

THE INTERACTION OF MICROWAVE RADIATION
WITH PAPER-WATER SYSTEMS

Project 3322

Report One
A Progress Report
to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

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Appleton, Wisconsin

DYNAMIC INTERACTIONS OF LIQUIDS WITH
SURFACES AND FIBERS

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December 15, 1978

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SUMMARY

The importance of understanding the interactions of liquids with solids is well recognized in the paper industry. However, the lack of fundamental information with regard to these wetting interactions has limited adequate control, prediction and improvement of many industrial processes. The information gap is particularly evident in the area of wetting dynamics. Consequently, this report is a review of the pertinent scientific literature describing both static and dynamic interactions of liquids with solids.

Contact angle measurements are the most direct means of evaluating solid-liquid interactions. The contact angle can be related to the various surface and interfacial free energies for a solid-liquid system via the well-known equation credited to Thomas Young. However, this expression is of limited utility to the practical scientist since two of the four unknown quantities cannot be reliably or conveniently measured or calculated. However, developments in recent years have circumvented or overcome these difficulties to enable significantly more information to be garnered from contact angle measurements.

Zisman and coworkers developed an empirical technique to characterize low energy (<100 ergs/cm²) solids. This method permitted evaluation of a parameter called the critical surface tension of the solid. Liquids with surface tensions less than this critical value would wet the solid with a zero contact angle. Liquids possessing surface tensions greater than the solid's critical value would incompletely wet the solid and form finite contact angles. This method provided

a convenient manner to characterize low energy solids and permitted predictions of wetting behavior.

Good and coworkers developed a theoretical way to determine the surface energy of a solid. An interaction parameter was introduced into the theory which quantitatively described the molecular attractive interactions across an interface. This parameter could be calculated from the available properties of the solid and liquid. The solid's surface energy was determined from the calculated interaction parameter and experimental measurements of the surface tension of the liquid and the contact angle. Characterization of the solid in this manner then permitted wetting predictions for any liquid of known surface tension with this solid.

Fowkes extended the theory of Good and presented the stimulating idea that the surface energy of a solid was composed of additive components. Likewise, the surface tension of a liquid could be separated into individual components. He then proposed that the interaction of a solid with a liquid occurred only by the common components of each. For example, a nonpolar liquid would be insensitive to the dipoles in a polar solid, and interaction would occur via the London forces common to both. These ideas led to vigorous activity for experimentalists to characterize the various components of low energy solids. However, certain precautions and reservations must be observed with this technique to insure that the data are not overinterpreted.

Contact angle hysteresis results when more than the single contact angle predicted by the Young equation is observed under equilibrium conditions. Adequate theories to explain this phenomenon have been developed. Contact angle hysteresis is generally attributed to the characteristics of the solid surface which do not adhere to the stringent surface properties assumed in developing the theory. The idealized solid is considered flat, smooth, isotropic and nondeformable. Real

solids have varying degrees of roughness, heterogeneity and porosity, each of which can be the cause of contact angle hysteresis. Evidence exists that the microscopic contact angle obeys the Young equation for a liquid on a rough solid: In summary, the theory of static contact angles and contact angle hysteresis is well developed and adequately documented by experiment. Consequently, it is possible for the investigator to account for the observed equilibrium contact angle behavior in most practical systems.

Many of the considerations valid in static systems also apply to the interactions of solids and liquids under dynamic conditions. However, there are several important distinctions and differences. Liquid inertial and viscous effects must be considered in addition to the surface and interfacial forces. Dynamic contact angles reflect the solid-liquid interactions and are fundamentally different from the static situation. Thermodynamic or force balance static treatments are inadequate to describe the wetting kinetics. The subject of dynamic contact angles is best considered a branch of fluid dynamics. A brief summary of the current state of the art of contact angle rate effects follows.

A number of physical and surface chemists have measured the relationship between dynamic contact angles and velocity of the moving contact line. A lack of agreement on the observed effects as well as a number of explanations for the dynamic contact angle behavior have resulted from these studies. These controversies have not been resolved. However, this area is currently receiving considerable attention; consequently, it is in a rapid state of development.

A limited number of treatments of moving liquid contact lines on solids have been presented by fluid dynamicists. These workers have made valuable contributions to the field of wetting kinetics. The major difficulty of treating moving contact lines with conventional fluid dynamics has been dealing with the

flow in the region of the three phase line. Theoretical analyses have predicted infinite forces and stresses at the contact line. This behavior violates the fundamental no-slip boundary condition of fluid mechanics. It has been suggested, without justification, that a slip coefficient would alleviate these complications.

A theoretical justification has recently been presented for the origin of the forces which generate a slip velocity. A model which permitted a molecular analysis of the three phase zone led to the discovery that directional intermolecular forces are generated in the vicinity of the contact line. Computations of the slip velocity established the relationships with regard to the distance from the three phase line and the magnitude of the dynamic contact angle. A combination of such a molecular analysis in the region of the contact line and conventional fluid dynamics appears to offer the greatest hope of a unified treatment of wetting dynamics. Furthermore, many practical complications resulting from roughness, heterogeneity and porosity of the surface of the solid will have to be dealt with and incorporated into the theory. Significant steps along these lines have already been taken so that interested workers can optimistically anticipate an operational theory suitable for predicting the wetting behavior of practical systems in the near future.

INTRODUCTION

The importance of understanding and controlling the interactions of liquids with surfaces and fibers under dynamic conditions has long been recognized in the paper industry. Numerous liquid-solid phenomena are encountered in paper and board processing and converting operations such as sizing, coating, corrugating, saturating, etc. In addition, liquid wetting, spreading, adsorption and penetration often determine the suitability of paper and board products for a particular end use application such as printing, bonding or coating. In view of the significance of liquid interactions in papermaking, it is surprising that detailed knowledge and understanding of these processes do not exist. The lack of fundamental information is particularly evident with regard to the kinetics and dynamics of liquid-solid interactions. A more thorough understanding of wetting dynamics would assist the industry in improved control of current systems as well as enable increased processing speeds to be achieved.

The goals and objectives of this program are to develop a fundamental understanding of the interactions of liquids with surfaces and fibers. The approach taken will involve establishing satisfactory methods for characterizing the important surface properties of solids and determining the relationships of these properties to wetting and penetration rates. In addition, the significance of surface roughness, heterogeneity and porosity of the solids will be assessed. The ultimate long-range goal of this work is to be able to accurately predict the interaction behavior of liquids and solids under dynamic conditions in order to optimize the various processing variables encountered in the paper industry.

The first phase of our program has utilized the concepts of contact angles of liquids on solids as a measure of the relative interactions. The

characteristic static contact angle produced when a liquid drop contacts a smooth solid is an inverse measure of the wettability of the system. The dynamic situation obtained by movement of the liquid relative to the solid creates stresses in the droplet which result in the formation of advancing and receding contact angles which generally differ from the equilibrium value. The magnitude of the dynamic contact angle changes or hysteresis can be related to the liquid-solid interactions. However, a review of the literature prior to our experimental program indicated considerable advancement in the general fields of solid surface characterization and static contact angles in the last 10-15 years. Furthermore, the theory of contact angle hysteresis and the effect of rates is not well understood and is currently in a rapid state of development. More than a half-dozen independent causes of hysteresis have been proposed, some of which predict independence of rate effects.

In view of the recent progress in quantitatively describing the interactions of liquids and solids and in the understanding of dynamic contact angle hysteresis, we felt a critical review of the literature was necessary prior to proposing a meaningful research program. Consequently, this report reviews the scientific literature on the interaction of liquids with solids under both static and dynamic conditions. The recent advances in the theories of contact angles and contact angle hysteresis are covered. The current state of the art of contact angle rate effects are also reviewed. A subsequent report will cover the experimental program designed to assess the surface properties of solids important to the dynamics of wettability.

LITERATURE REVIEW

SURFACE ENERGY AND STATIC CONTACT ANGLE CONCEPTS

A brief review of the concepts of surface energy and contact angles appears to be a logical place to begin a discussion of the interaction of liquids with solids. The existence of the surface tension of liquids is readily observed by the presence of what appears to be a contractile "skin" surrounding the liquid. The intermolecular forces between fluid molecules are responsible for this surface tension. The liquid density is lower in the surface layer as a result of reduced intermolecular attractions between a surface molecule which has fewer nearest neighbors compared to a bulk fluid molecule. Consequently, the surface of a liquid has a higher free energy than an equivalent quantity of bulk material, and energy must be expended to create new surface. A liquid will form as nearly a spherical shape as possible (dependent on other external forces, e.g., gravity) in an attempt to minimize the surface-to-volume ratio and surface free energy.

