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The generalized Laplace equation of capillarity II. Hydrostatic and thermodynamic derivations of the Laplace equation for high curvatures

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Abstract

Two derivations are given of the generalized Laplace equation of capillarity, which assume constant surface tensions and constant curvature potentials over the surface for highly curved interfaces *a priori*: one based on hydrostatics and the other on thermodynamics. The excess hydrostatic equation is integrated across the interfacial zone, leading to the Boruvka and Neumann (BN) generalized Laplace equation. Based on the minimum free energy principle, a straightforward derivation is presented, also resulting in the BN generalized Laplace equation. The agreement between the two independent approaches provides a confirmation of the BN generalized Laplace equation for high curvature systems.

Contents

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I. Introduction

The previous paper [1] re-confirmed the Boruvka and Neumann (BN) fundamental equation of their generalized theory of capillarity [2]. Based on this fundamental equation, the generalized Laplace equation can be derived by considering the mechanical equilibrium condition in the direction normal to the surface. The original derivation [2] for BN generalized Laplace equation was complex because of its generality, and the resulting Laplace equation was given in the most general form, cf. Eq. (18) of the previous paper [1]. For a constant surface tension and constant curvature potentials over the surface, the Laplace equation was obtained only by simplification of the general form. Interestingly, a derivation of the Laplace equation, which assumes constant surface tensions and constant curvature potentials *a priori*, does not appear in the literature. This paper will provide two such derivations: one based on hydrostatics and the other on thermodynamics.

The hydrostatic approach to capillarity was developed by Buff [3]; it is based on the analysis of an interfacial stress tensor field in which the excess hydrostatic equation is integrated across the interface, leading to the Laplace equation. However, Buff used his thermodynamic variables [3–5] in his hydrostatic analysis; while his thermodynamic development [3–5] is believed to lack thermodynamic rigor [1], the Laplace equation resulting from his hydrostatic analysis is not proper. The present paper will employ the definitions of variables in the BN thermodynamic theory to develop a hydrostatic approach leading to the BN Laplace equation. This hydrostatic approach will provide an independent confirmation of the BN Laplace equation.

A procedure of minimizing the free energy will also be presented. The free energy is obtained through a Legendre transformation from the internal energy in the BN fundamental equation [6], and the resulting Laplace equation will be compared with the hydrostatic results. The agreement between the two approaches will provide further justification for the BN generalized Laplace equation.

II. Hydrostatic equation

Consider a macroscopic system consisting of two fluid phases separated by an interface. The system is in both thermal and chemical equilibrium with the surrounding media, and the appropriate thermo-

dynamic potential is, therefore, the grand canonical free energy [6]. The system can be treated as a continuum mechanical system; in other words, spatial smoothing is carried out for the variables under consideration. The hydrostatic description is essentially given in the previous paper [1], only the key relations are presented below, which are necessary for the following derivation.

The basic equation of hydrostatics can be written as follows:

$$\nabla \cdot \sigma = \rho \nabla \phi \tag{1}$$

where σ is the stress tensor, ρ is the mass density, and ϕ is the potential of an external body force, such as gravity. Inside a bulk phase, away from the influence of the interface, the stress tensor becomes isotropic, and the hydrostatic equation reduces to

$$\nabla P = -\rho \nabla \phi \tag{2}$$

where P is the bulk pressure.

In order to treat the interface, one follows Gibbs [7] to span the interfacial zone (transition zone) by a family of parallel dividing surfaces [1]. The parallel dividing surface description has been demonstrated thoroughly by Buff [3–5]. When generalized surface coordinates u, v are introduced, a point $\boldsymbol{r}$ of a given dividing surface A may be represented parametrically by $\boldsymbol{r} = \boldsymbol{r}(u,v)$, while a point $\boldsymbol{R}$ of the parallel surface A', located at a constant distance λ along the normal from the surface A, is expressed by [3]

$$\boldsymbol{R} = \boldsymbol{r}(u,v) + \lambda \boldsymbol{n}(u,v) \tag{3}$$

where $\boldsymbol{n}$ is the coincident outward unit normal to both surfaces A and A'.

