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Thermodynamics of Thin Films and Three-Phase Contact Regions

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SUMMARY

The classical, equilibrium thermodynamic relationships for a film of one fluid phase between two similar or dissimilar fluid or solid phases are derived. The results differ from the conventional Gibbs approach in that the distance separating the interfaces, that is, the film thickness, is now a thermodynamic variable. In particular, the interfacial tensions are functions of film thickness. The change in the interfacial tensions can be expressed in terms of the disjoining pressure. The spreading coefficient can be expressed as an integral of the disjoining pressure. It can then be used to determine the macroscopic contact angle of the three-phase contact region. Additional relationships that are derived are the augmented Laplace-Young equation for the pressure drop across a fluid–fluid interface, the augmented Gibbs adsorption equation, and the augmented Kelvin equation for capillary condensation and/or multilayer adsorption.

The condition for the equilibrium coexistence of films of different thicknesses is derived. The local stability of a film is examined at constant temperature and chemical plus gravitational potential by the use of the interaction potential, Ω. The gravitational potential and surface curvature are introduced to show their effect on the film tension, spreading coefficient, and contact angle. Film elasticity is derived for an equilibrium film.

Most measurement methods and prediction models of the disjoining pressure are limited to thicknesses greater than several monolayer thickness. Adsorption isotherms provide measurement methods and prediction models down to zero thickness. It will be shown that the adsorption isotherms can be used to extend the disjoining pressure isotherms down to zero thickness. The relationship between the initial spreading coefficient, equilibrium spreading coefficient, and film pressure is given.

I. INTRODUCTION

Wettability has been recognized as an important factor in remaining oil saturation, capillary pressure curves, and relative permeability curves. This chapter describes some of the physics of the contact angle between mineral surfaces, water, oil, and gas. Description of a particular system will require a chemical description of the mineral, brine, and oil. While the wettability of a rock–brine–oil system cannot be described by a single contact angle, it is the multitude of contact angles at the various three-phase contact regions in the pore spaces that determine the wettability of the system. Description of wettability will require a morphological description of the pore space with the contact angles as a boundary condition for the fluid distribution. However, regardless of the morphology, the wettability will be dependent on the contact angles.

In this chapter, the thermodynamics of thin films and the three-phase contact region is reviewed. The shape of the meniscus/film transition region is discussed in a following chapter.

During the 1930s, a previously unrecognized "surface force" was discovered when one dimension of a fluid phase became sufficiently small (~0.1 μm). The name of the theory describing the phenomenon, the DLVO theory [1, 2], is attributed to its discoveries, Dergajuin and Landau from the Soviet Union and Verwey and Overbeek from The Netherlands. The primary forces are the electrostatic forces and the London–van der Waals forces. Other forces, described as structural or solvation forces and hydrophobic interactions, are currently under investigation.

The greatest success of this theory was in explaining the stability of lyophobic (solvent-fearing) colloids. It has also advanced the understanding of thin films and wetting (three-phase contact region) phenomena.

The DLVO theory recognizes that when one dimension of a fluid phase becomes sufficiently small, it no longer has the properties of a homogeneous phase. Thus, the thermodynamic functions must include this dimension when it becomes sufficiently small. This dimension will be referred to in this work as the thickness. There is a lower limit of thickness where it is still practical to apply the DLVO theory. When the thin phase becomes a monolayer or sub-monolayer, the thickness can be replaced by a surface excess concentration in these very thin films and the DLVO theory can be augmented by theories of adsorption.

Since 1960, numerous articles have described the thermodynamics of thin films and the three-phase contact region [3–24]. The treatment is best summarized in reference 3. It is the purpose of this report to organize the thermodynamics of these systems by assuming that the thickness of a phase is a thermodynamic variable and deducing the consequence of this assumption using thermodynamic principles [25–27].

The thermodynamic analysis of thin films follows the development of Gibbs [25] with several important differences. This analysis considers a pair of Gibbs dividing surfaces with the distance of separation denoted by the thickness h. When Gibbs considered a single dividing surface, it was possible to define a pair of imaginary surfaces that are near the dividing surface but "at such a distance as to lie entirely beyond the influence of the discontinuity in its vicinity" (p. 220). If the thickness of a film becomes sufficiently small, it is no longer possible to define such a surface in the interior of the film once the regions of influence of the interfaces (surfaces of discontinuity) overlap. Thus, Gibb's analysis loses its validity once the film thickness becomes sufficiently small.

Gibbs suggested that the contradiction between his analysis and the observed stability of vertical soap films was due to a gelatinous

condition of the film. An alternative explanation is proposed in the present work. The basic premise in the following analysis is that when the thickness of a film becomes sufficiently small for the regions of interaction of the pair of interfaces to overlap, the internal energy of the system is a function of the thickness. It will be shown that the consequence of this premise is that, at equilibrium, the interfacial and film tensions of a thin film are functions of thickness. Furthermore, a vertical film can be in mechanical and chemical equilibrium with respect to all of its components.

The gravitational field is included from the outset. This has required the inclusion of the gravitational potential [27] along with the chemical potential (electrochemical potential, to be more general) in the energy balance. Guggenheim [27] clarifies the definition of a phase in a gravitational field: "Since a phase was defined as completely homogeneous in its properties and state, two portions of matter of identical temperature and composition must be considered as different phases if they are differently situated with respect to a gravitational field. It follows that the mere presence of a gravitational field excludes the possibility of a phase of a finite depth in the direction of the field. In the presence of a gravitational field even the simplest possible kind of system must be considered as composed of a continuous sequence of phases each differing infinitesimally from its neighbors."

The derivation of the Gibbs–Duhem equation requires the integration of the extensive parameters at fixed values of the intensive parameters. As pointed out by Guggenheim, this will require a fixed value of the gravitational potential.

The effects of interfacial curvature and gravitational field are included in the following analysis. The inclusion of these two parameters allows a change in the film thickness at a fixed value of the electrochemical plus gravitational potentials. This freedom is required when evaluating the three-phase contact region of an equilibrium system. Prior analysis that considered neither curvature nor gravitational potential required a change in the chemical potential in order to have a change in film thickness.

The additional degree of freedom with curvature can be illustrated for the case of vapor-liquid equilibrium of a single component system. According to Gibb's phase rule, there is only on degree of freedom when both phases coexist. For example, there is a unique relation between temperature and pressure. Now consider a system in which the interfacial curvature is a parameter. There are now two degrees of freedom. For example, there is a relation between the pressure and curvature at a fixed temperature described by the Kelvin equation. If, in addition, the film thickness is a thermodynamic variable, there will be three degrees of freedom for a thin, curved, single component film in equilibrium with its vapor. This augmented Kelvin equation will be derived in the following.

Prior stability analysis [25] considered the amount rather than chemical potential of one or two components held fixed in the film. This is justified when the film extends to infinity and these components are not present in either bulk phase. The present analysis considers the case in which all of the components have fixed chemical plus gravitational potential. This condition is justified in systems in which the thin film is connected to the same phase in bulk and on a time scale that is sufficient for the components to reach equilibrium by diffusion. Nonequilibrium processes can be studied as special cases in which the amount of certain components rather than the chemical potential is held fixed.

Adsorption isotherms provide the measurement methods and models for films down to zero thickness. In the following, the relation between adsorption isotherms and disjoining pressure isotherms will be developed.

The absence of any discussion of the statistical thermodynamics of thin films and three-phase contact region is not due to absence of activity in this area but rather to the unfamiliarity of the writer with the subject. The reader is referred to the book by Rowlinson and Widom [37] and the book edited by Ivanov [3] for a discussion of this subject.

II. ANALYSIS

A. Treatment of a Film as Two Gibbs Dividing Surfaces

The approach of using two Gibbs dividing surfaces [14–18] was originated by Rusanov (1966) [14]. He makes the following distinction between thick films and thin films:

> . . . by definition, a thick film is a combination of a layer of volume phase bounded by surface layers on both sides, and is characterized by additivity of all the extensive properties (including energy) of these three constituent parts. When we pass to thin films, additivity of certain properties breaks down owing to interactions of the two surface layers. In particular, in a thin film the energy of the surface layers is not additive, because the potential energy of their interaction cannot be assigned to either of the surface layers separately, thus the distinction between thick and thin films lies in the fact that the two surfaces of a thick film may be considered independently of each other, whereas in the case of a thin film such separation is impossible.

The disjoining pressure is a force (per unit area) that tends to separate two interfaces when it is positive and tends to attract two interfaces when it is negative. In order to treat the disjoining pressure as a thermodynamic quantity from which other quantities such as film tension, contact angle, spreading coefficient, and adhesion energy can be derived, it is necessary to give an exact thermody-

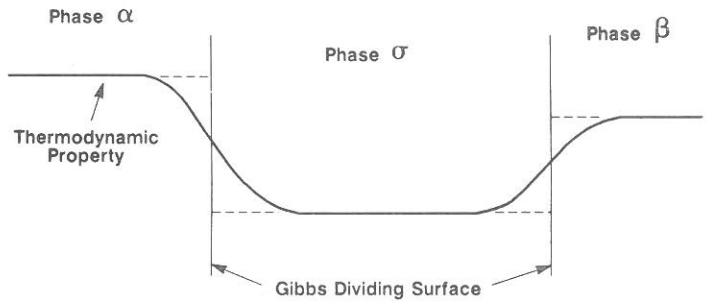

FIG. 1 Interfacial region for thick film where regions of inhomogeneity do not overlap.

namic definition. The starting point for deriving the disjoining pressure is J. W. Gibb's treatment of interfaces between phases.

Figure 1 is a schematic profile of a thermodynamic property across three phases. There is a gradient of the property when going from one phase to another in the interfacial region. Gibbs described how to define a dividing surface such that the thermodynamic property can be treated as if it is equal to the value of the homogeneous, bulk phase up to the dividing surface, and the difference between this step profile and the actual profile can be assigned to a surface excess quantity for this thermodynamic property. For example, if the thermodynamic property is energy, then the surface excess energy is the interfacial or surface tension. When the two interfaces on Fig. 1 are far enough apart such that the thermodynamic property in the middle phase reaches the homogeneous bulk phase value, then the surface excess quantities are independent of the distance of separation. For example, the interfacial tensions will be independent of the thickness of the middle phase. Such a system will be called a thick film, and disjoining pressure is not a consideration.

Figure 2 is a schematic profile of a thermodynamic property when the thickness of the middle phase is such that the inhomogeneous regions of the two interfacial regions overlap, and there is no homogeneous region in the middle phase. This will be called a thin film. In this case, the surface excess quantity for each of the interfaces will not be the same as that for Fig. 1. In particular, where does the inhomogeneous region of one interface end and that for the other begin? In this case, the interfacial tensions are a function of the film thickness and the choice of the location where one inhomogeneous region ends and the other begins. Since the surface excess quantities are a function of the film thickness, the film thickness should be a thermodynamic variable. The differential of the excess energy (difference between total energy and the sum of the energy of each

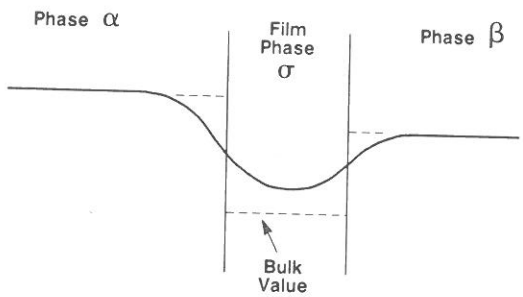

FIG. 2 Interfacial region for thin film where regions of inhomogeneity overlap.

phase if the phase was homogeneous up to the dividing surface) will then include the partial differential of the excess energy with respect to the thickness multiplied by the differential of the thickness. The partial differential of energy with respect to thickness (a measure of distance) is a force. This force per unit area of the film is called the disjoining pressure. Thermodynamic arguments show that this disjoining pressure is equal to the negative of the partial differential of the sum of the interfacial tensions with respect to thickness at constant temperature and chemical potential. The film tension, spreading coefficient, and contact angle can be expressed as functions of the integral of the disjoining pressure isotherm. The condition for equilibrium in a system with a pair of interfaces results in the inclusion of the disjoining pressure in the Young–Laplace equation.

The distance over which the disjoining pressure is significant is a function of the contributions from the various surface forces. For example, the distances are a fraction of a micrometer for electrostatic forces at low electrolyte concentrations, a few nanometers for van der Waals forces, and a few angstroms for structural forces.

The phases considered are phase σ interposed between phases α and β as shown on Fig. 3. The surfaces between the phases will be identified by Gibbs dividing surfaces. The surfaces can have different curvatures, but it is assumed that the radii of curvature are sufficiently large compared to the interfacial transition region so that the contribution of the curvature to the surface excess energy is not significant [3, 25, 28]. The exact location of each surface can be defined such that the surface excess of the substrate is zero on one surface and the amount of material of the primary component of the film is equal to the distance to the second surface (thickness) multiplied by the bulk phase density. In the case of a symmetric film such as a foam film, the first condition can be replaced with the condition of symmetry. This specification will be utilized when ad-

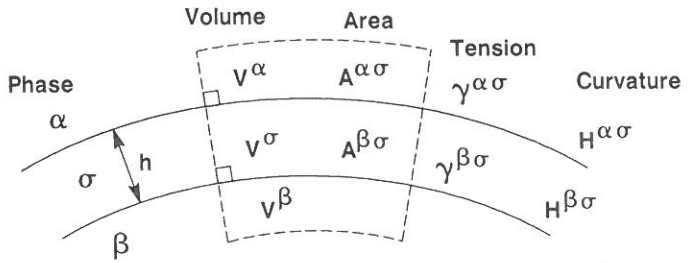

FIG. 3 Representation of a film as two Gibbs dividing surfaces.

sorption isotherms are discussed. The phases will be denoted by superscripts and components by subscripts. The surfaces are denoted by double superscripts and the excess quantities for the pair of surfaces by a pair of double superscripts.

The differential of the energy of the bulk phases and the excess energy, respectively, is given by

$$dU^{j} = T^{j}\,dS^{j} - P^{j}\,dV^{j} + \sum_{i}(\mu_i^{j} + M_i\Phi)\,dn_i^{j} \tag{1}$$

$$j = \alpha,\beta,\sigma$$

and

$$dU^{\alpha\sigma,\beta\sigma} \equiv dU - \sum_{j} dU^{j} \tag{2}$$

$$= T^{\alpha\sigma,\beta\sigma}\,dS^{\alpha\sigma,\beta\sigma} + \sum_{i}(\mu_i^{\alpha\sigma} + M_i\Phi)\,dn_i^{\alpha\sigma} + \sum_{i}(\mu_i^{\beta\sigma} + M_i\Phi)\,dn_i^{\beta\sigma}$$

$$+ \gamma^{\alpha\sigma}\,dA^{\alpha\sigma} + \gamma^{\beta\sigma}\,dA^{\beta\sigma} - A^{f}\Pi\,dh \tag{3}$$

The disjoining pressure is defined as

$$\Pi \equiv -\frac{1}{A^{f}}\left(\frac{\partial U^{\alpha\sigma,\beta\sigma}}{\partial h}\right)_{S^{\alpha\sigma,\beta\sigma},n_i^{\alpha\sigma},n_i^{\beta\sigma},A^{\alpha\sigma},A^{\beta\sigma}} \tag{4}$$

and the film area as

$$A^{f} \equiv \overline{(A^{\alpha\sigma},A^{\beta\sigma})} \tag{5}$$

The film area is a mean value between the areas of the two dividing surfaces. To be exact, it should be defined as the area of the surface of tension. For details the reader is suggested to read the chapter on curved thin films in reference 3. The interfacial tensions in Eq. (3) are the partial derivatives of energy with interfacial area at a fixed value of thickness, entropy, and amount of material. These interfacial tensions are equal to the usual interfacial tension between bulk phases when the thickness becomes large. Equation (3) differs from that found in Gibbs's approach [25] for a pair of noninteracting interfaces by the terms $A^{f}\Pi\,dh$. This term denotes the contribution to the energy due to the change in the distance separating the surfaces (film thickness). The term Π is called the disjoining pressure, for reasons that will become apparent later.

