The generalized Laplace equation of capillarity
I. Thermodynamic and hydrostatic considerations of the fundamental equation for interfaces

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Abstract

Theories of capillarity are reviewed. The limitations of the classical theory as developed by Gibbs are demonstrated. The generalized theories of capillarity initiated by Buff, and later by Murphy, Kondo, Kralchevsky, and Boruvka and Neumann are scrutinized by considering the basic requirements of formulating thermodynamic fundamental equations. The different generalized Laplace equations of different theories stem from the different setups of the fundamental equation. It is concluded that only Boruvka and Neumann's (BN) generalized theory satisfies all the requirements of thermodynamics and mathematics.

Further, to test the BN theory, a hydrostatic treatment of a two phase capillary system is presented. This non-thermodynamic approach is based on the concept of virtual work as the condition for equilibrium of a capillary system, and on the concept of parallel surfaces for evaluating the stress tensor field and excess properties within the interfacial region. Following a straight-forward procedure, it is shown that the hydrostatic results for surface tension γ and two bending moments, C_1, and C_2, agree with the results of the BN generalized thermodynamic theory of capillarity. This agreement indicates that the form of the BN fundamental equation for surfaces with the extensive geometric curvatures ($\mathcal{J}$ and $\mathcal{K}$, total mean and total Gaussian curvatures, respectively) is the proper expression required to generalize the theory of capillarity.

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Contents

I. Review of the Gibbsian classical theory of capillarity

The classical theory of capillarity as developed by Gibbs [1] is the basis of all surface thermodynamics. In Gibbsian thinking, the key element of a thermodynamic theory is the fundamental equation. In order to describe a curved interfacial (surface) system, two curvature terms are necessarily included in the fundamental equation. Gibbs postulated the fundamental equation of an interface as follows [1]

$$U = U\left(S, N_i, A, c_1, c_2\right) \tag{1}$$

where U is the internal energy of the interface, S is the entropy, N_i is the mole number of component i, A is the surface area, c_1 and c_2 are the two principal curvatures of the surface. The differential form of Gibbs' fundamental equation, Eq. (1), is written as

$$dU = T\,dS + \Sigma\mu_i\,dN_i + \gamma\,dA + C_{1g}\,dc_1 + C_{2g}\,dc_2 \tag{2}$$

where T is the temperature of the system, μ_i is the chemical potential of component i, γ is the surface tension, and C_{1g} and C_{2g} are the curvature coefficients associated with the principal curvatures [1], respectively. Rearrangement of Eq. (2) leads to

$$dU = T\,dS + \Sigma\mu_i\,dN_i + \gamma\,dA + \frac{1}{2}\,(C_{1g}{+}C_{2g})\,d(c_1{+}c_2) + \frac{1}{2}\,(C_{1g}{-}C_{2g})\,d(c_1{-}c_2) \tag{3}$$

Next Gibbs showed that it is possible to select a particular position of the dividing surface [1] so that $C_{1g} + C_{2g}$ is zero. This particularly positioned dividing surface is identified as the 'surface of tension' [1]; the term 'surface of pure tension' would be a more descriptive name [1]. The second curvature term is eliminated by assuming that the interface is moderately curved and the difference between the two principal curvatures, $c_1 - c_2$, is of the second order. Therefore, by introducing the concept of the surface of tension and the assumption of moderate curvature, the Gibbs fundamental equation, Eq. (3), is reduced to

$$dU = T\,dA + \Sigma\mu_i\,dN_i + \gamma\,dA \tag{4}$$

which no longer contains the curvatures explicitly. Based on this reduced fundamental equation, Gibbs derived the classical Laplace equation

$$J\gamma = P_1 - P_2 \tag{5}$$

where $J = c_1 + c_2$ is the mean curvature, and $P_1 - P_2$ is the pressure difference between the two adjacent bulk phases. Equation (5) is the mechanical equilibrium condition and determines the shape of the interface.

II. Different approaches to generalize the Laplace equation of capillarity

From the above analysis, it can be seen that the classical theory of capillarity is limited to situations of moderately curved interfaces. However, when the curvatures of a surface are large, and their corresponding radii are comparable to the thickness of the interface, the moderate-curvature assumption does not hold, and the second curvature term cannot be eliminated from the fundamental equation. When high curvatures exist, the selection of the surface of tension also becomes obscure, and it may not fall within the physical interfacial zone [1,2]. Therefore, Eq. (4) is not an adequate fundamental equation, and as a consequence, the classical Laplace equation, Eq. (5), is not applicable to high curvature systems, such as microemulsions, lipid bilayers and certain biomembranes [3-6]. For both theoretical and practical reasons, it is necessary to generalize the classical theory of capillarity and retain the curvature terms in the fundamental equation of the interface, which

in turn can be expected to play a role in the mechanical equilibrium condition.

The first generalized version of the theory of capillarity was given by Buff et al. [7–9]; they retained the first curvature term in the fundamental equation as the cornerstone of their theory. Buff's fundamental equation in differential form was postulated as follows

$$dU = T\,dS + \sum \mu_i\,dN_i + \gamma\,dA + C\,d(c_1 + c_2) \tag{6}$$

where C was called the mean curvature coefficient [7]. The corresponding mechanical equilibrium condition, i.e. Buff's Laplace equation reads

$$(c_1 + c_2)\,\gamma - (c_1^2 + c_2^2)\,C_1 = P_1 - P_2 \tag{7}$$

where $C_1 = C/A$ is the first curvature potential. Equation (7) can be re-written as follows

$$J\gamma - (J^2 - 2K)\,C_1 = P_1 - P_2 \tag{8}$$

where $K = c_1 c_2$ is the Gaussian curvature.

Following Buff's strategy for retaining curvature terms, i.e. using the intensive curvature combinations, Murphy [2] developed a generalized theory of capillarity, with the fundamental equation postulated as follows

$$U = U(S, N_i, A, J, K) \tag{9}$$

written in differential form as

$$dU = T\,dS + \sum \mu_i\,dN_i + \gamma\,dA + C_1 A\,dJ + C_2 A\,dK \tag{10}$$

where C_2 is the second (Gaussian) curvature potential. Thus, both curvature terms are included in Eqs. (9,10), in contrast to Buff's fundamental equation, Eq. (6), where only one curvature term was retained. The Laplace equation derived from Eq. (9) can be written as

$$J\gamma - (J^2 - 2K)C_1 - JKC_2 = P_1 - P_2 \tag{11}$$

which differs from Buff's Laplace equation, Eq. (7), by the term with the second curvature potential, C_2.

