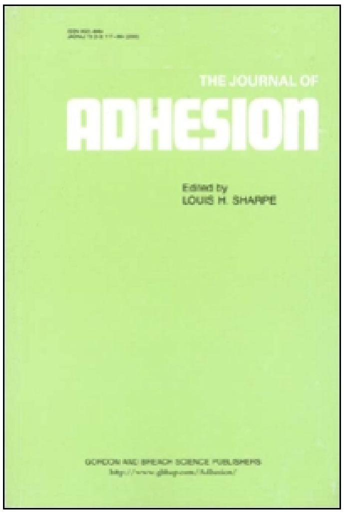

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ON THERMODYNAMICS OF THIN FILMS: THE MECHANICAL EQUILIBRIUM CONDITION AND CONTACT ANGLES

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A thermodynamic model for plane parallel thin liquid films applicable to solid-liquid-vapor systems was presented using the detailed method. The film was modeled as a bulk phase bound by two dividing surfaces. The thermodynamic thickness of the film was established as well as excess properties such as film tension. The analysis using this model yielded disjoining pressure definition identical to the literature reports. The effect of definition for contact angle on the resulting mechanical equilibrium condition was also demonstrated. It was concluded that from a theoretical perspective it is important to clearly define contact angles as the angle a sessile drop makes with either the solid phase or the thin film. However, on a practical level for most cases, the difference between using either of the two mechanical equilibrium conditions to determine film tension or contact angle will be minimal (ascertained by an order of magnitude analysis). The attempt was also made to bring about clarity concerning some of the questions in the literature regarding the thermodynamic model for thin films presented by Li and Neumann.

Keywords: Thin films; Contact angle; Wetting; Disjoining pressure; Film tension; Interfacial tension; Mechanical equilibrium condition; Equation of state

INTRODUCTION

The study of thin films is important in both practical and theoretical aspects. Thin films are present in emulsion and foam systems and to a great extent determine the properties of such systems

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(*e.g.*, stability); several thin film properties are determined by the same forces that also govern the stability of lyophbic colloids [1]. Thin films are also an important factor influencing contact angle phenomena. Contact angle studies have been long established as a very sensitive measure to investigate adhesion [2]. Contact angles are also a determining factor in attachment of particles to air bubbles in processes such as froth floatation and stabilizing emulsions by solid particles [3]. This article studies the influence of thin films on contact angles for solid-liquid-vapor systems using a macroscopic thermodynamics model. It specifically considers the commonly encountered case of a sessile drop, which is studied using a "detailed" approach (unlike the approaches used in past studies).

The subject of liquid films received considerable stimulus beginning in 1930s when Derjaguin and others realized that the thickness of some films is in the range of a few nanometers to 100 nm. Such minute thickness brings about the possibility of interaction between the two interfaces a thin film makes with neighboring bulk phases and gives it some unique characteristics. In a thin film it is virtually impossible to distinguish between the surface layers and the bulk phase. To address this unique situation, Derjaguin [4] introduced the notion of the disjoining pressure, which was not included in the original thermodynamic treatment by Gibbs in his theory of capillarity [5] (Gibbs confined himself to only thick films, which makes it possible to overlook the interaction of the two interfaces of a film with adjacent bulk phases).

There have been various thermodynamics treatments of the thin film and its effect on contact angle mainly concerning vapor-liquid-vapor systems [1, 4, 6–18]. The main approaches to thermodynamically model thin films are as follows: a Derjaguin-type analysis where the thin film is modeled as a plane of almost zero thickness and all excess properties (*e.g.*, entropy, free energy) of the film are attributed to this plane and form the basis for the analysis (this method is sometimes called the membrane approach); the approach that was pioneered by Rusanov [7–9], in which a film is assumed to have a thickness and be generally composed of three parts, *i.e.*, bulk and two interfaces (or dividing surfaces); the film thickness for the film's bulk phase (or better described as the distance between the pair of dividing surfaces) is defined by thermodynamic analysis (this method is known as the "detailed" approach or three-dimensional). The important aspect to note in this model is that the bulk phase of the thin film does not necessarily have properties similar to the bulk phase that the film is connected to (or made of) and its properties may need to be defined by thermodynamic analysis. The same applies to the two interfaces (see below). Among the analyses that have not explicitly used one of the above two approaches has been the work of Li and Neumann [17]; they have used a macroscopic thermodynamic approach based on fundamental equations and a variation principle to derive the equilibrium condition (with special focus on the mechanical equilibrium condition).

