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# On the lack of structure of Defay–Prigogine $2D$ -continua

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IN THIS PAPER it is proved that the bidimensional continua modelling the interfaces between fluid phases have to be endowed with a shell-like structure. Indeed (generalizing the result due to TOLMAN [1]) the Gibbs–Tolman formula is proved to be universally valid for the class of fluid interfaces introduced by DEFAY and PRIGOGINE in [3]. The starting assumption is that (following DELL'ISOLA and ROMANO [2]) the interfaces between different phases can be modelled by nonmaterial bidimensional ( $2D$ -)continua, whose independent constitutive variables are the temperature and the interfacial mass density. Moreover, for this class of  $2D$ -continua (their introduction is suggested in [3]) we prove the Gibbs phase rule, Kelvin relation between interfacial curvature and vapour pressure, and propose a formula which could allow for experimental evaluation of the surface mass density for plane and curved interfaces. Unfortunately, as discussed in ADAMSON [4], the dependence of surface tension on the curvature which is experimentally measured is inconsistent with the Tolman formula. Our result implies that, in order to supply theoretical forecasting consistent with experimental data, it is useless to look for new constitutive equations for interfacial free energy: therefore, the conjecture formulated by DEFAY and PRIGOGINE in [3] seems to be not true. Instead, to account experimental evidence, it is necessary to construct  $2D$ -continua endowed with a more complex structure. The minimal set of independent constitutive variables which seem to be necessary to this aim is determined in the epilogue.

## 1. Introduction

IN HIS FUNDAMENTAL series of paper [1, 5, 6] TOLMAN, developing the ideas of GIBBS [7], could obtain a formula (then generalized by KOENIG [8] to the case of mixtures) which relates the equilibrium surface tension acting on a liquid drop surrounded by its vapour to its radius. The fundamental assumptions accepted by Tolman are:

- T1. The vapour is a Van der Waals gas.
- T2. The liquid phase incompressible.
- T3. The interface is a mixture between liquid and vapour: all properties of this mixture are postulated on a heuristic ground.<sup>(1)</sup>

The utility of this formula, which in the literature is sometimes called also Gibbs–Tolman formula, has been tested in many experimental conditions. ADAMSON [4], while underlining its conceptual importance, quotes many papers, for example LAMER and POUND [13], in which is shown that the dependence of the surface tension on curvature, as predicted from Tolman's results, is in poor agreement with experimental data. The first attempt to point out the theoretical reasons of the quoted failure is due to DEFAY and PRIGOGINE [3]; they conjecture that Tolman's results have to be improved by taking into account the dependence of the equilibrium surface mass density at the interface upon the curvature. We remark explicitly here that if one decides to model the interface by a bidimensional ( $2D$ -)nonmaterial continuum, this conjecture clearly implies that the

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<sup>(1)</sup> In our opinion it is possible to deduce the quoted properties in the framework of the theories of the second gradient (see for instance SEPPECHER [9] or the series of papers CASAL-GOUIN [10, 11, 12]). Indeed, these theories provide a unique constitutive description for all the three phases (including the interface) coexisting in the systems considered.

constitutive assumption

$$(1.1) \quad \gamma = \gamma(\vartheta),$$

where  $\gamma$  is the surface tension and  $\vartheta$  the interfacial temperature, which seems to be generally accepted in the literature, has to be generalized as follows:

$$(1.2) \quad \gamma = \gamma(\vartheta, \rho_\sigma),$$

where  $\rho_\sigma$  is the interfacial surface mass density.

We will call the  $2D$ -continua for which Eq. (1.2) is accepted Defay–Prigogine continua. The results experimentally found by KAYSER [14], once Eq. (1.2) is assumed, should be reinterpreted: he actually measured the values of the following function

$$(1.3) \quad \gamma_P^*(\vartheta) := \gamma(\vartheta, \rho_{\sigma P}^*(\vartheta)),$$

where  $\rho_{\sigma P}^*(\vartheta)$  is the equilibrium surface mass density for plane interfaces. The aim of this paper is to prove, by modelling the interface between different phases of the same material as proposed in [2], that:

R0. The function  $\rho_{\sigma P}^*(\vartheta)$  is determined when the functions  $\gamma_P^*(\vartheta)$  and  $E_{\sigma P}^*(\vartheta)$  (the equilibrium surface tension and the surface inner energy per unit area for plane interface) are known.

R1. (1.1) is not consistent with the Gibbs phase rule.

R2. (1.2) implies Gibbs phase rule and enables, once a constitutive choice of interfacial free energy is made, a theoretical evaluation, in terms of the function  $\rho_{\sigma P}^*(\vartheta)$ , of the function  $\rho_\sigma^*(\vartheta, H)$ , i.e. the equilibrium interfacial surface mass density corresponding to curvature  $H$  and fixed temperature  $\vartheta$  (obviously  $\rho_{\sigma P}^*(\vartheta) = \rho_\sigma^*(\vartheta, 0)$ ).