Kralchevsky [10] also developed a similar generalized theory of capillarity by considering the same two curvature terms as Gibbs, i.e. Eq. (3). His fundamental equation (Ref.[10], Eq. (4.17)) is expressed as

$$dU = T \, dS + \sum \mu_i \, dN_i + \gamma \, dA + C_{1k} A \, dJ + C_{2k} A \, dK_k \tag{12}$$

where C_{1k} is the curvature potential corresponding to J, $K_k \equiv c_1 - c_2$, and C_{2k} is the curvature potential corresponding to K_k. Note that K_k can be related to the Gaussian curvature through $K_k^2 = J^2 - 4K$. The curvature potentials in different approaches can be obtained through the partial derivative definitions in the respective theories. Based on Eq. (12), the Laplace equation is obtained as (Ref. [10], Eq. (5.10))

$$J\gamma - (J^2 - 2K)C_{1k} - JK_kC_{2k} = P_1 - P_2 \tag{13}$$

Kondo [11] developed a generalized theory of capillarity in terms of spherical interfaces. In order to maintain conservation of the total free energy of the system during the shifting of the dividing surface, he derived his version of the fundamental equation as

$$dU = T \, dS + \mu \, dN + \gamma \, dA + \left[\frac{\partial \gamma}{\partial a} \right] A \, da \tag{14}$$

where a is the radius of curvature of a spherical dividing surface. In Eq. (14), Kondo introduced a non-physical derivative term $[\partial\gamma/\partial a]$, called a formal derivative. His version of the Laplace equation is

$$\gamma + \frac{1}{2} a \, \frac{\partial \gamma}{\partial a} = \frac{1}{2} a \, (P_1 - P_2) \tag{15}$$

Boruvka and Neumann [12] in their approach started out by a consideration of the requirements of thermodynamics for any fundamental equation and of the differential geometry in three dimensional space. They stated that, in accordance with Gibbsian thermodynamics, an independent parameter in the fundamental equation has to be [12,13]: (i) a scalar and (ii) an extensive property of the same type as entropy and mass for surface systems (see the next section). They stated further that specifically for surfaces in three dimensional space there is an additional, mathematical requirement, that the geometric variables

should be the lowest order scalar differential invariants of the surface [14,15]. With these considerations, Boruvka and Neumann [12] developed a generalized theory of capillarity, and their postulated fundamental equation for a homogeneous portion of a surface is

$$U = U\left(S, N_i, A, \mathcal{J}, \mathcal{K}\right) \tag{16}$$

with the differential form

$$dU = T\,dS + \Sigma\mu_i\,dN_i + \gamma\,dA + C_1\,d\mathcal{J} + C_2\,d\mathcal{K} \tag{17}$$

where $\mathcal{J}$ and $\mathcal{K}$ are the total mean and total Gaussian curvatures of the surface with an area A

$$\mathcal{J} = \int\int_{(A)} J\,dA, \qquad \mathcal{K} = \int\int_{(A)} K\,dA \tag{18}$$

and C_1 and C_2 are the potentials of $\mathcal{J}$ and $\mathcal{K}$, respectively. The relations between these extensive variables in Eq. (16) and their densities can be explicitly written as

$$U = uA, \quad S = sA, \quad N_i = n_iA \quad (i = 1,2,...),$$

$$\mathcal{J} = JA, \quad \mathcal{K} = KA \tag{19}$$

where u, s, and n_i are the area density of the internal energy, the entropy, and the mole number of component i, respectively. The above relations are also considered to be the transformation equations between the extensive variables and their densities [12]. In the case of a non-homogeneous surface, the density form of the fundamental equation is necessarily employed [12]

$$u = u\left(s, n_i, J, K\right) \tag{20}$$

The Boruvka and Neumann (BN) generalization of the Laplace equation which follows from Eq. (20) is written, in the most general form, as follows

$$J\gamma + 2KC_1 - \nabla_2^2\,C_1 - K\nabla_2^* \cdot (\nabla_2 C_2) = P_1 - P_2 \tag{21}$$

where ∇_2^* is a special surface operator [12,15], and ∇_2 is the two-dimensional analog to the three-dimensional gradient. When the surface tension and the two curvature potentials C_1 and C_2 are constant along the surface (homogeneous surface conditions), Eq. (21) reduces to [12]

$$J\gamma + 2KC_1 = P_1 - P_2 \qquad (22)$$

It is evident that the various versions of Laplace equation (Eqs. (7), (11), (13), (15) and (22)) are all different in form. To elucidate this point, it may be helpful to consider the special case of spherical surfaces, where the two principal curvatures are equal, i.e. $c = c_1 = c_2$ and the difference between the two principal curvatures is zero. In this case, the generalized Laplace equations reduce to

Buff:
$$2c\gamma - 2c^2C_1 = P_1 - P_2 \qquad (7a)$$

Murphy:
$$2c\gamma - 2c^2C_1 - 2c^3C_2 = P_1 - P_2 \qquad (11a)$$

Kralchevsky:
$$2c\gamma - 2c^2C_{1k} = P_1 - P_2 \qquad (13a)$$

Boruvka and Neumann:
$$2c\gamma + 2c^2C_1 = P_1 - P_2 \qquad (22a)$$

Note that the Kondo equation, Eq. (15), was derived for spherical surfaces in the first place. While the Buff and the Kralchevsky equations become identical in this special case, the Murphy and the BN equations remain distinct. It has been argued [16–19] that any two of the above Laplace equations can be transformed into the other equation by mathematically redefining the parameters. However, this is prohibited by the thermodynamic requirements for the fundamental equation and the structure and proceedings of thermodynamics [13], see also below.

III. The necessity to distinguish between extensive and intensive properties

To work towards a resolution of the above impasse, it is convenient to return to the three requirements stated in the work of Boruvka and

Neumann (BN). The requirement that the independent variables in the fundamental equation have to be scalar quantities is of no particular concern and in any case rather obvious, since the internal energy on the left-hand side of the various formulations of the fundamental equation is a scalar. The requirement of differential invariance might be argued to be nothing more than a matter of mathematical convenience. However, the necessity for the independent parameters to be extensive is a fundamental thermodynamic issue. We would like to point to the book of Callen [13], who writes in the preface to his second edition that his book is now "...the thermodynamic reference most frequently cited in physics research literature, and... the postulational formulation which it introduced is now widely accepted" [13]. Callen's Postulate 2, which represents part of the second law of thermodynamics reads: "There exists a function (called the entropy *S*) of the *extensive* parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the *extensive* parameters ... are those that maximize the entropy ...". Clearly, in the fundamental equation, the independent variables involved must be extensive.

Thermodynamically, the requirement of extensivity makes good sense: the partial derivatives of U with respect to the independent variables, e.g. $\partial U / \partial S$, which represents the temperature, must be intensive. Since U is extensive, this is possible only if S and all the other variables are also extensive.