Clarity has been brought to the field (*e.g.*, see Marmur [16]) regarding sometimes inconsistent results for pressure inside a thin film (*e.g.*, Toshev and Ivanov [10] and De Feijter *et al.* [12]) that results from application of the first two approaches. However, questions (*e.g.*, regarding the appropriate treatment of disjoining pressure and measurement of film tension [19]) in the approach taken by Li and Neumann [17] have remained unanswered, especially when dealing with the effect of thin films on contact angles. This short article, unlike past studies, uses a detailed approach to construct a thin film model connected to a sessile drop to verify the findings by Li and Neumann [17] regarding the disjoining pressure, mechanical equilibrium conditions, and film tension; it also aims to bring about clarity regarding questions raised by some researchers [19] concerning the appropriateness of the model and conclusions presented in Li and Neumann [17] (*e.g.*, applicability of the equation of state for contact angles in the presence of thin films).

THERMODYNAMIC FORMULATION OF THIN FILMS FOR SOLID-LIQUID-VAPOR SYSTEMS

The thermodynamic analysis below is presented for the class of plane parallel (or uniform) films [20] (this is the system studied by Li and Neumann [17]). The film was modeled using the detailed approach and is assumed to have three parts; a bulk phase and two interfaces. The film bulk phase was assumed to be made of a *mother* liquid bulk phase (λ), the composition of which is assumed to be identical to the film bulk phase; the film bulk phase may be considered inhomogeneous due to close proximity of its two interfaces with the neighboring bulk phases (*i.e.*, vapor (α) and solid (β) phases). The two interfaces are $\beta\lambda$ and $\alpha\lambda$ (see Figure 1) at film-solid and film-vapor dividing surfaces, respectively. The distance between the two dividing surfaces is chosen to represent the thickness of the thin film, h (see below). The film thickness is an important thermodynamic quantity that yields the unique characteristics of thin films as a result of overlapping interface regions. The other important property for thin films is the film tension that will be discussed later. As will be shown, these two properties could affect the observed contact angle

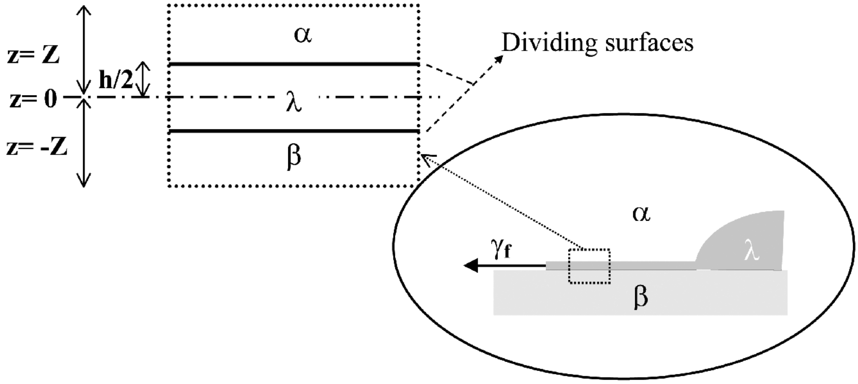

FIGURE 1 Schematic of the closed thermodynamic system including the thin film (with film tension of γ_f) and bulk phases, *i.e.*, solid (β), liquid sessile drop (λ), and surrounding vapor (α) phases. The enlarged box shows a subsystem containing a planeparallel film; it also shows the detailed view of the thermodynamic model used for the thin film, which depicts the pair of dividing surfaces at a distance, h, from each other (heavy lines). The bulk phases adjacent to the thin film are β and α, which, at a distance of $|Z|$ from centerline of the thin film, do not have any influence on the excess properties at the dividing surfaces.

