

Application of diffusive internal variables in complex fluids

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Abstract

A thermodynamical phenomenological approach to complex fluids is presented in which the underlying microstructure is accounted for through a so-called internal variable of state. The latter may diffuse. It is shown that both the bulk evolution–diffusion equation of this variable and the required associated boundary conditions can be deduced from a thermodynamical reasoning that exploits the second law in the bulk and at the boundary considered as an interface. © 2001 Published by Elsevier Science B.V.

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1. Introduction

In this work we aim at introducing some generalization of the notion of *internal variables* in order to deal with a more accurate phenomenological description of *complex fluids* and of their *rheology*. This generalization, accounting for the *diffusion* of the relevant internal variable, should, paradoxically, be achieved in the simplest possible manner.

We remind the reader that a fruitful modeling of the complex fluids of interest uses the notion of *internal variable of state*, hence a thermodynamical framework (cf. [17,21]) even though both wording and framework are not acknowledged by all authors. Such an internal variable must be most representative of the *microstructure* of the fluid, a good example being the so-called *conformation* of macromolecules [13,18]. The thermodynamic approach (applying the second law of thermodynamics as a mathematical constraint) that accounts for the *time evolution* of such a variable imposes a certain form to the governing equation which traditionally is a pure *evolution equation*; only the variable and its time derivative and some other fields — the latter parametrically — are involved in that equation which, therefore, has no boundary conditions associated with it. These ‘classical’ internal variables of state are not controlled by such conditions. This is the essential difference between that class of thermodynamic variables and the

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class of *observable* variables of state — temperature, quantities related to the macroscopic motion — that generally satisfy *field equations* including inertial terms and accompanied by boundary conditions, and thus requiring more data in both time and space. Such a framework — here referred to as the ‘classical one’ — has borne fruits in a lot of applications in various branches of phenomenological physics (mechanical solid and fluid, and electromagnetic, applications in [17]). In the case of fluids on which we focus attention, this approach gives interesting results in the absence of substantial gradients. Accordingly, regions near walls are excluded. Similarly, in solids, regions with localized strains are excluded.

Classically, at the starting point in a general thermodynamical description we have to provide information about the microstructure of the considered medium, the different constituents present in it, and their possible interactions. At this point we are not able to introduce balance laws for all the quantities governing the macroscopic behavior of the medium. So we try to guess what are the most relevant variables. To do this we must be helped by experimental results that play a guidance role in this selection. Such a choice being done, one must build an appropriate thermodynamical framework in order to formulate the missing constitutive equations, and then solve some exemplary problems in order to test the validity of the working assumptions. Taking account of important spatial gradients requires more sophistication. A rather direct approach consists in introducing gradients of internal variables of state in the set of independent variables. Accordingly, the Helmholtz free energy ψ depends on this enlarged set and the relevant internal variable α is shown to be governed by an evolution–diffusion equation, where the flux is related to the functional derivative of ψ with respect to the internal variable (cf. [9,16]).

Another viewpoint consists in adding some quantities that play a determining role in the mechanical behavior of the considered medium. Again this requires some guidance from experimental data or microscopic physics. Then the relevant internal variable is a priori assumed to satisfy an evolution–diffusion equation that contains unknown divergence and rate of production terms. This approach has been initially developed by Hess and Pardowitz [6,7,9] for the description of isotropic and nematic phases of liquid crystals. Obviously, both initial and *boundary* conditions are needed in such a formulation. The method used by Waldman [25] to construct such boundary conditions will be exploited, our aim being to develop an approach that deviates the least from the framework of the thermodynamics of irreversible processes with internal variables (expanded, e.g. [17]). To that purpose we assume that classical balance laws are formally not modified by the presence of these internal variables. In the process we will justify the case where this assumption holds good. A critical comparison between the two viewpoints is given for the case of dilute polymer solutions.