R3. The Gibbs–Tolman formula is universally valid for the interfaces modelled in [2].

We explicitly remark here that we supply a proof of Gibbs–Tolman which:

H1 — is independent of the assumptions T1 and T2: the only hypothesis we need is that both liquid and vapour are perfect fluids;

H2 — is independent also of the “physically grounded” assumption T3: we only accept that the interface between phases is a perfect (Defay–Prigogine)  $2D$ -continuum;

H3 — is almost independent of the classical one supplied by Tolman: since the model used carefully ignores the concepts of Gibbs surface excess and Gibbs dividing surface, our proof is simpler.

The results quoted in statement R0 and R2 seems to supply an experimental method for evaluating the interfacial mass density. Statement R3 implies that the models proposed in [2] need to be improved in order to produce a theoretical approach to the problem of curvature depending on surface tension which is consistent with experimental evidence. Indeed, in this paper we prove that a perfect Defay–Prigogine  $2D$ -continuum is not endowed with sufficient structure to see, in equilibrium conditions, the difference between nonmaterial and material interfaces. In the epilogue some hints of future developments are sketched: following the ideas stemming from the work of CAPRIZ and PODIO-GUIDUGLI [15] (generalized to  $2D$ -nonmaterial continua), the introduction of further independent constitutive variables to describe the state of the interface seems unavoidable. It has to be cleared up how many of these variables should be introduced: indeed, there are many possible choices. We list here the two which are subject to our investigations: i) one could generalize the model proposed by DICARLO, GURTIN and PODIO-GUIDUGLI [16], introducing the curvature itself as a further independent variable (this approach implies the introduction of interfacial couple stresses) or ii) if the ideas exposed by CHOI *et al.* [17] or

by FISHER and ISRAELACHVILI [18, 19] in their comments to their experimental data are founded) one could, using the results found in DELL'ISOLA and KOSIŃSKI [20], introduce a surface scalar field modelling the thickness of the interface.

## 2. Constitutive equations for Defay-Prigogine 2D-continua. Gibbs' phase rule

Following [2] we assume that the independent constitutive variable characterizing the state of the interface are  $\vartheta$  and  $\rho_\sigma$ , i.e. the temperature and the surface mass density.

Therefore the interfacial free energy per unit mass  $\psi_\sigma$  has to be determined as a function of  $(\vartheta, \rho_\sigma)$ . Once this function is known, the entropy principle implies that all the other constitutive laws are determined. Indeed, in [2] the following relations are proved:

$$(2.1) \quad \eta_\sigma = -\frac{\partial \psi_\sigma}{\partial \vartheta}, \quad \varepsilon_\sigma = \vartheta + \psi_\sigma, \quad \gamma = -\rho_\sigma^2 \frac{\partial \psi_\sigma}{\partial \rho_\sigma},$$

where  $\eta_\sigma$  and  $\varepsilon_\sigma$  denote the interfacial entropy and inner energy per unit mass. If we define the interface Gibbs' potential per unit mass as follows

$$(2.2) \quad g_\sigma = \psi_\sigma - \frac{\gamma}{\rho_\sigma}$$

and if we assume that

**HYPOTHESIS 1.** *Once  $\vartheta$  is fixed, Eq. (2.1)<sub>3</sub> determines a one-to-one correspondence between  $\gamma$  and  $\rho_\sigma$ ;*

then the Eq. (2.1) trivially implies that (if instead of  $\rho_\sigma$  we choose  $\gamma$  as independent variable)

$$(2.3) \quad \frac{\partial g_\sigma}{\partial \gamma} = -\frac{1}{\rho_\sigma}.$$

On the other hand, if we assume that the interface is incompressible, i.e. if we assume that

IC1)  $\rho_\sigma$  is independent of the tension  $\gamma$  and is given as a function of the variable  $\vartheta$  alone;

IC2) all the other thermomechanical quantities are functions of the variables  $\gamma$  and  $\vartheta$ ;

then the Eq. (2.3), with reasoning completely analogous to those one can find in [2], can be proved to start from the entropy principle.

**DEFINITION 1.** *We will call Defay-Prigogine continua those bidimensional nonmaterial continua whose free energy satisfies Hypothesis 1 and whose entropy, inner energy and surface tension satisfy Eq. (2.1).*

We will prove that Gibbs' Phase Rule holds for Defay-Prigogine continua in all the cases of planar or spherical interfaces.

We start from the equilibrium condition deduced in [2] from the reduced entropy inequality, specified to the case of plane and spherical interfaces:

$$(2.4) \quad 2H\gamma = p_l - p_v, \quad g_v = g_l, \quad g_v = g_\sigma,$$

where  $H$  is the curvature of the interface,  $p_l$  and  $g_l$ ,  $p_v$  and  $g_v$ , are, respectively, the pressure and Gibbs' potential in the liquid and in the vapour phases: in what follows  $g_l$  and  $g_v$  are assumed to be, respectively, function of  $\vartheta$  and of  $p_l$  and  $p_v$ .