According to Buff [3], within the transition zone it is assumed that the stress ellipsoid is axi-symmetrical about the direction normal $\boldsymbol{n}$. If the stress tensor is symmetrical, then it is always possible to find a transformation which reduces it to a diagonal form whose components lie along the mutually orthogonal axes of the coordinate system (u, v, λ). In addition, if the system is invariant to a rotation about the direction normal to the interface, then these three components may be further reduced to two: one of them, σ_N, normal to the interface and two equal components, $\sigma_T = \sigma_{uu} = \sigma_{vv}$, along the mutually orthogonal directions parallel to the interface. Thus, the stress tensor may be expressed as

$$\sigma = \sigma_T \boldsymbol{I}_2 + \sigma_N \boldsymbol{nn} \tag{4}$$

where $\boldsymbol{I}_2$ is the unit surface tensor [1], and σ_T and σ_N are the tangential and normal components of the stress tensor, respectively.

Now a dividing surface is placed within the interface and the bulk properties such as the pressure and the density are extrapolated up to the dividing surface. The differences between the actual system properties and the extrapolated ones are the interfacial excess quantities assigned to the dividing surface, such as:

$$\sigma_E = \sigma + P_e \boldsymbol{I} \tag{5}$$

where $\boldsymbol{I}$ is the three-dimensional unit tensor, subscript E denotes the interfacial excess properties and subscript e denotes the extrapolated bulk properties. Furthermore Eq. (5) can be written, by using Eq. (4), as [1]:

$$\sigma_E = \sigma_{TE} \boldsymbol{I}_2 + \sigma_{NE} \boldsymbol{nn} \tag{6}$$

Subtracting Eq. (2) from Eq. (1) and using the definition of Eq. (5), the hydrostatic equation for the interfacial excess stress follows as:

$$\nabla \cdot \sigma_E = \rho_E \nabla \phi \tag{7}$$

The integration of this hydrostatic equation across the interfacial zone will lead to the Laplace equation [3].

III. Laplace equation

In preparation for the following analysis it will be convenient to outline some mathematical identities for the parallel surfaces. First the volume element dV may be written as [1,3,8]:

$$dV = (1 + c_1\lambda)\,(1 + c_2\lambda)\,dA\,d\lambda \tag{8}$$

where c_1 and c_2 are the principal curvatures of the chosen dividing surface A at $\lambda = 0$, dA is the area element of the dividing surface. As shown in Fig. 1, the radius $r_1(\lambda)$ of the principal curvatures $c_1(\lambda)$ of surface A' passing through point $\boldsymbol{R}$ can be expressed as:

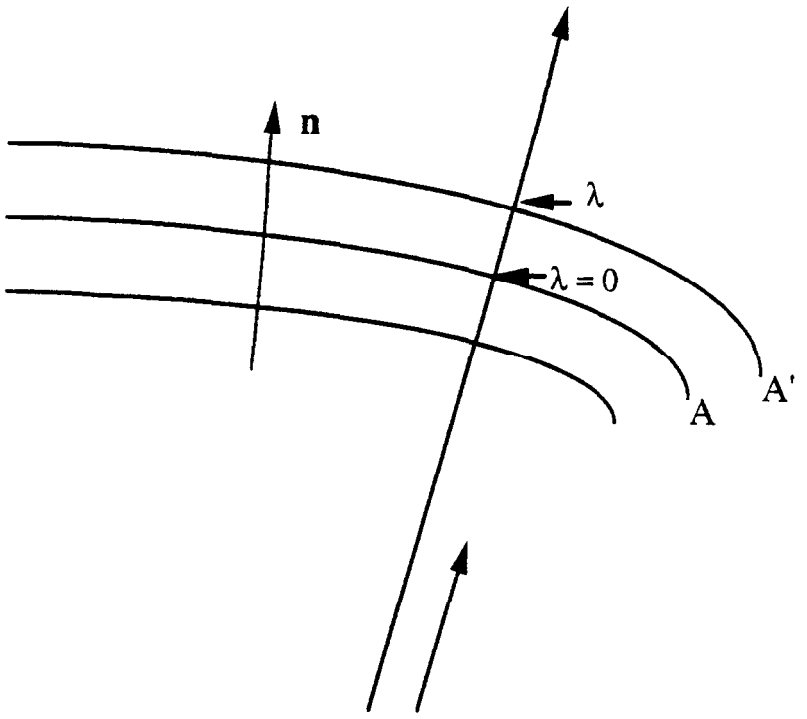

Fig. 1. Coordinate system for parallel surfaces.

