

Thermodynamics of Flat Thin Liquid Films

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The two main themes of this study aim to resolve conflicting results in the literature regarding the thermodynamics of flat (uniform thickness) thin liquid films. One of the themes concerns the augmented Young equation, which is a condition for mechanical equilibrium. Two different expressions for the augmented Young equation have appeared in the literature. It is shown that under certain assumptions, the two expressions can be made equivalent. The second main theme addresses thermodynamic functions describing systems with non-pressure-volume (non-PV) work. In thin liquid films, the non-PV work is the film tension work. Two different expressions that relate the film's Gibbs energy to its internal energy have appeared in the literature. This ambiguity is resolved by showing that only one of the Gibbs energies can be used to determine the equilibrium state via energy minimization. The analysis can be readily generalized to systems with other types of non-PV work. © 2015 American Institute of Chemical Engineers AIChE J, 61: 3104–3115, 2015

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Introduction

Thin liquid films have a diverse array of applications in surface science. They have been observed on crystalline surfaces at temperatures below the melting point of the bulk crystalline material. For example, thin liquid films appear as premelted layers on the surface of ice crystals and snowflakes.¹ The melting temperature of gold nanoparticles can be theoretically modeled with high accuracy if the model accounts for the presence of thin liquid films on the surface of the nanoparticles.² The thermodynamics of thin liquid films have been used to explain the wetting behavior of thin polymer films,^{3,4} which have applications in electronics and the design of anti-reflective coatings. Thin liquid films have also served as a model for studying lung surfactants.⁵ The surfactants are essential for normal physiological function because they allow the lung tissues to expand and contract more easily during the breathing cycle.

Wettability alteration of mineral surfaces by CO₂^{6,7} and by low-salinity waterflooding,^{8–12} both of which have applications to improved oil recovery (CO₂ wettability alteration is also important for geological carbon sequestration), may be related to the thin liquid films, specifically thin brine films, that wet the mineral surfaces. One such wettability alteration mechanism involving thin brine films is double-layer expansion.

In this mechanism, injection of low-salinity brine expands the two electrical double layers in the film (one at the film/oil interface and another at the film/rock interface) and increases the electrostatic repulsion between these two interfaces of the film. As a result, the film becomes thicker, and the rock becomes less oil-wet, leading to oil release and improved recovery. Recent efforts have been made to experimentally measure¹³ and theoretically predict¹⁴ the thickness of brine films in the presence of CO₂ under conditions relevant to subsurface CO₂ injection.

The thermodynamics of thin liquid films have been studied for the past several decades, starting with the pioneering work of Derjaguin.^{15,16} The foundation he developed has been improved by Toshev,¹⁷ Ivanov,¹⁸ Rusanov,¹⁹ de Feijter,²⁰ Hirasaka,²¹ and several others. Many studies focus on flat (uniform thickness) films, although there has also been work on curved films and other types of films with a nonuniform thickness.^{22–26} These studies have done much to further our understanding of thin liquid films. For example, it is now well known that pressure in the film is anisotropic and generally different from the pressure in the corresponding bulk liquid. The augmented Young-Laplace equation and the concept of the disjoining pressure were developed to describe these phenomena. The work done on the film when its area is changed is commonly modeled using a quantity called the film tension.

The past studies have improved our understanding of thin liquid films, but there are some conflicting results that have not been addressed. Two different expressions for the augmented Young equation, which is a condition for mechanical equilibrium, have been proposed in the literature. Similarly,

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two different expressions for the Gibbs energy of thin liquid films have been presented, creating ambiguity over which expression should be used in thermodynamic analyses. This work addresses both of these issues. The Formulation Section establishes the foundation for the rest of our study. It introduces a model system composed of a droplet (which can be treated as a bulk liquid), a flat thin liquid film formed from the droplet, and a surrounding gas phase; all of which are contained in an isothermal, closed container. We derive both expressions for the augmented Young equation in the Mechanical Equilibrium and the Augmented Young Equation Section and show that the two are equivalent for films that can be idealized under certain conditions. The Thermodynamic Relations for Thin Liquid Films Section examines the appropriate physical context in which the two proposed Gibbs energy functions may be applied. We show that each of the two functions has a unique physical interpretation and fulfills specific roles. For example, only one of the Gibbs energies can be used to determine the equilibrium state in the general case when the work involving the film tension is nonzero. We conclude with a summary of our main results in the Conclusions Section.

Formulation

System description

We consider a liquid droplet resting on a flat, smooth, and chemically homogeneous solid surface. The solid surface forms part of the walls of a nondeformable container that encloses the droplet and a surrounding gas phase. After the droplet is placed on the surface, part of it may eventually spread out to form a thin liquid film that wets the surface. The droplet changes shape during this process.^{27,28} When thermodynamic equilibrium is eventually established, the film ceases spreading and the droplet assumes a definite shape with a contact angle θ that is defined with respect to the extrapolated surface of the film. Both the droplet and the film are not necessarily axisymmetric in shape. It is instructive to compare the typical physical dimensions of the droplet and the film in the equilibrium state. The droplet may be large enough to be visible to the naked eye. In contrast, the film thickness h is less than 100 nanometers (nm), and usually less than 10 nm, in many studies that have examined thin liquid films on smooth surfaces.^{13,14,21,27,28} However, the horizontal dimensions of the film (i.e., the extent to which it spreads out away from the base of the droplet) are at least tens of microns large²⁷ and may be on the order of millimeters. Taking into account the great disparity between the film's thickness and its horizontal dimensions, we idealize the film as being uniform in thickness so that its volume is $V^f = hA^f$. This idealization has been used by many authors.^{17,18,20,29–32} In accordance with Ref. 33, the flat film covers the entire solid surface on which it rests. We define our system to be the entire contents of the closed container. This includes the liquid droplet (l), the thin liquid film (f) formed by the droplet, the gas (g) surrounding the droplet and film, and three interfaces between the bulk phases: liquid-gas (lg), liquid-solid (ls), gas-solid (gs). All interfaces in this study are treated as Gibbs dividing surfaces of zero volume. The system is isothermal and nonreactive. We also neglect the influence of external fields like gravity and treat the droplet and the film as being sufficiently large enough that we may neglect line tension effects. A two-dimensional cross section of our system is depicted in Figure 1. For clarity, the thickness of the film has been exaggerated in the figure.

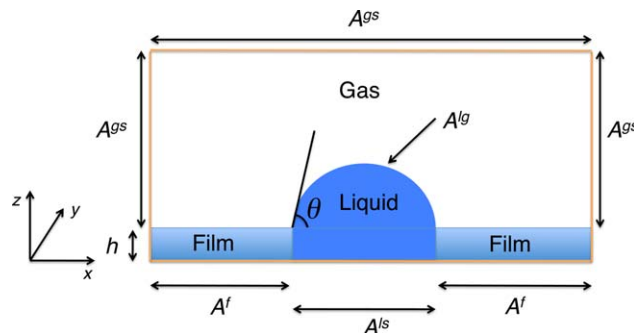


Figure 1. Two-dimensional cross section of our system.

It is not necessarily axisymmetric. It consists of two bulk phases (the droplet l and the gas g), the thin liquid film (f), and three interfaces that separate the bulk phases: liquid-gas (lg), liquid-solid (ls), gas-solid (gs). All of these fluids are held inside an isothermal, closed container. The film is characterized geometrically by its thickness h , area A_f , and volume $V_f = hA_f$. It covers the entire solid surface on which it rests. The contact angle θ forms at the liquid-film-gas contact line. The horizontal double-headed arrows represent the portions that contribute to the interfacial areas or to A_f . For clarity, h has been exaggerated in this figure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Pressure anisotropy, disjoining pressure, and the augmented Young–Laplace equation