Solid surface molecules also experience a similar intermolecular attraction difference compared to the bulk as in the case of a liquid. This gives rise to a higher free energy in the surface of the solid. However, unlike in a liquid, the surface molecules of a solid are not readily mobile and cannot rapidly reorient themselves to satisfy a more favorable energy condition. Solids readily attract and adsorb vapor molecules in the vicinity of the surface as a result of the excess free energy located at the interface. An overall reduction in the total free energy of the system results. Adsorption, of the type described above, gives rise to an intermolecular attractive force between the dissimilar vapor and solid molecules. Likewise, liquids in contact with a solid will experience the constraining surface tension forces due to intermolecular attraction between the fluid molecules and expansive forces as a result of attraction between the liquid

and solid molecules in the contacting surface layers. The balance of these forces determines the wettability behavior of a particular liquid-solid system.

Thomas Young (1) recognized the interrelationship of the various surface-free energies as early as 1805. He qualitatively stated the well known expression shown below for a pure liquid on a smooth, flat, rigid, isotropic solid.

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

The γ 's refer to the surface or interfacial free energies and the subscripts lv, sv, and sl denote the liquid-vapor, solid-vapor and solid-liquid interfaces, respectively. It is important, as we shall see, to recognize that γ_{sv} represents the free energy of the solid surface in equilibrium with the vapor of the liquid. θ represents the characteristic equilibrium contact angle formed by a nonwetting liquid on a solid and is the angle measured through the liquid to the line tangent at the point of intersection of the solid-liquid-vapor interface as shown in Fig. 1.

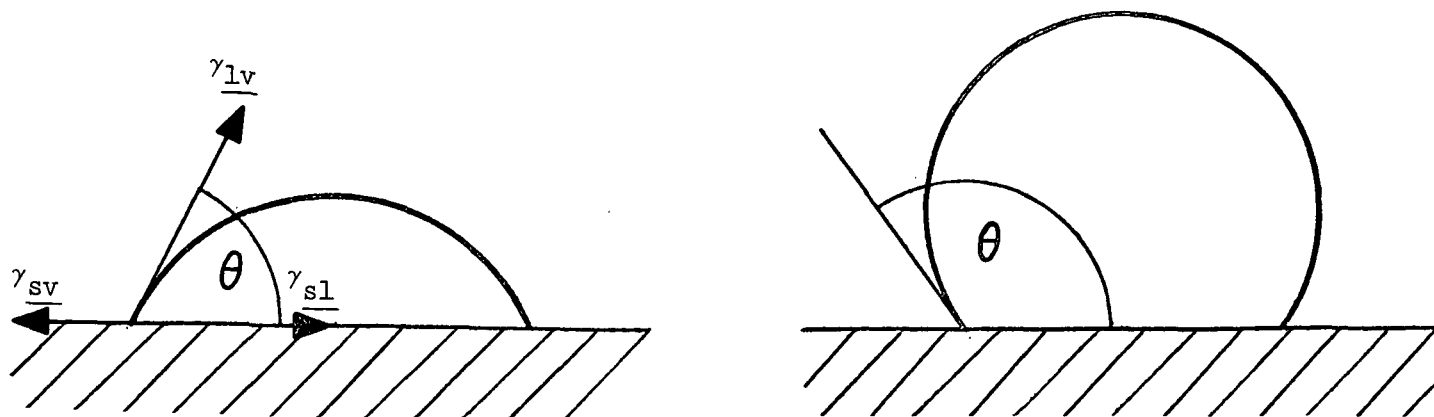


Figure 1. Representation of the Surface Tension Forces and an Acute and Obtuse Contact Angle for Idealized Liquid Drops on a Solid

Equation (1) can be obtained from a simple mechanical balance of surface tension forces in Fig. 1. However, this approach has been criticized by Bikerman (2,3) because of the disregard for the vertical component of the liquid surface tension ($\gamma_{lv} \sin \theta$). Lester (4) has also commented on the importance of this force for normal solids. Evidence exists (3,5) that a ridge is raised on soft solids at the periphery of the liquid drop. However, the elastic properties of harder solids are apparently able to withstand these forces since no visible evidence for surface deformation exists. Equation 1 has also been derived from strict thermodynamic principles (6,7).

The work of adhesion between a liquid and solid, W_{sl} , was defined by Dupre in 1869 (8) and is shown in Equation (2):

$$W_{sl} = \gamma_s + \gamma_{lv} - \gamma_{sl} \quad (2)$$

where γ_s represents the free energy of the solid in equilibrium with its own vapor. Thus γ_s differs from γ_{sv} defined above by nature of the vapor in contact with the surface. W_{sl} is defined as the work necessary to separate a unit area of solid-liquid interface into an equivalent area each of liquid-vapor interface and pure solid surface. Utilizing the following expression for the film pressure (π_e) of a foreign vapor on a solid:

$$\pi_e = \gamma_s - \gamma_{sv} \quad (3)$$

Equations (1) and (2) can be combined to give the useful expression so familiar to adhesion chemists:

$$W_{sl} = \gamma_{lv} (1 + \cos \theta) + \pi_e \quad (4)$$

π_e is often assumed (sometimes erroneously) to be negligibly small. With this simplification, the wetting behavior or adhesion between a solid and a liquid

can be determined using Equation (4) from the experimentally obtainable quantities $\gamma_{\ell v}$ and θ . Equation (4) is invalid when $\theta = 0$.

The theory presented up to this point does not allow the surface of a solid to be characterized in easily measured experimental quantities (i.e., γ_s and/or γ_{sv} cannot be measured conveniently or reliably). This was a serious shortcoming for the practical use of contact angle data for many years. Several significant and useful concepts and theories have been developed in the last twenty years which have allowed considerable progress in the understanding of solid-liquid interactions. This work will be briefly reviewed in chronological order of development.

DETERMINATION OF THE SURFACE ENERGY OF SOLIDS

Zisman and coworkers (9,10) were the first to show a regular relationship between the contact angle and the surface tension of the liquid. Fox and Zisman (11) classified solids into high and low energy surfaces and arbitrarily chose 100 ergs/cm² as the dividing line. The major contribution of this work was the discovery of an empirical rectilinear relation between the cosine of the equilibrium contact angle, θ , and the surface tension, $\gamma_{\ell v}$, for a homologous series of organic liquids on low energy solids. Figure 2 demonstrates this behavior. Some curvature is observed for the higher surface tension liquids which has been attributed to the hydrogen bonding capability of these fluids with the solid. Extrapolation of the linear portion of the curve to zero contact angle ($\cos \theta = 1.0$) gives a characteristic value termed the critical surface tension, γ_c , of the solid. The data correspond to an equation of the form:

$$\cos \theta = 1 - b (\gamma_{\ell v} - \gamma_c) \quad (5)$$

where γ_c represents the slope of the line. Liquids which have surface tension values equal to or less than γ_c have a zero contact angle and, therefore, wet and spread on the solid. γ_c has proved to be a useful empirical parameter with which to characterize the relative wettabilities of numerous low energy surfaces. The critical surface tension values obtained with the same series of liquids were related to differences in composition and molecular orientation and packing of the solid surfaces. This work demonstrated that the attractive intermolecular forces at an interface are almost completely controlled by only the surface atoms and molecules. Characterization of low energy solid surfaces in this manner permitted wettability predictions for a particular solid-liquid system from knowledge of γ_c and the surface tension of the liquid, γ_{lv} . This technique has been frequently utilized for the surface energy characterization of cellulose and other wood-related compounds (12-17). Such studies have proved useful in predicting adhesion behavior in paper systems (13,14).