$$r_1(\lambda) = r_1 + \lambda \tag{9}$$

where r_1 is the radius of curvature c_1 of surface A. By using the definition: $r_1 = 1/c_1$, the following identity can be obtained from Eq. (9):

$$c_1(\lambda) = \frac{c_1}{1 + \lambda c_1} \tag{10}$$

Similarly, the relationship between the other principal curvature $c_2(\lambda)$ of surface A' and c_2 can be written as:

$$c_2(\lambda) = \frac{c_2}{1 + \lambda c_2} \tag{11}$$

Choosing $\boldsymbol{i}$ and $\boldsymbol{j}$ as the unit tangent vectors on the surface, corresponding to the two principal curvatures, and taking x and y as the arc lengths in these two directions, the surface gradient is defined as:

$$\nabla_2 \equiv \boldsymbol{i}\frac{\partial}{\partial x} + \boldsymbol{j}\frac{\partial}{\partial y} \tag{12}$$

Operation of the surface gradient on the unit normal $\boldsymbol{n}$ produces the first scalar of the surface dyadic, $\nabla_2\boldsymbol{n}$ [3,6]:

$$\nabla_2 \cdot \boldsymbol{n} = c_1(\lambda) + c_2(\lambda) = J \tag{13}$$

where J is the mean curvature of surface A' passing through point $\boldsymbol{R}$.

The Laplace equation is the mechanical equilibrium condition along the direction normal to the interface. It follows from Eq. (7), with the use of Eqs. (6) and (13), that the normal component of the hydrostatic equilibrium condition is given by ([3], see also Appendix A):

$$\begin{aligned}(\nabla\cdot\sigma_E)\cdot\boldsymbol{n} &= \nabla\cdot(\sigma_E\cdot\boldsymbol{n}) - \nabla\boldsymbol{n}:\sigma_E \\ &= \nabla\cdot(\sigma_{NE}\,\boldsymbol{n}) - [c_1(\lambda) + c_2(\lambda)]\sigma_{TE} \\ &= \rho_E\nabla\phi\cdot\boldsymbol{n}\end{aligned} \tag{14}$$

The dividing surface A splits the whole system into two subvolumes v_1 and v_2 which are bounded by A and A_1, and A and A_2; A_1 and A_2 are outer boundaries of the system (Fig. 2). Integrations of Eq. (14) over the regions v_1 and v_2, with the use of the divergence theorem (Appendix B), leads to

$$\iint\sigma_{NE}\,dA - \iint\sigma_{NE}\,dA_1 = \iiint\left\{[c_1(\lambda) + c_2(\lambda)]\sigma_{TE} + \rho_E\nabla\phi\cdot\boldsymbol{n}\right\}dv_1 \tag{15}$$

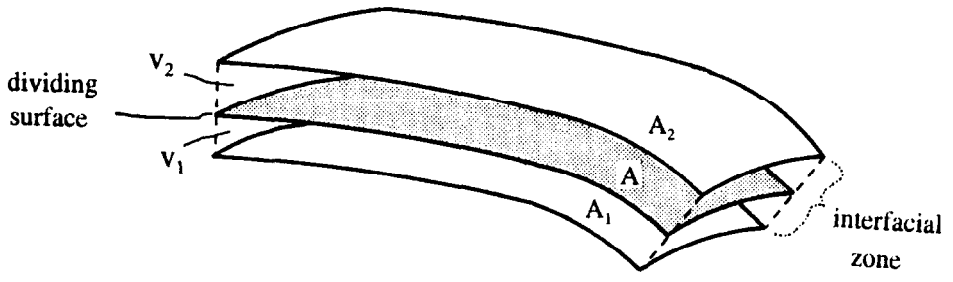

Fig. 2. Schematic drawing of the dividing surface A splitting the system into two subvolumes v_1, and v_2 which are bounded by A and A_1, and by A and A_2.

and

$$-\iint \sigma_{NE}\, dA + \iint \sigma_{NE}\, dA_2 = \iiint \left\{ [c_1(\lambda) + c_2(\lambda)]\sigma_{TE} + \rho_E \nabla\phi \cdot \boldsymbol{n} \right\} dv_2 \tag{16}$$