and, hence, adhesion. It is worth nothing that the methodology proposed above is not a new finding or approach, but the specific system studied, *i.e.*, sessile drops connected to a thin liquid film, has not been analyzed thus far using a detailed approach. This is significant because the detailed approach, as compared with the membrane approach, is a more intuitive methodology, which will more effectively aid in clarifying outstanding issues in the literature, as mentioned above.

To determine film thickness, the dividing surfaces and their excess properties need to be defined. In defining film thickness and excess properties, we have adapted the detailed approach as outlined in De Feijter [1] and Rusanov [15]. The solid phase is assumed ideal (smooth, homogenous, nonreactive, and nondeformable), and the presence of external fields is not considered; the assumption of homogeneity also applies to the vapor phase. As such, the excess surface energy for each of the film interfaces (*i.e.*, $u_f^{\alpha\lambda}$ and $u_f^{\beta\lambda}$) can be written for the system shown in Figure 1 as follows. Note that, in general, to consider the inhomogeneity of the film bulk phase the excess energy definition for the film interfaces are not the same as that of the *mother* (sessile drop) bulk phase (λ) with the neighboring phases α and β, *i.e.*, $u_f^{\alpha\lambda} \neq u^{\alpha\lambda}$ and $u_f^{\beta\lambda} \neq u^{\beta\lambda}$:

$$u_f^{\alpha\lambda} = \frac{U_f^{\alpha\lambda}}{A_f} \equiv \int_0^{h/2} \left[u(z) - u^{\lambda}\right]dz + \int_{h/2}^{\infty} \left[u(z) - u^{\alpha}\right]dz, \tag{1}$$

$$u_f^{\beta\lambda} = \frac{U_f^{\beta\lambda}}{A_f} \equiv \int_{-h/2}^{0} \left[u(z) - u^{\lambda}\right]dz + \int_{-\infty}^{-h/2} \left[u(z) - u^{\beta}\right]dz, \tag{2}$$

where u(z) is the volume density of the energy in the inhomogeneous film region; u^{α}, u^{β}, and u^{λ} are the volume densities of the energy in the homogenous bulk phases α, β, and λ, respectively (in this model all excess properties are ascribed to the two interfaces and as such the homogeneous bulk volume density, u^{λ}, of the original phase can be used in the above definition); A_f is the area for each of the film interfaces; U denotes the magnitude of the energy, and subscript *f* refers to film properties. The excess entropy and concentration of species at each of the interfaces can be defined in a similar fashion.

Considering the system shown in the enlarged box in Figure 1 (a hypothetical subsystem free to exchange matter with the rest of the system) and assuming that the bulk phases adjacent to the thin film, β and α, at a distance of |Z| from centerline of the thin film, do not have any influence on the excess properties at the dividing surfaces for the system in thermal equilibrium, one can write the following relations for total energy (U_T) and total concentration of *i*th species in the system (N_{iT}):

$$U_T = U^{\alpha} + U^{\beta} + U_f = A_f \int_{-Z}^{Z} u(z)dz, \tag{3}$$

$$N_{iT} = V^{\alpha}n_i^{\alpha} + V^{\beta}n_i^{\beta} + N_{fT} = A_f \int_{-Z}^{Z} n_i(z)dz, \tag{4}$$

where *V* and n_i denote the total volume and volume density of component *i*, respectively. Note that Equations (3) and (4) are written independent of the original phase (λ) because the focus is on the film itself. Combining Equations (1) and (2) with Equation (3) (noting that $z \leq \pm Z$) and the condition that the total volume for the system is constant will result in

$$U_f = A_f(u_f^{\alpha\lambda} + u_f^{\beta\lambda} + hu^{\lambda}) = U_f^{\alpha\lambda} + U_f^{\beta\lambda} + U_f^{b}, \tag{5}$$