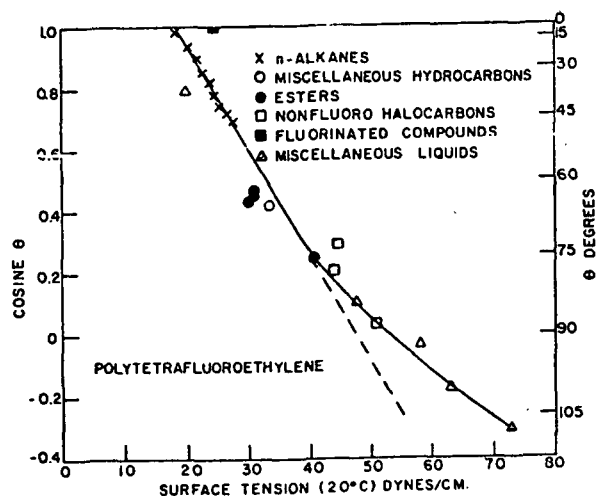


Figure 2. Wettability of Polytetrafluoroethylene by Various Liquids (10)

Girifalco and Good (18,19) presented a theory that the interfacial free energy between two immiscible phases could be determined from the individual surface-free energies and the nature of the attractive interaction across the interface. The equation for a solid-liquid system is:

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 2 \Phi \sqrt{\gamma_s \gamma_{lv}} \quad (6)$$

All of the free energy, γ , terms have the same meaning as before. Φ is an interaction parameter which describes the interaction of the solid and liquid molecules at the interface. Good (20) has given the quantitative expression for Φ in terms of the molecular polarizabilities, dipole moments and the ionization energies of the liquid and solid. $\Phi \approx 1$ for nonpolar liquids on nonpolar solids, however, values between about 0.5 and 1.0 are more typical for systems normally encountered in contact angle work.

The following expression results when Equation (6) is combined with Young's equation, Equation (1), to eliminate γ_{sl} :

$$\cos \theta = -1 + 2 \Phi (\gamma_s / \gamma_{lv})^{1/2} - \pi_e / \gamma_{lv} \quad (7)$$

A plot of $\cos \theta$ against $1/(\gamma_{lv})^{1/2}$ is linear for liquids with similar Φ values on a solid assuming the π_e term is negligible. When the above expression is solved for the surface-free energy of the solid, γ_s , the following equation is obtained:

$$\gamma_s = \frac{[\gamma_{lv} (1 + \cos \theta) + \pi_e]^2}{4 \Phi^2 \gamma_{lv}} \quad (8)$$

Equation (8) simplifies further if $\pi_e \approx 0$ resulting in an expression relating γ_s to the experimentally measurable quantities γ_{lv} and θ and a calculated value of Φ . Characterization of the surface of solids is possible utilizing Equation (7) and suitable contact angle data for a single liquid. The reader is referred to

Good's (20) discussion with regard to the limitations of the molecular properties of the solid-liquid pair which must be considered in the calculation of Φ .

Fowkes (21-24) extended the ideas of Girifalco and Good and presented the stimulating concept that the surface-free energy of a solid or liquid is composed of additive components. For example, the surface-free energy of a solid, γ_s , could be broken up into various components:

$$\gamma_s = \gamma_s^L + \gamma_s^P + \gamma_s^I + \gamma_s^H + \dots \quad (9)$$

where the superscripts L, P, I and H denote the surface-free energy components of the solid due to London (or dispersion), polar, induction force and hydrogen bonding components, respectively. Fowkes reasoned that saturated hydrocarbons are capable of only London interactions as a result of their nonpolar nature and uniform molecular charge distribution. Consequently, a nonpolar liquid should be relatively insensitive to the dipoles of a polar solid, and the total interaction of such a liquid and solid would be via London forces. Fowkes used a modified form of the Girifalco-Good expression, Equation (7), to obtain Equation (10):

$$\cos \theta = -1 + 2 (\gamma_s^L / \gamma_{lv}^*)^{1/2} - \pi_e / \gamma_{lv}^* \quad (10)$$

γ_{lv}^* denotes the use of a liquid which is completely nonpolar. When $\pi_e \simeq 0$, a graphical representation of $\cos \theta$ versus $1/(\gamma_{lv}^*)^{1/2}$ results in a straight line as Fig. 3 shows. The London component of the solid surface free energy, γ_s^L , determines the slope. Additionally, the London component of the surface tension, γ_l^L , was obtained from measurements of the interfacial tension of a liquid against liquid hydrocarbons using a modified form of Equation (6). The difference, $\gamma_{lv} - \gamma_l^L$, was attributed to all polar contributions, γ_l^P . In this manner, tables were made of the London and polar components of a number of common liquids and low energy solids (23,27).

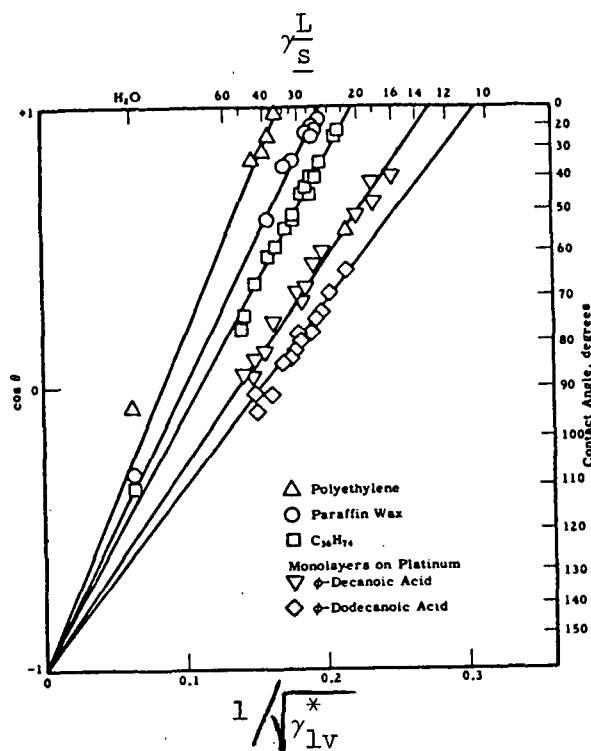


Figure 3. Contact Angles of a Number of Liquids on Five Low Energy Surfaces (21)

Fowkes' line of reasoning was carried further by Owens and Wendt (25) and Kaelble (26,27). These treatments were identical, and an equation of the following form was obtained for a solid-liquid system:

$$\cos \theta = -1 + 2 (\gamma_{\ell}^L \gamma_s^L)^{1/2} / \gamma_{\ell v} + 2 (\gamma_{\ell}^P \gamma_s^P)^{1/2} / \gamma_{\ell v} \quad (11)$$

π_e is assumed negligible; also γ_s and $\gamma_{\ell v}$ are composed of additive London and polar components only. The similarity to Equations (7) and (10) are obvious. Equation (11) has been used to characterize low energy solids by measuring the contact angles of two liquids whose γ_{ℓ}^L and γ_{ℓ}^P values are known. This treatment of data enables the London and polar components of the solid, γ_s^L and γ_s^P , to be determined. A number of low energy solids (28-33) have been characterized in this manner including cellulose, hemicellulose, lignin and wood surfaces (15,16,34-36). Wu (37) has recently suggested, on an empirical basis, the use of a reciprocal mean

instead of the geometric mean interfacial interaction proposed by Girifalco and Good (18,19). Wu showed that the reciprocal mean gave better results in characterizing the London and polar interactions of polar polymers.

Certain criticisms of the Fowkes-Kaelble-Owens-Wendt method for the characterization of low energy solids using Equations (9)-(11) should be mentioned. Firstly, a variety of interactions (e.g., dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.) are all lumped together under a general polar contribution. It has been suggested that the individual components are not strictly additive, and a certain amount of cross interaction is likely with polar liquids on polar solids. Furthermore, as we shall see in the next section, typical solids used for contact angle measurements cannot be considered to be smooth, planar and isotropic, which is a requirement of the theory. Such considerations must be borne in mind when the data are analyzed. Consequently, the investigator must not be tempted to over-interpret the data and draw conclusions based on subtle differences in the calculated London or polar contributions to the surface energy of a solid.

Zisman (38) and Good (20) have cautioned against the use of liquid mixtures to obtain a variation in γ_{lv} for contact angle measurements. Numerous difficulties arise as a result of uncertainties regarding selective adsorption of one of the components of a binary mixture at the three different interfaces. Furthermore, the selective adsorption at each of the interfaces is likely to be quite different. Consequently, Good (20) strongly urges that in order to avoid interpretation complications only pure liquids be used in contact angle determinations.

