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Abstract

In this paper is proved that the Gibbs-Tolman formula is universally valid for a class of interfaces larger than that first described by Tolman [1]. The starting assumption is that 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. Unfortunately the dependence of surface tension on curvature which is experimentally measured is inconsistent with 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. To account experimental evidence , it is necessary to construct $2D$-continua endowed with more complex structure.

1 Introduction

In his fundamental series of paper [1,2,3] Tolman, developing the ideas of W.Gibbs [4], could obtain a formula (then generalized by Koenig [5] 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.

The utility of this formula, which in the literature is sometimes also called Gibbs-Tolman formula, has been tested in many experimental conditions, but the dependence of the surface tension on curvature as predicted from Tolman's results is in poor agreement with experimental data [6,7]. It is due to Defay and Prigogine [8] a first effort to point out the theoretical reasons of quoted failure: they conjecture that Tolman's results have to be improved taking into account the dependence of equilibrium surface mass density at the interface on the curvature. We remark explicitly

here that if one accepts to model the interface with a bidimensional $2D$-nonmaterial continuum, this conjecture clearly implies that the constitutive assumption $\gamma = \gamma(\vartheta)$ where γ is the surface tension and ϑ the interfacial temperature, which seems to be generally accepted in the literature, has to be generalized as follows:

$$\gamma = \gamma(\vartheta, \rho_\sigma) \tag{1.1}$$

where $\rho_\sigma$is the interfacial surface mass density. We will call the $2D$-continua for which (1.1) is accepted Defay-Prigogine continua (DP-continua, see below for a more precise definition) [9].

The aim of this paper is to prove, using the model for the interface between different phases of the same material proposed in [10], that:

R) the Gibbs-Tolman formula is universally valid for the interfaces modelled as DP-continua.

As by product of this result it si possible to prove also the following three assertions:

$R1$) (1.1) implies Gibbs' phase rule and allows, once a suitable 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 and temperature fixed (obviously we have that $\rho^*_{\sigma P}(\vartheta) = \rho^*_\sigma(\vartheta, 0)$).

$R2$) the assumption that $\gamma(\vartheta)$ is not consistent with the Gibbs' phase rule;

$R3$) the function $\rho^*_{\sigma P}(\vartheta)$, the equilibrium surface mass density for plane interfaces, is determined once the functions $\gamma^*_P(\vartheta)$ and $E^*_{\sigma P}(\vartheta)$ (the equilibrium inner surface energy per unit area for plane interface) are known.

We explicitly remark here that we supply a proof of Gibbs-Tolman formula which: i) is independent of the assumptions $T1$) and $T2$): the only hypothesis we need is that both liquid and vapour are perfect fluids; ii) is independent also of the "physically grounded" assumption $T3$): we only accept that the interface between phases is a nonmaterial perfect DP-continuum; iii) is pretty 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.

Moreover our proof implies that the models proposed in [10] need to be improved in order to produce a theoretical treatment of the problem of curvature dependence of surface tension which is consistent with experimental evidence. In the conclusion some hints of future developments are sketched: following the ideas stemming from the work of Capriz and Podio-Guidugli [11] (generalized to $2D$-nonmaterial continua) the introduction of further independent constitutive variables to describe the state of the interface seems unavoidable. It rest to be cleared up which and how many of these variables need to be introduced: indeed many are the possible choices.

2 Constitutive equations for DP-continua. Gibbs' phase rule.

Following [10] we assume that the independent constitutive variable characterizing the state of the interface are ϑ and ρ_σ. Therefore the interfacial free energy per unit mass ψ_σ has to be determined as a function of (ϑ, ρ_σ). Once this function is known the entropy principle implies that all the other constitutive laws are determined. Indeed in [10] the following relations are proved:

$$\eta_\sigma = -\frac{\partial \psi_\sigma}{\partial \vartheta}; \quad \epsilon_\sigma = \psi_\sigma + \vartheta \eta_\sigma; \quad \gamma = -\rho_\sigma^2 \frac{\partial \psi_\sigma}{\partial \rho_\sigma} \tag{2.1}$$

where η_σ and ϵ_σ denote the interfacial entropy and inner energy per unit mass. If we define the interface Gibbs' potential per unit mass as follows:

$$g_\sigma = \psi_\sigma - \frac{\gamma}{\rho_\sigma} \tag{2.2}$$

We assume that: H0) *once fixed* ϑ, Eq.$(2.1)_3$ *determines a one-to-one correspondence between* γ *and* ρ_σ. Moreover we assume: H1) *both vapour and liquid phase are perfect fluids.* H0 plus the Eq.s (2.1) trivially implies that [12]:

$$\frac{\partial g_\sigma}{\partial \gamma} = -\frac{1}{\rho_\sigma}, \tag{2.3}$$

