

Invariance of free energy against a shift of the dividing surface of arbitrary geometry

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Received 10 August 1995; revised 8 May 1996

This paper demonstrates that within the context of the generalized theory of capillarity, the free energy remains invariant against an arbitrary shift of the dividing surface for a general surface geometry. The Gibbs adsorption equation is used to illustrate the importance of being able to shift the dividing surface. The mathematical proof makes use of an equation describing the change of free energy for a shift of the dividing surface, derived in an independent development of a hydrostatic approach to capillarity.

1. Introduction

Capillarity is an important phenomenon in colloid and surface chemistry. Many biological problems, such as simple models for lipid vesicles [1], and technological problems, such as soil physics and recovery of petroleum [2] are closely linked with the study of capillarity. Other examples which illustrate the significance of capillarity include microemulsions [3,4] and surfactant micelles [5,6].

Gibbs [7] first developed formulations to study capillary phenomena at surfaces of arbitrary shape. The dividing surface is a fundamental element of the Gibbsian model. As shown by the solid line in Fig. 1, the properties of the two bulk fluid phases change continuously from one to the other through an "interfacial" region. This interfacial region has a finite thickness, and thus, the phenomenon is three dimensional in nature. However, since this thickness is typically many orders of magnitude less than the dimensions of the surface area, the interfacial region is modelled as two dimensional by placing a dividing surface within the region. The conservation requirements for mass, entropy and energy are satisfied by assigning excess quantities to the dividing surface so that the bulk fluid phases can be considered homogeneous up to the dividing surface as shown by the dotted line in Fig. 1.

It is easy to see that an arbitrary shift in the dividing surface position will change the extensive properties of the bulk fluid phases, and hence the surface excess quantities in order to guarantee the conservation requirements.

Thus, previous researchers have realized the advantage of choosing a specific position for the dividing surface to simplify their mathematical problems. A well

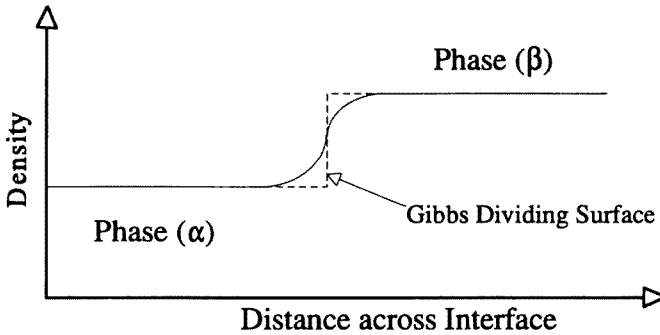


Fig. 1. Continuous change of bulk properties from Phase (α) to Phase (β). (Density is used here as an example.)

known example to demonstrate the desirability of shifting the dividing surface is the Gibbs adsorption equation [8]:

$$\Gamma = -\frac{a}{RT} \left(\frac{d\gamma}{da} \right), \quad (1)$$

where Γ is the excess surface density per unit area of a solute, a is the activity of the solute, γ is the surface tension, T is the temperature and R is the universal gas constant. Here the dividing surface was chosen so that the excess surface density of the solvent is zero.

To accommodate any arbitrary geometry of an interface, Gibbs included curvature terms in his theory. However, he then removed all curvature dependence from analytical consideration by: (i) considering only moderately curved surfaces, and (ii) placing the dividing surface in a unique position which he called the “surface of tension” [7,9]. Hence, this classical theory suffers from a central restriction: curved interfaces have their dividing surface fixed at the surface of tension. It should be noted that in Adamson’s derivation of eq. (1) [8], the specific case of a flat interface was treated. This was necessary due to the assumptions of the Gibbsian model.

Many interesting cases of capillary phenomena, however, involve curved interfaces. Common examples include liquid-vapour and liquid-liquid interfaces. In these instances, in the context of the classical theory, the dividing surface is restricted to the surface of tension position [7,9].

In the case of a curved interface for the adsorption equation given above, if we leave the dividing surface in the surface of tension position, we obtain [8]

$$d\gamma + \Gamma_1 \frac{RT}{a_1} da_1 + \Gamma_2 \frac{RT}{a_2} da_2 = 0, \quad (2)$$

where 1, 2 are the two components of the system.