The set  $\mathcal{S}$  of the parameters which describe the equilibrium of a liquid and its vapour, when capillarity phenomena can't be neglected and the interface is plane or spherical, is

$$(2.5) \quad \mathcal{S} = \{\vartheta, H, p_l, \rho_l, p_v, \rho_v, \rho_\sigma, \gamma\}.$$

We explicitly remark that, in view of H1 and H2, the constitutive relations for the vapour, liquid and interfacial phases reduce to the five independent variables appearing in  $\mathcal{S}$ .

#### Gibbs phase rule

If  $H = 0$ , i.e. if the interface is plane, the four independent quantities appearing in (2.5) are constrained by the three equations (2.4). If these equations are independent, then there is a one-to-one correspondence between one parameter chosen in  $\mathcal{S}$  and the equilibrium states of the system. In what follows this parameter will always be the temperature  $\vartheta$ : all the other quantities in  $\mathcal{S}$  will become function of  $\vartheta$ , these functions we will denote by the same letter with the superscript \* and the subscript  $p$ .

On the other hand, if  $H$  is not vanishing then there are two degrees of freedom of the system. This is exactly what was forecast by the suitably generalized form of Gibbs' Rule (for more details cf. ADAMSON [4], LEVINE [21] or GIBBS [7]).

We prove now the following

PROPOSITION 1. The assumption  $\gamma$  independent of  $\rho_\sigma$  is

i) a consequence of the relation (which is often accepted in the literature)

$$(2.6) \quad \gamma = \rho_\sigma \psi_\sigma;$$

ii) not consistent with the Gibbs' Phase Rule.

To prove ii) we remark that the hypothesis  $\gamma = \gamma(\vartheta)$  implies (because of (2.1)<sub>3</sub>) the following relation

$$(2.7) \quad \psi_\sigma = \frac{\gamma(\vartheta)}{\rho_\sigma} + \hat{\psi}_\sigma(\vartheta),$$

where  $\hat{\psi}_\sigma(\vartheta)$  is a function of the variable  $\vartheta$  alone which does not depend on  $\gamma$ .

Equation (2.7) implies, together the definition (2.2), that

$$(2.8) \quad g_\sigma(\psi, \rho_\sigma) = \hat{\psi}_\sigma(\vartheta).$$

The consequences of (2.8) are remarkably inconsistent with the Gibbs' Phase Rule: indeed, even if one could always believe that  $\rho_\sigma$  is very small or vanishing or negligible, so that he is not interested in determining its value at the equilibrium states, he could never ignore (2.4)<sub>3</sub> (which was established by Gibbs himself) which, together with (2.8), states that

a) in the case of planar interfaces there exists a unique equilibrium state characterized by a fixed couple of values for temperature and pressure;

b) in the case of spherical interfaces there exists for every temperature a unique equilibrium radius.

Both the statements a) and b) are in obvious disagreement with the experimental evidence which supports Gibbs' Phase Rule.

To prove i) it is sufficient to remark that Eq. (2.6) together with Eq. (2.1)<sub>3</sub> leads to the following implications

$$\left( \psi_\sigma = -\rho_\sigma \frac{\partial \psi_\sigma}{\partial \rho_\sigma} \right) \Rightarrow \left( \psi_\sigma = \frac{k(\vartheta)}{\rho_\sigma} \right) \Rightarrow \gamma \text{ depends only on } \vartheta.$$

We remark explicitly that the relation (2.6) implies that

$$(2.9) \quad g_\sigma(\vartheta, \rho_\sigma) = 0.$$

The last equation is equivalent, because of (2.1)<sub>1</sub> and (2.2), to

$$-\rho_\sigma \eta_\sigma = \frac{\partial \gamma}{\partial \vartheta},$$

which is Eq. III-5 in ADAMSON [4]. The validity of the last equation and of Eq. (2.6) is therefore really doubtful.

### 3. Proof of Gibbs-Tolman formula

In this section we assume that

H1) both vapour and the liquid phase are perfect fluids, therefore the following equalities hold:

$$(3.1) \quad \frac{\partial g_v}{\partial p_v} = \frac{1}{\rho_v}, \quad \frac{\partial g_l}{\partial p_l} = \frac{1}{\rho_l};$$

H2) the set of equilibrium equations (2.4) is independent: therefore once the temperature  $\vartheta$  is fixed, the choice of the variable  $p_v$ , determines the equilibrium state of the system and therefore all the equilibrium values of the other quantities in  $\mathcal{S} - \{\vartheta\}$ ; we will denote  $H^*$ ,  $\gamma^*$ ,  $p_l^*$ ,  $\rho_l^*$ ,  $\rho_v^*$  and  $\rho_\sigma^*$  the functions which map  $(p_v, \vartheta)$  onto the corresponding equilibrium values.