2. Some experimental data

A most remarkable effect observed in polymer solutions is known as the ‘apparent slip phenomenon’. For this we refer to the study of Müller-Mohnsen [23]. These authors use a laser differential anemometer and a total-reflection microscope anemometer. They obtained characteristic velocity and concentration profiles in rectangular ducts with walls made of two different materials, lucite in one case, glass in the other. The fluid is aqueous polyacrylamide solution. They were able to obtain the velocity profile in a boundary layer of which the thickness δ is of the order of 0.15 μm . This is of the same order as the spatial resolution of the apparatus. Indeed, they show that the velocity profiles evolve from zero at the wall to a finite value at distance δ . Different values are observed for the two walls, and the thickness δ depends on the concen-

tration, and the latter itself is observed to be lower in the boundary layer than in the bulk of the solution. Other authors, in particular, Aussere [1], has observed such depletion layers near walls. From these experiences we retain the idea of the presence of a *boundary layer*, a zone with large velocity gradients, and the influence of the nature of the wall that introduces the notion of *interaction* between the polymer solution and the material boundaries. A relevant question then is ‘what are the tools to be used to account for this interaction’? One possibility is that boundary conditions for some unknown quantities have to be postulated. Because of this specification at the boundary the said variable — that we would like to identify — becomes controllable, in contradistinction with now classical internal variables of state. On account of this remark, we now set forth the general thermodynamically admissible framework to model the above-noted phenomena.

3. General framework

First we assume for the fluid material under consideration that we can define the set of thermodynamical state variables (see [17] for this notion), as also the associated balance laws. Second, an additional ‘internal’ variable of state noted α —independently of its precise tensorial order— is introduced. We suppose that the presence of α does not formally modify the above-mentioned balance laws. This, in particular, means that α does not contribute any kinetic energy to the system (a classical working assumption of internal — variable theory in contradistinction with what happens with additional ‘degrees of freedom’). However, α will be governed by an evolution–diffusion equation of the type

$$\dot{\alpha} + \text{div } \mathbf{b} = \hat{\alpha}, \quad (1)$$

where a superimposed dot denotes the material time derivative D/Dt . Eq. (1) involves a rate source term $\hat{\alpha}$ and a divergence term of the quantity \mathbf{b} representing the flux within an elementary volume. This is the relevant ingredient in the modeling of *spatial non-uniformities*. These two quantities are as yet unknown. We, therefore, need a procedure to formulate expressions for them. To that purpose we work within the frame of the thermodynamics of irreversible processes and exploit the Clausius–Duhem inequality and the entropy production. In the process we will have to define appropriately the *entropy flux vector*. To illustrate this procedure in a more vivid manner, we consider an example corresponding to dilute polymer solutions.

4. Example of dilute polymer solutions

Here we combine ingredients from various approaches. First, the solution is viewed as a *binary mixture*. The concentration in polymer is an important state variable. Its gradient and diffusion are known to be present near walls and solid boundaries (see above). Next the solution is also considered as a *microstructured continuum*. The nature of macromolecules should influence the behavior of the solution. We must, therefore, specify that quantity α that will model these microstructural effects. Here we adopt the classical viewpoint of internal-variable theory [18] and choose as internal variable the *conformation* of macromolecules that is represented by a second-order tensor. We can proceed thus.

4.1. Binary mixture theory

Compared with traditional *homogeneous* media, we have to account for the additional state variable called the concentration in polymer. Let ρ_P and ρ_S be the mass density of polymer molecules and solvent, respectively, so that the mixture mass density is $\rho = \rho_P + \rho_S$ and the concentration c is defined by

$$c = \frac{\rho_P}{\rho}. \quad (2)$$

Let \mathbf{v} denote the barycentric velocity of the macroscopic solution. In the absence of chemical reactions (mass exchange) between constituents, the balance of mass yields

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0, \quad (3)$$

$$\rho \frac{Dc}{Dt} + \nabla \cdot \mathbf{J} = 0, \quad (4)$$

where \mathbf{J} is the *diffusion flux* such that

$$\mathbf{J} = \rho c (\mathbf{v}_P - \mathbf{v}), \quad (5)$$

if \mathbf{v}_P is the polymer molecule velocity.

