On evolution of notion of the capillarity tensor

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ABSTRACT: The concept of the surface capillarity tensor has grown up from the notion of the surface tensor. In the paper we present the evolution of the notion of the capillarity tensor starting from the basic procedures of Buff and Tolman. The main aim is to present how Gurtin’s solution can be involved into the general thermodynamic concept.

1 CAPILLARITY FORCE FROM THE PSEUDO MOMENTUM JUMP

In 1995 Gurtin demonstrated a new role of configurational forces in modeling the laws of evolution and dynamics of interfaces during phase transitions. Gurtin (1995). If the standard Newtonian forces associated with continua are responsible for the motion of material points, the independent, additional configurational forces may be needed to describe an internal microstructure evolution. Configurational forces are related with the pseudo-momentum flux balance, which is an analog of Newtonian balances of forces. The pseudo-momentum flux, called also the Eshelby stress tensor, is responsible for an internal transport of the pseudo-momentum and undergoes the configurational balance. The evolution relation for some internal micro-structure, like an interfacial layer, can be formulated as the jump relation within the configurational balance (Gurtin 1995, eq. (5.11)):

\[ \mathbf{C} \mathbf{n} + \mathbf{e} + \text{div} \mathbf{C} = 0. \]  

(1)

Here \[ \mathbf{C} \] is the jump of the 3D Eshelby tensor over the interfacial layer, \[ \mathbf{e} \] is an Eshelby interfacial tensor which undergoes two-dimensional surface divergence, and \[ \mathbf{n} \] represents internal forces distributed over the interface. As a special form of eq. (1), Gurtin was able to transform a general driving force equation to the condition of “motion-by-curvature”, an interface motion neglecting bulk behavior, a Stefan-type motion of a melting surface, etc.

Continuing Gurtin’s approach, the authors have extended the notion of pseudo-momentum, pseudo-momentum flux, pseudo-energy and pseudo-energy flux from the Lagrangian to the Eulerian description, thus giving a new approach to the pseudo-momentum balance in the form appropriate for fluids, see Badur & Badur (2005). The present paper tries to continue Gurtin’s idea in relation to interphase phenomena. Searching for a proper evolution equation that governs motion of a phase transition zone occurring in a thin shell-like domain, one can choose a few equivalent approaches to the mathematical modeling. For instance, such a governing equation has recently been found by using the Gibbs variational principle, see Eremeyev & Pietraszkiewicz (2004).

In this paper, we propose another way applying an integration of the pseudo momentum flux tensor through the layer thickness. At the same time, the classical Kirchhoff shell assumptions are introduced into consideration. Finally, a few particular cases are discussed.

1.1 Tolman and Buff generalization

When in 1927 Weatherburn proposed general principles of balances of the two-dimensional interfacial layer, Weatherburn (1927), we had an impression that the theory of capillarity attained its limit. However, the variational approach, along the line of Laplace–Gauss–Skiba–Gibbs was still incompatible with the “forced” approach of Monge-Young-Maxwell. In the latter approach, the capillarity laws were stated from an ordinary balance of vector forces. Then in 1948 Tolman proposed to renovate the original Gibbs’ energetic line of reasoning. His analyses of Gibbs arguments were precised and deeply stated; finally Tolman proposed a new definition of interfacial layer called by him the “Gibbs’ dividing surface”, which mathematically is a surface endowed with \textit{a priori} physical properties like “surface tension”, “surface entropy” or “surface mass content”. A variation of the total surface energy for that continuum Tolman writes to be (Tolman 1948, eq. (4.2)):

\[ \delta E = \delta E^\prime + \delta E^\prime + \delta E^G \]

\[ = T \delta S^I + \mu_1 \delta m_1^I + \mu_2 \delta m_2^I + ... + \sigma \delta \sigma \]

\[ + T \delta S^II + \mu_1 \delta m_1^{II} + \mu_2 \delta m_2^{II} + ... + \sigma \delta \sigma \]

\[ + T \delta S^G + \mu_1 \delta m_1^G + \mu_2 \delta m_2^G + ... + \sigma \delta \sigma + C_1 \delta c_1 + C_2 \delta c_2. \]  

(2)
Next, Tolman assumes a thermal equilibrium \( T' = T'' = T \) and a chemical equilibrium \( \mu_1' = \mu_2' = \mu_1 = \mu_2 \), and following Gibbs he takes the mechanical non-equilibrium \( p' \neq p'' \neq \sigma \). Having these assumptions, and putting \( \delta^2 = 0 \), Tolman obtains from the mechanical equilibrium (Tolman 1948, eq. (5.4)):

\[
(p' - p'') \delta x' = \sigma \delta s.
\]