Consider small elements of volume that include the film such that the sides of the elements are perpendicular to the surfaces and the elements have the same gravitational potential. Then $S^{\alpha\sigma,\beta\sigma}$, $n_i^{\beta\sigma}$, $A^{\alpha\sigma}$, and $A^{\beta\sigma}$ are extensive parameters, but not h. Thus, due to the first-order homogeneity property of energy with respect to extensive variables, we have

$$U^{\alpha\sigma,\beta\sigma} = T^{\alpha\sigma,\beta\sigma}S^{\alpha\sigma,\beta\sigma} + \sum_{i}(\mu_i^{\alpha\sigma} + M_i\Phi)n_i^{\alpha\sigma} + \sum_{i}(\mu_i^{\beta\sigma} + M_i\Phi)n_i^{\beta\sigma}$$

$$+ \gamma^{\alpha\sigma}A^{\alpha\sigma} + \gamma^{\beta\sigma}A^{\beta\sigma} \tag{6}$$

with constant Φ.

By differentiating Eq. (6) and subtracting Eq. (3), we have a Gibbs–Duhem type equation:

$$0 = S^{\alpha\sigma,\beta\sigma}\,dT^{\alpha\sigma,\beta\sigma} + \sum_{i} n_i^{\alpha\sigma}\,d\mu_i^{\alpha\sigma} + \sum_{i} n_i^{\beta\sigma}\,d\mu_i^{\beta\sigma}$$

$$+ A^{\alpha\sigma}\,d\gamma^{\alpha\sigma} + A^{\beta\sigma}\,d\gamma^{\beta\sigma} + A^{f}\Pi\,dh \tag{7}$$

at constant Φ.

Using A^{f} to approximate $A^{\alpha\sigma}$ and $A^{\beta\sigma}$, we derive the relationship between the disjoining pressure and the change in the sum of the interfacial tensions with thickness [6, 14]:

$$\Pi = -\left[\frac{\partial(\gamma^{\alpha\sigma} + \gamma^{\beta\sigma})}{\partial h}\right]_{T,\mu,\Phi} + O(Hh) \tag{8}$$

The term 0(Hh) denotes terms that approach zero in proportion to the product, Hh. The term H is defined as the mean curvature of the interface. For a detailed discussion on the effect of curvature on the disjoining pressure, chapter 2 of reference 3 is suggested.

B. Equilibrium Conditions for Film with Two Gibbs Dividing Surfaces [14–18]

Consider a closed system containing phases α, β, and σ and having boundaries perpendicular to the surfaces as shown in Fig. 3. At equilibrium, energy, volume, and amount of substance are conserved and entropy is maximized [26]:

$$dU = \sum_j dU^j + dU^{\alpha\sigma,\beta\sigma} = 0 \tag{9}$$

$$dS = \sum_j dS^j + dS^{\alpha\sigma,\beta\sigma} = 0 \tag{10}$$

$$dV = \sum_j dV^j = 0 \tag{11}$$

and

$$dn_i = \sum_j dn_i^j + dn_i^{\alpha\sigma} + dn_i^{\beta\sigma} = 0 \tag{12}$$

If the interfaces are flat, the area cannot change as a result of a displacement of the interfaces. However, since the interfaces can be curves, we have to consider the change in area with an arbitrary displacement of the interfaces. Denote by $dz^{\alpha\sigma}$ and $dz^{\beta\sigma}$ the displacement of the interfaces (dz is positive for a displacement directed outward from σ, and H is positive for σ concave relative to α or β). We have

$$dA^{\alpha\sigma} = -2H^{\alpha\sigma}A^{\alpha\sigma}\, dz^{\alpha\sigma} \tag{13}$$

$$dA^{\beta\sigma} = -2H^{\beta\sigma}A^{\beta\sigma}\, dz^{\beta\sigma} \tag{14}$$

$$dV^{\alpha} = -A^{\alpha\sigma}\, dz^{\alpha\sigma} \tag{15}$$

$$dV^{\beta} = -A^{\beta\sigma}\, dz^{\beta\sigma} \tag{16}$$

$$dV^{\sigma} = A^{\alpha\sigma}\, dz^{\alpha\sigma} + A^{\beta\sigma}\, dz^{\beta\sigma} \tag{17}$$

and

$$dh = dz^{\alpha\sigma} + dz^{\beta\sigma} \tag{18}$$

Substituing Eqs. (1), (3), and (13)–(18) into Eq. (9) gives

$$\begin{aligned} 0 = {} & \sum_j T^j dS^j + T^{\alpha\sigma,\beta\sigma}\, dS^{\alpha\sigma,\beta\sigma} \\ & + \sum_i \left[\sum_j (\mu_i^j + M_i\Phi)\, dn_i^j + (\mu_i^{\alpha\sigma} + M_i\Phi)\, dn_i^{\alpha\sigma} + (\mu_i^{\beta\sigma} + M_i\Phi)\, dn_i^{\beta\sigma} \right] \\ & + (P^{\alpha} - P^{\sigma} - \Pi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma})A^{\alpha\sigma}\, dz^{\alpha\sigma} \\ & + (P^{\beta} - P^{\sigma} - \Pi - 2H^{\beta\sigma}\gamma^{\beta\sigma})A^{\beta\sigma}\, dz^{\beta\sigma} \\ & + 0(Hhdz) \end{aligned} \tag{19}$$

Equation (19) along with the constraints of Eqs. (10)–(12) yields the equilibrium conditions:

$$T^{\alpha\sigma,\beta\sigma} = T^{\alpha} = T^{\beta} = T^{\sigma} \tag{20}$$

$$\mu_i^{\alpha\sigma} + M_i\Phi = \mu_i^{\beta\sigma} + M_i\Phi = \mu_i^{\alpha} + M_i\Phi = \mu_i^{\sigma} + M_i\Phi = \mu_i^{\beta} + M_i\Phi \tag{21}$$

$$P^{\alpha} - P^{\sigma} = \Pi + 2H^{\alpha\sigma}\gamma^{\alpha\sigma} \tag{22}$$

and

$$P^{\beta} - P^{\sigma} = \Pi + 2H^{\beta\sigma}\gamma^{\beta\sigma} \tag{23}$$

Equations (20) and (21) are the usual conditions for heterogeneous equilibrium. The condition of Eq. (21) is limited to those components and phases in which the amount of material can change. Equations (22) and (23) are the augmented Laplace–Young equations [4, 6]. These latter equations could also have been derived from a force balance [29]. The pressure drop across an interface, called the capillary pressure, now includes a new term, the disjoining pressure [15] term, which differs from zero when the film is sufficiently thin. The role of the disjoining pressure can be illustrated with these equations. Consider the case when the surface curvature is

zero. The disjoining pressure is then the additional pressure (when Π is positive) that the film exerts on the phases α and β as the film is thinned. This pressure (when positive) tends to disjoin the two interfaces. When the disjoining pressure is negative, it tends to contract the film.

In addition to the thermodynamic approach used here, the concept of the disjoining pressure can be developed from mechanical approach introduced by Dergajuin and Kussakov in 1937 [31] and (1939) [32]. In 1955, Dergajuin, in a review paper, defines the concept of the disjoining pressure:

> The disjoining pressure of a plane-parallel layer of liquid situated between any two different or identical phases, is equal to the jump in pressure, $P_e - P_i = P(h)$, which must be assumed to exist at the boundary of separation between the thin layer and either of the phases bordering on it (in which the hydrostatic pressure is equal to P_e), in order that in a condition of equilibrium of the system, the pressure, P_i, in the layer should satisfy the equations of hydrostatics and of capillary theory. The jump in pressure, P(h), should, for a given (planar) system, depend only on the thickness of the layer, h.

Dergajin and Churaev [33] in 1978 described the disjoining pressure in terms of the stress tensor.

> A more general and strict definition of the disjoining pressure applicable to any liquid or gaseous interlayer found between any phases that are in any aggregate state is now introduced; it is that at mechanical equilibrium, the disjoining pressure, $\Pi(h)$, is equal to the difference existing between the component, P_{zz}, of the pressure tensor in the interlayer and the pressure, P_0, set up in the bulk of the phase from which it has been formed by thinning out (Plateau border):
>
> $$\Pi = P_{zz} - P_0 = P_N - P_0$$
>
> In the simplest case of a one-component liquid phase, mechanical equilibrium under isothermal conditions implies thermodynamic equilibrium. In that case, the disjoining pressure is a . . . function of the interlayer thickness, h, and is a . . . thermodynamic characteristic of a thin interlayer which makes it different from the mother bulk phase.

This mechanical approach has been reviewed recently by Mohanty [29] and Teletzke [30]. According to Mohanty,

> The (energy contributions of) intermolecular forces experienced by a volume element in the interior of a thin-film at equilibrium are different from those acting on an identical element in the interior of the bulk phase of the same fluid. Consequently, the state of stress inside a film is different from that in the bulk, and, in fact, it is non-isotropic. Disjoining pressure, Π, is the normal principal stress a film of thickness h has over and above (if $\Pi > 0$) the isotropic pressure of the bulk phase . . . .

Another point of view is taken by Toshev and Ivanov [9], who state,

> We shall prove now that the disjoining pressure is the equilibrium pressure difference between the film and the (bulk phase enclosed by the) meniscus. This result follows directly from the fact mentioned above that the normal component, P_N, of the pressure tensor does not depend on z and must have the same value in the film and in the gas phase, i.e.,
>
> $$P_N = P_f = P_g,$$
>
> P_g being the pressure in the gas phase.

Although the conditions of mechanical equilibrium may be consistent with this assumption, the condition of chemical equilibrium is not satisfied. The difference in pressure between the film and the bulk phase enclosed by the meniscus will result in a difference in the chemical potential between the film and the bulk phase enclosed by the meniscus.

The augmented Laplace–Young equation also describes the relationship between capillary pressure, curvature, and disjoining pressure in the three-phase contact region. Here there is a transition in the curvature of the interface from that of the meniscus to that of the solid substrate. This is illustrated in Figs. 4 and 5.

Subtraction of Eq. (23) from (22) yields the expression for the pressure drop across a curved film:

$$P^{\alpha} - P^{\beta} - 2\,(H^{\alpha\sigma}\gamma^{\alpha\sigma} - H^{\beta\sigma}\gamma^{\beta\sigma}) = 0 \qquad (24)$$

If the two surfaces are parallel, the mean curvatures are equal in magnitude and opposite in sign. This results in the conventional expression for the pressure drop across a curved film [27]. However, it must be recognized that the two interfacial tensions of a sufficiently thin film can be different from the interfacial tensions between bulk phases.

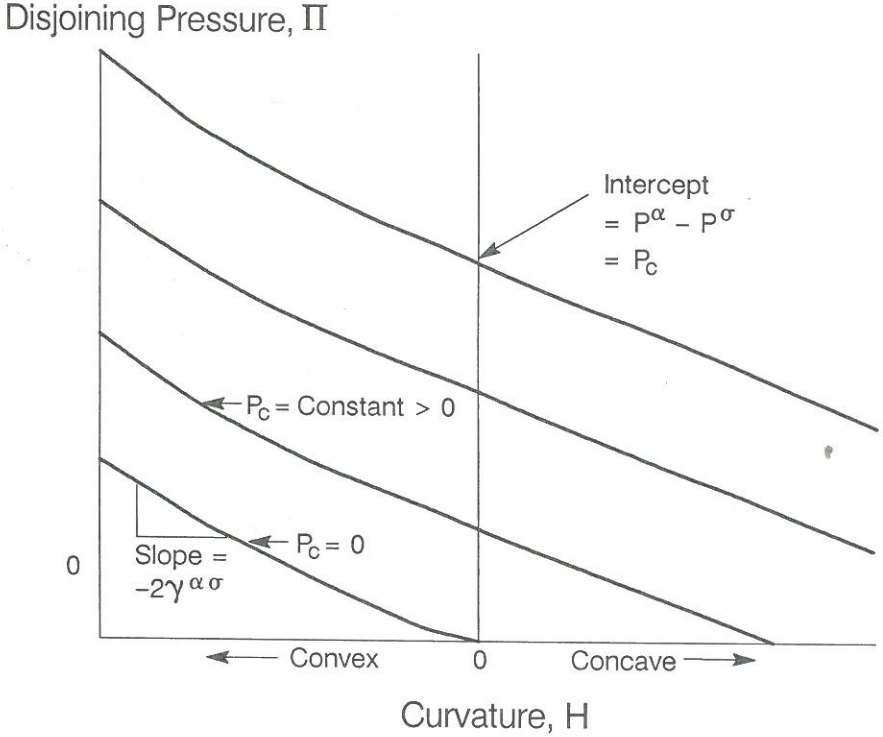

FIG. 4 The augmented Laplace–Young equation.

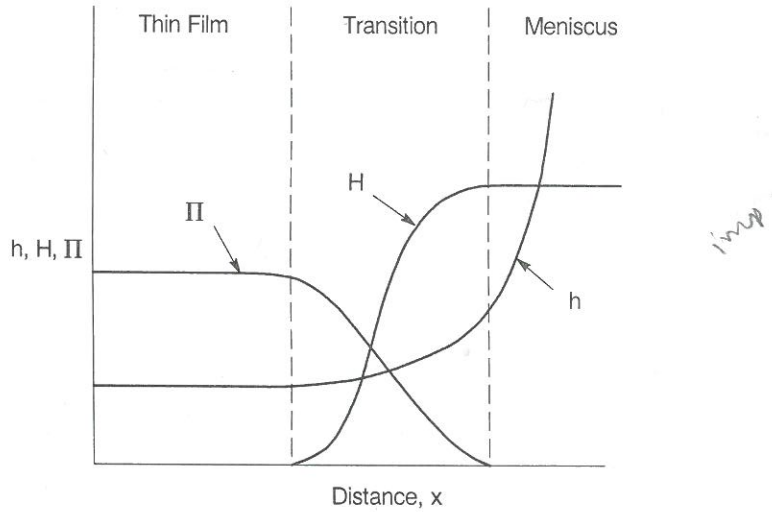

FIG. 5 Thickness, curvature, and disjoining pressure in a three-phase contact region.