It is clear from the above equation that we do not have an explicit solution for Γ_1 or Γ_2 and that we can not proceed unless we shift the dividing surface, and set the

excess surface density for one component equal to zero. This shift, however, is not permitted within the framework of the classical theory.

Kondo [10] attempted to overcome the limitations of the Gibbsian theory by introducing a special curvature term into the classical fundamental equation

$$dU = TdS + \mu dN + \gamma dA + \left(\frac{\partial \gamma}{\partial R}\right) AdR, \quad (3)$$

where U is the internal energy, S is the entropy, μ is the chemical potential, N is the number of moles, A is the surface area and R is the radius of a drop with a spherical interface.

The term $[\partial \gamma / \partial R]$, also called a “formal derivative”, accounts for a change in the value of γ due to the arbitrary choice of the dividing surface, but not due to the change associated with an increase in the radius of the physical interface [9]. Hence, eq. (3) obviously allows for the dividing surface to be shifted, but in our opinion, the formal derivative is an *ad hoc* term, without fundamental mathematical and thermodynamic meaning. The intensive parameters of the fundamental equation are defined as partial derivatives of the internal energy with respect to the associated extensive parameter. For example, T is defined as $\partial U / \partial S$. The formal derivative, however, does not follow this simple definition. It is clear that formulations based on the classical theory should adhere to Gibbsian thinking. Terms such as the formal derivative cannot arise rigorously from the classical fundamental equation [11].

Boruvka and Neumann [12] developed a “generalized” theory of capillarity by retaining curvature terms in their fundamental equation. Later, Rotenberg et al. [9] studied the prospect of shifting the dividing surface in both the classical and generalized theory of capillarity. They showed that the dividing surface was restricted to the surface of tension position in the classical theory. In the case of the generalized theory, the dividing surface was free to be shifted. The paper by Rotenberg et al. illustrated the capacity to shift the dividing surface in the generalized theory by considering two simple geometries, namely spherical and cylindrical. The present paper extends their work to show that the generalized theory can accommodate a shift of the dividing surface for any arbitrary geometry.

2. Generalized theory of capillarity considerations

The generalized theory of capillarity retains both curvature terms in the fundamental equation *via* two scalar differential invariants of the surface, i.e. the first (mean) curvature, J , and the second (Gaussian) curvature, K , defined by

$$J = C_1 + C_2, \quad (4)$$

$$K = C_1 \cdot C_2, \quad (5)$$

where $C_1 = 1/R_1$ and $C_2 = 1/R_2$, and where R_1 and R_2 are the principal radii of curvature.

Hence the fundamental equation for surfaces per unit area can be written as

$$u = u[s, \rho_1, \dots, \rho_i, \dots, \rho_r, J, K], \quad (6)$$

where u is the surface internal energy density, s is the specific entropy, ρ is the density and i is the i th component of the system ($1 \leq i \leq r$).

Analogous to the surface tension, γ , defined as $\partial U/\partial A$, the temperature, T , as $\partial u/\partial s$ and the chemical potential, μ_i , as $\partial u/\partial \rho_i$, the corresponding intensive parameters for the mean and Gaussian curvatures are

$$C_J = \left(\frac{\partial u}{\partial J} \right), \quad (7)$$

$$C_K = \left(\frac{\partial u}{\partial K} \right), \quad (8)$$

where C_J is the first bending moment of the interface and C_K is the second bending moment of the interface. The associated extensive parameters of J and K for a finite surface area, A , are defined as

$$\mathcal{J} = \int \int_A J dA, \quad (9)$$

$$\mathcal{K} = \int \int_A K dA, \quad (10)$$

where \mathcal{J} is the total mean curvature and \mathcal{K} is the total Gaussian curvature. Although the quantities \mathcal{J} and \mathcal{K} are not used as frequently as J and K , they have been discussed in differential geometry literature [13].

It has been shown [14] that neither the Gibbs, nor the Helmholtz potentials are as well-suited to study capillary systems, as is the free energy (or *grand canonical potential*), Ω . Since capillary problems involve conditions of thermal and chemical equilibrium, it is more convenient to use the free energy potential rather than the internal energy.