Because we explicitly consider only the three interfaces that separate the bulk phases, the region labeled as the film in Figure 1 includes not only its body, which we refer to as the film volume, but also the four interfaces that separate the film volume from the rest of the system. Since the film is thin, we neglect the contribution to the film's internal energy from its two lateral interfaces and consider only the contribution from the film-gas and film-solid interfaces. These two interfaces are parallel to each other and separated by a distance h . Each is defined by an area A^f . The small thickness allows the film-gas and film-solid interfaces to be sufficiently close in proximity so that the properties of the film (e.g., density) exhibit spatial heterogeneity.²⁹ The properties of thin flat films generally depend on z . The pressure in the film is also anisotropic and can be described by a second-order Cartesian tensor $\mathbf{P}$ with diagonal components $P_{xx}^f, P_{yy}^f, P_{zz}^f$ and vanishing off-diagonal components. We denote P_{zz}^f as P_n^f , since it gives the pressure normal to the film-gas interface. It has been shown for flat films that P_n^f does not have any spatial dependence while $P_{xx}^f(z) = P_{yy}^f(z)$ is a function of only z .²⁹ We briefly discuss that derivation here because we will use some of the results in our work. The interfacial balance of momentum normal to the static liquid-gas interface or film-gas interface yields the Young-Laplace equation

$$P_n - P^g = 2\gamma\kappa \quad (1)$$

where P_n is the normal pressure on the liquid or film side of the interface, P^g is the gas phase pressure, γ is the interfacial tension, and

$$\kappa = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

is the mean curvature defined by the two principal radii of curvature R_1 and R_2 . Since $P_n = P^I$ in the droplet, the Young–

Laplace equation for the liquid-gas interface states that $P^l - P^g = 2\gamma^{lg}\kappa$. The film-gas interface in our study is flat ($\kappa = 0$) so that upon applying (1), we obtain $P_n^f(z=h) = P^g$. For the hydrostatic thin liquid film, the Navier–Stokes equation simplifies to

$$\nabla \cdot \mathbf{P} = 0$$

which is a vector equation that leads to three separate scalar equations

$$\frac{\partial P_{xx}^f}{\partial x} = 0 \quad (3)$$

$$\frac{\partial P_{yy}^f}{\partial y} = 0 \quad (4)$$

$$\frac{\partial P_z^f}{\partial z} = 0 \quad (5)$$

The geometry of the film allows it to be thought of as a planar sheet of finite thickness h and horizontal dimensions much larger than h . Symmetry requires that all pressure components be independent of x and y [this is consistent with (3) and (4)] and that $P_{xx}^f(z) = P_{yy}^f(z)$ for all z . We represent $P_{xx}^f(z)$ and $P_{yy}^f(z)$ by a single pressure $P_t^f(z)$, where the subscript t is chosen because $P_t^f(z)$ gives the pressure along directions that are tangent to the film-gas interface. Equation 5 combined with the previously derived relation $P_n^f(z=h) = P^g$ require that P_n^f be uniform throughout the film and equal to gas-phase pressure P^g . This result shows that even though the film is formed from the droplet, its normal pressure is different from the bulk liquid pressure P^l . To describe this phenomena, Derjaguin^{15,16} introduced the concept of the disjoining pressure Π , which he defined as the excess normal pressure in a liquid film

$$\Pi(h) = P_n - P^l \quad (6)$$

The disjoining pressure is a locally defined quantity whose magnitude sharply decreases with the local thickness of the film because the interactions between the film-gas and film-solid interfaces become weaker with increasing separation. If the film is of uniform thickness, its disjoining pressure is everywhere equal to $P^g - P^l$. The film's thickness is therefore a reflection of the difference between the two bulk phase pressures. The definition in (6) can also be applied to the droplet with the understanding that its "thickness" (the distance between the liquid-gas and liquid-solid interfaces) is everywhere sufficiently large that $\Pi = 0$. In other words, the entire droplet is described by an isotropic pressure P^l .

On a macroscopic scale, the pressure from the properties of the film to those of the bulk liquid appears to be abrupt. On a scale comparable with the film thickness, however, this transition occurs gradually.^{21,29} Figure 2a shows that on this scale (we choose a representative value of $h = 10$ nm), there exists a transition zone between the film and the bulk liquid.^{34–36} The bulk liquid and gas phases are described by isotropic pressures P^l and P^g , respectively. The pressure in the transition zone is anisotropic, with the normal pressure P_n and the tangential pressures P_t being generally unequal to each other and unequal to P^l . We therefore have three liquid regions (the bulk, the transition zone, and the film) where the normal pressure in each region is different from the normal pressure in the other two regions. Nevertheless, P_n in all three regions can be related to P^g by a single, unified equation. We may substitute the definition (6) of the disjoining pressure into (1) to obtain

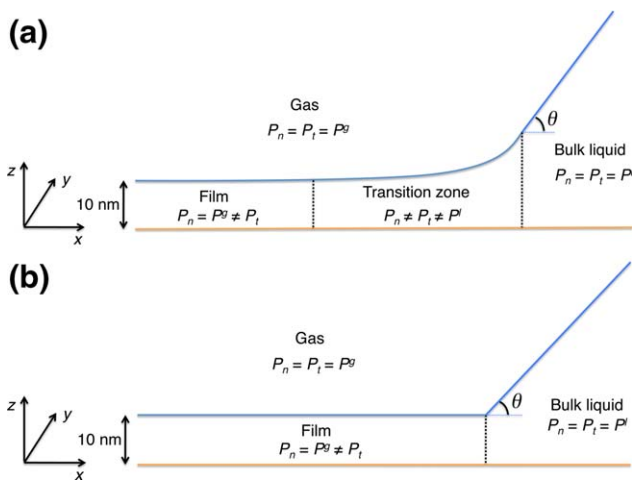


Figure 2. Two-dimensional cross section of the system near the liquid-film-gas contact line at a scale comparable with h .

The curvature of the liquid-gas interface is not noticeable at this scale. The bulk liquid and gas phases are described by isotropic pressures P^l and P^g , respectively. The pressure is anisotropic in the film and in the transition zone. We represent the anisotropy by denoting the pressure normal to the interface as P_n , and the pressures tangent to the interface as P_t . The uniform thickness model approximates the real behavior in (a) with the idealized picture in (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$P^l - P^g = 2\gamma\kappa - \Pi(h) \quad (7)$$

This result is called the augmented Young–Laplace equation and was first proposed by Derjaguin.¹⁵ Applied to the bulk liquid where $\gamma = \gamma^{lg}$ and $\Pi = 0$, Equation 7 becomes the traditional Young–Laplace equation. Applied to the flat film where $\kappa = 0$, Eq. 7 simplifies to $\Pi = P^g - P^l$. For the transition zone, (7) is equivalent to (1), where γ and P_n refer to the local interfacial tension and the local normal pressure, respectively.

The augmented Young–Laplace equation, which is derived purely from mechanical considerations, serves as a check on the consistency of our results. The conditions for mechanical equilibrium derived in the Mechanical Equilibrium and the Augmented Young Equation Section must be consistent with (7). We make one additional simplification. Because the transition zone is typically much smaller in x and y than the other two liquid regions, the uniform thickness model approximates the real behavior depicted in Figure 2a with the idealized picture illustrated in Figure 2b. The approximation avoids the difficulties in modeling the transition zone, where $P_n = P_n(x, y, z)$ and $P_t = P_t(x, y, z)$ may be complicated functions of the spatial coordinates.

Film thickness, work, and energy

We have stated that the internal energy of the film is equal to the internal energy of the film volume (f_v) plus the internal energies of the film-gas (f_g) and film-solid (f_s) interfaces. More generally, any extensive property E^f of the film (except for the area A^f) can be written as $E^f = E^{f_v} + E^{f_g} + E^{f_s}$. In accordance with Gibbs' treatment, the film-gas and film-solid interfaces have zero volume and are described by interfacial tensions γ^{fg} and γ^{fs} , respectively. The work done on the interfaces in an

