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Contact Angles and Wettability of Cellulosic Surfaces: A Review of Proposed Mechanisms and Test Strategies

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Contact angle methods are widely used to evaluate the wettability of cellulose-based surfaces and to judge their suitability for different applications. Wettability affects ink receptivity, coating, absorbency, adhesion, and frictional properties. There has been a continuing quest on the part of researchers to quantify the thermodynamic work of adhesion between cellulosic surfaces and various probe liquids and to account for such components of force as the London/van der Waals dispersion force, hydrogen bonding, and acid and base interactions. However, due in part to the rough, porous, and water-swellable nature of cellulosic materials, poor fits between various theories and contact angle data have been observed. Such problems are compounded by inherent weaknesses and challenges of the theoretical approaches that have been employed up to this point. It appears that insufficient consideration has been given to the challenging nature of cellulosic materials from the perspective of attempting to gain accurate information about different contributions to surface free energy. Strong hysteresis effects, with large differences between advancing and receding contact angles, have been overlooked by many researchers in attempting to quantify the work of adhesion. Experimental and conceptual approaches are suggested as potential ways to achieve more reliable and useful results in future wettability studies of cellulosic surfaces.

Keywords: Contact angles; Surface free energy; Cellulose; Wood; Water-repellent treatments

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Contents of Article

INTRODUCTION

Wettability can be generally defined as the tendency of a selected liquid to spread out and make intimate contact with a surface of interest. The most common way to assess wettability is to evaluate the angle of contact between a probe liquid and the surface. This review focuses on the wettability of natural or modified cellulosic surfaces, with emphasis on those characteristics of cellulosic surfaces that can make wettability assessments more challenging. In the context of this article, the term “cellulosic” will include such materials as cellulose itself, as well as wood, paper, cotton, lignin isolates, and regenerated cellulose products such as Cellophane®, Rayon®, and lyocell, as well as chemically modified cellulosic materials.

Reasons to Study Wettability of Cellulosic Surfaces

Evaluation of the relative wettability of a surface can be helpful for predicting or controlling the outcome of various industrial processes. As noted by Berg (1993), wettability measurements can be used to optimize the coating of paper, as well as its adhesion to various resins. The compatibility of a paper surface for specific xerographic toner particles also can be monitored, making it possible to select the best chemical modification of the surface groups to improve the printing (Erbil 1997). Also, the geometry of mineral particles used in the coating of paper can be designed in such as a way as to optimize the degree of permeation of aqueous solution during ink-jet printing (Kent and Lyne 1989).

It turns out that the wettability of a surface by selected glue formulations can be the key to achieving strong adhesion (Freeman and Wangaard 1960; Bodig 1962; Collett 1972; Borch 1991; Berg 1993; Shi and Gardner 2001; Baldan 2012; Petrič 2013; Qin *et al.* 2014). As noted by Cheng and Sun (2006), a good adhesive for wood needs to be able to wet and penetrate into the pores to achieve effective bonding. Hiziroglu *et al.* (2014) showed that the roughness of wood surfaces affected their wettability by bonding formulations and ultimately affected the strength of bonding.

Measurements related to contact angles have been carried out to evaluate the wettability of many different kinds of cellulosic surfaces. Examples include hydrophobic treatments (sizing agents) for paper (Aspler and Lyne 1984; Aspler *et al.* 1984, 1987; Etzler *et al.* 1995; Huang *et al.* 1995), effects attributable to the recycling of paper fibers (Wistara *et al.* 1999; Tze and Gardner 2001a,b), the beneficial action of compatibilizers used in preparation of wood-polymer composites (Cantero *et al.* 2003; Li 2014a), and hot-press treatment that may affect the bondability of wood (Li *et al.* 2014). Various studies have focused on factors that affect wood’s wettability, such as beetle attack (Little *et al.* 2013), antifungal agents (Maldas and Kamdem (1998), the type of wood species (Soumya *et al.* 2011), the passage of time after the creation of freshly-cut surfaces (Stehr *et al.* 2001), and extraction with hot water (Paredes *et al.* 2009). As shown by Rossi *et al.* (2012) the wettability of wood can also be a function of the location in the tree from which it was obtained, and there are also relationships between wettability and the chemical and structural composition of the wood.

Challenges of Assessing Wettability of Cellulosic Materials

Efforts to quantify the wetting and adhesion characteristics of cellulosic materials face challenges. In particular, the complex porous and fibrillar morphology of cellulosic surfaces poses obstacles for the accurate quantification of contact angles at such surfaces. When the values of contact angles are in doubt, then any estimates of thermodynamic work of adhesion and other fundamental properties are likely to be inaccurate. This article reviews work aimed at overcoming these challenges using a variety of experimental and interpretive approaches.

In addition to the experimental approaches to be emphasized in the present review, industrialists employ a range of practical tests for purposes of quality control. Such tests have been reviewed in greater detail elsewhere (Tai and Yamauchi 2013). For paper industry applications, the most widely used tests related to wettability and absorption are the weight-gain tests (*e.g.* the Cobb test, TAPPI T441), the penetration time tests (*e.g.* the Hercules size test, TAPPI T530), and the inkjet printing of paper to evaluate such aspects as the spreading, feathering, and resulting print density (Borch 1991; Fischer 1999; Calvert 2001). Also, many papermaking operations have made use of the Bristow wheel method (Bristow 1967), as well as tests to assess the dynamic wettability relative to high-speed fluid-based printing operations.

Two Tracks of Theoretical Development

Scientists who have attempted to apply the concepts of wettability to real surfaces have generally followed either one or the other of two contrasting conceptual tracks. On the one hand, a great many studies have focused on issues related to physical chemistry, attempting to account for the degree of interaction between a probe liquid and a solid. On the other hand, a smaller group of scientists have focused on issues related to morphological effects – especially the effects of roughness and porosity on contact angles. Very few investigators appear to have attempted to include both aspects in the interpretation of experimental results (for instance, Shen *et al.* 2000). Background related to the chemical aspects and forces of interaction has been provided in a series of review articles (Fowkes 1964b; Good 1979, 1992; Etzler 2013). For background related to the effects of roughness and porosity, the following sources are recommended (Fortes 1981; Wålinder and Gardner 2002b; Samyn 2013). Also, experimental aspects of wettability determination for cellulose-based materials have been reviewed (Berg 1993; de Meijer *et al.* 2000; Petrič and Oven 2015). The two tracks of research will first be considered separately in this article, and then, at the end, an attempt will be made to bring them together in a discussion of results of experimental work.

Apparent contact angles

As will be discussed in the sections that follow, both of the two conceptual tracks mentioned above can give rise to uncertainty as to whether the contact angles that one measures on a cellulosic surface can be regarded as ideal or equilibrium quantities. Non-equilibrium contact angles, penetration of the fluid into the pores of the material, and swelling of the cellulosic substance, especially in the case of water, tend to make the measurements difficult to account for theoretically (Kamdem and Riedl 1992). Thus, it has been proposed that the term "apparent contact angle" be employed (Shuttleworth and

Bailey 1948; Huh and Mason 1977; Stehr *et al.* 2001; Wålinder and Gardner 2002a; Marmur 2006; Kutnar 2012; Rossi *et al.* 2012). For example, to minimize effects of inertia and absorption on their contact angle data, Kalnins *et al.* (1988) had to specify an observation time of 3 to 5 seconds after placement of a droplet onto wood. Liptáková *et al*. (1998) analyzed problems with determination of the equilibrium state during the wood wetting process and came up with a recommendation for choosing an apparent "equilibrium" contact angle on wood. Though the simpler term "contact angle" will be mainly employed within this article, it should be kept in mind that the chemically heterogeneous, rough, porous, and often absorbent nature of cellulosic materials can be expected to lead to poor fits of various idealized models that will be discussed.

Much energy has been spent, by many researchers, in an effort to account for wettability effects in terms of fundamental contributions to surface free energy. Though it is a noble idea to want to fully understand the mechanisms underlying such events as the wetting of surfaces, it can be argued that the progress of industrial applications may not need to wait for such goals to be achieved. In fact, as will be discussed in the course of this article, many theoretical aspects do not appear to have been adequately resolved.

Organization of the article

The two tracks of *chemical aspects* and *morphological aspects* will be considered from several different viewpoints in this work.

The first main section will provide some background regarding the surfaces of typical cellulosic surfaces. From a chemical perspective, the goal will be to describe, based on the literature, what are the main functional groups present at cellulosic surfaces and what is the known about the ability of these groups to interact with different kinds of molecules, including non-polar compounds, polar ones, those that can hydrogen bond, and those with Lewis acid or Lewis base character. From a morphological perspective, the goal will be to define the likely scale of roughness and the sizes of different kinds of pores associated with cellulosic surfaces.

The second main section will deal with theoretical concepts. On the chemical side, the concepts to be reviewed, with emphasis on cellulosic surfaces, will include the Young equation (Young 1805), the work of adhesion (Dupré 1869), critical surface tensions (Fox and Zisman 1950), and different ways of accounting for acidic or basic character of surfaces (Drago and Wayland 1965; Gutmann *et al.* 1966; Mayer *et al.* 1975; Drago *et al.* 1987). From a morphological perspective, the concepts to be reviewed will include Wenzel's (1936) modification of Young's equation to account for some predicted equilibrium effects of roughness, various hysteresis effects related to roughness, and effects attributable to porosity of cellulosic surfaces (Cassie and Baxter 1944).

The third main section deals with experimental findings and their interpretation. Here the primary emphasis will be placed on results of studies attempting to shed light on the chemical aspects of the wettability of cellulose. Results will be discussed relative to their self-consistency and also in terms of what is known about cellulosic surfaces by other means. It will be argued that, even when systematic errors cannot be ruled out or accounted for, the trends revealed by different kinds of experiments can be highly useful for industrial development efforts. While the practical evaluation and prediction of wettability and adhesion outcomes can be expected to remain a challenge, it is possible to gain a lot of useful information from some relatively easy-to-apply tests. Examples will be highlighted in which researchers have attempted to bridge the gap between chemical-based concepts and morphology-based concepts.

The final main section of the article will consider what additional steps might be taken in future work to more successfully apply wettability concepts to cellulosic surfaces. Four main approaches will be reviewed, based on the published literature. First to be considered will be ways to render cellulosic surfaces smooth and non-porous as a means of more accurately applying some of the chemical approaches to analysis of wetting phenomena. Secondly, the question of quantitative prediction rather than just qualitative explanation of effects of roughness and porosity will be considered. Thirdly, attempts to incorporate roughness and porosity concepts into analysis of components of surface free energy will be considered, with emphasis placed on the idea that wettability phenomena can be dominated by minor impurities and morphological imperfections in a cellulosic surface. And finally, it will be advocated that many published results should be viewed as useful estimations that require calibration, rather than as sources of quantitative information regarding the free energy of the surfaces.