The specific free energy of a dividing surface, ω , can be defined [14] as

$$\omega = \gamma + C_J J + C_K K. \quad (11)$$

In a two phase capillary system, when gravity is neglected, and thus all intensive parameters are constant, the overall free energy (comprised of the total surface and bulk free energies), Ω , is written as

$$\Omega = \int \int_A \omega dA - \int \int \int_V \Delta P dV = \gamma A + C_J \mathcal{J} + C_K \mathcal{K} - \Delta P V, \quad (12)$$

where ΔP is the pressure difference across the interface and V is the volume.

Rotenberg et al. [9] compared the free energy expression for the virtual work of the internal forces in a dividing surface, derived from the hydrostatic formulation, to the expression obtained from the thermodynamic approach to capillarity. They obtained the following expressions:

$$\gamma = \int \sigma_{TE} d\lambda, \quad (13)$$

$$C_J = - \int \lambda \sigma_{TE} d\lambda, \quad (14)$$

$$C_K = \int \lambda^2 \sigma_{TE} d\lambda, \quad (15)$$

where σ_{TE} is the tangential excess stress tensor component about the dividing surface (at $\lambda = 0$) and λ is the distance from the dividing surface.

Using eqs. (13) to (15) and by considering two arbitrary positions of the dividing surface, Rotenberg et al. then determined some relations describing the interdependence of γ , C_J and C_K . In addition, they showed that the dependency on the stress tensor component σ_{TE} cancelled out, and that a shift of the dividing surface caused changes in γ , C_J , C_K and ΔP . Using the expressions which describe these changes and eq. (12), they derived the following expression describing the difference in the overall free energy of the capillary system for two positions of the dividing surface:

$$\begin{aligned} \Omega^{(2)} - \Omega^{(1)} = & \gamma^{(1)}(A^{(2)} - A^{(1)} + \Delta\lambda\mathcal{J}^{(2)} + \Delta\lambda^2\mathcal{K}^{(2)}) \\ & + C_J^{(1)}(\mathcal{J}^{(2)} - \mathcal{J}^{(1)} + 2\Delta\lambda\mathcal{K}^{(2)}) \\ & + C_K^{(1)}(\mathcal{K}^{(2)} - \mathcal{K}^{(1)}) \\ & + \Delta P(V^{(1)} - V^{(2)} - \Delta\lambda A^{(2)} - \frac{1}{2}\Delta\lambda^2\mathcal{J}^{(2)} - \frac{1}{3}\Delta\lambda^3\mathcal{K}^{(2)}), \quad (16) \end{aligned}$$

where $^{(2)}$ denotes the final position of the dividing surface, $^{(1)}$ denotes the initial position of the dividing surface and $\Delta\lambda$ is the displacement (distance between) of the dividing surface.

Rotenberg et al. [9] proceeded to illustrate the invariance of free energy by considering specific geometries of cylindrical and spherical bubbles. In the case of the cylindrical geometry the total Gaussian curvature, \mathcal{K} , is equal to zero, rendering the second bending moment, C_K , immaterial. However, the first bending moment, C_J , is still necessary in the free energy expression, permitting the dividing surface to be shifted [9]. For the spherical geometry both principal radii of curvature are identical, resulting in a free energy expression which is specific and not applicable to any other geometry. Hence, the generalization of the geometry is a non-trivial matter; the proof which follows extends the work of Rotenberg et al. [9] by showing the

invariance of free energy when shifting the dividing surface for a general geometry.

3. Invariance of the free energy for an arbitrary shift of the dividing surface for a general surface geometry

Consider the elemental volume shown in Fig. 2. As depicted, it should be noted that the two principal radii of curvature (R_1 and R_2) are offset by a distance, D ; and that the displacement (distance between) of the dividing surface $\Delta\lambda$ is equal to $-\delta z$ for both R_1 and R_2 . The initial area is x_0y_0 , and the area after the shift is $x^{(2)}y^{(2)} = (x_0 + \delta x)(y_0 + \delta y)$.

