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Review Article

Progress in Wettability Study of Reactive Systems

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A review of various factors affecting wetting and spreading has been presented. Various methods for wettability studies and critical issues concerning contact angle measurement are discussed. Reactive wetting has been given a special attention in the paper and recent developments in this area are summarized and discussed. Although advanced understanding of nonreactive wetting is currently available in the literature, complete understanding of reactive wetting is still lacking due to the complexity of the phenomenon. To date, there is no single model that is generally applicable to all reactive wetting systems. Reaction between the liquid drop and substrate can take the form of dissolution, intermetallic formation, or combination of both processes. Factors affecting wettability have been summarized and discussed as well as the major available techniques to investigate wetting behaviour.

1. Introduction

Wettability study is an age-old field with the pioneering theoretical work being credited to Young and Laplace [1]. It is of great importance to many industrial practices such as soldering, coating, and composite manufacturing [2–15]. It gives an indication of the extent of intimacy in contact between a liquid and a solid, making it, therefore, an important behaviour to evaluate the success of an industrial operation like brazing [16].

The earliest approach to wettability study was to use physical theory of surface tension to explain and characterize the phenomenon [1, 17, 18]. This idea is well reflected in Young's equation, which is expressed as [19–22]

$$\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}} = \gamma_{\mathrm{lv}} \cos\theta, \tag{1}$$

where θ represents the contact angle measured and γ_{sv}, γ_{sl}, and γ_{lv} represent the solid-vapour, solid-liquid, and liquid-vapour interfacial tension, respectively.

Laplace, on the other hand, gave the mathematical description of the pressure difference between the two sides of a curved surface as [23]

$$\Delta P = \gamma_{\mathrm{lv}} \left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{2}$$

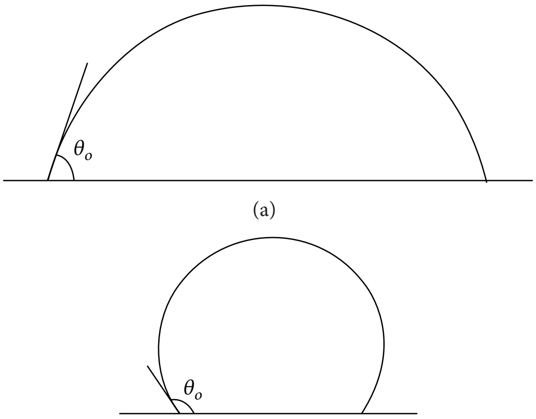
where R_1 and R_2 represent the two principal radii of curvature.

Dupre defined the work of adhesion between a solid and a liquid, yielding the famous Young-Dupre equation [24]. The significance of the Young-Dupre equation lies in the fact that it relates the work of adhesion to the measurable quantities, surface tension of the liquid, and the equilibrium contact angle, rather than to the inaccessible interfacial tensions involving the solid surface as [25, 26]

$$W_{\mathrm{sl}} = \gamma_{\mathrm{lv}} (1 + \cos\theta). \tag{3}$$

However, wetting is more complex than as described by (3) [27]. The derivations of Young's and Young-Dupre equations are made under the assumptions of spreading of nonreactive liquid on an ideal (chemically inert, smooth, homogenous, and rigid) solid. It also assumed that the contact angles are large enough to allow accurate measurement. However, these conditions are rarely met in practical situations [24].

1.1. Wetting and Spreading. With respect to the literature, there seems to be no generally accepted distinction between wetting and spreading. According to Kumar and Prabhu [24], wetting is essentially a surface phenomenon in which a liquid covers the surface of a solid when it is placed over such



(a)

(b)

Figure 1: Profiles of (a) wetting (b) nonwetting sessile drops resting on horizontal surface [37].

a surface, while spreading is considered as a physical process by which the liquid wets the surface of the solid. Yin et al. [29] considered wetting to be a process confined to the contact line region only and spreading as a macroscopic process which involves the flow of a liquid mass over a solid surface in response to an external effect such as capillary force. However, Sharps et al. [30] stated that for spreading to occur, the apparent contact angle must be zero; otherwise, it is wetting or at best good wetting, depending on how close the angle is to zero. This view [30] represents the clearest distinction between wetting and spreading.

The degree of wetting of a substrate by a liquid is usually quantified by the equilibrium or static contact angle, θ, which the liquid metal drop forms on such a substrate [5, 7, 31–36]. The system is usually described as wetting or nonwetting if the contact angle is lesser or greater than 90° as shown in Figures 1(a) and 1(b), respectively [37].

If the liquid droplet wets the substrate with a finite equilibrium contact angle, θ_e, it is referred to as partial wetting; but when θ_e is equal to zero, it is called complete wetting [38, 39].

In the case of nonequilibrium situation whereby the surface energy of the solid is larger than the addition of the solid/liquid and liquid/vapour interfacial energies, then the difference is referred to as spreading coefficient, S, and there will be complete spreading [1]:

$$S = \gamma_{\mathrm{so}} - \gamma_{\mathrm{sl}} - \gamma, \qquad (4)$$

where γ_{so} is the surface energy of a solid with a dry surface and γ is the same as liquid/vapour surface energy.

1.2. Critical Issues with Contact Angle and Its Measurement. In nonreactive wetting systems, the final contact angle is truly the equilibrium contact angle because of the lack of reactivity in the system. However, in systems undergoing reactive wetting, chemical equilibrium is hardly achieved or takes a long period of time to achieve, making the use of equilibrium contact angle to assess the degree of wetting lose its meaning in some circumstances or cases. For a system in which the reaction leads to the formation of solid phases either at the contact line or throughout the brazing droplet, this might lead to isothermal solidification, thus leading to a premature arrest of the spreading [32]. Also, in cases involving the dissolution of the substrate, the contact angle that is observed at the macroscopic level is the apparent contact angle [40]. The true contact angle can only be observed through metallographic inspection. Therefore, the use of contact angle to quantify the degree of wetting in such systems has to be approached with caution.

1.3. Experimental Methods for Wettability Study. Various techniques abound in the literature to evaluate spreading and measure the equilibrium contact angle. Conventional sessile drop method is probably the most used technique in wettability studies [7, 16, 30]. This is due to its simplicity and ease of use. The conventional sessile drop approach/methodology for studying wettability involves placing a solid particle (pure metal, alloy, etc.) on the substrate and then heating up the assembly until the particle melts and flows on the substrate. However, there are some serious concerns with this approach.

In the course of this process, for the case of an alloy, its composition may change due to evaporation and/or diffusion. Also, it can be very difficult to identify when the solid particle is fully molten, which can affect the reference time for wetting/spreading in the study [41]. Equally, the wettability study is usually carried out at a temperature above the melting point of the solid particle. Therefore, this process cannot be described as strictly isothermal because while the pure metal or alloy is melting, the temperature of the furnace is still increasing or yet to stabilize. This might explain some of the discrepancies in the spreading time reported in the literature.

