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THERMODYNAMICS OF WETTING

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ABSTRACT

The thermodynamics of a solid-liquid-vapor system both under chemical equilibrium and non-equilibrium conditions, based on the model of Gibbs, is discussed. Under chemical equilibrium conditions, the degree of wetting or non-wetting of a flat and non-deformable solid by the liquid is defined by Young's equation in terms of the static interfacial tensions. Under chemical non-equilibrium conditions, mass transfer across an interface results in a transient decrease in the corresponding specific interfacial free energy and the interfacial tension by an amount equal to the free energy of the effective chemical reaction per area at that interface. When the reaction is between the solid and the liquid, this transient lowering of the interfacial tension can cause the liquid drop to spread on the solid substrate if the interfacial energy reduction is large enough and also if the diffusion rates of the reacting components in the solid phase are slow enough relative to the flow rate of the liquid to cause the liquid at the periphery of the drop to be in dynamic contact with unreacted solid.

I. INTRCDUCTION

The degree of wetting of a solid by a liquid in a solid-liquid-vapor system is characterized by the conditions of thermodynamic equilibrium. Young,[2] from a mechanistic approach, expressed the relationship between the horizontal components of the three interfacial tensions of such a system at the three-phase contact as

$$\gamma_{sv}-\gamma_{s\ell} = \gamma_{\ell v} \cos \theta , \qquad (1)$$

where γ is the interfacial tension between solid-vapor (sv), solid-liquid ($s\ell$), and liquid-vapor (ℓv) phases, and θ is the contact angle measured through the liquid phase as shown in Fig. 1.

The first exact treatment of the thermodynamics of a solid-liquid-vapor system is due to Gibbs[3] who derived Young's equation for the non-gravitational case and outlined its derivation for a system in a gravitational field. A more rigorous treatment of the thermodynamics of a solid-liquid-vapor system, using the method of Gibbs, has more recently been provided by Johnson.[4] In both Gibbs' and Johnson's treatment of the conditions of mechanical equilibrium, the system was assumed to be at chemical equilibrium, i.e., no mass transport across the interfaces. Johnson explicitly defined the conditions for mechanical equilibrium in a solid-liquid-vapor system and emphasized that Young's equation is not the only requirement for total mechanical equilibrium and that the effect of the gravitational field and of curvature on pressure also has to be considered.

In wetting studies at elevated temperatures, the phases of a solid-liquid-vapor system are not often at chemical equilibrium prior to an experiment. Under chemical non-equilibrium conditions, the effect of chemical reactions on the interfacial tensions have to be considered. It has frequently been suggested[5-13] that an interfacial reaction or diffusion of a component from one bulk phase to the other results in the lowering of the corresponding interfacial tensions. Attempts have consequently been made[6,9,12] to correlate the wetting tendency with the free energy of interfacial reactions. This suggestion has been refused by others[14] on the grounds that interfacial reactions do not necessarily correlate with changes in wetting behavior.

The objectives of this study are to expand on the thermodynamic treatment of Gibbs and Johnson in order (i) to establish the correlation between the degree of wetting and the corresponding interfacial tensions under total thermodynamic equilibrium conditions (Section II) and (ii) to establish the effect of interfacial chemical reactions on the wetting mechanics under chemical non-equilibrium conditions (Section III).

II. MECHANICS OF WETTING UNDER CHEMICAL EQUILIBRIUM CONDITIONS

Let us consider a solid-liquid-vapor system as presented in Fig. 1, where the effect of the gravitational field is neglected. The total differential of the free energy of this three-phase system[15] (at constant temperature and pressure, after neglecting the effect of curvature on the pressure and assuming that interfacial tensions are independent of orientation) is

$$dG = \sum_i \mu_i^s dn_i^s + \sum_i \mu_i^\ell dn_i^\ell + \sum_i \mu_i^v dn_i^v + \gamma_{s\ell} dA_{s\ell} + \gamma_{sv} dA_{sv} + \gamma_{\ell v} dA_{\ell v} +$$

$$\sum_{\alpha,\beta} \left\{ \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^\alpha} \right) dn_i^\alpha + \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^\beta} \right) dn_i^\beta + \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^{\alpha\beta}} \right) dn_i^{\alpha\beta} \right\}, \qquad (2)$$

where μ_i is the chemical potential of component i in the designated phases; n_i is the total number of moles of component i in the designated phase obtained by multiplying the concentration of component i in the homogeneous region of the phase by its volume, i.e. $C_i^\alpha V^\alpha$ or $C_i^\beta V^\beta$ or by multiplying the adsorption of component i at an interface by the corresponding interfacial area, i.e. $\Gamma_i^{\alpha\beta} A^{\alpha\beta}$; G is the total free energy of the designated phase obtained by multiplying the free energy of a unit volume in the homogeneous region of the phases by the volume of the corresponding phase, i.e. $g^\alpha V^\alpha$ or $g^\beta V^\beta$ or by multiplying the specific interfacial free energy by the corresponding interfacial area, i.e. $g^{\alpha\beta} A^{\alpha\beta}$, and where the subscripts of the partial derivatives are omitted for brevity and the summation $\sum_{\alpha,\beta}$ is taken over all three interfaces.

At total thermodynamic equilibrium, dG = 0; then since the variations of mass are independent of the variations of area,

$$\gamma_{s\ell} dA_{s\ell} + \gamma_{sv} dA_{sv} + \gamma_{\ell v} dA_{\ell v} = 0, \qquad (3)$$

and

$$\sum_i \mu_i^s dn_i^s + \sum_i \mu_i^\ell dn_i^\ell + \sum_i \mu_i^v dn_i^v + \sum_{\alpha,\beta} \left\{ \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^\alpha} \right) dn_i^\alpha + \right.$$

$$\left. \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^\beta} \right) dn_i^\beta + \sum_i \left(\frac{\partial G^{\alpha\beta}}{\partial n_i^{\alpha\beta}} \right) dn_i^{\alpha\beta} \right\} = 0. \qquad (4)$$

These two equations outline the conditions for mechanical and chemical equilibrium of the system, respectively; at chemical equilibrium Eq. (4) is satisfied and γ has a static value. Now, let us assume that the liquid is a small enough drop so that its equilibrium configuration in the absence of attractive forces is spherical due to negligible gravitational effects. If such a drop is placed on a flat and rigid solid surface, a solid-liquid interface will form if

$$\delta G = \delta \int_{s\ell} \gamma_{s\ell} dA_{s\ell} + \delta \int_{sv} \gamma_{sv} dA_{sv} + \delta \int_{\ell v} \gamma_{\ell v} dA_{\ell v} < 0 \qquad (5)$$

This free energy decrease results in a driving force for the deformation of the liquid drop. The solid-liquid interfacial area increases, and the deformation continues until the minimum energy state is reached as defined by Eq. (3). Thus, for a given system, when the bulk volumes are non-reactive, the free energy changes for the system are associated with changes in the interfacial areas.