According to Eqs. (5) and (6), the interfacial excess stress tensor can be written explicitly as:

$$\begin{aligned} \sigma_{NE} &= \sigma_N - \sigma_{12} \\ \sigma_{TE} &= \sigma_T - \sigma_{12} \end{aligned} \tag{17}$$

where

$$\sigma_{12} = -P_1[1 - H(\lambda)] - P_2 H(\lambda) \tag{18}$$

with

$$\begin{aligned} H(\lambda) &= 0, \quad \lambda < 0 \\ &= 1, \quad \lambda \geq 0 \end{aligned} \tag{19}$$

The case $\lambda < 0$ corresponds to the subvolume v_1, and $\lambda \geq 0$ corresponds to the subvolume v_2. The interfacial excess stress σ_{NE} is zero inside the bulk and away from the influence of the interface. Therefore, the integrations at the outer boundaries A_1 and A_2 in Eqs. (15) and (16) disappear. Substituting Eq. (17) into Eqs. (15) and (16), the area integrals of σ_N cancel in the summation of Eqs. (15) and (16). With the use of Eqs. (8), (10) and (11), this summation can therefore be expressed as:

$$\begin{aligned} \iint [(P_1 - P_2) - (c_1 + c_2) \int \sigma_{TE} d\lambda - 2c_1 c_2 \int \sigma_{TE} \lambda\, d\lambda \\ - \int \rho_E \nabla\phi \cdot \boldsymbol{n}(1 + c_1\lambda)\,(1 + c_2\lambda)\, d\lambda]\, dA = 0 \end{aligned} \tag{20}$$

By using the assumption of parallel dividing surfaces and considering constant densities along each parallel surface, the area integration drops out, and Eq. (20) is further written as:

$$P_1 - P_2 = J\gamma + 2KC_1 + \int \rho_E \nabla\phi \cdot \boldsymbol{n}(1 + J\lambda + K\lambda^2)\, d\lambda \tag{21}$$

where $K = c_1 \cdot c_2$ is the Gaussian curvature, and γ and C_1 are the surface tension and the first moment about $\lambda = 0$ (these can be realized by

comparing Eq. (21) with the BN Laplace equation, e.g. Eq. (19) of the previous paper):

$$\gamma = \int \sigma_{TE} d\lambda \tag{22}$$

and

$$C_1 = \int \sigma_{TE}\, \lambda\, d\lambda \tag{23}$$

When the external force is gravity

$$\nabla\phi = g\, \boldsymbol{k} \tag{24}$$

where g is the gravitational constant and $\boldsymbol{k}$ is the unit vector directed along the space-fixed z axis [3]. Substitution of Eq. (24) into Eq. (21) results in

$$P_1 - P_2 = J\gamma + 2KC_1 + (g\boldsymbol{k}\cdot\boldsymbol{n})\Gamma \tag{25}$$

where Γ is the interfacial excess mass density:

$$\Gamma = \int \rho_E(1 + c_1\lambda)\,(1 + c_2\lambda)\, d\lambda \tag{26}$$

It can be seen that Eq. (25) is the BN Laplace equation [2] for constant surface tensions and constant curvature potentials. When gravity $g\boldsymbol{k}$ is absent, or the surface mass Γ is negligible, Eq. (25) is identical to Eq. (19) of the previous paper [1]. As expressed in Eqs. (22) and (23), the surface tension and the first moment (the mean curvature potential) are dependent on the choice of the position of the dividing surface [1].

In the derivation of the Laplace equation, Eq. (25), the only approximation is to assume the parallel dividing surfaces for the interfacial zone, and that all variables (properties) are transversely isotropic at each parallel surface. This may well reflect many actual cases of fluid interfaces. However, this assumption is not valid in the case of a solid surface where two-dimensional anisotropy prevails.

