

# Thermomechanics of Interstitial Working at Liquid Boundaries <sup>1</sup>

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Dedicated to Professor Wolfgang Muschik on the occasion of his 65-th birthday.

*A model of material interface, for which the metric tensor is regarded as an internal variable, is considered. Both a local and a non-local evolution equation for such a variable are analyzed. The consequences of the second law of thermodynamics are derived in both cases.*

## 1 Introduction

Interfacial phenomena arise frequently in nature and have useful applications in science and technology. For instance, they are observed in the thin layer between different phases of the same material, or in a film of a given substance spread on a surface (Adamson, 1982). Within a certain approximation, these systems behave as two-dimensional continua carrying suitable material properties. For instance, in a soap bubble in mechanical equilibrium the pressure jump is proportional to the mean curvature. The proportionality factor is a force per unit of area, which is referred to as *surface tension*. Analogously, a *surface internal energy* and a *surface free energy* can be measured by standard techniques (Adamson, 1982). The presence of material passing through the interface is accounted for by certain jumps of three-dimensional fields appearing in the balance equations. Two cases are possible: the interface is *material*, i.e. it is formed at any instant of time by the same particles; the interface is *non-material*, i.e. it is a propagating geometrical surface occupied at different instants of time by different particles. When the interface is material the related model describes films; when the interface is not material the model applies to phase transitions. In both cases that region is regarded as a two-dimensional non-Euclidean continuum the geometrical and material properties of which influence each other. In the classical theory of interfaces (Moeckel, 1987; Müller, 1985), the metric tensor is regarded as a standard thermodynamic variable, playing the role of the two-dimensional strain tensor. A stress-strain relation follows from the second law of thermodynamics. Such an approach excludes the possibility of a dissipation of energy related to the interface deformation. To our opinion such a dissipation is possible. For example, let us consider an interface which contains a granular material, as it happens in many detergent substances. Then the grains migrate and diffuse inside the interstitial volume but such a *micromotion*, which is superposed to the surface *macromotion* and influences its deformation, cannot be described by any three-dimensional field since, in that picture, the thickness of the interfacial region is zero. However, the diffusive motion of the grains, besides influencing the surface macromotion, yields an additional entropy production inside the interstitial region. These observations suggest that the metric tensor defined on the interface should be considered as a dissipative material field related to the intrinsic nature of the actual three-dimensional volume. Hence, following the point of view already expressed in Valanis (1998) and Ciancio et al. (2001), in the present paper we regard the metric tensor as an internal thermodynamic variable. Its evolution is controlled by a differential equation which depends on certain material fields such as the surface mass density or the surface temperature. Both the local and the gradient approaches will be considered since, at the interfacial scale, the long range interactions could be important (Cimmelli and Starita, 1990). In this framework we determine the conditions under which a stress-strain relation, involving the physical metric, exists. It turns out that this is true only if the evolution of the metric is controlled by a partial differential equation (non-local theory). In such a case the metric tensor is nothing but the local strain at the interface and, moreover, no dissipation of energy results from the surface deformation. If, instead, the internal variable is ruled by an ordinary differential equation (local theory) then we have the dissipation of the interstitial working, and a stress-strain relation does not exist in general. In such a case one can apply the standard procedures of Onsager's non-equilibrium thermodynamics (Verhás, 1997) in order to obtain the evolution equation for the generalized force conjugated to the metric time rate.

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## 2 Material Interface with an Internal Variable

Let us consider a material interface  $\sigma_*$ , separating two regular regions  $C_*^+$  and  $C_*^-$  of the point space  $E_3$ . We define a motion of  $C_* = C_*^+ \cup C_*^-$  and of  $\sigma_*$  through the couple of vector functions