Several progressive geometric configurations of the drop and the change in the areas of the liquid-vapor and the solid-liquid interfaces vs the contact angle, θ, (or the height of the drop, h) are shown in Fig. 2. It should be noted that the liquid-vapor interfacial area decreases from 180° to 90° and then increases as the contact angle decreases to 0°, whereas the solid-liquid interface increases continuously. Since $dA_{s\ell} = - dA_{sv}$, Eq. (5) becomes

$$\delta G = \delta \int_{s\ell} \left(\gamma_{s\ell}-\gamma_{sv}\right) dA_{s\ell} + \delta \int_{\ell v} \gamma_{\ell v} dA_{\ell v}, \tag{6}$$

or

$$\frac{dG}{dh} = \left(\gamma_{s\ell}-\gamma_{sv}\right) \frac{dA_{s\ell}}{dh} + \gamma_{\ell v} \frac{dA_{\ell v}}{dh} . \tag{7}$$

It is now possible by use of Eq. (7) to determine whether the contact angle will be acute or obtuse for any combination of relative interfacial tensions as shown in Table I which gives the sign of the terms of the equation. A net negative dG/dh indicates that the solid-liquid interface will continue to form and the contact angle will continue to decrease; the minimum energy configuration is obtained when dG/dh is zero which is realized when a balance is achieved between the two terms of the equation. It thus can be seen that when $\gamma_{sv}>\gamma_{s\ell}>\gamma_{\ell v}$ (case c), the contact angle is always acute; and when $\gamma_{sv}<\gamma_{s\ell}<\gamma_{\ell v}$ (case b), the contact angle is always obtuse. When $\gamma_{sv}<\gamma_{s\ell}>\gamma_{\ell v}$ (case a) and $\gamma_{s\ell}<\gamma_{sv}+\gamma_{\ell v}$, regardless of whether $\gamma_{sv} \gtrless \gamma_{\ell v}$, the contact angle is obtuse; but when

$\gamma_{s\ell}=\gamma_{sv}+\gamma_{\ell v}$, no interface forms and the measured contact angle is 180°. When $\gamma_{sv}>\gamma_{s\ell}<\gamma_{\ell v}$ (case d), regardless of whether $\gamma_{sv}\gtrless\gamma_{\ell v}$, the contact angle is acute. When $\gamma_{sv}-\gamma_{s\ell}>\gamma_{\ell v}$, an equilibrium contact angle is not obtained since the free energy decrease on wetting the rigid solid is greater than the increase due to the extension of the liquid surface; spreading, a dynamic condition, then continues as long as the bulk liquid is available. A reduction of the total surface energy of the solid by the liquid ($\gamma_{sv}>\gamma_{s\ell}$) is defined as wetting; a condition of $\gamma_{s\ell}>\gamma_{sv}$ is defined as non-wetting of the solid. Then, $\gamma_{sv}-\gamma_{s\ell}$ can be considered as the driving force for wetting.

The formation of a solid-liquid interface due to the wetting of the solid results in forces acting on the liquid drop that, because of the rigid nature of the solid, result in resisting forces generated by the liquid because of the imposed deformation of the liquid drop whose minimun energy state is a spherical shape. From the viewpoint of mechanics, there must be a balance of forces acting on the liquid drop at its periphery, as shown in Fig. 1. If an unbalance of these forces occurs, due to unequal chemical conditions around the periphery of the drop, the drop will move, as has been observed.[17] Likewise, there must be a balance of all the forces acting at any point; a balance of the horizontal forces at the "triple point" (solid, liquid, and vapor in equilibrium) provides the familiar Young's equation directly from mechanics (Eq. (1)). A balance of the vertical forces acting at the triple point also occurs; the magnitude of the attractive force exerted by the solid, B_v, is determined[18] by the vertical component of the surface tension of the liquid at the triple point, which does not exceed

the bonding force at the interface and normally does not distort the solid. The resultant of the horizontal and vertical forces exerted by the solid on the liquid becomes a balancing force, B, equal and opposite to the surface tension force of the liquid at the triple point (Fig. 1).

The formation of a solid-liquid interface due to minimum energy requirements but with no wetting of the solid becomes possible because of a reduction of the surface energy, $\int \gamma_{\ell v} dA$, of the liquid in contact with the solid ($\gamma_{sv} < \gamma_{s\ell} < \gamma_{\ell v}$). Again, there is a balancing force equal and opposite to the surface tension of the liquid, which is the resultant of the vertical attractive force (equal and opposite to the vertical component of $\gamma_{\ell v}$) and the force developed due to $\gamma_{s\ell} - \gamma_{sv}$, as seen in Fig. 1b.

It is now worthwhile to consider the boundary conditions which are not indicated by the mathematical analysis just employed. Under chemical equilibrium conditions, the formation of a true interface can be considered to be analogous to the formation of a solution and corresponds to an adjustment of surface structures to form some intermediate interfacial structure whose interfacial tension ($\gamma_{s\ell}$) then is between γ_{sv} and $\gamma_{\ell v}$ (cases b and c). The actual magnitude of $\gamma_{s\ell}$, however, is dependent upon the degree of chemical bonding or minimization of structural discontinuity across the interface developed in the system; $\gamma_{s\ell}$ thus becomes smaller with increasing chemical bonding at the interface. For $\gamma_{\ell v} > \gamma_{sv}$, then, $\gamma_{s\ell}$ approaches γ_{sv} with the development of chemical bonding, resulting in a limiting contact angle of 90°. For $\gamma_{sv} > \gamma_{\ell v}$, $\gamma_{s\ell}$ approaches $\gamma_{\ell v}$; experimental evidence,[17,19] however, suggests that the maximum reduction of γ_{sv}

by the liquid is by an amount equal to $\gamma_{\ell v}$ resulting in a limiting nominal zero contact angle as long as $\gamma_{sv}-\gamma_{\ell v}\geq\gamma_{\ell v}$, as can be seen from Eq. (1).

If $\gamma_{s\ell}$ is greater than both γ_{sv} and $\gamma_{\ell v}$ (case a), a true interface actually has not formed. It is visualized that the two surfaces are actually attracted to reduce the total interfacial energy but that they have not lost their individual identity; the contact angle approaches 180° with decreasing attraction. If $\gamma_{s\ell}$ is less than both γ_{sv} and $\gamma_{\ell v}$ (case d), a transient condition involving chemical reactions exists (Section III).

III. MECHANICS OF WETTING UNDER CHEMICAL NON-EQUILIBRIUM CONDITIONS

The conditions of chemical equilibrium at constant temperature and pressure are given by Eq. (4). When the conditions of Eq. (4) are not satisfied throughout the system, the phases of the solid-liquid-vapor system will react with each other through the interfaces to achieve a state of chemical equilibrium. During these non-equilibrium dynamic conditions, the interfacial tensions and thus the contact angle will be continuously changing until the system reaches a state of chemical equilibrium. Volume changes occurring during the reactions, if significant, will affect the physical configuration of the system.