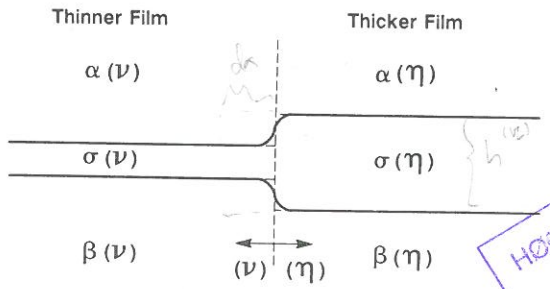

FIG. 6 Coexistence of two films.

C. Equilibrium Coexistence of Films of Different Thicknesses

The previous section described the equilibrium between a film and bulk phases. The film thickness is an unconstrained variable in this system. It is possible for films of different thicknesses to coexist at equilibrium. An example of this is the coexistence from the first and second black films in soap films. The analysis given here is for a planar film.

The coexistence of different thicknesses at fixed chemical potential and capillary pressure is analogous to the coexistence of phases with different specific volumes at fixed chemical potential and pressure.

The system is illustrated in Fig. 6. The system is similar to that of Fig. 3 except that the film is planar, and the system is a composite of two subsystems that have different film thicknesses. The transition region between the different film thicknesses will be treated as a step change. A proper description of this region would require knowledge of the effect of the gradient of thickness on the surface energy to determine the line tension. It is assumed that the contact line is a straight line so that line tension will not have to be considered.

The two subsystems will be denoted by the superscripts (η) and (ν). Since a flat film is being considered, the pressure of the α and β phases is equal and will be denoted by P. There is no constraint on the position of the transition region. Displacement of the transition region along the film by the distance dx will change the areas and volumes of the subsystems. The conservation conditions stated in the previous section apply to the total system. However, new relationships are needed to describe the changes in the areas and volumes of the subsystems as the transition region is displaced. For the sake of clarity, only the new relationships that contain dx will be shown in the following.

$$dA^{\alpha\sigma(\eta)} = dA^{\beta\sigma(\eta)} = +w\,dx \tag{25}$$

$$dA^{\alpha\sigma(\nu)} = dA^{\beta\sigma(\nu)} = -w\,dx \tag{26}$$

$$dV^{\sigma(\eta)} = +wh^{(\eta)}\,dx \tag{27}$$

$$dV^{\alpha(\nu)} + dV^{\beta(\nu)} = -wh^{(\eta)}\,dx \tag{29}$$

$$dV^{\alpha(\nu)} + dV^{\beta(\nu)} = +wh^{(\nu)}\,dx \tag{30}$$

where w is the width of the contact line. Equations (22) and (23) apply to each subsystem. The differential of the energy is:

$$dU = \sum_{k=\eta,\nu} \left[\sum_{j} dU^{j(k)} + dU^{\alpha\sigma,\beta\sigma,(k)} \right] \tag{31}$$

$$\begin{aligned} dU = {} & (T\,dS) + [(\mu + M\Phi)\,dn] + (P - P^{\sigma} - \Pi - 2H\gamma)\,dz \\ & + [(\Pi^{(\eta)}h^{(\eta)} + \gamma^{\alpha\sigma(\eta)} + \gamma^{\beta\sigma(\eta)}) \\ & + (\Pi^{(\nu)}h^{(\nu)} + \gamma^{\alpha\sigma(\nu)} + \gamma^{\beta\sigma(\nu)})]w\,dx \end{aligned} \tag{32}$$

The first three terms in Eq. (32) yield the same equilibrium conditions as derived in the previous section; see Eq. (19). The conservation of energy for arbitrary variations in dx requires that the last term in brackets vanish. Thus the additional condition for the equilibrium coexistence of two different film thicknesses is as follows [9, 24]:

$$[\Pi h + \gamma^{\alpha\sigma} + \gamma^{\beta\sigma}]^{(\eta)} = [\Pi h + \gamma^{\alpha\sigma} + \gamma^{\beta\sigma}]^{(\nu)} \tag{33}$$

We will see later that this is the condition of equality of film tensions, that is, the tension of the film as a whole.

If the contact line is curved, so that the line tension explicitly enters the equilibrium conditions, Eq. (33) must be replaced by the condition that the discontinuity in $\Pi h + \gamma^{\alpha\sigma} + \gamma^{\beta\sigma}$ is equal to $\kappa^{\ell}H^{\ell}$ where κ^{ℓ} is the line tension and H^{ℓ} is the curvature of the contact line [24].

Dergajuin, Martynov, and Gutop [9] derived the conditions for the equilibrium coexistence of two film regions of different but uniform thicknesses. The condition of equilibrium requires the equality of the film tension and the chemical potentials. The chemical potential between the two regions can be expressed as an integral of the film tension [9].

D. Representation of Film as a Single Dividing Surface

An alternate approach to thin films, attributed to Dergajuin [7], is to consider the film as a single Gibbs dividing surface having a volume associated with it. The differential of the energy of the open film system with this representation is

$$dU^{f} = T\,dS^{f} - P^{f}\,dV^{f} + \sum_{i} (\mu_i + M_i\Phi)\,dn_i^{f} + \gamma^{f}\,dA \tag{34}$$

The variables are denoted by the superscript f to indicate that it applies to the film as a whole. In particular, γ^{f} is the film tension, that is, the tension of the film as a whole. In this representation the film thickness does not appear explicitly.

The relationship between single dividing surface representation, Eq. (34), and the two dividing surfaces representation will be shown by utilizing Eqs. (1)–(15). The film phase consists of phase σ and the surface excess quantities:

$$\begin{aligned} dU^{f} &= dU^{\sigma} + dU^{\alpha\sigma,\beta\sigma} \\ &= T(dS^{\sigma} + dS^{\alpha\sigma,\beta\sigma}) - P^{\sigma}\,dV^{\sigma} \\ &\quad + \sum_{i} (\mu_i + M_i\Phi)\,(dn_i^{\sigma} + dn_i^{\alpha\sigma} + dn_i^{\beta\sigma}) \\ &\quad + (\gamma^{\alpha\sigma} + \gamma^{\beta\sigma})\,dA - A\Pi\,dh \end{aligned} \tag{35}$$

The thickness, volume, and area of the film are related by

$$dV^{\sigma} = A\,dh + h\,dA \tag{36}$$

Elimination of dh between Eqs. (35) and (36) results in

$$\begin{aligned} dU^{f} = {} & T\,(dS^{\sigma} + dS^{\alpha\sigma,\beta\sigma}) - (P^{\sigma} + \Pi)\,dV^{\sigma} \\ & + \sum_{i} (\mu_i + M_i\Phi)\,(dn_i^{\sigma} + dn_i^{\alpha\sigma} + dn_i^{\beta\sigma}) \\ & + (\gamma^{\alpha\sigma} + \gamma^{\beta\sigma} + \Pi h)\,dA \end{aligned} \tag{37}$$

Comparing Eq. (37) term by term with Eq. (34) yields the relationships between the single dividing surface representation and the two dividing surface representations:

$$dS^f = dS^\sigma + dS^{\alpha\sigma,\beta\sigma} \tag{38}$$

$$dV^f = dV^\sigma \tag{39}$$

$$dn_i^f = dn_i^\sigma + dn_i^{\alpha\sigma} + dn_i^{\beta\sigma} \tag{40}$$

$$P^f = P^\sigma + \Pi \tag{41}$$

and

$$\gamma^f = \gamma^{\alpha\sigma} + \gamma^{\beta\sigma} + \Pi h \tag{42}$$

These relationships show the "pressure of the film" P^f to be greater than the pressure of the σ phase by an amount equal to the disjoining pressure. Also, the "film tension" γ^f is greater than the sum of the interfacial tensions by the amount Πh [14, 18–20, 35].

The Gibbs–Duhem equation for the film and the σ phase can be derived from Eqs. (34) and (1) at constant gravitational potential:

$$0 = S^f\, dT - V^f\, dP^f + \sum_i n_i^f\, d\mu_i + A\, d\gamma^f \tag{43a}$$

and

$$0 = S^\sigma\, dT - V^\sigma\, dP^\sigma + \sum_i n_i^\sigma\, d\mu_i \tag{43b}$$

at constant ϕ.

The difference between the variables for the film and the σ phase is determined from Equations (38)–(41) and from

$$hA = V^f = V^\sigma \tag{44a}$$

$$(\Gamma_i^{\alpha\sigma} + \Gamma_i^{\beta\sigma})\, A = n_i^f - n_i^\sigma = n_i^{\alpha\sigma} + n_i^{\beta\sigma} \tag{44b}$$

$$\Delta sA = (S^f - S^\sigma) = S^{\alpha\sigma,\beta\sigma} \tag{44c}$$

The Gibbs–Duhem equation for the film becomes [35]

$$0 = \Delta s\, dT - h\, d\Pi + \sum_i (\Gamma_i^{\alpha\sigma} + \Gamma_i^{\beta\sigma})\, d\mu_i + d\gamma^f \tag{45a}$$

at constant ϕ and

$$d\gamma^f = h\, d\Pi - \sum_i (\Gamma_i^{\alpha\sigma} + \Gamma_i^{\beta\sigma})\, d\mu_i \tag{45b}$$

at constant T and ϕ.

This equation is the augmented Gibbs adsorption equation. It contains a term, $h\, d\Pi$, that is nonzero if the film is thin enough.

E. Spreading Coefficient and Contact Angles

Three different cases are possible for the contact angle. Figure 7 shows that the three-phase contact region can be described with a single contact angle either when one bulk phase is a solid or if both bulk phases (on either side of the film) are identical. The contact region between three different fluid phases will require two contact angles for its description. In this latter case, the spreading coefficient (defined below) can still be used to determine whether or not the film is spreading.

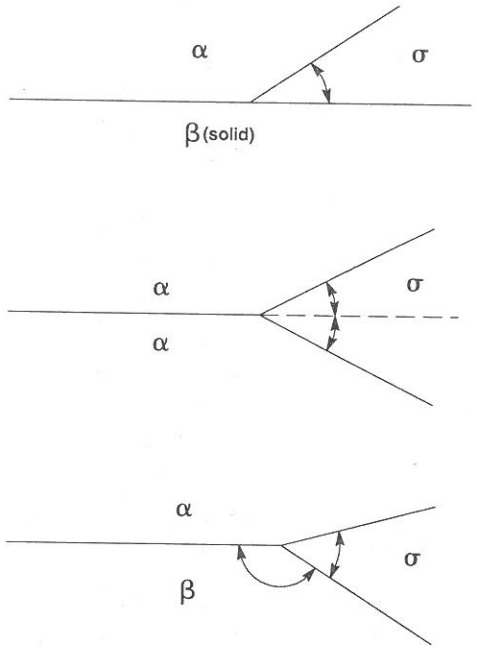

FIG. 7 Contact angle systems.

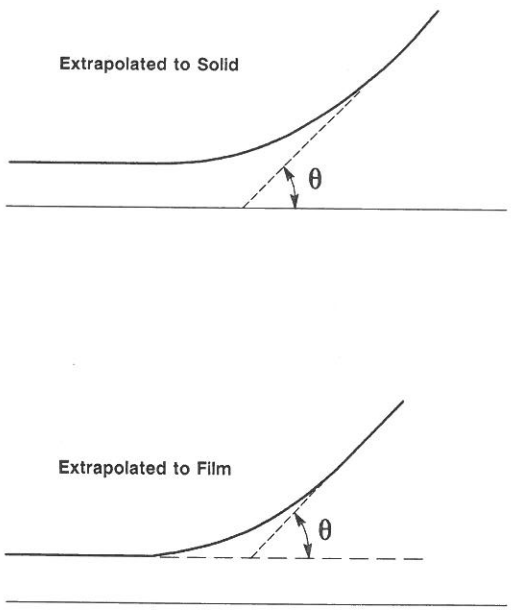

FIG. 8 Contact angle definitions.

The macroscopic contact angle can be defined in two different ways as shown on Fig. 8 [20, 24, 34, 35]: either as the angle that the extrapolated meniscus makes with the extrapolated surface of the film, or as the angle that the extrapolated meniscus makes with the solid substrate (or the center of the film in the case of identical bulk phases). In the following, the contact angle is with respect to the solid substrate (or the center of the film in the case of identical bulk phases) in order to be consistent with the Young equation. For cases in which the contact angle is very small, such as in the cases of a transition between different thicknesses in a symmetrical film (i.e., film surrounded by identical bulk phases) or between a symmetrical film and its meniscus, it may be advantageous to define the contact angle with respect to the extrapolated surface of the film [35]. If the contact angle is with respect to the extrapolated surface of the film, the term Πh must be added to the Young equation. Also, the expression for the contact angle in terms of the disjoining pressure will be the integral of Π dh rather than h dΠ.

The term macroscopic is used to describe the contact angle when the meniscus is extrapolated from a location on the meniscus where the curvature of the meniscus is not affected by the film thickness. If the meniscus is flat, then the extrapolation of the meniscus is a straight-line extrapolation. If the meniscus is curved, as in the case

of finite capillary pressure, then the extrapolation is with a constant curvature as explained in the next chapter. At small film thicknesses, the curvature of the interface is affected by the film thickness and the "microscopic" contact angle has sometimes been used to refer to the angle that the interface makes with the solid where the film thickness approaches the uniform film thickness. We will show in the next chapter that this microscopic contact angle should be zero.

The equilibrium spreading coefficient [36] (to be distinguished from the initial spreading coefficient to be discussed later) $S^{eq}_{\sigma/\alpha\beta}$ for the phase σ between phases α and β is the difference between the interfacial tensions of phases α and β separated by a thin equilibrium film of σ, γ^f, and the sum of the bulk phase interfacial tensions, $\gamma^{\alpha\sigma}_\infty$ and $\gamma^{\beta\sigma}_\infty$:

$$S^{eq}_{\sigma/\alpha\beta} \equiv \gamma^f - (\gamma^{\alpha\sigma}_\infty + \Gamma^{\beta\sigma}_\infty) \tag{46}$$

The tension, γ^f, is the film tension defined earlier. The bulk-phase interfacial tensions are denoted by infinity to signify that the film thickness is infinite or that σ acts as a bulk fluid. Either Eq. (8) and (42) or (45) enable one to express the spreading coefficient in terms of the disjoining pressure [35]:

$$\gamma^{\alpha\sigma} + \gamma^{\beta\sigma} = \gamma^{\alpha\sigma}_\infty + \gamma^{\beta\sigma}_\infty - \int_\infty^{h_{eq}} \Pi' \, dh' \tag{47}$$

$$\gamma^f = \gamma^{\alpha\sigma}_\infty + \gamma^{\beta\sigma}_\infty - \int_\infty^{h_{eq}} \Pi' \, dh' + (\Pi h)_{eq} \tag{48}$$

$$\gamma^f = \gamma^{\alpha\sigma}_\infty + \gamma^{\beta\sigma}_\beta + \int_0^{\Pi(h_{eq})} h' \, d\Pi' \tag{49}$$

at constant T, μ_i, and ϕ.

Thus

$$S^{eq}_{\sigma/\alpha\beta} = \int_0^{\Pi(h_{eq})} h' \, d\Pi' \tag{50}$$

The above equations contain integrals of $\Pi(h)$. These integrals exist only if $\Pi(h)$ vanishes rapidly enough as h approaches infinity.