The balance of linear and angular momenta are those of a classical continuum (no couple stress) and read in Cartesian tensor notation that needs no further explanation

$$\rho \frac{Dv_i}{Dt} = \sigma_{ij,j} + f_i \quad (6)$$

and

$$\sigma_{ij} = \sigma_{ji}, \quad (7)$$

where σ_{ij} are the components of the Cauchy stress tensor and f_i those of the body force. The balance of (internal) energy in the absence of bulk heat source, is given by (cf. [17])

$$\rho \frac{De}{Dt} - \sigma_{ij} D_{ji} + q_{j,j} = 0. \quad (8)$$

Here, e is the internal energy per unit mass of the mixture, q_j are the components of the heat flux vector, and D_{ij} are those of the strain-rate tensor, i.e.

$$D_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}) = D_{ji}. \quad (9)$$

Eq. (8) means that only stress and heat flux are involve at the boundary.

4.2. Description of the microstructure

This is effected through the introduction of the symmetric *conformation* tensor \mathbf{K} of components $K_{ij} = K_{ji}$. Such a tensor is often used to describe first-order deviations from a spherical shape (cf.

[12,13,18–20]). Here we suppose nothing concerning \mathbf{K} except its symmetry and the fact that, in agreement with Section 3, we postulate the following evolution–diffusion equation for \mathbf{K}

$$D_J \mathbf{K} + \text{div } \mathbf{b} = \mathbf{R}, \quad (10)$$

where D_J denotes the Jaumann (co-rotational) derivative of \mathbf{K} , \mathbf{b} is a third-order tensor symmetric in its first two indices, hence of components $b_{ijk} = b_{jik}$ (the divergence of \mathbf{b} is taken on the last index), and \mathbf{R} is a symmetric second-order tensor of components $R_{ij} = R_{ji}$. The last two quantities are unknown. The thermodynamics of irreversible processes and the entropy production are used to derive thermodynamically admissible expressions (constitutive equations) for them.

Finally, the entropy inequality, without specific hypothesis concerning the entropy flux, reads at any point

$$\rho \frac{Ds}{Dt} + \phi_{i,i} \geq 0, \quad (11)$$

where the entropy flux vector Φ of components ϕ_i has to be specified, s is the entropy per unit mass, and T is the absolute temperature.

Gibbs differential equation reads in the present case

$$\frac{Ds}{Dt} = T^{-1} \left(\frac{De}{Dt} + p \frac{D\tau}{Dt} - \tilde{\mu} \frac{Dc}{Dt} \right) + T^{-1} \rho^{-1} F_{ij} \frac{DK_{ij}}{Dt}, \quad (12)$$

where p is the pressure, τ the specific volume, μ is the chemical potential, and

$$F_{ij} \equiv -\rho \frac{\partial g}{\partial K_{ij}} = F_{ji}, \quad (13)$$

defines the thermodynamical force associated to \mathbf{K} if g is the Gibbs energy associated to the variable \mathbf{K} . For example, in a simple approach the latter is assumed to be quadratic and involving only one scalar dimensionless coefficient A , i.e.

$$\rho g = \frac{1}{2} (n k_B T) A K_{ij} K_{ji}, \quad (14)$$

where k_B is the Boltzmann's constant, and n is the number of macromolecules per unit volume. A non-quadratic expression involving higher-order terms is possible, in the tradition of Landau's theory of phase transitions (cf. [22]), but this sophistication is not required here. In Eq. (12) we shall distinguish the classical contribution and that one due to \mathbf{K} , i.e. with a straightforward identification, we write

$$\rho \frac{Ds}{Dt} = \rho \left(\frac{Ds}{Dt} \right)^0 + T^{-1} F_{ij} \frac{DK_{ij}}{Dt}. \quad (15)$$

We have at hand the following ingredients: (i) Eq. (15) which represents a statement of Gibbs Equation, (ii) Eq. (8) that stands for the *energy theorem* (the variable \mathbf{K} does not produce any power in that expression; that is, in agreement with [10], this would be an *internal variable* in its own right), and (iii) Eq. (10) in which we have to give appropriate expressions to \mathbf{b} and \mathbf{R} under the constraint (11). Accounting to Eq. (10), we transform Eq. (15) to

$$\rho \frac{Ds}{Dt} = \rho \left(\frac{Ds}{Dt} \right)^0 + T^{-1} F_{ij} (R_{ij} - b_{ijk,k}). \quad (16)$$