Transfer of mass across the interfaces can be regarded as absorption from one phase to the other in the interfacial region. This process is more critical than adsorption (no mass transfer across the interfaces when the bulk phases are at equilibrium) since the degree of compositional and corresponding volume changes both in the bulk phases and the interphase could be substantially higher than the changes observed during

adsorption. Volume changes of the condensed phases during adsorption can normally be neglected.

Mass transfer across the interfaces must result in a net decrease of the free energy of the system at any time, for the reaction, otherwise, will not proceed. At the first instant of formation of an interface, however, only the interfacial region is involved in the chemical reaction, and thus the corresponding initial decrease in the free energy of the system is totally attributed to the decrease in the free energy of the interfacial region. The magnitude of the decrease in the specific interfacial free energy, $(-)\Delta g^{\alpha\beta}$, then is directly equal to $(-\Delta G^{\alpha\beta}/A)$. The corresponding interfacial tension is similarly reduced by an amount equal to $(-)\Delta g^{\alpha\beta}$ since[15]

$$\gamma_{\alpha\beta} = g^{\alpha\beta} - \sum_i \mu_i^{\alpha\beta} \Gamma_i \quad , \tag{8}$$

as schematically shown in Fig. 3. If it is assumed that the free energy of the reaction between the phases in the interfacial region is comparable but not necessarily equal to that between the bulk phases, the value of $(-\Delta G^{\alpha\beta}/A)$ could be substantially high, and for an approximate interfacial region thickness of 20Å, a decrease of as much as 1000 ergs/cm^2 (see Appendix A) could be realized in the magnitude of the specific interfacial energy and thus the interfacial tension. Experimentally, negative interfacial tensions are often measured during such chemical reactions that result in spontaneous spreading[5-9,12,20] or emulsification phenomena.[13]

Under chemical equilibrium conditions, however, specific interfacial free energies and static interfacial tensions are always positive since the bulk phases are more stable than the interfaces. Thus, after the completion of the reaction at the interface followed by its continuation into the bulk regions by diffusion, the incremental contributions of the $\sum_i \left(\partial G^{\alpha\beta}/\partial n_i^{\alpha}\right) dn_i^{\alpha}$ and $\sum_i \left(\partial G^{\alpha\beta}/\partial n_i^{\beta}\right) dn_i^{\beta}$ terms in Eq. (2) must be such that $\gamma_{\alpha\beta}$ increases towards a static interfacial tension value. With time, the contributions of these terms will decrease and become minimal because of the decrease in the chemical potential or composition gradient from the interface into the bulk phases. Therefore, after the initial decrease, $\gamma_{\alpha\beta}$ increases and gradually approaches the static interfacial tension of the reacted bulk phases (Fig. 3), which could be higher or lower than the pure dynamic interfacial tension, γ^0, of the unreacted phases but should not differ from it drastically. In comparison, Fig. 3 also shows the variation of the interfacial tension with time for a pure adsorption process which differs from that for a mass transfer across the interface since a transient minimization of the interfacial tension is not realized with adsorption.

Let us now consider the specific effects of several types of reactions on the solid-liquid vapor system of Fig. 1, assuming that chemical equilibrium exists between the vapor and the condensed phases but not between the solid and the liquid. The reactions to be considered are those that result because (i) only the solid is not saturated with some or all of the components of the liquid, (ii) only the liquid is not saturated with some or all of the components of the solid, (iii) both phases are unsaturated with respect to the other, and (iv) a compound

forms at the interface.

Several dynamic stages associated with the first type of reaction are shown schematically in Fig. 4. At the time t_o, Fig. 4a illustrates the instantaneous quasichemical equilibrium involving no interfacial reaction between the liquid and the solid. Young's equation (Eq. (1)) may then be expressed only in terms of the initial dynamic surface tensions. Now, as the solid solution reaction proceeds at the interface, the dynamic specific interfacial free energy, $g^{0,s\ell}$, will change by an amount $\Delta g^{s\ell}$ due to the free energy of the reaction; a corresponding change in $\gamma_{s\ell} = \gamma^o_{s\ell} + \Delta g^{s\ell}$ with time occurs, as shown in Fig. 3. When the diffusion rates of the reacting components and thus the growth rate of the reaction product are slow enough relative to the flow rate of the liquid drop (see Appendix B), the liquid at the periphery of the drop will remain in contact with unreacted solid that has an unaltered γ^o_{sv} as long as $\Delta A_{s\ell}$ is positive; the driving force for wetting $\gamma^o_{sv}-(\gamma^o_{s\ell} + \Delta g^{s\ell})$ which is increased by the amount $(-)\Delta g^{s\ell}$ remains constant. If the maximum driving force at t_m (Fig. 3) exceeds $\gamma_{\ell v}$, then spreading occurs;[20] and if the force does not exceed $\gamma_{\ell v}$, the contact angle continues to decrease until a transient mechanical equilibrium is reached as represented by t_1 in Fig. 4b. At this point, however, diffusion in the solid continues as shown schematically in Fig. 4c; γ^o_{sv} ahead of the liquid periphery then is also decreased by an amount $\approx (-)\Delta g^{s\ell}$.[21] The driving force for wetting therefore decreases, and the contact angle increases to a new value of θ_ε corresponding to the one for mechanical and chemical equilibria for the system (Fig. 4d). During this pull-back stage, the drop may break into isolated smaller drops if the thickness of the

original drop decreases considerably during the transient spreading stage.[20]

On the other hand, when the diffusion rates of the reacting components in the solid are fast relative to the flow rate of the liquid drop (see Appendix B), both γ^{o}_{sv} and $\gamma^{o}_{s\ell}$ will simultaneously decrease by an amount $(-)\Delta g^{s\ell}$, and the liquid at the periphery of the drop will remain in contact with reacted solid, as represented schematically in Fig. 4b'. The driving force for wetting in this case does not change drastically from that due to the initial dynamic surface tensions (Fig. 4a) and remains essentially constant while the system moves to chemical equilibrium (Figs. 4b', 4c', and 4d).

Throughout these entire sequences, and in Fig. 4, the amount of material dissolved by the solid was considered to be small enough to be neglected so that the solid surface remained flat. However, if the specific volume of the solid solution phase at the interface differs appreciably from that of the unreacted solid, analysis by use of Young's equation as applied to experimentally measured contact angles could be misinterpreted because of the resulting non-existence of a flat solid surface.