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t), \quad \mathbf{r} = \mathbf{r}(\mathbf{R}, t), \quad (2.1)$$

where  $\mathbf{X}$  and  $\mathbf{R}$  are the vector position of a given point  $X$  of  $C_*$  and a given point  $R$  of  $\sigma_*$ , while  $\mathbf{x}$  and  $\mathbf{r}$  mean the vector position of  $X$  and  $R$  in the actual configurations  $C_t = C_t^+ \cup C_t^-$  and  $\sigma_t$ . Let us denote by  $u^\alpha$ ,  $\alpha = 1, 2$ , a system of curvilinear coordinates defined on  $\sigma_t$  and by

$$\mathbf{a}_\alpha := \frac{\partial \mathbf{r}}{\partial u^\alpha} \quad (2.2)$$

the tangent vectors to the coordinate curves. The plane  $(\mathbf{a}_1, \mathbf{a}_2)$  is tangent to  $\sigma_t$  and the matrix

$$a_{\alpha\beta} := \mathbf{a}_\alpha \cdot \mathbf{a}_\beta \quad (2.3)$$

yields the coefficients of the first fundamental form

$$ds^2 = a_{\alpha\beta} du^\alpha du^\beta, \quad (2.4)$$

representing the infinitesimal length on  $\sigma_t$ . In (2.4) and in the following the conventional summation over repeated indices is assumed. It results from (2.4) that  $a_{\alpha\beta}$  stands for the non-Euclidean metric tensor. Its determinant and inverse matrix will be denoted by  $a$  and  $a^{\alpha\beta}$  respectively. The unitary normal vector on  $\sigma_t$  is defined by

$$\mathbf{n} := \frac{\mathbf{a}_1 \times \mathbf{a}_2}{|\mathbf{a}_1 \times \mathbf{a}_2|}. \quad (2.5)$$

Finally, the trihedron  $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{n}\}$  will represent a basis for the three-dimensional vector space  $\mathbf{E}_3(\sigma_t)$ . Moreover, if  $f_\sigma$  is a regular function defined on  $\sigma_t$ , the convected time derivative of  $f_\sigma$  is given by

$$\dot{f}_\sigma = \frac{\partial f_\sigma}{\partial t} + \nabla_\sigma f_\sigma \cdot \mathbf{v}_\tau, \quad (2.6)$$

where  $\mathbf{v}_\tau$  is the projection of  $\mathbf{v} = \frac{\partial \mathbf{r}}{\partial t}$  on the interface and  $\nabla_\sigma$  is the gradient operator defined on  $\sigma_t$ . The following relation holds (Fergola and Romano, 1985)

$$\dot{a}_{\alpha\beta} = 2\eta_{(\alpha\beta)}, \quad (2.7)$$

where

$$\eta_{\alpha\beta} := \tau_{\alpha|\beta} - b_{\alpha\beta} \dot{\mathbf{r}} \cdot \mathbf{n}, \quad \eta_{(\alpha\beta)} = \frac{1}{2}(\eta_{\alpha\beta} + \eta_{\beta\alpha}), \quad (2.8)$$

$b_{\alpha\beta} := \mathbf{a}_\alpha \cdot \mathbf{n}_{,\beta}$  is the second fundamental form (Romano, 1982), a comma stands for the partial derivative, and a vertical bar denotes the covariant derivation. For a material interface we have (Romano, 1982)

$$\dot{\mathbf{x}}^+ \cdot \mathbf{n} = \dot{\mathbf{r}} \cdot \mathbf{n} = \dot{\mathbf{x}}^- \cdot \mathbf{n} \quad (2.9)$$

where  $f^+$  and  $f^-$  mean a function  $f$  evaluated on both sides of the interface. Under the hypothesis (2.9) the following balance equations for mass, linear momentum and energy are valid (Romano, 1982; Moeckel, 1987)

$$\dot{\rho}_\sigma + \rho_\sigma \eta_\alpha^\alpha = 0, \quad (2.10)$$

$$[\mathbf{T}] \cdot \mathbf{n} + \rho_\sigma \dot{\mathbf{r}} - \nabla_\sigma \cdot \mathbf{T}_\sigma - \rho_\sigma \mathbf{b}_\sigma = 0, \quad (2.11)$$

$$\rho_\sigma \dot{\epsilon}_\sigma - [\mathbf{h}] \cdot \mathbf{n} - T_\sigma^{(\alpha\beta)} \eta_{(\alpha\beta)} - \nabla_\sigma \cdot \mathbf{h}_\sigma = 0. \quad (2.12)$$