An improved form of the conventional sessile drop method for wettability study is the "drop-transfer technique" [13, 41]. In this approach, the brazing alloy is heated up until it is completely molten on a plate or material with which the alloy is known to have little or no reactivity. Once the furnace temperature is stabilized, the molten alloy is then "transferred" to the substrate as shown in Figure 2 [41]. However, the drawback attached to this approach is that the drop might be driven at the beginning by the transfer inertia. Also, there might be interaction between the wetting process and the drop transfer mechanism.

Another method being employed in wettability study is the dispensed drop method [28, 42]. In this method, the droplet is extruded through a capillary introducer as shown in Figure 3 [42]. However, this method is not free from the problem of perturbation which occurs as the droplet initiates a contact with the substrate.

One of the impediments to comprehensive understanding of reactive wetting, especially in high temperature experiments, is the difficulty of having in situ and real-time monitoring of the interface between the solid and the spreading droplet; hence, quenching and subsequent microstructural analyses are usually the method used to study the interface [43]. However, a new drop experiment technique has been

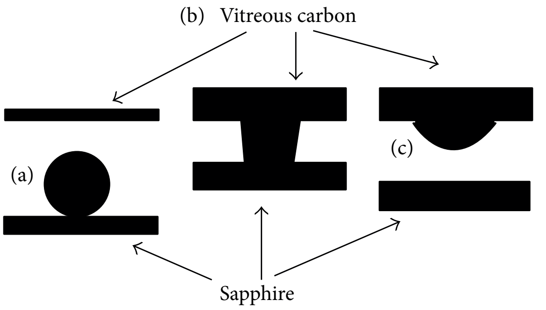


Figure 2: Shadow pictures of drop configuration in a transferred drop wetting experiment of Cu-Cr alloy on vitreous carbon: (a) initial configuration, (b) drop configuration upon initial contact, and (c) hanging drop after separation from lower substrate [41].

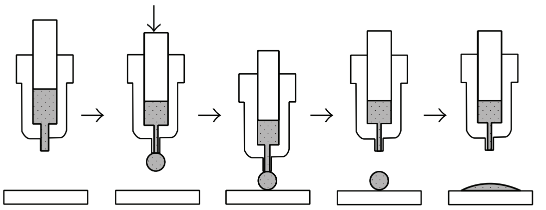


Figure 3: Schematic representation of dispense drop method [42].

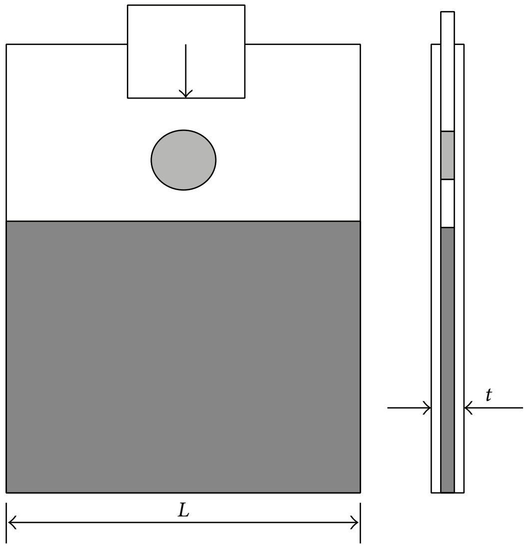


Figure 4: Schematic of the two-dimensional experimental set-up [44].

introduced that allows for real-time monitoring and observation of both the solid-liquid and liquid-vapour interface evolution. This was achieved by performing high temperature reactive wetting experiments in Hele-Shaw cells [29, 44]. This technique was based on drop transfer technique in a very small gap geometry. The transparent cell walls made a real-time observation of the interfaces possible; a schematic of the experimental set-up is shown in Figure 4 [44]. The drop in this experiment is essentially 2-dimensional.

1.4. Contact Angle Hysteresis. For many surfaces, different values of contact angle can be observed or measured depending on whether the measurement is performed with a drop of increasing size (the advancing contact angle, θ_a) or of diminishing size (the receding contact angle, θ_r) [22, 25]. This phenomenon of the existence of more than one contact angle for a particular drop is referred to as contact angle hysteresis [24]. θ_a corresponds to the highest static value that θ can attain [20]. The difference between the advancing and the receding contact angle gives the measure of the hysteresis [45, 46]. Hysteresis plays a special role in practical capillary problems, especially where superhydrophobicity of a surface is required [47–49]. This phenomenon is mostly attributed to surface roughness and chemical heterogeneity of a geometrical surface, among other factors [20, 46, 50, 51]. A very detailed theoretical analysis on contact angle hysteresis has been done by Joanny and de Gennes [52]. Also, Shanahan [22] linked the second order force ripple occasionally observed during dynamic experiments using the Wilhemy plate technique to the phenomenon of contact angle hysteresis leading to the formation of protrusions on the wetting front. There are several other relevant and important works that have been done on the study of contact angle hysteresis such as [53–58].

1.5. Factors Affecting Wetting. According to Shibata et al. [59], issues such as metal purity, gas-phase oxygen content, surface roughness, and substrate purity must all be controlled in order to accurately carry out a wettability study.

1.5.1. Substrate Surface Roughness. The influence of roughness of the solid surface on the contact angle obtained in practice was first discussed by Wenzel [60, 61]. Wenzel [62] argued that for a drop of water resting on a horizontal solid surface, the specific energy content of the solid interface will, in general, be different for the wetted area under the drop than for the dry area around it. He stated that for identically the same increase in the free liquid area at the upper surface of the drop, a greater amount of actual surface is wetted under it, when the surface of the solid is rough than when it is smooth. Consequently, for the process involving the rough surface, there is a greater net energy decrease to induce spreading, and the rough surface is wetted more rapidly. The same reasoning applies for a water-repellent surface, in which case the dry interface has the lower specific energy. The drop will then spontaneously assume a more spherical form. He proposed an equation that gives a relation between equilibrium contact angle and the apparent angle formed on a rough surface as [24, 61]

$$\cos\theta_w = r\cos\theta, \tag{5}$$

where θ is the equilibrium contact angle on a smooth surface, θ_w is the apparent contact angle on a rough surface (generally known as Wenzel angle), and r is the average roughness ratio, the factor by which roughness increases the solid-liquid interfacial area.

From this equation, it can easily be deduced that for any equilibrium contact angle less than 90°, the apparent contact angle will decrease with increase in roughness and vice versa.

Effect of Surface Roughness on Hysteresis. Kandlikar and Steinke [63] observed the interfacial behaviour of deionized (DI) water on copper and stainless steel to investigate the effect of surface roughness and surface temperature on advancing and receding contact angles. For the studied surface roughness range, always the equilibrium contact angle was found to be in between the two limits of the corresponding advancing and receding contact angles. In the case of copper, the highest advancing contact angle was obtained with the smoothest surface while equilibrium contact angle remained relatively constant with increase in surface roughness. For stainless steel, however, the equilibrium contact angle decreased with increase in surface roughness.

It is worth mentioning the fact that, in reactive wetting systems, the asperities and grooves associated with surface roughness may act as preferable sites for reaction and adsorption. Hence, the effect of surface roughness on wettability might be confounded with the effect of other factors [24].