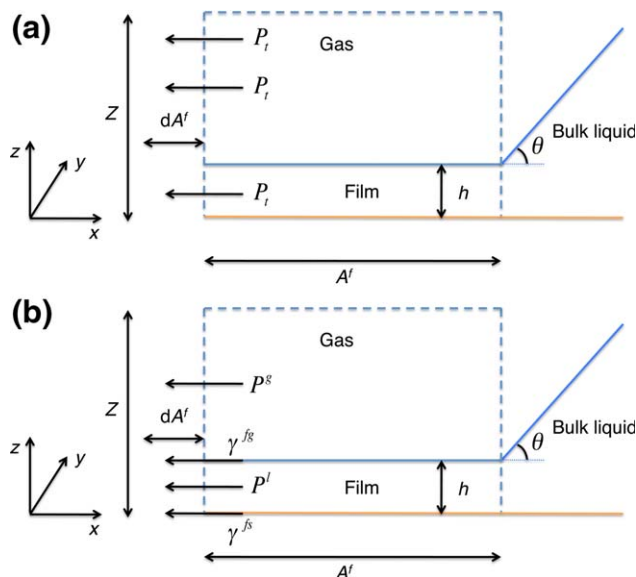


Figure 3. The dashed lines depict an imaginary partition of the system. The work required to expand the portion of the system inside the partition by dA^f is given by the integral on the left-hand side of (8). The film thickness h is defined so that (a) is mechanically equivalent to (b), as expressed by (8). The “excess tangential pressure” is encoded in the interfacial tensions γ^{fg} and γ^{fs} . To be consistent with this figure, the properties of the film are defined according to (11) and (12).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

infinitesimal process are $\gamma^{fg}dA^f$ and $\gamma^{fs}dA^f$. In the film volume, there is only pressure-volume (PV) work. Following the studies of Amirfazli³² on wetting films and de Feijter on free thin liquid films,²⁹ we define h so that the PV work done on the film volume in changing the film’s area by dA^f is mechanically equivalent to what it would be if the contents of the film volume were replaced with bulk liquid. Let Z represent a distance along z that is sufficiently large to ensure that the properties at Z are homogeneous (i.e., located in the bulk gas phase). As illustrated in Figure 3, mechanical equivalence is achieved if

$$-\left[\int_0^Z P_t(z)dz\right]dA^f = -P^l h dA^f + \gamma^{fg}dA^f + \gamma^{fs}dA^f - P^g(Z-h)dA^f \quad (8)$$

which can be rearranged to

$$\gamma^{fg} + \gamma^{fs} = -\int_0^h [P_t(z) - P^l]dz - \int_h^Z [P_t(z) - P^g]dz \quad (9)$$

With the thickness defined in this manner, the work done on the film in changing its area by dA^f is

$$(\gamma^{fg} + \gamma^{fs})dA^f - P^l h dA^f \quad (10)$$

The extensive properties $E^f = E^{fv} + E^{fg} + E^{fs}$ of the film are defined to be consistent with (8) and (9). In the region near the film, the volumetric density e of an extensive function E varies with z , so we may write

$$E^{fg} + E^{fs} = A^f \left\{ \int_0^h [e(z) - e^l]dz + \int_h^Z [e(z) - e^g]dz \right\} \quad (11)$$

$$E^{fv} = e^l V^f \quad (12)$$

In addition to (10), there is also work done on the film in changing its thickness by dh . This work is

$$-P_n^f A^f dh \quad (13)$$

The differential of the internal energy of the film as a whole is $dU^f = dU^{fv} + dU^{fg} + dU^{fs}$. Combining (10) and (13), dU^f during a reversible process is

$$dU^f = T^f dS^f - P_n^f A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h)dA^f + \sum_{k=1}^c \mu_k^f dN_k^f \quad (14)$$

where T^f is the temperature of the film, S^f is the entropy, μ_k^f is the chemical potential of component k in the film, N_k^f is the moles of k , and c is the number of components. The internal energy (14) can be decomposed into a film-volume contribution dU^{fv} and a surface excess contribution $d(U^{fg} + U^{fs})$ represented by

$$\begin{aligned} dU^{fv} &= T^f dS^{fv} - P^l dV^f + \sum_{k=1}^c \mu_k^f dN_k^{fv} \\ d(U^{fg} + U^{fs}) &= T^f d(S^{fg} + S^{fs}) - \Pi A^f dh \\ &\quad + (\gamma^{fg} + \gamma^{fs})dA^f + \sum_{k=1}^c \mu_k^f d(N_k^{fg} + N_k^{fs}) \end{aligned} \quad (15)$$

The differential of the Helmholtz energy $F^f = U^f - T^f S^f$ of the film is

$$dF^f = -S^f dT^f - P_n^f A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h)dA^f + \sum_{k=1}^c \mu_k^f dN_k^f \quad (16)$$

Thermal and phase equilibrium

The system in Figure 1 is isothermal, constrained in size by a constant-volume container, and closed to the surroundings so that the conditions for thermodynamic equilibrium are obtained by minimizing the Helmholtz energy F of the system.³⁷ Since F is an extensive property, it can be expressed as a sum of the Helmholtz energy of its constituent subsystems

$$F = F^l + F^g + F^f + \sum_i F^i, \quad i = lg, ls, gs$$

A necessary condition for the minimum of F is

$$dF = dF^l + dF^g + dF^f + \sum_i dF^i = 0 \quad (17)$$

for all processes that cause an infinitesimal change in the system’s state variables. For a reversible process

$$dF^l = -S^l dT^l - P^l dV^l + \sum_{k=1}^c \mu_k^l dN_k^l \quad (18)$$

$$dF^g = -S^g dT^g - P^g dV^g + \sum_{k=1}^c \mu_k^g dN_k^g \quad (19)$$

$$dF^i = -S^i dT^i + \gamma^i dA^i + \sum_{k=1}^c \mu_k^i dN_k^i \quad (20)$$

where V is the volume, and γ^i is the interfacial tension of interface i . The system is isothermally constrained at a temperature T and is closed so that

$$dT^l = dT^g = dT^f = dT^i = 0, \quad i = lg, ls, gs \quad (21)$$

$$dN_k^l = -dN_k^g - dN_k^f - \sum_i dN_k^i, \quad k = 1, \dots, c \quad (22)$$

Substituting (16) and (18)–(22) into (17), we obtain

$$\begin{aligned} dF = & -P^l dV^l - P^g dV^g - P_n^f A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h) dA^f + \sum_i \gamma^i dA^i \\ & + \sum_{k=1}^c (\mu_k^g - \mu_k^l) dN_k^g + \sum_{k=1}^c (\mu_k^f - \mu_k^l) dN_k^f + \sum_i \sum_{k=1}^c (\mu_k^i - \mu_k^l) dN_k^i = 0 \end{aligned} \quad (23)$$

Because the differentials dN_k^g , dN_k^f , and dN_k^i , are independent of each other, we have

$$\mu_k^l = \mu_k^g = \mu_k^f = \mu_k^i, \quad i = lg, ls, gs, \quad k = 1, \dots, c \quad (24)$$

The conditions for thermodynamic equilibrium in our system include spatial uniformity of the temperature (thermal equilibrium) and the chemical potential of each component (phase equilibrium). We now proceed to derive the conditions for mechanical equilibrium, which is our last, but least trivial, set of conditions for thermodynamic equilibrium.

Mechanical Equilibrium and the Augmented Young Equation

The augmented Young equation proposed by Amirfazli

In the absence of a film, the contact angle θ formed when a droplet contacts a bare solid surface immersed in a gas is described by the well-known Young equation, which is a condition for mechanical equilibrium of the system. If the droplet forms a film as in Figure 1, mechanical equilibrium is instead described by an augmented Young equation that takes into account the effect of the film on the contact angle. For flat thin liquid films, two different expressions for the augmented Young equation have been proposed in the literature. Amirfazli³² obtains

$$\gamma^{lg} \cos \theta = \gamma^{fs} + \gamma^{fg} - \gamma^{ls} \quad (25)$$

In this section, we use the concept of virtual work to derive (25). Virtual work is widely used in analytical mechanics^{38,39} and has also been used for thermodynamic minimization problems by Gibbs and others.^{30,36,40,41} This concept forms the framework of Li and Neumann's study on thin liquid films,³⁰ but our work differs from theirs in that they represent the film in terms of only the surface excess so that their expression for the differential of the internal energy is given by (15) instead of (14). In The augmented Young equation proposed by Hirasaki Section, we extend the analysis to derive the other augmented Young equation proposed in the literature and show that it is equivalent to (25) under the conditions described in that section.