We shall call *entropy flux vector* associated to the internal variable \mathbf{K} the vector Φ^K of components

$$\Phi_k^K = T^{-1} F_{ij} b_{ijk}. \quad (17)$$

Eq. (16) therefore reads

$$\rho \frac{Ds}{Dt} + \text{div } \Phi^K = \rho \left(\frac{Ds}{Dt} \right)^0 + T^{-1} (b_{ijk} F_{ij,k} + F_{ij} R_{ij}). \quad (18)$$

The energy theorem (Eq. (8)) allows us to write the following expression:

$$\rho \left(\frac{Ds}{Dt} \right)^0 = T^{-1} (\sigma_{ij}^v D_{ij} - q_{i,i} + \tilde{\mu} J_{i,i}), \quad (19)$$

after decomposition of the stress tensor into pressure and viscous terms

$$\sigma_{ij} = -p \delta_{ij} + \sigma_{ij}^v. \quad (20)$$

Considering only the ‘classical’ expression (19), we can identify an *entropy flux vector* and a *source of entropy* as

$$\Phi_k^0 = T^{-1} (q_k - \tilde{\mu} J_k), \quad (21)$$

$$\Sigma^0 = T^{-1} (\sigma_{ij}^v D_{ij} + q_i (T^{-1})_{,i} - J_i (\tilde{\mu}_i / T)_{,i}). \quad (22)$$

The total entropy flux and entropy production are given by

$$\Phi = \Phi^0 + \Phi^K, \quad \Sigma = \Sigma^0 + \Sigma^K, \quad (23)$$

where Σ^K is given by the last contribution in Eq. (18). That is,

$$\Sigma^K = T^{-1} (F_{ij} R_{ij} + F_{ij,k} b_{ijk}). \quad (24)$$

The entropy flux (21) is of a classical form in diffusion (cf. [11], p. 345). The additional entropy flux due to \mathbf{K} -diffusion is of the form proposed by Maugin [16] in general considerations on *weakly non-local* theories of internal-variable thermodynamics (the weak non-locality concept was introduced in [14,15]). In both cases we are far from the assumptions that prevail in the so-called ‘rational thermodynamics’ (cf. [24]). We are rather in the realm of *extended thermodynamics* although we shall strictly adhere to the procedure of irreversible thermodynamics (see below).

5. Irreversible thermodynamics

5.1. Constitutive equations

In the classical theory of irreversible processes, which is used here as the main tool, the entropy production that should be non-negative is considered as the starting point for the formulation of linear (irreversible) constitutive equations:

$$T(\Sigma^0 + \Sigma^K) \geq 0. \quad (25)$$

Examination of the parity of terms present in the expressions (22) and (24) allows one to envisage *couplings* between the quantities \mathbf{q} , \mathbf{J} , and \mathbf{b} — which are the ‘fluxes’ — the quantities ∇T , ∇c , and $\nabla \mathbf{K}$ — which are the associated ‘forces’. That is, spatial non-uniformities in \mathbf{K} will contribute to both \mathbf{q} and \mathbf{J} . We also recall the formulation that was exploited by Drouot and Berrajaa [3] in so far as the terms in \mathbf{b} and \mathbf{R} are concerned. For instance, introducing the deviatoric and spherical parts of \mathbf{R} and \mathbf{F} by

$$R_{ij} = R_{ij}^d + \frac{1}{3} R_{kk} \delta_{ij}, \quad F_{ij} = F_{ij}^d + F_{kk} \delta_{ij}, \quad (26)$$

simple isotropic relations that satisfy automatically — sufficient conditions (Eq. (25)) — in the absence of flow, are given by

$$R_{ij}^d = +\tau_k^{-1} F_{ij}^d, \quad R_{kk} = +\tau_{K'}^{-1} F_{kk}, \quad b_{ijk} = +D_K F_{ij,k}, \quad (27)$$