Hysteresis of a Wenzel drop (a drop that wets the groove of a rough surface) on a rough hydrophobic surface made of polydimethylsiloxane (PDMS) was studied by He et al. [45]. The experiments were conducted to measure both the advancing and receding contact angles. The advancing contact angle for the Wenzel drop on the rough surface was found to lie between 142 and 143°. However, no conclusion could be drawn regarding the receding contact angle of a Wenzel drop because the apparent contact angle kept decreasing with decreasing droplet size down to the smallest drop volume that could be handled. They [45] predicted the advancing contact angle of the Wenzel drop using the Wenzel's formula in the form of

$$\cos\theta_{\text{adv}}^{w} = r\cos\theta_{\text{adv}}^{f}, \tag{6}$$

where f is the area fraction of the peaks of the square pillars on the horizontal surface, subscript "adv" denotes advancing angle, w denotes a wetted contact area, and r is the solid roughness, defined as the ratio of the actual solid-liquid contact area to the contact area projected on the horizontal plane.

Equation (6) gave the value of θ_{adv}^{w} as 149°.

1.5.2. Heterogeneity of the Surface. The equilibrium contact angles are influenced by, among other factors, any surface impurities that may be present on the liquid-vapor interface or the solid surface [64]. Many materials of practical interest are multiphase solids with heterogeneous surfaces [65].

Cassie extended Wenzel's treatment of rough surfaces to heterogeneous surfaces. He derived an important equation analogous to Wenzel's for such surfaces [24, 65, 66] as

$$\cos\phi = \sigma_1\cos\theta_1 + \sigma_2\cos\theta_2, \tag{7}$$

where ϕ is the contact angle on the heterogeneous surface, σ_1 is fraction of the surface having the intrinsic contact angle θ_1, and σ_2 is the fraction of the surface having the intrinsic angle θ_2.

Effect of Surface Heterogeneity on Contact Angle Hysteresis. He et al. [45] equally quantified the hysteresis of a Cassie drop (a drop that sits on the peak of the surface roughness) on a rough PDMS surface by measuring the advancing and receding contact angles. An advancing contact angle between 152 and 153° was observed experimentally for a Cassie drop on the rough substrate. The corresponding receding contact angle for the Cassie drop was found to be about 132°. They [45] predicted the advancing contact angle of the Cassie drop using Cassie formula of the form:

$$\cos\theta_{\text{adv}}^{c} = f\cos\theta_{\text{adv}}^{f} + f - 1, \tag{8}$$

where c represents composite contact, f is the area fraction of the peaks of the square pillars on the horizontal surface, and subscript "adv" denotes advancing angle.

Using (8), a value of 153.5° was obtained for θ_{adv}^{c}.

They [45] also estimated the receding contact angle of the Cassie drop using an equation of the form:

$$\cos\theta_{\text{rec}}^{c} = f\cos\theta_{\text{rec}}^{f} + f - 1, \tag{9}$$

where rec represents receding angle.

An estimated value of 143° was obtained for θ_{rec}^{c} from (9). They [45] equally estimated the receding contact angle of the Cassie drop using a model proposed by Patankar [67]. A value of 127.6° was obtained for θ_{rec}^{c}, which was much more close to the experimental value. It must be noted that in the model proposed by Patankar [67], the droplet was assumed to leave a thin film of liquid behind on the peaks of the pillars of the surface roughness as against leaving behind a dry surface as assumed in (9).

1.5.3. Atmosphere. The surface tension of liquid metals is very sensitive to impurities and, in particular, to the oxygen concentration in the liquid phase [68]. If the liquid filler metal is to wet and flow over the base metal, any intervening oxide layers must be removed. Three methods are used in practice to reduce and control the formation of oxide layers in wettability studies: fluxing with molten salts, heating in a reducing atmosphere, and heating in a vacuum [2, 69].

Takao et al. [70] investigated the effect of fluxes (ULF-300R and PO-Z-7) on the ability of Sn-3.5Ag to wet Cu substrate at 270°C. UFL-300R is a more activated flux containing halogen while PO-Z-7 has no halogen. For UFL-300R, a final contact angle (θ) and interfacial liquid-flux tension (γ_{lf}) of 38° and 0.406 N/m were obtained, respectively. While for PO-Z-7, the values of θ and γ_{lf}, were reported to be 43° and 0.470 N/m, respectively. The relative decrease of 5° in the contact angle was attributed to the relative 0.064 N/m decrease in γ_{lf} values of the two fluxes.

López and Kennedy [16] investigated the effect of a K-Al-F-based flux on the spreading of Al on TiC, at temperatures up to 900°C, in Ar and in air. They reported that, while obtuse contact angles were observed without flux, the flux facilitated rapid spreading to a perfect wetting condition, in both Ar and air.

In all cases involving the use of reducing atmosphere, the active reducing constituent is hydrogen or carbon monoxide [2]. For a few metals, hydrogen is satisfactory as a reducing atmosphere [71]. Practical limits are set to the use of hydrogen reduction: firstly in techniques for drying the gas and secondly in keeping it dry because it takes up moisture from the surfaces of the tubes through which it passes into the test chamber [69].

1.5.4. Temperature. The wetting behaviour of a liquid on a solid is sensitive to temperature changes as temperature affects a number of properties of liquid such as viscosity and surface tension [72].

Samarasekera and Munir [73] investigated the contact angles formed by liquid tin, indium, and gallium on zirconium and niobium over temperature range of 303–923 K. They observed three characteristic regions of the temperature dependence of contact angles. A steady-state region in which θ was relatively independent of temperature was preceded and followed by regions in which θ decreased rapidly with increasing temperature.

An experimental investigation into contact angle temperature dependence for water droplets on practical aluminum surfaces was carried out by Bernardin et al. [64]. They observed two distinct temperature-dependent regimes. In the lower temperature regime, below 120°C (surface temperature), a relatively constant contact angle of 90° was observed; while in the high temperature regime, above 120°C, the contact angle decreased in a fairly linear manner. It is worth noting that they [64] used a pressure vessel to increase the water temperature up to 170°C.

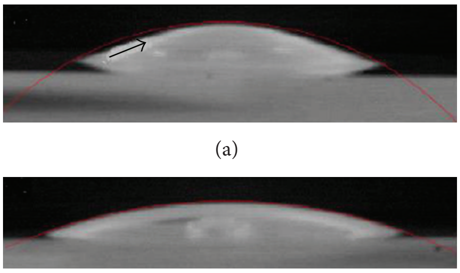
Feduska [74] studied the reactions between five high-temperature base metals and six high-temperature brazing alloys in three different atmospheres at nominal and superheat brazing temperature levels. He observed that the wettability of the substrates by the brazing alloys decreased as the brazing temperature was increased above the nominal level. This trend was attributed to an increase in reactivity between the brazing alloy elements and the base metal at the higher brazing temperature.

Also, contact angle of pure aluminum on the surface of polycrystalline alumina substrate was studied in the temperature range of 750–1100°C by Sangghaleh and Halali [75]. In this system, contact angle was observed to reduce with increasing temperature. In temperatures in excess of 1050°C, the condition of the system changed from nonwetting to wetting.