The necessity of extensivity of thermodynamic variables is also supported by the variational analysis. For an interface, whether it is homogeneous or not, the total internal energy U of the interface is an integral of the internal energy density u over the area (c.f. Eq. (20)). A variation in the total internal energy can be written as

$$\delta U = \delta \int u \, dA = \int \delta u \, dA + \int u \delta(dA) \tag{23}$$

When dealing with the density form of the internal energy u, the question of the extensivity of independent variables does not occur since all the parameters under consideration are in intensive form. The standard variation of the internal energy density is written as

$$\delta u = T\delta s + \mu_i \delta n_i + C_1 \delta J + C_2 \delta K \tag{24}$$

which can be obtained from all the different generalized theories [2,4,7–10,12) except that of Kondo's [11]. Clearly, the difference in the definitions

of J and K in the different approaches is of no consequence for the present mathematical argument. Note that, e.g., in the framework of Kralchevsky's theory, the Gaussian curvature variation δK in Eq. [24] only has to be replaced by δK_k (cf. Eq. (12)). Therefore, for the purpose of the present mathematical argument, we can treat Eq. (24) as a commonly accepted, standard variation of the internal energy density. To evaluate the right-hand side of Eq. (23), the Euler form of the internal energy density may be used in addition to Eq. (24); hence the variation of the total internal energy δU becomes

$$\delta U = \int [T\delta(sdA) + \mu_i\delta(n_idA) + \gamma\delta(dA) + C_1\delta(JdA) + C_2\delta(KdA)] \tag{25}$$

In the case of a homogeneous dividing surface, Eq. (25) integrates into

$$\delta U = T\delta(sA) + \mu_i\delta(n_iA) + \gamma\delta A + C_1\delta(JA) + C_2\delta(KA) \tag{26}$$

Upon using the transformation equations between the extensive variables and their densities, Eq. (19), the Boruvka and Neumann fundamental equation, Eq. (17), is recovered. In the above variational analysis, Eqs. (23–26), the only knowledge used is the calculus of variations. Therefore, by considering both pure mathematical and thermodynamic [13] requirements, we can conclude that the choice of extensive variables (J and K) is a necessity in formulating the fundamental equation.

While the above mathematical requirements are clearly violated in the majority of approaches discussed here, they are by no means unknown in the field. An example of proper handling of the distinction between extensive and intensive properties is the work of Helfrich [6,20,21] in the treatment of the effects of curvature on the shape of closed membranes.

Returning to the above generalized theories, it is apparent that all three criteria of thermodynamics and mathematics in setting-up the fundamental equations are only satisfied by the approach of Boruvka and Neumann. Buff et al. [7–9] mixed intensive and extensive thermodynamic parameters in their fundamental equation, Eq. (6). Murphy [2], who recognized the need for differential invariance, also mixed intensive curvature terms with extensive parameters such as the surface area and the surface entropy, Eq. (9). Kralchevsky [10], in his fundamental equation, Eq. (12), has both intensive (J, K_k) and extensive

(surface area and surface entropy) parameters. Moreover, the difference between the two principal curvatures used by Kralchevsky [10] is not a scalar differential invariant [15].

Seemingly, Kralchevsky's fundamental equation has the merit of being identical with that of Gibbs [1], Eq. (3). However, it has been argued elsewhere [14] that it is likely that Gibbs was aware of the shortcomings of Eqs. (1) and (3), although they served his purposes well. He was quick to suggest possible generalization of his theory, e.g. in the case of line tension; in the much more central question of the curvatures, he remained totally silent.

In Kondo's generalization, the formal derivative expresses a change in the value of the surface tension γ due to a shift of the dividing surface, and it is not to be confused with a change accompanying an increase in the radius of the physical interface [22]. It can be seen from Eq. [14] that the differential form of Kondo's fundamental equation is not a standard formulation [13,14]. The formal derivative, which is the coefficient of the 'A da' term in Eq. (14), is not the partial derivative of the internal energy U with respect to the radius of the curvature, and cannot arise from a proper formulation of the fundamental equation. It may be concluded that the formulation of Kondo's fundamental equation violates the standard requirements of derivative definitions of thermodynamics.

In contrast, it can be seen that the Boruvka and Neumann fundamental equation, Eqs. (16–18), not only retains both curvature terms (in Buff's theory only one curvature term is retained) but also eliminates the problem with mixing intensive and extensive thermodynamic parameters in the fundamental equation. The *total* mean and Gaussian curvatures $\mathcal{J}$ and $\mathcal{K}$ are extensive variables. The two curvature potentials were defined as the partial derivatives of the internal energy with respect to the two corresponding total curvatures [12]. Moreover, the surface geometric parameters $\mathcal{J}$ and $\mathcal{K}$ are the first and the second scalar invariants of the surface dyadic [15,23].

IV. The scope of non-thermodynamic continuum approaches to capillarity

The correctness of the generalized Laplace equation depends on the correctness of its fundamental equation. While the Boruvka and Neumann (BN) fundamental equation satisfies all thermodynamic and

geometric requirements, it is still a postulate and as such remains in need of verification and interpretation. Also, the retaining of the second curvature term (the Gaussian curvature term) needs to be justified, i.e. the term which was left out in Buff's analysis.

Major credit in this area is due to Buff, who not only pioneered the idea of a generalized thermodynamic theory of capillarity, but also developed strategy and methodology for independent testing of the thermodynamic results. Specifically, he developed [7] a hydrostatic approach to capillarity based on the analysis of the interfacial stress tensor field. Through the integration of the excess hydrostatic equation across the interface, he recovered his generalized Laplace equation, Eq. (7), by relating the thermodynamic parameters to the interfacial stress field. However, Buff carried over, from his thermodynamic theory, the use of the intensive parameters as the variables in his hydrostatic derivation. Equations (6) and (7) are believed to lack thermodynamic rigour, and hence the expressions for the thermodynamic parameters in terms of the stress field of the interfacial zone are not proper. Nevertheless, he presented a useful approach to confirm the thermodynamic theory.

Boruvka et al. [24] also developed a hydrostatic approach to capillarity using tools developed by Buff [7]. However, in contrast to Buff [7] whose hydrostatic approach is to confirm the Laplace equation of his thermodynamic theory, Boruvka et al. [24] developed the hydrostatic approach to verify and confirm the postulated BN fundamental equation. The hydrostatic approach of Boruvka et al. provided a complete verification and confirmation of the BN thermodynamic theory. However, rather complicated differential geometry was involved [24] which made the paper somewhat difficult to read.

In view of the importance of the question and the inconsistencies and discrepancies between the various existing versions of generalized Laplace equations as shown above, we propose to reconsider here the hydrostatic approach. With a reasonably simple tensor analysis, the present paper re-examines the derivation of the BN fundamental equation by using a more transparent hydrostatic approach than that of Boruvka et al. [24]. The physical meaning of the curvature terms will also be explored.

The hydrostatic equation (sometimes called equilibrium equation [25]) can be written as

$$\nabla \cdot \sigma = \rho \, \nabla \, \phi \tag{27}$$

where σ and ρ are the stress tensor and density, respectively, and external body forces are represented by the potential ϕ. Integration of the excess hydrostatic equation across the interface leads to the mechanical equilibrium condition, i.e., the Laplace equation [7]. An alternative formulation of the conditions for equilibrium of a system is the principle of virtual work which will appear later in this paper, cf. Eqs. (38–43). The analysis of the virtual work of the interfacial system will provide the proper form of the free energy and hence of the fundamental equation. Thus, the connection between the hydrostatic approach and thermodynamic fundamental equation can be attained by considering virtual work [24]. For this reason the present hydrostatic approach is again based on the virtual work principle rather than the hydrostatic equation.

V. Stress tensor field in a capillary system

Consider a two phase capillary system with a plane-parallel interfacial zone. Inside each bulk phase, away from the influence of the interface, the stress tensor becomes isotropic, i.e.

$$\sigma = - PI \qquad (28)$$

where P is the pressure and I is the three-dimensional unit tensor.