where the τ ’s are non-negative relaxation times and D_K is a non-negative diffusion coefficient. Then the evolution–diffusion equation satisfied by \mathbf{K} in this simple case reads as follows:

$$\frac{\partial}{\partial t} K_{ij} + D_K \nabla^2 F_{ij} = \left(\tau_K^{-1} F_{ij}^d + \frac{1}{3} \tau_{K'}^{-1} F_{kk} \delta_{ij} \right), \quad (28)$$

or, separating spherical and deviatoric parts,

$$\frac{\partial}{\partial t} K_{kk} + D_K \nabla^2 F_{kk} = +\tau_{K'}^{-1} F_{kk}, \quad (29)$$

$$\frac{\partial}{\partial t} K_{ij}^d + D_K \nabla^2 F_{ij} = +\tau_K^{-1} F_{ij}^d, \quad (30)$$

where F_{ij} is in fact linearly related to $-K_{ij}$, so that Eqs. (29) and (30) are ‘good’ equations with non-negative τ ’s and D_K .

Generalizations of Eq. (30) in the presence of flow but without diffusion of the variable \mathbf{K} may be found in [18], where only the deviation from spherical ‘shapes’ are of interest (\mathbf{F} was isochoric in that approach). In general, however, Eqs. (29) and (30) are evolution–diffusion equations that require *boundary conditions* in problem solving. But the way \mathbf{K} was introduced — no alteration of the energy equation (8), which means no work related to \mathbf{K} at the boundary — makes that we are short of these boundary conditions which, like Eqs. (29) and (30), must be obtained on some thermodynamical basis. This is examined next following ideas put forth by Waldman [25].

5.2. Boundary conditions

In the approach advocated by Waldman [25] which, although old, is fully pertinent, the boundary is naturally considered as an *interface* between two different media. But, viewed on our macroscopic scale, this interface structure will result in the consideration of phenomenological coefficients relating various quantities (forces and fluxes) at the interface; the solution to our problem of formulating boundary conditions at the boundary is, from that viewpoint, one of irreversible thermodynamics of an interface. The latter is first considered as an interface between two immiscible fluids, and attention is focused on the relevant quantity, the interfacial entropy production. Two possibilities may be considered depending on whether this interface does or does not carry momentum and energy per unit area. Working along this line Waldman [25] writes the equations of discontinuity (at the interface) associated with the classical balance

laws, and the discontinuity (jump) condition for entropy including an interfacial entropy (a source term at the interface). Exploiting then the theory of irreversible processes at the interface, he is able to write Onsagerian linear relations between ‘forces’ and ‘fluxes’. This does provide the missing information. For instance, when the interface carries neither momentum nor energy, this author finds a mechanical slip for the velocity field related to the temperature jump. A similar line of thought was considered more recently by Hess and Koo [8] to obtain some boundary conditions in molecular fluids. This type of approach allowed these authors to take the influence of the boundary on the molecular alignment into account. In that approach the molecular alignment is mathematically represented by a second-order tensor that satisfies an equation of the type (1) or (10), so that this is very close to our present interest. Hess and Koo [8] were particularly interested in the boundary conditions in the isothermal case and in the absence of surface heat flux, focusing thus on mechanical considerations. Let us apply a similar approach in our case where Eqs. (4), (6), (8) and (10) are the relevant bulk equations.

Let Σ the regular boundary between the two media labeled $i=1$ and 2 , respectively, the ‘complex fluid’ and the solid boundary. We see Σ as a flattened transition zone Σ' . This bulk, but thin ‘third body’ Σ' , is limited by surfaces Σ_2 and Σ_1 , respectively, on the fluid and solid sides, with outside pointing unit normals \mathbf{n}_2 and \mathbf{n}_1 , respectively. As Σ' flattens to Σ , Σ_2 comes to coincide with $\Sigma_1=\Sigma$ and the unit normals \mathbf{n}_2 and \mathbf{n}_1 comes to coincide with \mathbf{n} and $-\mathbf{n}$, where \mathbf{n} is the unit outward normal to the solid boundary. What happens at the lateral ends of Σ' during the shrinking procedure is irrelevant in the absence of surface tension. In this procedure it is checked that, in the absence of mass transport through Σ , we have from Eq. (3) the following jump relation at Σ :