In what follows we do not indicate the functional dependence on  $\vartheta$ .

According to our notation, Eqs. (2.3), (2.4)<sub>3</sub> and (3.1), we have the following chain of implications:<sup>(2)</sup>

$$(3.2) \quad (g_\sigma(\gamma^*(p_v)) = g_v(p_v)) \Rightarrow \left( \frac{\partial g_\sigma}{\partial \gamma} \frac{d\gamma^*}{dp_v} = \frac{\partial g_v}{\partial p_v} \right) \Rightarrow \left( \frac{d\gamma^*}{dp_v} = -\frac{\rho_\sigma^*}{\rho_v^*} \right).$$

Moreover, starting from Eqs. (2.3)<sub>1,2</sub> we establish the hypothesis of the following implication, its thesis being obtained by making use of Eq. (3.1) and the last equality in (3.2)

$$(3.3) \quad \left\{ \begin{array}{l} \frac{\partial g_v}{\partial p_v} = \frac{\partial g_l}{\partial p_l} \frac{dp_l^*}{dp_v} \\ \frac{dp_l^*}{dp_v} = 1 + 2 \frac{dH^*}{dp_v} \gamma^* + 2H^* \frac{d\gamma^*}{dp_v} \end{array} \right\} \Rightarrow \left( \frac{dH^*}{dp_v} = \frac{(\rho_l^* - \rho_v^*) + 2H^* \rho_\sigma^*}{2\gamma^* \rho_v^*} \right).$$

Finally, the Gibbs-Tolman formula is obtained by evaluating the ratio of the last equalities appearing in (3.2) and (3.3), after having observed that the nonvanishing expression we have obtained for the derivative  $dH^*/dp_v$  allows us to chose, instead of  $p_v$ , the variable  $H$  in order to characterize the equilibrium states:

$$(3.4) \quad \frac{d\tilde{\gamma}}{dH} = -\frac{2\tilde{\gamma}\delta}{1 + 2H\delta},$$

where  $\delta(H) := \tilde{\gamma}_\sigma / (\tilde{\gamma}_l - \tilde{\gamma}_v)$  and where the upper tilde indicates the generic composite function  $\tilde{f}(H) := f^*(p_v(H))$ .

<sup>(2)</sup> This relation seems to represent a reasonable reformulation of Eq. (III-22) on p. 56 in ADAMSON [4].

Trivial integration by parts allows us to obtain the following equivalent expression, which can be more easily compared with those found in literature, and in particular in TOLMAN [1]:

$$(3.5) \quad \tilde{\gamma} = \gamma_0 \frac{e^{\Delta(H)}}{1 + 2\delta(H)H},$$

where

$$\Delta(H) := \int (1 + 2H\delta(H))^{-1} \left( 2H \frac{d\delta}{dH} \right) dH.$$

#### 4. Interfacial free energy and the dependence of interfacial mass density on temperature and curvature

Once Eq. (3.5) is obtained, the problem of determining the function  $\delta(H)$  arises. It is easy to forecast, simply by observing Eq. (2.4), that  $\delta(H)$ , which is the ratio of the functions  $\tilde{\rho}_\sigma$  and  $\tilde{\rho}_l - \tilde{\rho}_v$ , has not many chances to be independent of the constitutive law assigning the interfacial free energy  $\psi_\sigma$ .

We remark explicitly here that the classical treatment due to Tolman hides this circumstance behind some Gibbsian reasoning which seems to be neither logically nor physically well grounded. However, it is our belief that these "Gibbsianism" could be made understandable (and the dependence of  $\delta(H)$  on the constitutive law for  $\psi_\sigma$  explicit) once that the theory of the second gradient or interstitial working (see for instance SEPPECHER [9] or CASAL-GOUIIN [10, 11] or DUNN-SERRIN [22]) is introduced to describe the behaviour of the interfacial phase.

##### 4.1 Determination of surface mass density for plane interfaces. The case of compressible Defay-Prigogine 2D-continua

In this subsection we aim to determine a relation between equilibrium surface mass density, surface tension and surface inner energy per unit area, which is valid in the case of plane interfaces and which we could not find in the literature. In our opinion it could be very useful in determining experimentally the magnitude of interface mass density involved in capillarity phenomena.