Within the interfacial zone, a special treatment must be considered. Buff [7] introduced the following parametrization of the position vector R, in the space occupied by the interface

$$R = R(u,v,\lambda) = r(u,v) + \lambda n(u,v) \qquad (29)$$

where r is the position vector of a selected dividing surface, n is the unit normal to the surface and λ is the distance from the dividing surface. This representation of the interfacial zone is shown in Fig. 1 where $u–v$ is a curved surface representing the dividing surface.

From the figure we have

$$n = \frac{r_u \times r_v}{|r_u \times r_v|} \qquad (30)$$

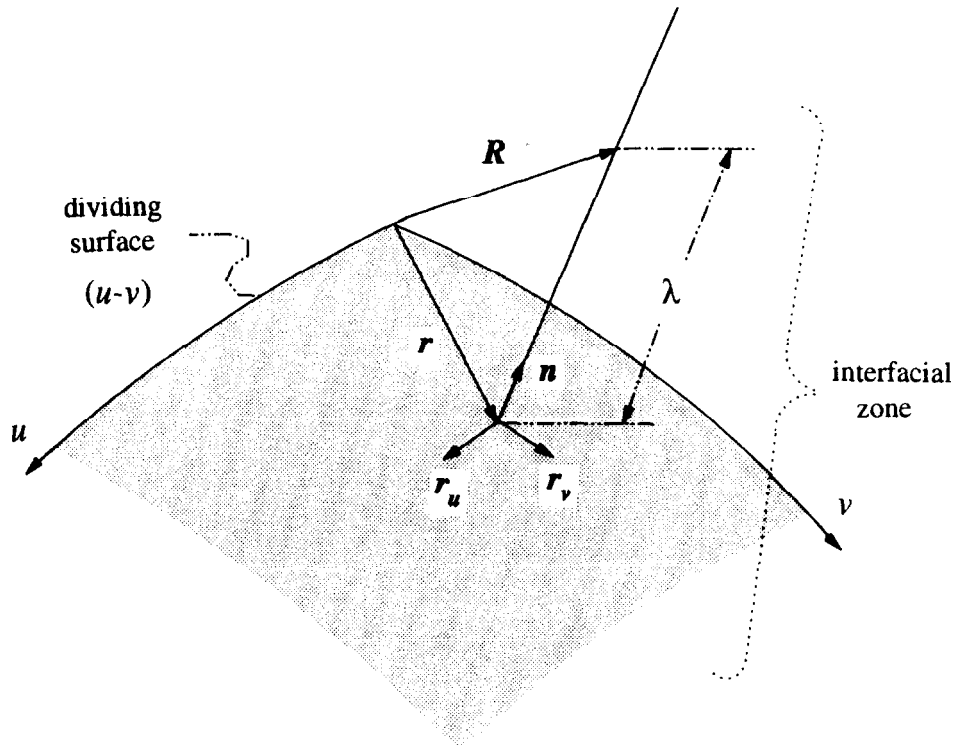where r_u and r_v are the unit vectors on the interface at the point under consideration.

Fig. 1. Buff's representation of the interface.

By definition, the surfaces, **R** (λ = *constant*), represent a one parameter family of parallel surfaces with the dividing surface at λ = 0 (Fig. 2).

Within the interfacial zone, all physical properties like density ρ and stress tensor σ vary quickly but smoothly along the direction λ which is normal to the dividing surface. The variation of density within the interface is shown schematically in Fig. 3 [26].

Because of the rapid variation of density in the direction λ, the isotropy of the stress tensor in the interfacial zone is destroyed. Using the parametrization of **R**(u,v,λ), Buff [27] assumed that within the transitional zone, the stress ellipsoid is axi-symmetric along the normal to the dividing surface passing through the point under consideration. For the case of a spherical interface (i.e. u–v surface in Fig. 1 is part of a sphere), he offered the following relation for the stress tensor

$$\sigma = \sigma_T(\lambda) \, (r_u r_u + r_v r_v) + \sigma_N(\lambda) \, nn \tag{31}$$

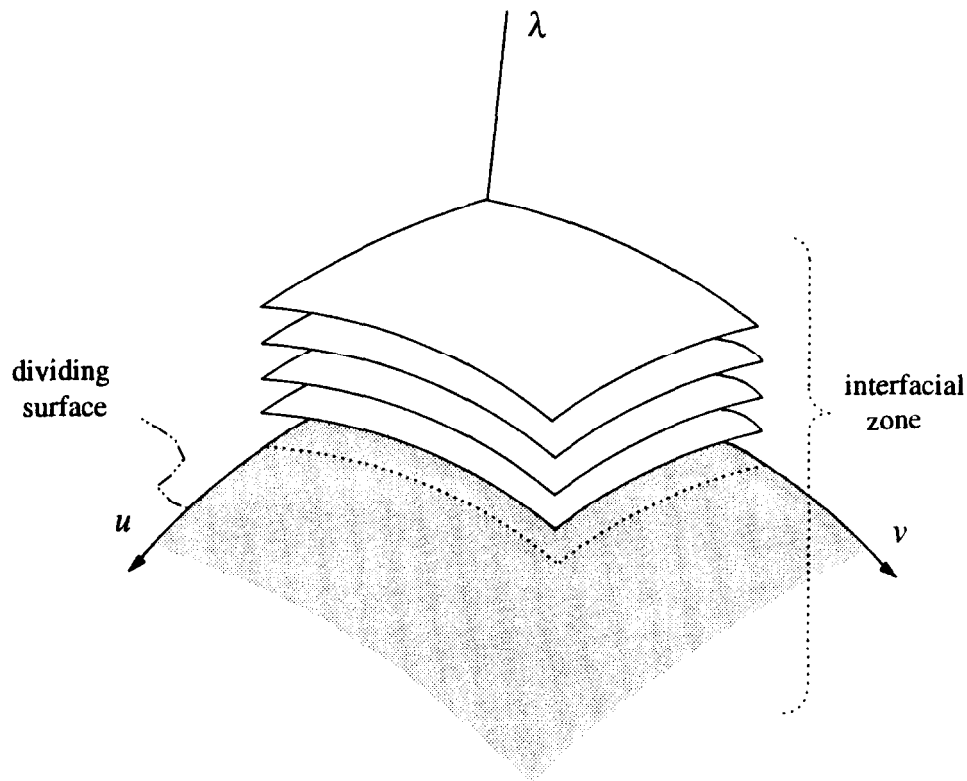where $r_u r_u$, $r_v r_v$ and nn represent the unit line tensors in the u, v and λ

Fig. 2. 'λ = *constant*' surfaces within the interfacial zone.

directions, respectively, at the point under consideration. In this equation $(r_u r_u + r_v r_v)$ may be replaced by I_2 the unit surface tensor ($I_2 = I - nn$), so that Eq. (31) is replaced by [7]

$$\sigma = \sigma_T(\lambda)\, I_2 + \sigma_N(\lambda)\, nn \tag{32}$$

where σ_T represents the two identical isotropic, tangential stress components and σ_N represents the normal stress component[*] of the interface which is equal to the negative pressure at the point under consideration. In the interior of each bulk phase the tangential stress component σ_T reduces to $-P$; therefore in the bulk phases Eq. (32) reduces to Eq. (28).