Several dynamic stages associated with a reaction of type (ii), where only the liquid is not saturated with the solid, are shown schematically in Fig. 5. Figure 5a shows the configuration at t_o when the liquid phase first comes into contact with the solid and Young's equation may be used to express the conditions for mechanical equilibrium in terms of the dynamic interfacial tensions. After the initial reaction the composition of the liquid around the periphery and at the solid-

liquid interface rapidly approaches equilibrium compositions relative to the solid; correspondingly, $\gamma^{o}_{s\ell}$ and $\gamma^{o}_{\ell v}$ decrease because of the free energy contribution of the reaction, but then they rapidly approach their static interfacial tension values $\gamma_{s\ell}$ and $\gamma_{\ell v}$ (Fig. 3). During the initial reaction stage, thus, an instantaneous lowering of the contact angle or spreading may be observed[20] which is immediately followed by the drop pulling back to an equilibrium contact angle θ_{ε} which is retained until the system reaches equilibrium (Figs. 5b and 5c). With high-viscosity liquids and fast diffusion rates, however, the initial spreading may not be realized because the static interfacial tensions are attained faster than the liquid can spread. Again, as in the previous case, the amount of solid dissolved by the liquid was considered to be small enough to be neglected. In actual fact, however, as the reaction proceeds, the solid-liquid interface will drop below the solid-vapor surface,[22] complicating the analysis of mechanical equilibrium.

The same sequences would occur in the case of a sessile drop with an obtuse contact angle, $\gamma^{o}_{s\ell}>\gamma^{o}_{sv}$, experiencing reactions. If the $\Delta g^{s\ell}$ contribution is large enough to reduce $\gamma_{s\ell}$ to a value smaller than γ_{sv}, an initial acute contact angle will form; and if $\Delta g^{s\ell}$ is large enough to increase $\gamma^{o}_{sv}-\gamma^{o}_{s\ell}-\Delta g^{s\ell}$ to a value larger than $\gamma_{\ell v}$, initial spreading will occur.

A type (iii) reaction is expected to be similar in behavior either to type (i) or (ii) reaction depending on whether an increase or decrease of volume of the solid occurs at the interface, but the kinetic analysis of the reaction and determination of the nature of the physical configuration become more complicated. The formation of a compound at the

interface (type (iv) reaction) is also expected to cause the mechanical behavior of the system to be similar to that for one with type (i) reaction. The analysis in this case could be even more complicated, particularly if the compound should isolate the liquid from direct contact with the reacting solid.

IV. CONCLUSIONS

The conditions of thermodynamic equilibrium, i.e. the minimization of the free energy, of a solid-liquid-vapor system define the degree of wetting of the solid by the liquid phase. When chemical equilibrium exists throughout the system, the free energy changes for the system are associated only with changes in the interfacial areas. The equilibrium contact angle of a liquid drop on a flat and rigid solid surface, then, is determined by Young's equation in terms of the static interfacial tension values. The relative magnitudes of the interfacial tensions indicate whether the contact angle will be acute or obtuse: (i) when $\gamma_{sv} > \gamma_{s\ell} \lesseqgtr \gamma_{\ell v}$, the contact angle is always acute (the condition of wetting of the solid), and (ii) when $\gamma_{sv} < \gamma_{s\ell} \gtreqless \gamma_{\ell v}$, the contact angle is always obtuse (the condition of non-wetting of the solid). Experimental observations, however, indicate that, under chemical equilibrium conditions, $\gamma_{s\ell}$ is always in between γ_{sv} and $\gamma_{\ell v}$. With increasing degree of chemical bonding at the interface, $\gamma_{s\ell}$ approaches the lower value of the two, γ_{sv} or $\gamma_{\ell v}$.

Under chemical non-equilibrium conditions, the free energy changes for the system are associated not only with changes in the interfacial areas but also with changes in mass. Mass transfer across an interface initially results in a decrease in the corresponding specific interfacial free energy and the interfacial tension by an amount equal to the magnitude of $(-\Delta G/A)$ for the effective chemical reaction at the interface. However, after the completion of the reaction at the interface followed by its continuation into the bulk regions by diffusion, the specific interfacial free energy and the interfacial tension gradually increase towards their static values. When the reaction is between the solid and the liquid, this transient lowering of the interfacial tension can cause the liquid drop to spread on the solid substrate if the interfacial tension reduction is large enough and if the diffusion rates of the reacting components, and thus the growth rate of the reaction product, are slow enough relative to the flow rate of the liquid.

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APPENDIX A

EFFECTIVE FREE ENERGY OF REACTION AT AN INTERFACE

Consider a solid-liquid-vapor system[20] where an interfacial reaction,

$$MgO_{(s)} + R_2O_3 \text{ (in liquid)} \rightarrow MgR_2O_4 \text{ (in MgO)}, \qquad \text{(A1)}$$

takes place at the solid (MgO)-liquid interface that results in the formation of an MgO solid solution with MgR_2O_4, where R_2O_3 denotes a sesquioxide Al_2O_3, Cr_2O_3, or Fe_2O_3. At 1673K, an average value for the standard free energy of this reaction,[23] ΔG^o, is -8000 cal/mole. The free energy of the reaction (A1), then, is

$$\Delta G = RT \ln \frac{a_{MgR_2O_4}}{a_{R_2O_3}} - 8{,}000, \qquad \text{(A2)}$$

where R is the gas constant. Assuming that Raoult's law is applicable, $a_{MgR_2O_4}$ is equal to the concentration of MgR_2O_4 in the MgR_2O_4 solid solution at equilibrium with the MgO solid solution. A typical value[20] for $a_{MgR_2O_4}$ is ≈ 0.9. Similarly, $a_{R_2O_3}$ depends on the concentration of R_2O_3 in the liquid phase. Assuming a value of 0.5 for $a_{R_2O_3}$, $\Delta G = -6050$ cal/mole. The effective contribution of this reaction at the solid-liquid interface depends on the volume of the effective interfacial region and the extent of the solid solution in MgO. Consider a liquid drop of 0.5 cm in diameter on an MgO substrate. Assume the effective thickness of the interfacial region at the solid-liquid interface to be

≈ 20 Å. The volume of this interfacial disc is 3.94×10^{-8} cm^3. The number of moles of MgR_2O_4 going into solution in MgO in this volume depends on the extent of the solubility of MgR_2O_4 in MgO. The density and the molecular weight of this solid solution can be estimated assuming that the molar volumes of the pure components are equal to the partial molal volumes and thus the molar volumes of the pure components are additive. The molecular weight of an MgO solid solution with 50 mol% $MgFe_2O_4$, then, is 120.16 gms. Similarly, the density, ρ, of this solid solution is 4.04 gms/cm^3 based on the $\rho_{MgO} = 3.58$ and $\rho_{MgFe_2O_4} \cong 4.5$ gm/cm^3 values.[24] Therefore, the number of moles of the MgO ($MgFe_2O_4$) solid solution forming in the interfacial volume is 1.32×10^{-9}, and thus the number of moles of $MgFe_2O_4$ going into solution is 6.6×10^{-10}. The ΔG of the interfacial reaction becomes -4×10^{-6} cal or -167 ergs; and in terms of unit area, $\Delta g^{s\ell} = -850$ ergs/cm^2.