where U_f^b is the energy for the bulk phase of the thin film; and the superscripts denote the interfaces/phases involved. As mentioned above, in analogy to Equations (1) and (2), expressions for excess concentration of species at each of the interfaces can be defined similar to Equations (1) and (2) and, if combined with Equation (4), the concentration for the *i*th species in the film can be written as

$$N_{if} = A_f(\Gamma_{if}^{\alpha\lambda} + \Gamma_{if}^{\beta\lambda} + hn_i^{\lambda}) = N_{if}^{\alpha\lambda} + N_{if}^{\beta\lambda} + N_{if}^{b}, \tag{6}$$

where Γ is the density per unit area of the *i*th species. Similar to a case where a single dividing membrane is used in modeling a thin film (*i.e.*, the membrane approach) and, in keeping with the conventional Gibbsian approach to define the location of dividing surfaces, the location of the two dividing surfaces in this model were set where concentration of one of the species (say component one) is zero. Therefore, at both interfaces $\alpha\lambda$ and $\beta\lambda$, one would have $N_{1f}{}^{\alpha\lambda} = N_{1f}{}^{\beta\lambda} = 0$. As such,

$$N_{1f}^{b} = N_{1f} = A_f h n_{1f}^{\lambda},$$

and, therefore, according to Equation (6) the film thickness, h, is defined as,

$$h \equiv \frac{N_{f1}}{A_f n_{f1}^{\lambda}}. \tag{7}$$

The above definition for film thickness can be further improved, if one applies the approach used by DeFeijter *et al.* [12], for thin liquid films in contact with similar vapor phases (*e.g.*, foams). To obtain a more rigorous definition for film thickness for solid-liquid-vapor systems (*e.g.*, a thin film in contact with a solid phase on one side and a vapor phase on the other side, see Figure 1), the volume constraint for the system as given by Equation (8) can be combined with Equations (4) and (7) to yield Equation (9). Equation (9) provides the rigorous thermodynamic definition for film thickness for solid-liquid-vapor systems; in principle, all parameters in this equation are measurable:

$$V_T = V^{\alpha} + V^{\beta} + V_f = (2Z - h)A_f + A_f h, \tag{8}$$

$$h \equiv \frac{N_{T1} - V^{\alpha}n_1^{\alpha} - V^{\beta}n_1^{\beta}}{A_f(n_1^{\lambda} - n_1^{\alpha} - n_1^{\beta})}. \tag{9}$$

To complete the thermodynamic analysis of the excess quantities for thin films, the film tension is introduced. Film tension (γ_f) is the excess of the tangential forces per unit area of the film relative to the surrounding phases [6, 11, 13]. The definition for film tension is given by Equation (12); this equation is constructed in analogy to the expression of surface excess convention used to define surface tension of a film for a symmetrical film surrounded by two similar phases (*e.g.*, foams as presented by Toshev and Ivanov [21]). Since there are two different phases present on either side of the film in a solid-liquid-vapor system, to define film tension correctly unlike the definition in Toshev and Ludnov [21] for each of the film interfaces, the tension should be defined separately as in Equations (10) and (11) for liquid–vapor and solid–liquid interfaces, respectively:

$$\gamma_f^{\alpha\lambda} = -\int_0^{h/2} (P^n(z) - P^\lambda)dz - \int_{h/2}^{\infty} (P^n(z) - P^\alpha)dz, \tag{10}$$

$$\gamma_f^{\beta\lambda} = -\int_{-h/2}^{0} (P^n(z) - P^\lambda)dz - \int_{-\infty}^{-h/2} (P^n(z) - P^\beta)dz, \tag{11}$$

$$\gamma_f = -\int_{-\infty}^{0} (P^n(z) - P^\beta)dz - \int_{0}^{\infty} (P^n(z) - P^\alpha)dz, \tag{12}$$