Using the principles of similar triangles:

$$\frac{dx}{x} = \frac{dz}{z} \tag{17}$$

and if we consider that initially, at $z = z_0$, $x = x_0$, after integrating we get

$$x = \frac{x_0}{z_0} z. \tag{18}$$

Similarly, for y ,

$$\frac{dy}{y} = \frac{dz}{z'}, \tag{19}$$

where z' corresponds to the second principal radii of curvature, R_2 , which is offset from R_1 by D and hence

$$z' = z + D. \tag{20}$$

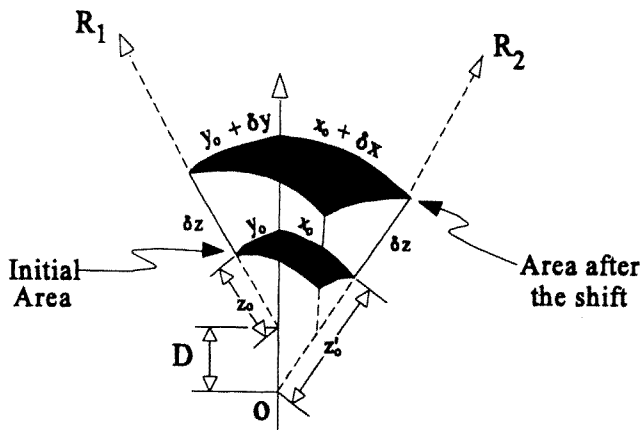


Fig. 2. Elemental volume: R_1 and R_2 are the principal radii of curvature (R_2 is offset from R_1 by a distance D). Initial area is x_0y_0 . The dividing surface is shifted by a distance δz . The area after the shift is $(x_0 + \delta x)(y_0 + \delta y)$. The origin is indicated by O .

Again, if we consider that initially at $z = z'_0, y = y_0$, then

$$y = \frac{y_0}{z'_0} z'. \tag{21}$$

It has been shown elsewhere [15] that the variation of the total Gaussian curvature, i.e. $\delta\mathcal{K}$, for an arbitrary shift in the dividing surface, is equal to zero. Hence it follows that $\mathcal{K}^{(1)} = \mathcal{K}^{(2)}$.

In the proof that follows, each term on the right hand side of eq. (16) will be dealt with individually, starting with the first term on the right hand side of eq. (16):

$$\gamma^{(1)}(A^{(2)} - A^{(1)} + \Delta\lambda\mathcal{J}^{(2)} + \Delta\lambda^2\mathcal{K}^{(2)}) = \gamma^{(1)}(x^{(2)}y^{(2)} - x_0y_0 - \Delta z\mathcal{J}^{(2)} + \Delta z^2\mathcal{K}^{(1)}). \tag{22}$$

If all surface properties are uniform or constant at each point on the surface, then \mathcal{J} and \mathcal{K} may be replaced by JA and KA , respectively. Rotenberg et al. derived eq. (16) under this condition, and hence, we make this substitution and proceed:

$$\begin{aligned} &\gamma^{(1)}(x^{(2)}y^{(2)} - x_0y_0 - \Delta zJ^{(2)}A^{(2)} + \Delta z^2K^{(1)}A^{(1)}) \\ &= \gamma^{(1)}\left[\frac{x_0y_0}{z_0z'_0}(z_0 + \Delta z)(z'_0 + \Delta z) - x_0y_0 \right. \\ &\quad \left. - \Delta zJ^{(2)}\frac{x_0y_0}{z_0z'_0}(z_0 + \Delta z)(z'_0 + \Delta z) + \Delta z^2K^{(1)}x_0y_0\right]. \end{aligned} \tag{23}$$