In case of the formation of the compound MgR_2O_4 at the interface, $\Delta g^{s\ell}$ is higher due to the higher number of moles of MgR_2O_4 forming in the interfacial region. The number of moles of $MgFe_2O_4$ solid solution forming in the same interfacial region is then 8.86×10^{-10}, and $\Delta g^{s\ell}$ becomes -1140 ergs/cm^2.

APPENDIX B

KINETICS OF SPREADING

The kinetics of spreading of a spherical liquid droplet on a flat and rigid solid surface has been discussed by Yin[25] based on the assumption that spreading is impelled by the horizontal components of the surface tensions at the three-phase boundary and retarded by the viscous flow of the droplet. Yin showed that the instantaneous rate of spreading, in terms of area per unit time, is

$$\frac{dA}{dt} = K\,(S_o I_1 + \gamma_{\ell v}\, I_2), \text{ with} \tag{B1}$$

$$K = \left(\frac{4\pi}{\eta}\right)\left(\frac{3V_o}{\pi}\right)^{1/3}, \tag{B2}$$

where η is the viscosity of the liquid (poise), V_o is the volume of the droplet (cm^3), $S_o = \gamma_{sv} - \gamma_{s\ell} - \gamma_{\ell v}$ is the spreading coefficient, and I_1 and I_2 are definite integrals as functions of the instantaneous contact angle only. For the system shown in Fig. 4, when an original instantaneous contact angle of 50° is assumed $I_1 = 0.5$ and $I_2 = 0.05$.[25] Furthermore, when values of $V_o = 0.03\ cm^3$, $\gamma_{\ell v} = 500$, $\gamma_{sv} = 1000$, $\gamma_{s\ell} \cong 0$ dynes/cm (chemical reaction case), are assumed, $S_o = 500$ dynes/cm, and

$$\frac{dA}{dt} = \frac{107}{\eta}\ (cm^2/sec), \text{ or } \frac{dr}{dt} = \frac{51.2}{\eta}\ (cm/sec). \tag{B3}$$

Now, let us consider the spreading of an R_2O_3 containing silicate liquid on an MgO substrate which is unsaturated with respect to MgR_2O_4. When R_2O_3 diffuses into MgO, in order for the reaction product to grow ahead of the liquid periphery, i.e. into the solid-vapor interface, the flow rate of the drop has to be slower than the growth rate of the diffusion product. The concentration, C, of a component diffusing rapidly in the surface region of a substrate, from a stationary cylindrical source, is[26]

$$C(r,t) = \frac{C_o r_o}{r(D_s t)^{1/2}} \operatorname{erfc} \left\{ \frac{r-r_o}{(D_s t)^{1/2}} \right\} , \qquad (B4)$$

where C_o is the concentration of the diffusing component in the surface region of the substrate beneath the circular source, r_o is the radius of the source, D_s is the surface diffusion coefficient, and erfc is the complementary error function. For an instantaneous contact angle of 50° and $V_o = 0.03\ cm^3$, $r_o = 0.33$ cm. Taking $D_s = 10^{-6}\ cm^2/sec$,[27] the concentration front of $C/C_o = 0.9$ at $t = 1.0$ sec is at $r = 0.332$, and $\Delta r = 2.35 \times 10^{-3}$ cm. In order for the liquid to spread faster than the diffusion product can grow, a liquid viscosity of $<2.56 \times 10^4$ poise is required (Eq. (B3)). Thus, when dealing with high viscosity liquids (silicates), lowering of the contact angle or spreading may not necessarily be observed during an interfacial reaction.

Table I. The sign of the terms in Eq. (14) for possible γ relationships

γ Relationship	First Term	Second Term
For contact angles of 180° → 90°		
(a) $\gamma_{sv} < \gamma_{sl} > \gamma_{lv}$	(+)	(-)
(b) $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$	(+)	(-)
(c) $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$	(-)	(-)
(d) $\gamma_{sv} > \gamma_{sl} < \gamma_{lv}$	(-)	(-)
For contact angles of 90° → 0°		
(a) $\gamma_{sv} < \gamma_{sl} > \gamma_{lv}$	(+)	(+)
(b) $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$	(+)	(+)
(c) $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$	(-)	(+)
(d) $\gamma_{sv} > \gamma_{sl} < \gamma_{lv}$	(-)	(+)

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FIGURE CAPTIONS

Fig. 1. Equilibrium of forces on the periphery of a sessile drop of an (a) acute contact angle and (b) obtuse contact angle. B is the resultant balancing force equal and of opposite direction to $\gamma_{\ell v}$, and B_v is the vertical component. The liquid drops are small enough to neglect gravitational forces.

Fig. 2. Variation of the solid-liquid and the liquid-vapor interfacial areas vs decreasing contact angle, θ, or the height of the drop, h. V_o is the volume of the liquid drop.

Fig. 3. Variation of dynamic interfacial tension with time during a chemical reaction between two phases. The initial or pure dynamic interfacial tension is indicated by $\gamma^o_{\alpha\beta}$. The degree of minimization of the interfacial tension at t_m is proportional to $\Delta g^{\alpha\beta}$ (see Appendix A). In case of a pure adsorption process, no minimum is observed (top curve).

Fig. 4. Schematic representation of the various dynamic stages of a sessile drop when the initial solid is not saturated with some or all of the components of the liquid. The path "abcd" corresponds to the case where the growth rate of the reaction product is slower than the flow rate of the liquid drop; and path "ab'c'd" corresponds to the case where the growth rate of the reaction product is faster than the flow rate of the liquid drop.

Fig. 5. Schematic representation of the dynamic stages of a sessile drop when the initial liquid is not saturated with some or all of the components of the solid.