where $\gamma^{\alpha\lambda}{}_f$ and $\gamma^{\beta\lambda}{}_f$ are film surface tensions and $P^n(z)$ is the normal pressure component in the pressure tensor acting parallel to the mid plane of the film. Note that the pressure inside a thin film is not the same as the bulk phase from which the film is made (see Figure 1). This is because in physical terms the bulk phase in the film is an inhomogeneous layer. Pressures P^λ, P^α, and P^β are the isentropic pressures in the homogeneous bulk phases of λ, α, and β, respectively. (As the film becomes thick (*i.e.*, $h = \infty$), for the case of a planar film all isentropic bulk pressures will have to be equal and, consequently, the classical definition for surface tension of two neighboring homogeneous bulk phases can be recovered from Equation (10) or (11). In the absence of external field forces, the pressure component acting perpendicular to the plane of the film must be constant, *i.e.*, $P^\alpha = P^\beta$. Therefore, combining Equation (12) with Equations (10) and (11) will result in the relation between the film tension (γ_f) and surface tensions of the film with its adjacent bulk phases (*i.e.*, $\gamma^{\alpha\lambda}{}_f$ and $\gamma^{\beta\lambda}{}_f$) as follows:

$$\gamma_f = \gamma_f^{\alpha\lambda} + \gamma_f^{\beta\lambda} - h(P^\lambda - P^\alpha). \tag{13}$$

The last term on the righthand side of the above equation has been expressed using the definition of disjoining pressure (Π) as $h\Pi$. The disjoining pressure is the difference between the pressure of the phase surrounding the thin film (P^{α}) and the pressure of the bulk phase that the film has been drawn from (P^{λ}), *i.e.*, $\Pi = P^{\alpha} - P^{\lambda}$ [5]. There is also a more refined definition for disjoining pressure available [11] that better describes the inhomogeneity of thin films, *i.e.*, the difference between the normal component of the pressure tensor perpendicular to the interface in the layer (P^{N}) and the pressure of the bulk phase that by thinning has yielded the thin film (*i.e.*, the original/mother phase); therefore, $\Pi = P^{N} - P^{\lambda}$. Considering the refined definition for Π, in general, the disjoining pressure is not necessarily directly connected to the definition of the film tension according to Equation (13). The thermodynamic expression for disjoining pressure (*i.e.*, Equation (15)) can be found based on the differential form of the fundamental equation for the system, *i.e.*, Equation (14) (for detailed derivation of Equation (14), see the Appendix), as:

$$dU_f^{\alpha\lambda,\beta\lambda} = TdS_f^{\alpha\lambda,\beta\lambda} - \Pi d(hA_f) + \gamma_f dA_f + \sum \mu_i dN_f^{\alpha\lambda,\beta\lambda}, \tag{14}$$

$$\Pi = -\frac{1}{A_f}\left(\frac{\partial U_f^{\alpha\lambda,\beta\lambda}}{\partial h}\right)_{T,n_i}, \tag{15}$$

where superscripts $\alpha\lambda$ and $\beta\lambda$ represent the excess quantities with respect to bulk phase, λ, of the film. Equation (15) yields the definition for disjoining pressure similar to findings in Rusanov [15] for constant temperature and concentration of the ith species.

MECHANICAL EQUILIBRIUM CONDITION

The system considered in this section is identical to the one investigated by Li and Neumann [17], *i.e.*, a sessile drop connected to a thin liquid film that is placed on an ideal solid surface (see Figure 2). Consistent with the system in Li and Neumann [17], no transition zone between the thin film and sessile drop is considered. At equilibrium it is understood that, for such a system, temperature and chemical potentials are constant throughout all phases in the system [17]. The mechanical equilibrium condition can be obtained by setting the changes in the free energy of the system for a small displacement in the system to zero (note that the bulk solid phase is considered ideal, and as such its free energy will always remain constant, *i.e.*, it will not enter into the mathematical treatment of the variational analysis). The generic treatment of such an approach is well documented in the literature [10, 14, 22, 23], and so here, to avoid repeating mainly