Equations (23) and (24) together require that

$$-P^l dV^l - P^g dV^g - P_n^f A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h) dA^f + \sum_i \gamma^i dA^i = 0 \quad (26)$$

This result states that the work done on the subsystems during an infinitesimal, reversible process must sum to zero. The system is constrained in total volume so that $d(V^l + V^g + V^f) =$

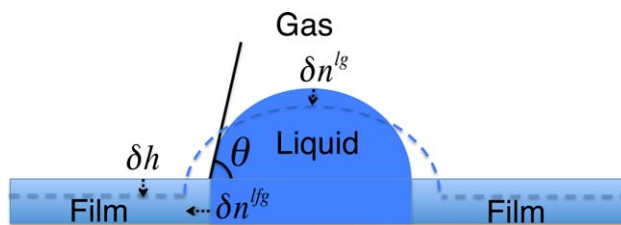


Figure 4. The three virtual displacements (δn^{lg} , δh , and δn^{lf}) are admissible with the constraint of a constant-volume container. The resultant shape of the droplet and film after the displacements is shown with dashed lines. From the sign convention described in the text, δn^{lg} and δh are negative, but δn^{lf} is positive.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0 and $d(A^f + A^{ls} + A^{gs}) = 0$. Substituting these constraints into (26), we have

$$\begin{aligned} & (P^g - P^l) dV^l + (P^g - P_n^f) A^f dh \\ & + [(\gamma^{fg} + \gamma^{fs} - P^l h) - \gamma^{gs} + P^g h] dA^f + (\gamma^{ls} - \gamma^{gs}) dA^{ls} + \gamma^{lg} dA^{lg} = 0 \end{aligned} \quad (27)$$

Some of the differentials in (27), such as dV^l and dA^{lg} , may be related to each other in a complicated way. The differentials correspond to real displacements in the system that occur during the reversible process. For our problem, we focus on the virtual work associated with virtual displacements, which are infinitesimal perturbations in the system's configuration consistent with the mechanical constraints. The virtual displacements in our system must be consistent with the constraint that the total volume is a constant. An alternative, but equivalent condition to (27) is that the virtual work due to the virtual displacements within the system must sum to zero. Figure 4 shows the three virtual displacements considered in The augmented Young equation proposed by Amirfazli Section. We represent displacements normal to the liquid-gas interface, film-gas interface, and liquid-film-gas contact line as δn^{lg} , δh , and δn^{lf} , respectively. We use the sign convention where $\delta n^{lg} > 0$ if the displacement is directed away from the droplet, $\delta h > 0$ if h increases, $\delta n^{lf} > 0$ if the displacement is directed away from the bulk liquid.

The virtual work associated with δn^{lg} is

$$\begin{aligned} & - \int_{A^{lg}} P^l \delta n^{lg} dA^{lg} - \int_{A^{lg}} P^g (-\delta n^{lg}) dA^{lg} + \int_{A^{lg}} 2\gamma^{lg} \kappa \delta n^{lg} dA^{lg} \\ & = \int_{A^{lg}} (P^g - P^l + 2\gamma^{lg} \kappa) \delta n^{lg} dA^{lg} \end{aligned} \quad (28)$$

The first two integrals on the left-hand side of (28) represent the pressure-volume work done on the liquid and gas phases, while the third represents the interfacial work from the change in the surface area of the liquid-gas interface due to the displacement δn^{lg} . The expression for this interfacial work may be derived formally using differential geometry, but it can also be understood from Figure 5. The virtual work associated with δh is

$$-P_n^f A^f \delta h - P^g A^f (-\delta h) = (P^g - P_n^f) A^f \delta h \quad (29)$$

The virtual work associated with δn^{lf} is

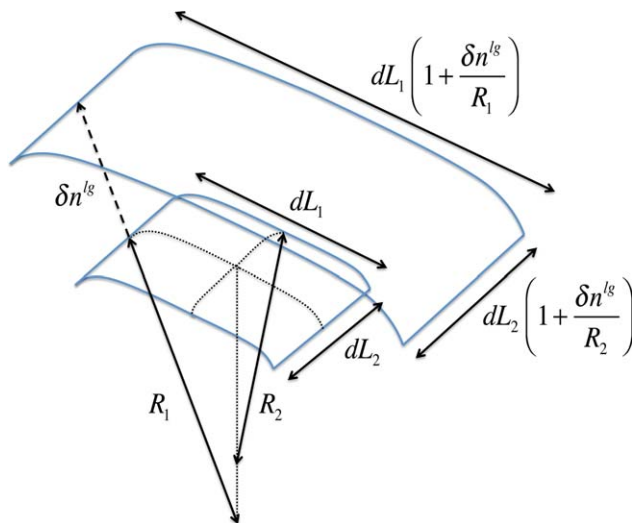


Figure 5. Sketch of a differential element of the liquid-gas interface (defined by radii of curvature R_1 and R_2) and the resultant shape of the element after the virtual displacement δn^{lg} is applied.

Before undergoing the displacement, the area of the element is approximately $dL_1 dL_2$. After the displacement, the element becomes deformed so that its area is approximately $dL_1(1 + \delta n^{lg}/R_1) dL_2(1 + \delta n^{lg}/R_2)$, which simplifies to $(1 + 2\kappa \delta n^{lg}) dL_1 dL_2$ if the quadratic term in δn^{lg} is neglected.⁴² The mean curvature κ is defined in (2). Thus, the displacement δn^{lg} maps an area dA^{lg} of the interface to an area $(1 + 2\kappa \delta n^{lg}) dA^{lg}$. This reasoning justifies the expression for the interfacial work term in (28). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\begin{aligned} & \int_{L^{lg}} \gamma^{ls} \delta n^{lg} dL^{lg} + \int_{L^{fg}} \gamma^{fg} (-\delta n^{fg}) dL^{fg} + \int_{L^{fs}} \gamma^{fs} (-\delta n^{fs}) dL^{fs} \\ & + \int_{L^{fg}} \gamma^{lg} \cos \theta \delta n^{fg} dL^{fg} - \int_{L^{fg}} P^l h \delta n^{fg} dL^{fg} - \int_{L^{fg}} P^l h (-\delta n^{fg}) dL^{fg} \\ & = \int_{L^{fg}} [-(\gamma^{fg} + \gamma^{fs}) + \gamma^{lg} \cos \theta + \gamma^{ls}] \delta n^{fg} dL^{fg} \end{aligned} \quad (30)$$

where dL^{fg} is the length of a differential element of the liquid-film-gas contact line (Figure 6). The first integral on the left-hand side is the interfacial work from the change in the liquid-solid interfacial area A^{ls} . This is coupled with the interfacial work done on the film in changing A^f (the second and third integrals). The integral $\int_{L^{fg}} \gamma^{lg} \cos \theta \delta n^{fg} dL^{fg}$ is the work done on the liquid-gas interface, where $\gamma^{lg} \cos \theta$ is the force in the direction of the displacement δn^{fg} per unit length of the liquid-film-gas contact line. The last two integrals on the left-hand side of (30) are the pressure-volume work terms (with differential volume element $h \delta n^{fg} dL^{fg}$) of the bulk liquid and the film volume, respectively.

Mechanical equilibrium requires that the right-hand sides of (28)–(30) sum to zero. However, because the three virtual displacements are independent of each other, each of the right-hand sides individually must be zero. As a result, we obtain three conditions for mechanical equilibrium

$$P^l - P^g = 2\gamma^{lg} \kappa \quad (31)$$

$$P_n^f = P^g \quad (32)$$

$$\gamma^{lg} \cos \theta = \gamma^{fg} + \gamma^{fs} - \gamma^{ls} \quad (33)$$

The Young–Laplace equation for the liquid-gas interface is expressed in (31). Equation (32) shows that equilibrium requires $P_n^f = P^g$ so that the disjoining pressure in the film is $\Pi = P^g - P_n^f$. Both (31) and (32) are consistent with the augmented Young–Laplace equation 7 discussed earlier. Equation 33 is the augmented Young equation (25) presented by Amirfazli.³²

Note that for a single-component fluid the Kelvin equation can be derived based on (21), (24), and (31), and making the assumptions that the gas phase is ideal and the liquid in the droplet is incompressible.² In that case, the equilibrium droplet will be oversaturated. However, oversaturation applies only to single-component fluids. It may not apply to multicomponent, nonideal mixtures, such as the ones considered in our study.²

The augmented Young equation proposed by Hirasaki

Hirasaki⁴³ has suggested, but has not derived, an augmented Young equation of the form

$$\gamma^{lg} \cos \theta = \gamma^{gs} - \gamma^{ls} - \Pi h \quad (34)$$

Through a simple extension of the previous section, we may show that (34) is compatible with (25) for flat films with volume $V^f = hA^f$ that terminate before the film reaches the edge of the solid surface. This idealized geometry can be relaxed by considering films of nonuniform thickness that terminate gradually at their edges. Yeh et al. have derived an augmented Young equation for such films.^{23,24} Up until now, we have considered the film to cover the entire solid surface on which it rests (see Figure 1).