The acute, macroscopic contact angle can be determined from the spreading coefficeint and the fluid–fluid interfacial tension. If β is a rigid, solid phase, the contact angle extrapolated to h = 0 in

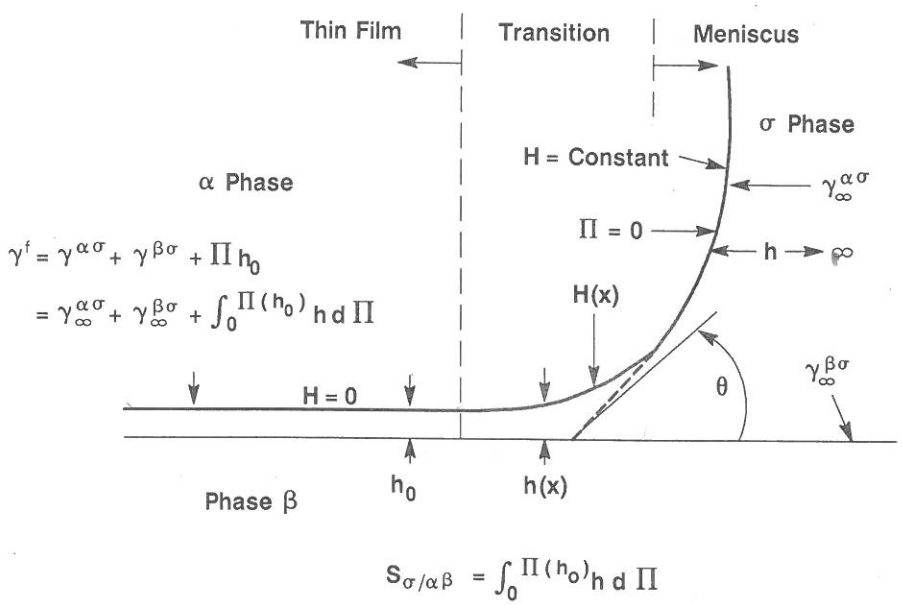

FIG. 9 Schematic of the macroscopic contact angle between a solid and two fluids.

a translationally invariant (i.e., straight contact line) system is derived from Young's equation as follows. The system is illustrated in Fig. 9.

$$\gamma^f = \gamma_\infty^{\alpha\sigma} \cos\theta + \gamma_\infty^{\beta\sigma} \tag{51a}$$

$$\cos\theta = 1 + \frac{\int_0^{\Pi(h_{eq})} h'\, d\Pi'}{\gamma_\infty^{\alpha\sigma}} \tag{51b}$$

for

$$\int_0^{\Pi(h_{eq})} h'\, d\Pi' \leq 0 \tag{51c}$$

If α and β are the same phase, as in a foam or emulsion film, the acute, macroscopic contact angle extrapolated to the midplane in a translationally invariant system is as follows:

$$\gamma^f = 2\gamma_\infty^{\alpha\sigma} \cos\theta \tag{52a}$$

$$\cos\theta = 1 + \frac{\int_0^{\Pi(h_{eq})} h'\, d\Pi'}{2\gamma_\infty^{\alpha\sigma}} \tag{52b}$$

for

$$\int_0^{\Pi(h_{eq})} h'\, d\Pi' \leq 0 \tag{52c}$$

The upper limit of the integrals is the equilibrium value of the disjoining pressure in the thin film. This value is determined from the capillary pressure and curvature as described by Eqs. (22) and (23). The contact angle is nonzero only if the integrals in Eqs. (51) and (52) are negative. Equations (49), (50), and (51) show that a nonzero contact angle requires that the film tension be less than the sum of the bulk phase interfacial tensions, so that the spreading coefficient must be negative.

If the capillary pressure (i.e., the pressure drop across the interface) and curvature and zero and thus the equilibrium disjoining pressure is zero, one may get the mistaken notion that the value of the integral in Eq. (50) is always zero. The integration by parts in Eqs. (48) and (49) shows that a zero equilibrium value of the disjoining pressure results in the integral being equal to the negative of the integral of Π with respect to thickness from infinity to a finite thickness at which Π is equal to zero, provided that such a thickness exists. This latter integral represents the negative of the potential energy required to bring the surfaces from infinite separation to the equilibrium thickness at zero capillary pressure. Equations (51) and (52) show that a nonzero contact angle at zero capillary pressure and curvature can exist only if this potential energy is negative.

Figure 10 illustrates the conditions required to have a nonzero contact angle. The equilibrium disjoining pressure (equal to the capillary pressure when the curvature of the solid is zero) is shown to be nonzero for the sake of generality. In the upper figure, the disjoining pressure is everywhere positive. The integral in Eqs. (51) and (52) is shown by the hatched area in Fig. 10. In the

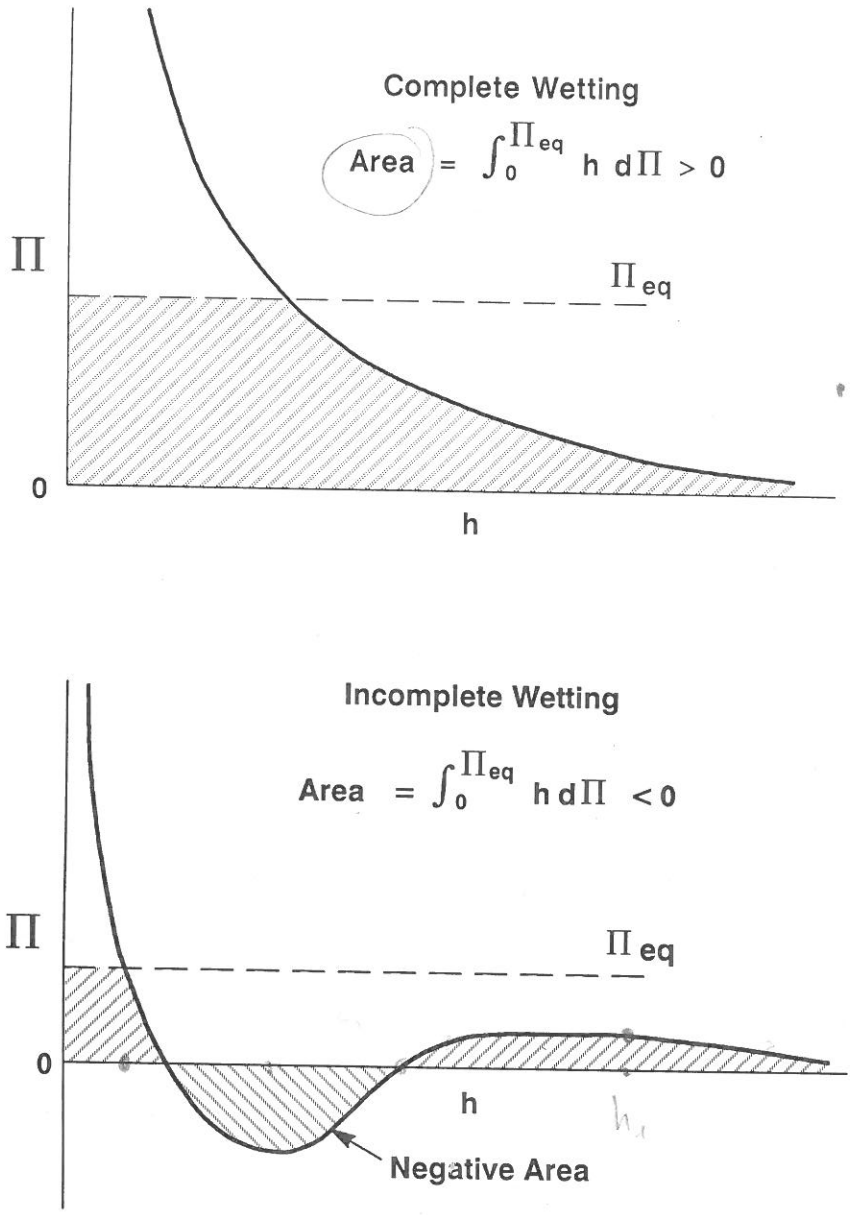

FIG. 10 Disjoining pressure for complete wetting (zero contact angle) and incomplete wetting (nonzero contact angle).

upper figure, the integral is positive and the contact angle is zero. In the lower figure, negative values of disjoining pressure representing a net attraction are shown. The negative contribution to the integral is hatched in the opposite direction. If the net area is negative, the contact angle will be nonzero. The equilibrium wetting transition occurs when the integral is equal to zero.

Antonow's rule states that when the film phase completely wets the interface of the bulk phases, the interfacial tension of the film is equal to the sum of the interfacial tensions of the spreading phase and the surrounding bulk phases. From the definition of the equilibrium spreading coefficient, Eq. (46), Antonow's rule implies that the equilibrium spreading coefficient is equal to zero for a complete wetting system, that is, the equilibrium spreading coefficient cannot be positive. Rowlinson and Widom [37] argue that the equilibrium spreading coefficient can never be positive. Their argument, the same as that given by Gibbs [25] (p. 258) and more recently by Davis and Scriven [38], is that at equilibrium, the very structure of the film phase would then be that of the bulk phase. The surface energy per unit area (i.e., film tension) is then equal to the sum of the interfacial tensions between the bulk phase comprising the film, and the surrounding bulk phases, and therefore the spreading coefficient is equal to zero.

In contrast to this conclusion, the analysis given earlier shows that a positive equilibrium spreading coefficient is possible in a system that has a positive equilibrium disjoining pressure. This can occur in the case of two fluids in a capillary in which one fluid completely wets the solid and the meniscus between the fluids is curved. For example, if the disjoining pressure isotherm is positive and the equilibrium disjoining pressure is positive, then the integral in Eq. (50) is also positive, resulting in a positive equilibrium spreading coefficient. Equation (49) shows that the film tension differs from the sum of the interfacial tensions between the bulk phases by an amount equal to the integral of the disjoining pressure isotherm, the integral extending from zero to the equilibrium value of the disjoining pressure. Another example of a positive spreading coefficient is a system with a positive disjoining pressure isotherm due to an adsorbed film at a chemical potential that is less that the saturation value. The section describing adsorption explains how this results in a positive spreading coefficient.

Therefore, Antonow's rule is limited to complete wetting systems in which the equilibrium disjoining pressure is zero, that is, systems in which the film phase exists in bulk at the same pressure as the other bulk phases. This limitation was recognized by Davis and Scriven [38].

F. Disjoining Pressure Expressed in Terms of Chemical Potential or Vapor Pressure (Kelvin Equation)

The previous sections expressed the disjoining pressure as a function of the capillary pressure (pressure difference across an interface). In this section, the disjoining pressure will be expressed as a function of the chemical potential. In the case of a film with a single volatile component, the chemical potential and thus the disjoining pressure can be expressed as a function of the vapor pressure relative to the saturation pressure.

The relationship between the disjoining pressure and the chemical potentials is determined by considering the total differential of energy for the σ phase only as described by Eq. (1) and Figure 3. Since this is a subsystem of the system considered earlier, the equilbrium relation, Eq. (22), applies to it. Combining Eqs. (1) and (22) gives:

$$dU^\sigma = T\,dS^\sigma - (P^\alpha - 2H^{\alpha\sigma}\gamma^{\alpha\sigma} - \Pi)\,dV^\sigma + \sum_i (\mu_i + M_i\Phi)\,dn_i^\sigma \tag{53}$$

Since, at fixed gravitational potential, U^σ is homogenous of order one in S^σ, V^σ, and n_i^σ, the Gibbs–Duhem equation can be derived to show the relationship between the intensive variables. Dividing by the film volume V^σ yields the desired relationship for the σ phase:

$$0 = (S^\sigma/V^\sigma)\,dT - dP^\alpha + d(\Pi + 2H^{\alpha\sigma}\gamma^{\alpha\sigma}) + \sum_i c_i^\sigma\,d\mu_i \tag{54}$$

Gibbs-Duhem $\sum n_i\,d\mu_i = 0$

at constant Φ, where

$$c_i = n_i/V$$

The corresponding relationship for the α phase is

$$(S^\alpha/V^\alpha)\,dT - dP^\alpha + \sum_i c_i^\alpha\,d\mu_i = 0 \tag{55}$$

at constant Φ. The term P^α can be eliminated to yield the relationship between the disjoining pressure and chemical potential at constant temperature and gravitational potential:

$$d(\Pi + 2H^{\alpha\sigma}\gamma^{\alpha\sigma}) = -\sum_i (c_i^\sigma - c_i^\alpha)\,d\mu_i \tag{56}$$

at constant T and Φ.

If the film is formed by changing the chemical potential of a single component that is a liquid in phase σ, a vapor that satisfies the ideal gas law in phase α, and satisfies the condition

$$c^\sigma = \text{constant} \gg c^\alpha \tag{57}$$

then Eqs. (54) and (55) can be easily integrated. [Eliminate $d\mu_i$ between Equations (54) and (55).] At saturation pressure, the vapor is in equilibrium with bulk liquid with a flat interface:

$$\Pi + 2H^{\alpha\sigma}\gamma^{\alpha\sigma} \cong -c^\sigma RT \ln (P^\alpha/P^{\text{sat. flat}}) \tag{58a}$$

If phase α is a perfect gaseous mixture, the chemical potential of the component in the film can be expressed in terms of the partial pressure, P_1^α of the component in phase α (see Ref. 27, p. 224). Integration of Eq. (56) gives:

$$\Pi + 2H^{\alpha\sigma}\gamma^{\alpha\sigma} \cong -c^\sigma RT \ln(P_1^\alpha/P_1^{\text{sat. flat}}) \tag{58b}$$

These equations are the augmented Kelvin equation for curved interfaces and thin films [6, 33]. One of its uses is measuring the disjoining pressure in the capillary condensation and/or multilayer adsorption of water on quartz.

Equation (58) can be used in the interpretation of film condensation or dropwise condensation on surfaces. When the vapor pressure is equal to the saturation pressure, the right side of Eq. (58) is equal to zero. This will require that the left side of the equation be equal to zero, and for a flat surface will require that the disjoining pressure be equal to zero. If the disjoining pressure is zero only for infinite thickness, then film condensation will occur. If the disjoining pressure becomes zero for a finite value of the thickness, then dropwise condensation is possible, since the nonzero contact angle can exist if the area under the curve is negative.

G. Thermodynamic Potentials for Thin Films

So far, the only thermodynamic potential or energy function that has been introduced is the internal energy U. Other thermodynamic potentials are useful for determining the work required to form a thin film or the work required to cause a departure from equilibrium.

The thermodynamic potential that will be introduced will include an integral of the disjoining pressure.

The thermodynamic potential [24] that can be used to describe processes conducted at constant temperature (isothermal), volume, and chemical plus gravitational potential is the potential Ω, called the interaction potential, where

$$\Omega \equiv U - TS - \sum_i (\mu_i + M_i\Phi)n_i \tag{59}$$

This potential has also been called the potential energy [5], Kramer's function [24], and the grand potential [26]. It replaces the Helmholtz free energy and amount of substance in the fundamental relation with the temperature and chemical plus gravitational potentials as independent variables [26]. It is a minimum at equilibrium for processes at fixed temperature, volume, and chemical plus gravitational potential.