CELLULOSIC SURFACES

Chemistry of Cellulosic Surfaces

There is widespread agreement that surface chemical composition plays a major role with respect to wettability and adhesion. Surface chemical aspects of cellulosic materials have been reviewed (Gardner *et al.* 2008; Gray *et al.* 2010; Gamelas 2013; Samyn 2013; Petrič and Oven 2015). This section provides an overview of such topics, with an emphasis on functional groups that are commonly found at cellulosic surfaces and how they can be expected to influence the free energy of the surface. It is well known (Vassilev *et al.* 2012; Vaz 2014) that the main chemical components of most cellulosic materials such as wood are cellulose, hemicellulose, and lignin, in addition to minor amounts of extractable monomeric compounds, *i.e.* the “extractives”.

Cellulose

Cellulose, because of its strong tendency to crystallize into relatively stiff, straight fibrillar forms at the nanometer scale, can be regarded as the skeleton of plant materials. The most notable functional group to be concerned with is the –OH group, which is known to participate in extensive hydrogen bonding (Medronho and Lindman 2014). Within the cellulose crystal, the hydrogen bonds act in a highly regular pattern, linking the –OH···O– structures both within and between adjacent cellulose chains (Pönni *et al.* 2012; Yuan *et al.* 2013; French *et al.* 2014). As a consequence, the majority of –OH groups can be regarded as “already occupied”, and not necessarily available for interaction with liquid probes or other materials placed at a cellulosic surface. Nevertheless, it is clear that –OH groups at cellulosic surfaces play a major role in wettability and adhesion phenomena, especially with respect to interactions with water and other hydrogen-bonding materials (Yamane *et al.* 2006). The subject of hydrogen bonding has been well reviewed elsewhere (Jeffrey 1997), so only brief comments will be given here.

The –OH group can be regarded as "polar", which implies that net-positive or net-negative parts of the molecule may be electrostatically attracted (at least weakly) to certain parts of adjacent polar compounds. The oxygen atom is highly electronegative, and as a consequence the electron pair associated with covalent bonding to hydrogen tends to spend a disproportionate amount of time (or wave density) closer to the oxygen atom, giving rise to a net positive charge on the hydrogen. Attractive forces arising from such interactions between dipoles can be regarded either in terms of Keesom forces (Rosenholm 2010), or as a manifestation of acid-base interactions (van Oss *et al.* 1988a,b; Sun and Berg 2003), and there appears to be a need for more work to consider whether these different categories of interaction should be regarded as separate from each other.

What is easy to overlook when considering the surface interactions of cellulose is that different crystal faces of pure cellulose differ greatly with respect to the availability of –OH groups (Biermann *et al.* 2001). Yamane *et al.* (2006) showed that depending on the conditions under which cellulose solutions are regenerated in the preparation of films or fibers, the degree to which polar –OH groups end up facing outwards can be greatly affected. For instance there are many –OH groups in the equatorial position of glucopyranose rings, associated with the (1-10) crystal face of regenerated cellulose, and if this crystal face is dominant at the exterior of the regenerated material, this will give rise to a water-loving surface. By contrast, the (110) plane is expected to be hydrophobic. Such differences help to account for why the medium in which regeneration occurs has a strong influence on the resulting external surface and its wettability.

Hemicelluloses

Hemicelluloses are present in most plant cell walls, with the exception that they are a very minor component in seed hairs such as cotton (Tampa and Triplett 1993; Komuraiah *et al.* 2014). The most striking attribute of hemicelluloses from a structural standpoint, in comparison to cellulose, is their somewhat irregular nature (Scheller and Ulvskov 2010). Their side groups tend to discourage the formation of crystalline domains within hemicelluloses, and as a consequence hemicelluloses tend to act as an adhesive or as a "matrix polymer" rather than providing structural rigidity to wood or paper. One of the consequences of the non-crystalline nature is that hemicelluloses can be expected to offer greater availability for interaction with adjacent molecules. For instance, it is known that hemicelluloses are largely responsible for the tendency of cellulosic materials to swell in water (Laine and Stenius 1997). Accordingly, the wettability of cellulosic materials by water tends to be decreased when hemicellulose is removed (Hosseinaei *et al.* 2011).

A characteristic functional group that is quite common in hemicellulose, depending on its source and also its subsequent processing, is the carboxylic acid group, –COOH, or its corresponding carboxylate form, *e.g.* $–COO^- Na^+$, which is present when the pH is near to or above the midpoint pH for its dissociation (the pK_a value). According to Laine *et al.* (1996), the pKa value of carboxylic acid groups on hemicelluloses is about 3.3. The charged form ($–COO^- Na^+$), which is fully expressed at about two pH units above the p*K*a value, is especially interesting as a contribution to electrostatic attractions and repulsions. Despite the strength of such interactions and their importance in such fields as biology and the manufacture of paper (Hubbe 2006), such interactions are often overlooked in research work aimed at understanding the wettability and adhesion. The reason appears to be that researchers are often particularly interested in adhesion to solids that do not contain significant levels of ionic species, and in any case, many situations of high interest to industrial clients in the past have involved non-aqueous systems where the ionic forms are not stabilized.

Lignin

Lignin is a glassy, irregularly structured, highly aromatic polymer that serves as an additional matrix material in cellulosic materials such as wood and grasses (Lu *et al.* 2013; Norgren and Edlund 2014). The lignin in different plant materials can have markedly different proportions of three kinds of monomeric groups – guaiacyl, syringyl, and *p*-hydroxyphenyl – within the lignin structure, which is itself bonded by a seemingly random arrangement of ester, ether, –C-C–, and other connections among the monomer units.

From the standpoint of surface interactions it is notable that the ratio of oxygen to carbon in softwood kraft lignin can be estimated as about 0.44 (Dodd *et al.* 2014), which is much lower than the value of 1.11 in the case of pure cellulose (based on a molecular formula of ($C_6H_{10}O_5$)). Hollertz *et al.* (2013) reported an O/C ratio of 0.41 based on surface analysis of a spin-coated lignin sample. It follows that native lignin can be expected to be much more hydrophobic in comparison to cellulose and hemicellulose. Lee and Luner (1972) evaluated the wetting properties of six different lignin preparations and found them all to be similar; this result was tentatively attributed to the likely presence of adsorbed moisture on the materials under ambient conditions.

The delocalization of electrons within the aromatic rings of lignin can give rise to a somewhat higher Hamaker constants (Shen and Rosenholm 1998; Hollertz *et al.* 2013), meaning that the London dispersion component of van der Waals forces will be somewhat higher in comparison to the other chemical components present in wood (Shen 2009). However, such effects can sometimes be outweighed by the higher density of cellulose within crystalline regions (Hollertz *et al.* 2013). The other functional group that is worth emphasizing in lignin is the free phenolic group, which is present, for instance, at a level of 0.6 to 0.9 mmoles per gram of lignin in *Eucalytpus globulus* wood (Guerra *et al.* 2008). The phenolic group is a very weak acid, having a pK_a value near to 10.5 in the case of lignin materials (Norgren and Lindström 2000).

Evidence of lignin's importance relative to the wettability of wood comes from observations of the effects of weathering. Weathered wood tends to become depleted of lignin near to its surface, which is attributable to photodegradation of the aromatic structures. Indeed, the depletion of lignin in the surface layers of wood exposed to outdoor sunlight has been shown to result in increased wettability by water (Kalnins and Feist 1993; Huang *et al.* 2012b). Weathering also can be expected to cause other changes, some of them associated with chemical decomposition, evaporation of low-mass compounds, and solubilization of some hydrophilic compounds, *etc*.

Contamination

Because of the multicomponent character of typical cellulose-related materials, especially in their raw form, the word "contamination" should be understood to include minor ingredients of the biomass itself, such as fatty acids, resin acids, triglyceride fats, and other such extractable compounds (Chen 1970; Collett 1972; Wålinder and Gardner

2000; Petrič and Oven 2015). According to Petrič and Oven (2015), levels of extractives in the range of 2 to 5% are common for wood grown in temperate zones, whereas an extractives level of 20% can be found in tropical woods. Santoni and Pizzo (2011) reported that softwoods generally have higher contact angles than hardwoods, and they attributed this difference to the higher level of extractives, and also the presence of the hydrophobic resin acids in the softwoods. As was noted by Collett (1972), it takes only a monomolecular layer of contamination to completely change the wettability characteristics of a surface, and woody material is loaded with potential contaminants.

Various researchers have reported substantial changes in wettability characteristics because of the presence of trace ingredients in a solid (de Gennes 1985; Piao *et al.* 2010). Even a material as seemingly simple as paraffin wax can show large differences in contact angle caused by minor components. For instance, when ordinary wax is cooled from a melt in contact with water, the resulting surface has been found to have a much greater hydrophilic character relative to cooling it in contact with air (Adam and Jessop 1925). Wood extractives will also have a preferential molecular orientation depending on the environmental conditions to which the wood is exposed (Gardner *et al*. 1996; Carpenter 1999).

Sodium hydroxide is regarded as an effective wetting liquid for wood surfaces (Hse 1972; Wellons 1980; Casilla *et al.* 1981); a likely explanation is that the NaOH is able to convert some of the fatty acids, resin acids, and esters into saponified, ionically charged forms that have a higher affinity for water.

In addition to affecting the wettability of cellulosic surfaces, the various extractable materials also can be expected to contaminate the probe liquids that are employed in an effort to evaluate contact angles. For instance, Wålinder and Johansson (2001) found that the types of probe liquids used for evaluation of surface free energy attributes tend to be highly susceptible to changes in interfacial tension when wood extractives become dissolved in them.

Though water is usually not regarded as a contaminant, at least not by technologists who routinely deal with cellulosic materials under ambient conditions, it is important to bear in mind that even a film of moisture can lead to huge changes in wettability characteristics of certain high-energy surfaces. As noted by de Gennes (1985), dry metallic surfaces can have free energies in the range of hundreds of mNm^{-2}. Such values fall to about 60 mNm^{-2}, *i.e.* below the surface tension of pure water, after moistening with water.

Additives

Chemicals that are added during the processing of cellulosic materials, including those that enter the process on account of recycling of materials, also can be regarded as contaminants. For example, Ayrilmis (2011) showed that addition of certain fire retardants tended to increase the water-wettability of wood-plastic composite panels. Given the increasing importance of recycling of cellulosic materials – especially in the case of paper – one can expect there to be increasing challenges related to predicting the composition of such raw materials used in manufacturing.