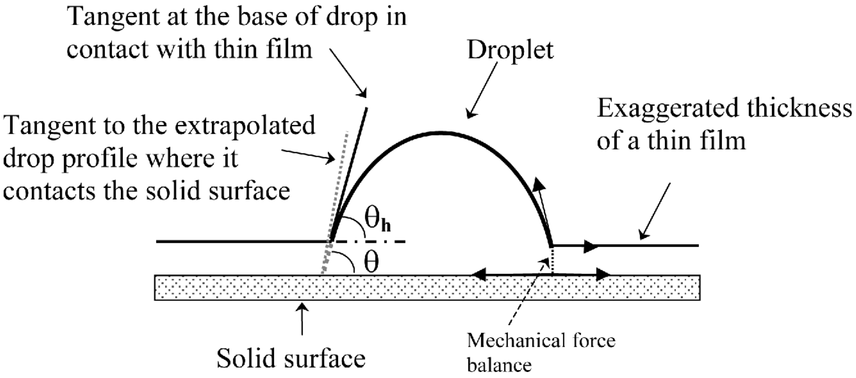

FIGURE 2 A sessile drop in equilibrium with a thin liquid film on an ideal solid substrate. This figure highlights the two definitions used for contact angle that can result in different forms for the mechanical equilibrium condition. At the right contact point, the force balance at the junction of the thin film and sessile drop is depicted.

mathematical derivations that are especially well detailed in Toshev and Ivanov [10], only the final result is provided, *i.e.*,

$$\gamma^{\lambda\alpha}\cos\theta = \gamma_f - \gamma^{\lambda\beta}. \tag{16}$$

Equation (16) is obtained by assuming the same theoretical definition for contact angle, θ (*i.e.*, the angle where the extrapolated profile of the drop meets the solid surface (*i.e.*, at $\mathrm{h} = 0$): see Figure 2), as in Li and Neumann [17] (note that typically θ_h (see Figure 2) is the angle that is observed in an experiment). However, if instead of the above definition for contact angle, its practical definition, *i.e.*, the angle that the drop makes with the thin film, θ_h, is used, (intersection of the dividing surface for film and drop with vapor phase; see Figure 2), the mechanical equilibrium condition will become

$$\gamma^{\lambda\alpha}\cos\theta_h = \gamma_f - \gamma^{\lambda\beta} - \Pi h. \tag{17}$$

A simple way to arrive at Equation (17) is to consider the mechanical equilibrium where the thin film meets the sessile drop (see the right contact point in Figure 2 for a force balance) and noting that according to Equation (13), $\gamma_f - \Pi\mathrm{h} = \gamma^{\alpha\lambda} + \gamma^{\alpha\beta}$. Equation (17) is consistent with the reported mechanical equilibrium condition stated by Ivanov *et al.* [14] and DeFeijter *et al.* [12] for vapor-liquid-vapor systems. Equation (17) is also consistent with Equation (16), *i.e.*, as the film thickness approaches zero, θ_h will change to θ, and hence both Equations (16) and (17) will be identical. When the film thickness is zero, the term γ_f will no longer represent the film tension, but the solid–vapor surface tension; hence, the classical Young equation for mechanical equilibrium at the three-phase line will be recovered.