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[*] It should be mentioned that σ_T and σ_N are normal (i.e. not shear) stresses but since they are in the directions parallel and normal to the interface at the point under consideration, respectively, σ_T is called tangential stress component and σ_N normal stress component.
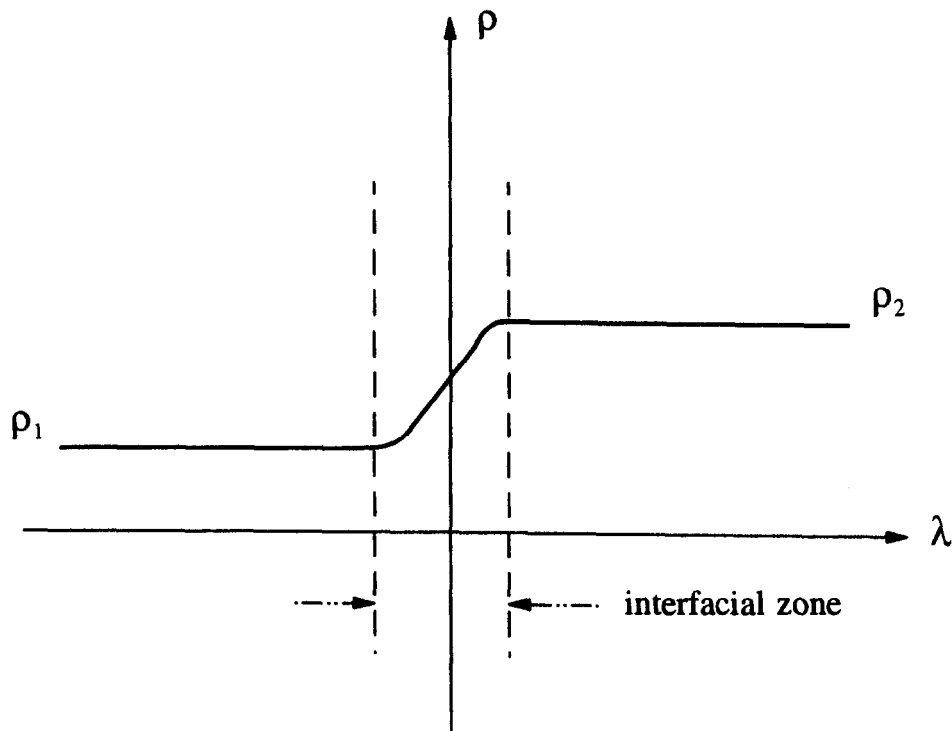
Fig. 3. A schematic of the variation of density within the interface.

As observed from Eq. (32), σ_T and σ_N for the spherical interface are only functions of λ, the direction normal to the dividing surface. In the cases with non-uniform curvatures, i.e. nonspherical interfaces, Eq. (32) is expected to be a good approximation (to the first order) of the actual form of the interfacial stress tensor. The implicit assumption invoked *via* this construction is that the constant density surfaces (Fig. 2) within the interface are taken as parallel and that the stress is transversely isotropic. In other words, it is assumed that the fluid is isotropic and homogenous in every parallel surface within the interfacial region regardless of whether or not non-uniform curvatures exist.

According to the above development of the stress tensor representation for a capillary system, the variation of the tangential and normal stress components against the direction normal to the dividing surface may be drawn schematically as shown in Fig. 4 [26]. It should be noted that the variation of $\sigma_T(\lambda)$ is quantitatively studied in the microscopic approach to capillarity [28].
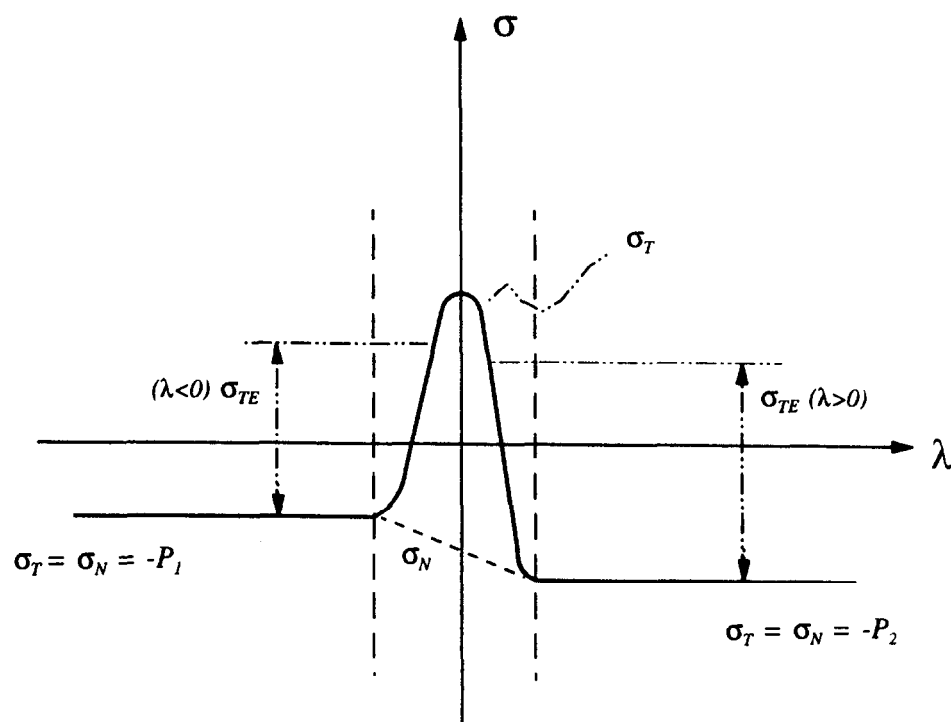
Fig. 4. A schematic of the variation of the stress tensor components across the interface.

VI. Interfacial excess properties

The interfacial zone may be considered (to the first order approximation), as done by Gibbs [1], as a mathematical (two-dimensional) boundary between two bulk phases which extend uniformly right up to the mathematical dividing surface. From the Gibbsian viewpoint, the dividing surface or surface of discontinuity is a mathematically constructed surface of only two dimensions which is sensibly placed within the thin interfacial zone to separate the bulk regions that make contact when forming the interface.

As a result of this model, when a dividing surface is placed within the interface in a hydrostatic system and the actual bulk phases are approximated by the extrapolated bulk phases right up to the dividing surface, the interfacial excesses of physical properties have to be assigned to the dividing surface. Otherwise, the system totals of physical properties would not be preserved. This is the main idea of the dividing

surface concept. The simplest way of assigning the interfacial excess properties to the dividing surface is by making use of the parallel surfaces (Fig. 2).

Extrapolated and excess quantities with respect to the surface are defined in terms of both the position of the dividing surface and the orientation of the surface. The excess quantities of the surface like $\rho^{(A)}$, $u^{(A)}$, $s^{(A)}$ etc. are assigned to a particular point on the surface and obtained by integration through the interfacial zone.