Surface characterization of high energy surfaces (e.g., metals, metal oxides, silica, glass, etc.) possessing γ_s values in excess of 100 ergs/cm² is

complicated by practical considerations. Certain low energy amphipathic liquids (liquids possessing polar and nonpolar portions of their molecules) do not wet high energy surfaces (39,40). Such autophobic liquids prevent wetting by adsorption of an oriented monomolecular film whose critical surface tension is less than the surface tension of the liquid. Consequently, the liquid cannot spread on its own adsorbed film. Additionally, the high surface free energy of such solids makes them particularly susceptible to adsorption of trace contaminants. Consequently, extreme care and rigor in sample preparation do not always guarantee a clean homogeneous surface. Additionally, suitable liquids that have γ_{lv} values high enough to form finite contact angles on these high energy solids are not readily available, making the experimental characterization difficult or impossible. Therefore, the Zisman critical surface tension technique has been restricted to solids possessing surface energies $<100 \text{ ergs/cm}^2$. However, recent studies (41) have reported the determination of the London and polar components of the surface free energy of a high energy solid, mica. A modified form of the Fowkes-Kaelble-Owens-Wendt method was used.

One interesting controversy between Zisman and Fowkes which remains unresolved is whether water wets high-energy surfaces ($\gamma_s > 100 \text{ ergs/cm}^2$) such as metals. Zisman (10) predicts water should spread on metal surfaces which possess γ_s (likewise γ_c) values in excess of the surface tension of water. On the other hand, Fowkes (42) has calculated that water should form a finite contact angle on a gold surface based on his treatment of the London interaction components of this solid-liquid system. Experimental verification of the water contact angle has not been conclusive as a result of difficulties in preparing uncontaminated gold surfaces.

CONTACT ANGLE HYSTERESIS

In the derivation of Young's equation, Equation (1), the solid was assumed to be ideal, i.e., uniform, plane and nondeformable. For a liquid spreading on such a solid, this relationship predicts a single unique equilibrium contact angle. However, this behavior is rarely encountered in practice. A number of stable equilibrium contact angles can often be determined for a given solid-liquid system. One way to illustrate this behavior is to change the volume of the liquid drop on a solid by adding or withdrawing fluid as illustrated in Fig. 4. The largest and smallest equilibrium contact angles can be measured with a reasonable degree of reproducibility. These angles are indicated in Fig. 4 and are called the advancing, θ_a , and receding, θ_r , contact angles, respectively. Several recent reviews (43-45) have been written concerning this type of hysteresis. This behavior should be distinguished from the contact angle variations that are observed during motion of the liquid relative to the solid. This subject, referred to as dynamic contact angles, will be discussed in a subsequent section.

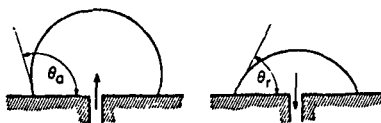


Figure 4. Technique for Obtaining Advancing and Receding Contact Angles (43)

The causes of equilibrium contact angle hysteresis are generally attributed to the properties of the solid which cause it to deviate from the ideal homogeneous, planar, and nondeformable surface. However, it has been speculated that true hysteresis can result with certain solid-liquid pairs as a result of a change of state in the vicinity of the three phase boundary line (TPL) located at the solid liquid-vapor

interface (45). Surface roughness, heterogeneity, and porosity as well as penetration of liquid molecules into the surface have all been shown to result in contact angle hysteresis.

Wenzel (46,47) was the first to predict the effect of roughness on the contact angle. He proposed the following relationship between the observed, θ_{obs} , and the intrinsic, θ , contact angles and a roughness factor, r . The roughness

$$\cos \theta_{\text{obs}} = r \cos \theta \quad (12)$$

factor was defined as the ratio of the real to the apparent geometric surface areas such that $r \geq 1$. Consequently, surface roughness will decrease the observed contact angle when $\theta < 90^\circ$ and increase θ_{obs} when $\theta > 90^\circ$ as shown for a number of situations in Fig. 5. It should be stressed that the relative effects of roughness are more pronounced at very low or high intrinsic contact angles. For example, the accurate measurement of low angles requires a smoother surface than for values around 90° . However, as Johnson and Dettre (43) point out, θ_{obs} as predicted by the Wenzel equation corresponds to the contact angle which has the lowest free energy on the rough surface but does not account for the numerous possible metastable states usually encountered in practice. Consequently, θ_{obs} is seldom, if ever, the measured contact angle.

The magnitude, scale and orientation of the roughness are also important factors in determining the contact angle. The effect of macroscopic roughness of the type readily discernible in an electron microscope is shown in Fig. 6. The macroscopic contact angles, θ_a and θ_r in Fig. 6 would correspond to the measured values obtained using conventional techniques. However, closer inspection of the leading and trailing edges of the drop would indicate that the equilibrium contact angle, θ (θ_o in the figure), is maintained at both peripheries. This behavior has

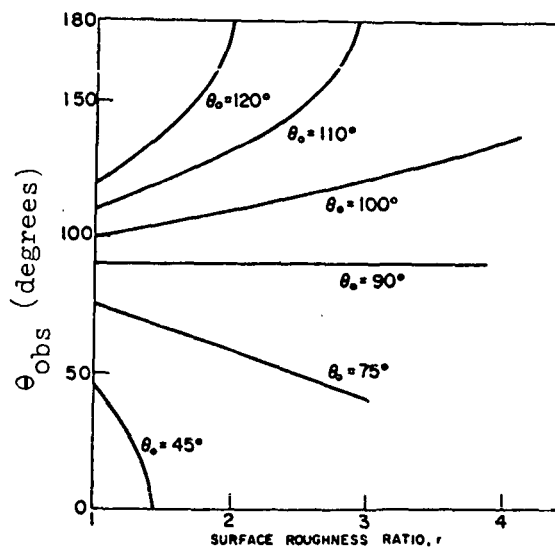


Figure 5. Wenzel's Angle as a Function of Surface Roughness for Various Intrinsic Contact Angles (43)

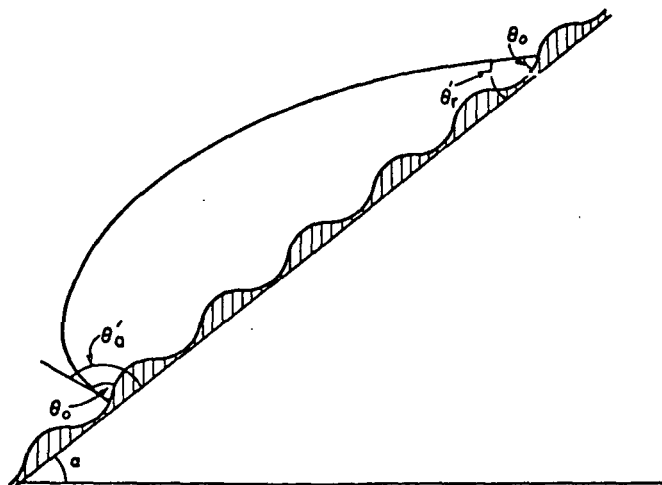


Figure 6. A Liquid Drop on a Tilted Rough Surface (43)

been documented experimentally (48). The contact angle behavior on surfaces with microscopic roughnesses on the scale of molecular dimensions is more difficult to predict and confirm experimentally. The effect of orientated ridges and valleys (e.g., parallel grooves) generally has the effect of promoting wetting in the direction of the grooves. Similarly, surfaces with nonrandom and nonuniform roughness will generally show preferential directional wetting.

Surface heterogeneity has also been shown to result in contact angle hysteresis (43,49,50). Cassie and Baxter (51,52) extended Wenzel's treatment of roughness to heterogenous and composite surfaces. Their equation is given below which described the observed contact angle when a surface is composed of small random "islands" of a second material which has a different wettability from the remaining solid.

$$\cos \theta_{\text{obs}} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (13)$$

f_1 represents the fraction of the surface having contact angle θ_1 , and f_2 is the fraction having angle θ_2 such that $f_1 + f_2 = 1$. Analogous to the case of surface roughness, θ_{obs} is rarely, if ever, measured since a number of metastable states are possible giving rise to hysteresis (43). Figure 7 shows how contact angles and contact angle hysteresis vary with the percentage of the surface covered with a more wettable (low contact angle) material. The center curve corresponds to θ_{obs} ($\hat{\theta}$ in Fig. 7) calculated from Equation (13). Curves above and below the center curve represent possible advancing and receding contact angles, respectively, for drops of varying vibrational energy. Curves for high energy drops appear closer to the center curve which corresponds to the lowest free energy state. It was concluded from the wetting behavior presented in Fig. 7 that an advancing angle is a good measure of the wettability of the low-energy (high contact angle) part of the surface, and a receding angle is more characteristic of the high energy part.