Now we can state the definition of DP-continua:

Definition: *We will call DP-continua those bidimensional nonmaterial continua whose free energy verifies* H0 *and whose entropy, inner energy and surface tension verify* Eq.s (2.1).

We will prove that Gibbs' Phase Rule holds for DP-continua in *all the* cases of planar *or* spherical interfaces. We start from the equilibrium condition deduced in [10] from the reduced entropy inequality, particularized to the case of plane and spherical interfaces:

$$2H\gamma = p_l - p_v; \quad g_v = g_l; \quad g_v = g_\sigma \tag{2.4}$$

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 ϑ and respectively of p_l and p_v. The set $\mathcal{S}$ of the parametres which describe the equilibrium of a liquid and its vapour, when capillarity phenomena cannot be neglected and the interface is plane or spherical, is:

$$\mathcal{S} = \{ \vartheta, H, p_l, \rho_l, p_v, \rho_v, \rho_\sigma, \gamma \} \tag{2.5}$$

We explicitly remark that because of perfect fluids and DP-continua hypothesis the constitutive relations for the vapour, liquid and interfacial phases reduce the independent variables to only five among that appearing in $\mathcal{S}$. 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 the following we assume that, together H0 and H1, also the independence of Eq.s (2.4) will be satisfied, we call this hypothesis H2. In what follows this parameter will always be the temperature ϑ: all the other quantities in $\mathcal{S}$ will become function of ϑ, which we will denote with the same letter with the superscript *and the subscript $_P$.

On the other hand if H is not vanishing then the degrees of freedom of the system are two. This is exactly what forecast by the suitably generalized form of Gibbs' Rule (for more details cfr. Adamson [7], Gibbs [4] or Levine [13], and see also [14]).
In connection with the above cited assertion $R2$, we prove now the following:
Proposition: *The assumption γ independent of ρ_σ is : i) not consistent with the Gibbs' Phase Rule; ii) equivalent to the relation $\gamma = \rho_\sigma \psi_\sigma$ which is often accepted in the literature.*
To prove i) we remark that the hypothesis $\gamma = \gamma(\vartheta)$ implies (because of $(2.1)_3$) the following relation:

$$\psi_\sigma = \frac{\gamma(\vartheta)}{\rho_\sigma} + \hat{\psi}_\sigma(\vartheta) \tag{2.6}$$

where $\hat{\psi}_\sigma(\vartheta)$ is a function of the variable ϑ *alone* which does not depend on γ. *Eq.*(2.6) implies, together the definition (2.2), that:

$$g_\sigma(\vartheta, \rho_\sigma) = \hat{\psi}_\sigma(\vartheta) \tag{2.7}$$

The consequences of (2.7) are remarkably inconsistent with the Gibbs' Phase Rule: indeed, even if one could always believe that ρ_σ is very small or vanishing or negligible so that he is not interested in determining its value at the equilibrium, however he could *never* ignore $(2.4)_3$ (which was established by Gibbs himself) which, together with (2.7) would implies that: a) in the case of planar interfaces there exists an 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 radius an unique equilibrium state.