Migration

In many cases it has been found that the wettability properties of cellulosic surfaces can change as a function of time (Herczeg 1965; Nguyen and Johns 1979; Casilla *et al.* 1981; Gardner *et al.* 1991; Gray 1992; Nussbaum 1999; Wålinder and Ström 2001; Wålinder 2002; Gindl *et al.* 2004; Englund *et al.* 2009; Tang *et al.* 2012). In most of the cited cases the cellulosic surfaces became less wettable by water with the passage of time. A similar effect has been observed when wood samples are subjected to heating (Jennings *et al.* 2006; Unsal *et al.* 2011; Huang *et al.* 2012a; Kutnar *et al.* 2012) or densification of the woody material (Jennings *et al*. 2006; Unsal *et al.* 2011; Kutnar *et al.* 2012). Such observations have often been attributed to the migration of oleophilic monomeric compounds to the solid surface (Swanson and Cordingly 1959; Gray 1992; Nussbaum 1999; Wålinder 2002; Piao *et al.* 2010). Evidence of such migration can be obtained by surface-sensitive analytical methods such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Liptáková *et al.* 1994; Englund *et al.* 2009). For instance, Englund *et al.* (2009) found that the ratio of oxygen to carbon atoms at the outermost surfaces of wood tended to decrease with the passage of time after freshly cutting a piece of wood. Huang *et al.* (2012b) likewise reported an inverse proportionality between the O/C ratio and the contact angle of water droplets on wood. Gunnells *et al.* (1994) found evidence that the migration of hydrophobic substances to the wood surface is facilitated if the material is heated above the glass transition temperatures of such substances. Since the migration of hydrophobic compounds to the surface of cellulosic material can be accelerated by heating, it makes sense that drying and heat-treatment processes generally tend to increase the hydrophobic character of wood (Gerardin *et al.* 2007; Wang *et al.* 2007; Kutnar *et al.* 2012).

Oxidation

Another time-dependent factor is the state of oxidation of cellulosic surfaces. It is well known that the water-wettability, as well as the gluability of cellulosic surfaces, can be increased by oxidative treatments (Back 1991; Lai *et al.* 2013). For example, plasma treatment can be used to increase the content of polar oxygen-containing functional groups at a surface (Podgorski *et al.* 2000; Deshmukh and Bhat 2003; Bhat *et al.* 2011; Peršin *et al.* 2012; Tang *et al.* 2012). When such treatments are carried out in air, the term corona discharge is often used (Podgorski *et al.* 2000). Since plasma treatments often give rise to transient, high-energy species at a surface, the induced changes in wettability may rapidly revert in the direction of the untreated material with further passage of time (Tang *et al.* 2012). Alternatively, selective oxidation of the C6 groups of cellulose by means of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) has also been found to increase water-wettability (Lai *et al.* 2013). Payne *et al.* (2001) found that certain kiln-drying practices tended to make the wood subsequently more prone to development of increased wettability by water. Winfield *et al.* (2001) showed that flame ionization can be used to increase the water-wettability of wood, thus increasing the performance of water-based adhesives.

Hydrophobic modifications

As discussed in recent review articles (Wang and Piao 2011; Petrič 2013; Hubbe *et al.* 2015), there have been many studies dealing with the hydrophobic modification of cellulosic surfaces. One of the prime goals has been to increase compatibility and adhesion of cellulosic reinforcing elements with various plastic matrix materials, for the manufacture of composites (Wålinder and Gardner 2002a; Tze *et al.* 2006; Heng *et al.* 2007; Mei *et al.* 2013; Li 2014a). The impact of such treatments on the wettability behavior of the cellulosic materials has been widely reported (Toussaint and Luner 1993; Erbil 1997; Cantero *et al.* 2003; Kannangara *et al.* 2006; Černe *et al.* 2008; Mohammed-Ziegler *et al.* 2008; Bhat *et al.* 2011; Payne *et al.* 2012; Samyn 2013; Li 2014a). Also, hydrophobic treatments are widely used in the manufacture of paper (Hubbe 2007; Lindström and Larsson 2008).

Superhydrophobic modifications

There has been much interest recently in certain treatments that can render a surface very highly resistant to wetting, *i.e.* superhydrophobic modifications. A superhydrophobic surface can be defined as one on which a water droplet exhibits an angle of contact greater than 150 degrees and a sliding angle of less than ten degrees (Song and Rojas 2013). For reasons that will be explained later in this article (Cassie and Baxter 1944), such treatments typically involve a combination of low (or very low) free energy of the surface layer, combined with a very high level of nano-scale roughness. Superhydrophobic treatments of cellulosic surfaces have been reported (Mahlberg *et al.* 1998; Piao *et al.* 2010; Samyn 2013; Song and Rojas 2013).

Morphology of Cellulosic Surfaces

To provide a context for discussions later in this article, this section will briefly review some of what is known about the roughness or porous nature of some common types of cellulosic surfaces – with emphasis on wood, paper, and regenerated cellulose films and fibers. As will be discussed later, morphological aspects can play a decisive role in the wettability of surfaces (de Gennes 1985). In particular, it will be noted that the dimensions of surface features of cellulosic materials may be expected to influence whether or not an advancing liquid front will be able to proceed without interruptions, *i.e.* "stick-slip" effects. Since cellulose itself constitutes an essential part of each of these kinds of materials or products, the morphological aspects of pure cellulose will be considered first.

Cellulose

The cellulose macromolecule has a strong tendency to arrange itself into elongated crystals (Kadla and Gilbert 2000; Xu *et al.* 2013). Common cellulosic materials have crystalline contents in the range of about 26 to 80%. As is the case with many man-made polymers, cellulose typically comprises alternating crystalline and somewhat disordered regions (Schurz and Lenz 1994; Dufresne 2012). The latter, which are sometimes called "amorphous regions" are mainly responsible for the ability of pure cellulose to absorb water and swell. According to Nishiyama *et al.* (2003), these disordered zones are quite limited in extent – perhaps involving only about 4 to 5 contiguous anhydro-glucose units of the polymer chains. There is also reason to suspect that amorphous regions constitute the boundaries between cellulose nanocrystals (CNC) having dimensions in the range of about 3 to 30 nm thickness and length from tens to hundreds of nm, *i.e.* the dimensions of CNC particles that can be obtained by hydrolysis of cellulose using strong acid (Elazzouzi-Hafraoui *et al.* 2008; Eichhorn 2011). Also, according to Driemeier and Bragatto (2013) there is a strong correlation between the width of cellulose crystallites in plant material and the amount of water that can be taken up. In general, thinner crystallites give rise to more disordered area within the structure, allowing for more associations with water.

Wood

The morphological situation is much more complex when one considers wood, which is porous across multiple ranges of dimensions (Bryne and Wålinder 2010; Piao *et al.* 2010; Petrič and Oven 2015). On the microscopic scale, wood has an extensive network of lumen spaces, which are connected by pit openings between adjacent fibers. The lumen openings, which run the lengths of tracheids and fibres, allow substantial permeability in the longitudinal direction of wood. Piao *et al.* (2010) gave a range of 5 to 170 μm for pit openings in a variety of wood species. In the case of hardwoods, the main conduit for fluid transport up the truck of the tree is by means of multi-cellular vessels (Gardner *et al.* 1991; Cheng and Sun 2006), which have diameters in a range of about 20 to 350 μm, depending on the species and other factors (Huber and Schmidt 1936; Piao *et al.* 2010). The permeability of wood via these passages varies greatly with different wood species, different seasons of growth, and also as a consequence of the aging of wood layers, *e.g.* sapwood *vs.* heartwood (Flynn 1995; Nasroun and Al-Shahrani 1998; Taylor *et al.* 2002). For instance, in some species the pit openings between tracheids become blocked as a natural course of growth and maturation of a softwood tree (Panek *et al.* 2013). In hardwoods the vessels may become occluded either by tyloses or by deposition of gums (Bonsen 1991; Sorz and Hietz 2006). To supplement the longitudinal transport of aqueous solution, wood species also have ray cells that allow passage of liquid in a radial direction (Kitin *et al.* 2009). Notably, such radial connections are absent in bamboo, which is not wood but a member of the grass family (Lucas 2013). Studies have shown that occluded passages within wood can be reopened to some extent by microwave treatment (He *et al.* 2014; Wang *et al.* 2014a) or by enzymatic decay (Lehringer *et al.* 2010; Panek *et al.* 2013). Also, the flow of various liquids through wood with constant pressure has been found to decrease with time (Anderson *et al.* 1941), and effect that might be attributable to swelling (Heng *et al.* 2007; Li 2014b) or because of plugging of the channels with debris (Hubbe *et al.* 2009).

On the nano scale, the cell walls of natural wood are relatively impervious to the flow of water, especially in comparison to the kraft fibers that will be discussed later (Petty and Palin 1983). This is because the cellulose within a cell wall is embedded in a dense matrix of hemicellulose and lignin. The hemicellulose is subject to swelling in response to moisture, but the extent of such swelling is constrained by the stiffness of the adjacent cellulose and lignin.

As one might expect, the surface of a wooden object depends on the manner of cutting or machining it (Sinn *et al.* 2009). First, one can expect strong differences depending on whether the end grain, the transverse, or the radial surface is exposed (Dunisch 2013). Void spaces associated with fiber lumens and with vessels will be presented in different orientations on different cut faces of wood. The roughness of wooden surfaces can be greatly reduced by such processes as planing and sanding. The morphology also can be influenced by chemical processes. For instance, Hosseinaei *et al.* (2011) showed that tiny droplets of lignin can become redeposited onto wood surfaces after certain extraction procedures. As will be shown later, the resulting heterogeneity and texture of a wood surface, at a nano-scale level, can be expected to inhibit water-wettability in many cases.

Paper

A typical paper surface is profoundly porous. On the microscopic scale there are spaces between the fibers that make up the paper sheet. An initial estimate of the maximum size of such openings might be made based on the diameters of typical fibers. Piao *et al.* (2010) listed hardwood fiber widths in the range 10 to 30 μm and softwood tracheid widths in the range 17 to 60 μm. Yamauchi and Murakami (2002) found a modal pore size of 5 μm and a range of pore sizes between 0.1 and 20 μm in handsheets prepared from unrefined pulp fibers. However, the spaces among fibers in a sheet of paper will be greatly affected by the degree of refining of fibers before forming the sheet. Application of relatively large amounts of energy during the mechanical refining of fiber can reduce the typical pore sizes markedly. For instance, Corte (1982) reported that sheets made from unrefined pulp having a Schopper Riegler refining degree of 24 °SR had a modal pore size of about 1.5 μm. This was reduced to about 1 μm after refining to 64 °SR and to 0.5 μm after refining to 87 °SR. Likewise, Villar *et al.* (2009) showed that the Gurley Densometer porosity of the resulting paper was increased from about 3 to 20 seconds (per 100 cm^3) when bast fibers were refined; but values as high as 100 s were obtained for paper comprised of 100% core fiber, which is finer and more compliant. The transformation can be attributed to the increased conformability of the cell walls, which is brought about by delamination within the water-swollen cellulosic structure. Nano-scale delamination within the cell wall allows the fibers to collapse into compliant ribbons, which can drape over one another and more effectively resist the passage of air through paper. The reduced porosity of paper resulting from refining also can be partly attributed to generation of cellulosic fines, which tend to fill in the spaces among the fibers of paper. Bristow (1986) found that the modal pore size within laboratory-formed paper sheets could be reduced from 1 μm, in the case of unfilled paper, to either 0.5 or 0.25 μm in the case of talc filler addition, depending on the particle size of the talc.