IV. Thermodynamic derivation

The most often encountered external field is gravity. Because of the thinness of the interface, the gravity effects on an interface are rather

small and may be ignored. In the following treatment, the external force field is then assumed to be negligible. For an interfacial system with a constant surface tension and constant curvature potentials along the surface, i.e., the interfacial system is assumed homogeneous over the dividing surface, the free energy at constant temperature T and constant chemical potential μ_i (i = 1,2,...,r) is the grand canonical potential Ω [2,6]. The grand canonical potential of a bulk phase can be written as:

$$\Omega^{\nu} = U^{\nu} - TS^{\nu} - \sum \mu_i N_i^{\nu}$$

$$= -PV \tag{27}$$

where superscript ν denotes the bulk phase, U is the internal energy, S the entropy, N_i the mole number of component i, P the pressure, and V the volume of the bulk phase. In differential form Eq. (27) becomes

$$d\Omega^{\nu} = -S^{\nu}dT - \sum N_i^{\nu} d\mu_i - PdV \tag{28}$$

For a surface, on the basis of the fundamental equation derived in the previous paper [1], the grand canonical potential can be expressed as:

$$\Omega^{A} = U^{A} - TS^{A} - \sum \mu_i N_i^{A}$$

$$= \gamma A + C_1 \mathcal{J} + C_2 \mathcal{K} \tag{29}$$

where superscript A denotes the surface phase, i.e., the dividing surface; γ is the surface tension, $\mathcal{J} = JA$ is the total mean curvature, and $\mathcal{K} = KA$ is the total Gaussian curvature. The fluid system is represented by the dividing surface and two bulk phases extrapolated up to the dividing surface. The differential form of the grand canonical potential for the dividing surface can be written as:

$$d\Omega^{A} = -S^{A}dT - \sum N_i^{A} d\mu_i + \gamma dA + C_1 d\mathcal{J} + C_2 d\mathcal{K} \tag{30}$$

The total free energy of the system consisting of one surface and two bulk phases is

$$\Omega^{tot} = \Omega^{\nu_1} + \Omega^{\nu_2} + \Omega^{A} \tag{31}$$

When minimizing the system free energy, the total volume of the system has to be maintained constant, i.e.,

$$V^{tot} = V^1 + V^2 = constant \tag{32}$$

where V_1 and V_2 are the volumes of the two bulk phases.

In order to apply the minimum free energy principle, a small variation δz is produced in the direction normal to the interface, Fig. 3. The corresponding variations of all the other variables can be obtained. In Fig. 3, x and y are the side-lengths of a small rectangular surface with an area A. The variation of the dividing surface area δA due to δz can be written as:

$$\begin{aligned}\delta A &= (x + \delta x)(y + \delta y) - xy \\ &= x\,\delta y + y\,\delta x\end{aligned} \tag{33}$$