Both the statements a) and b) are in cogent disagreement with the experimental evidence which supports Gibbs' Phase Rule.
To prove ii) it is sufficient to remark that Eq.(2.6) together with $Eq.(2.1)_3$ leads to the following implications

$$(\psi_\sigma = -\rho_\sigma \tfrac{\partial \psi_\sigma}{\partial \rho_\sigma}) \Leftrightarrow (\psi_\sigma = \tfrac{k(\vartheta)}{\rho_\sigma}) \Leftrightarrow \gamma \textit{ is depending only on } \vartheta$$

3 Proof of Gibbs-Tolman formula

Because of H1 the following equalities hold:

$$\frac{\partial g_v}{\partial p_v} = \frac{1}{{}_v\rho}; \qquad \frac{\partial g_l}{\partial p_l} = \frac{1}{{}_l\rho}; \tag{3.1}$$

From H2 *once fixed the temperature* ϑ 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 ρ_σ^* the functions which map (p_v, ϑ) in quoted equilibrium values. With our denotation Eq.s (2.3), $(2.4)_3$ and (3.1) implies the following chain of implications:

$$(\, g_\sigma(\gamma^*(p_v)) = g_v(p_v)\,) \Leftrightarrow (\, \tfrac{\partial g_\sigma}{\partial \gamma}\tfrac{d\gamma^*}{dp_v} = \tfrac{\partial g_v}{\partial p_v}\,) \Leftrightarrow (\, \tfrac{d\gamma^*}{dp_v} = -\tfrac{\rho_\sigma^*}{\rho_v^*}\,) \tag{3.2}$$

Moreover starting from Eq.s $(2.3)_{1,2}$ we establish the hypothesis of the following implication, whose thesis is obtained making use of Eq.(3.1) and the last equality in (3.2):

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

Finally the Gibbs'-Tolman formula is obtained evaluating the ratio of the last equalities appearing in (3.2) and (3.3), after having remarked that the *non-vanishing* expression we have obtained for the derivative $\frac{dH^*}{dp_v}$ allows us to chose, instead of p_v, the variable H in order to characterize the equilibrium states:

$$\frac{d\tilde{\gamma}}{dH} = -\frac{2\tilde{\gamma}\delta}{1 + 2H\delta} \tag{3.4}$$

where:

$$\delta(H) := \frac{\tilde{\rho}_\sigma}{\tilde{\rho}_l - \tilde{\rho}_v}$$

and where the upper tilde indicates the generic composed function $f(H) := f^*(p_v(H))$. 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]:

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

where $\Delta(H) := \int (\, 1 + H\delta(H)\,)^{-1} (\, H\frac{d\delta}{dH}\,)\, dH$ and γ_0 is the value of γ for $H = 0$. Once obtained Eq.(3.5) the problem of determining the function $\delta(H)$ arises. It is easy to forecast, simply observing Eq.(2.4), that $\delta(H)$, which is the ratio between the functions ρ_σ and $\rho_l - \rho_v$, does not has many chances to be independent of the constitutive law assigning the interfacial free energy ψ_σ.

4 Interfacial Free Energy and the dependence of Interfacial Mass Density on Temperature and Curvature.

4.1 Determination of Surface Mass Density for Plane Interfaces: the case of Compressible DP-Continua.

In this subsection we aim to present a relation among equilibrium surface mass density, surface tension and surface inner energy per unit area which we is valid in the case of plane interfaces and which we could not find in the literature (cfr. assertion R3 in the Introduction). In our opinion it could be very useful in determining experimentally an evaluation of the magnitude of interface mass density involved in capillarity phenomena.
We prefer discuss directly the result, the reader interested to deduction of it can refers to Appendix. We obtain:

$$\rho^*_{\sigma P} = \frac{\rho^*_{lP} - \rho^*_{vP}}{(\rho h)^*_{lP} - (\rho h)^*_{vP}}(-\gamma + \vartheta \frac{d\gamma^*_P}{d\vartheta} + E^*_{\sigma P}) \tag{4.1}$$

where h is the enthalpy for unit mass.

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 conceivable to use it to indirectly determine the interfacial mass density. Before discussing shortly the prediction which could be drawn from Eq.(4.1) it is necessary to shortly compare it with the theoretical results found in the literature in order to warn the reader about a pitfall in which one should avoid to fall. Indeed in the literature sometimes a little approximation is done: "*as a good approximation surface enthalpy per unit area and surface inner energy per unit area are not distinguished*" (cfr. pag.50 in Adamson [7]). The reasons of this statement, whose exegesis we leave to those readers which are familiar with Gibbsian thermodynamics, most likely can be found in the papers of Gibbs himself [4]. We limit ourselves to remark that as a consequence of this statement we obtain that (cfr. Eq.(III-8) on pag.50 in [7]):