To examine systems where there may be a flat film which does not cover the entire solid surface, let us consider a

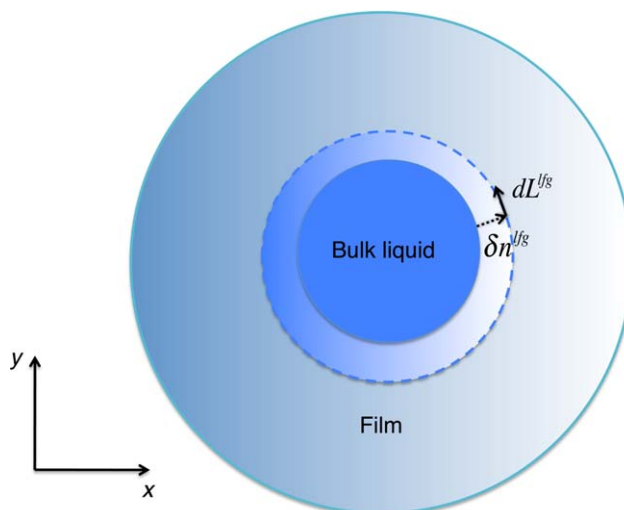


Figure 6. Overhead view of the system, where for clarity we depict the droplet as being spherical and the thin liquid film as being cylindrical.

The discussion in the text applies in the general case of more complicated shapes. The change in the area A^{ls} of the liquid-solid interface due to the virtual displacement δn^{lg} is $\int_{L^{lg}} \delta n^{lg} dL^{lg}$, which is represented by the annulus between the dashed curve and the bulk liquid. This annulus is also equal to minus the change in the area A^f of the film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thought experiment where we have an ensemble of systems, each of which is composed of a droplet made of a nonvolatile liquid surrounded by a gas phase placed inside an isothermal, closed container. The premise is that the contact angle θ is an equilibrium measure of the wettability of the liquid droplet to the solid surface. For sufficiently large droplets (those for which line tension and other size-dependent effects are negligible), the value of θ depends only on the temperature, the pressure of the surrounding gas phase, and the equilibrium chemical composition (identity) of the liquid droplet, film, gas, and solid. The value of θ should be independent of the size of the container. Suppose that the temperature, gas phase pressure, and the equilibrium composition of the droplet, film, gas, and solid are the same in all systems of the ensemble. The only difference among the systems is the size of the container and thus the area of the solid surface on which the droplet and film rest. As each system proceeds toward equilibrium, the film spreads until the equilibrium value of θ is established. Since the liquid is nonvolatile, the total mass of the liquid in the droplet plus the film is fixed. This requirement, when coupled with the fact that the equilibrium value of θ is the same in all the systems, means that there is a limit L to the lateral extent to which the film can spread. In practice, L may be on the order of centimeters for a droplet with a micron-sized radius. In all systems of the ensemble whose lateral dimensions of the container are larger than L , the film will terminate before it reaches the edge of the solid surface. If we model the film as terminating abruptly so that it maintains a uniform thickness h , we will overestimate the volume of the film by a negligible fraction that is on the order of $h/L \ll 1$.

If we consider a system that is the same as in Figure 1, except that now the film does not cover the entire solid surface, the conditions for mechanical equilibrium may be obtained from the four virtual displacements depicted in Figure 7. Three of the displacements (δn^{lg} , δh , and δn^{lf}) in this figure are the same ones examined in Figure 4, so all of the results we have derived up until now continue to be valid. In addition, we now include δn^{fgs} , which represents a virtual displacement of the film-gas-solid contact line. We define $\delta n^{fgs} > 0$ if the displacement is directed away from the film. Following the same reasoning as we did for (30), we may show that the virtual work associated with δn^{fgs} is

$$\begin{aligned} & \int_{L^{fgs}} \gamma^{fg} \delta n^{fgs} dL^{fgs} + \int_{L^{fgs}} \gamma^{fs} \delta n^{fgs} dL^{fgs} + \int_{L^{fgs}} \gamma^{gs} (-\delta n^{fgs}) dL^{fgs} \\ & - \int_{L^{fgs}} P^l h \delta n^{fgs} dL^{fgs} - \int_{L^{fgs}} P^g h (-\delta n^{fgs}) dL^{fgs} \\ & = \int_{L^{fgs}} [(\gamma^{fg} + \gamma^{fs} - P^l h) - \gamma^{gs} + P^g h] \delta n^{fgs} dL^{fgs} \end{aligned} \quad (35)$$

where dL^{fgs} is the length of a differential element of the film-gas-solid contact line. As a result, the system in Figure 7 is described by four conditions for mechanical equilibrium: (31)–(33), plus an additional fourth condition that we obtain from setting the integrand in (35) equal to zero

$$\gamma^{fg} + \gamma^{fs} = \gamma^{gs} - (P^g - P^l)h \quad (36)$$

Equation 36 is a mechanical equilibrium condition that must be satisfied for the film to cease spreading. Substituting (36) and the identity $\Pi = P^g - P^l$ into (33) yields the augmented Young equation 34 proposed by Hirasaki.⁴³ Thus, the two

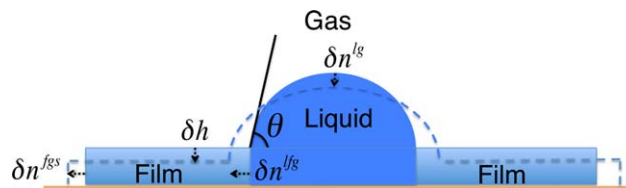


Figure 7. The four virtual displacements (δn^{lg} , δh , δn^{lf} , and δn^{fgs}) are admissible with the constraint of a constant-volume container. The resultant shape of the droplet and film after the displacements is shown with dashed lines. The displacement δn^{fgs} is allowed if the film does not cover the entire solid surface (see the discussion in the text).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

expressions (25) and (34) that have appeared in the literature are equivalent for thin liquid films that can be modeled as described in this section.

As a check on our results, we now show that (36) together with (31)–(33) form a self-consistent set of conditions for mechanical equilibrium. The disjoining pressure in a thick film (on smooth and flat surfaces, we may consider a film to be thick if $h > 100 \text{ nm}$ ²⁴) is virtually zero because, as we have mentioned previously, the disjoining pressure sharply decreases in magnitude with h . The properties of the thick film resemble those of the bulk liquid so that $\gamma^{fg} = \gamma^{lg}$ and $\gamma^{fs} = \gamma^{ls}$. Equation 33 in the large thickness limit requires that $\cos \theta = 1$, which implies $\theta = 0^\circ$. Physically, this means that a thick film can be possible only if the liquid droplet is completely wetting so that it spreads to become flat in shape. Since the disjoining pressure in the thick film is zero, we have from (32) that $P_n^f = P^g = P^l$. From (31), $P^g = P^l$ only if the droplet is flat ($\kappa = 0$). In the large thickness limit, (36) can be written as $\gamma^{lg} = \gamma^{gs} - \gamma^{ls}$, which is the form of the Young equation for a flat (i.e., film-shaped) droplet.

Film tension

According to (14), the work done on the film is $-P_n^f A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h) dA^f$. Since $P_n^f = P^g$ in flat films, this expression may be written as

$$\begin{aligned} & -P^g A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h) dA^f \\ & \gamma^f = \gamma^{fg} + \gamma^{fs} + \Pi h \end{aligned} \quad (37)$$

It is convenient in thermodynamic analysis to divide the work into a dV^f term and a dA^f term. Traditionally,^{17,29,32,36} this has been done by defining a film tension γ^f so that

$$-P^g A^f dh + (\gamma^{fg} + \gamma^{fs} - P^l h) dA^f = -P^g dV^f + \gamma^f dA^f \quad (38)$$

Combining (9) and (37), we have

$$\gamma^f = - \int_0^z [P_t(z) - P^g] dz$$

The definition (37) of the film tension is analogous to the expression $\gamma^f = 2\gamma^{fg} + \Pi h$ that has been derived for free thin liquid films.^{17,18,20,29,31} These are films where instead of resting on a solid surface, they are surrounded by the gas phase on both of their parallel interfaces.