The differential of this potential can be derived from Eqs. (1)–(3) and (59).

$$\begin{aligned} d\Omega = &- \left(\sum_j S^j + S^{\alpha\sigma,\beta\sigma}\right) dT \\ &- \sum_i \left(\sum_j n_i^j + n_i^{\alpha\sigma} + n_i^{\beta\sigma}\right) d(\mu_i + M_i\Phi) \\ &- \sum_j P^j\, dV^j + \gamma^{\alpha\sigma}\, dA^{\alpha\sigma} + \gamma^{\beta\sigma}\, dA^{\beta\sigma} - A^f \Pi\, dh \end{aligned} \tag{60}$$

The first two terms on the right side of Eq. (60) are zero for constant temperature and chemical plus gravitational potential. They will just be denoted by (S dT) + [n d(μ + MΦ)]. The equilibrium conditions will be determined for a composite system as before except that the walls of the system allow mass and heat transfer. The area, volume, and thickness are related by Eqs. (13)–(18). With these relations, the differential of the potential is

$$\begin{aligned} d\Omega = &-(S\, dT) - [n\, d(\mu + M\Phi)] \\ &+ (P^\alpha - P^\sigma - \Pi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma})A^{\alpha\sigma}\, dz^{\alpha\sigma} \\ &+ (P^\beta - P^\sigma - \Pi - 2H^{\beta\sigma}\gamma^{\beta\sigma})A^{\beta\sigma}\, dz^{\beta\sigma} \end{aligned} \tag{61}$$

The condition that Ω is a minimum at equilibrium for arbitrary variations in dz yields the same equilibrium condition as Eqs. (22) and (23).

The dependence of Ω on the disjoining pressure and thickness can be illustrated by replacing the pair ($dz^{\alpha\sigma}$, $dz^{\beta\sigma}$) by the pair (dh, $dz^{\beta\sigma}$) as the independent variables in Eq. (61).

$$\begin{aligned} d\Omega = &- (S\, dT) - [n\, d(\mu + M\Phi)] \\ &+ (P^\alpha - P^\sigma - \Pi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma})A^{\alpha\sigma}\, dh \\ &+ [P^\beta - P^\alpha - 2(H^{\beta\sigma}\gamma^{\beta\sigma} - H^{\alpha\sigma}\gamma^{\alpha\gamma})]A^f\, dz^{\beta\sigma} \\ &+ 0(Hh\, dz) \end{aligned} \tag{62}$$

The term in dh represents the change in potential with thickness and the term in $dz^{\beta\sigma}$ represents the change of the potential due to changes in position of the film at constant film thickness. The equilibrium conditions, Eqs. (22) and (24), result in these terms vanishing at equilibrium. The stability of the equilibrium state with respect to thickness can be examined by taking the second derivative of Ω. If the area is constant, the result can be expressed in terms of a specific interaction potential ω.

$$\left(\frac{\partial^2\omega}{\partial h^2}\right)_{T,\,\mu_i+M_i\Phi,\,z^{\beta\sigma},\,A^f} = -\frac{\partial\Pi}{\partial h} + \frac{\partial\Pi_{eq}}{\partial h} \tag{63a}$$

where

$$\omega = \frac{\Omega}{A^f} \tag{63b}$$

$$\Pi_{eq} = P^\alpha - P^\sigma - 2H^{\alpha\sigma}\gamma^{\alpha\sigma} \tag{63c}$$

If the equilibrium disjoining pressure Π_{eq} is constant, the necessary condition for a locally stable equilibrium is that $\partial\Pi/\partial h < 0$, that is, $\Pi(h)$ has a negative slope. The dependence of the potential ω on thickness for constant temperature, chemical plus gravitational potential, and position of the film can be determined by integrating Eq. (62):

$$\omega(h) = \int_h^\infty [\Pi' - (P^\alpha - P^\sigma - 2H^{\alpha\sigma}\gamma^{\alpha\sigma})]\, dh' \tag{64}$$

with constant T, $\mu_i + M_i\Phi$, $z^{\beta\sigma}$, and A^f. The change in ω with h is the work required to change the film thickness at constant temperature, chemical plus gravitational potential, position of the film, and area of the film.

Equation (64) can also be used to determine the change in potential for a departure from an equilibrium thickness. For example, the change in potential for a departure from the equilibrium thickness h_{eq} at constant temperature, chemical plus gravitational potential, position of the interface, and $(P^\alpha - P^\sigma - 2H^{\alpha\sigma}\gamma^{\alpha\sigma}) = \Pi_{eq}$ is

$$\Delta\omega(\Pi_{eq}, h_{eq}, \Delta h) = \Pi_{eq}\,\Delta h + \int_{h_{eq}+\Delta h}^{h_{eq}} \Pi'\,dh' \qquad (65a)$$

$$= \int_{h_{eq}+\Delta h}^{h_{eq}} (\Pi' - \Pi_{eq})\,dh' \qquad (65b)$$

Equation (65) can be used t determine whether a local equilibrium is global or metastable and the energy barrier that must be overcome to reach another local equilibrium state. This is illustrated on Fig. 11. The area between h_{eq} and h_1 represents the energy barrier. The net area between h_{eq} and h_2 is the energy difference between the local equilibrium states.

The classical problem treated in the DLVO theory is the case where $P^\alpha - P^\sigma + 2H\gamma = \Pi_{eq} = 0$ and $h_{eq} \to \infty$. In this case the interaction potential is just equal to the integral of the disjoining pressure and the potential approaches zero as h approaches infinity. This potential has been referred to as the potential energy [5] or the interaction free energy [35]. The DLVO theory did not include the short-range repulsive forces that result in positive disjoining pressures at small separations.

The condition for coexistence of two different film thicknesses is illustrated in Fig. 12. Coexistence requires equality of disjoining pressure and equal area between the curve of $\Pi(h)$ and the horizontal line, $\Pi = \Pi_{eq}$. This latter condition results in equal potential for the coexisting films. The condition for coexistence of films is analogous to the conditions for the coexistence of a liquid and vapor. In the latter case, the disjoining pressure and potential, ω, are replaced by pressure and chemical potential.

It can be easily shown that equality of disjoining pressure and potential ω between equilibrium coexisting flat films of different thickness imply the equality of the film tensions. The equality of film tensions can be shown by integration by parts of Eq. (64) and substitution of Eq. (49). This substantiates Eq. (33).

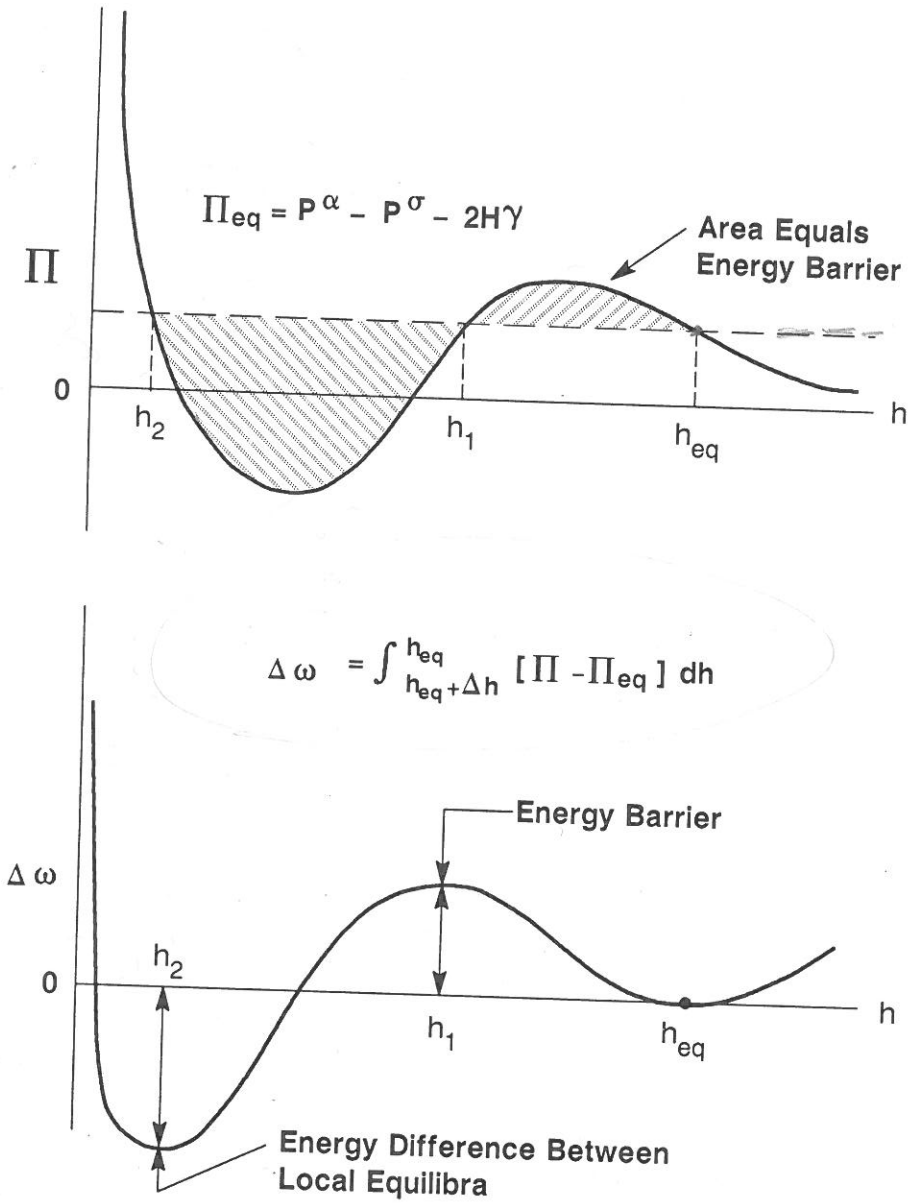

FIG. 11 Illustration of the relationship between disjoining pressure and the specific interaction potential ω.

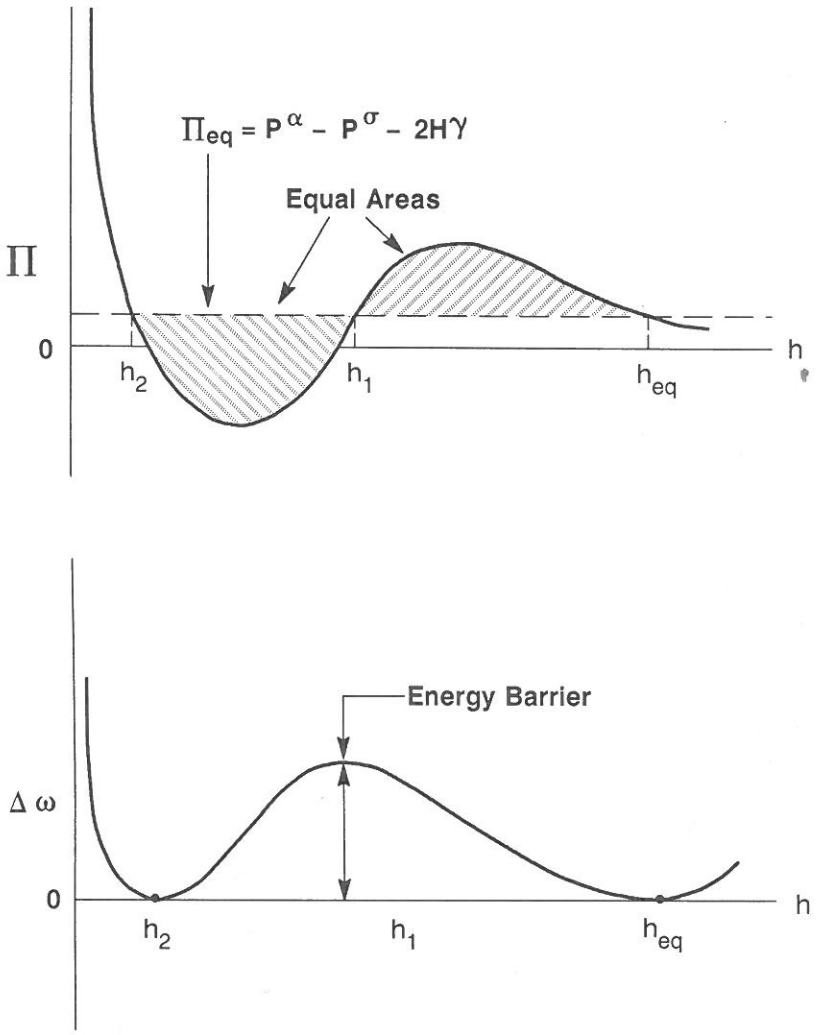

FIG. 12 Condition for the coexistence of two films.

Equilibrium coexisting flat films of different thicknesses will have a difference in the value of the sum of the interfacial tensions. This difference can be derived from the definition of the film tension, Eq. (42):

$$\Delta(\gamma^{\alpha\sigma} + \gamma^{\beta\sigma}) = -\Pi_{eq}\,\Delta h$$

This equation shows that the thinner film will ha
the sum of the interfacial tensions for a positiv

H. Gravitational Field and Curved Surfaces

The effect of a gravitational field was included in the prece
analysis with the addition of the product, $M_i\Phi$, of the molecular
weight and gravitational potential to the chemical potential [27]. In addition, the equilibrium pressure difference (capillary pressure), $P^{\alpha} - P^{\sigma}$, can be expressed in terms of the hydrostatic pressure difference relative to the gravitational potential datum where $P^{\alpha} = P^{\sigma}$:

$$(P^{\alpha} - P^{\sigma})_{static} = (\rho^{\alpha} - \rho^{\sigma})\,\Delta\Phi \tag{66}$$

where

$$\rho^{i} = \sum_{i} c_i^j M_i$$

The equilibrium value of the disjoining pressure is [33] from Eq. (22),

$$\Pi_{eq} = (\rho^{\sigma} - \rho^{\alpha})\,\Delta\Phi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma} \tag{67}$$

Equation (65) can now be expressed in terms of the gravitational potential:

$$\Delta\omega = \int_{h_{eq}+\Delta h}^{h_{eq}} \{\Pi - [(\rho^{\sigma} - \rho^{\alpha})\,\Delta\Phi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma}]\}\,dh' \tag{68}$$

The effect of the gravitational potential (or capillary pressure) and curvature on the local stability of a film is illustrated on Fig. 13. The horizontal lines represent different equilibrium values of the disjoing pressure equal to $(\rho^{\sigma} - \rho^{\alpha})\,\Delta\Phi - 2H^{\alpha\sigma}\gamma^{\alpha\sigma}$. It was mentioned in the previous section that the energy barrier between a thicker film and a thinner film is the area above the line representing the equilibrium value of the disjoining pressure and the disjoining pressure curve. When the gravitational potential (in the case where the film is the more dense phase) and/or curvature becomes sufficiently large, the thicker film will no longer be stable, as in Fig. 14. This explains why a film that is metastable can thin or rupture to a lower potential if it is connected to a region where