With reference to the works of López and Kennedy [16], the spreading process was seen to exhibit a temperature dependency. The spreading time was considered to follow an Arrhenius behaviour of the form:

$$\frac{1}{t_0} = K \exp\left(-\frac{E_a}{RT}\right), \qquad (10)$$

where t_0 corresponds to the spreading time, with K being a preexponential constant.



(a)

(b)

Figure 5: Spreading of (a) pure Cu and (b) saturated Cu-Si on Si substrates after 50 ms [29].

1.5.5. Alloying Elements. Yang et al. [76] investigated, in detail, the effects of Ni and Cr contents and wetting temperatures on the wettability and the wetting mechanisms of copper on tungsten substrate. The results showed that the wetting angles of Cu on the W substrate decreased with an increase in the content of Ni or Cr and also decrease with increase in the wetting temperatures.

Equally, wettability at a liquid Al-alloy/SiC interface was evaluated by the sessile drop method at 750°C by Candan [77]. The wetting angle, θ, of the sessile drop on SiC substrate was equally reported to decrease with the addition of Pb, Mg and Ca to pure Al. The reduction in θ obtained with the Al-Pb alloy drop was proportional to the reduction in surface tension, γ_{lv}, of Al; whereas for Al-Mg and Al-Ca alloys, the reduction in θ was greater than the reduction in γ_{lv} of Al. The reduction in contact angle was attributed to reactions that took place at the Al-alloy/SiC interface.

Yu et al. [78] studied the interfacial microstructure and wetting property of Sn-Zn-Cu solders with Cu substrate. They reported that wettability improved remarkably with increasing Cu content in the solder.

1.6. Marangoni Convention. In reactive wetting systems where there is alloying between the chemical species of the liquid and the solid substrate, there is a likely tendency for solute-capillary effect, if the difference in surface tension between the two chemical species is large [28, 29]. In the early stages of reactive regime in wetting where there is dissolution of the substrate into the liquid droplet, the concentration of the solute is usually larger at the contact line/solid-liquid interface than at the top of the droplet. This concentration gradient is likely to set up a solute-capillary flow. The presence of this effect was demonstrated in the spreading of pure Cu and saturated Cu-Si drops on pure Si substrate after 50 ms from the initiation of wetting as shown in Figure 5 [29]. This observation was related to the fact that the surface tension of pure Cu (1280 mNm^{-1}) is higher than that of saturated Cu-Si solution (840 mNm^{-1}) at 1100°C. The effect of early dissolution of Si into the drop at the contact line reduces the surface tension at the contact line relative to that at the top of the drop. Therefore, spreading will be retarded at this stage. On the other hand, spreading will be accelerated if the surface tension of the solute is higher than that of the liquid [28].

1.7. Nonreactive Wetting. When a liquid spreads on a dense and nonporous solid substrate without any reaction, it is referred to as a nonreactive or an inert wetting [79]. For this kind of system, the interface remains flat and unchanged materially [30]. The system is in chemical equilibrium and the degree of wetting is determined by the Young's equation for a flat and nondeformable solid [19]. Also, the spreading time for a metallic millimeter sized droplet in a nonreactive system in which the equilibrium contact angle value is higher than 20° is reported to be less than 10^{-1} s [28, 80]. For the case of complete wetting of a solid surface by a liquid, wetting dynamics are reportedly dominated by a precursor film which spreads ahead of the main body of fluid [1, 38]. A precursor film can either be a bulk liquid phase identical to the drop phase or an adsorption layer [51].

Contact line motion is normally correlated with the dynamic contact angle to describe the kinetics of a wetting system using both theoretical (hydrodynamic, molecular kinetics, and combined hydrodynamic-molecular kinetics) and empirical approach [6].

For droplet spreading where the effect of gravitation is minimal, the macroscopic shape of the droplet is found to be close to a spherical cap [1, 81]. In the case of complete wetting, at late times of spreading, the shape of the drop is spherical and the flow dynamics can be described by Tanner's law [82, 83]:

$$\frac{r}{R} \sim \left(\frac{\gamma t}{\eta R}\right)^{1/10}, \tag{11}$$

where r is the instantaneous radius of the wetted area, R is the initial radius of the drop at the start of spreading, t is time, η is viscosity, and γ represents the liquid surface tension.

Tanner's law does not apply to early stages of spreading where the shape of the drop is completely different (high curvature at the contact line) from that at late time [15]. At short time of spreading, Biance et al. [81] reported the presence of an inertial regime in the spreading drop of water on glass plate. The duration of this regime was found to be in the order of 1 ms for a millimetric water drop and the wetting rate followed a square root growth of the form:

$$r^2(t) \sim \sqrt{\frac{\gamma R}{\rho}}\, t. \tag{12}$$

The characteristic time or duration of this inertial regime was found to be mainly dependent on the drop size.

In partial wetting experiment of different water-glycerol mixtures on solid surfaces with various degree of wettability, early-time inertially dominated wetting was also reported [39]. The spreading dynamics was fit with a power law in the form of:

$$\frac{r}{R} = C\left(\frac{t}{\tau}\right)^{\propto}, \quad \text{where } \tau \equiv \sqrt{\frac{\rho R^3}{\gamma}}, \tag{13}$$

where C is a prefactor and $\propto$ is an exponent.

They [39] found that for low equilibrium angles (θ_e < 10°), $\propto \approx 0.5$, and the spreading dynamics is similar to that of complete wetting. However, both $\propto$ and C were found to decrease with increase in contact angle.

In the short time dynamics of viscous drop spreading investigated by Eddi et al. [15], however, spreading did not follow a pure power-law growth. The spreading velocity was, instead, found to decrease logarithmically in time and the dynamics was reported to be identical to that of coalescing viscous drop. The initial stage of wetting was also found to be independent of substrate wettability. The effective exponent for coalescence was derived as

$$\propto = \frac{\ln(r/R)}{\ln(r/R) - 1}. \tag{14}$$

Lavi and Marmur [6] investigated the partial spreading of organic liquids on coated silicon wafer. An exponential power law was suggested for the kinetics in systems with partial wetting as

$$\frac{A}{A_f} = 1 - \exp\left(-\frac{K}{A_f}\tau^n\right), \tag{15}$$

where A is the normalized and dimensionless drop base area, A_f is the final, equilibrium value of the normalized wetted (solid-liquid) area, τ is the dimensionless time, and K and n are empirical constants.

Another empirical model for describing the mobility relations of partially wetting systems is [43]

$$\frac{\cos\theta_0 - \cos\theta_D}{\cos\theta_0 - 1} = \tanh\left(4.96\mathrm{Ca}^{0.702}\right), \tag{16}$$

where Ca is the capillary number (ratio of viscous force to surface tension force), while θ_0 and θ_D represent the static and dynamic contact angles, respectively. There are other relevant works that have been done on nonreactive wetting [54, 84–94].