The roughness of typical uncoated paper and paperboard surfaces, when evaluated by profilometry (Alam *et al.* 2012), were found to be within the range of 3 to 5 μm. Lower values were found in the case of coated samples. At the rough end of this range are course paperboard products and filter paper. Similarly, Eriksen *et al.* (2007) measured average roughness values in the range of 2 to 5 μm on paper handsheets prepared with thermomechanical pulp fibers blended with different types and amounts of chemical pulp fibers. These values can be generally attributed to the dimensions of the fibers in the paper, as well as in their conformability. Piao *et al.* (2010) estimated that a 1 mm droplet placed on the surface of paper will cross about 33 to 100 hardwood fibers, or 17 to 58 softwood tracheids. The smoothness of paper surfaces is profoundly affected by calendering operations in which the sheet is passed through the nips between smooth rolls at high pressure.

The nano-scale porosity of chemically pulped cellulosic fibers can be very much different from that of wood fibers. Never-dried kraft fibers, for instance, are known to be suffused with pores having their least dimensions within the range of about 2 to 100 nm, depending on the materials, as well as on the means of measurement and the assumptions used in interpretation of the results (Stone and Scallan 1968a; Li *et al.* 1993; Alince and van de Ven 1997; Alince 2002). The presence of pores or gel structures smaller than 10 nm in water-wet kraft pulp fiber walls is also supported by the results of streaming potential measurements carried out at different salt concentrations (Hubbe *et al.* 2007). The surfaces of cellulosic fibers used in papermaking can be profoundly affected by the procedures employed during preparation of the pulp. For instance, Stone and Scallan (1968b) and Berthold and Salmén (1997) observed a progressive increase in the typical size of pores within spruce wood fibers in the course of kraft or sulfite pulping; the effects were attributed to the progressive removal of lignin. The drying of a sheet of paper results in semi-irreversible closure of a portion of its pores (Stone and Scallan 1966). In the cited work, the surface area of the never-dried kraft fibers was found to be about 93 m^2/g, and this value fell to about 1 m^2/g when paper was dried.

Textile fibers

Cellulose-based textile fibers come in a wide variety of forms, ranging from continuous filaments of regenerated cellulose (see next) to cotton, flax, and hemp. As shown by Bismarck *et al.* (2002), flax fibers exhibit fine-scale ridges, with a period of about 1 μm. Natural cotton surfaces are known to be somewhat hydrophobic, and this has been attributed to the presence of waxes (Choi and Cloud 1992; Buchert *et al.* 2001). Various treatments of natural fibers can be employed to remove such waxes, and their removal generally results in a rougher exposed surface (Kalia *et al.* 2009). Diameters of filaments and spun fibers used in textile manufacture are typically in the range of 0.1 to 30 μm, and these are typically spun into much larger threads and yarns (Chattopadhyay 2010). It follows that textile fabrics tend to be quite rough relative to the scale of a droplet of water placed on their surface.

Regenerated cellulose

Relatively pure films and fibers of regenerated cellulose, *i.e.* Cellophane,® lyocell, Rayon®, and similar products can be prepared by controlled precipitation from specialized solutions such as cellulose xanthate (viscose process) or n-methylmorpholine oxide (lyocell process) (Schurz and Lenz 1994). Remarkably, even when such transformations are brought about at industrial speeds, the resulting crystallinity is typically in the range of about 40 to 80% (Colom and Carrillo 2002). Regenerated cellulose fibers are usually in a range of 10 to 20 μm in diameter, although coarser fibers, such as 60 μm, are also available (Hearle 2001). Multi-lobed cross-sections are typical, such that there can be deep grooves along the lengths of regenerated cellulose fibers (Hearle 2001). Analysis following water-equilibration of regenerated cellulose revealed a relatively high specific surface area of 26 to 240 m^2/g, depending on the subsequent drying method (Lee *et al.* 1983); these results suggest that there can be substantial amorphous character of such materials, allowing them to swell. As shown by Kontturi *et al.* (2006), it is possible to prepare ultra-thin films of regenerated cellulose by means such as a “spin-coating” method. The resulting films were found to have a relative roughness of 10%, which translates to about 2 nm variations as measured by profilometry.

Nanocellulose films

In recent years there has been great interest in cellulosic nanomaterials, including cellulose nanocrystals (Elazzouzi-Hafraoui *et al.* 2008). Because of the small dimensions of such materials, there is potential to prepare films that are very smooth, at least based on profilometric measurements (Edgar and Gray 2003; Rodionova *et al.* 2012). Rodionova *et al.* (2012) observed roughness levels in the range of about 0.2 to 2 μm in the case of cast films of cellulose nanocrystals. Roughness has been observed to have profound influence on contact angles of water on conventional cellulosic surfaces (Wålinder and Gardner 2002b; Kannangara and Shen 2008; Samyn 2013). Dankovich and Gray (2011) found that contact angle measurements on cast films of cellulose nanocrystals exhibited unusually low levels of hysteresis, as defined by the difference between advancing and receding contact angles. An advancing contact angle can be defined as the angle obtained when the static liquid front has recently been moving forward sufficiently to yield a maximum value (when the angle is measured through the probe liquid). By contrast, the receding contact angle is the corresponding static value when the liquid front recently has been moving back from the previously wetted area, sufficient to give a minimum value. Presumably, the low extent of hysteresis effects can be attributed to the low scale of the roughness.

MECHANISTIC INTERPRETATION OF CONTACT ANGLES

Chemical Aspects

In reviewing published work aimed at understanding the mechanisms underlying contact angles and wettability, attention will be first directed towards explanations based on physical chemistry, and the fact that cellulosic surfaces are rough and porous will be temporarily set aside. In other words, studies will be considered in which the authors – either explicitly or by omission – treated the surfaces as if they were ideally flat and non-porous. General background is provided in earlier review articles (Fowkes 1964b; Good 1979; Kalnins 1987; Berg 1993; Etzler 2013).

Surface tensions of liquids

To understand the contact angles of liquids with solids, it is perhaps best to begin with an explanation of why surface tensions arise at the interface between a liquid and a gas phase (Lyklema 1999). As explained by Fowkes (1964a; 1965), surface tension is a natural consequence when there is an imbalance of forces at a fluid interface. Within the bulk phase of a pure liquid each molecule will experience molecular attractions with adjacent molecules on all sides. But right at the surface, a molecule will experience a void in one direction. This situation will cause molecules to be generally drawn into the interior of the liquid phase, until the surface layer becomes slightly depleted, and in a sense stretched. Thus the tension at the interface is necessary to balance the preference of molecules to diffuse into the interior of the liquid phase.

A corollary to the explanation just given is that the surface tension of a pure liquid is always a function of its cohesive energy density (van Oss *et al.* 1988a). To give an illustrative example, the very high surface tension of mercury metal in air can be attributed to its strong metallic bonding forces (Aqra and Ayyad 2011). Likewise, the relatively high surface tension of water can be attributed to its high density of hydrogen bonding capability (Ishiyama *et al.* 2012). Indeed, just by knowing the atoms and structures that make up a given liquid, it is possible to quite accurately estimate its surface tension (Stefanis *et al.* 2005; Gharagheizi *et al.* 2011; Roosta *et al.* 2012; Albahri and Alashwak 2013). The fact that reasonably good correlations are possible is consistent with the close relationship between surface tension and the sum of attractive forces within the condensed phase.

Lack of "dynamic" character in case of solids

The description given above to account for the surface tension of a liquid is based on an assumption of thermodynamic equilibrium. However, there is reason to doubt that such an assumption can be rightly applied to the case of a solid surface. In the first place, even if a solid surface has a surface tension, there is generally no way to directly measure it (Johnson 1959). Thus, in this article, the term "surface free energy" will be used to refer to an analogous quantity associated with a solid-vapor or solid-liquid interface. Secondly, there is no assurance, in the case of a solid, that the free energy of the surface has a uniform value from point to point, as is the case for a liquid. Indeed, any crystal defects would be expected to give rise to locally less favorable energy states (Bonzel 2001; Lasaga and Luttge 2004). And unlike a liquid, the surface molecules are not free, at any moment, to diffuse into the interior of the phase. Based on such considerations, the solid surface is not in true thermodynamic equilibrium, which is an inherent assumption in Gibbs' theory of surface free energy at interfaces (Gibbs 1961). Because of concerns of this type, it can be argued that experiments involving contact angles cannot provide complete information about the free energy of a solid surface (Shuttleworth 1950; Johnson 1959), and much of the related theoretical work needs to be regarded as a series of approximate models having no reliable means of calibration. This point will be brought up again later in this article when it comes time to judge the ability of different theoretical approaches to explain various sets of data.

Equating surface tension and free energy

If one makes the hypothesis that solid surfaces have a quantifiable value of surface free energy, then a variety of potentially useful calculations and estimates can be made, as will be discussed. It is reasonable to assume that the ability of a surface to become wetted by various fluids and ultimately to develop adhesive bonding with a variety of glues and resins depends on the excess free energy of its surface (Owens and Wendt 1969; Kaelble and Uy 1970; Jameson and del Cerro 1976; Fowkes *et al.* 1990; Good 1992; Della Volpe *et al.* 2004). In theory, the free energy associated with the surface is the amount of energy needed to create a unit area of interface in equilibrium with its vapor – for instance by changing the shape of the interface. But in the case of a solid material such changes cannot be brought about without causing structural damage, especially in the case of a highly crystalline, isotropic, solid cellulosic materials. There is just no realistic way to "keep everything else equal" while attempting such a change. The mechanical strength of a typical solid is so great relative to surface tension forces that there is no way to independently evaluate something like a surface tension of a solid. It follows that all attempts to evaluate the surface free energy of cellulosic surfaces must necessarily be indirect – sensing how the surface interacts either with liquids (contact angle methods) or gaseous components (inverse gas chromatography and related methods). The practical details of such methods will be considered only after dealing with some basic concepts.

The Young equation

In 1805, which happens to be the same year that the first major hydrophobic sizing system for papermaking was first announced (Illig 1805), Young made a bold proposal: He proposed that the contact angle of a pure liquid on a smooth, uniform solid surface would be related to a balance between three force vectors at the three-phase line of contact (Young 1805). The equation can be expressed in the following form,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \qquad (1)$$

where γ_{SV} is the interfacial tension at the solid-vapor boundary, γ_{SL} is the interfacial tension at the solid-liquid boundary, and γ_{LV} is the well-known surface tension of the liquid, in the presence of its own vapor in the gas phase. As discussed by Johnson (1959), Eq. 1 appears to be valid for a wide range of situations, as long as one bears in mind that the quantities γ_{SV} and γ_{SL} should not be assumed to necessarily equal the free energy associated with those interfaces (Shuttleworth 1950).