In (2.10)-(2.12) a subscript  $\sigma$  denotes the quantities defined on the interface. In particular,  $\rho_\sigma$  is the surface mass density,  $\epsilon_\sigma$  the surface specific internal energy,  $\mathbf{T}_\sigma$  the surface stress tensor,  $\mathbf{h}_\sigma$  the surface heat flux vector and  $\mathbf{b}_\sigma$  the surface body force. Moreover,  $\mathbf{h}$  and  $\mathbf{T}$  mean the heat flux vector and the stress tensor in the bulk materials and  $[f] =: f^+ - f^-$ . Here we restrict our attention to non polar continua, which have no intrinsic spin or couple. Consequently, the surface density of production of moment of momentum vanishes. This is equivalent to

$$T_\sigma^{\alpha 3} = 0, \quad T_\sigma^{\alpha\beta} = T_\sigma^{\beta\alpha}. \quad (2.13)$$

Moreover, the Clausius-Duhem inequality is (Moeckel, 1987)

$$-[\mathbf{h}] \cdot \mathbf{n} + \rho_\sigma \dot{s}_\sigma - \nabla \cdot \mathbf{h}_\sigma - \frac{h_\sigma^\alpha \theta_{\sigma,\alpha}}{\theta_\sigma} \geq 0, \quad (2.14)$$

with  $\theta_\sigma$  the surface temperature and  $s_\sigma$  the interfacial specific entropy. Once the Helmholtz free energy  $\Psi_\sigma =: \epsilon_\sigma - \theta_\sigma s_\sigma$  is introduced and, owing to (2.12), the divergence of  $\mathbf{h}_\sigma$  is eliminated from (2.14), one obtains

$$-\rho_\sigma \dot{\Psi}_\sigma - \rho_\sigma s_\sigma \dot{\theta}_\sigma - T_\sigma^{\alpha\beta} \eta_{(\alpha\beta)} - \frac{1}{\theta_\sigma} h_\sigma^\alpha \theta_{\sigma,\alpha} \geq 0. \quad (2.15)$$

Inequality (2.15) may be exploited to restrict the constitutive equations for surface quantities in such a way that all process directions in the state space are allowed (Muschik et al., 2001). Let us assume that the space of the states of  $\sigma_t$  is spanned by the surface mass density  $\rho_\sigma$ , the surface temperature  $\theta_\sigma$  and its gradient  $\theta_{\sigma,\alpha}$  together with the metric tensor  $a_{\alpha\beta}$ . The main difference between the present approach and the classical ones (Moeckel, 1987; Fergola and Romano, 1985; Romano, 1982) is that  $a_{\alpha\beta}$  is no longer a standard observable quantity but an internal state variable. We will show that such an assumption leads to more general thermodynamic results including the classical ones as a particular case. Because of (2.7), a kinetic equation for  $a_{\alpha\beta}$  may be assigned through a suitable constitutive equation for  $\eta_{(\alpha\beta)}$ . Such a function can be defined on the state space but also on a wider thermodynamic space including the gradient of the internal variable. These different hypotheses lead to different thermodynamic properties of the system (Cimmelli and Rogolino, 2001). A discussion of both cases will be developed in the next section.

### 3 Thermodynamics of the Interface

In our analysis we disregard the bulk materials and derive the consequences of (2.15) on the physical properties of  $\sigma_t$ . The following two cases will be discussed:

1. both the constitutive equations and the kinetic equation are local with respect to  $a_{\alpha\beta}$ ;
2. the constitutive equations are local but the kinetic equation is non-local, i.e., it is a partial differential equation with respect to  $a_{\alpha\beta}$ .