We can express Amirfazli's augmented Young equation 25 and the mechanical equilibrium condition (36) in terms of the film tension by substituting (37) into these equations to obtain

$$\gamma^{lg} \cos \theta = \gamma^f - \gamma^{ls} - \Pi h \quad (39)$$

$$\gamma^f = \gamma^{gs} \quad (40)$$

respectively. Equation 40 is a direct consequence of the equivalence between the augmented Young equations 39 proposed by Amirfazli and (34) proposed by Hirasaki. It states that at equilibrium, the thickness h of the film assumes a value so that γ^f , which is a function of h , is balanced at the edge of the film by the gas-solid interfacial tension γ^{gs} . If γ^{gs} is modified (such as by changing the identity of the solid surface), the thickness of the film changes so that (40) remains satisfied.

As we have noted previously, (36) and (40) are not general results that apply to all thin liquid films. They apply only to flat films that terminate before reaching the edge of the solid surface. Examples of such films may be the thin alkane films considered by Li and Neumann.³⁰ They present correlations for $\gamma^{fg} + \gamma^{fs}$ (their study labels this sum as γ^f) and γ^{gs} in terms of experimentally measurable quantities like γ^{lg} and θ . Using experimental data for four different alkane (decane, dodecane, tetradecane, and hexadecane) films that wet siliconized glass surfaces, their correlations show that in all four cases, $\gamma^{fg} + \gamma^{fs}$ is virtually equal to γ^{gs} . Li and Neumann state the mean curvature κ to be 1000 m^{-1} , and γ^{lg} for the alkanes are in the range $23\text{--}28 \text{ mJ/m}^2$ so that the magnitude of the disjoining pressure $|\Pi| = |P^g - P^l| = 2\gamma^{lg}\kappa$ is approximately 50 Pa . Since the thickness of the films are assumed to be less than 100 nm ,³⁰ the product Πh is at least four orders of magnitude smaller than $\gamma^{fg} + \gamma^{fs}$, which are calculated to be between 23 and 25 mJ/m^2 , depending on the particular alkane considered. Thus, Li and Neumann's correlations imply that $\gamma^f = \gamma^{fg} + \gamma^{fs} + \Pi h$ is virtually equal to γ^{gs} , in agreement with (40).

Thermodynamic Relations for Thin Liquid Films

Two expressions for the Gibbs energy

In this section, we discuss the relation between the Gibbs energy and the internal energy (i.e., the Legendre transform between the two functions) of thin liquid films. As we will soon see, the form of this relation has not been clearly resolved in the literature. We start by combining (38) and (14) to obtain the differential of a thin liquid film's internal energy U^f

$$dU^f = T^f dS^f - P^g dV^f + \gamma^f dA^f + \sum_{k=1}^c \mu_k^f dN_k^f \quad (41)$$

The internal energy is an Euler homogeneous function of the extensive variables⁴⁴ whose differential we integrate to obtain

$$U^f = T^f S^f - P^g V^f + \gamma^f A^f + \sum_{k=1}^c \mu_k^f N_k^f \quad (42)$$

Four other common thermodynamic energy functions of a thin liquid film are its Helmholtz energy F^f , grand potential Ω^f , enthalpy, and Gibbs energy. For reasons that will soon become clear, we do not assign the last two functions a symbol for now. There is agreement that

$$F^f = U^f - T^f S^f \quad (43)$$

$$\Omega^f = U^f - T^f S^f - \sum_{k=1}^c \mu_k^f N_k^f = F^f - \sum_{k=1}^c \mu_k^f N_k^f \quad (44)$$

$$\text{Enthalpy} = \text{Gibbs energy} + T^f S^f \quad (45)$$

Thus, (42)–(45) provide four equations for the five functions U^f , F^f , Ω^f , enthalpy, and Gibbs energy. An equation that expresses the Gibbs energy in terms of U^f (or alternatively, enthalpy in terms of U^f) is needed to completely specify these functions. Two different expressions for the Gibbs energy of a film have appeared in the literature. According to Iyota et al.⁴⁵ and Toshev,⁴⁶ the Gibbs energy is

$$G^f = \sum_{k=1}^c \mu_k^f N_k^f \quad (46)$$

so that the relation between G^f and U^f is

$$G^f = U^f - T^f S^f + P^g V^f - \gamma^f A^f = F^f + P^g V^f - \gamma^f A^f \quad (47)$$

In this expression, the chemical potentials take on their familiar role as the partial molar Gibbs energy, as shown in (46). de Feijter⁴⁷ provides a different expression for the film's Gibbs energy

$$\mathcal{G}^f = \gamma^f A^f + \sum_{k=1}^c \mu_k^f N_k^f = G^f + \gamma^f A^f \quad (48)$$

where we denote this alternative expression as $\mathcal{G}^f$. The difference between G^f and $\mathcal{G}^f$ is the $\gamma^f A^f$ term that appears due to the film tension work $\gamma^f dA^f$, which is a type of non-pressure-volume (non-PV) work. The relation (48) requires that

$$\mathcal{G}^f = U^f - T^f S^f + P^g V^f = F^f + P^g V^f \quad (49)$$

Eriksson and Toshev⁴⁸ also express the Gibbs energy according to (49). Ikeda et al. use both G^f and $\mathcal{G}^f$ in a parallel manner in their study.⁴⁹ The studies above present the Gibbs energy in a matter-of-fact way, with no physical justification for why a particular expression is chosen. As a result, there is ambiguity over which of the two functions should be used in thermodynamic analyses. The goal of this section is to clarify this fundamental issue by discussing the appropriate physical context in which each of the two proposed expressions may be applied.

To gain a deeper appreciation of the historical background to the problem we have posed, we briefly consider the simpler, but analogous problem of writing the Gibbs energy of a system where there is only one interface. Thin liquid films are more complicated because they have more than one interface of interest. A typical example of a single-interface system is the interface that separates a gas bubble from a surrounding bulk liquid. This liquid-gas interface, which we treat as a Gibbs dividing surface of area A^{lg} and zero volume, is assigned properties that represent excess quantities. There is no controversy over how to express the Gibbs energy of the gas and bulk liquid phases, but there is discrepancy in the literature over how to write the Gibbs energy of the interface. Just like for thin liquid films, two different expressions have appeared

$$G^{lg} = U^{lg} - T^{lg} S^{lg} - \gamma^{lg} A^{lg} = \sum_{k=1}^c \mu_k^{lg} N_k^{lg} \quad (50)$$

$$\mathcal{G}^{lg} = U^{lg} - T^{lg} S^{lg} = \gamma^{lg} A^{lg} + \sum_{k=1}^c \mu_k^{lg} N_k^{lg} \quad (51)$$

where γ^{lg} is the interfacial tension. As in the case of thin liquid films, the ambiguity arises because of non-PV work.

For the liquid-gas interface, the non- PV work is the interfacial work $\gamma^{lg} dA^{lg}$. The Gibbs energy in (51) is the same as the Helmholtz energy F^{lg} of the interface, which is defined as $F^{lg} = U^{lg} - T^{lg} S^{lg} = G^{lg}$. Equation 51 is the expression for the Gibbs energy recommended by Alberty, although he also recognizes (50) to be a valid expression.⁵⁰ His study considers not only interfacial work, but several other types of non- PV work (e.g., work done by electric, magnetic, and gravitational fields). He recommends to write the Gibbs energy as $U - TS + PV$ for all systems, presumably to keep this relation invariant with respect to the different types of non- PV work. In the case of the liquid-gas interface where $V^{lg} = 0$, Alberty's recommendation simplifies to (51). Equation 50 is the expression for the Gibbs energy adopted by the International Union of Pure and Applied Chemistry (IUPAC), as described in the IUPAC manual published by Everett in 1972.⁵¹ Everett states firmly in this manual that (50) is the only way to express the Gibbs energy of the interface. In (50), the chemical potentials are equivalent to the partial molar Gibbs energy. Some authors present the two expressions (50) and (51) in a parallel manner.⁵² Thus, despite several decades of studies, the relation between the Gibbs energy and the internal energy of single-interface systems has still not been clearly resolved.

Our analysis of thin liquid films can be understood more clearly by considering the case of bulk fluids, where the Gibbs energy defined as $G = U - TS + PV$ is used for two types of calculations. One purpose is to determine the equilibrium state of the system. Specifically, the equilibrium state of a closed system at constant (T, P) with only PV work is found by minimizing G .³⁷ The other purpose of G is to calculate the reversible non- PV work obtainable from the system. For a closed system at constant (T, P) with both PV and non- PV work, $-dG$ equals the maximum differential amount of non- PV work that can be done by the system. It is because of this physical interpretation that G was for a long time known as, and is still sometimes called, the "Gibbs free energy." Of these two purposes, the Gibbs energy is far more commonly used to determine the equilibrium state than to calculate the reversible non- PV work.