Later in this article a “film pressure” term will be added to Eq. 1 to deal with uncertainties in the effects related to molecular adsorption onto the solids. However, the main approach to be used here assumes that such effects are adequately represented by the term γ_{SV}, *i.e.* the surface tension term for a surface in equilibrium with the vapors of the probe liquid. In other words, if there is a film pressure attributable to adsorbed molecules on the solid, then the effects of such molecules are assumed usually to already be included in Eq. 1.

Some researchers have criticized the Young equation for its failure to take into account some other contributions to free energy, such as the “line tension” associated with the location of meeting between the three phases (Jameson and del Cerro 1976). Wang *et al.* (2014b) proposed a general equation in which line tension was incorporated into the Young equation in a consistent manner. However, other studies have shown that line tension, which can be attributed to torsion in the vicinity of the three-phase contact line, has a negligible effect on contact angles in typical cases (Marmur 2006). White (1977) and de Gennes (1985) showed that Young’s equation is valid when applied in a macroscopic sense, such that the contact angle is evaluated far enough from the three-phase line of contact so that one is beyond the range of influence of, for instance, London dispersion forces and electrostatic double layer effects (Adamson and Gast 1997). Starting with Dupré (1869), many investigators have made a further assumption that each of the three force vectors defined by Young can be identified with the free energies associated with the three kinds of interfaces at the contact line (Owens and Wendt 1969; Kaelble 1970; Kaelble and Uy 1970; Fowkes *et al.* 1990; Good 1992).

The equation of Good and Girifalco

The fact that the quantities γ_{SV} and γ_{SL} cannot be measured directly has not prevented researchers from attempting to estimate these quantities. One of the most important models, in this regard, was proposed by Girifalco and Good (Girifalco and Good 1957; Good and Girifalco 1960). They proposed the following relationship,

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\Phi\ [\gamma_{SV} \times \gamma_{LV}]^{0.5} \qquad (2)$$

where the new term Φ is an interaction parameter, expressing the degree to which the forces acting within each of the two phases also are able to act between the phases at the interface. For instance, let us suppose that the two phases are identical in composition, such that Φ equals 1; in that case it is easy to show that the right side of the equation sums to zero, as one might intuitively expect. By contrast, if the two phases are rather incompatible with each other, then the value of Φ will be relatively low; it follows that the interfacial tension in the solid-liquid boundary is predicted to be relatively high. The seeming reasonableness of Eq. 2 provides some encouragement for further investigation of force contributions to the interactions at interfaces.

Criteria for a successful model

Before considering various approaches to estimating contributions to the work of adhesion at interfaces, as a means of accounting for contact angles, it is worth reviewing some criteria of what to expect in a successful model, with particular focus on models that can be usefully applied for characterization and understanding of cellulosic surfaces. Such criteria are spelled out in Table 1.

Table 1. Criteria by Which to Judge the Success of a Model to Account for the Surface Tensions and Contact Angles Associated with Wetting

The model is self-consistent and doesn't contradict itself or physical laws.
Results do not depend on an arbitrary choice of probe liquids.
Results are physically reasonable: A: The dispersion component does not *exceed* that of an equivalent liquid. B: The *total* surface free energy is not *less* than that of an equivalent liquid.

With respect to item "A" in Table 1, data compiled by Fowkes *et al*. (1990) suggest that the chemical groups associated with typical cellulosic materials are consistent with dispersion force components of surface free energies in the range of about 20 to 35 mJ/m^2. With respect to item "B", a wide assortment of surface tension data have been compiled by Roosta *et al.* (2012). These values will be considered later in this article when discussing different systems of interpretation of contact angle data.

Critical surface tension

One of the most important advances in accounting for contact angles based on energy concepts was contributed by Zisman and collaborators (Fox and Zisman 1950; Fox *et al.* 1955). They defined a critical surface tension based on a series of tests in which probe liquids having different surface tensions (γ_{lv}) were placed on a solid surface of interest. The value of critical surface tension γ_c is the highest value of surface tension of a hypothetical liquid that will still wet the surface. It should be noted that values of γ_{lv} can be easily measured with a du Nouy tensiometer (Harkins and Jordan 1930) or a Wilhelmy plate instrument (Wilhelmy 1863). Some data from Fox and Zisman (1950) are replotted in Fig. 1 to illustrate the method. As shown, the authors draw a linear regression line through $\cos\theta$ values as a function of γ_{lv}.

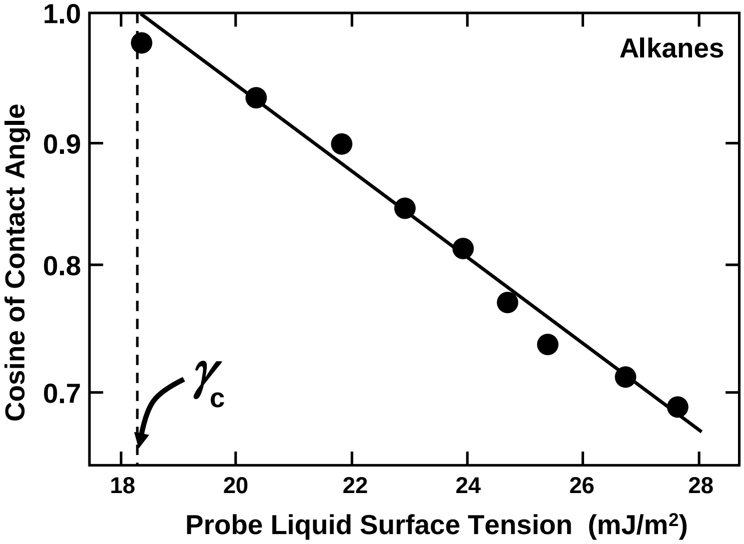


Fig. 1. Plot of the cosine of contact angle *vs.* the fluid-vapor surface tension of a series of alkane test liquids placed on a smooth fluorochemical solid surface, illustrating how extrapolation can be used to define the value of critical surface tension. Data replotted from Fox and Zisman (1950).

By extrapolating the regression line to the point where $\cos\theta$ is equal to 1 (implying that θ is equal to zero or "perfect wetting"), one can determine the value of γ_c, the critical surface tension. Although more sophisticated approaches have been developed subsequently, Zisman's system of obtaining γ_c values remains widely used, possibly on account of its simplicity and its ability to characterize surfaces in terms of a single value.

Although critical surface tension values have been used in industry for many years, it is widely appreciated that values of γ_c should be regarded as a low estimate of the true surface free energy (Piao *et al.* 2010). One reason for this is that the selection of probe liquids is somewhat arbitrary; there is no assurance that the set of probe liquids employed will embody all of the components of interaction that are expressed by the solid material of interest. To give an illustrative example, Shafrin and Zisman (1967) used a series of alkane probe liquids to determine the critical surface tension of pure water; their obtained value of 22 mJ/m^2 was far below water's known surface tension of about 72 mJ/m^2. The explanation is that none of the probe liquids that were employed had hydrogen bonding capability; thus they were blind to that contribution to water's surface tension. On a more practical level, Zhu *et al.* (2010) noted cases in which values of $\cos\theta$ failed to fall on a line as a function of surface tension of probe liquids. A poor regression fit leads to doubt about how precisely the values of γ_c can be defined in practice.

Some odd effects can be obtained if one attempts to evaluate critical surface tensions or related phenomena by means of impure probe liquids, for instance in cases where the probe liquids become contaminated by the surface that is under study. Such impurities can cause a spreading liquid to actually retract, following the adsorption of a lower-surface tension component onto the surface (Fox *et al.* 1955). In addition, detailed studies have shown that very thin “precursor films” will often precede the wetting liquid (de Gennes 1985; Good 1992; Leger and Joanny 1992; Decker *et al.* 1999).

Work of adhesion estimates from contact angles

When one separates two condensed phases, forming two surfaces in contact with air or vapor, one needs to add energy (work) into the system. The amount of energy, per unit area, can be defined as the work of adhesion. According to Dupré (1869) the work of adhesion between a probe liquid and a solid can be defined as follows:

$$W_{\text{adhesion}} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (3)$$

One of the fascinating aspects of Eq. 3 is that two of the variables, γ_{SV} and γ_{SL}, cannot be directly measured. Surface tensions at liquid-liquid or liquid-vapor phase boundaries can be measured by various means, including use of spinning-drop, Wilhelmy plane, and drop mass methods (Joseph *et al.* 1992; Lee *et al.* 2008). However, at a solid surface the strength and elasticity of the material precludes evaluation of any capillary contribution to stretching or contraction of the surface. The fact that the equation has two unknowns would seem to pose a severe challenge to those attempting a definitive analysis. Readers are urged to keep in mind the fact that neither term can be compared to a known standard. Later in this article it will be shown that many attempts to fit contact angle to various theoretical models have resulted in severe inconsistencies, and it seems likely that many such problems can be traced all the way back to whether or not Eq. 3 can be regarded as valid and meaningful.

Though it has not been convincingly shown that γ_{SV} and γ_{SL} truly exist as separate quantities, their difference ($\gamma_{SV} - \gamma_{SL}$) can be evaluated by means of contact angles, subject to some simplifying assumptions (Adam and Jessop 1925). According to these authors, Pockels in 1914 may have been the first to point out that the relationship shown in Eq. 3 could be combined with the Young equation (Eq. 1) to yield the Young-Dupré equation:

$$W_{\text{adhesion}} = \gamma_{LV}\,(1 + \cos\theta) \qquad (4)$$

This equation is widely used to predict the effectiveness of adhesives, especially those that rely upon physical attractions with the solid surfaces. In fact, Fowkes *et al.* (1990) urged their readers to regard W_{adhesion} values as being much more theoretically sound and useful quantities than any known system of estimating components of surface free energy. Again, it should be kept in mind that the value of W_{adhesion} is not the same thing as either the surface tension of the solid or its surface free energy (Rosenholm 2010). This makes intuitive sense because, as shown in Eq. 4, the definition of W_{adhesion} does not require the evaluation of either of the unmeasurable quantities, γ_{SV} or γ_{SL}. The work of adhesion is also capable of direct measurement (Fröberg *et al.* 1999).

A possible source of error when applying Eq. 4 is that a solid surface to be tested in practical cases is not necessarily at equilibrium with the vapor of the probe liquid. To deal with such situations it is possible to express Eq. 4 in a more extended form as,

$$W_{\text{adhesion}} = \gamma_{S} + \pi + \gamma_{LV} - \gamma_{SL} \qquad (5)$$

where π is the spreading pressure exerted by an adsorbed film of vapor-derived molecules on the surface. Although this term is often set to zero in theoretical work, it is possible to envision many situations where such a term might be important during processing of cellulosic materials in various applications.