2. Reactive Wetting

This type of wetting is characterized with dissolution of the substrate and/or formation of intermediate compounds at the interface between the liquid alloy and the substrate [29]. The wetting kinetics, in this case, is controlled not by viscous dissipation but by the rate of interfacial reaction and the spreading time is reported to be in the range of 101–104 s [41, 42, 80, 95–97]. A spreading time of 0.06 s was reported for eutectic Ag-Cu liquid droplet on Cu substrate by Sharps et al. [30]. Reactive wetting is very important in metal-metal joining processes such as brazing and soldering [43].

The main difference between wetting in purely dissolutive systems and wetting in compound forming systems is the formation of intermetallic compounds in the latter, which tend to arrest the spreading at the triple line [44]. Interfacial reactions have often been suggested to lead to the reduction of the corresponding interfacial energy and attempts have been made to relate the degree of wetting with the free energy of interfacial reactions by replacing the γ_{sl} term in (1) by [98]

$$\gamma_{\mathrm{sl}}(t) = \gamma_{\mathrm{sl}} + \Delta G_r(t), \tag{17}$$

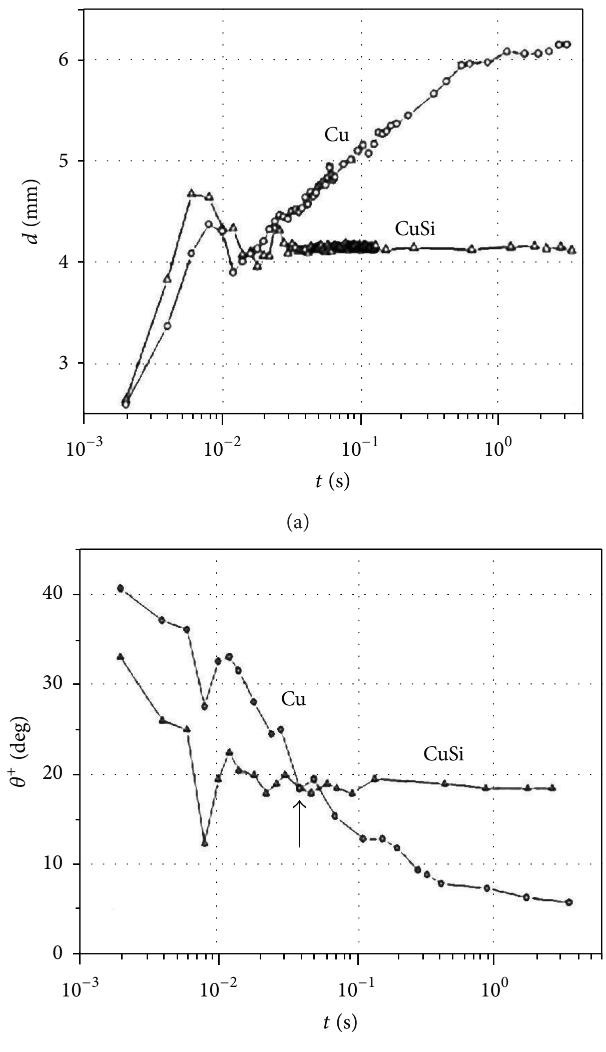
where $\Delta G_r(t)$ corresponds to the change in Gibbs energy released per unit area by the reaction in the "immediate vicinity of the solid/liquid interface" [98].

2.1. Purely Dissolutive Reactive Wetting. This kind of wetting is synonymous with high degree of dissolution of the substrate in the molten alloy, leading to a nonplanar solid-liquid interface [43]. It occurs not only in metal/metal systems but also in metal/ceramic systems.

Protsenko et al. [40] studied the wetting of single crystal silicon wafers (0 0 1) by pure copper and silicon-saturated CuSi alloy, using the dispensed drop technique at 1100°C under high vacuum. This was done to investigate both dissolutive (nonequilibrium) and nonreactive (equilibrium) wetting for the same system. The spreading time for the nonreactive CuSi/Si was observed to take place in a few milliseconds with an average final visible contact angle of $19 \pm 3^\circ$. In the Cu/Si system, wetting occurred in two different stages. In the first stage (nonreactive), a visible contact angle close to 40° (angle formed by pure Cu on nearly unreacted Si) was observed after a few milliseconds. The second stage (dissolutive) led to the formation of a visible contact angle of 5° on a nonplanar interface within 1-2 s. This second reactive or dissolutive stage was subsequently broken down into two steps. The first step involved the decrease of the contact angle from 40° to 19° which is formed on Si by Si-saturated copper. This angle decrease took place rapidly in about 40 ± 10 ms. At this point, the solid Si was reportedly in equilibrium with the liquid at the solid-liquid interface but not in equilibrium with the bulk liquid. The implication of this is that dissolution rate at the solid-liquid interface was faster than the transport rate of the Si atoms from the interface to the bulk liquid. The second reactive step led to the decrease of the visible contact angle from 19° to 5° couple with the formation of a crater at the interface. The variation of the drop base diameter and visible contact angle with time, on a logarithmic scale, is shown in Figure 6 [40]. It is important to know that Protsenko et al. [99] obtained similar result on (1 1 1) Si wafers.

Recently, an interesting study was made into the wetting of Ag-Cu alloys on Cu substrates at 900°C, using dispensed drop technique [28]. Equilibrium and nonequilibrium systems were considered by using Cu-saturated and non-Cu-saturated liquid. The plotted variation of the drop base diameter, d, and contact angle, θ, with time on a logarithmic scale is shown in Figure 7 [28].

For both the equilibrium and nonequilibrium systems, the spreading curves were nearly overlapping up to 20–30 ms. Based on this observation, the early stage of wetting was described as nonreactive, suggesting the absence of dissolution and its effects in the nonequilibrium system at this stage. However, after 30 ms, the spreading of the non-Cu-saturated drop became faster than the Cu-saturated drop. This observed faster spreading in the nonequilibrium system was attributed to the dissolution of Cu into the Ag-Cu alloy. In both cases, the spreading time exceeded 100 s. This observed long spreading time in the equilibrium Ag-Cu/Cu system is unusual, considering the lack of any significant reaction between the solid and liquid phases. The long spreading time observed in the equilibrium system was attributed to the very low equilibrium contact angle, about 1°, of the system.



(a)

(b)

Figure 6: Drop base radius (a) and visible contact angle (b) as a function of time plotted on a logarithmic scale for Cu and Cu presaturated in Si on a (0 0 1) Si surface at 1100°C. The arrow in the $\theta^+(t)$ diagram indicates the time when the visible contact angle equalled the value of 19° observed with Si presaturated Cu (CuSi) [40].

Three distinct spreading stages were observed in the non-Cu-saturated system as shown in Table 1 [28]. The highlight of this is the presence of nonreactive spreading both before and after the dissolutive stage. Schematic representation of the spreading stages for both nonequilibrium and equilibrium Ag-Cu/Cu systems are shown in Figure 8 [28].

2.2. Compound Forming Systems. One way of improving the wetting of a substrate by a metal is to alloy such a metal with chemical species that react with the substrate to form a reaction product that is more wettable than the original substrate [41, 42, 76, 97]. One of the earliest efforts

Table 1: Spreading regimes in nonequilibrium Ag-Cu/Cu system [28].