DISCUSSION

A comparison between the fundamental equation for a planeparallel thin film obtained here (Equation (A2) or the differential form given by Equation (14)) and the relations presented by Li and Neumann (*i.e.*, Equation (6) or (8) in Li and Neumann [17]) reveals that the interpretation of disjoining pressure in Li and Neumann [17] is not necessarily consistent with the classical definition (*i.e.*, $\Pi = P^{\alpha} - P\lambda$). For a planeparallel film the term labeled *disjoining pressure* in the formulation presented in Li and Neumann [17] is equal to the normal component of the pressure tensor perpendicular to the interface of the thin film, *i.e.*, the surrounding bulk pressure (P^{α}), when the system is in equilibrium. For the system shown in Figure 2, this implies that the pressure jump across the thin film is equal to the pressure in the surrounding phase and, hence, fixed at all times regardless of the film thickness. Knowing that disjoining pressure is a function of film thickness according to its definition (see Equation (15)), the finding that Π is equal to P^{α} cannot be accepted. The terminology in Li and Neumann [17] has caused some confusion in the literature; for example, Lee [19] has questioned the validity of the equation of state formulation for contact angles presented in Li and Neumann (17) on the basis that the parameter called disjoining pressure should have included additional terms to account for molecular, ionic, and steric forces. However, the argument by Lee [19] to refute the findings regarding the existence of an equation of state in Li and Neumann [17] is not valid, as Lee has not recognized the imprecise use of the term disjoining pressure in that study. Although the term *disjoining pressure* is not used appropriately in the context of the mechanical equilibrium relation, if the term labeled *disjoining pressure* in Li and Neumann [17] is considered as bulk pressure (as it should be), the definition of the film tension and mechanical equilibrium condition by Li and Neumann will be consistent with its thermodynamic definition provided in this article and, hence, their conclusion regarding the equation of state would hold.

As shown above, depending on which definition for contact angle is used, the mechanical equilibrium condition will take a different form (*i.e.*, Equation (16) or (17)). In Li and Neumann [17], when defining the system the theoretical definition of contact angle as indicated by

θ in Figure 2 was used, which means Equation (16) will provide the mechanical equilibrium condition; however, in effect, when solving the variational problem to find the mechanical equilibrium condition, Li and Neumann have applied the more commonly used practical definition for contact angle (*i.e.*, θ_h in Figure 2) and found a relation similar to Equation (17). The nonexplicit switching of the definition for contact angle in Li and Neumann [17] has led to misinterpreting their phase rule arguments in the literature (*e.g.*, Lee [19]). Such confusion is similar to that regarding the relations that can be used to find the free energy of interaction for thin films from contact angle data (see *e.g.*, De Feijter *et al.* [12] and Scheludko *et al.* [22]). In this article, however, the mechanical equilibrium condition presented in Li and Neumann [17] is confirmed by an independent method and, as such, the arguments presented in Li and Neumann [17] regarding the existence of an equation of state for contact angles and the effect of thin films on drop size dependence of contact angles can be accepted, as long as the intrinsic contact angle of the system is above $\sim 10^\circ$. If the contact angle is below 10°, neglecting or adding the Πh term in the mechanical equilibrium condition could cause error in the surface energetics interpretation of contact angles (*e.g.*, if h is of the order of 10^{-7} m and Π has a typical value of $5 \times 10^2\,\mathrm{N/m^2}$, then including or neglecting the Πh term in the mechanical equilibrium condition would result in a numerical error in the order of $10^{-3;}$ this error is of the order of $1 - \cos\theta$ when the interfacial tension of the system is of the order of $10^{-2}\,\mathrm{J/m^2}$ and the contact angle observed is, say, 3°).

CONCLUSION

In conclusion, a thermodynamic model for planeparallel thin liquid films applicable to solid-liquid-vapor systems was presented using the detailed method pioneered by Rusanov. The film was modeled as a bulk phase bound by two dividing surfaces. The thermodynamic thickness of the film was established as well as excess properties such as film tension. The analysis using our model yielded a disjoining pressure definition identical to the one reported earlier by Rusanov [15] and others (*e.g.*, Kralchevsky and Ivanov [24]) for vapor-liquid-vapor systems. The effect of the definition of contact angle on the resulting mechanical equilibrium condition was also demonstrated. This finding highlights the importance of a clear definition for contact angles and consistent application of the definition in thermodynamic analysis of thin films. On a practical level, to determine film tension for low surface energy solid surfaces where contact angles are generally large, the difference between using Equations (16) and (17) will be minimal. As such, the findings of our model suggest that the method proposed by Li and Neumann to determine film tension is acceptable, and the criticism raised in Lee [19] is not significant on a practical level.