If the dividing surface is put at $\lambda = 0$ and extrapolated bulk properties are denoted by subscript e, then the interfacial excess density ρ_E can be written as

$$\rho_E = \rho - \rho_e \tag{33}$$

Similarly for the excess stress tensor

$$\sigma_E = \sigma - \sigma_e \tag{34}$$

where σ_e is the stress tensor of the bulk phase; therefore using Eq. (28) we have

$$\sigma_E = \sigma + P_e \boldsymbol{I} \tag{35}$$

so that

$$\sigma_{TE} = \sigma_T + P_e \, , \qquad \sigma_{NE} = \sigma_N + P_e \tag{36}$$

Now using Eq. (32) we have

$$\sigma_E = \sigma_{TE}(\lambda) \, \boldsymbol{I}_2 + \sigma_{NE}(\lambda) \, \boldsymbol{nn} \tag{37}$$

It should be mentioned that the extrapolated quantities, denoted by subscript e, for the two regions of $\lambda < 0$ and $\lambda > 0$ are different on the two sides and, therefore, the excess quantities for the two regions will also be different. The tangential component of the excess stress tensor in the interfacial zone is shown schematically in Fig. 4 [26].

VII. Virtual work in a hydrostatic system

The equation of hydrostatics, Eq. (27), is a necessary condition for the equilibrium of a static fluid body. An alternative formulation of the conditions for equilibrium of a system is the principle of virtual work (sometimes called the principle of virtual displacements). The method of virtual work may be used instead of writing the equilibrium equations to solve for unknown reactions or to determine the equilibrium configuration of the system [29]. By applying this method for a static fluid body, Eq. (27) is replaced by another necessary condition as follows

$$\delta W = 0 \tag{38}$$

That is, the total virtual work in a static fluid body is zero at equilibrium.

Notice that in a hydrostatic analysis, thermal and chemical equilibria are tacitly assumed; therefore the principle of virtual work, Eq. (38), is equivalent to the minimum principle of the free energy (grand canonical potential).

The appropriate expression for δW is

$$\delta W = \delta W_i + \delta W_\phi + \delta W_o \tag{39}$$

where δW_i, δW_ϕ and δW_o are the virtual work done by the internal forces (stress tensor σ), the external body forces $(-\rho \, \nabla \phi)$ and the external surface forces, respectively. If the virtual work expression is set up correctly, the hydrostatic equation should follow from Eq. (38).

Since the main purpose of this paper is to confirm the proper form of the fundamental equation for an interface we are concerned only with the virtual work arising from the internal forces. The appropriate expression for δW_i is

$$\delta W_i = -\int\int\int_{(V)} \sigma : \nabla \delta \boldsymbol{R} \, dV \tag{40}$$

where $\nabla \, \delta \boldsymbol{R}$ is the virtual strain tensor ($\delta \boldsymbol{R}$ is the virtual displacement vector) and the sign ':' is the double dot product. For a two phase capillary system, the usual treatment is applied (as explained before): the Gibbs' dividing surface is placed within the interface, the bulk properties are extrapolated right up to the dividing surface, and the interfacial excess quantities are introduced. Substituting for σ from Eq. (35), the virtual work of the internal forces, Eq. (40), separates into two parts as follows

$$\delta W_i = \delta W_{ie} + \delta W_{iE} \tag{41}$$

where δW_{ie} and δW_{iE} are the virtual work in the extrapolated bulk phases and the interfacial excess part of δW_i, respectively, and we have

$$\delta W_{ie} = \int\int\int_{(V)} P_e \, \boldsymbol{I} : \nabla \delta \boldsymbol{R} \, dV \tag{42}$$

$$\delta W_{iE} = -\int\int\int_{(V)} \sigma_E : \nabla \delta \boldsymbol{R} \, dV \tag{43}$$

Note that

$$\boldsymbol{I} : \nabla \delta \boldsymbol{R} = (\nabla \delta \boldsymbol{R})_{ii} = \nabla \cdot \delta \boldsymbol{R} \qquad i=1,2,3 \tag{44}$$

and from the variation of volume integrals we have

$$\delta \, dV - (\nabla \cdot \delta \boldsymbol{R}) \, dV \tag{45}$$

Therefore combining Eqs. (42), (44) and (45), the virtual work in the extrapolated bulk phases may be expressed as

$$\delta W_{ie} = \int\int\int_{(V)} P_e \, \delta dV \tag{46}$$

δW_{iE}, the interfacial excess part of δW_i, will be evaluated in the next section.

VIII. Hydrostatic properties of a dividing surface

Having defined the excess quantities of an interface in a capillary system, we are able to assign the interfacial excess properties to a selected dividing surface. This can be accomplished in a simple way by making use of the parallel surfaces (Fig. 2) and integrating the excess quantities through the interfacial region. For example, the mass of the dividing surface may be written as

$$M_E = \int\int\int_{(V)} \rho_E \, dV \tag{47}$$

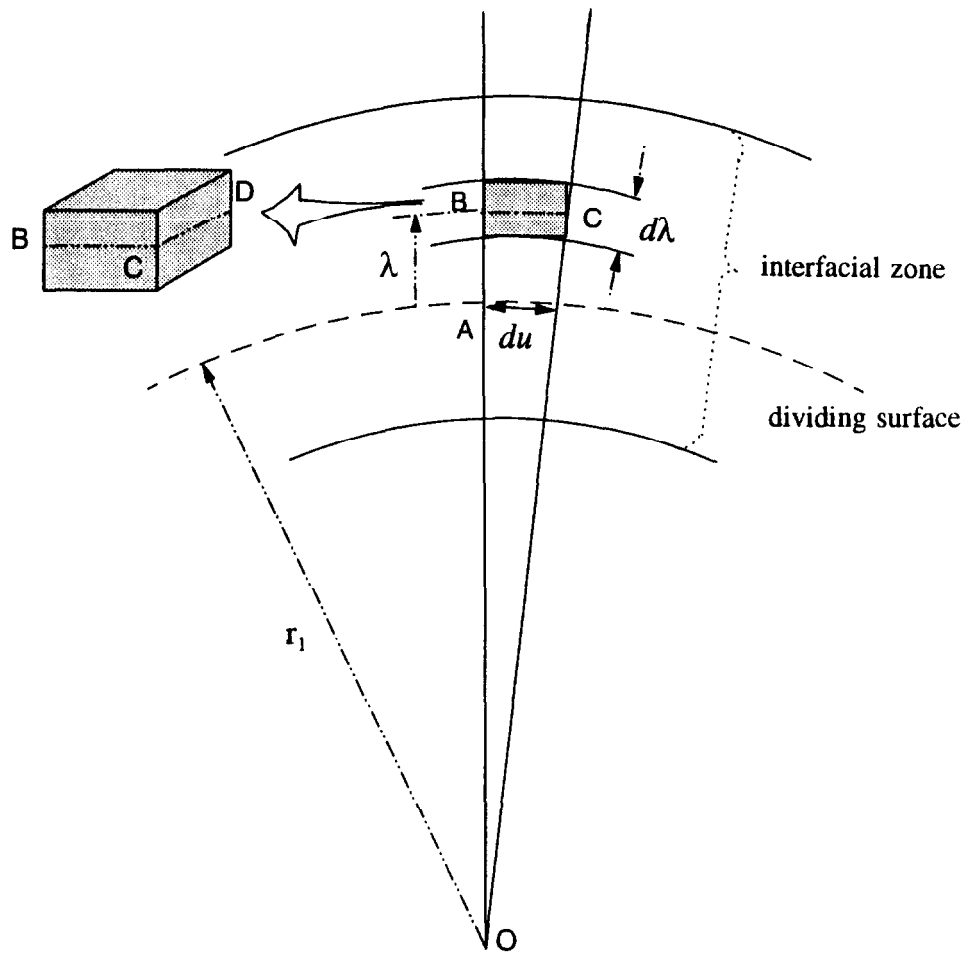Therefore, as observed, a volume element of the interfacial region, dV,