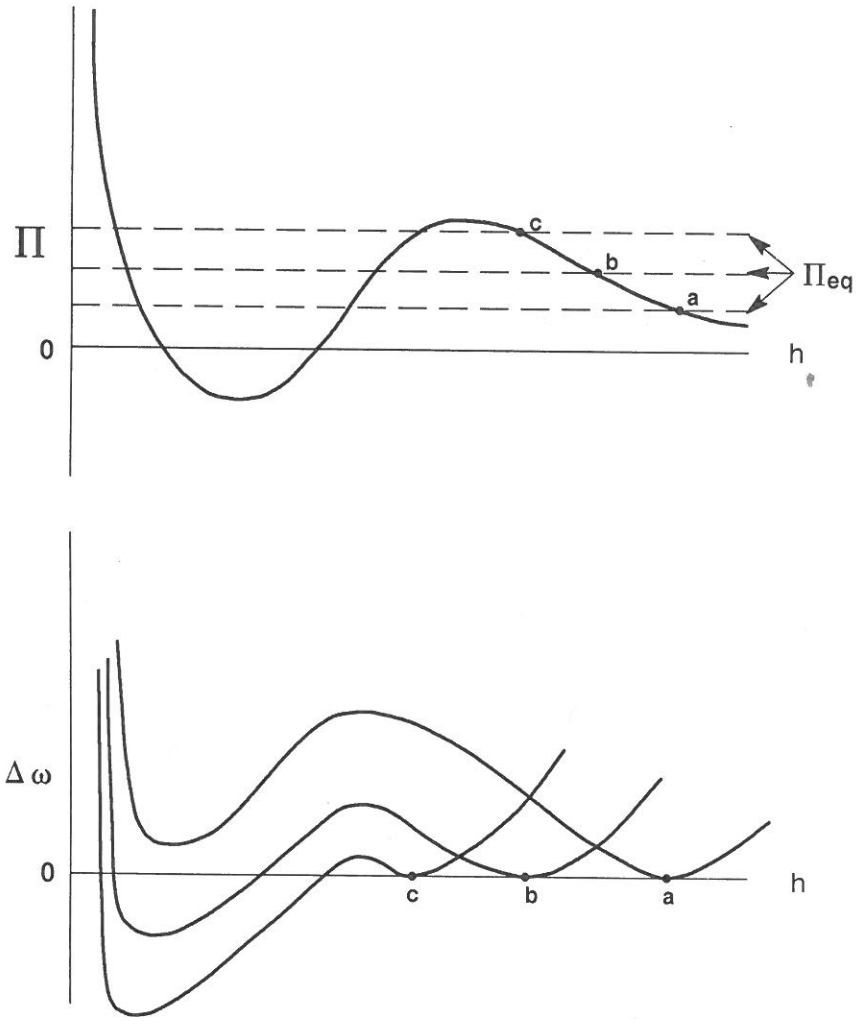

FIG. 13 Illustration of the effect of different gravitational potentials (or capillary pressure) on the specific interaction potential ω.

it is unstable due to a large sufficiently large gravitational potential and/or curvature, that is, large capillary pressure.

The augmented Kelvin equation, Eq. (58), gave the relationship between disjoining pressure and vapor pressure for a fixed gravitational potential. Equation (67) shows how the disjoining pressure changes with gravitational potential. The two equations imply that

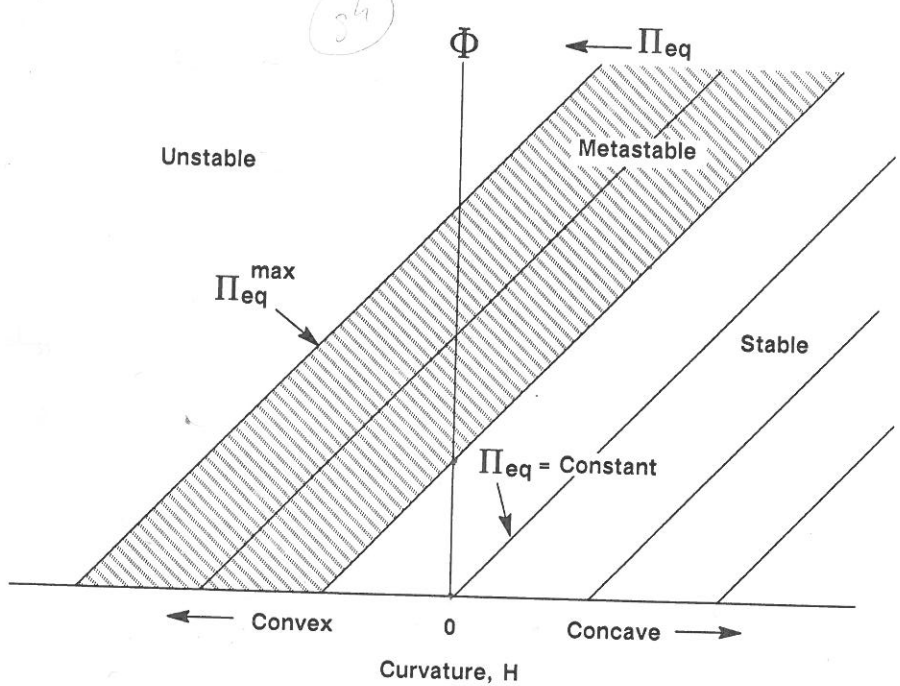

FIG. 14 Stability regions in the presence of gravity and curvature ($\rho^{\sigma} > \rho^{\alpha}$).

the vapor pressure will change with gravitational potential. The natural question that arises is whether or not the varying vapor pressure will result in a departure from chemical equilibrium at different levels of gravitational potential as suggested by Gibbs (Ref. 25, p. 310). Substitution of Eq. (67) into Eq. (56) shows that the sum of the chemical potential and the product of the molecular weight and gravitational potential are constant for components with nonzero concentrations. This is a necessary condition for equilibrium given by Eq. (21). The vapor pressure can be expressed as a function of the gravitational potential by substituting the ideal gas law and Eq. (67) into the augmented Kelvin equation, Eq. (58):

$$p^{\alpha} \cong p^{sat} - \rho^{\alpha sat}(\Phi - \Phi^{sat}) \tag{69}$$

This equation shows that the vapor pressure changes corresponding to the hydrostatic pressure of the vapor. This will result in chemical equilibrium between the film and vapor phase. Therefore the

augmented Kelvin equation describes the condition of mechanical and chemical equilibrium of a film with changing gravitational potential.

The profiles of the equilibrium disjoining pressure, thickness, surface tensions, and film tensions as a function of the gravitational potential can be derived from Eq. (67) (constant density is assumed in the following):

$$d\Pi = (\rho^{\sigma} - \rho^{\alpha})d\Phi - d(2H^{\alpha\sigma}\gamma^{\alpha\sigma}) \tag{70}$$

$$dh = \frac{d\Pi}{(\partial\Pi/\partial h)_T} \tag{71a}$$

$$= -\frac{(\rho^{\sigma} - \rho^{\alpha})}{(-\partial\Pi/\partial h)_T} d\Phi + \frac{d(2H^{\alpha\sigma}\gamma^{\alpha\sigma})}{(-\partial\Pi/\partial h)_T} \tag{71b}$$

$$d(\gamma^{\alpha\sigma} + \gamma^{\beta\sigma}) = -\Pi\, dh \tag{72a}$$

$$= \frac{(\rho^{\sigma} - \rho^{\alpha})\Pi\, d\Phi}{(\partial\Pi/\partial h)_T} - \frac{\Pi\, d(2H^{\alpha\sigma}\gamma^{\alpha\sigma})}{(\partial\Pi/\partial h)_T} \tag{72b}$$

$$d\gamma^{f} = d(\gamma^{\alpha\sigma} + \gamma^{\beta\sigma}) + d(\Pi h) \tag{73a}$$

$$= (\rho^{\sigma} - \rho^{\alpha})\, h\, d\Phi - h\, d(2H^{\alpha\sigma}\gamma^{\alpha\sigma}) \tag{73b}$$

These profiles are illustrated on Fig. 15.

Equation (73) is the condition for hydrostatic mechanical equilibrium of the film. This condition for mechanical equilibrium was established under the condition that the chemical plus gravitational potential of all of the components is constant. Failing to recognize that the disjoining pressure is nonzero, Gibbs [25] showed that at least two components must have their mass rather than their chemical plus gravitational potential held fixed for mechanical equilibrium to exist for a vertical film. Here it has been shown that mechanical equilibrium is possible with all components having constant chemical plus gravitational potential.

Equation (73) also shows how the curvature of the surface can change the film tension. The effect of gravitational potential and curvature on the spreading coefficient and contact angle can be seen from Eqs. (46), (51), (52), and (73). These equations show that a small increase in the gravitational potential and/or decrease in surface curvature (the surface becoming more convex or less concave) will increase the film tension and spreading coefficient and decrease the contact angle if it is not already zero. However, a sufficiently large increase in the gravitational potential and/or decrease in the curvature can result in the instability of a metastable film and the

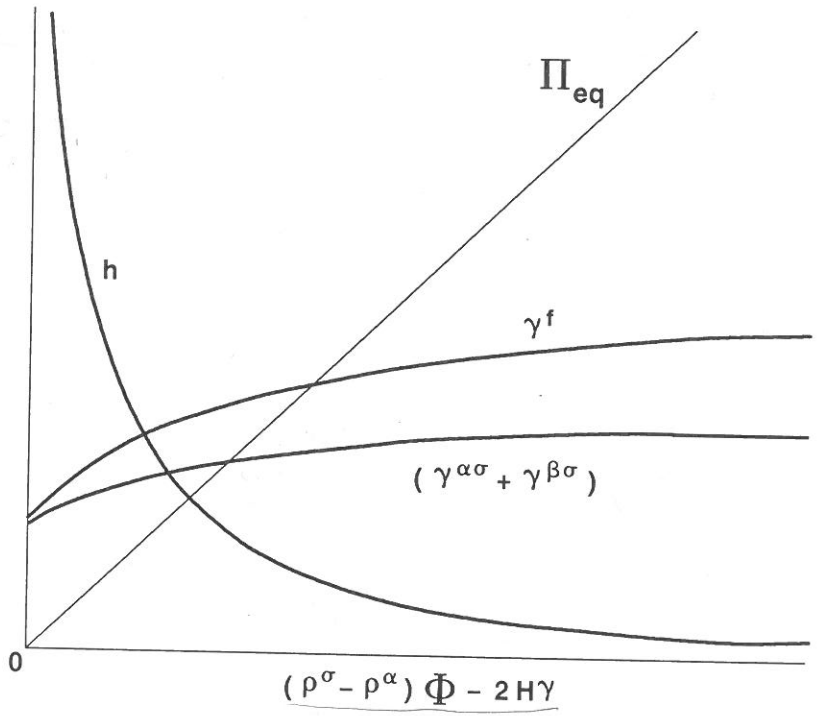

FIG. 15 Profiles of disjoining pressure, thickness, interfacial tensions, and film tension as a function of gravitational potential and curvature.

formation of a thinner film with a smaller film tension and spreading coefficient and a larger contact angle.

This change in film tension with a curvature should not be mistaken with the change in tension that would have resulted if curvature terms were included in Eq. (3). The effect of curvature discussed here is only that due to a curved substrate and meniscus shape. Such an effect occurs, for example, at the junction of a thin film and the Plateau border, at the three-phase contact region, or due to the change in curvature that results from the roughness of the solid substrate.

I. Film Elasticity

Gibbs [25] (pp. 300–303) also considered the elasticity (i.e., the infinitesimal increase of the tension of the film divided by the infinitesimal increase of area in a unit of surface) of a film in which the mass of two components was held constant as the film was ex-

tended. A positive elasticity is necessary for stability [14]. Gibbs explains that for a vertical film to be mechanically stable, there must be a gradient in the surface tension to balance the weight of the film. Also, for the liquid in the film to be stable with respect to drainage, the liquid must be in hydrostatic equilibrium. However, because a vertical film is made from flat interfaces, the pressure of the liquid must be equal to the pressure of the gas and thus cannot be in hydrostatic equilibrium. Gibbs speculated that the drainage was arrested by the liquid in the film having a "gelatinous consistency."

The previous section discussed the stability of films in a gravitational field with the restriction that the sum of the chemical plus gravitational potentials is constant. Such a film will be in mechanical and chemical equilibrium. The elasticity of such a film will be denoted by E^{eq} to distinguish it from the E used by Gibbs, which was based on constant mass of two components. Moreover, the elasticity will be based on the film tension, which differs from the sum of the surface tensions by the term Πh:

$$E^{eq} \equiv \left(\frac{\partial \gamma^f}{\partial \ln A} \right)_{T,\mu_i+M_i\Phi,V^\sigma} \tag{74}$$

$$= \frac{\partial \gamma^f}{\partial h} \frac{\partial h}{\partial \ln A} \tag{75}$$

A change in film area with constant chemical plus gravitational potential and film volume is possible, for example, if for a given element of the film, the disjoining pressure is changes by changing the elevation of the film relative to the elevation where the disjoining pressure is equal to zero (i.e., where the film phase exists as a bulk phase):

$$V^\sigma = Ah = \text{constant} \tag{76}$$

$$\frac{\partial h}{\partial \ln A} = -h \tag{77}$$

$$\frac{\partial \gamma^f}{\partial h} = h \frac{\partial \Pi}{\partial h} \tag{78}$$

$$E^{eq} = -h \frac{\partial \gamma^f}{\partial h} \tag{79a}$$

$$E^{eq} = -h^2 \frac{\partial \Pi}{\partial h} \tag{79b}$$

From Eq. (8), the elasticity can be expressed in terms of the interfacial tensions [14]:

$$E^{eq} = h^2 \left[\frac{\partial^2 (\gamma^{\alpha\sigma} + \gamma^{\beta\sigma})}{\partial h^2} \right]_{T,\mu_i+M_i\Phi,V^\sigma} \tag{80}$$

Equation (63) shows that $\partial\Pi/\partial h$ must be negative for the film to be locally stable. This condition will result in a positive value for E^{eq} for a locally stable film. Equation (80) expresses E^{eq} in terms of the change in interfacial tensions with thickness. This term was zero in Gibbs's analysis since he assumed that "difference of thickness does not necessarily involve any difference of tension" [25] (p. 303) when a film is stretched at constant chemical plus gravitational potential.

J. Relationship Between Disjoining Pressure and Adsorption Isotherm

Most attention on the disjoining pressure has been in the thickness range from a finite equilibrium thickness (i.e., multimolecular layers) to infinite thickness. Thus most models for the study of disjoining pressure isotherms are continuum models (with the exception of the structural forces) that apply only to multilayer films. The thermodynamic arguments presented here are not limited to multilayers if the definition of thickness is carefully defined with respect to the surface excess or the amount of material adsorbed. Measurement of adsorption isotherms permits examination of the disjoining pressure isotherm in the film thickness region that is dominated by structural forces (e.g., zero to a few molecular layers). Also, adsorption results in a film pressure, which is the reduction of the substrate surface tension or energy. This film pressure accounts for the difference between the initial and equilibrium spreading coefficients, initial and equilibrium contact angles, and part of the difference between the advancing and receding contact angles. This approach should make it possible to calculate film tensions all the way from the value equal to the interfacial tension of the bulk phases in the absence of the spreading phase (i.e., zero film thickness) to the value equal to the sum of the interfacial tensions between the spreading phase and the bulk phases (i.e., infinite film thickness).

It is assumed that only one component will be changing in chemical potential. We denote this component 1. The two Gibbs dividing surfaces bounding the film will be located such that the surface excess concentration is zero for the component that is changing in chemical potential, that is, the amount adsorbed is accounted for by the thickness. It is assumed that the film is flat, that is,

has zero curvature. The Gibbs–Duhem equation is obtained from Eq. (43):

$$0 = -V^f \, dP^f + \sum_i n_i^f \, d\mu_i + A \, d\gamma^f \tag{81}$$

at constant T and Φ. The pressure p^f can be expressed in terms of the bulk-phase pressure P^α by using Eqs. (22) and (41):

$$P^f = P^\sigma + \Pi \tag{82a}$$

$$= P^\alpha \tag{82b}$$

at constant H.