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APPENDIX

In order to construct the fundamental thermodynamic equation of thin films, one can consider the process of film formation under suitably chosen conditions. In the system shown in Figure 1, it is assumed that all works are done reversibly; the overall volume of the system remains constant and equal to the summation of the film and phases α and β; concentration of all species in the system is the summation of the concentrations of each in the film, and phases α and β; and finally, the total entropy and internal energy of the system is equal to the summation of each property in the film, and α and β, phases. If, under the conditions stated above, the area of the film is increased by dA_f and, further, that this change does not affect the thermodynamic state of other parameters (*i.e.*, temperature (T), chemical potential (μ_i), number of moles of each species (N_i), and the volume of the bulk phases α, β, and λ, being constant), then following the conventional method (*e.g.*, see De Feijter [1]), the work to extend the thin film will be

$$W_1 = (P^\alpha - P^\lambda)hdA_f,$$

$$W_2 = \gamma_f^{\beta\lambda}dA_f - \gamma^{\alpha\beta}dA^{\alpha\beta},$$

$$W_3 = \gamma_f^{\alpha\lambda}dA_f.$$

Using the definition of film tension (Equation (13)) and the above relations, one will have:

$$W_4 = W_1 + W_2 + W_3 = \gamma_f dA_f - \gamma^{\alpha\beta}dA_f$$

The above process requires that material for forming the extended film be brought into the film from its surroundings; consequently, the "material work" associated with the film will be:

$$W_5 = \sum \mu dN_{if}$$

The increase in volume of the film, dV_f, is equal to the decrease in the volume of the bulk phase, α (β is an ideal nondeformable solid phase) and, according to the assumption of constant total volume for the system, one has:

$$W_6 = P^\alpha dV^\alpha = -P^\alpha dV_f$$

The summation of the above works (*i.e.*, W_{4-6}) on the system should be equal to the change in the total free energy of the system (F_T) for a reversible and isothermal system. Noting that the thermodynamic state of the bulk phases α, β and λ were kept constant in this process, as mentioned above, there will not be any change in their free energies. Therefore,

$$dF_T = dF_f + dF^{\alpha\beta} = W_4 + W_5 + W_6,$$

where

$$dF_f = dF_f^{\beta\lambda} + dF_f^{\alpha\lambda} + dF_f^b.$$

From the above the free energy for the thin film can be found as

$$dF_f = -P^{\alpha}dV_f + \gamma_f dA_f + \sum \mu_i dN_{if}.$$

If one allows thermal exchange between the thin film system and its surroundings, *i.e.*, relaxing the isothermal condition of the system, the above relation will take the following form:

$$dF_f = -S_f dT_f - P^{\alpha}dV_f + \gamma_f dA_f + \sum \mu_i dN_{if}.$$

To find the internal energy change (dU_f) for this system the Legendre transformation can be utilized:

$$dU_f = T_f dS_f - P^{\alpha}dV_f + \gamma_f dA_f + \sum \mu_i dN_{if}. \qquad (A1)$$

To find the film's internal energy (U_f), the Euler theorem can be applied to Equation (A1), *i.e.*,

$$U_f = T_f S_f - P^{\alpha}V_f + \gamma_f A_f + \sum \mu_i N_{if}. \qquad (A2)$$

The change in the internal energy for the bulk portion of the modeled thin film can be written as follows (analogous to the usual formulation for any other bulk phase):

$$dU_f^b = TdS_f^b - P^{\lambda}d(hA_f) + \gamma_f dA_f + \sum \mu_i dN_{if}^{\lambda}, \qquad (A3)$$

where the superscript *b* refers to the bulk portion of the thin film. Subtracting Equation (A3) from Equation (A1) will result in the following equation, which can be used to define thermodynamically the film tension and disjoining pressure, among other properties for a thin film:

$$dU_f^{\alpha\lambda,\beta\lambda} = TdS_f^{\alpha\lambda,\beta\lambda} - \Pi d(hA_f) + \gamma_f dA_f + \sum \mu_i dN_f^{\alpha\lambda,\beta\lambda}. \qquad (A4)$$