This behavior and means to characterize a heterogeneous surface have been documented (53).

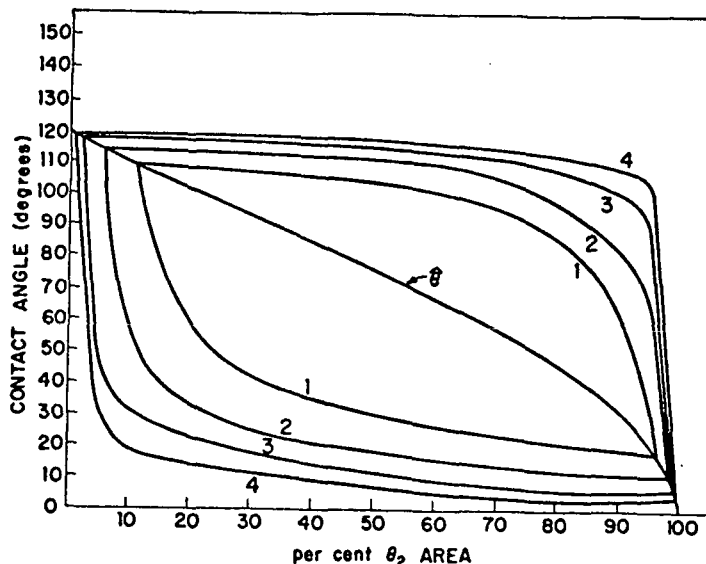


Figure 7. Contact Angle Hysteresis on a Model Heterogeneous Surface (43)

Porous surfaces or very rough surfaces can produce composite interfaces which result from liquids being unable to completely penetrate the surface. A certain fraction of the underlying liquid is in contact with air instead of the pores or crevices of the solid. Liquids which form high intrinsic contact angles are susceptible to the formation of composite interfaces. Spontaneous wetting is the general rule for porous solid-liquid systems where $\theta < 90^\circ$ due to capillarity considerations. Composite interfaces are treated by a modified form of the Cassie and Baxter relationship, Equation (13). Region 2 which consists of air has a contact angle of 180° , and the following equation results:

$$\cos \theta_{\text{obs}} = f_1 \cos \theta_1 - f_2 \quad (14)$$

Johnson and Dettre (43) concluded from their calculations and experiments that the

receding angle on a composite interface depends strongly on the wettability of the solid portion of the surface and is insensitive to surface porosity.

Penetration of liquids into the surface of solids is also thought to contribute to contact angle hysteresis. Timmons and Zisman (54) have reported a number of examples of varying degrees of hysteresis for a selection of probe liquids of different molecular size. However, the observed contact angle variability may not be a true hysteresis since it could be the result of nonattainment of equilibrium if one supposes that the penetration is a slow process.

DYNAMIC WETTING OF SOLIDS

The industrial importance of the interaction of liquids with solids under dynamic conditions has long been recognized, and some of the specific applications of interest to the papermaker have already been mentioned. Similar considerations apply to the dynamic wetting situation as outlined earlier for the static case; however, there are several important differences as we shall see. The macroscopic behavior of liquids on solids under dynamic conditions is controlled by the interfacial free energies, the dynamic contact angle, and liquid inertial and viscous effects. A liquid front moving over a solid displaces another fluid (either a gas or an immiscible liquid) and constantly encounters new surface. Such a dynamic system cannot be considered to be in thermodynamic equilibrium. Consequently, the interpretation of the dynamic contact angle, defined as the instantaneous or steady state angle obtained during motion of the TPL, is fundamentally different from the equilibrium contact angles discussed so far. Thermodynamic or force balance static treatments are inadequate to describe and predict the behavior of dynamic contact angles. However, a meaningful approach can be accomplished by considering the subject of dynamic contact angles as a branch of fluid dynamics.

Dynamic Contact Angles

There are two methods used to determine dynamic contact angles when a fluid interface traverses a solid surface. One method stems from the spontaneous spreading of a liquid on a solid corresponding to the case of a zero static contact angle. The driving force results from the imbalance of the interfacial free energies as described by Young's equation, $\gamma_{sv} - \gamma_{sl} > \gamma_{lv}$. This type of wetting behavior is of great importance and interest in the formation of thin films. Examples are lubrication, foliar applications of herbicides and pesticides, and applications of molten waxes, hot melts, printing inks and other oils and organic films to paper and board. The spontaneous spreading of molten polymers on solids has been studied and the influence of dynamic contact angles measured (55-58). Bascom and coworkers (59) have studied the spreading rates and shapes of advancing oil films on metal surfaces. A related branch of spontaneous wetting deals with liquids in contact with solids with a significant internal void network. Capillary penetration into the voids results when the liquid forms a contact angle less than 90° with the solid. Considerable interest in liquid penetration exists in the fields of paper, textiles, and more recently, in oil recovery from underground porous media. However, the subject of liquid penetration in porous structures is a subject worthy of a separate treatment and, consequently, will not be dealt with in any detail here. The interested reader should consult the following references for a more thorough coverage of this topic (60,61).

The second technique to determine dynamic contact angles is to impress motion of the liquid-vapor interface relative to the solid. Such forced motion of the TPL is accomplished by applying a suitable external force. Systems most often consist of a liquid which forms a finite contact angle with the solid; however, solid-liquid pairs which exhibit zero static contact angles can also be measured

when the forced velocity is larger than the spontaneous movement of the TPL.

Studies of forced spreading were primarily concerned with the dynamic contact angle behavior with variations in velocity of the TPL.

The earliest observations of dynamic contact angles (62,63) from forced spreading on smooth solids demonstrated a dependence on the velocity of the moving liquid front and a significant deviation from the equilibrium contact angle. Advancing contact angles increased, and receding contact angles decreased with increasing speeds. Later studies (64-69) confirmed a dynamic contact angle dependence on velocity; however, considerable lack of quantitative agreement was found in the results from one laboratory to another. A few selected examples will be shown for illustration.

Figure 8 shows the results obtained by Elliott and Riddiford (66) where they identified three regions of contact angle-velocity dependence. A close inspection of their data at the lowest velocities (<1 mm/min) revealed that the dynamic contact angles were equal to the equilibrium contact angles. The angle rose sharply at some critical velocity and then leveled off and became essentially independent of velocity at speeds in excess of 10 mm/min. These data suggested that the factors controlling the velocity-dynamic contact angle behavior were different at various speed ranges. Similar variations of the dynamic contact angle over certain velocities were found by Schwartz and Tejada (69), and a typical relationship is shown in Fig. 9. Although the data are plotted differently from Fig. 8, it is readily seen that two distinct linear contact angle-log velocity regions exist up to speeds of approximately 50 cm/sec (30 m/min). These same workers (69) also demonstrated that solid-liquid systems possessing zero or positive static contact angles behaved similarly under dynamic conditions. Finally, the recent results of Johnson and coworkers (70) showed little or no dependence of the dynamic contact angle on velocity of the three-phase boundary. Figure 10 shows some typical results

over a velocity region up to approximately 250 mm/min. Johnson, *et al.* (70) have plotted the data of Elliott and Riddiford (66) (Curves 4 and 5) with their own results. Curves 2 and 4 are direct comparisons for the same solid-liquid systems in the two different laboratories. Quite striking differences in dynamic contact angle-velocity behavior are evident between these two research groups. Curve 3 is the result obtained with a known heterogeneous solid. In order to explain the effect of velocity on dynamic contact angles and also the discrepancies that exist between researchers it is necessary to look into the reasons and explanations for the observed behavior.