In case 1. the constitutive equations and the right hand side of the kinetic equation depend on the same set of variables. We have therefore

$$\Phi_\sigma = \Phi_\sigma^*(\rho_\sigma, \theta_\sigma, \theta_{\sigma,\alpha}, a_{\alpha\beta}), \quad (3.1)$$

$$\eta_{(\alpha\beta)} = f_{\alpha\beta}(\rho_\sigma, \theta_\sigma, \theta_{\sigma,\alpha}, a_{\alpha\beta}), \quad (3.2)$$

where  $\Phi_\sigma^*$  stands for an element of the set  $\{\epsilon_\sigma, \Psi_\sigma, \mathbf{h}_\sigma, \mathbf{T}_\sigma\}$ , and  $f_{\alpha\beta}$  is a symmetric smooth function of the denoted arguments.

In case 2. instead we assume

$$\Phi_\sigma = \Phi_\sigma^*(\rho_\sigma, \theta_\sigma, \theta_{\sigma,\alpha}, a_{\alpha\beta}), \quad (3.3)$$

$$\eta_{(\alpha\beta)} = f_{\alpha\beta}(\rho_\sigma, \theta_\sigma, \theta_{\sigma,\alpha}, a_{\alpha\beta}, a_{\alpha\beta,\gamma}). \quad (3.4)$$

In the following we will show that if (3.1) and (3.2) are valid then the material's behaviour is viscoelastic, while it is thermoelastic if (3.3) and (3.4) hold true. Let us start by supposing Eq.s (3.1)-(3.2) hold. Then we may calculate the time derivative of  $\Psi_\sigma$  and rearrange (2.15) as follows

$$\begin{aligned} & -\rho_\sigma \left( \frac{\partial \Psi_\sigma}{\partial \theta_\sigma} + s_\sigma \right) \dot{\theta}_\sigma - \rho_\sigma \frac{\partial \Psi_\sigma}{\partial \theta_{\sigma,\alpha}} \dot{\theta}_{\sigma,\alpha} + \\ & + \left( -2\rho_\sigma \frac{\partial \Psi_\sigma}{\partial a_{\alpha\beta}} + \rho_\sigma^2 \frac{\partial \Psi_\sigma}{\partial \rho_\sigma} a^{\alpha\beta} - T_\sigma^{\alpha\beta} \right) f_{\alpha\beta} - \frac{1}{\theta_\sigma} h_\sigma^\alpha \theta_{\sigma,\alpha} \geq 0. \end{aligned} \quad (3.5)$$

The inequality above must be satisfied whatever the values of  $\dot{\theta}_\sigma$ ,  $\dot{\theta}_{\sigma,\alpha}$ ,  $f_{\alpha\beta}$ ,  $\theta_{\sigma,\alpha}$  are. By applying the Coleman-Gurtin technique (Coleman and Gurtin, 1967), we get the following thermodynamic restrictions

$$s_\sigma = -\frac{\partial \Psi_\sigma}{\partial \theta_\sigma}, \quad (3.6)$$

$$\Psi_\sigma = \Psi_\sigma^*(\rho_\sigma, \theta_\sigma, a_{\alpha\beta}), \quad (3.7)$$

$$A_\sigma^{\alpha\beta} f_{\alpha\beta} - \frac{1}{\theta_\sigma} h_\sigma^\alpha \theta_{\sigma,\alpha} \geq 0, \quad (3.8)$$

where

$$A_\sigma^{\alpha\beta} = -2\rho_\sigma \frac{\partial \Psi_\sigma}{\partial a_{\alpha\beta}} + \rho_\sigma^2 \frac{\partial \Psi_\sigma}{\partial \rho_\sigma} a^{\alpha\beta} - T_\sigma^{\alpha\beta}. \quad (3.9)$$

As already observed in Cimmelli and Rogolino (2001) the Coleman-Gurtin technique does not allow to put  $A_\sigma^{\alpha\beta} = 0$  since such a function depends on the same variables of the coefficient standing in front of it, i.e.  $f_{\alpha\beta}$ . Thus,  $A_\sigma^{\alpha\beta}$  contributes to the local entropy production at the interface between the bulk materials. Moreover, no relation between stress and deformation follows from the second law. The relations (3.8) and (3.9) characterize the dissipative behaviour of the medium. By applying the standard procedures of Onsager's irreversible thermodynamics (Verhás, 1997), we obtain the following phenomenological evolution equations for  $A_\sigma^{\alpha\beta}$  and  $h_\sigma^\alpha$