The Gibbs energy of thin liquid films is used for the same two types of calculations. We show in the rest of this section that whether we should apply G^f in (47) or $\mathcal{G}^f$ in (49) in thermodynamic analyses is univocally determined by what we wish to compute with the Gibbs energy. In particular, G^f must be used if our goal is to determine the equilibrium state through an energy minimization. This is true regardless of whether the film is closed (see next paragraph) or is part of a larger system and can exchange matter and energy with the rest of the system (see the Equilibrium in systems containing thin liquid films Section). We will show that, except in a very specialized case, it is not correct to use $\mathcal{G}^f$ in determining equilibrium states. Nevertheless, $\mathcal{G}^f$ can still be useful because its differential indicates the maximum amount of film tension work (i.e., non- PV work) that can be done by the film.

In analogy to the case described above for bulk fluids, we may show that since G^f in (47) is a natural function of $(T^f, P^g, \gamma^f, \mathbf{N}^f)$, where $\mathbf{N}^f = (N_1^f, N_2^f, \dots, N_c^f)$ represents the mole numbers of all species in the film, G^f is a minimum at equilibrium for a closed film held at constant (T^f, P^g, γ^f) . This may be demonstrated in the same way that we may prove the analogous statement for bulk fluids.³⁷ We start by writing the energy balance and entropy balance of a closed film, which state

$$dU^f = \delta Q^f - P^g dV^f + \gamma^f dA^f \quad (52)$$

$$dS^f = \delta Q^f / T^f + dS_{\text{gen}}^f \quad (53)$$

respectively. In these equations, δQ^f is the heat flow across the boundaries of the film, $-P^g dV^f + \gamma^f dA^f$ is the work done on the film, and dS_{gen}^f is the entropy generated in the film by irreversible processes. According to the second law of thermodynamics, $dS_{\text{gen}}^f \geq 0$. Combining (52) and (53), we obtain

$$dU^f - T^f dS^f + P^g dV^f - \gamma^f dA^f = -T^f dS_{\text{gen}}^f \leq 0 \quad (54)$$

At constant (T^f, P^g, γ^f) , the left-hand side of (54) equals dG^f so that

$$dG^f = -T^f dS_{\text{gen}}^f \leq 0$$

This result shows that under conditions of constant (T^f, P^g, γ^f) , the Gibbs energy G^f always either decreases or remains the same, depending on whether the heat flow and work done on the film occur irreversibly or reversibly. Therefore, at the equilibrium state, which is characterized by the cessation of all irreversible processes, G^f is a minimum.

We may follow the same reasoning as in the preceding paragraph to show that since $\mathcal{G}^f$ in (49) is a natural function of $(T^f, P^g, A^f, \mathbf{N}^f)$, $\mathcal{G}^f$ is a minimum at equilibrium for a closed film held at constant (T^f, P^g, A^f) . However, constant A^f implies that the film tension work $\gamma^f dA^f$ is constrained to be zero. Thus, $\mathcal{G}^f$ cannot be used to determine the equilibrium state of the film in the general case when $\gamma^f dA^f$ is nonzero. Nevertheless, $\mathcal{G}^f$ still has a physically meaningful interpretation: for a closed film at constant (T^f, P^g) , the maximum amount of film tension work $\gamma^f dA^f$ obtainable from the film is $-d\mathcal{G}^f$. To show this, we substitute $\mathcal{G}^f$ into (54) and rearrange the result to get

$$-\gamma^f dA^f = -d\mathcal{G}^f - T^f dS_{\text{gen}}^f \quad (55)$$

Note that $d\mathcal{G}^f \neq -T^f dS_{\text{gen}}^f$ (i.e., $\mathcal{G}^f$ is not necessarily a minimum at equilibrium) unless $dA^f = 0$ so that the film tension work is zero. Since $\gamma^f dA^f$ represents the film tension work done on the film, $-\gamma^f dA^f$ is the film tension work done by the film. For a reversible process, $dS_{\text{gen}}^f = 0$, and (55) simplifies to $-\gamma^f dA^f = -d\mathcal{G}^f$. For an irreversible process, $-\gamma^f dA^f < -d\mathcal{G}^f$ since $-T^f dS_{\text{gen}}^f < 0$. Therefore, the film tension work done by the film is always less than or equal to the amount $-d\mathcal{G}^f$ obtainable from a reversible process. In this sense, $\mathcal{G}^f$ gives an indication of the free energy available in the film.

Equilibrium in systems containing thin liquid films

If a thin liquid film is part of a larger system and the equilibrium state of the total system is obtained by minimizing the Gibbs energy of the total system, the film's Gibbs energy must be expressed as G^f and not $\mathcal{G}^f$. As an example, let us define the total system to be all of the fluid held inside the isothermal container depicted in Figure 1, where the container walls are subject to a constant external pressure P . The film in the system considered here is not closed. It can exchange matter and energy with the rest of the system. Also, since the film tension γ^f is a function of the thickness h of the film, the constraint of constant γ^f described previously requires that the work done on the film involves only changes in the area A^f and not in h . This restriction of constant γ^f does not apply to the film considered here. The only constraints are that the container is closed, its contents are held at a constant temperature T , and the only work done on the system by the surroundings is the

PV work due to the external pressure P . As a result, we may write $U=TS-PV+\sum_{k=1}^c \mu_k N_k$, where U, S, V, N_k are the internal energy, entropy, volume, and moles of component k , respectively, of the total system. Note that from simply examining the natural variables of G^f and G^i , we cannot resolve which of the two functions should be used, because none of the variables N^f, A^f , and γ^f are fixed.

Since the total system is closed, isothermal, and surrounded by a constant external pressure, the Gibbs energy $G=U-TS+PV=\sum_{k=1}^c \mu_k N_k$ of the total system is a minimum at equilibrium. Furthermore, by setting $dG=0$, we can show that one of the conditions for equilibrium is that the chemical potential μ_k must be constant throughout the system for all components k .^{37,44,53} We have stated that the system can be divided into six subsystems: the bulk liquid, the gas, the thin liquid film, and the three interfaces i where $i=lg, ls, gs$. The equilibrium state is obtained by minimizing $G=\sum_{k=1}^c \mu_k N_k$, where $N_k=N_k^l+N_k^g+N_k^f+\sum_i N_k^i$ is the total number of moles of component k . Since G is an extensive function, another way to express G is the sum of the Gibbs energies over all the subsystems. The objective is to define the Gibbs energy of the subsystems in a way so that the total Gibbs energy G is equal to $\sum_{k=1}^c \mu_k N_k$ when subject to the equilibrium condition $\mu_k^l=\mu_k^g=\mu_k^f=\mu_k^i=\mu_k$ for all k and $i=lg, ls, gs$.

It is clear that in order for the sum of the Gibbs energies over all constituent subsystems to be equal to $\sum_{k=1}^c \mu_k N_k$, the chemical potential μ_k must equal the partial molar Gibbs energy with respect to component k in all subsystems. For the bulk liquid and gas phases, this requirement is in agreement with the widely recognized relations $G^l=U^l-T^l S^l-P^l V^l=\sum_{k=1}^c \mu_k N_k^l$ and $G^g=U^g-T^g S^g-P^g V^g=\sum_{k=1}^c \mu_k N_k^g$. As we have discussed, the issue is over how to relate the Gibbs energy of the thin liquid film and the interfaces to their internal energy, since unlike the bulk phases, these subsystems are described by non-PV work. From our arguments, it is clear that the Gibbs energy of the film at equilibrium must be $G^f=U^f-T^f S^f+P^s V^f-\gamma^f A^f=\sum_{k=1}^c \mu_k N_k^f$, and the Gibbs energy G^i of interface i must be

$$G^i=U^i-TS^i-\gamma^i A^i=\sum_{k=1}^c \mu_k N_k^i, \quad i=lg, ls, gs \quad (56)$$

If we were to write the Gibbs energy of the film and the interfaces with the alternative expressions $G^f=\gamma^f A^f+\sum_{k=1}^c \mu_k N_k^f$ and $G^i=\gamma^i A^i+\sum_{k=1}^c \mu_k N_k^i$, the sum of the Gibbs energies over all the subsystems would not be equal to $\sum_{k=1}^c \mu_k N_k$ (which is the quantity that is actually a minimum at equilibrium)

$$G^l+G^g+G^f+\sum_i G^i=\gamma^f A^f+\sum_i \gamma^i A^i+\sum_{k=1}^c \mu_k N_k \neq \sum_{k=1}^c \mu_k N_k$$

Thus, for the purposes of determining the equilibrium state, the Gibbs energy of the thin liquid film and interface i are given unambiguously by G^f in (46) and G^i in (56), respectively, in which the chemical potentials are equivalent to the partial molar Gibbs energies. Our analysis is in agreement with the procedure employed in molecular dynamics simulations for computing the equilibrium state of isothermal, closed systems subject to only PV work from the surroundings with a constant external pressure.⁵⁴ For all such systems (regardless of whether they are single phase, multiphase, contains a thin liquid film, etc.), the equilibrium state is found by minimizing the quantity $\sum_{k=1}^c \mu_k N_k$, which represents the Gibbs energy

of the system. Quantities that arise from non-PV work that may occur internally within the system, such as interfacial tensions and film tensions, are not involved in the energy minimization.