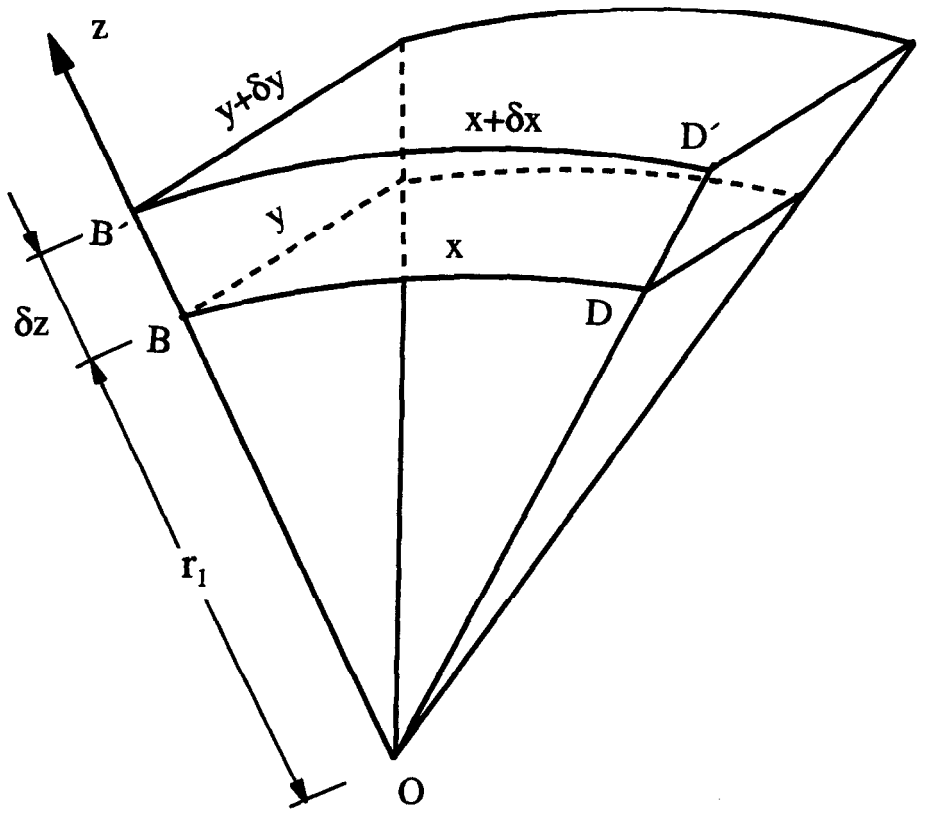

Fig. 3. The variation of the surface area due to the variation δz.

In order to find δx and δy, the following equality can be obtained by using the geometric similarity between ΔOBD and $\Delta OB'D'$ in Fig. 3:

$$\frac{x + \delta x}{x} = \frac{r_1 + \delta z}{r_1} \tag{34}$$

where r_1 is the radius of the principal curvature c_1 corresponding to side x. Furthermore, Eq. (34) can be written as:

$$\delta x = \frac{x}{r_1}\delta z = xc_1\delta z \tag{35}$$

Similarly, δy can be found:

$$\delta y = yc_2\delta z \tag{36}$$

Substitution of Eqs. (35) and (36) into Eq. (33) results in

$$\begin{aligned}\delta A &= xyc_2\delta z + yxc_1\delta z \\ &= (c_1 + c_2)xy\delta z \\ &= JA\delta z\end{aligned} \tag{37}$$

The variation of the volume of one of the bulk phases δV can easily be written as:

$$\delta V = A\delta z \tag{38}$$

The variation of the total mean curvature $\delta \mathcal{J}$:

$$\delta \mathcal{J} = \delta(JA) = A\delta J + J\delta A \tag{39}$$

where δJ may be evaluated

$$\begin{aligned}\delta J &= \delta(c_1 + c_2) = \delta\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \\ &= -\frac{1}{r_1^2}\delta z - \frac{1}{r_2^2}\delta z \\ &= -(c_1^2 + c_2^2)\delta z = (2K - J^2)\delta z\end{aligned} \tag{40}$$

Substitution of Eq. (40) into Eq. (39), with the use of Eq. (37), results in

$$\delta \mathcal{J} = 2KA\delta z \tag{41}$$

Similarly, the variation of the total Gaussian curvature $\delta\mathcal{K}$ is [9]

$$\begin{aligned}\delta\mathcal{K} &= A\delta K + K\delta A \\ &= -JKA\delta z + KJA\delta z \\ &= 0\end{aligned} \tag{42}$$

Differentiation of the free energy of the two bulk phases, Eq. (28), with respect to z leads to

$$\begin{aligned}\frac{d\Omega^{v}}{dz} &= -P_1\frac{dV^1}{dz} - P_2\frac{dV^2}{dz} \\ &= -P_1A - P_2(-A) \\ &= -(P_1 - P_2)A\end{aligned} \tag{43}$$

where Eq. (38) and the constant total volume Eq. (32) have been used. Differentiation of Eq. (30) with respect to z, with the use of Eqs. (37), (38), (41) and (42), results in

$$\begin{aligned}\frac{d\Omega^{A}}{dz} &= \gamma\frac{dA}{dz} + C_1\frac{d\mathcal{J}}{dz} + C_2\frac{d\mathcal{K}}{dz} \\ &= J\gamma A + 2KC_1A\end{aligned} \tag{44}$$

In both Eqs.(43) and (44), the constancy of temperature and chemical potentials has been used.

The minimum free energy principle implies

$$\frac{d\Omega^{tot}}{dz} = 0 \tag{45}$$

Substitution of Eqs. (31), (43) and (44) into Eq. (45) gives

$$J\gamma + 2KC_1 = P_1 - P_2 \tag{46}$$

which is immediately seen to agree with Eq. (25). Thus, the Laplace equation for high curvatures has been derived in two independent ways. Since Eq. (25) also follows from the more general thermodynamic derivation also starting with the fundamental equation [2], cf. Eqs. (18) and (19) of the previous paper [1], it would seem that Eq. (25) is well founded.