(3)

This is equivalent to the Young-Laplace equation (Tolman 1948, eq. (6.1)):

\[
p' - p'' = (c_1 + c_2) \sigma
\]

(4)

where \( c_1 \) and \( c_2 \) are the main values of curvature. However, in the extensive discussion Tolman suggests that introducing the surface moments \( C_1, C_2 \) to the Young-Laplace equation should be given in a similar variational way. Finally, Tolman introduces an idea of defining the surface tension by some "excess" pressure \( \rho \) (Tolman 1948, eq. (12.6)):

\[
\gamma = \int_a^b \frac{\lambda_1}{\lambda_2} (\sigma' - \sigma_{\text{surf}}) [1 + (c_1 + c_2) \lambda] d\lambda,
\]

(9)

\[
C = \int_a^b \frac{\lambda_1}{\lambda_2} (\sigma' - \sigma_{\text{surf}}) \lambda d\lambda,
\]

(10)

\[
\sigma_{\text{surf}} = \int_a^b (\rho - \rho_{\text{surf}}) d\lambda,
\]

(11)

Both above external pressures \( p', p'' \) are important and the interfacial surface curvature is present via the mean curvature \( c \).

1.2 Surface tension dyade

A quite independent starting point was taken by Buff (1956). It became clear that a new approach was proposed, and finally Buff presented his own generalization of the Young-Laplace equation. He wanted to explain sources of "surface tension" notion and the rules that govern the complicated interface behavior. He was the first who assumed that in the domain of interface layer the spherical pressure tensor may become non-spherical. It appears that in his approach the layer pressure has the normal component \( \sigma_n \) and the tangential component \( \sigma_t \). Therefore, going from the fluid \( \sigma \) to the fluid \( \beta \) across the interface layer we observe three different pressure tensors (Buff 1956, eq. (6.6)):

\[
\sigma_n = -\rho_n 1,
\]

\[
\sigma_2 = \sigma_t 1_2 + \sigma_{\text{surf}} N \otimes N
\]

(6)

\[
\sigma_{13} = -\rho_{13} 1,
\]

where, keeping Weatherburn’s notations, a two-dimensional identity dyade [idemfactor of Gibbs] reads \( 1_2 = -N \otimes N \). Buff, making an integration of force balance through the layer thickness

\[
\int [\text{div} \sigma + p g \underline{h} j] d\lambda,
\]

(7)

and using Weatherburn’s numerous achievements in surface differential geometry, Weatherburn (1927), provides the generalized Young-Laplace equation in the final form: \( \gamma = \sigma_2 = 0 \). The normal component of this equation, according to the Gibbs postulate, contains both the surface tension scalar \( \gamma \) and the surface tension moment \( C \) (Buff 1956, eq. (22)):

\[
p_n - p_{\beta} = (c_1 + c_2) \gamma - (c_1^2 + c_2^2) C + g \Gamma \underline{k} \cdot N_{\text{surf}}.
\]

(8)

During integration of (7) Buff takes an assumption that change of the normal pressure in the normal direction \( \partial \sigma / \partial N \) is so small that can be omitted. From integration one can simply find original definitions of the "surface tension" \( \gamma \), the surface moment \( C \) and the excess of density \( \Gamma \) (Buff 1956, eq. (23)):

\[
\gamma = \int_a^b \frac{\lambda_1}{\lambda_2} (\sigma' - \sigma_{\text{surf}}) [1 + (c_1 + c_2) \lambda] d\lambda,
\]

(9)

\[
C = \int_a^b \frac{\lambda_1}{\lambda_2} (\sigma' - \sigma_{\text{surf}}) \lambda d\lambda,
\]

(10)

\[
\sigma_{\text{surf}} = \int_a^b (\rho - \rho_{\text{surf}}) d\lambda,
\]

(11)

where \( \sigma_{\text{surf}}, \rho_{\text{surf}} \) are responsible for the pressure jump between \( p_n \) and \( p_\beta \) as well as for the density jump between \( \rho_n \) and \( \rho_{\beta} \), respectively. Additionally, what is important, the energetic Tolman definition of the surface tension (5) is compatible with the force approach of Maxwell. Buff shows that starting from the Gibbs reasoning and from (2) one can approach his generalized Young-Laplace equation (8) as well as the Thomson formulae of dependence of surface tension on curvature of condensation interface surface (Buff 1956, eq. (54)):

\[
\gamma = \gamma_{\text{surf}} + \left( C + \frac{T \gamma}{\rho_n - \rho_\beta} \right) (c_1 + c_2) + ...
\]