Liquids that can cause swelling of cellulosic material also may be expected to give rise to deviations from Eq. 5 and other relationships based on a two-dimensional analysis of wetting phenomena. Aqueous liquids, and some other liquids, clearly can interact with cellulose in three dimensions, *e.g.* as shown by swelling effects, but such interactions have not been incorporated into models that can account for static contact angles.

Possible Contributing Factors that Make Up the Surface Free Energy

In an effort to shed light upon the concept of surface free energy, the subsections that follow will consider a variety of components that possibly contribute to the free energy of solid and liquid surfaces (van Oss *et al.* 1988a,b). Contributions to be considered will include van de Waals forces, acid-base interactions, and hydrogen bonding, among others. In other words, it has been widely assumed that several physical chemical principles may work together to comprise the net free energy of a surface of interest. A question to bear in mind while considering various published concepts in this area is whether or not some of these suggested contributions are truly independent of each other or whether they overlap. Another question to consider is whether it is possible to come up with a sufficiently complete set of contributions so as to avoid the kind of underestimation observed by Shafrin and Zisman (1967) when using alkane probe liquids to estimate the critical surface tension of water.

Table 2 provides a preliminary list of some different kinds of force that might reasonably be expected to contribute to both the cohesive energy density of pure phases and the interfacial tensions that arise at their boundaries.

Table 2. Listing of Possible Components of Surface Free Energy

Component forces	**Terms needed (& comment)**	**Key citations**
van der Waals forces		Van der Waals 1873
London/Lifshitz dispersion	1	London 1930; Lifshitz 1955
Keesom	1	Keesom 1915
Debye	1 (probably not significant)	Debye 1920
Lewis acid and base	2 (or more if hard & soft)	Gutmann *et al.* 1966
Hydrogen bonding	1 (or possibly 2)	Karger *et al.* 1976
Ionic charge interactions	? (hard to predict)	see: Hubbe 2006
Metallic bonding	1	Aqra and Ayyad 2011

Note: In general, a single term in the defining expression is sufficient in the case of force components that are inherently symmetrical. Two terms may be more appropriate if the interaction is inherently asymmetrical, as in the case where each solid and each probe liquid can have differing values of Lewis acidity and basicity (see later discussion).

Combining multiple contributions to surface free energy

Fowkes (1972) proposed that various kinds of forces can be summed up as quasi-independent contributions in an overall equation to more fully characterize the interactions at phase boundaries. Ideally, such a summation would include terms for the London/Lifshitz dispersion force, hydrogen bonding, acid-base interactions, dipole-dipole interactions, and induced dipole-dipole interactions. The main assumption here is that the different contributions to free energy need to be independent and non-overlapping.

As an initial step in the direction of this multi-component vision, Fowkes' basic equation, to predict the value of interfacial tension between a non-polar solid (phase 1) and a probe liquid (phase 2), can be expressed as follows (Fowkes 1964a),

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2[\gamma_1^d \gamma_2^d]^{0.5} \qquad (6)$$

where the subscripts refer to the two condensed (non-gaseous) phases, and the superscript "d" refers to the dispersion component of surface free energy. Combining Eq. 6 with the Young equation (Eq. 1) yields,

$$1 + \cos\theta = 2[\gamma_1^d \gamma_2^d]^{0.5}/\gamma_{LV} \qquad (7)$$

Equation 7 was demonstrated by its application to the interactions of water with a series of non-polar, immiscible liquids. Computed values of the dispersion component of free energy for the water surface were within a narrow range (21.8 ± 0.7 mJm^{-2}), which provides at least partial validation of the approach.

Owen and Wendt (1969) extended the approach of Fowkes to include a separate polar term,

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \qquad (8)$$

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \qquad (9)$$

where the superscript "p" indicates a polar energy component. If one combines these relations with the previous equation, one obtains (Piao *et al.* 2010),

$$1 + \cos\theta = 2(\gamma_{SV}^d)^{0.5} (\gamma_{LV}^d)^{0.5}/(2\gamma_{LV}) + 2(\gamma_{SV}^p)^{0.5} (\gamma_{LV}^p)^{0.5}/(2\gamma_{LV}) \qquad (10)$$

To use Eq. 10, one can choose probe liquids that are well suited for sensing each of the two aspects, *i.e.* the London/Lifshitz dispersion forces and the polar contributions. The dispersion forces will be considered first before considering the polar term in Eq. 10.

London/Lifshitz dispersion forces

There is widespread agreement in the literature that the London-Lifshitz dispersion component of van de Waals forces (London 1930; Lifshitz 1955) accounts for a large part of the cohesive energy density within common materials and liquids, and thus accounts for a major share of the surface tension values of liquids (Hamaker 1937; van Oss *et al.* 1988a; Bowen and Jenner 1995; Hansen 2007; Shen 2009). Though dispersion force interactions are weaker than, say, hydrogen bonds, they are ubiquitous, not depending very much on the concentrations of different chemical groups at surfaces. This helps to explain why dispersion forces typically account for a major share of the cohesive and adhesive energy within and between phases of common materials. As stated by van Oss *et al.* (1988a), the dispersion component of force can be calculated with a greater degree of confidence than any of the others to be considered. Estimates of the dispersion components of free energy for materials of interest to researchers in the field of cellulosic science have been tabulated (Visser 1972) and strategies for use of such information have been laid out (Bowen and Jenner 1995).

The contribution of dispersion forces to wettability and adhesion can be estimated by measuring the contact angles of non-polar liquids. In particular, di-iodomethane (DIM) has been recommended as a probe liquid (Fowkes *et al.* 1991) on account of its nonpolar nature, its high Hamaker constant (indicating a strong dispersion interaction), and the fact that its surface tension is higher than many polymeric materials of interest to technologists. The high surface tension of DIM means that it is possible, in many cases, to evaluate non-zero contact angles on a wide variety of surfaces and thereby to estimate the dispersion contribution to the work of adhesion. Also, the high surface tension of DIM means that its contact angle on common surfaces will be high enough so that it is not quickly absorbed into a porous material, such as paper (Lyne and Huang 1993).

Because dispersion forces arise owing to the random movements and momentary lining up of transient electrical dipoles within atom and molecules, all materials experience an attractive force towards each other because of dispersion forces. However, species that have loosely-held electrons in their outermost valence shells (such as DIM) experience stronger attractions. As already noted, the delocalized electrons present in aromatic groups, such as those of lignin, give rise to somewhat higher Hamaker constants (French *et al.* 2007), indicating a greater influence of dispersion forces. By contrast, the electrons associated with alkyl chains, such as those of fatty acids or their triglyceride fats in the extractives component of woody materials, have somewhat lower Hamaker constants (Visser 1972; Takenaga *et al.* 2008; Troncoso and Acosta 2015). Among common organic chemicals there appears to be a difference of a factor of two between those with the lowest Hamaker constants (*e.g.* paraffin wax) and those with the highest (aromatic-containing polyesters and polystyrene) (Visser 1972). If a cellulosic surface were to be chemically derivatized so that it is fully covered by fluorocarbon chains, then the Hamaker constant could be about 39 zJ (note: 1 zJ = 1 x 10^{-21} J), which is about 70% of the corresponding value for pure alkyl hydrocarbon chains (Takenaga *et al.* 2008). In summary, though the London dispersion forces associated with cellulosic surfaces can be affected by drastic chemical transformations, most cellulosic surfaces can be expected to have Hamaker constants within the range of about 44 to 63 zJ in air (Bergstrom *et al.* 1999; Shen 2009), representing moderate tendency to interact with probe materials by the dispersion mechanism. Whang and Gupta (2000) noted that whereas the polar component of free energy at a cellulosic surface can change drastically depending on treatments, it takes a relatively profound chemical transformation of the outermost surface to significantly change the dispersion component. For example, Jennings *et al.* (2006) found that hydrothermal treatment and densification of poplar wood increased the contact angle when using bromonaphthalene as a probe liquid. As will be discussed later, bromonaphthalene interacts with surfaces almost exclusively via London dispersion forces. The effects are consistent with a lower Hamaker constant of alkyl chains in comparison with polysaccharide materials.

Calculating the London/Lifshitz dispersion component of free energy

When computing the contribution of dispersion forces to the free energy of interaction it has been customary to employ the geometric mean approach, as was shown in Eq. 6. Such an approach has been used in some of the most definitive articles on the topic (Girifalco and Good 1957; Good and Girifalco 1960; Fowkes 1964a; Fortes 1981).

However, there has been some concern that such an approach may over-estimate the influence of higher-energy components in some cases (Shen 2009; Piao *et al.* 2010). Somewhat lower values of dispersion energy of interaction are obtained when using a harmonic mean approach to the calculation (Wu 1971, 1982; de Meijer *et al.* 2000). The choice of which equation is employed has been shown to have a large effect on the predictions (Gardner 1996; Gindl *et al.* 2001a; Černe *et al.* 2008). Nguyen and Johns (1978) found good agreement with data for both types of relationship, but they preferred the harmonic mean model for purposed of characterizing wood surfaces. The harmonic equation proposed by Wu (1971) can be expressed as (Piao *et al.* 2010),

$$\gamma_{LV}\,(1+\cos\theta) = [4(\gamma_{LV}{}^{d}\ \gamma_{LV}{}^{d})/(\gamma_{LV}{}^{d} + \gamma_{LV}{}^{d})] + [4(\gamma_{LV}{}^{p}\ \gamma_{LV}{}^{p})/(\gamma_{LV}{}^{p} + \gamma_{LV}{}^{p})] \qquad (11)$$

where the final bracketed term of the equation refers to polar contributions, which will be discussed next.

Adding a polar term

The dispersion component of interaction energy, as just discussed, concerns only the non-polar aspects of interactions between molecules at close range. But it is well known that fixed dipole moments in the molecules that make up a pure liquid give rise to greater surface tension. It follows that a polar term of some kind is needed to provide a more complete accounting of components of cohesive energy. The simplest models used to account for polar contributions make no distinction between compounds having significant hydrogen bonding ability *vs.* other polar compounds (Owens and Wendt 1969; Janczuk *et al.* 1983). Such approaches will be considered first.

Keesom forces

The name Keesom is associated with a contribution of permanent molecular dipole moments to their close-range attractions (Keesom 1915; Rosenholm 2010). Such forces, which are considered to be a type of van der Waals force, arise as a result of random correlation of alignments among the molecular dipoles. To visualize such forces, consider a bunch of very weak bar-magnets each bouncing back and forth on a frictionless billiard table. In such a case even though the kinetic energy of the system is too large to allow clustering of the magnets (which would represent freezing), the tendency to correlate alignments contributes to a net attraction (less net pressure of bouncing against the walls of the billiard table. Owens and Wendt (1969) referred to such forces as justification for adding a polar term in their relatively early analysis of contact angles. Likewise, Kaelble and Uy (1970) supposed that a polar term in their equation could include the effects attributable to hydrogen bonding. Karger *et al.* (1976) suggested that Keesom forces could at least partly account for the greater surface tensions and contact angles of liquids able to undergo hydrogen bonding. More recent research has aimed to quantify the effects of dipole moments based on molecular dynamic simulations (Eggebrecht *et al.* 1987a,b; Mecke *et al.* 2001; Sánchez-Arellano *et al.* 2012), as well as other computational approaches (Stockmayer 1941; Frodl and Deitrich 1993).