$$E^*_{\sigma P} = \gamma - \vartheta \frac{d\gamma^*_P}{d\vartheta} \tag{4.2}$$

which trivially implies that, because of Eq.(4.1): $\rho^*_{\sigma P} = 0$. We can conclude that the approximation quoted by Adamson consists of neglecting the interfacial mass density. Two problems now arise: 1) it is not clear to us if Tolman in his papers accepts or not 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 measures are to be used one should check if the interfacial inner energy has been measured directly or indirectly by means of (4.2) (as it seems the case for instance

for the measures listed in Wolf [15]). If one makes use of tables of measures which apparently do not use (4.2) (for instance see [16]) he can obtain some interesting results, when organizing the data following Eq.(4.1). Indeed the numerical value obtained for water at $20°C$ are of the order of magnitude of $10^{-8} - 10^{-7} g/cm^2$, which is the order of magnitude in general accepted as the most likely in the literature (for a detailed discussion of this point see the series of papers of Alts and Hutter [17]). However we do not believe it is wise to rely much on Eq.(4.1) as we are aware of the simplicity of the model which allowed its deduction together with Tolman formula it has to be generalized into 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 after (3.3)) it leads, even when the simplest constitutive assumptions are made, to some technical problems in the explicit calculation of 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. Deriving Eq.s $(2.4)_{1,2}$ respect the variable H and using Eqs.(3.1) with simple algebra we obtain:

$$\left(1 - \frac{\rho_l}{\rho_v}\right) \frac{d\tilde{p}_v}{dH} = -\frac{d}{dH}(2H\tilde{\gamma}) \tag{4.3}$$

If we assume that: $C1$) the liquid phase is incompressible; $C2$) the vapour is a perfect gas so that the following relation holds: $p_v = R_v \vartheta_v \rho$; then from (4.3) we obtain:

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

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

$$\rho_l R_v \vartheta \ln\left(\frac{\tilde{p}_v}{p^*_{vP}}\right) = (p^*_{vP} - \tilde{p}_v) + 2H\tilde{\gamma} \tag{4.4}$$

Equation (4.4) is exactly Kelvin formula: we remark that already under the particular constitutive assumption $C1) - C2)$ the function mapping H into p_v is transcendent. Moreover in (4.4) the unknown function δ appears, as $\tilde{p}_v$ depends on it. When more general constitutive equations are to be introduced we can regard (4.4) as an equation which generalizes Kelvin formula.
In order to obtain some suggestions concerning the dependence of surface mass density on vapour pressure and an interesting expression for $\frac{d\delta}{dH}$ we assume $C1), C2)$ and

$C3$) the interface is a linearly compressible bidimensional fluid whose Gibbs potential is given by:

$$g_\sigma(\vartheta, \rho_\sigma) = g_v(p^*_{vP}(\vartheta), \vartheta) + \alpha(\vartheta) \ln\left(\frac{\rho_\sigma}{\rho^*_{vP}(\vartheta)}\right) \tag{4.5}$$

The function $\alpha(\vartheta)$, to our knowledge, was never introduced in the literature neither we could find some experimental data which could, suitably reinterpreted, allow its determination. However (4.5) is clearly related, via the thermodynamical relationships (2.1) to Eötvös relation (III-10) in Adamson [7]. Because of $C2$) we have that

$$g_v(\vartheta, p_v) = g_v(p^*_{vP}(\vartheta), \vartheta) + R_v \vartheta \ln\left(\frac{p_v}{p^*_{vP}(\vartheta)}\right) \tag{4.6}$$

so that $Eq.(2.4)_3$ implies that:

$$\left(\frac{\rho^*_\sigma}{\rho^*_{vP}(\vartheta)}\right)^{\frac{\alpha(\vartheta)}{R_v \vartheta}} = \left(\frac{p_v}{p^*_{vP}(\vartheta)}\right) \tag{4.7}$$

Finally we add the following assumption (cf. the experimental data listed by Fisher-Israelachvili in [18]) that: $C4$) in the range of considered measures $\rho_v << \rho_l$.
Therefore because of the definition of δ, the perfect gas law and Eq.s $(2.4)_3$, (4.3), (4.5) we have:

$$\frac{d\delta}{dH} = \frac{1}{\tilde{\rho}_l}\left(\alpha + \frac{\tilde{\rho}_v}{R_v \vartheta}\right)\frac{d\tilde{\gamma}}{dH} \tag{4.8}$$

which, taking account of (3.5) and (4.4) (in which first addend on LHS can be neglected in the range of measures performed by Fisher- Israelachvili), represents an equation which determines δ.