As stated above, $J = C_1 + C_2, K = C_1 \cdot C_2, C_1 = 1/R_1$ and $C_2 = 1/R_2$. We will use this notation and that of Fig. 2 (i.e. $R_1 = z$ and $R_2 = z'$). Also, since the two principal radii (R_1 and R_2) are offset by a distance $D, z' = z + D$. Using these relations we obtain, for the right hand side of eq. (23):

$$\begin{aligned} &\gamma^{(1)}x_0y_0\left[\left(\frac{z_0^2 + D(z_0 + \Delta z) + 2z_0\Delta z + \Delta z^2}{z_0(z_0 + D)} - 1\right) \right. \\ &\quad \left. - \frac{\Delta z(z_0 + \Delta z + z_0 + D + \Delta z)(z_0^2 + D(z_0 + \Delta z) + 2z_0\Delta z + \Delta z^2)}{z_0(z_0 + D)(z_0 + \Delta z)(z_0 + D + \Delta z)} + \Delta z^2\left(\frac{1}{z_0}\right)\left(\frac{1}{z_0 + D}\right)\right] \\ &= \gamma^{(1)}x_0y_0\left[\frac{z_0^2 + D(z_0 + \Delta z) + 2z_0\Delta z + \Delta z^2 - z_0(z_0 + D) + \Delta z^2}{z_0(z_0 + D)} \right. \\ &\quad \left. - \frac{(2\Delta zz_0 + 2\Delta z^2 + \Delta zD)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{z_0(z_0 + D)(z_0 + \Delta z)(z_0 + D + \Delta z)}\right] \\ &= \gamma^{(1)}x_0y_0\left[\frac{(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2 - z_0^2 - z_0D + \Delta z^2)(z_0 + \Delta z)(z_0 + D + \Delta z)}{z_0(z_0 + D)(z_0 + \Delta z)(z_0 + D + \Delta z)} \right. \\ &\quad \left. - \frac{(2\Delta zz_0 + 2\Delta z^2 + \Delta zD)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{z_0(z_0 + D)(z_0 + \Delta z)(z_0 + D + \Delta z)}\right] \\ &= 0. \end{aligned} \tag{24}$$

Proceeding to the second term of the right hand side of eq. (16),

$$C_J^{(1)}(\mathcal{J}^{(2)} - \mathcal{J}^{(1)} + 2\Delta\lambda\mathcal{K}^{(2)}) = C_J^{(1)}(J^{(2)}A^{(2)} - J^{(1)}A^{(1)} - 2\Delta zK^{(1)}A^{(1)}). \quad (25)$$

By making the same substitutions as above, we find

$$\begin{aligned} & C_J^{(1)}(J^{(2)}A^{(2)} - J^{(1)}A^{(1)} - 2\Delta zK^{(1)}A^{(1)}) \\ &= C_J^{(1)}x_0y_0 \left[\left(\frac{1}{z_0 + \Delta z} + \frac{1}{z_0 + D + \Delta z} \right) \left(\frac{z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2}{z_0(z_0 + D)} \right) \right. \\ & \quad \left. - \left(\frac{z_0 + z_0 + D}{z_0(z_0 + D)} \right) - \frac{2\Delta z}{z_0(z_0 + D)} \right]. \end{aligned} \quad (26)$$

Upon further simplification of the right hand side of eq. (26),

$$\begin{aligned} & C_J^{(1)}x_0y_0 \left[\left(\frac{2z_0 + 2\Delta z + D}{(z_0 + \Delta z)(z_0 + D + \Delta z)} \right) \left(\frac{z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2}{z_0(z_0 + D)} \right) \right. \\ & \quad \left. - \left(\frac{2z_0 + 2\Delta z + D}{z_0(z_0 + D)} \right) \right] \\ &= C_J^{(1)}x_0y_0 \left[\frac{(2z_0 + 2\Delta z + D)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right. \\ & \quad \left. - \frac{(2z_0 + 2\Delta z + D)(z_0 + \Delta z)(z_0 + D + \Delta z)}{z_0(z_0 + D)(z_0 + \Delta z)(z_0 + D + \Delta z)} \right] \\ &= 0. \end{aligned} \quad (27)$$

Moving to the third term of the right hand side of eq. (16), we again invoke the finding of Gaydos et al. [15] (i.e. that $\delta\mathcal{K} = 0$) and see that this term vanishes.