Time interval (s)	Drop base diameter (d/d_{dr}) evolution	Spreading regime	Average spreading rate (m/s)
0–0.03	0–2.6	Nonreactive	10^{-1}
0.03–1	2.6–4.6	Dissolutive	10^{-3}
1–100	4.6–7.3	Diffusion into the solid	10^{-5}

$T = 900^\circ$C.

towards understanding this type of reactive wetting was made by Aksay et al. [19]. Using a thermodynamic approach, they concluded that, under chemical nonequilibrium, mass transfer across the interface leads to a transient decrease in the corresponding interfacial energy.

Landry and Eustathopoulos [95] made a significant contribution towards understanding this reactive wetting by relating the experimentally obtained wetting radius, $R(t)$, curves for Al/C_v with the mechanism of growth of the interfacial reaction product (Al_4C_3) at 1100 K. The main feature of the $R(t)$ curve was the presence of a nearly linear spreading region/regime during which the liquid/solid interface was completely covered by a layer of (Al_4C_3). The wetting kinetics was suggested to be controlled by the kinetics of lateral growth of Al_4C_3 at the triple line.

Also in the experimental study of wetting of Cu-Si alloys on carbon substrate [98], linear spreading was observed. A 3-step change in contact angle and base radius were noticed. Spreading was described as rapid in the first stage before slowing down significantly in the second stage (linear spreading regime). The drop radius and contact angle remained steady in the third stage. The presence of a continuous layer of silicon carbide was noticed at the solid/liquid interface.

The concept of diffusion-limited reactive wetting was introduced in 1999 by Voitovitch et al. [41] in the study of the spreading kinetics of Cu-Cr alloys on carbon. A dense reaction layer, Cr_7C_3, was formed at the solid/liquid interface, with the thickness depending on Cr concentration and the time of holding. The observed triple line velocity was not constant with time, it was found to be a function of the contact angle. A final contact angle of 40° was observed, which was reported to be nearly equal to the contact angle of Cu-Cr alloy on a substrate of chromium carbide. The diffusion of chromium to the triple line was concluded to be the rate limiting factor in the spreading kinetics of Cu-Cr/C system.

2.2.1. Nonreactive Stage in Reactive Wetting.

Different stages have been observed in different reactive systems [7, 28, 40, 42, 80, 98, 100]. However, there has been a common observation among researchers of the existence of nonreactive stage at the onset of this wetting which is characterised with fast spreading with no reaction with the substrate, thereby leaving the solid/liquid interface in its original flat state. However, until recently, there was no physical proof of this due to lack of in situ and real-time observation of the solid/liquid interface.

Yin et al. [29] performed experimental investigation into dissolutive wetting of Bi-Sn system in Hele-Shaw cells. The obtained results, as shown in Figure 9 [29], tend to support the presence of this nonreactive stage at the onset of reactive wetting. At the early stage of wetting (less than 100 ms), no change in the solid/liquid interface was observed.

2.3. Cold Wetting.

Application of hysteresis phenomenon and reactive wetting to liquid droplets spreading on solid surfaces is well documented in the literature [101–105]. A surface having primarily polar groups will have a strong affinity for water and a low contact angle will be formed on it by water. Such a surface is referred to as being hydrophilic. On the other hand, if the surface is made up of nonpolar groups, a large contact angle will be formed on it by water and such a surface is termed hydrophobic [25]. The idea of free and rapid motion of liquid droplets on solid surface is essentially based on the ability of a liquid to modify a hydrophilic surface by some reactive mechanism and render if hydrophobic. The droplet would then be out of equilibrium between the hydrophilic surface it meets at the front and the hydrophobic trail it leaves behind, thereby leading to a free running droplet [102].

Chaudhury and Whitesides [105] equated the unbalanced force experienced by a drop placed on a surface with gradient in surface tension, as shown in Figure 10 [105], to the unbalanced Young's force (dF_Y), as given in the following [105]:

$$dF_Y = [(\gamma_{SV} - \gamma_{SL})_A - (\gamma_{SV} - \gamma_{SL})_B]\, dx, \qquad (18)$$

where dx is the thickness of the section of the drop.

In terms of contact angles at points A and B, the unbalanced Young's force was represented as

$$dF_Y = \gamma_{LV} (\cos\theta_A - \cos\theta_B)\, dx. \qquad (19)$$

They [105] stated that the presence of gradient in surface tension only on a solid surface is not sufficient to ensure motion of liquid drops, the surface must also have low hysteresis in contact angles and be free of defects that can pin the edge of the drop. By producing gradients in chemical compositions and surface tension on solid surfaces through silanization reaction, they [105] were able to cause 1-2 μL drops of water to move up a 15° slope along the direction of increasing surface free energy with average velocities of 1 to 2 mm/s.

Bain et al. [101] put to test the concept of reactive flow of liquid droplet on solid surface by experimenting with a drop of Decane containing a fluorinated fatty acid, $CF_3(CF_2)_6CO_2H$ (PFOA), on an ordinary glass microscope slide inclined at an angle of 43° to the horizontal. The drop was observed to flow up the slide as shown in Figure 11 [101].

The chemistry occurring at the surface of the glass was identified to be the key behind this behaviour. The PFOA was reported to adsorb from Decane to form an oriented

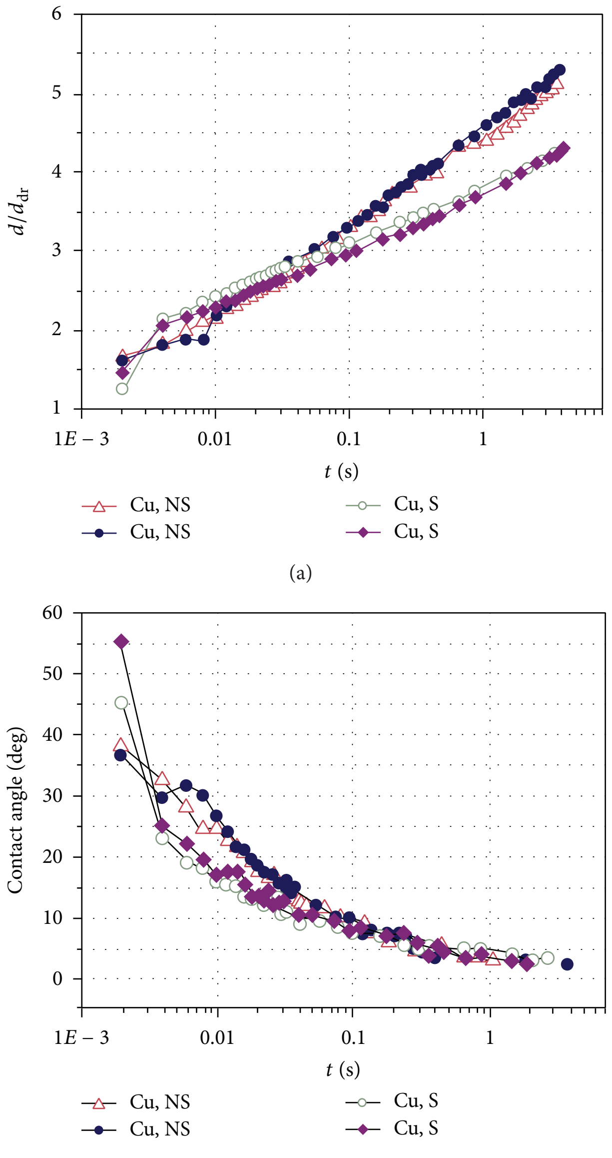


FIGURE 7: Normalised drop base diameter (a) and contact angle (b) as a function of logarithm of time for two saturated (S) and two nonsaturated (NS) Ag-Cu drops spreading on monocrystalline Cu at $t < 4$ s [28].