$$[\mathbf{v}] \cdot \mathbf{n} = 0, \quad (31)$$

where we defined the jump by $[A]=A_2-A_1$. Eq. (31) expresses the fact that the relative velocity of the two media at Σ is purely *tangential* [5]. That is,

$$\mathbf{v}_2 - \mathbf{v}_1 = \mathbf{v}_t \equiv P_\Sigma(\mathbf{v}_2 - \mathbf{v}_1), \quad P_\Sigma \equiv \mathbf{1} - \mathbf{n} \otimes \mathbf{n}, \quad (32)$$

where P_Σ is the projection operator onto Σ . Let Φ_2 and Φ_1 be the entropy influx from media 2 and 1 at Σ_2 and Σ_1 , respectively. The interfacial entropy production at Σ is obtained as

$$N = \lim_{\Sigma_2 \rightarrow \Sigma} \left(- \int_{\Sigma_2} \Phi_2 \cdot \mathbf{n}_2 \, ds - \int_{\Sigma_1} \Phi_1 \cdot \mathbf{n}_1 \, ds \right) = - \int_{\Sigma} [\Phi] \cdot \mathbf{n} \, ds \quad (33)$$

The second law of thermodynamics at Σ imposes the following restriction:

$$N \geq 0. \quad (34)$$

This is implemented for any surface element of the boundary, i.e. we impose that

$$-[\Phi] \cdot \mathbf{n} \geq 0 \text{ at any point } x \in \Sigma. \quad (35)$$

We are going to exploit this inequality for several exemplary cases.

5.2.1. Boundary condition in the absence of heat flux and concentration gradient (purely mechanical theory)

In this case, we have

$$\Phi_1 = \mathbf{0} \text{ (solid)}, \quad \Phi_2 = \Phi^K \text{ (complex fluid)}. \quad (36)$$

On account of Eqs. (17) and (36), condition (35) yields

$$-F_{ij}b_{ijk}n_k \geq 0. \quad (37)$$

By way of example, a simple (isotropic) linear relation between forces and fluxes involved in Eq. (37) reads

$$F_{ij} = -\beta b_{ijk}n_k, \quad \beta > 0. \quad (38)$$

This is a sufficient condition for Eq. (35) to be satisfied. On account of the last equation of Eq. (27), Eq. (38) also reads

$$F_{ij} + \lambda \frac{\partial F_{ij}}{\partial n} = 0, \quad \lambda = \beta D_K \geq 0. \quad (39)$$

The boundary conditions (38) or (39) are the conditions looked for. It involves a single scalar phenomenological coefficient, whose positiveness is a consequence of the second law. The condition is a linear combination of Dirichlet and Neumann conditions for the components of the symmetric tensor F_{ij} . This is akin to the *Robin* condition in electromagnetism. Pure Dirichlet and Neumann conditions are obtained in the following two limit cases:

$$\lambda = 0 \Rightarrow F_{ij} = 0 \text{ at } \Sigma, \quad (40)$$

$$\lambda \rightarrow \infty \Rightarrow \frac{\partial F_{ij}}{\partial n} = 0 \text{ at } \Sigma. \quad (41)$$

Conditions (39)–(41) characterize different types of *anchoring* at the solid boundary. This is similar to the considerations of Hess and Koo [8] if we remember that their alignment tensor is very similar to our K_{ij} .

Remark: The boundary condition (39) is also reminiscent of the general boundary condition that prevails for magnetic spin in the continuum theory of ferromagnets (cf. Eq. (9.3.35) and footnote in p. 453 of [4]). The analogy in fact is deeper than thought at first sight. In effect, magnetic spin is usually considered as an observable variable of state (this is the case in the just cited book). But in the magnetomechanical theory, it may also be considered as a *diffusive* internal variable of state — compared to mechanics that provide the main observable field; the *diffusive nature* of the internal variable then originates from the fact that Heisenberg exchange forces between neighboring spins are active. This second avenue was exploited by the author Maugin [15], but there remained then the problem of the associated boundary condition. A development analogous to the above-given one would render this *Robin* type of boundary condition for the magnetic spin. This answers a question raised more than 20 years ago.