Though there is widespread agreement about the existence of Keesom forces, in most practical cases they appear to be more than an order of magnitude smaller than the dispersion component of forces just discussed (Rosenholm 2010). In general, when hydrogen bonding is neglected, stronger dipole moments of the molecules are predicted to lead to only slightly higher surface tensions of liquids. There appears to be a gap in research, however. There is a need for future research to consider a model in which hydrogen bonding interactions, because of their strong influence and unique character (Jeffrey 1997), are explicitly separated from other polar interactions for evaluation of surface energies and contact angles.

Acid and base components of free energy

Fresh insights into the interactions between liquids and solid surfaces have followed from a realization that Lewis acids and bases may pay a prominent role with respect to contact angles (Drago and Wayland 1965; Gutmann *et al.* 1966; Mayer *et al.* 1975; Drago *et al.* 1971, 1977; Fowkes 1983). In other words, certain chemical compounds – known as Lewis bases – have significant capability to contribute electron pairs in the formation of adducts, whereas other compounds – known as Lewis acids – have significant capability to accept the participation of such pairs from other molecules. One should note that this definition of acidity is quite different from the usual Brønsted system of acids and bases that prevails in aqueous systems, where H_3O^+ and OH^- are the dominant acidic and basic species. Fortunately, it is possible by spectrographic analyses to determine which kind of interaction is involved in specific cases (Fowkes *et al.* 1990; Auroux 2008). One of the most interesting aspects of acid-base theory is the fact that a given compound can have both acidic and basic character – often to different degrees – at the same time (Sun and Berg 2003). This is in contrast to the analysis of Keesom forces, including the molecular dynamics simulation of effects attributable to molecular dipoles, as mentioned earlier. A consequence of this potentially dual, but often asymmetric nature of chemical compounds, relative to Lewis acidity and basicity, is that (as was shown in Table 2) two separate terms are generally required to give a full description of the resulting interactive forces or energies.

Drago and coworkers (Drago and Wayland 1965; Drago *et al.* 1971; 1977) were the first to systematically investigate the Lewis acidity and basicity of a variety of compounds, as reflected in their heats of interaction with a reference compound. One of the key contributions of these authors was a concept of hard and soft acidity and basicity (Drago *et al.* 1971). Thus, the most effective interactions are predicted when a soft acid interacts with a soft base (meaning that the outermost electrons are rather loosely bound to the respective molecules), or alternatively when a hard acid interacts with a hard base. Acid and base parameters derived from such an analysis have been tabulated (Drago *et al.* 1987). Li *et al.* (2005) presented evidence that the softness of a certain crystal face was important relative to wetting interactions. While the concept of hard-soft-acid-base (HSAB) appears to be well accepted, an inherent drawback of such an approach is a lack of quantification. At present it appears that HSAB concepts are mainly being used for qualitative descriptions, and there is a need to extend HSAB analysis to include quantitative aspects.

An inherently simpler approach was proposed by Gutmann *et al.* (1966) and Mayer *et al.* (1975). These authors developed scales of Lewis acidity and basicity on the basis of heats of mixing of various solvents with antimony pentachloride or by chemical shifts in nuclear magnetic resonance measurements of solutions of triethylphosphine oxide in the liquids under analysis (Sun and Berg 2003). This approach makes no distinction between hard *vs.* soft acidity or basicity. A correction to the acid donor number, obtained by subtracting a contribution of the London dispersion component of interactions to the observed spectral shifts, was provided by Riddle and Fowkes (1990).

The van Oss – Good – Chaudhury Model

The next key advance in the field involved a model in which surface free energies were attributed to a combination of dispersion forces and Lewis acid-base interactions (van Oss *et al.* 1988a; Good 1992). The dispersion forces were represented by a single geometric mean term, as discussed earlier. The Lewis acid and base contributions, because of their asymmetric nature, were represented by a pair of terms. In other words, the acidic character of the probe liquid was presumed to interact with the basic character of the solid under investigation (first term) and the basic character of the liquid was presumed to interact with the acidic nature of the solid. Such an analysis yields two contributions to acid-base interactions, and the effects of these need to be summed. Gardner *et al.* (2000) observed reasonably good agreement between different experimental and computational approaches when applying such concepts to the surfaces of several kinds of wood. In particular, the London dispersion components of free energy generally showed consistent values, especially when those terms were calculated first, before fitting the information related to acid or base probes. Oporto *et al.* (2011) observed improved mechanical properties in cases where there was a positive contribution to adhesion attributable to acid-base interactions. The review by Etzler (2013) provides a description of the approach by van Oss *et al.* (1988a) and also discusses some related models.

One of the most arbitrary, and therefore controversial aspects of the "van Oss-Chaudhury-Good" (vOCG) approach involves the manner in which acidity and basicity were assigned values. The authors decided to use water as the standard by which to judge the relative Lewis acidity and basicity of all other compounds. One of the consequences of this assignment is that analyses based on the vOCG model predict that almost every solid surface of practical interest is overwhelmingly basic in character, *i.e.* "monopolar" (van Oss *et al.* 1987; Chen and Chang 1991; Morra 1996; Della Volpe and Siboni 1997; van Oss *et al.* 1997; Dourado *et al*. 1998; Wolkenhauer *et al.* 2008; Shen 2009). Even solids that are widely regarded to being acidic in nature, *e.g.* polyvinylchloride, are classed as monobasic electron contributors according to such analyses (Morra 1996). Also, the vOCG results do not seem to line up with results of adhesion-based evaluations (Morra 1996).

Della Volpe *et al.* (2004) showed that the problem just described could be largely overcome by judicious fitting of the reference point to achieve self-consistency within a set of data. The research group used data from a wide assortment of test fluids in an attempt to obtain a well-conditioned fit of data from an "over-determined" system (Della Volpe and Siboni 1997). Unfortunately, it appears that almost all calculations of interaction energies presently in the literature have been based on the earlier arbitrary scale of acidity and basicity assumed in the vOCG model. However, without having a firm basis upon which to define a new acid-base scale, there does not yet appear to be sufficient reason to adopt the approach of Della Volpe *et al.* (2004) as a way to process data. Rather, the results can be regarded as a signpost indicating likely inaccuracies of work done to date using limited sets of acid and base probe liquids. Though a better overall fit can be achieved by using an updated scale of basicity and acidity, the results for a given analysis still are likely to depend on an arbitrary selection of probe liquids.

Given the mismatch between the vOCG predictions and general expectations regarding acidity and basicity of well-studied surfaces, it should perhaps not come as a surprise that there has been much controversy about this topic. One of the most persuasive articles to come out of this controversy involved a study in which different wetting models were used in an attempt to fit contact angles and interfacial free energies in systems involving mutually insoluble liquids in contact with their vapor (Fowkes *et al.* 1990). One of the liquids was squalene, which has a molecular mass of 411 g/mole and a completely saturated structure. A key difference between the studied system and almost every other study of contact angles is that in the cited system it was possible to precisely measure each of the interfacial tensions at phase boundaries. Based on the results, almost every known model of interfacial free energies based on contact angles was found to be very far away from reality. In addition, Kwok *et al.* (1994) found that attempts to fit data to the vOCG model resulted in the generation of theoretically untenable negative values of the square-roots of certain components of surface free energy. It is possible, however, that the cited authors were attempting to fit slopes of lines based on data points that were too close together.

A second type of problem inherent in the vOCG model is that it requires some rather aggressive number-crunching. In essence, one needs to solve simultaneous equations based on coefficients that might not be completely accurate (Wu *et al.* 1995). As a consequence, there is potential for errors to become magnified, especially when using probe liquids that are insufficiently different from each other (Kwok *et al.* 1994; Wu *et al.* 1995; Mantanis and Young 1997). One potential way to get around such problems is to employ probe liquids with more clearly differentiated Lewis acidity or basicity. However, to be practically useful, the probe liquids also each need to have a relatively high surface tension so that non-zero contact angles can be measured on a wide range of surfaces, and there are only relatively few liquids to choose among. Near the end of this article it will be suggested that such problems might be at least partly overcome by the design and preparation of specialized probe liquids that exhibit larger contrasts in terms of aspects such as acidity, basicity, and hydrogen bonding ability.

Ionic charge contributions

From the perspective of judging interactions with cellulosic surfaces, inherent drawbacks of a model based on Lewis acidity and basicity, as just discussed, involve a disregard for the potential effects of water and the lack of accounting for effects of ionic charges. Cellulosic materials are inherently somewhat hygroscopic, such that moisture levels in the range of 5 to 10% are common in paper products (Alava and Niskanen 2006), and even higher in natural plant materials (Jirjis 1995). Also, many applications of interest, such as many glues and coatings, are aqueous-based (Pizzi 2006). However, relatively few studies have considered effects related to ionic charges and Brønsted acidity or basicity on wettability and adhesion to solid surfaces (Labib and Williams 1984; Jacob and Berg 1993b; Sun and Berg 2003). As noted by Sun and Berg (2003), all Brønsted acids or bases are also Lewis acids or bases, but the converse is not true. In addition, very strong acids and bases in aqueous systems tend to be leveled to the strength of the H_3O^+ and OH^- ions (Shimizu *et al.* 2009).

The most concerted attempt to relate the ionically charged character of cellulosic surfaces to their wettability characteristics was undertaken by Jacob and Berg (1993b). The water-wettability of several types of wood pulp fibers was studied as a function of pH. However, data in the cited article were not consistent with the expected ionization of the surfaces. If contact angles were to be truly governed by the ionic charge of the fiber surfaces, then one would expected to observe increasing wettability as the pH is being increased within the range between about 3 and 7, which corresponds to the dissociation of various classes of carboxylic acid groups common at wood pulp surfaces (Herrington and Petzold 1992). However, not one of the sets of data presented by Jacob and Berg (1993b) showed such a relationship. Rather, the highest work of adhesion, in every case, was observed at a pH of 12, and some of the least wettable conditions were observed at neutral conditions, for all but one type of fiber. Only in the case of chemithermomechanical pulp (CTMP) was the work of adhesion found to be low at very low pH; in all the other cases a pH value of 1 yielded strong wettability, despite the fact that typical cellulosic fiber surfaces have a near-neutral charge under such conditions (Herrington and Petzold 1992). A general conclusion that can be drawn from the cited study (Jacob and Berg 1993b) is that ionic charges do not play a controlling role relative to wettability in such cases. According to Hawker *et al.* (2015), similar approaches involving “contact angle titrations” versus pH have been successful in the evaluation of various oxide surfaces. However, once again, the results of the cited studies did not show consistent relationships between the contact angles and the expected pH dependencies of ionic charge of the surfaces. An explanation for why this is so will have to wait for future research.