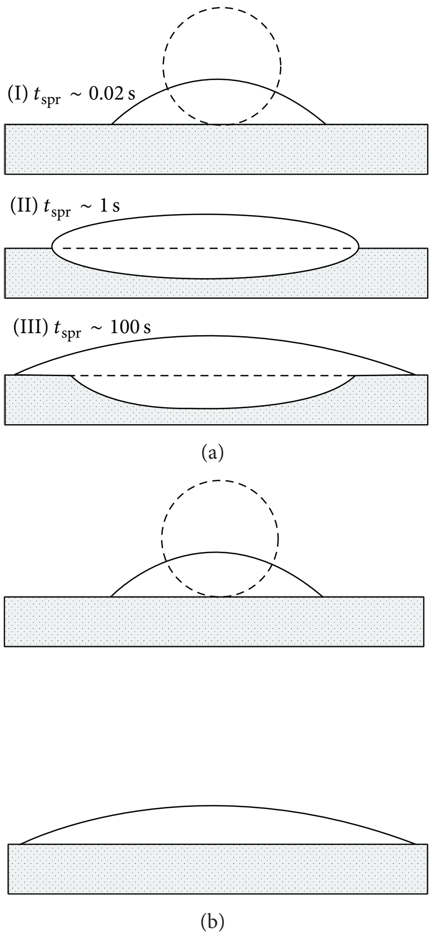


FIGURE 8: Schematic representation of spreading stages in (a) nonequilibrium and (b) equilibrium Ag-Cu/Cu systems [28].

monolayer attached to the glass through the carboxylic acid group. The outer surface of the monolayer allegedly consists of oil-repelling CF_2 and CF_3 groups. While Decane beads up on a fluorinated surface because of its lower surface energy; it spreads on a clean surface of glass.

The idea of reactive wetting in free-running droplet was also established by dos Santos and Ondarçuhu [102]. They experimented with the flow of droplets of *n*-alkanes (*n*-octane and *n*-dodecane) containing 1H,1H,2H,2H-perfluorodecyltrichlorosilane on glass surface. They reported that the silane molecules can form dense grafted monolayers on silicon or glass, thereby rendering the surface hydrophobic. Two types of droplets were used for the experiment, based on the capillary length ($\kappa^{-1} = (\gamma/\rho g)^{1/2}$; the capillary length: γ is the surface tension of the liquid and ρ is its density). After dropping the droplet on the glass surface, motion was initiated by pushing it with a pipette. The droplet was observed to move on the substrate and the self-supporting movement ended only when the droplet had no more hydrophilic surface available. The movement was equally observed on an inclined substrate with the droplet running uphill. For droplets with length smaller than the capillary length, they were observed to move with constant velocity V and constant length L. When the silane concentration of the small droplets was changed, the velocity initially increased with increase in concentration before reaching a saturation level at high concentrations, as shown in Figure 12 [102].

There are other important contributions to the field of liquid cold wetting [106, 107].

2.4. Modelling of Kinetics of Reactive Systems. Due to the lack of thorough understanding and complexity of reactive wetting systems, there is still no single model that is generally applicable to all reactive systems.

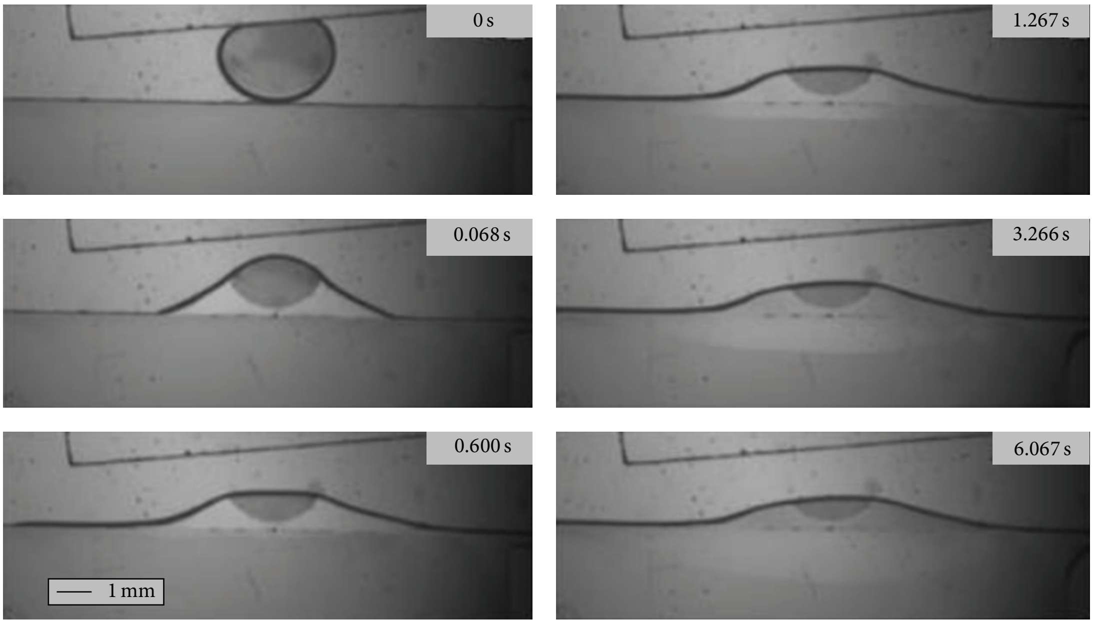


Figure 9: Images of a pure Sn drop wetting pure Bi in a Hele-Shaw cell [29].

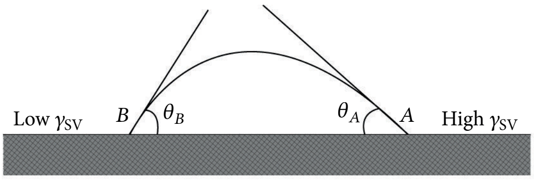


Figure 10: Idealized diagram of a thin cross section of a liquid drop on a gradient surface [105].

In the Cu/Si system studied by Protsenko et al. [40], the wetting rate was modelled by an equation of the form:

$$U = \frac{4}{3\theta_Y^2} \cdot \frac{D}{\delta} \left(\theta^+ - \theta_F^+\right), \tag{20}$$

where θ_Y, θ^+, θ_F^+, and D/δ represent Young's contact angle, instantaneous visible contact angle, final visible contact angle, and mass transport parameter, respectively.

When the transport of Si in the liquid was assumed to be purely diffusion based, the experimental data fit the equation well but with a much higher than usual value for the diffusion coefficient, indicating that the diffusion coefficient lost its physical meaning and became an adjustable parameter.