(12)

Having the useful mathematical tool, Buff proposes a generalization of notion of the surface tension. For him the surface tension cannot be further a scalar but a two-dimensional tensor of surface tension \( \sigma_2 \). It is anticipated in the following manner (Buff 1957, eq. (16)):

\[
\sigma_2 = \gamma 1_2 - C \nabla N_{\text{surf}}.
\]

(13)

Making appropriate manipulations on the curve of three interfaces intersections, Buff and Salzburg obtain also the generalized Neumann equation (Buff & Salzburg 1957, eq. (49)):

\[
\sigma_{\text{surf}}^{\text{HIL}} : \underline{t} \times N_{\text{HIL}} + \sigma_{\text{surf}}^{\text{HII}} : \underline{t} \times N_{\text{HII}}
\]

(14)

\[
+ \sigma_{\text{surf}}^{\text{HIII}} : \underline{t} \times N_{\text{HIII}} + kg \underline{t} \nabla_1 \cdot \sigma = 0.
\]

The first three terms of eq. (14) are analogous to the Neumann equation, but instead of single \( \gamma \)
they contain also the Gibbs surface moment $C$ contained in definition (13). Quite a new element is an original Buff conception that three-phase intersection curve has anisotropic properties that define a line tension denoted by $L^*$. If $t^*$ is a tangent vector to that three-phase intersection then such a line tension dyade should have the form (Buff 1957, eq. (48)) — for reconstruction see also Amirfazl & Neumann (2004):

$$\sigma_1^* = L^* t^* \otimes t^*.$$  \hfill (15)

This is the generalized Young contact line. A one-dimensional gradient should also be defined as a differential along the line, or as a one-dimensional Nabla operator, see Weatherburn (1927), Lord Rayleigh (1883):

$$\nabla_1 = t^* \frac{\partial}{\partial t^*}. \hfill (16)$$

Similarly to the density excess (10), Buff and Saltsburg introduce a priori the one-dimensional density excess $\Gamma_1$, Buff & Saltsburg (1957).

### 1.3 Further generalizations of the Young-Laplace equations

The Buff equations have frequently been verified and revalorized. There are a few important works based on some implementation as well as on some new theoretical assumptions. Here, important are contributions by Blinowski (1973), Povstenko (1991), Kosiński (1986). Goodrich proposed to take into account viscous properties of the interfacial layer, Goodrich (1981). Then, additionally to $\sigma_2$ dyade a new tensor should be added, based on a capillary excess viscosity, Goodrich (1961). He assumes, similarly to eq. (6), that the tensor of viscous stresses possesses in the interfacial layer different properties in tangential and normal directions. It means that the three-dimensional tensor $\sigma$ in eq. (7) has the following components (Goodrich 1961, eq. (44)):

$$\sigma_{xx} = -p_r + \mu' d_{xx}, \quad \mu' d_{yy} + \lambda d_{zz}, \hfill (17)$$

$$\sigma_{xz} = -p_r + \mu' d_{xz} + \mu d_{xy} + \lambda d_{zz}, \hfill (18)$$

$$\sigma_{yz} = -p_r + \mu' d_{yz} + \mu d_{xy} + \lambda d_{zz}, \hfill (19)$$

$$\sigma_{yy} = 2 \mu d_{yy}, \sigma_{zz} = 2 \mu'' d_{zz}, \sigma_{xy} = 2 \mu'' d_{zz}. \hfill (20)$$

Here, components of rate of deformation dyade are denoted as $d_{ij}$. Lamé viscous coefficients $\lambda$, $\mu$ within the interfacial layer possess the same anisotropy; therefore instead of the two coefficients Goodrich proposes five new: $\lambda_1$, $\lambda_2$, $\mu_1$, $\mu_2$, $\mu''$. In a quite similar manner the new transport of heat in the interface layer has been proposed in Bornhorst & Hatsopoulos (1967). This approach, originally proposed for a "naked" surface, can be extended to any nonnul equilibrium phenomena, see Konoski (1986). More difficult is extension of the Young-Laplace equation into the case when the interface surface is moving. In 1986, Kosiński started a new research direction on the complete formulation of governing equations for a multiphase layer, Kosiński (1986). Not only the Young-Laplace equation were examined but also rules that govern the peripatetic motion for chemical, heat, electrical forces were formulated. In the next paper by Dell'Isola & Kosiński (1993), the governing equations were extended for the two-dimensional case when the thickness of interface layer becomes independent from processes.

