed above. The mass flux and the stress depend on an additional state variable (namely $\rho_0(X, t)$) whose evolution is not controlled by the deformation.

7.2 Anelastic model

We have seen that in the adaptive elasticity model there exists a preferential global stress-free reference configuration, whose density $\rho_0(X, t)$ acts as an internal variable for the progress of the mass flux. Thus, the self-diffusion phenomenon becomes independent of the deformation. In the anelastic model, this is not the case. A stress-free configuration (which, in the case of a one-dimensional setting always exists) is not given a priori.

Rather, in the absence of porosity, as the density changes at a given body point the constitutive equation is referred to a local stress-free reference at a reference density k , prescribed once and for all. In other words, it can be said that, if we were to cut a small neighbourhood (with density $\rho_0(X, t)$) of the point in the global reference configuration, the cut piece would immediately jump to a relaxed state with density k . If the deformation gradient from the global (not generally stress-free) reference configuration is $x'(X, t)$, the deformation gradient from the locally relaxed reference configuration is given by:

$$f_k = x'(X, t) \frac{k}{\rho_0(X, t)}. \quad (7.16)$$

Concomitantly, the time-dependent constitutive law (assumed to be of the linear form (7.12), for the purposes of comparison), is now given by:

$$T(X, t) = E(f_k - 1) = E\left(x' \frac{k}{\rho_0(X, t)} - 1\right). \quad (7.17)$$

As far as the mass flux is concerned, we can no longer relate it to the density gradient in the global reference configuration, since the theory should be independent of it (unlike the case of adaptive elasticity, where there was a physically meaningful stress-free global reference configuration). Notice that, in a one-dimensional context, we can always construct a global stress-free reference configuration. This configuration, however, would be by definition of constant density k , and thus useless as the driving force for the mass flow. Our only remedy is to consider the *spatial* gradient of the *spatial* density, namely $\rho_{,i}$, and to propose the following law for the mass flux:

$$m_i = -D \rho_{,i}, \quad (7.18)$$

or, in the Lagrangian formulation:

$$M^I = J F^{-Ii} m_i = -D J F^{-Ii} \rho_{,i} = -D F^{-Ii} F_i^{-L} \left(-F_k^{-K} F_{K,L}^k \rho_0 + \rho_{0,L} \right). \quad (7.19)$$

In the one-dimensional case, this formula becomes

$$M = -\frac{D}{x'^2} \left(\rho'_0 - \frac{x''}{x'} \rho_0 \right). \quad (7.20)$$

In contrast with the adaptive elasticity case, we have here a second-grade material, as evidenced by the appearance of second derivatives of the deformation in this constitutive

equation. As a consequence, the field equations (which are obtained by introducing (7.17) and (7.20) into (7.10) and (7.11)) will be of the third order. Questions of appropriate boundary conditions and of exact or approximate thermodynamic restrictions are more difficult to answer in this case.

8 Summary and conclusions

A complete theory of self-diffusion has been presented on the basis of the introduction of an extra (diffusive) momentum field. It has been shown that, as a consequence of demanding observer independence of the balance of angular momentum, the mass flux vector must be equal to the diffusive momentum field. A remarkable feature of the theory is that it can be independently reinterpreted as that of a binary mixture obtained by arbitrarily partitioning the medium into two components and formulating the equations of the mixture from the vantage point of an observer attached to one of the two components. The resulting equations are independent of the partitioning. The consequences of the Clausius-Duhem inequality in terms of restrictions to possible constitutive equations were investigated and found to lead to somewhat paradoxical results. Assuming that the theory of mixtures is consistent with the Clausius-Duhem inequality, and taking into consideration that the two versions (self-diffusion and binary mixture) of the inequality are identical in form, we must conclude that there is no fundamental contradiction between the Second Law of Thermodynamics and the proposed theory. It is rather surmised that theories of open systems with additional state variables, such as those prevalent in processes of biological growth and remodelling, offer a challenge that the Clausius-Duhem inequality in its classical form may not be able to sustain.

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