5.2.2. Boundary condition in the presence of heat flux, but isothermal conditions and no concentration gradient

In this case we have to exploit the jump conditions associated with motion and energy. The second of these gives (this is independent of the flattening procedure of Σ')

$$[\mathbf{v} \cdot \boldsymbol{\sigma} \cdot \mathbf{n} - \mathbf{q} \cdot \mathbf{n}] = 0 \text{ at } \Sigma, \quad (42)$$

or, on account of Eqs. (31) and (32),

$$\mathbf{v}_t \cdot \mathbf{T}_t = [\mathbf{q}] \cdot \mathbf{n}, \quad \mathbf{T}_t \equiv P_\Sigma(\boldsymbol{\sigma}_2 \cdot \mathbf{n}). \quad (43)$$

For the entropy fluxes, we have

$$\Phi_1 = T^{-1} \mathbf{q}_1 \text{ (solid)}, \quad \Phi_2 = T^{-1} \mathbf{q}_2 + \Phi^K \text{ (complex fluid)}. \quad (44)$$

As a consequence of Eqs. (43) and (44) and the continuity of traction, the surface entropy production reads

$$N = - \int_{\Sigma} (T^{-1} [\mathbf{q}] \cdot \mathbf{n} + \Phi^K \cdot \mathbf{n}) \, ds, \quad (45)$$

or else

$$N = \int_{\Sigma} T^{-1} (\mathbf{v}_t \cdot \mathbf{T}_t + F_{ij} B_{ij}^{(n)}) \, ds \geq 0, \quad B_{ij}^{(n)} \equiv b_{ijk} n_k \text{ at } \Sigma. \quad (46)$$

Now we look for sufficient conditions to satisfy the first of Eq. (46) locally at each point of Σ . The question of parity here is important as we look for *coupled* expressions for the fluxes F_{ij} and \mathbf{v}_t . Furthermore, we should note that these expressions should be at least linear in the components of the normal vector \mathbf{n} (remembering that this is indeed the case of the quantities \mathbf{T}_t and $\mathbf{B}^{(n)}$). As F_{ij} is a symmetric tensor, and \mathbf{v}_t is obviously odd in time, and is purely tangential, one simple possibility is provided by the following expressions:

$$\mathbf{F} = -k_1 (\mathbf{T}_t \otimes \mathbf{n})_S - \beta \mathbf{B}^{(n)}, \quad \mathbf{v}_t = -a \mathbf{T}_t - k_2 P_{\Sigma} (\mathbf{n} \cdot \mathbf{B}^{(n)}), \quad (47)$$

with the conditions

$$\beta \geq 0, \quad a \geq 0, \quad k_2 = -k_1. \quad (48)$$

The last of these follows from the different time parity of \mathbf{v}_t and F_{ij} , leaving the sign of k_1 undetermined by thermodynamics. We have called such couplings ‘gyroscopic’ in the sense that they finally do not contribute to entropy production as they satisfy jointly an *orthogonality condition* between thermodynamical forces and associated generalized velocities (for such couplings between conformation and flow in the bulk, see [18]). The coefficient a accounts for *mechanical slip* at the solid boundary as it is checked by considering the special case where F_{ij} is absent and we take $\mathbf{v}_1 = \mathbf{0}$, resulting in a tangential traction opposite to the velocity of the fluid.

If the third simple bulk constitutive equation of Eq. (27) holds good, then after a simple calculation, Eq. (47) yields

$$F_{ij} + \lambda \frac{\partial F_{ij}}{\partial n} = -\frac{1}{2} k_1 (T_{ii} n_j + T_{ij} n_i), \quad v_{ti} = -a T_{ti} + k_1 D_K P_{\Sigma} \left(n_k \frac{\partial F_{ki}}{\partial n} \right). \quad (49)$$

If the cross coupling is neglected ($k_1 = 0$), then the first of Eq. (49) recurs to the ‘Robin’ condition (39) and the second condition of Eq. (49) reduces to the pure mechanical-slip condition.