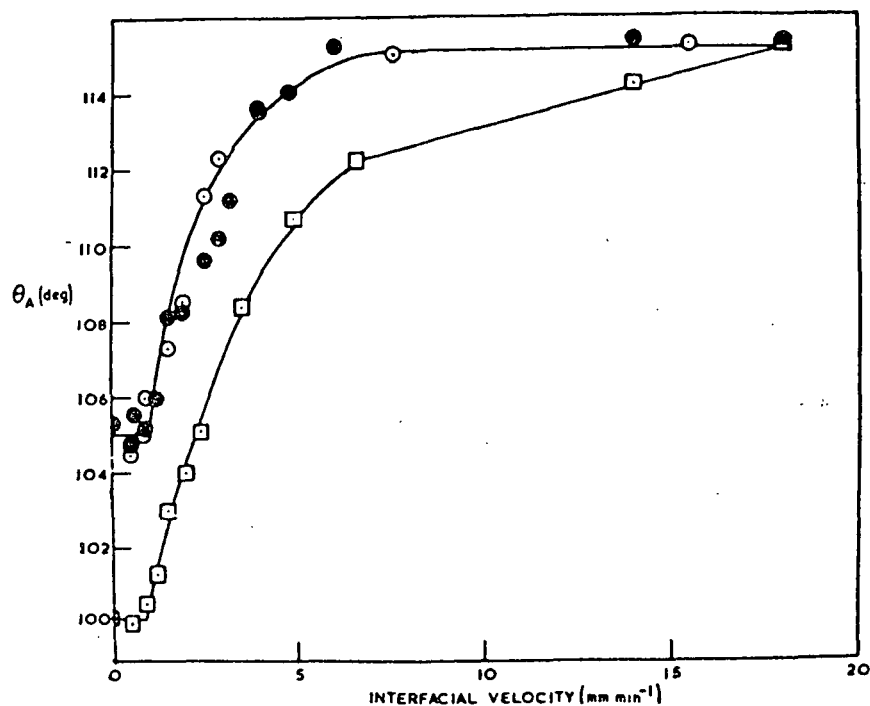


Figure 8. Advancing Contact Angles as a Function of the Velocity of an Air-water Interface Moving Over Siliconed Glass (Circles) and Polyethylene (Squares) (66)

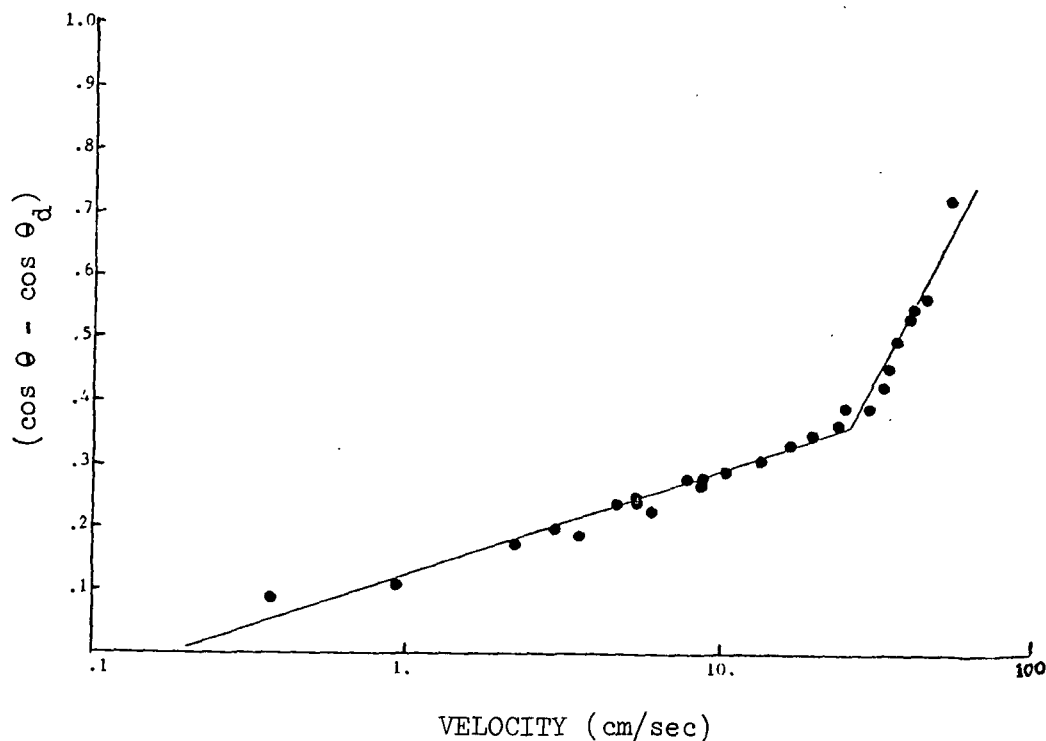


Figure 9. Advancing Contact Angles as a Function of the Velocity of an Air-octane Interface Moving Over a Teflon Surface (69)

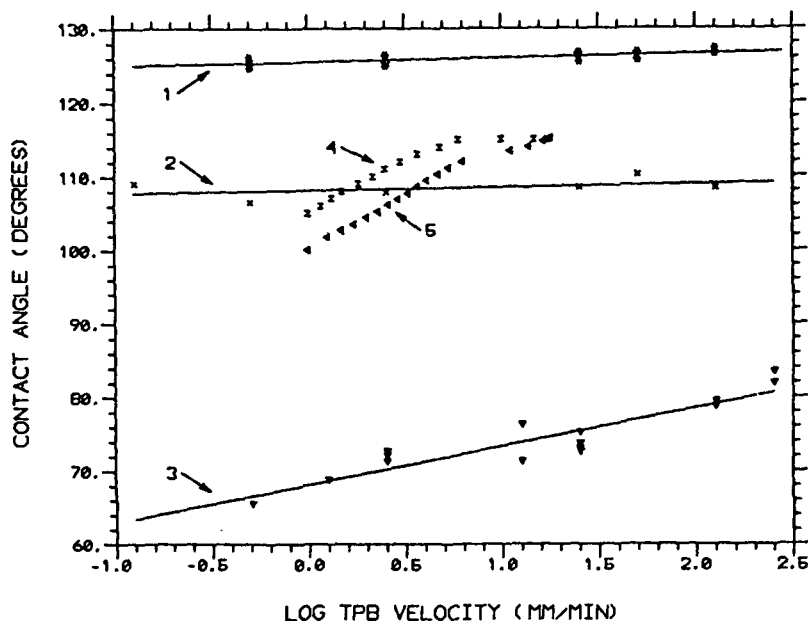


Figure 10. Advancing Contact Angles as a Function of the Velocity of an Air-water Interface Moving Over a Fluoropolymer (Curve 1), Siliconed Glass (Curves 2 and 4) and Polyethylene (Curve 5) Surfaces. [Curves 4 and 5 from Reference (66)] (70)

Hansen and Miotto (71) suggested that displacement of a TPL involves molecular disorientation in the immediate vicinity of the interface. They reasoned that the most energetically favorable orientation of the liquid molecules at the TPL would require some finite time to achieve. They proposed that some natural displacement velocity, $v_{\underline{n}}$, would be associated with the most slowly relaxing molecules at the interface. Hansen and Miotto reasoned that if the actual rate of displacement of the TPL was greater than $v_{\underline{n}}$, a certain amount of molecular disorientation would exist, and the interfacial free energies would exceed their equilibrium values. Consequently, the dynamic contact angle would unlikely be equivalent to the equilibrium angle. On the other hand, when the TPL displacement velocity was small compared to $v_{\underline{n}}$ the molecules at the interface should be able to orient themselves, and the dynamic contact angle should equal the static value. Displacement velocities between these two extremes would presumably involve some critical speed at which further increases in velocity would cause varying degrees of disorientation at the TPL.

Several investigators have adopted this plausible explanation by Hansen and Miotto to explain their experimental observations. Riddiford and coworkers (66,68) invoked this theory to explain the dynamic contact angle-velocity behavior described earlier in Fig. 8 as well as subsequent data. Lowe and Riddiford (72,73) have suggested that dynamic contact angle measurements can be utilized to determine the relative importance of polar and London interaction forces at the solid-liquid interface. They conclude that both polar and London forces are important at low velocities and that London forces dominate at higher velocities.

McIntyre (74) used an oscillating drop technique and concluded that energy variations associated with the advancing and receding solid-liquid interface resulted from molecular relaxation effects in the three-phase boundary

region. Estimates of the natural displacement velocity, v_n , led to the calculation of realistic relaxation times for water molecules on a paraffin surface in the range of 10^{-6} - 10^{-5} sec.