We start with the remark that, because of our definition, Eqs. (2.1) and Eq. (2.4)<sub>3</sub> we obtain (recall that the subscript  $P$  refers to the circumstance that all equilibrium functions which we consider are related to plane interfaces, and that all the functions considered have a unique variable, the temperature  $\vartheta$ )

$$(4.1) \quad E_{\sigma P}^* = \rho_{\sigma P}^* \varepsilon_{\sigma P}^* = \rho_{\sigma P}^* \psi_{\sigma P}^* - \rho_{\sigma P}^* \vartheta \left( \frac{\partial \psi_\sigma}{\partial \vartheta} \right)_P^*,$$

$$(4.2) \quad \gamma_P^* = -(\rho_{\sigma P}^*)^2 \left( \frac{\partial \psi_\sigma}{\partial \rho_\sigma} \right)_P^*,$$

$$(4.3)_1 \quad \psi_{\sigma P}^* + \rho_{\sigma P}^* \left( \frac{\partial \psi_\sigma}{\partial \rho_\sigma} \right)_P^* = g_{vP}^* = g_{lP}^*;$$

here we used the notations

$$(4.3)_2 \quad g_{vP}^*(\vartheta) := g_v(p_{vP}^*(\vartheta), \vartheta); \quad g_{lP}^*(\vartheta) := g_l(p_{lP}^*(\vartheta), \vartheta)$$

and the relations (resulting from (2.4)<sub>1,2</sub>)

$$(4.3)_3 \quad p_{vP}^*(\vartheta) = p_{lP}^*(\vartheta) \Rightarrow g_v(p_{vP}^*(\vartheta), \vartheta) = g_l(p_{lP}^*(\vartheta), \vartheta).$$

On the other hand, using the chain rule for the derivation of composed functions, we obtain

$$(4.4) \quad \left(\frac{\partial \psi_\sigma}{\partial \vartheta}\right)_P^* = \frac{d\psi_{\sigma P}^*}{d\vartheta} - \left(\frac{\partial \psi_\sigma}{\partial \rho_\sigma}\right)_P^* \frac{d\rho_{\sigma P}^*}{d\vartheta}.$$

Then, from Eqs. (4.2) and (4.3), using simple algebra we obtain

$$(4.5) \quad \psi_{\sigma P}^* = g_{vP}^* + \gamma_P^*(\rho_{\sigma P}^*)^{-1},$$

$$(4.6) \quad -\gamma_P^*(\rho_{\sigma P}^*)^{-2} = \left(\frac{\partial \psi_\sigma}{\partial \rho_\sigma}\right)_P^*.$$

Finally one has to

- i) substitute the LHS of Eq. (4.6) in the RHS of Eq. (4.4),
- ii) substitute the derivative of RHS of Eq. (4.5) again in the RHS of Eq. (4.4),
- iii) substitute the RHS of the so transformed Eq. (4.4) in the RHS of Eq. (4.1),
- iv) substitute the RHS of Eq. (4.5) again in RHS of Eq. (4.1), in order to obtain the following relation

$$(4.7) \quad \rho_{\sigma P}^* \left( g_{vP}^* - \vartheta \frac{dg_{vP}^*}{d\vartheta} \right) = -\gamma_P^* + \vartheta \frac{d\gamma_P^*}{d\vartheta} + E_{\sigma P}^*.$$

In order to compare Eq. (4.7) with the experimental data available in the literature, it is necessary to evaluate the second factor on LHS. We start by calculating the derivative appearing in (4.7),

$$(4.8) \quad \frac{dg_{vP}^*}{d\vartheta} = (\rho_{lP}^* - \rho_{vP}^*)^{-1} \left( \rho_l \frac{\partial g_l}{\partial \vartheta} - \rho_v \frac{\partial g_v}{\partial \vartheta} \right)_P^*.$$

The last expression is easily obtained by differentiating both expressions appearing in (4.3)<sub>2</sub> and recalling Eq. (3.1) and (2.4)<sub>2</sub>. In order to make the final step of our derivation clear it is useful to recall that the partial derivatives appearing in Eq. (4.8) are evaluated at fixed variables  $p_l$  and  $p_v$ . Indeed, as a consequence of Eq. (3.1), if  $\varepsilon_l$  and  $\varepsilon_v$  denote the inner energy per unit mass in the liquid and vapour phase, we have

$$(4.9) \quad g_l - \vartheta \frac{\partial g_l}{\partial \vartheta} = \varepsilon_l + p_l/\rho_l, \quad g_v - \vartheta \frac{\partial g_v}{\partial \vartheta} = \varepsilon_v + p_v/\rho_v$$

and therefore (using (4.8) and again recalling (2.4)<sub>2</sub>) we obtain

$$(4.10) \quad \left( g_{vP}^* - \vartheta \frac{dg_{vP}^*}{d\vartheta} \right) = (\rho_{lP}^* \varepsilon_{lP}^* - \rho_{vP}^* \varepsilon_{vP}^*) (\rho_{lP}^* - \rho_{vP}^*)^{-1}$$

and (here the enthalpy per unit mass  $h$  is introduced in both phases)

$$(4.11) \quad \rho_{lP}^* \varepsilon_{lP}^* - \rho_{vP}^* \varepsilon_{vP}^* = \rho_{lP}^* h_{lP}^* - \rho_{vP}^* h_{vP}^*.$$



In conclusion Eq. (4.7) becomes

$$(4.12) \quad \rho_{\sigma P}^* (\rho_{iP}^* h_{iP}^* - \rho_{vP}^* h_{vP}^*) = \left( -\gamma_P^* + \vartheta \frac{d\gamma_P^*}{d\vartheta} + E_{\sigma P}^* \right) (\rho_{iP}^* - \rho_{vP}^*),$$

which is the relation announced at the beginning of the section.