Fig. 5. One side of a volume element of the interfacial zone.

has to be evaluated first, in order to perform the integration across the interface. Consider one side of a volume element of the interfacial region as shown in Fig. 5. The area of the indicated side of the element may be approximated by the shaded rectangular region shown in the figure; this area is given by $BC\, d\lambda$. Now, from the triangle OBC:

$$\overline{BC} = \frac{\overline{OB}}{\overline{OA}}\, du = \frac{r_1 + \lambda}{r_1}\, du = \left(1 + \frac{\lambda}{r_1}\right) du$$

$$\therefore\ \overline{BC} = (1 + c_1\lambda)\, du \tag{48}$$

where c_1 is one of the principal curvatures of the dividing surface (c_1 = $1/r_1$). Similarly for the other side of the volume element we have

$$\overline{CD} = (1 + c_2\lambda)\, dv \tag{49}$$

By combining Eqs. (48) and (49) the area element of a parallel surface with a distance λ from the dividing surface (Fig. 5) may be written as

$$dA_s = \overline{BC}\ \overline{CD}$$

$$= (1 + c_1\lambda)(1 + c_2\lambda)\, du\, dv$$

$$= \{1 + (c_1 + c_2)\lambda + c_1c_2\lambda^2\}\, dA \tag{50}$$

$$= (1 + J\lambda + K\lambda^2)\, dA$$

where J, K and dA are the mean curvature, the Gaussian curvature and an element of the area of the dividing surface (at $\lambda = 0$), respectively.

Finally, for the volume element of the interfacial region (Fig. 5) we have

$$dV = dA_s d\lambda = (1 + J\lambda + K\lambda^2)\, dA\, d\lambda \tag{51}$$

Having determined dV, we can substitute Eq. (51) into Eq. (47) to obtain the total interfacial excess mass as follows

$$M_E = \int\int\int \rho_E(1 + J\lambda + K\lambda^2)\, d\lambda\, dA \tag{52}$$

Thus the interfacial excess mass density (per unit area) is given by

$$\rho^{(A)} = \int \rho_E(1 + J\lambda + K\lambda^2)\, d\lambda \tag{53}$$

and the mass of the dividing surface may also be written as

$$M_E = M^{(A)} = \int\int_{(A)} \rho^{(A)}\, dA \tag{54}$$

It is clear that, in general, we have

$$J = J(u,v), \qquad K = K(u,v), \qquad \rho_E = \rho_E(u,v,\lambda)$$

$$\therefore \rho^{(A)} = \rho^{(A)}(u,v) \tag{55}$$

It should be mentioned that the integration limits on λ in the above equations are implied by the vanishing of ρ_E and that all centres of the dividing surface are assumed to fall outside these limits.

Other properties of the dividing surface such as the excess internal energy $u^{(A)}$, and the excess entropy $s^{(A)}$ can be evaluated similarly as $\rho^{(A)}$. The virtual work of the excess internal forces, δW_{iE}, is the most important attribute of the dividing surface to be obtained. Substituting Eqs. (37) and (51) into Eq. (43) leads to

$$\delta W_{iE} = - \int \int \int [\sigma_{TE} I_2 + \sigma_{NE} \, nn] : \nabla \, \delta \, R \, dA_s \, d\lambda \tag{56}$$

An evaluation for δR with respect to the dividing surface may be obtained by taking the variation of Eq. (29), which leads to

$$\delta R = \delta r + \lambda \delta n + n \delta \lambda \tag{57}$$

On the other hand, by considering the parallel surface with a distance λ from the dividing surface (Figs. 1 and 5) we may write the following

$$\delta R = \delta R_s + \delta R_n \tag{58}$$

where δR_s and δR_n are projections of δR on and normal to the parallel surface, respectively. Comparing Eqs. (57) and (58) we have

$$\delta R_s = \delta r + \lambda \delta n \tag{59}$$

$$\delta R_n = n \delta \lambda \tag{60}$$

In a manner similar to Eq. (44) it can be shown that

$$I_2 : \nabla \delta R = (\nabla \delta R)_{jj} = \nabla_2 \cdot \delta R_s \qquad j = 1,2 \tag{61}$$

$$nn : \nabla \delta R = (\nabla \delta R)_{33} = \nabla_1 \cdot \delta R_n \tag{62}$$

where ∇_2 and ∇_1 are the surface- and the line-differential operators, respectively (similar to space gradient ∇). Substituting Eqs. (61) and (62) into Eq. (56) we get

$$\delta W_{iE} = - \int \int \int \sigma_{TE}(\nabla_2 \cdot \delta \boldsymbol{R}_s) \, dA_s \, d\lambda - \int \int \int \sigma_{NE}(\nabla_1 \cdot \delta \boldsymbol{R}_n) \, d\lambda \, dA_s \qquad (63)$$

Now, similar to Eq. (45) from the variation of surface and line integrals we have

$$\delta dA_s = (\nabla_2 \cdot \delta \boldsymbol{R}_s) \, dA_s \qquad (64)$$

$$\delta d\lambda = (\nabla_1 \cdot \delta \boldsymbol{R}_n) \, d\lambda \qquad (65)$$

and using an approximation that the 'λ= *constant*' surfaces spanning the interface (Fig. 2) remain parallel to the dividing surface and the distance between them does not change, we may write

$$\delta\lambda = 0 \quad \rightarrow \quad \delta d\lambda = 0 \qquad (66)$$

This approximation is in line with the assumptions already made. Thus, substituting Eqs. (64–66) into Eq. (63) we obtain the following

$$\delta W_{iE} = - \int \int \int \sigma_{TE} \, \delta dA_s \, d\lambda \qquad (67)$$

From Eq.[50] by applying Eq.[66] it can be shown that

$$\delta \, dA_s = \delta[(1 + J\lambda + K\lambda^2) \, dA]$$

$$= \delta \, dA + \lambda \, \delta(JdA) + \lambda^2 \, \delta(KdA) \qquad (68)$$

When introducing J and $\mathcal{K}$ the total mean and Gaussian curvatures, respectively, with the following definitions

$$J = \int \int_{(A)} J \, dA \,, \qquad \mathcal{K} = \int \int_{(A)} K \, dA$$

$$\therefore \; dJ = J \, dA \,, \qquad d\mathcal{K} = K \, dA \qquad (69)$$

and substituting Eq. (68) into Eq. (67) results in

$$\delta W_{iE} = -\int\int\int \sigma_{TE}\,(\delta dA)\,d\lambda - \int\int\int \sigma_{TE}\,\lambda(\delta d\,\mathcal{J})\,d\lambda - \int\int\int \sigma_{TE}\,\lambda^2(\delta d\mathcal{K})\,d\lambda \tag{70}$$

Using the following definition

$$\chi_k = \int \lambda^k\,\sigma_{TE}\,d\lambda\,;\qquad k = 0,\,1,\,2 \tag{71}$$

we obtain the final expression for the virtual work of the internal forces in a dividing surface

$$\delta W_{iE} = \delta W_i^{(A)} = -\int\int_{(A)} (\chi_0\,\delta dA + \chi_1\,\delta d\mathcal{J} + \chi_2\,\delta d\mathcal{K}) \tag{72}$$

Notice that in the procedure which resulted in Eq. (72) no restriction was made on where the dividing surface should be put inside the interfacial region; therefore this surface can be positioned arbitrarily.