$$A_\sigma^{\alpha\beta} = L_{(1)}^{\alpha\beta\gamma\delta} \dot{a}_{\gamma\delta} - \frac{1}{\theta_\sigma} M_{(1)}^{\alpha\beta\gamma} \theta_{\sigma,\gamma}, \quad (3.10)$$

$$h_\sigma^\alpha = L_{(2)}^{\alpha\beta\gamma} \dot{a}_{\beta\gamma} - \frac{1}{\theta_\sigma} M_{(2)}^{\alpha\beta} \theta_{\sigma,\beta}, \quad (3.11)$$

where the coefficients  $L_{(k)}$  and  $M_{(k)}$  depend on the basic fields  $\rho_\sigma$ ,  $\theta_\sigma$ ,  $\theta_{\sigma,\alpha}$ ,  $a_{\alpha\beta}$ . Because the internal variable is genuinely dissipative, the classical results do not apply in such a case.

If, instead, (3.3)-(3.4) are valid, then  $f_{\alpha\beta}$  is independent of  $A_\sigma^{\alpha\beta}$  so that, beside the equations (3.6) and (3.7), we get

$$T_\sigma^{\alpha\beta} = -2\rho_\sigma \frac{\partial \Psi_\sigma}{\partial a_{\alpha\beta}} + \rho_\sigma^2 \frac{\partial \Psi_\sigma}{\partial \rho_\sigma} a^{\alpha\beta}, \quad (3.12)$$

$$\frac{1}{\theta_\sigma} h_\sigma^\alpha \theta_{\sigma,\alpha} \leq 0. \quad (3.13)$$

Inequality (3.13) proves that no dissipation is due to the interface deformation since, as showed by (3.12), it behaves as an elastic fluid membrane. The classical theory is then recovered. In particular, if  $\Psi_\sigma$  depends only on  $a = \det(a_{\alpha\beta})$ , then, due to the derivation rule  $\frac{\partial a}{\partial a_{\alpha\beta}} = a a^{\alpha\beta}$ , and after applying the chain rule to (3.12), we obtain

$$T_\sigma^{\alpha\beta} = \gamma a^{\alpha\beta}, \quad (3.14)$$

where

$$\gamma := -2a\rho_\sigma \frac{\partial \Psi_\sigma}{\partial a} + \rho_\sigma^2 \frac{\partial \Psi_\sigma}{\partial \rho_\sigma} \quad (3.15)$$

represents the surface tension of classical thermochemistry (Defay and Prigogine, 1951). In general, the

stress tensor may be decoupled as follows (Kluitenberg and Ciancio, 1978)

$$T_{\sigma}^{\alpha\beta} = T_{\sigma(rev)}^{\alpha\beta} + T_{\sigma(int)}^{\alpha\beta} , \quad (3.16)$$

where for the non-dissipative stress  $T_{\sigma(rev)}^{\alpha\beta}$  the restriction (3.12) holds. As a consequence the inequality (3.8) reduces to

$$T_{\sigma(int)}^{\alpha\beta} f_{\alpha\beta} - \frac{1}{\theta_{\sigma}} h_{\sigma}^{\alpha} \theta_{\sigma,\alpha} \geq 0, \quad (3.17)$$

i.e. the internal forces are responsible for the mechanical dissipation, and the intrinsic stress may be regarded as the generalized force (affinity) conjugated to the time rate of the physical metric.

#### 4 Conclusions

The classical theory of material interfaces (Moeckel, 1987; Müller, 1985), has been revisited in order to model a dissipation of energy following from the surface deformation. The physical metric has been no longer considered as a standard observable quantity, but as an internal state variable. Such an approach applies to the material interfaces, which contain grains migrating and diffusing inside the interstitial volume. This is the case for many detergent substances where the grains are necessary to remove the surfacial impurities (Adamson, 1982). In such a case an energy dissipation due to the micromotion of the grains must be taken into account. An additional entropy production takes also place as well in other interfacial phenomena such as lubrication, flotation, and wetting (Adamson, 1982). All these applications could be modeled by applying the present approach.

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