5 Conclusion

In this paper some classical results of chemical physics are generalized making use of the simple model for the interface between the phases of a material proposed in [10] In our opinion the relative simplicity of our deduction compared with those proposed by Tolman [2] or Adamson [7] is due to our use of the methods of Rational Thermodynamics exposed by Truesdell in his classical work [19]. We remark explicitly here that the classical treatment due to Tolman hides this circumstance behind some Gibbsian reasoning which does not seem neither logically nor physically deeply grounded. However it is our belief that these "Gibbsianism" could be made understandable (and the dependence of $\delta(H)$ on ψ_σ explicit).

We can indicate here two improvements of the model proposed in [10] which could improve our understanding of quoted phenomena, at least for what concerns the influence on capillarity of curvature.

i) In the literature (see for instance [6,18]) it is often stated that is conceivable an influence of the thickness of the interface on equilibrium surface tension. For this reason Choi et Al. [20] 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 so defined thickness. However these results, when used together with Tolman's ones, lead to some results inconsistent with experimental data. In [21] an heuristic method is proposed to add more detailed structure to bidimensional nonmaterial continua introduced to describe capillarity phenomena. In this contest a concept of thickness is also introduced, which plays a relevant rôle in determining the behaviour of considered continua: however we think that its physical nature is pretty different from that introduced by Choi et Al. Indeed in Ref. [21] the spatial region in which is localized the interface can be identified with the region in which the material in consideration shows a behaviour of the type Korteweg (see [22]) or of the type of second gradient (see [23,24]). To make complete, from a physical point of view, the set of equations proposed in [21] it is necessary to specify the properties of the interfacial layer. This is done: 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 [24]); b) postulating (or deducing in the sense of [21]) the evolution equation for such a field. The interfacial free energy for bidimensional continua endowed of this structure will depend also on the thickness, and this circumstance could lead to a solution of proposed problem. Unfortunely just in the static case the non-linearity of the problem posed in term of second gradient theory make the solution very difficoult, though we can get novel insight about the behavior of interface. A very preliminar study shown that: i) $\tilde{\gamma}$ is a non-monodromic function of equilibrium paramenter (whenever this is p_v or H); ii) exists a minimal radius for a small vapour bubble in liquids; iii) a thickness for the interface can be defined rely on thermodynamic (a la Gibbs) quantities and second gradient quantities. In conclusion this approach seems suitable for the description of the behaviour of the interfaces between fluid phases.

ii) Following the ideas developed by Di Carlo et Al. [25] one could introduce non-material 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 suitably 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: a first formulation of the model could assume that this vector always coincides with the normal direction to the interface thus introducing some unknown reaction part of both surface stress and couple-stress tensor. In this model the dependence of interfacial free energy on curvature is allowed by the second principle of thermodynamics: it seems therefore possible to obtain, suitably choosing a constitutive equation for it, a generalized Tolman formula more consistent with experimental evidence. This approach seems more reasonably founded for describing the interfaces, for instance, between solid crystals and their melt.

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

where $\rho_{\sigma P}^*(\vartheta)$ is the equilibrium surface mass density for plane interfaces.

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Appendix: deduction of Eq.(4.1)

We start remarking that, because of our definition, Eqs.(2.1) and Eq.$(2.4)_3$ we obtain (recall that the pedex P refers to the circumstance that all equilibrium functions which we consider are relative to plane interfaces, and that all considered function have as unique variable the temperature ϑ):

$$E^*_{\sigma P} = \rho^*_{\sigma P}\epsilon^*_{\sigma P} = \rho^*_{\sigma P}\psi^*_{\sigma P} - \rho^*_{\sigma P}\vartheta\left(\frac{\partial\psi_\sigma}{\partial\vartheta}\right)^*_P \qquad (A.1)$$

$$\gamma^*_P = -(\rho^*_{\sigma P})^2\left(\frac{\partial\psi_\sigma}{\partial\rho_\sigma}\right) \qquad (A.2)$$