We underline that some tables of measures for all equilibrium quantities which appear in this equation, except the interfacial mass density, are available in the literature: therefore it is possible to use it to determine indirectly the interfacial mass density. Before discussing shortly the numerical information which could be drawn from Eq. (4.12), it is necessary to compare it with the theoretical results found in the literature in order to warn the reader about a danger which one should avoid. Indeed in the literature (see for example ADAMSON [4]) sometimes a little approximation (cf. 50, the lines between Eq. (III-6) and Eq. (III-7) in [4]) is made: "as a good approximation surface enthalpy per unit area and surface inner energy per unit area are not distinguished". The reasons for this statement, its explanation being left to those readers which are familiar with Gibbsian thermodynamics, most likely can be found in the papers of GIBBS himself [7]. We limit ourselves to remark that, as a consequence of this statement, we obtain (Eq. (III-8) at p. 50 in [4])

$$(4.13) \quad E_{\sigma P}^* = \gamma_P^* - \vartheta \frac{d\gamma_P^*}{d\vartheta},$$

which trivially implies that, because of Eq. (4.12),

$$(4.14) \quad \rho_{\sigma P}^* = 0.$$

We can conclude that the approximation quoted by Adamson consists in neglecting the interfacial mass density. Two problems now arise:

1. It is not clear to us if Tolman in his papers accepts or not the quoted approximation, but it is certain that he needs to evaluate equilibrium surface mass density as it appears in the definition of the function  $\delta(H)$ .

2. When the tables of measurements are to be used, one should check if the interfacial inner energy has been measured directly or indirectly by means of (4.13) (as it seems to be the case, for instance, in case of the measures listed in WOLF [23]).

If we make use of tables of measurements which apparently do not use (4.13) (for instance see [24]), we can obtain some interesting results, when organizing the data following Eq. (4.12). Indeed,

i) we can observe that the second factor on its RHS is negative (what is physically obvious in view of the meaning of enthalpy);

ii) its LHS is also always negative (we believe that this circumstance is related to the nonlinearities in the dependence of the equilibrium  $\gamma$  on the temperature, measured by KAYSER [14]);

iii) the numerical value obtained for water at 20°C are of the order of magnitude of  $10^{-8} - 10^{-7}$  g/cm<sup>2</sup>, which is the order of magnitude generally accepted as the most likely in the literature (for a detailed discussion of this point see the series of papers of ALTS and HUTTER [25]).

However, we do not believe it would be wise to rely much on Eq. (4.12) since we are aware of simplicity of the model which allowed for its deduction; together with the Tolman

formula it should be generalized to a more reliable one, once a more sophisticated model for the interface will be available.

**4.2 Spherical interfaces. The Kelvin formula for vapour pressure and the influence of surface free energy on surface mass density**

In order to simplify the comparison between the theoretical results and experimental data, in the literature instead of the vapour pressure  $p_v$  all equilibrium quantities are often expressed as functions of the variable  $H$ . While this choice is legitimate (at least in the framework of the model we use in this paper, see considerations following Eq. (3.3)) it leads, even when the simplest constitutive assumptions are made, to some technical problems in the explicit calculation of the quoted equilibrium function. A typical example of this situation is represented by the relationship between the curvature  $H$  and the vapour pressure, which in the literature is named after Kelvin.

Differentiating Eqs. (2.4)<sub>1,2</sub> with respect to the variable  $H$  and using Eqs. (3.1), we obtain

$$(4.15) \quad \left(1 - \frac{\rho_l}{\rho_v}\right) \frac{d\tilde{p}_v}{dH} = -\frac{d}{dH}(2H\tilde{\gamma}).$$

If we assume that

C1. The liquid phase is incompressible.

C2. The vapour is a perfect gas so that the following relation holds:

$$(4.16) \quad p_v = R_v \vartheta \rho_v,$$

then from (4.15) we obtain

$$(4.17) \quad \frac{d}{dH}(-\rho_l R_v \vartheta \ln(\tilde{p}_v) + \tilde{p}_v + 2H\tilde{\gamma}) = 0$$

which becomes (as  $\tilde{p}_v(0, \vartheta) = p_{vP}^*(\vartheta)$ )

$$(4.18) \quad \rho_l R_v \vartheta \ln\left(\frac{\tilde{p}_v}{p_{vP}^*}\right) = -(p_{vP}^* - \tilde{p}_v) + 2H\tilde{\gamma}.$$

Equation (4.18) is exactly the Kelvin formula: it is seen that already under the particular constitutive assumption C1–C2 the function mapping  $H$  into  $p_v$  is transcendental. Moreover, in (4.18) the unknown function  $\delta$  appears, since  $\tilde{\gamma}$  depends on it.