Finally we proceed to the last term of the right hand side of eq. (16). We find that this expression involves $V^{(1)} - V^{(2)}$. Here we have to determine $V = V(z)$ and integrate to find ΔV , that is

$$\Delta V = \int_1^2 \delta V. \quad (28)$$

We find, from Fig. 2, that if second order terms are neglected $\delta V = A\delta z$. Also, using eqs. (18), (20) and (21) we find

$$\Delta V = \left[\frac{x_0y_0}{z_0(z_0 + D)} \right] \int_1^2 (z^2 + Dz)dz. \quad (29)$$

Upon integration and appropriate substitutions,

$$\Delta V = \left[\frac{x_0 y_0}{6z_0(z_0 + D)} \right] (6\Delta z z_0^2 + 6\Delta z^2 z_0 + 2\Delta z^3 + 6Dz_0\Delta z + 3D\Delta z^2). \quad (30)$$

Replacing this into the expression

$$\begin{aligned} & \Delta P(V^{(1)} - V^{(2)} - \Delta\lambda A^{(2)} - \frac{1}{2}\Delta\lambda^2 \mathcal{J}^{(2)} - \frac{1}{3}\Delta\lambda^3 \mathcal{K}^{(2)}) \\ &= \Delta P x_0 y_0 \left[\frac{-(6\Delta z z_0^2 + 6\Delta z^2 z_0 + 2\Delta z^3 + 6Dz_0\Delta z + 3D\Delta z^2)}{6z_0(z_0 + D)} \right. \\ & \quad + \frac{\Delta z(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{z_0(z_0 + D)} \\ & \quad - \frac{1}{2}\Delta z^2 \left(\frac{(2z_0 + 2\Delta z + D)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right) \\ & \quad \left. + \frac{1}{3} \left(\frac{\Delta z^3}{z_0(z_0 + D)} \right) \right]. \quad (31) \end{aligned}$$

Simplifying the right hand side of eq. (31),

$$\begin{aligned} & \Delta P x_0 y_0 \\ & \times \left[\frac{-6z_0^2\Delta z - 6\Delta z^2 z_0 - 6Dz_0\Delta z - 3D\Delta z^2 + 6\Delta z z_0^2 + 6\Delta z Dz_0 + 6D\Delta z^2 + 12z_0\Delta z^2 + 6\Delta z^3}{6z_0(z_0 + D)} \right. \\ & \quad \left. - \frac{1}{2}\Delta z^2 \left(\frac{(2z_0 + 2\Delta z + D)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right) \right] \\ &= \frac{\Delta P x_0 y_0}{2} \left[\frac{D\Delta z^2 + 2z_0\Delta z^2 + 2\Delta z^3}{z_0(z_0 + D)} - \frac{\Delta z^2(2z_0 + 2\Delta z + D)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right] \quad (32) \end{aligned}$$

With additional mathematical manipulations on the right hand side of the equation above,

$$\begin{aligned} & \frac{\Delta P x_0 y_0}{2} \left[\frac{(D\Delta z^2 + 2z_0\Delta z^2 + 2\Delta z^3)(z_0 + \Delta z)(z_0 + D + \Delta z)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right. \\ & \quad \left. - \frac{(2\Delta z^2 z_0 + 2\Delta z^3 + \Delta z^2 D)(z_0^2 + Dz_0 + D\Delta z + 2z_0\Delta z + \Delta z^2)}{(z_0 + \Delta z)(z_0 + D + \Delta z)(z_0)(z_0 + D)} \right] \\ &= 0. \quad (33) \end{aligned}$$

Hence, what we have shown is that

$$\Omega^{(2)} - \Omega^{(1)} = 0 \quad (34)$$

for an arbitrary shift of the dividing surface for a general surface geometry.

4. Conclusions

This paper extends previous studies of Boruvka and Neumann [12] and of Rotenberg et al. [9]. The former introduced the generalized theory of capillarity, while the latter showed that this theory permits shifts of the dividing surface. The study by Rotenberg et al. confirmed the generality of this theory, since in the classical theory any position of the dividing surface other than the position of pure tension is prohibited. Rotenberg et al. illustrated their findings by considering only spherical and cylindrical geometries. The present study has considered a shift of the dividing surface for an arbitrary surface geometry and has shown that the generalized theory of capillarity allows freedom of placement of the dividing surface without violating the free energy conservation requirement of the system.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (grant #A8278), Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (A.J.) and a University of Toronto Open Fellowship (P.C.).

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