Adsorption isotherms provide the measurement methods and models for films down to zero thickness. In the following section, the relation between adsorption isotherms and disjoining pressure isotherms will be developed.

Substituting Eq. (82) into Eq. (81) and dividing by V^f, we have

$$0 = -dP^\alpha + \sum_i c_i^f \, d\mu_i + d\gamma^f/h \tag{83}$$

(at constant T, Φ, and H) where

$$h = V^f/A \tag{84a}$$

$$c_i^f = n_i^f/V^f \tag{84b}$$

The Gibbs–Duhem equation for the bulk phase gives

$$0 = -dP^\alpha + \sum_i c_i^\alpha \, d\mu_i \tag{85}$$

at constant T and Φ. Subtracting Eq. (85) from (83) yields the Gibbs adsorption equation for the film:

$$0 = h \sum_i (c_i^f - c_i^\alpha) \, d\mu_i + d\gamma^f \tag{86}$$

at constant T, Φ, and H. It can be seen from this equation that the excess concentration per unit area of the film can be defined in terms of the thickness and the excess concentration:

$$\Gamma_i^f = h \, (c_i^f - c_i^\alpha) \tag{87}$$

Since the Gibbs dividing surfaces were defined in such a way that the surface excess concentration of the component with the changing chemical potential is zero, the concentration of this component in the film is equal to the concentration within the spreading phase of the film:

$$c_1^f = c_1^\sigma \tag{88}$$

The relationship between the disjoining pressure and the chemical potential is obtained from Eq. (56):

$$d\Pi = -\sum_i (c_i^\sigma - c_i^\alpha) \, d\mu_i \tag{89}$$

at constant T, Φ, and H. The relationship between the disjoining pressure and the film tension is obtained by eliminating the chemical potential between Eqs. (86) and (89) and using Eq. (88):

$$d\gamma^f = h \, d\Pi \tag{90}$$

at constant T, Φ, H, and μ_i for $i \neq 1$. This relationship is the same as that in the case when the temperature and chemical plus gravitational potential are held constant with the curvature free to vary; see Eq. (45b).

The relationships between chemical potential, disjoining pressure, thickness, excess concentration, and film tension are expressed as functions of chemical potential from Eqs. (86) and (89). Therefore, the film tension can be expressed as a function of the disjoining pressure as in Eq. (90). The excess concentration of the film per unit area is related to the film thickness and the excess concentrations by Eqs. (87) and (88).

The relationships between film pressure and spreading coefficient can now be expressed by integrals of the disjoining pressure isotherm. The "film presure" will be denoted by a lower case π to distinguish it from the disjoining pressure Π. We have

$$\pi \equiv \gamma^{\alpha\beta} - \gamma^f \tag{91a}$$

$$= -\int_{\gamma^f(h=0)}^{\gamma^f(h)} d\gamma^f \tag{91b}$$

$$= -\int_{\Pi(h=0)}^{\Pi(h)} h'\, d\Pi \tag{91c}$$

and

$$S^{eq}_{\sigma/\alpha\beta} = \gamma^{f} - \gamma^{\alpha\sigma}_{\infty} - \gamma^{\beta\sigma}_{\infty} \tag{92a}$$

$$= \lim_{h^*\to\infty} \int_{\Pi(h)}^{\Pi(h^*)} h'\, d\Pi \tag{92b}$$

It can be seen from Eqs. (91) and (92) that the film pressure and the spreading coefficient are the continuation of the same integral. If each integral is evaluated to a common limit, then the "initial spreading coefficient" (i.e., the interfacial tension of the α and β phases evaluated in the absence of the σ phase, $\gamma^{\alpha\beta}$) can be evaluated from the sum of the film pressure and the equilibrium spreading coefficient:

$$S^{I}_{\sigma/\alpha\beta} \equiv \gamma^{\alpha\beta} - \gamma^{\alpha\sigma}_{\infty} - \gamma^{\beta\sigma}_{\infty} \tag{93a}$$

$$S^{I}_{\sigma/\alpha\beta} = \pi + S^{eq}_{\sigma/\alpha\beta} = -\lim_{h^*\to\infty} \int_{\Pi(h=0)}^{\Pi(h^*)} h'\, d\Pi \tag{93b}$$

The preceding analysis makes it possible to extend the disjoining pressure isotherm to zero thickness by using an adsorption isotherm. A schematic diagram showing the disjoining pressure, thickness, and film tension as a function of the chemical potential is shown in Fig. 16. In this case, the thickness is a monotonic function of the chemical potential. Such a case will yield a positive or zero spreading coefficient, that is, a zero contact angle.

For cases in which the thickness is not a monotonic function of the chemical potential, it will not be possible to measure the entire isotherm because some region of the isotherm will be unstable. By using a model for the isotherm, it may be possible to fit the small thickness region of the isotherm using adsorption data and the large thickness region of the isotherm using measurements of the disjoining pressure. The model can then be used to predict the isotherm across the region of the isotherm where no data exist. This case is illustrated on Fig. 17.

In this example, the point of intersection of the film pressure curve corresponds to two different thicknesses that have the same disjoining pressure and film pressure. This is a point of coexistence of films of different thickness and is a first-order phase transition. An example is the gaseous–expanded liquid transition of an adsorbed

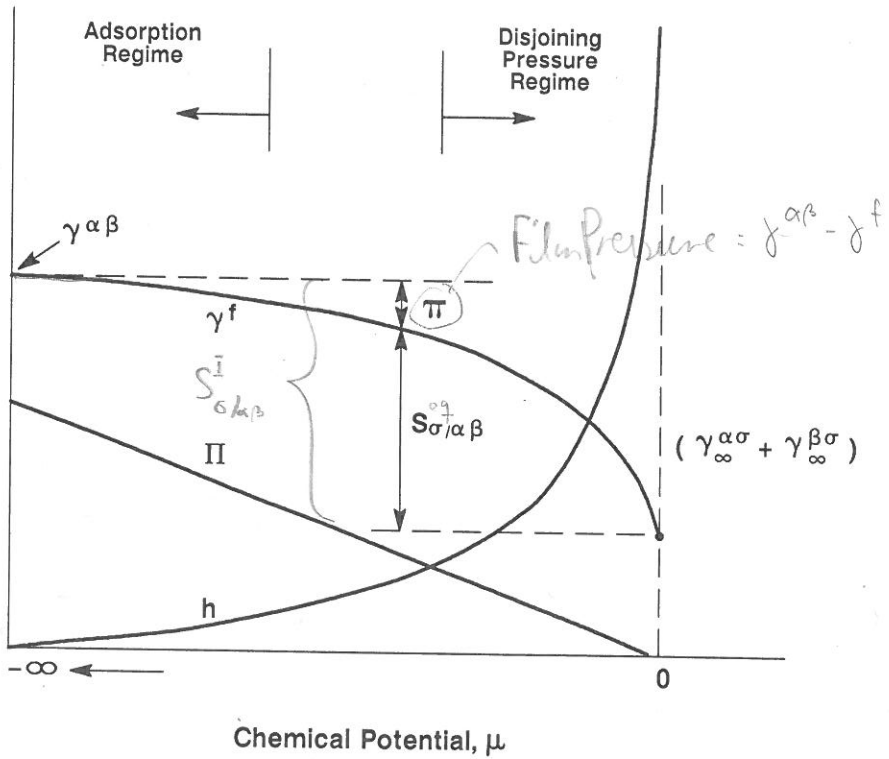

FIG. 16 Disjoining pressure, thickness, and film tension for monotonic isotherm.

monolayer. At saturation (zero disjoining pressure) the only stable film is the infinite thickness film, and thus the equilibrium spreading coefficient with saturated bulk liquid is zero.

Figure 18 is an illustration of a nonwetting system. This system is similar to the previous system except that saturation is reached before the isotherms intersected at the point of thin–film coexistence. At saturation, a thin film has a lower film tension than the infinite thickness film and thus is the stable film. A film tension less than that of the infinite thickness film is equivalent to a negative spreading coefficient and also to a finite contact angle.

The verification of the van der Waals interaction in the region of thin films was made by Blake [39, 40] from adsorption measurements on oxidized aluminum foil and for thick films by pressing a bubble against an alumina plate. His adsorption data are shown on Fig. 19 along with his calculation of the van der Waals interaction using the Hamaker theory. This theory fails below 6 Å. The ad-

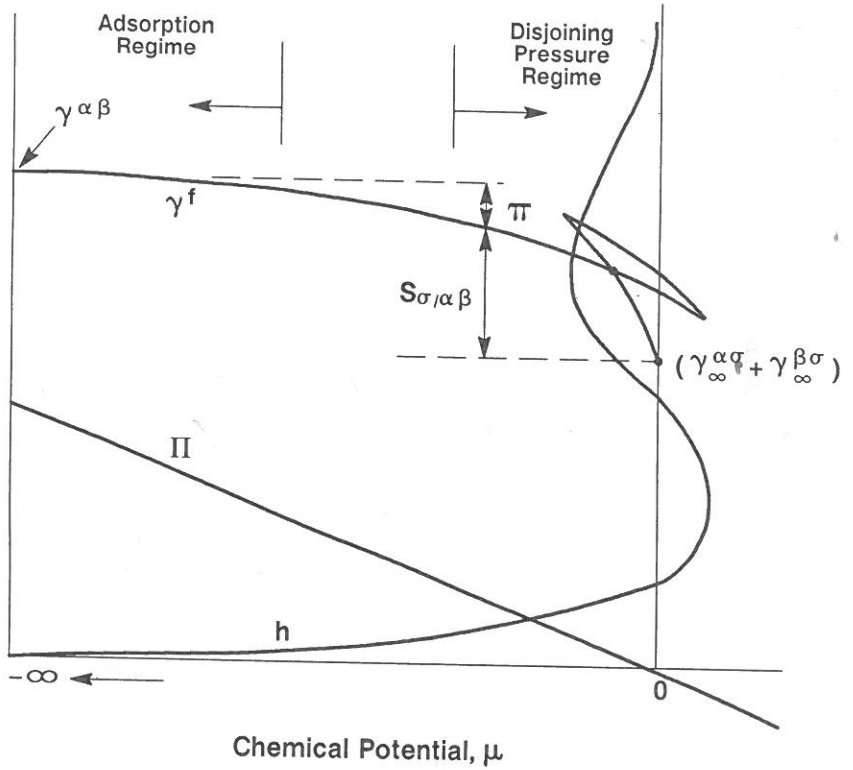

FIG. 17 Disjoining pressure, thickness and film tension for triple-valued isotherm.

sorption data for the smaller film thickness were fit by a two-dimensional van der Waals equation of state. This latter theory models the discrete nature of the adsorbate, and thus it models the structural effects.

A system where the disjoining pressure isotherm goes below the axis is the system vapor/benzene/water. The measured disjoining pressure isotherm from the data of Ottewill [41] is shown on Fig. 20. The data were fit with a two-dimensional van der Waals equation of state, and the fitted isotherm was extrapolated to intersect the van der Waals interaction isotherm from the Hamaker theory. The vertical line is where the Hamaker theory must be cut off in order to have an equilibrium spreading coefficient equal to the observed value of 1.63 mJ/m^2. For this system, the disjoining pressure isotherm from adsorption and Hamaker theory combined to give a spreading coefficient that corresponded with observation.

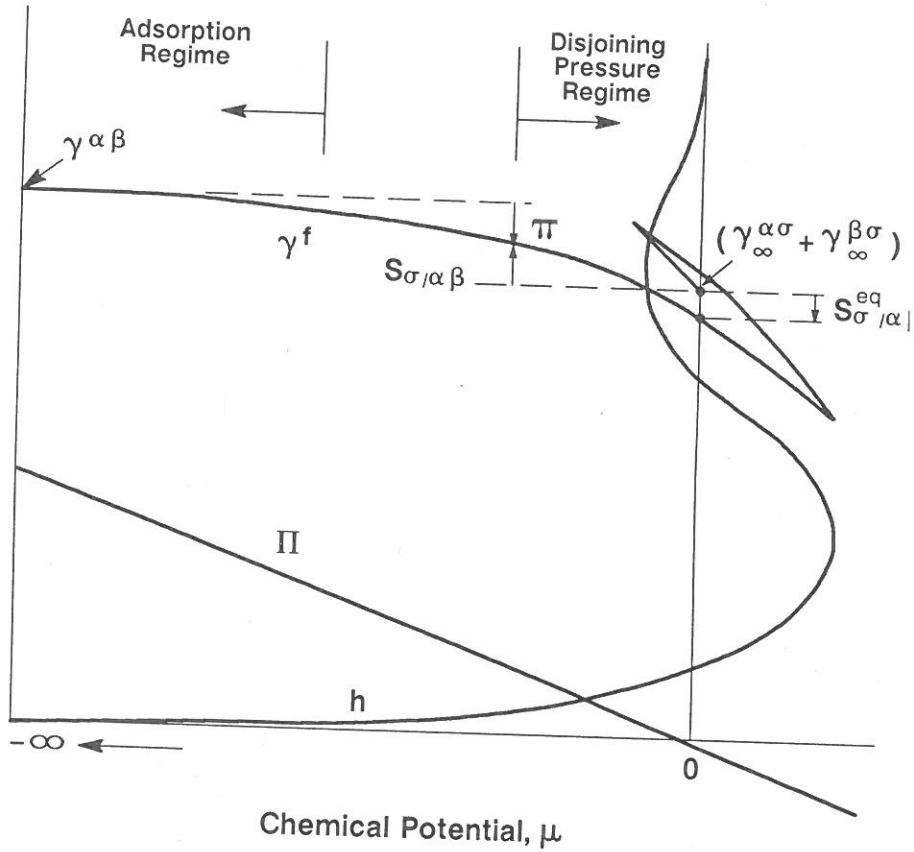

FIG. 18 Disjoining pressure, thickness, and film tension for non-wetting system.

Adamson et al. [42–45] interpreted a number of adsorption isotherms to compare the calculated contact angle with the observed contact angle on the same system. Those results showed that a low-energy material such as PTFE has an adsorbed film. The intersection and slope of the intersection of the adsorption isotherm with the zero disjoining pressure axis was an indication of the magnitude on the contact angle. Figures 21 and 22 show the isotherms for n-hexane and bromobenzene, which have small and large contact angles, respectively. The adsorption isotherms are fit with a two-dimensional van der Waals equation of state. The vertical line indicates where the Hamaker theory must be cut off in order to have the correct angle.