$$\psi^*_{\sigma P} + \rho^*_{\sigma P}\left(\frac{\partial\psi_\sigma}{\partial\rho_\sigma}\right)^*_P = g^*_{vP} = g^*_{lP} \qquad (A.3)_1$$

where we used the denotations $g^*_{vP}(\vartheta) := g_v(p^*_{vP}(\vartheta),\vartheta)$ and $g^*_{lP}(\vartheta) := g_l(p^*_{lP}(\vartheta),\vartheta)$ and the relations (arising from $(2.4)_{1,2}$)

$$p^*_{vP}(\vartheta) = p^*_{lP}(\vartheta) \qquad g_v(p^*_{vP}(\vartheta),\vartheta) = g_l(p^*_{lP}(\vartheta),\vartheta) \qquad (A.3)_2$$

On the other hand, using the chain rule for the derivation of composed functions, we have that:

$$\left(\frac{\partial\psi_\sigma}{\partial\vartheta}\right)^*_P = \frac{d\psi^*_{\sigma P}}{d\vartheta} - \left(\frac{\partial\psi_\sigma}{\partial\rho_\sigma}\right)^*_P\frac{d\rho^*_{\sigma P}}{d\vartheta} \qquad (A.4)$$

Then, from Eqs.(A.2) and (A.3), with simple algebra we obtain:

$$\psi^*_{\sigma P} = g^*_{vP} + \gamma^*_P(\rho^*_{\sigma P})^{-1} \tag{A.5}$$

$$-\gamma^*_P(\rho^*_{\sigma P})^{-2} = \left(\frac{\partial \psi_\sigma}{\partial \rho_\sigma}\right)^*_P \tag{A.6}$$

Finally combining the above equations from (A.1) to (A.6) is possible to find the following interesting relation:

$$\rho^*_{\sigma P}\left(g^*_{vP} - \vartheta \frac{dg^*_{vP}}{d\vartheta}\right) = -\gamma^*_P + \vartheta \frac{d\gamma^*_P}{d\vartheta} + E^*_{\sigma P} \tag{A.7}$$

The LHS can be simplified further calculating the derivative:

$$\frac{dg^*_{vP}}{d\vartheta} = (\rho^*_{lP} - \rho^*_{vP})^{-1}\left(\rho_l \frac{\partial g_l}{\partial \vartheta} - \rho_v \frac{\partial g_v}{\partial \vartheta}\right)^*_{vP} \tag{A.8}$$

Last expression is obtained with simple algebra, deriving both equations appearing in $(A.3)_2$ and recalling $Eq.(3.1)$ and $(2.4)_2$. In order to make clearer the final step of our derivation it is useful to recall that the partial derivatives appearing in $Eq.(A.8)$ are evaluated with the variables p_l and p_v fixed.
Indeed as a consequence of $Eq.(3.1)$, if ϵ_l and ϵ_v denote the inner energy per unit mass in the liquid and vapour phase, we have that

$$g_l - \vartheta \frac{\partial g_l}{\partial \vartheta} = \epsilon_l + p_l/\rho_l; \qquad g_v - \vartheta \frac{\partial g_v}{\partial \vartheta} = \epsilon_v + p_v/\rho_v$$

and therefore (using (A.8) and again recalling $(2.4)_2$) we obtain:

$$g^*_{vP} - \vartheta \frac{dg^*_{vP}}{d\vartheta} = (\rho^*_{lP}\epsilon^*_{lP} - \rho^*_{vP}\epsilon^*_{vP})\,((\rho^*_{lP} - \rho^*_{vP})^{-1}) \tag{4.9}$$

and (here the enthalpy per unit mass h is introduced in both phases) $\rho^*_{lP}\epsilon^*_{lP} - \rho^*_{vP}\epsilon^*_{vP} = \rho^*_{lP}h^*_{lP} - \rho^*_{vP}h^*_{vP}$. In conclusion we obtain the Eq.(4.1):

$$\rho^*_{\sigma P} = \frac{\rho^*_{lP} - \rho^*_{vP}}{(\rho h)^*_{lP} - (\rho h)^*_{vP}}(-\gamma + \vartheta \frac{d\gamma^*_P}{d\vartheta} + E^*_{\sigma P}) \tag{4.1}$$