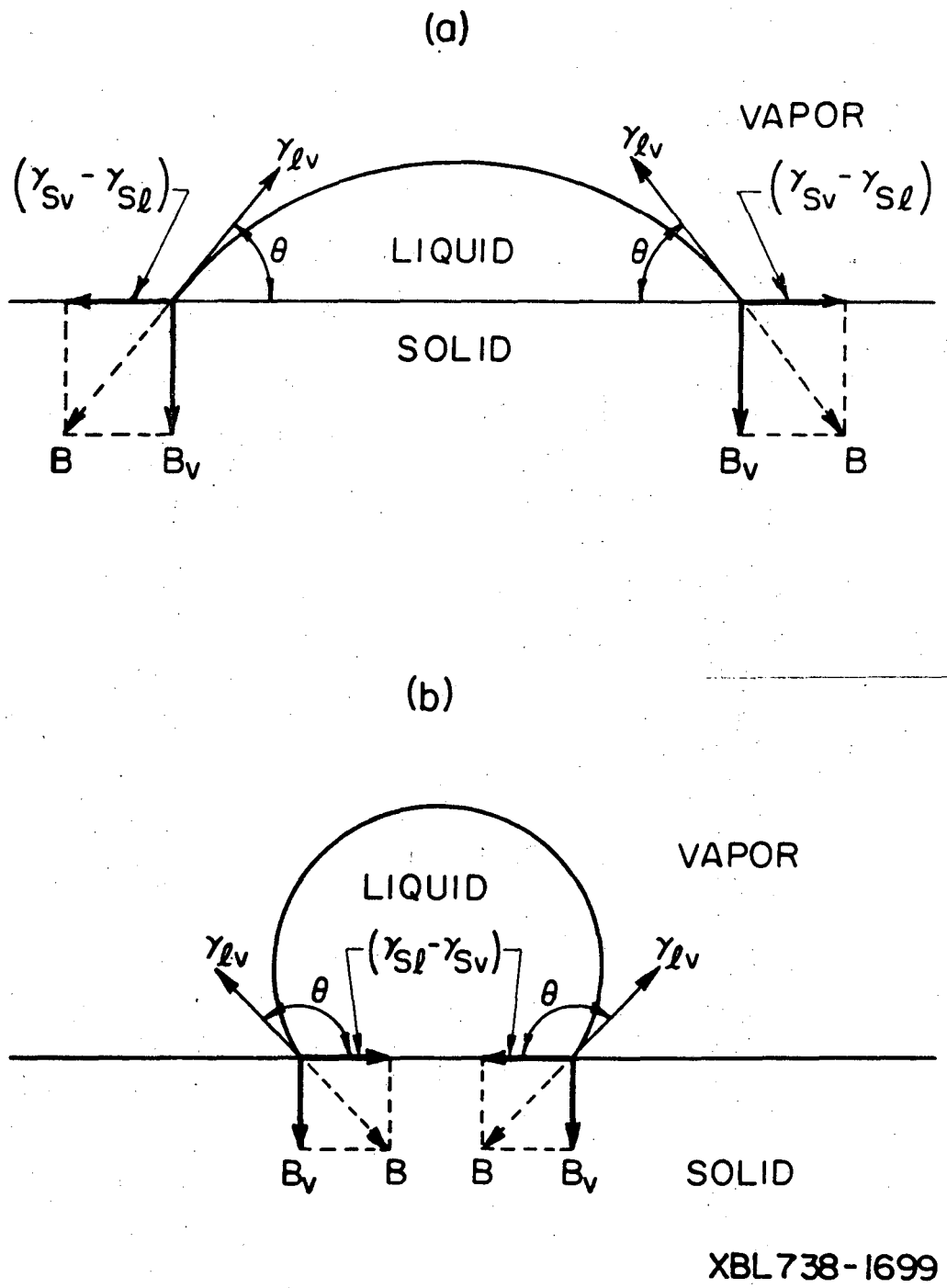
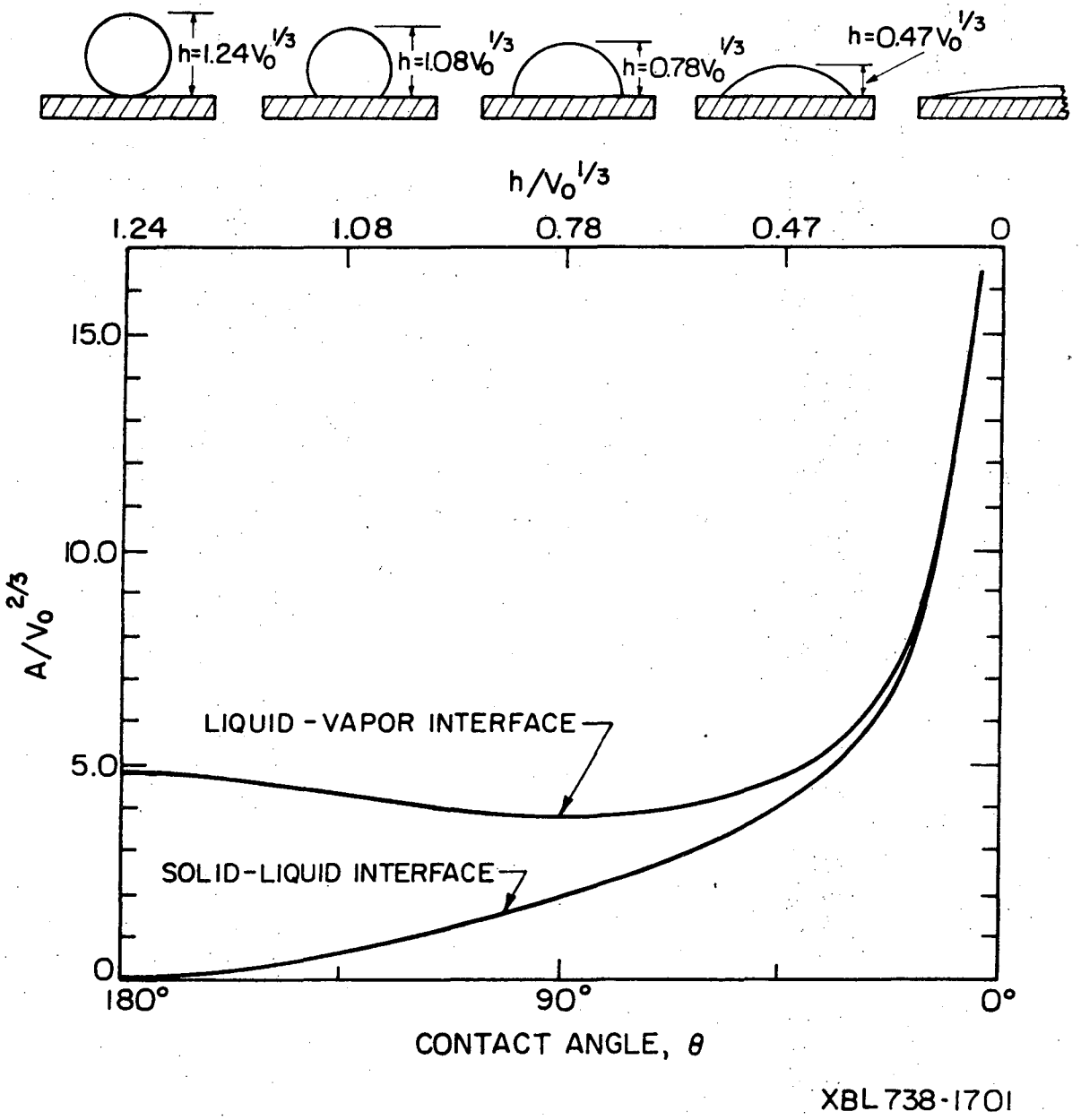