5.2.3. Boundary conditions without thermal effects

In this case cross effects are considered in the bulk of the complex fluid, heat flux and temperature gradients being neglected. This, in particular, means couplings between flow and the dynamical behavior of the internal variable K_{ij} . The bulk entropy production contains all terms, except that of heat flux. The coupled bulk constitutive equations in that case have been given in a previous work for an incompressible

isothermal flow and isochoric conformation K_{ij} . Let $\bar{\mathbf{K}}$, $\bar{\mathbf{F}}$ and $\bar{\mathbf{D}}$ denote then the traceless conformation, associated thermodynamical force, and strain rate. From Eqs. (26.2) through (26.4) in [2] we have the relations

$$\begin{aligned}\bar{F}_{ij} &= (nk_B T)(\tau_K \bar{R}_{ij} + \tau_0 \bar{D}_{ij}), & b_{ijk} &= D_K \bar{F}_{ij,k} + \chi_{ijkp} \left(\frac{\tilde{\mu}}{T} \right)_{,p}, \\ J_p &= -k \left(\frac{\tilde{\mu}}{T} \right)_{,p} + \chi_{ijkp} \bar{F}_{ij,k}.\end{aligned}\quad (50)$$

This renders the system of bulk equations (4), (6) and (10) fully coupled. Again the missing boundary condition that relates to Eq. (10) will be obtained by considering the positive nature of the interfacial entropy production at the boundary Σ . In the present case, we have

$$\Phi_1 = \mathbf{0} \text{ (solid)}, \quad \Phi_2 = -T^{-1} \tilde{\mu} \mathbf{J} \text{ (complex fluid)}.\quad (51)$$

Then the entropy production at Σ reads

$$N = - \int_{\Sigma} \left(\left(\frac{\tilde{\mu}_2}{T} \right) \mathbf{J}_2 \cdot \mathbf{n} + \Phi^K \cdot \mathbf{n} \right) ds.\quad (52)$$

The jump equation associated with Eq. (4) reads

$$[\mathbf{J}] \cdot \mathbf{n} = 0.\quad (53)$$

But $\mathbf{J}_1 = \mathbf{0}$, so that with Eq. (53), the first contribution in the integrand of Eq. (52) vanishes and the expression of N reduces to that already obtained in Eqs. (36) and (37), since only the entropy flux related to \mathbf{K} remains involved. The natural boundary condition (53) and a condition such as Eq. (39) complete the full set of boundary conditions.

6. Conclusions

Investigation of boundary-value problems on the basis of the three sets of extra boundary conditions obtained in Section 5 may be a difficult task. Practically, a relatively simple approach consists in the study of the influence of the variable \mathbf{K} alone on the rheology of the considered complex fluid, with special attention paid to the interaction between walls and microstructure. The validity of the proposed modeling has to be tested on some exemplary problems, and the results obtained compared to experimental data, when these are available. This is outside the aim of the present contribution whose main purpose was to demonstrate a powerful application of irreversible thermodynamics to the formulation of the rheology of complex fluids, a type of approach altogether too much neglected.

We have considered an extension of the notion of internal variable of state. This internal variable represents, in some sense, the additional degrees of freedom corresponding to a microstructure hidden to our naked eye but responsible for some apparent irreversibilities. The strength of the formalism of thermodynamics lies in its application in domains and regimes where we do not know precisely, or it is an insuperable task, to relate the underlying microscopic structure and macroscopic parameters. Here, in implementing the strategy of internal variables of state, we have first to identify the nature of, and define in a precise mathematical manner, the relevant internal variable. The latter then is supposed to satisfy before

hand an evolution–diffusion equation. The analysis of the bulk entropy production and of the interfacial entropy production, at boundaries, then allows one to characterize both irreversible bulk behavior and the non-classical boundary conditions by a few phenomenological parameters. Experimental data remains, in the end, the final test for the validity of this type of approach unless a complete precise transition from the microscopic level to the macroscopic one provides the expression of those phenomenological parameters in terms of essential features of the components of the complex fluid, a goal not reached for the moment.

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