When more general constitutive equations are to be introduced, we can regard (4.15) as an equation which generalizes the Kelvin formula.

Let us now briefly consider the system of equations which governs the equilibrium of drops separated from their vapour by compressible Defay–Prigogine 2D-continua (we do not indicate the dependence on the temperature  $\vartheta$  which is assumed to be fixed),

$$(4.19) \quad \begin{aligned} p_l &= p_v + 2H\gamma, \\ g_l(p_l) &= g_v(p_v), \\ g_\sigma(\rho_\sigma) &= g_v(p_v), \end{aligned}$$

to which we must add the constitutive relation

$$(4.20) \quad \gamma = \gamma(\rho_\sigma) / \frac{\partial \gamma}{\partial \rho_\sigma} > 0,$$

which is invertible, so that we can regard the Gibbs potential also as a function of  $\gamma$ .

Now we recall that ROMANO in [26], using the consequences of the second principle of thermodynamics together with some well-grounded physical assumptions on the Gibbs potential, could prove the existence and the uniqueness of the solutions of the system (4.19)<sub>1,2</sub>. Therefore, to complete the proof of the validity of Gibbs phase rule we started in Sec. 2, we only need to prove the existence and uniqueness of the surface density  $\rho_\sigma^*$  which is a solution of (4.19)<sub>3</sub> when  $p_v = p_v^*$ .

To this aim we assume (as done in the second part of the hypothesis iii) on p. 261 in [26]) that

$$(4.21) \quad \lim_{\rho_\sigma \rightarrow \infty} g_\sigma(\rho_\sigma) = \infty, \quad \lim_{\rho_\sigma \rightarrow 0} g_\sigma(\rho_\sigma) = -\infty.$$

Moreover, we remark that we do not need to introduce any hypothesis similar to that formulated in [26] (cf. Eq. (3.7) there): indeed, starting from the thermodynamical relations (2.1) we can easily prove that for every  $\vartheta \in ]\vartheta_*, \vartheta_c[$  ( $\vartheta_*$  — temperature of the triple point,  $\vartheta_c$  — critical temperature) there exists a unique solution  $\rho_{\sigma P}^*$  for (4.19)<sub>3</sub> once the value  $p_{vP}^*$  is substituted on its RHS. When (4.21) is accepted, the proof parallels step-by-step that presented in [26] to which we refer. In principle, therefore, once all constitutive assumptions for liquid, vapour and interfacial phases are made and, in particular, when the interfacial free energy is chosen in such a way that the hypotheses (4.20)–(4.21) are respected, the equilibrium functions  $\delta(p_v)$ ,  $\gamma^*(p_v)$ ,  $\rho_v^*(p_v)$  and  $\rho_l^*(p_v)$  can be determined. Using the thesis in (3.3) and the definition of  $\delta$ , the function  $\delta(H)$  can also be found. In order to obtain some suggestions concerning the dependence of surface mass density on vapour pressure and an interesting expression for  $d\delta/dH$  we assume C1, C2, and

C3. The interface is a linearly compressible bidimensional fluid, and its Gibbs potential is given by

$$(4.22) \quad g_\sigma(\vartheta, \rho_\sigma) = g_v(p_{vP}^*(\vartheta), \vartheta) + \alpha(\vartheta) \ln \left( \frac{\rho_\sigma}{\rho_{\sigma P}^*(\vartheta)} \right).$$

The function  $\alpha(\vartheta)$ , to our knowledge, was never introduced in the literature, neither we could find any experimental data which could, suitably reinterpreted, allow for its determination. However, (4.22) is clearly related, via the thermodynamical relationships (2.1), to Eötvös relation (III-10) in ADAMSON [4]. Because of C2 we have

$$(4.23) \quad g_v(\vartheta, p_v) = g_v(p_{vP}^*(\vartheta), \vartheta) + R_v \vartheta \ln \left( \frac{p_v}{p_{vP}^*(\vartheta)} \right),$$

so that Eq. (2.4)<sub>3</sub> implies that:

$$(4.24) \quad \left( \frac{\rho_\sigma^*}{\rho_{\sigma P}^*(\vartheta)} \right)^{\frac{\alpha(\vartheta)}{R_v \vartheta}} = \left( \frac{p_v}{p_{vP}^*(\vartheta)} \right).$$

Finally we add the following assumption (cf. the experimental data listed by FISHER-ISRAELACHVILI in [18, 19]) that in the range of considered measures