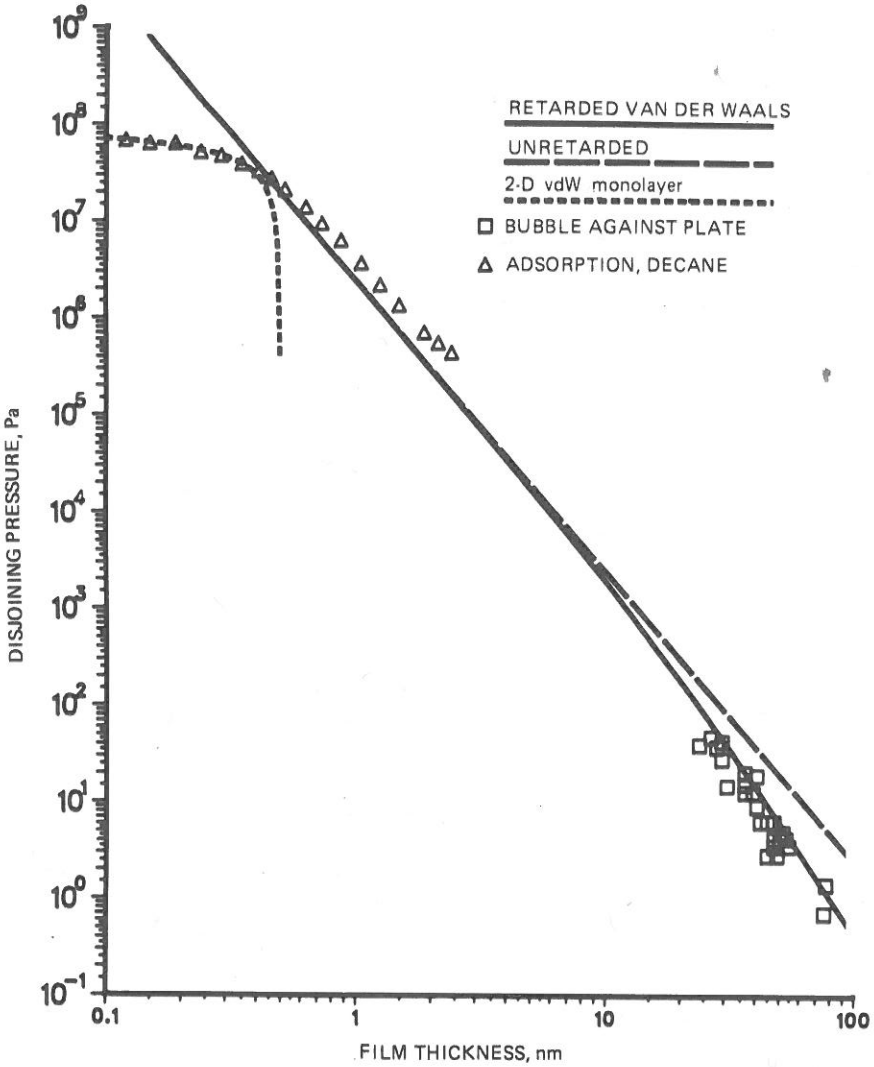

FIG. 19 Adsorption of decane on oxidized aluminum and bubble with octane and decane on alumina. (Data from Refs. 39 and 40.)

Gee [46] measured the adsorption of water on quartz using ellipsometry to measure the film thickness. Figure 23 shows the disjoining pressure isotherms for hydroxylated quartz, heat dehydoxylated quartz, and the isotherm calculated from van der Waals interaction alone. The heat dehydroxylated isotherm follows that of

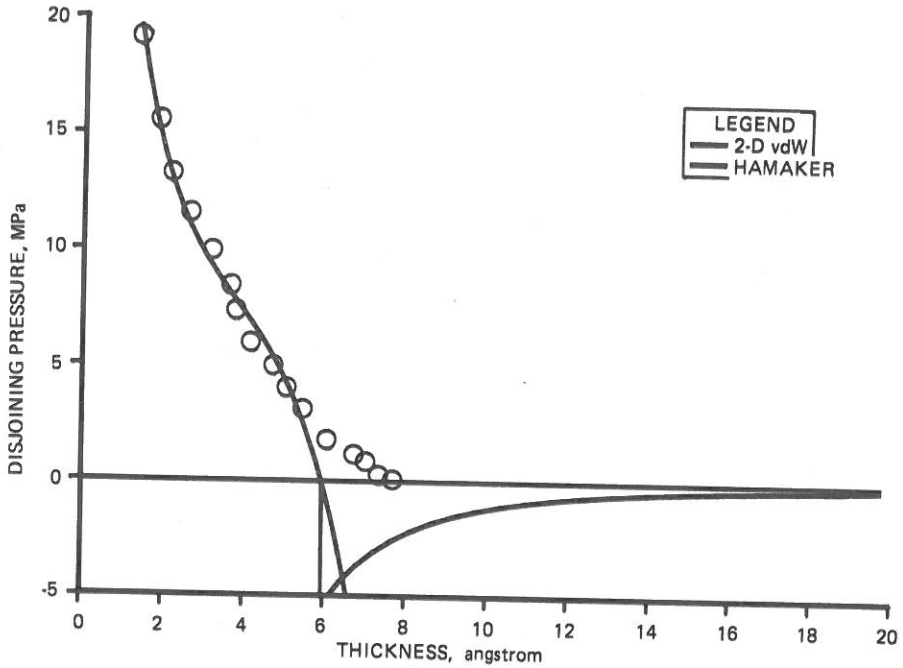

FIG. 20 Adsorption of benzene on water, S_{eq} = 1.63. (Data from Ref. 41.)

the van der Waals interactions at small thickness with the exception of the step at about 30 MPa. However, the contact angle of 43 degrees indicates that the isotherm must go below the axis. The hydroxylated quartz is water wetting and has a much greater thickness than can be accounted for by van der Waals and electrostatic interactions alone. These results suggest that surface force calculations for water must include structural or hydration forces due to hydrogen bonding.

K. Surface Forces

A model of the surface forces that describe the disjoining pressure isotherm is needed to study specific systems. The writer recently reviewed the effect of the surface forces on the contact angle [47]. For a general review of surface forces, the reader is referred to references 3, 48, and 49.

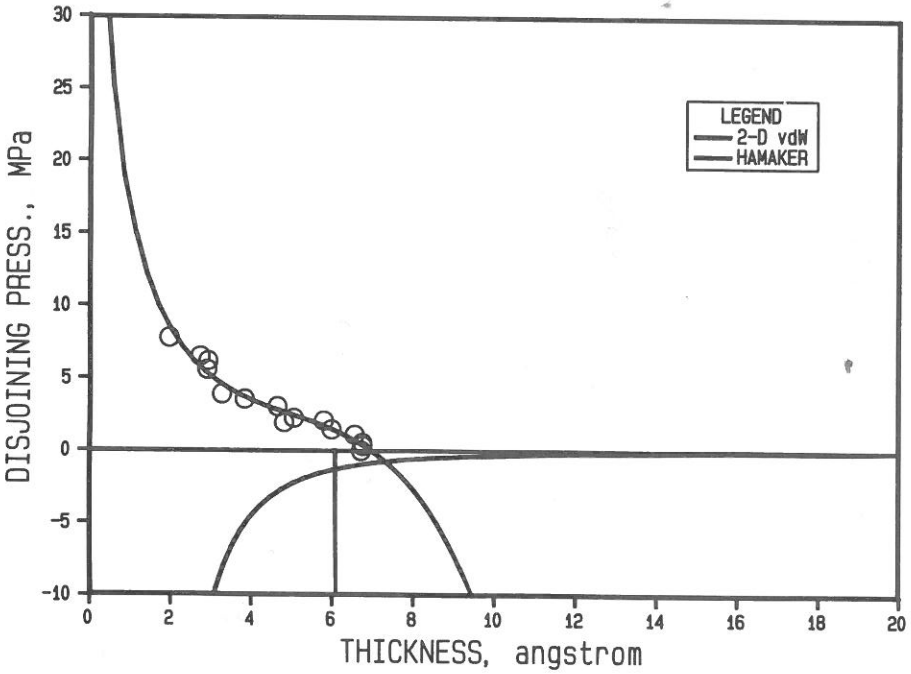

FIG. 21 Adsorption of hexane on PTFE, 12°C. (Data from Ref. 44.)

For a comprehensive review of wettability, the reader is referred to the article by de Gennes [50].

III. CONCLUSIONS

The classical, equilibrium thermodynamics of thin fluid films and the three-phase contact region has been derived by taking into consideration the disjoining pressure of the DLVO theory. This disjoining pressure is equal to the change in the sum of the interfacial tensions with thickness at a constant temperature, chemical potential, and gravitational potential.

The condition of equilibrium yields the augmented Laplace–Young equation, which includes the disjoining pressure. The augmented Kelvin equation describes the vapor pressure of a film as a function of the disjoining pressure (i.e., thickness), curvature, and gravatational potential.

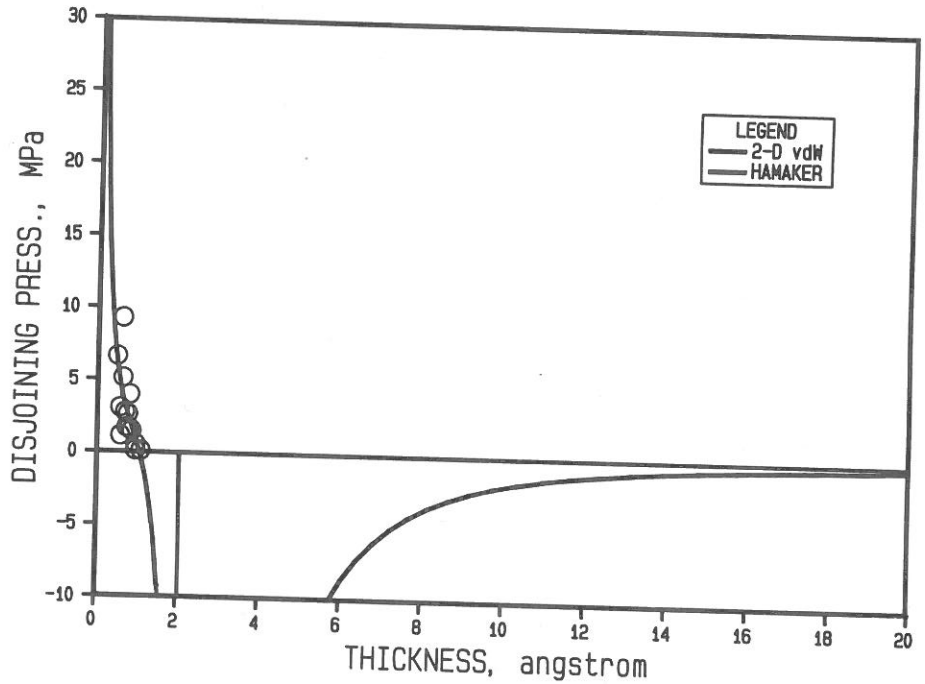

FIG. 22 Adsorption of bromobenzene on PTFE, 70°C. (Data from Ref. 44.)

The stability of an equilibrium state at constant temperature and chemical plus gravitational potential can be examined by use of the potential Ω. The effect of gravity can be examined by the effect of the gravitational potential. A sufficiently large increase (when the film is the more dense phase) in the gravitational potential can lead to the rupture of a thicker, metastable film and formation of a thinner film.

The spreading coefficient and contact angle of the three-phase contact region can be expressed in terms of an integral of the disjoining pressure isotherm. A nonzero contact angle can exist only if the value of the integral from zero disjoining pressure to its equilibrium value is negative.

A nonzero film elasticity can be derived for a film that has constant temperature and chemical plus gravitational potential for every component. This equilibrium elasticity was not recognized by Gibbs, since he assumed that the tensions would not change with thickness.

A particular specification of the Gibbs dividing surfaces also gives relationships for the changes of disjoining pressure and of film

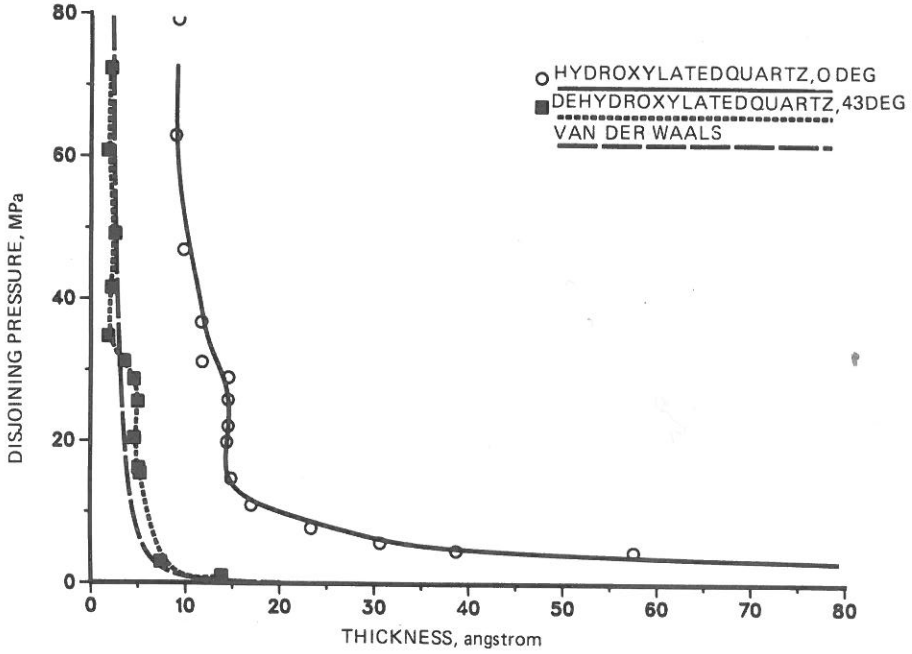

FIG. 23 Adsorption of water on quartz. (Data from Ref. 46.)

tension with change in chemical potential. Thus, the isotherm of disjoining pressure and thickness can be obtained from an adsorption isotherm. The adsorption isotherm will extend the disjoining pressure isotherm to zero thickness. Also, these relationships show the relation of film pressure, initial spreading coefficient, and equilibrium spreading coefficient.

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SYMBOLS

A	area, m
c	concentration, mol m^{-3}
E	elasticity, N m^{-1}

h	film thickness, m
H	mean curvature, m^{-1}
n	amount of substance, mol
M	molar mass, kg mol^{-1}
P	pressure, Pa
P_1	partial pressure of component 1, Pa
P_c	capillary pressure, Pa
psat	saturated vapor pressure, Pa
S	entropy, J K^{-1}
$S^{eq}_{\sigma/\alpha\beta}$	spreading coefficient, Nm^{-1}
$S^{I}_{\sigma/\alpha\beta}$	initial spreading coefficient, N m^{-1}
T	temperature, K
U	internal energy, J
V	volume, m^3
w	width, m
x	displacement of film transition parallel to film, m
z	displacement of film perpendicular to film, m
Γ	surface excess concentration, mol m^{-2}
γ	interfacial tension, N m^{-1}
κ	line tension, N
μ	chemical potential, J mol^{-1}
π	film pressure, N m^{-1}
Π	disjoining pressure, Pa
ρ	density, kg m^{-3}
Φ	gravitational potential, J Kg^{-1}
Ω	interaction potential, J
ω	specific interaction potential, J m^{-2}

Superscripts

f	film phase
j	phase index
α	bulk phase
β	bulk phase
σ	phase contained within film
η	one state of film
ν	another state of film
1	contact line
*	variable taken to the limit of infinity

Subscripts

i	component index
eq	equilibrium value
∞	evaluated at infinite thickness (bulk phase)

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