(a)
VAPOR
$\gamma_{\ell v}$
$\gamma_{\ell v}$
$(\gamma_{Sv} - \gamma_{S\ell})$
$(\gamma_{Sv} - \gamma_{S\ell})$
θ
LIQUID
θ
SOLID
B
B_v
B_v
B
(b)
VAPOR
LIQUID
$\gamma_{\ell v}$
$(\gamma_{S\ell} - \gamma_{Sv})$
$\gamma_{\ell v}$
θ
θ
B_v
B
B
B_v
SOLID
XBL738-1699

Fig. 1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h/V0^1/3
1.24
1.08
0.78
0.47
0
15.0
10.0
5.0
0
A/V0^2/3
LIQUID - VAPOR INTERFACE
SOLID-LIQUID INTERFACE
180°
90°
0°
CONTACT ANGLE, θ
XBL 738-1701

Fig. 2

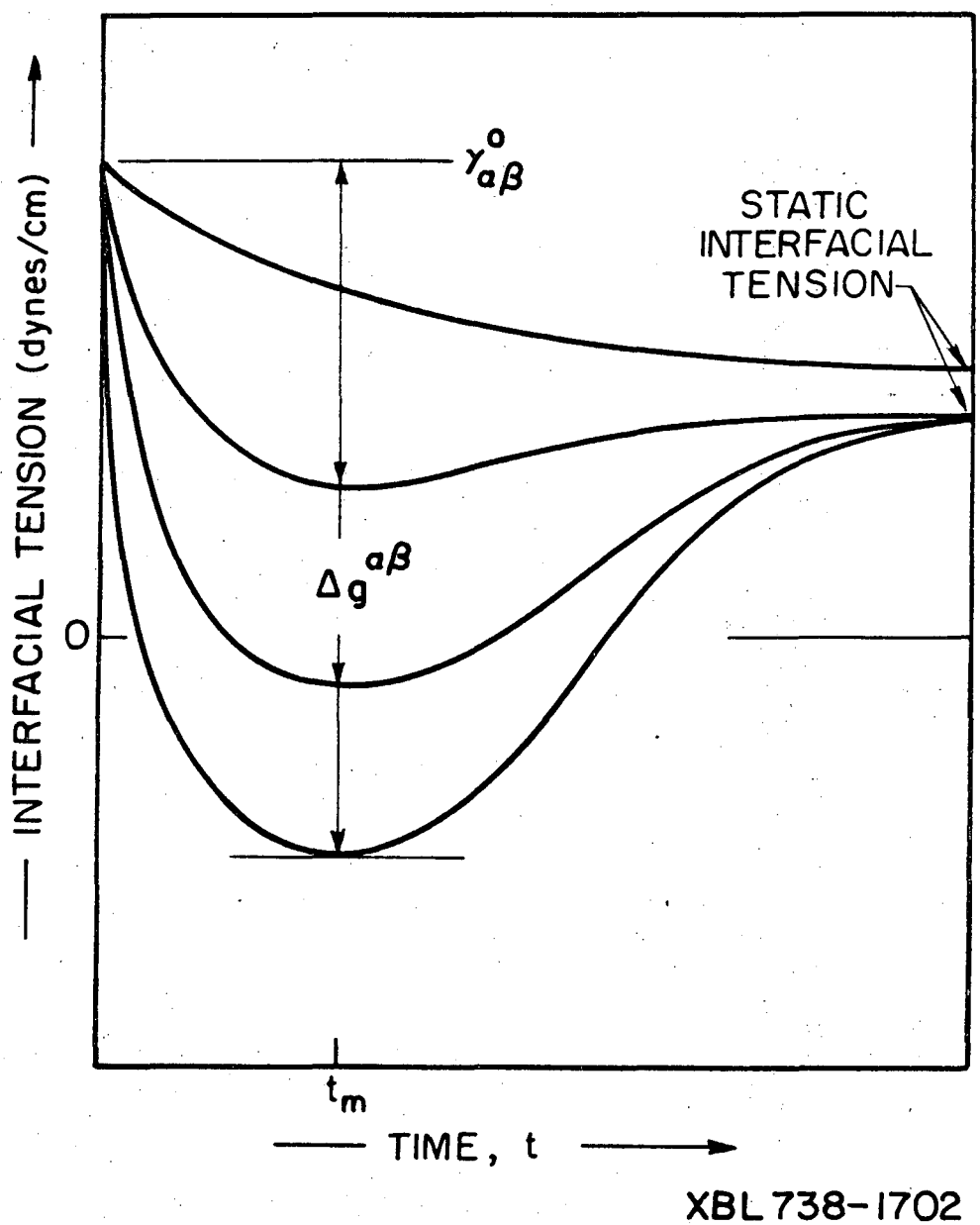
$\gamma^{o}_{\alpha\beta}$
STATIC
INTERFACIAL
TENSION
$\Delta g^{\alpha\beta}$
0
INTERFACIAL TENSION (dynes/cm)
t_m
TIME, t
XBL 738-1702