IX. Comparison with the generalized thermodynamic theory

From the generalized thermodynamic theory of capillarity [12] via the free energy formalizations [30], it has been shown that the virtual work of internal forces in a dividing surface is expected to be

$$\delta W_i^{(A)} = -\int\int_{(A)} (\gamma\,\delta dA + C_1\,\delta d\mathcal{J} + C_2\,\delta d\mathcal{K}) \tag{73}$$

where γ is the surface tension and C_1 and C_2 are the first and second bending moments, respectively. Equation (73) is matched term by term to Eq. (72) together with Eq. (71) by setting:

$$\gamma = \chi_0 = \int \sigma_{TE}\,d\lambda \tag{74}$$

$$C_1 = \chi_1 = \int \lambda\,\sigma_{TE}\,d\lambda \tag{75}$$

$$C_2 = \chi_2 = \int \lambda^2\,\sigma_{TE}\,d\lambda \tag{76}$$

These equations show that the thermodynamic quantities, γ, C_1 and C_2 correspond to the first three moments of the tangential excess stress component σ_{TE}, about the dividing surface at $\lambda = 0$. Recalling the case of a distributed loading on a beam from solid mechanics, we may infer from the above equations that the surface tension γ represents the total force per unit length acting along the interface and the two bending moments C_1 and C_2 indicate how this force, which results from the tangential excess stress tensor, is distributed across the interface. The close correspondence between Eqs. (72) and (73) indicates that the hydrostatic approach to capillarity is equivalent to the mechanical part of the generalized thermodynamic theory and thus proves the correctness of the generalized fundamental equation for surfaces. This confirms that A, $\mathcal{J}$, and $\mathcal{K}$ do indeed constitute the proper set of extensive geometric properties one must consider when generalizing the classical theory of capillarity.

Barring mathematical errors in the BN derivation of the generalized Laplace equation, Eq. (22), this generalized equilibrium condition must be considered as the correct one. In view of the complexities of the original BN derivation, we shall present two more elementary derivations of Eq. (22), one hydrostatic and one thermodynamic, in the subsequent paper.

X. Conclusions

A hydrostatic approach for a two phase capillary system with a single interface has been presented with a straightforward tensor analysis.

By applying the concept of virtual work in a capillary system and comparing the results of the treatment with the generalized thermodynamic theory, agreement between the hydrostatic and thermodynamic approaches was reached which led to an appropriate verification of the surface tension γ, and two bending moments C_1 and C_2. The agreement between the two approaches indicates that the form of the fundamental equation for surfaces [12] with the extensive geometric curvatures given by the total mean curvature $\mathcal{J}$, and the total Gaussian curvature $\mathcal{K}$ is the proper expression required to generalize the theory of capillarity.

The hydrostatic expressions for the two bending moments provide a justification and a physical interpretation of these previously postulated parameters.

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Appendix. The dependence of interfacial tension on the position of the dividing surface

The final point regarding our hydrostatic approach is about the position of the dividing surface. If the location of this surface in the interfacial zone is changed then, from Eq. (74), γ will change also, i.e. γ depends on the position of the dividing surface. To show this clearly, consider Fig. 6 [26].

If the dividing surface is positioned at $\lambda = 0$, then γ is equal to the shaded area in the figure. Now, if the dividing surface is put at $\lambda = \lambda_1$, then the area of 'abcda' will be added to the shaded area, i.e. $\gamma_1 > \gamma$, but if it is put at $\lambda = \lambda_2$, then the area of 'cdefc' will be subtracted from the shaded area so that $\gamma_2 < \gamma$. Thus, changing the dividing surface from $\lambda = \lambda_1$ to $\lambda = \lambda_2$ will decrease the surface tension by the area 'abfea', i.e.

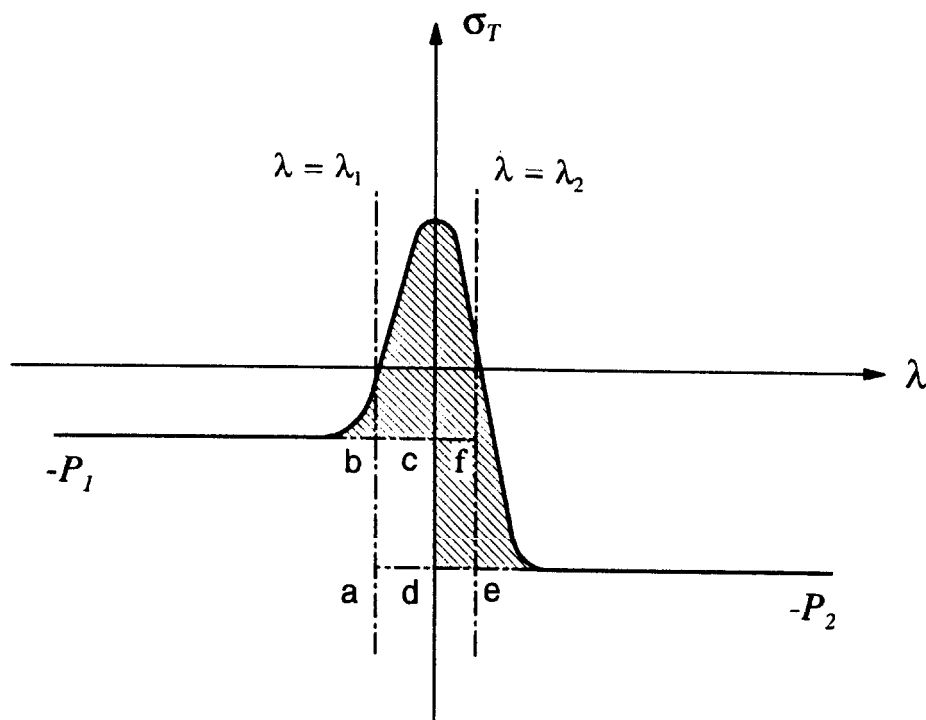$$\gamma_1 - \gamma_2 = \text{the area of 'abfea'} = \Delta P \cdot \Delta\lambda$$

Fig. 6. A schematic of the variation of σ_{TE} across the interface indicating the location of the dividing surface.