Also, Kozlova et al. [28] reported that the spreading kinetics of saturated Ag-Cu alloy on Cu followed the relation:

$$R^n \sim At, \tag{21}$$

where R represents the droplet base radius, t is the time, and n and A are empirical constants.

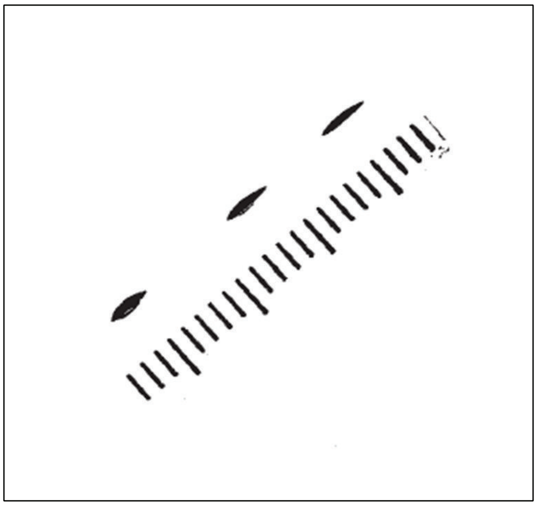


Figure 11: Photograph of a 2 μL drop of Decane containing 1.5 mM pentadecafluorooctanoic acid (PFOA) flowing up a glass microscope slide inclined at an angle of 43° from the horizontal. Three photographs taken at 0.45 s intervals have been superimposed in the same image with the first photograph being on the left [101].

The diffusion-limited spreading kinetics of Cu-Cr/C_v was equally described with an equation of the form [41]:

$$\frac{dR}{dt} = \frac{2DF_{(t)}}{en_v} \left(C_0 - C_e\right)\theta, \tag{22}$$

where D is the diffusion coefficient in the liquid phase, n_v is the number of moles of reactive solute per unit volume of the reaction product, e is the reaction thickness at the triple line, $F_{(t)}$ is the dynamic spreading force, C_o is the bulk drop

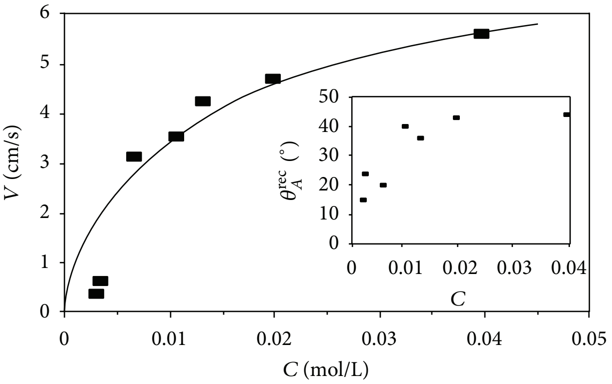


FIGURE 12: Plot of the velocity of octane droplets of length $L = 3.5$ mm as a function of the concentration in silane. Inset: receding contact angle of pure octane measured on the hydrophobic trail left by the same droplets [102].

concentration, and C_e is the concentration of the reactive solute at the triple line.

However, the experimental results obtained for this system, Cu-Cr/C_v, disagreed with this model. The intercept of the line described by (22) should be at $\theta = 0$. But for this system, it was at finite angle of 40°. Equation (22) was based on the assumption that all solute flux is consumed by the reaction at the triple line, therefore neglecting any thickening of the reaction layer behind the triple line. This was cited as the reason for the disagreement between the model and the experimental results for this system [80]. On the other hand, experimental results obtained for CuSn-Ti/C_v system were successfully modelled by (3) [80].

For reaction-limited spreading, Dezellus et al. [42] suggested that instantaneous contact angle, $\theta(t)$, could be defined by the relation:

$$\cos\theta_F - \cos\theta = (\cos\theta_F - \cos\theta_0)\cdot\exp(-kt) \tag{23}$$

with k being the kinetic constant.

For liquid droplet spreading in cold wetting systems, Raphael [108] showed that for an ideal surface, the droplet will reach a constant velocity given by

$$V = \frac{\gamma}{6l\eta}\tan\theta^*\left(\cos\theta_{Pe} - \cos\theta_{Ae}\right), \tag{24}$$

where γ is the surface tension of the liquid, η is its viscosity, l is a logarithmic factor ($l = \ln(x_{\max}/x_{\min})$, the ratio of macroscopic and molecular lengths), θ_{Pe} is the equilibrium angle on the hydrophilic surface (P), θ_{Ae} is the equilibrium angle on the hydrophilic surface (A), and θ^* is the dynamic contact angle of the droplet given as

$$2\cos\theta^* = \cos\theta_{\mathrm{Ae}} + \cos\theta_{\mathrm{Pe}}. \tag{25}$$

Dos Santos and Ondarçuhu [102] applied (24) and (25) to real surface by replacing θ_{Pe} and θ_{Ae} by $\theta_{\mathrm{P}}^{\mathrm{adv}}$ (advancing contact angle on P) and $\theta_{\mathrm{A}}^{\mathrm{rec}}$ (receding contact angle on A), respectively, and they succeeded in fitting the obtained experimental results.

For a droplet with size lesser than the capillary length, Brochard-Wyart and de Gennes [109] presented a model predicting the steady state velocity V as a function of the drop size L, while incorporating the reaction kinetics as

$$L = V\tau\ln\left(\frac{V_1}{V_1 - V}\right), \qquad V_1 = \frac{\gamma_1\theta^*}{6l}, \tag{26}$$

where τ is the reaction time and γ_1 is a constant.

3. Conclusion

The level of understanding of inert wetting is quite good. Models that can successfully describe the process are available in the literature. Reactive wetting systems, on the other hand, are quite complex to study. The nature of reaction in these systems could take the form of dissolution, intermetallic formation, or combination of both processes. Microstructural changes in such systems can occur within a fraction of seconds. Equally, different stages are involved in reactive wetting. The early stage of reactive wetting is usually very fast and independent of any reaction. However, the kinetics of the latter stages is usually controlled by the nature of the reaction. It is difficult, if not impossible, to find a single model that will perfectly describe the kinetics of all the stages involved in any reactive system. Variation of contact angle, with respect to advancing and receding droplets, has been reflected upon. Reactive wetting, as it applies to cold systems, has also been reviewed.

The Hele-Shaw reactive wetting experiment has the potential to radically advance the state of knowledge in interfacial dynamics of reactive systems. Identification and clarification of the different wetting regimes in the Cu-Si/Si system is a great development considering the importance of this system to the electronic industry. Also, the identification of two nonreactive spreading regimes before and after the dissolutive spreading in Ag-Cu/Cu system is a new development. Equally, the effect of solutal Marangoni convection during the early stage of reactive regime has been clearly identified in the literature. The development of reaction and diffusion limited spreading models will also go a long way in shedding more light on compound-forming reactive wetting systems.

Conflict of Interests

The authors declare that there is no conflict of interests of any sort that might have influenced the discussions or conclusions of this paper.

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