V. Conclusions

The excess hydrostatic equation has been integrated across the interfacial zone, leading to the Boruvka and Neumann (BN) generalized Laplace equation for constant surface tensions and constant curvature potentials. It confirms the correctness of the BN Laplace equation. Based on the minimum free energy principle, a straightforward thermodynamic derivation has been presented, also leading to the BN Laplace equation. The agreement between the hydrostatic equation and the minimum free energy principle provides further justification for the BN Laplace equation.

Acknowledgement

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Appendix A. Derivation of Equation (14)

The gradient operation on the dot product of a tensor of the second order σ_E and a vector $\boldsymbol{n}$ can be written as [A1]:

$$\nabla \cdot (\sigma_E \cdot \boldsymbol{n}) = (\nabla \cdot \sigma_E) \cdot \boldsymbol{n} + \nabla \boldsymbol{n} : \sigma_E \tag{A.1}$$

Rearrangement of Eq. (A.1) leads to

$$(\nabla \cdot \sigma_E) \cdot \boldsymbol{n} = \nabla \cdot (\sigma_E \cdot \boldsymbol{n}) - \nabla \boldsymbol{n} : \sigma_E \tag{A.2}$$

The surface gradient ∇_2, the two-dimensional analog of the three dimensional gradient ∇, may be written as

$$\nabla_2 = \boldsymbol{i} \frac{\partial}{\partial x} + \boldsymbol{j} \frac{\partial}{\partial y} \tag{A.3}$$

where $\boldsymbol{i}$ and $\boldsymbol{j}$ are two orthogonal unit tangent vectors on the surface, corresponding to the two principal curvatures $c_1(\lambda)$ and $c_2(\lambda)$, and x and y are the arc lengths in these two directions. Regarding $\boldsymbol{n}$ as the unit normal to the surface, the surface dyadic $\nabla_2 \boldsymbol{n}$ can be written as

$$\begin{aligned} \nabla_2 \boldsymbol{n} &= \boldsymbol{i} \frac{\partial}{\partial x} \boldsymbol{n} + \boldsymbol{j} \frac{\partial}{\partial y} \boldsymbol{n} \\ &= c_1(\lambda)\, \boldsymbol{ii} + c_2(\lambda)\, \boldsymbol{jj} \\ &= \nabla \boldsymbol{n} \end{aligned} \tag{A.4}$$

where the last equality of Eq. (A.4) is obtained by considering the unit normal $\boldsymbol{n}$ as constant along its direction. Regarding σ_E as the surface excess stress tensor:

$$\sigma_E = \sigma_{TE}(\boldsymbol{ii} + \boldsymbol{jj}) + \sigma_{NE} \boldsymbol{nn} \tag{A.5}$$

By using Eqs. (A.4) and (A.5), the double dot product in Eq. (A.2) can be written as

$$\begin{aligned} \nabla \boldsymbol{n} : \sigma_E &= [c_1(\lambda)\, \boldsymbol{ii} + c_2(\lambda)\, \boldsymbol{jj}] : [\sigma_{TE}(\boldsymbol{ii} + \boldsymbol{jj}) + \sigma_{NE} \boldsymbol{nn}] \\ &= [c_1(\lambda) + c_2(\lambda)] \sigma_{TE} \end{aligned} \tag{A.6}$$

Substitution of Eq. (A.6) into Eq. (A.2) results in

$$(\nabla \cdot \sigma_E) \cdot \boldsymbol{n} = \nabla \cdot (\sigma_{NE}\boldsymbol{n}) - [c_1(\lambda) + c_2(\lambda)]\sigma_{TE} \tag{A.7}$$

i.e., Eq. (14) of the main text.

Appendix B. The Divergence Theorem

The divergence theorem states:

Let E be a simple solid region whose boundary surface S has positive (outward) orientation. Let $\boldsymbol{F}$ be a vector field whose component functions have continuous partial derivatives on an open region that contains E. Then

$$\iint_S \boldsymbol{F} \cdot d\boldsymbol{S} = \iiint_E \nabla \cdot \boldsymbol{F}\, dV \tag{B.1}$$

The proof of this theorem can be found in many calculus textbooks, such as Ref. [B1].

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