In the paper by Badur & Przanowska (1997) the exact integration throughout the layer thickness of the same "excess flux" was used. In this case, the problem of an exact integration of pseudo-momentum excess was evaluated. This is possible only when we take the three-dimensional balance of pseudo-momentum and, additionally, the balance of moment of pseudo-momentum. This also leads to a general form of the Young-Laplace equation, new not only in the normal but also in the tangential direction. Now, a surface tension tensor [see eq. (13)] is postulated in the following form (Badur & Przanowska 1997, eq. (4.26), (5.8)):

$$\sigma_2 = \gamma_{(s)} - b \gamma_{(1)} + N \otimes I_2 \text{div}(\gamma_{(1)} - b \gamma_{(2)}). \hfill (21)$$

A few elements are reformulated here: a surface stretch given as $\gamma_{(s)}$, a three-fold, Gibbs-like surface moment $\gamma_{(1)}$, and, finally, a surface bi-moment $\gamma_{(2)}$. As it follows from the analysis of Povstenko (1991), the bi-moment is responsible for growing of ripples on the interface surface; that phenomenon was discovered by Povstenko & Badur (1998). In the above formula $b = \gamma_{(s)} N = N \otimes \nabla_2 = c_1 e_1 \otimes e_1 + c_2 e_2 \otimes e_2$ is the surface curvature. The vector $N$ is the unit vector normal to the surface identical with Buff's vector $N_{ib}$ directed from the phase $a$ to the phase $b$.

Let us recall that definition (21) not only extends Buff's definition of the surface bi-moment $\gamma_{(2)}$, but, what is essentially new, it also adds the transversal components. Mathematically, if we denote by a some surface vector

$$a = I_2 \text{div}(\gamma_{(1)} - b \gamma_{(2)}), \hfill (22)$$

then from (21) it follows that the generalized Buff tensor possesses a surface part and a transversal part — for analogy see Cermelli & Gurtin (1994):

$$\sigma_2 = \gamma_{(s)} - b \gamma_{(1)} + N \otimes a, \hfill (23)$$

Thus the generalized Young-Laplace equation takes the form (Badur & Przanowska 1997, eq. (5.9)):

$$\text{div} \sigma_2 + \| \sigma_2 \| N + f = 0, \hfill (24)$$

Here $f$ contains a "driving force" for equilibrium. The jump of the three-dimensional pseudo-momentum flux $\| \sigma_2 \|$ through the interfacial layer in the normal direction, in the case of fluid in rest, is equal to the difference of pressures between phases $a$ and $b$:

$$\| \sigma_2 \| N = (p_a - p_b) N. \hfill (25)$$

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It is clear that the normal component of equation (25) leads to the generalized Young-Laplace equation (Badur & Przanowska 1997, eq. (5.13)):

\[ (\gamma_{(1)}^{nl} - b_{(1)}^{nl}) \cdot n + h_{n0}(\gamma_{(0)}^{nl} - b_{(0)}^{nl}) \cdot n = 0, \]

\[ + (\mu_n - \mu) + J = 0. \]  

(26)

According to the idea of general interface state (2), postulated by Gibbs, the surface moment \( \gamma_{(1)}^{nl} \) can differ from a "spherical state". Poewsteno has introduced the compete set of components of \( \gamma_{(0)}^{nl} = \gamma_{(0)}^{nl} e_e \otimes e_e \), and has shown that the shear stresses \( \gamma_{(n)} \) are responsible for forming of the interfacial shape between liquid and crystallized metal, Poewsteno (1993). Stryla and Kuczyński have determined experimentally, for nematic fluids in contact with air, that \( \gamma_{(0)} \) is not a spherical tensor but it possess two main directions of tension. Existence of shear stresses indicates anisotropic properties of the interfacial layer, Stryla & Kuczyński (1986). From above it also follows that the generalized Gibbs variation \( \delta E^S \) [see eq. (2)] should have a complete form:

\[ \delta E^S = \gamma_{(0)}^{nl} \delta n_{nl} + \gamma_{(1)}^{nl} \delta n_{nl} + \gamma_{(2)}^{nl} \delta n_{nl}, \]

(27)

where 9 intensive and 9 extensive state parameters appear, like change of the metric tensor, change of the curvature and change of the bi-curvature.

REFERENCES