C4. The vapour mass density is negligible with respect the liquid mass density (i.e.  $\rho_v \ll \rho_l$ ); therefore because of the definition of  $\delta$  and the constitutive equation (4.16), we have

$$(4.25) \quad \frac{d\delta}{dH} = \frac{1}{\rho_l} \left( \left( \frac{d\tilde{\rho}_\sigma}{dH} \right) + \tilde{\rho}_\sigma (R_v \vartheta)^{-1} \frac{d\tilde{p}_v}{dH} \right).$$

Owing to (4.15), (2.4)<sub>3</sub> and (4.22), this becomes

$$(4.26) \quad \frac{d\delta}{dH} = \frac{1}{\tilde{\rho}_l} (\alpha + \tilde{\rho}_v (R_v \vartheta)^{-1}) \frac{d\tilde{\gamma}}{dH}$$

which, taking account of (3.5), (4.16) and (4.18) (in which the first term on RHS can be neglected in the range of measurements performed by Fisher-Israelachvili), represents an equation which determines  $\delta$ . Indeed,

$$(4.27) \quad \delta(0) = \frac{\tilde{\rho}_{\sigma P}}{\tilde{\rho}_{lP} - \tilde{\rho}_{vP}}.$$

## 5. Epilogue. Comments and program for further investigations

In this paper some classical results of chemical physics are generalized making use of the simple model for the interface between different phases of a single material proposed in [2].

In our opinion, the relative simplicity of our deduction compared with those proposed by TOLMAN [1] or ADAMSON [4] is due to our use of the methods of Rational Thermodynamics exposed by TRUESDELL in his classical work [27].

Therefore we expect that a further improvement in the modellization of the interfacial structure leading to the introduction of directed bidimensional nonmaterial continua could allow for the theoretical deduction of a relation between the equilibrium surface tension, surface mass and curvature, consistent with available experimental data. Moreover, we urge (cf. our discussion in subsec. 4.1) for the development of a more precise theoretical framework for the study of capillarity phenomena, as, in our opinion, the actual state of the art is pretty confuse. Too many theoretical prejudices make the appropriate interpretation of experimental evidence very difficult.

We can indicate here two improvements of the model proposed in [2] which could modify our understanding of the quoted phenomena, at least for what concerns the influence of capillarity on curvature.

i. Following the ideas developed by DICARLO-PODIO-GUIDUGLI-GURTIN [16], one could introduce nonmaterial constrained bidimensional continua, similar to those material bidimensional continua introduced in the theory of shells. Together with surface stress tensor, a couple-stress tensor and a suitable complex family of directors (spins, etc.) describe the state of the interface. One of these directors could model the direction of the flux of mass through the interface: the first formulation of the model could assume that this vector always coincides with the direction normal to the interface, thus introducing some unknown reaction terms of both surface stress and couple-stress tensor. In this model (contrary to the model we used in this paper), the dependence of interfacial free energy on curvature is allowed by the second principle of thermodynamics: therefore it seems possible to obtain, by a suitable selection of a constitutive equation for it, a generalized Tolman formula more consistent with the experimental evidence. This approach seems more reasonably founded for describing the interfaces, for instance, between solid and melted crystals.

ii. In the literature (see for instance [13, 17, 18, 19]) it is often stated that an influence of the thickness of the interface on equilibrium surface tension is possible. For this reason CHOI *et al.* [17] develop a theoretical method (using statistical mechanics) to define a

dividing thickness between different phases of some carbon compound, and an experimental method to determine the thickness so defined. However these results, when used together with Tolman's data, lead to some results inconsistent with the experimental data. In [20] a heuristic method is proposed to add a more detailed structure to bidimensional nonmaterial continua used to describe capillarity phenomena. In this approach a concept of thickness is also introduced, which plays a relevant role in determining the behaviour of continua considered. However, we think that its physical nature is different from that introduced by CHOI *et al.* Indeed, the spatial region in which in [20] the interface is localized can be identified with the region in which the material in consideration shows a behaviour of the Korteweg type (see [22]) or of the second grade type (see [9, 10, 11, 12]).

The interfacial region so identified is more likely macroscopic than those introduced by means of the methods of statistical mechanics, and it could be defined as that region in which the constitutive equations for the Stokes–Navier simple materials cannot be considered to be valid.

To make the set of equations proposed in [20] complete from a physical point of view, it is necessary to specify the properties of the interfacial layer. This is done by

a) introducing one further surface scalar field modelling the thickness of the thin but macroscopic capillarity region (such a region is studied for instance by SEPPECHER in [9]), and

b) postulating (or deducing in the sense of [20]) the evolution equation for such a field.

The interfacial free energy for bidimensional continua endowed with this structure will depend also on the thickness, and this circumstance could lead to a solution of the proposed problem.

This approach seems more suitable for the description of the behaviour of the interfaces between fluid phases.

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