Blake and Haynes (67) using a method similar to that of Cherry and Holmes (60) have quantitatively developed the model proposed by Hansen and Miotto (71). These workers postulate that molecules slide along the solid surface from the liquid to the vapor side of the TPL, which involves activated energy transitions of certain surface sites. They obtained an equation relating the TPL velocity to the variation of the dynamic contact angle from its static value. Blake and Haynes regard the retarding force of the fluid flow to be an interfacial viscosity. Their equations appeared to adequately describe data up to a velocity of 200-300 mm/min.

Schwartz and Tijada (69) concluded from their numerous forced spreading experiments that three different modes of dynamic contact angle-velocity behavior exist up to speeds of 30 m/min. A region exists at the lowest velocities where the dynamic contact angle is the same as the equilibrium value. This corresponds to speeds less than the natural displacement velocity proposed by Hansen and Miotto (71). The behavior above this region can be quantitatively expressed by the equations of Blake and Haynes (67) where the interfacial viscosity is the primary retarding force. Finally, at the highest speeds a different mechanism becomes increasingly important. Under these conditions, the dynamic contact angle-velocity relationship is adequately described by fluid flow effects which regard the major retarding force as the bulk viscosity.

Johnson and coworkers (70) concluded from their dynamic contact angle studies that the effect of TPL velocity up to 250 mm/min is zero or very small on homogeneous stable systems. However, heterogeneous solids exhibited a significant

dependence on velocity. Their results do not support the Hansen and Miotto (71) concept of dynamic contact angle-velocity dependence because of reorientation of liquid molecules at the TPL. Their explanation involves an extension of a theory of contact angle hysteresis developed earlier (43). The conclusions drawn from their work indicated velocity dependence of contact angles was related to surface heterogeneity.

The majority of the studies of dynamic contact angles mentioned up to this point deal with relatively modest velocities up to a few hundred millimeters per minute. Additionally, most of the work was carried out on smooth, flat, and homogeneous surfaces in order to eliminate or minimize complications arising from roughness, heterogeneity, and porosity. In spite of these efforts to simplify the system, there is currently a lack of complete agreement as to the effect of velocity on dynamic contact angles as well as suitable explanations for the phenomenon when rate dependency is observed. Furthermore, the majority of the literature consists of determinations of the nature and magnitude of the dynamic contact angle-velocity dependence. A complete picture supported by proven theory is currently lacking to describe the interactions between solids and liquids under dynamic conditions. It has been recognized (45,71,75) that significant advancement will most likely come from a thorough and suitable molecular analysis of the three-phase zone itself. It is more realistic to consider the solid-liquid-vapor interface as a zone or region consisting of at least molecular dimensions rather than a line which connotes a sharp division with no thickness. A molecular analysis of this zone is complicated theoretically and difficult to explore experimentally. However, we will see in the next section that significant progress has recently been made in this area.

It should be mentioned at this point that several investigators have made attempts directly or indirectly to deduce the influence of dynamic contact

angles on the wettability of cellulose fibers and paper. Knight (76) found a decreased wettability of paper surfaces with increasing speed of liquid application implicating a dynamic contact angle-velocity dependence. Unexplained liquid penetration behavior in a paper and paperboard coating study (77) was ascribed to differences in the dynamic contact angles. Recent scanning electron micrographs and movie films (78) have shown the type of irregular and erratic wetting behavior that exists on a fibrous mat such as paper on a microscopic scale. Such studies emphasize the difficulty in attempting to model and describe the wetting phenomena on a paper or paperboard surface.

Fluid Mechanics Approach to Dynamic Wetting

Hydrodynamicists and engineers, in addition to surface chemists, have also recognized the significance and importance of moving interfaces in many industrial processes. As a result of this interest, the problems associated with dynamic wetting and moving three phase contact lines have been approached with a different point of view from that already discussed. In general, fluid dynamicists have analyzed the problem in terms of typical hydrodynamic forces (e.g., inertial and viscous forces) in addition to the conventional surface and capillary considerations. Such treatments are, however, relatively few and have contributed significantly to the understanding of the whole complex area of wetting dynamics. Additionally, the fluid dynamicists and engineers were generally interested in processes that involved relatively higher rates of movement of the TPL than concerned most surface chemists. Consequently, their treatments were orientated toward the range of speeds most often encountered in many high speed industrial applications.

Scriven (79) presents one of the earliest treatments of the dynamics of wetting which recognized the profound influences that interfacial effects can have on the flow behavior of systems. This work was followed by a theoretical

development (80) of a model to describe the steady state movement of a solid-liquid-vapor contact line. This was the first attempt by a hydrodynamicist to deal theoretically with a moving TPL. A creeping flow approximation to the problem led to the presentation of several sample diagrams depicting the velocity field in the vicinity of the TPL for selected dynamic contact angles and fluid viscosities. However, the proposed model did not adequately describe the flow behavior in the vicinity of the three-phase line. In fact, this treatment predicted that shear stresses, pressure and viscous dissipation rate increased without bound as the three-phase contact line was approached. Such behavior violates the adherence or "no-slip" boundary condition of fluid mechanics. It was clearly recognized that the process of one fluid displacing another on a solid involves movement of both of these fluids relative to the solid sometime during the process. This behavior is incompatible with the accepted hypothesis of fluid dynamics that fluid immediately adjacent to a solid does not move or slip.

The difficulty of treating the behavior of the moving TPL with conventional fluid mechanics was also recognized by other investigators (81,82). In order to apply the classical concepts of hydrodynamics these researchers chose to recognize the inapplicability of such a treatment within short distances (molecular dimensions) of the interface. This resulted in an arbitrarily chosen thickness adjacent to the TPL for which the theory did not apply. Then, they each considered the system to be controlled by the normal macroscopic interfacial and viscous forces. In effect, an analysis of the flow field in the vicinity of the TPL was avoided, and the justification given was the reasonable agreement obtained between theory and experiment.

In order to analyze the fluid flow in the vicinity of the three phase line, it was necessary to understand the nature of the motion there. Several

investigators (83-86) utilizing moving liquid indexes in cylindrical tubes concluded that liquid moved along the tube via a rolling mechanism. The fluid spread outward from the center portion of the front meniscus and rolled inward toward the central region at the rear meniscus. No sliding of the liquid along the tube wall was observed. Rose (85) termed this behavior the "fountain effect." Dussan and Davis (87) recently photographically demonstrated this rolling behavior in several simple but illustrative experiments. They describe the fluid motion at a TPL as follows (87): "...the interfacial motion is reminiscent of a moving tractor tread." These authors concluded from this mechanism of fluid movement over a solid that the no-slip condition at the wall of the solid was kinematically compatible with a moving TPL.

An example of the motion of a dynamic contact line is given in Fig. 11 which is taken from an illustration by Dussan and Davis (87). The fluid represented by F_2 undergoes the rolling action described above where material points on F_1F_2 are mapped onto the solid represented as SF_2 during movement of the common line (CL). The motion of the displaced fluid, designated by F_1 (an immiscible liquid or a gas), is more complex as it is transported from SF_1 into the interior of F_1 . However, the theoretical analysis of Dussan and Davis (87) predicted the ejected movement of fluid F_1 as illustrated by the dashed line in Fig. 11.

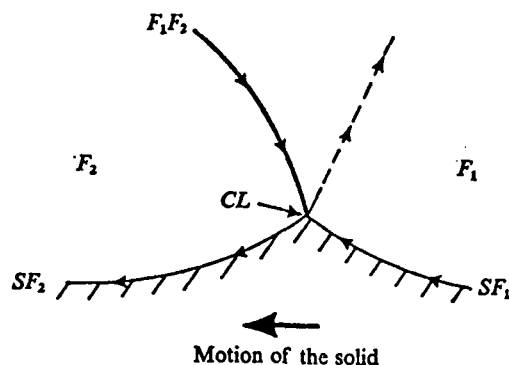


Figure 11. Fluid Motion of Liquid F_2 Displacing Fluid F_1 on the Surface of a Solid (87)

The complete theoretical treatment of Dussan and Davis (87) of a moving contact line resulted in a multivalued velocity field as well as the prediction of infinite forces at the TPL. It was pointed out (80,87) that the use of a slip coefficient would alleviate these problems; however, no justification based on measurable physical quantities has been given for such interfacial behavior. Furthermore, no theoretical reason for the existence of slip at the contact line has been given until recently.