Fig. 3

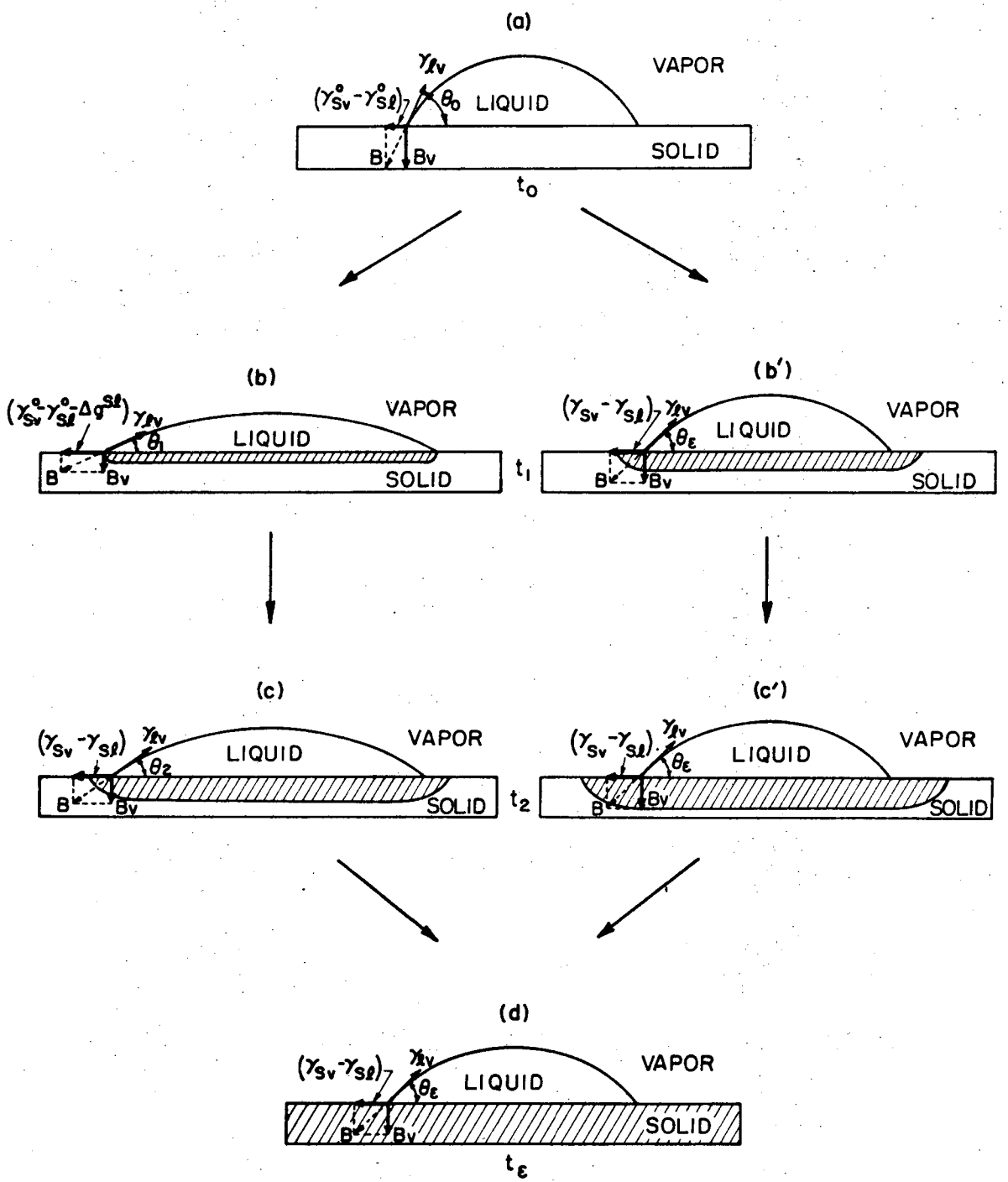
(a)
VAPOR
LIQUID
SOLID
B
Bv
t_0
(b)
VAPOR
LIQUID
SOLID
B
Bv
t_1
(b′)
VAPOR
LIQUID
SOLID
B
Bv
(c)
VAPOR
LIQUID
SOLID
B
Bv
t_2
(c′)
VAPOR
LIQUID
SOLID
B
Bv
(d)
VAPOR
LIQUID
SOLID
B
Bv
t_ε
XBL 738-1703

Fig. 4

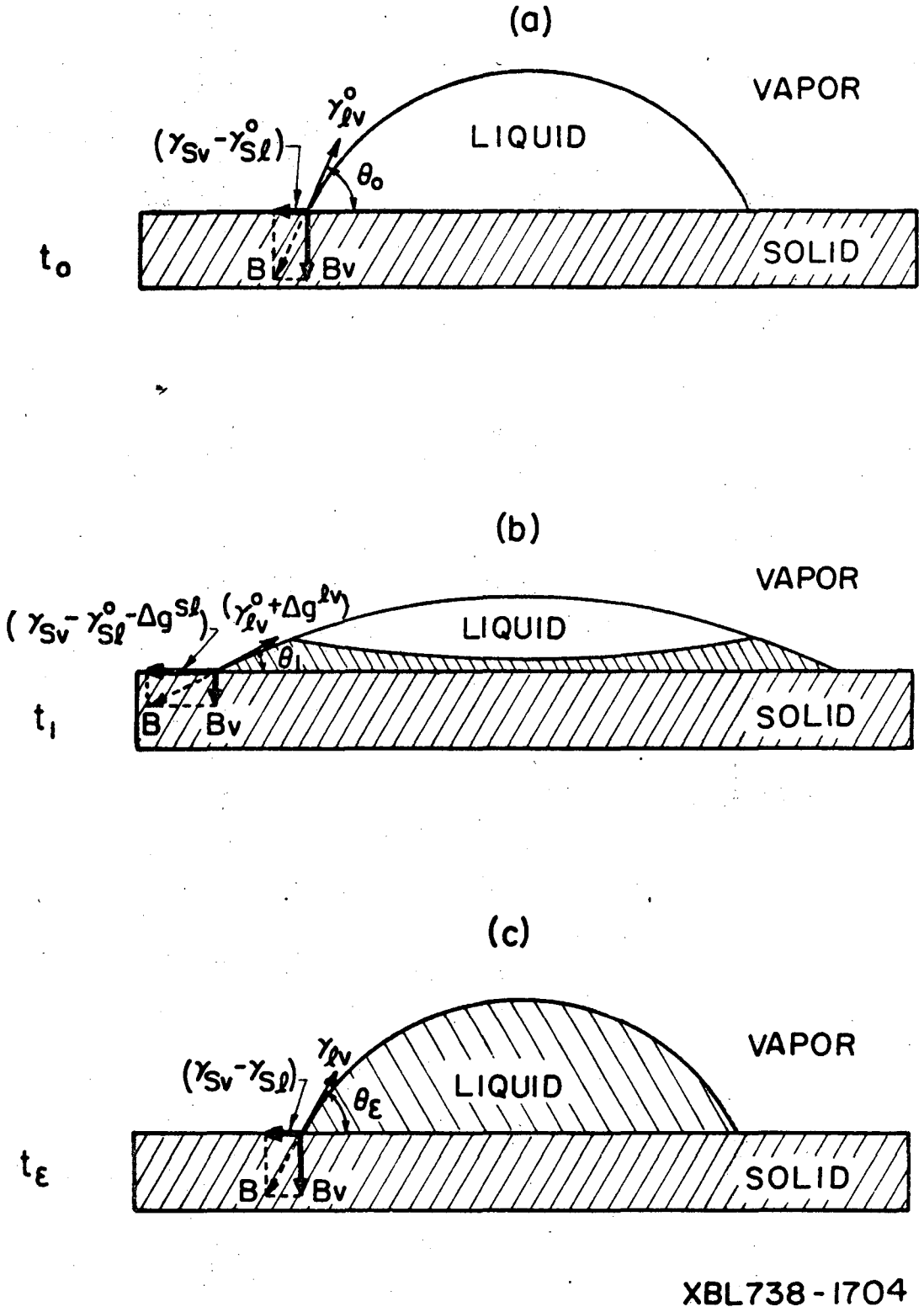
(a)
VAPOR
LIQUID
SOLID
$\gamma^o_{\ell v}$
$(\gamma_{Sv}-\gamma^o_{S\ell})$
θ_o
t_o
B
Bv
(b)
VAPOR
LIQUID
SOLID
$(\gamma_{Sv}-\gamma^o_{S\ell}-\Delta g^{S\ell})$
$(\gamma^o_{\ell v}+\Delta g^{\ell v})$
θ_1
t_1
B
Bv
(c)
VAPOR
LIQUID
SOLID
$\gamma_{\ell v}$
$(\gamma_{Sv}-\gamma_{S\ell})$
θ_ε
t_ε
B
Bv
XBL738-1704

Fig. 5

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