Enthalpy and generalization to systems with other types of non-PV work

Once the Gibbs energy is established, the enthalpy becomes fixed because it is related to the Gibbs energy via (45). If the Gibbs energy is expressed as $G^f=U^f-T^f S^f+P^s V^f-\gamma^f A^f$, the enthalpy is

$$H^f=G^f+T^f S^f=U^f+P^s V^f-\gamma^f A^f=T^f S^f+\sum_{k=1}^c \mu_k^f N_k^f$$

Substituting H^f into the energy balance (52) yields the relation $dH^f=dQ^f$ for closed films at constant (P^s, γ^f) . This result is analogous to the expression $dH=dQ$ for a closed system consisting of a bulk fluid that is subject to only PV work at constant P , where $H=U+PV$ is the enthalpy of the bulk fluid. The relation $dH=dQ$ is widely used in thermal science, especially in thermochemistry. If the Gibbs energy is instead expressed as $G^f=U^f-T^f S^f+P^s V^f$, the enthalpy is

$$\mathcal{H}^f=G^f+T^f S^f=U^f+P^s V^f=T^f S^f+\gamma^f A^f+\sum_{k=1}^c \mu_k^f N_k^f$$

Substituting $\mathcal{H}^f$ into (52) leads to the relation $d\mathcal{H}^f=\gamma^f dA^f$ for adiabatic, closed films at constant P^s . The analysis of the Gibbs energy and enthalpy that we have presented completes the specification of five commonly used thermodynamic energy functions of thin liquid films: U^f, F^f, Ω^f , enthalpy, and Gibbs energy. Other thermodynamic relations for thin liquid films can be derived from these functions. One such important relation is the Gibbs–Duhem equation

$$d\gamma^f=-\frac{S^f}{A^f}dT^f+hdP^s-\sum_{k=1}^c \frac{N_k^f}{A^f}d\mu_k^f$$

which is obtained by taking the differential of (42) and comparing the result to (41). The Gibbs–Duhem equation can be used to derive the Gibbs adsorption equation for the film^{29,36} and the Derjaguin–Frumkin equation that relates the disjoining pressure in the film to the contact angle.^{16,19,55}

Our analysis can be readily adapted to systems with other types of non-PV work where there is ambiguity regarding the Gibbs energy and the enthalpy. In all cases, it is straightforward to write the Helmholtz energy and the grand potential in terms of the internal energy. This is because the Helmholtz energy and the grand potential are related to the internal energy through Legendre transforms that do not involve work variables like pressure. The Gibbs energy and the enthalpy are more complicated because they involve Legendre transforms of the work variables. As we have illustrated for thin liquid films and interfaces, the issue is whether to include the non-PV work variables in the Legendre transform. Suppose, we have a system where there is non-PV work that may be represented as XdY , where X is an intensive variable (e.g., film tension, gravitational potential, and electrostatic potential) and Y is an extensive variable (e.g., area, mass, and electric charge). If the internal energy U of the system is

$$U = TS - PV + XY + \sum_{k=1}^c \mu_k N_k$$

where the symbols have their usual meaning, two expressions for the Gibbs energy may be proposed

$$G = U - TS + PV - XY = \sum_{k=1}^c \mu_k N_k \quad (57)$$

$$\mathcal{G} = U - TS + PV = XY + \sum_{k=1}^c \mu_k N_k \quad (58)$$

Following the reasoning above, it can be shown that G is a minimum at equilibrium for the system if it is closed and held at constant (T, P, X) . Furthermore, $\mathcal{G}$ cannot be used to determine the equilibrium state in closed systems because $\mathcal{G}$ is not a minimum at equilibrium, except in the special case when $dY = 0$ (i.e., when there is no non- PV work in the first place). More generally, if a system with $X dY$ work is part of a larger, closed, isothermal system subject to a constant external pressure, Eq. 57, and not (58), should be applied in the Gibbs energy minimization for computing the equilibrium state of the total system. This is because in equilibrium state calculations, the Gibbs energy of all subsystems must be defined so that the chemical potentials μ_k are equal to the partial molar Gibbs energies in all subsystems. This requirement is clearly not satisfied by $\mathcal{G}$ in (58). Nevertheless, $\mathcal{G}$ gives an indication of the free energy available since $-d\mathcal{G}$ represents the maximum amount of $X dY$ work obtainable at constant (T, P) . Thus, whether we should work with G or $\mathcal{G}$ is unambiguously determined by what we wish to compute with the Gibbs energy. Similar statements can be made for the role of enthalpy.

Conclusions

We have addressed two sets of conflicting results in the literature regarding the thermodynamics of flat thin liquid films. One of the two main topics in our study involves the augmented Young equation, for which two different expressions, (25) and (34), have been proposed in the literature. By applying the definition (37) of the film tension γ^f , (25) can be cast in the alternative, but equivalent form (39). We have shown that (25) [or (39)] and (34) are equivalent for thin liquid films that can be idealized as described in The augmented Young equation proposed by Hirasaki Section. Our analysis is based on the framework developed by Li and Neumann,³⁰ which uses the concept of virtual work. For films where (25) and (34) are equivalent, one of the implications is (40), which states that at equilibrium the film thickness h must assume a value so that $\gamma^f = \gamma^f(h)$ is balanced at the edge of the film by the gas-solid interfacial tension γ^{gs} . This condition for mechanical equilibrium is consistent with other widely accepted equilibrium conditions (31)–(33). It is also in agreement with the conclusions reached by Li and Neumann, who have developed correlations that can be used to calculate γ^f and γ^{gs} . Using experimental data presented in their study, their correlations show that γ^f is virtually equal to γ^{gs} for the systems considered by the experiments.

The second main topic addressed in our study concerns the Gibbs energy and enthalpy of thin liquid films. Two different expressions for the Gibbs energy, G^f in (46) and $\mathcal{G}^f$ in (48), have appeared in the literature, creating ambiguity over which expression should be used in thermodynamic analyses. The underlying reason for this issue is that for systems which

undergo non- PV work, it is unclear whether to include non- PV work variables in the Legendre transforms that relate the Gibbs energy and the enthalpy to the internal energy. This complexity is not present in thermodynamic functions like the Helmholtz energy and the grand potential, since the Legendre transforms that relate them to the internal energy do not involve work variables. In thin liquid films, the non- PV work is the film tension work, which can be expressed as $\gamma^f dA^f$. We have shown that to determine the equilibrium state via minimization of the Gibbs energy, G^f must be used. The function G^f has the important property that its partial molar quantities are equivalent to the chemical potentials. In equilibrium state calculations, G^f must be used regardless of whether the film is closed (see the Two expressions for the Gibbs energy Section) or is part of a larger system and can exchange matter and energy with the rest of the system (see the Equilibrium in systems containing thin liquid films Section). In contrast, $\mathcal{G}^f$ is not useful for determining equilibrium states. Rather, it indicates the free energy available in the film because $-d\mathcal{G}^f$ represents the maximum amount of film tension work that can be done by the film. Thus, whether we should apply G^f or $\mathcal{G}^f$ in thermodynamic analyses is uniquely determined by what we wish to compute with the Gibbs energy. Similar statements can be made regarding the enthalpy of thin liquid films, which is related to the Gibbs energy via (45). Our analysis can be readily generalized to systems with other types of non- PV work where there is ambiguity regarding the expression and interpretation of the Gibbs energy and the enthalpy.

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