Ruckenstein and coworkers (88,89) have presented a molecular analysis of the three-phase region which explains the origin of the forces which generate the slip velocity. Furthermore, a theoretical analysis was given for the computation of the slip velocity. A treatment of the intermolecular forces in the region of the TPL revealed a gradient of the chemical potential in the liquid along the solid-liquid interface. This gradient in the liquid is produced because the interactions of neighboring molecules in the vicinity of the TPL are different from that of a similar region of solid-liquid interface located at large distances from the contact line. This gradient of the chemical potential is also dependent on the location relative to the TPL. The analysis of Ruckenstein and Dunn (89) demonstrated that the chemical potential gradient produced a net translational liquid velocity parallel to the solid surface in the vicinity of the contact line. The mathematical relationships developed to describe this behavior correctly predicted that liquid moves away from the TPL when the dynamic contact angle is less than the equilibrium value. This corresponds to the receding contact angle case. Conversely, an advancing liquid front is associated with liquid moving toward the contact line corresponding to a dynamic contact angle which exceeds the equilibrium value. Figure 12 illustrates the dependency of slip velocity (V_s) on the distance (x) from the TPL as calculated by Ruckenstein and Dunn (89). These calculations

were made for various advancing and receding contact angles (represented by α in the figure) which corresponded to a solid-liquid system possessing an equilibrium value of 40° . The slip velocity-distance relationships for the advancing and receding contact lines in Fig. 12 demonstrated quite different behavior. The results of these calculations showed that the slip velocity varied with the inverse fourth power of the distance ($1/x^4$); consequently, this phenomenon is important over rather short distances from the contact line. Additionally, the rate of decay of the slip velocity exhibited a dependence on the dynamic contact angle.

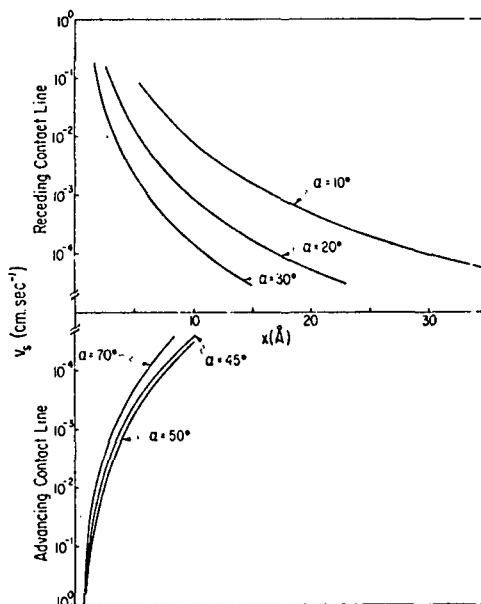


Figure 12. Slip Velocity as a Function of Distance from the Three Phase Line. Equilibrium Contact Angle Equals 40° . The Slip Velocity is Negative for Advancing and Positive for Receding Contact Angles (89)

The treatment of Ruckenstein and coworkers (88,89) appears to hold the greatest immediate promise for inclusion of the intermolecular interactions which occur at a moving TPL in the treatment and analysis of fluid motion. Their analysis does illustrate the cause and nature of fluid flow which results from

directional intermolecular forces generated in the vicinity of the contact line. These authors have recognized the limitations of their treatment with regard to the simplicity of the model. Their representation of the intermolecular forces and the nature of the solid were idealized. Consequently, practical aspects of wetting such as the roughness, heterogeneity, and porosity of the solid surface have not been addressed as yet. Such extensions of the theory appear feasible as soon as a unified treatment including fluid motion has been worked out and verified.

One last significant aspect of wetting kinetics deserves mention at this point but will not be treated in detail. Dynamic contact of liquids with solids in air can result in entrainment of air at the solid-liquid interface. This behavior has been observed in various coating operations and in the polymer processing and textile manufacturing industries and is most often found at high speeds. Systems which exhibit a dynamic contact angle-velocity dependence may reach a point at high speeds where the advancing contact angle approaches 180° and air is admitted into the interfacial region. Inclusion of air, usually in the form of fine bubbles, prevents good solid-liquid contact which may be detrimental to the adhesional or processing characteristics of the applied fluid film. The nature and importance of air entrainment under dynamic wetting conditions has been addressed recently (90,91). The interested reader is referred there for additional details.

CONCLUSIONS

The use of surface and interfacial free energies and contact angles is one of the most direct means of evaluating solid-liquid interactions. Useful theories and techniques of data analysis have been developed for equilibrium contact angles. Adequate theories and explanations for static contact angle hysteresis have been presented. Consequently, it is possible for the investigator to account for the observed equilibrium contact angle behavior in all but the most complex practical systems.

The kinetics of wetting and dynamic contact angles are less well understood. Useful information concerning solid-liquid interactions is available from dynamic contact angle measurements; however, the situation is fundamentally different in many respects to the static contact angle case. A number of investigators have measured the velocity dependence of dynamic contact angles. However, a lack of agreement on the observed effects as well as the explanation for these effects have resulted. These controversies have not been resolved in spite of the considerable amount of attention and effort currently being devoted to this area.

The problems of wetting dynamics and moving contact lines have been addressed by fluid dynamicists. The major difficulty in using this approach has been describing the liquid flow in the region of the contact line. Theoretical treatments predicted infinite forces and stresses at the three-phase line, violating the fundamental no-slip boundary condition of fluid mechanics. However, recent theoretical justification for a slip velocity in the region of the contact line solves this dilemma. Analysis of the model indicated the presence of directional intermolecular forces in the zone of the contact line. A combination of such a molecular analysis with conventional fluid dynamics appears to offer the greatest

hope of a unified treatment of wetting dynamics. Developments have proceeded to the point that interested workers can optimistically anticipate a theory suitable for predicting dynamic solid-liquid wetting behavior in the near future.

LIST OF SYMBOLS

CL	contact line of a fluid with a solid
cm	centimeter
f_1	fraction of surface of component 1
f_2	fraction of surface of component 2
m	meter
mm	millimeter
min	minute
r	roughness factor, dimensionless
TPL	three phase line (used interchangeably with CL)
V_s	slip velocity at CL, cm/sec
W_{sl}	work of adhesion of solid-liquid interface, ergs/cm ²
x	distance from CL, Angstrom units (10^{-8} cm)

Greek Symbols

γ_c	Zisman's critical surface tension, ergs/cm ²
γ_{lv}	liquid-vapor interfacial free energy, ergs/cm ²
γ_{lv}^*	nonpolar liquid-vapor interfacial free energy, ergs/cm ²
γ_i^L	London force component of the surface free energy of substance i , ergs/cm ²
γ_i^P	polar force component of the surface free energy of substance i , ergs/cm ²
γ_s	solid surface free energy, ergs/cm ²

γ_{sl}	solid-liquid surface free energy, ergs/cm ²
$\gamma_{\frac{I}{s}}$	induction force component of the solid surface free energy, ergs/cm ²
$\gamma_{\frac{H}{s}}$	hydrogen bond force component of the solid surface free energy, ergs/cm ²
γ_{sv}	solid-vapor surface free energy, ergs/cm ²
θ	equilibrium contact angle, degrees
$\theta_{\frac{a}{s}}$	static advancing contact angle, degrees
θ_{obs}	observed or real contact angle, degrees
$\theta_{\frac{r}{s}}$	static receding contact angle, degrees
$\pi_{\frac{e}{s}}$	equilibrium film pressure of adsorbed vapor, ergs/cm ²
Φ	intermolecular interaction parameter, a dimensionless constant

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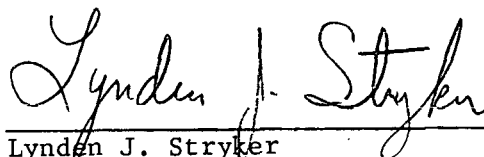
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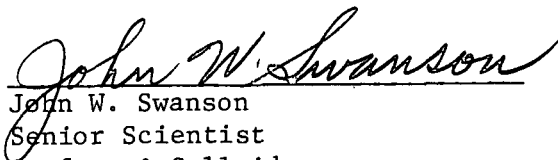
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A handwritten signature in cursive script, reading "Lynden J. Stryker". The signature is written in dark ink and is positioned above a horizontal line.

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A handwritten signature in cursive script, reading "John W. Swanson". The signature is written in dark ink and is positioned above a horizontal line.

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