Equation of state

An approach called the “Equation of state” deserves mention, despite the fact that Fowkes *et al.* (1990) criticized the approach on theoretical grounds and also found that it failed to predict the liquid-liquid interfacial tensions of probe liquids on squalane. The developers of the equation of state approach began with the premise that the surface free energy of a solid material will be governed by adsorption processes (Ward and Neumann 1974; Li and Neumann 1992; Kwok and Neumann 1999). They also assumed that a functional relationship has to exist between the values of γ_{SV}, γ_{LV}, and γ_{SL}, and that it should be possible to discover that relationship by means of data fitting. In follow-up work, computer fitting was used to optimize parameters to fit contact data corresponding to several different probe liquids (Neumann *et al.* 1974; Kwok and Neumann 1999).

One of the criticisms that Fowkes *et al.* (1990) leveled at the equation of state model is that it did not have a way to account for the effect of hydrogen bonding. None of the probe liquids selected by the developer of the approach had any hydrogen bonding capability. In fact, the equation of state approach does not have a way to incorporate effects of Lewis acidity or basicity either. Johnson and Dettré (1989) found that the equation of state approach gave erroneous predictions related to the spreading of one liquid on another. The equation of state approach was criticized by van de Ven and co-authors (1983) based on “erroneous and impractical assumptions”. In a follow-up essay, van de Ven (1984) criticized the approach based on its unsupported hypotheses and challenged the authors to come up with a theory to explain their seemingly relatively good ability to fit data. Among the assumptions challenged by van de Ven (1984) were the uniqueness of the critical surface free energy for a given surface, the identification of γ_c with surface free energy, and the assumed invariant nature of slopes in plots of the interaction parameter *vs.* the surface tensions of probe liquids. In any case, the results from the equation of state calculations tend to be quite different from those that follow from the vOCG approach (Černe *et al.* 2008). The fact that the equation of state approach could not predict the ability of both water and glycerol to spread onto certain gel surfaces was noted by Van Oss *et al.* (1988b).

Industry-oriented Approaches

Given the limited success of either the vOCG approach (with Lewis acids and bases) or the equation of state approach just considered to accurately fit data at the surface of squalene (Fowkes *et al.* 1990), it makes sense to take a closer look at some less theoretical approaches that continue to be widely used in industry. In particular, one can draw upon correlations to predict the solubility of pure solids, especially polymers, in a wide variety of liquids, including mixtures (Hansen 2007). The cited work shows how such considerations can be used to predict contact angles in a systematic way.

Dispersion and polar terms

A relatively simple model in which a dispersion term is combined with a polar term has been considered by several researchers (Owens and Wendt 1969; Kaelble 1970; Kaelble and Uy 1970). Using just two probe liquids, such as di-iodomethane and water, one can efficiently classify different surfaces with respect to their dispersion force capability (Hamaker constant) and their polar nature. The strength of this approach is that by using water as a probe, the method can provide very useful guidance in applications where hydrogen bonding may be important. The approach has been used to characterize the components of wood-polymer composites (Mantanis and Young 1997; Mei *et al.* 2013; Li 2014a), as well as regenerated cellulose samples (Peršin *et al.* 2012).

Dispersion and polar and hydrogen bonding terms

The system advocated by Hansen (2007) goes one step further and contains separate terms for general polar interactions and for hydrogen bonding, which is regarded as a unique contribution. The approach has been used to evaluate the effects of different wood components relative to wettability (Hansen and Björkman 1998). The latter authors pointed out that solubility characteristics can be expected to cause certain groups within lignocellulose to co-locate during either biosynthesis or regeneration of cellulose. For example, the sides of hemicellulose macromolecules bearing acetyl groups might be expected to adsorb facing towards lignin phases.

Shi (2007) attempted to fit data to both the vOCG model (van Oss *et al.* 1988a) and Hansen's (2007) system. Though Shi (2007) declares that a good fit was achieved, a close inspection shows that the vOCG model failed to show differences arising from the strongly differing hydrogen bonding abilities of different test liquids. On the other hand, the Hansen approach failed to discriminate between the effects of non-hydrogen-bonding liquids of differing Lewis acidity or basicity. It follows that the two systems, each in its own way, views only part of the potentially important information. Possible future steps to overcome this situation are considered in the final part of this article.

Karger *et al.* (1976) went yet an additional step further in their consideration of hydrogen bonding interactions. It has been often pointed out that hydrogen bonding is a kind of acid-base interaction, with the proton bonded to oxygen acting as the electron acceptor and an adjacent oxygen serving as the electron pair donor. It follows that one can separately consider the acidic and the basic character involved in the hydrogen bonding of each of the interacting materials. As was suggested in Table 2, such an approach would require two terms, rather than one, to account for hydrogen bonding contributions. Thus, part of Karger's analysis turns out to have been analogous to the vOCG Lewis acidity and basicity analysis (van Oss *et al.* 1988a). Navarro-Lupión *et al.* (2005) applied the Karger *et al.* (1976) concept to the study of swelling of hydroxypropylmethylcellulose.

Fitting based on UNIFAC equation

The systems considered so far, for the modeling of contact angle data, have each been based on reasonable equations to estimate different kinds of forces of interaction. But as pointed out by Banerjee and Etzler (1995), another approach is just to employ widely available information about interactions between different compounds. The UNIFAC system is a way to empirically predict activity coefficients of various soluble species in non-ideal mixtures of solvents (Gani 2004). Banerjee and Etzler (1995) showed that such a system could be used to predict contact angles of various pure liquids onto common polymeric solids to within seven degrees of the measured data. The activity coefficients of liquids at infinite dilution were used as the input.

Chemical Heterogeneity as a Source of Hysteresis

Before leaving the topic of physical chemical interactions, it is important to consider possible effects of chemical heterogeneity of surfaces. Based on the descriptions of the surfaces of wood, paper, and textile fibers given near the start of this article, it should be easy to understand how these surfaces could differ in composition from point to point. In addition, measures to modify the wettability of cellulosic surfaces will not necessarily result in uniform distributions of chemical composition. Liu *et al.* (1995) employed a lattice model to show ways in which micro-domains of hydrophilicity and hydrophobicity can be expected to affect the wettability of a polymer surface. Related effects have been observed in practice following treatment with hydrophobic sizing agents. Modaressi and Garnier (2002) observed contact angle hysteresis on hydrophobically treated paper, and they attributed this to the nonuniform distribution or curing of the sizing agent. Neumann *et al.* (1974) proposed that the presence of low-energy patches on a solid surface can be effective in retarding the spreading of water.

A model able to predict the effects of chemical heterogeneity, when it is on a scale much smaller than the droplet or the width of a meniscus on a strip of paper (Marmur 2006), was first advanced by Cassie and Baxter (1944). According to this system, the contact angle is predicted to be governed by the weighted average of the cosines of contact angles for areas having different wettability (Marmur 2006). The general equation, for use with chemically heterogeneous surface (Cassie and Baxter 1944), can be expressed as,

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{12}$$

where θ is the observed contact angle, θ_1 is what the value of contact angle would have been if all of the surface had been of type "1", θ_2 is what the value of contact angle would have been if all of the surface had been of type "2", and f_1 and f_2 are proportional amounts of interface corresponding to the two compositions, each in comparison to a hypothetical planar surface area.

Though the model, as described thus far, assumes equilibrium wetting, it is easy to imagine how such a model can account for hysteresis effects, especially if the regions of differing wettability are sufficiently large relative to the scale of the droplet or the width of a paper strip dipping into a slowly rising liquid, *etc*. The following authors have predicted that chemical heterogeneity should lead to hysteresis effects, meaning that the advancing contact angle will be significantly larger than the receding angle (de Meijer *et al.* 2000; Modaressi and Garnier 2002).

Accounting for Roughness and Porosity

Almost all of the theoretical approaches considered so far in this review report have been based on an explicitly or unstated assumption that the surfaces in question are absolutely smooth, or at least can be treated as being such for purposes of fitting data. The present section will relax that assumption and reveal a very prominent source of error. Excellent review articles have been written emphasizing the effects of roughness and porosity on the wetting of solid surfaces (de Gennes 1985; Piao *et al.* 2010).

A case can be made that the effects of roughness and porosity, to be discussed below, are of a magnitude (but not necessarily a direction) that they might account for various data fitting problems already encountered while discussing physical chemical effects. A number of authors have blamed such factors as the roughness, porosity, absorption, and swelling of cellulosic materials for observed poor fits of data to expected models (Lee and Luner 1972; Shen *et al.* 2000; de Meijer *et al.* 2000; Wålinder and Gardner 2002a).

Equilibrium aspects of roughness and contact angles

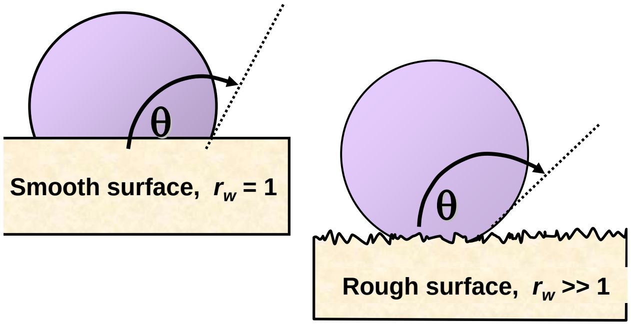
The wettability and contact angle concepts discussed so far all assume a smooth, uniform surface, *i.e.* a situation quite different from that of a cellulose surface, as already discussed. As a first step toward accounting for the morphological complexities of cellulosic surfaces – while still envisioning systems at equilibrium – one can consider the effect of fine-scale, moderate roughness. Wenzel (1936) started such an analysis by noting that the real surface area of practical materials, even non-porous ones, can be much greater than that of a plane or smoothly curved geometric model representing the real surface. A roughness factor can be defined as,

$$r_w = A_{\text{real}} / A_{\text{model}} \tag{13}$$

where A_{real} is the actual surface area if one considers all of the detailed morphology at the scale of the molecules of the probe liquid, and A_{model} is the corresponding area of a simple geometric model (plane or gradually curving representation) corresponding approximately to the object. Since A_{real} is always at least equal to and usually a lot greater than A_{model}, it follows that the amount of surface free energy associated with the surface must be greater than what would be predicted based on simple measurements and application of the Young equation. Thus, in practical cases, the Young equation needs a correction. The result is shown as Eq. 14:

$$r_W\,[\gamma_{SV} - \gamma_{SL}] = \gamma_{LV}\cos\theta \tag{14}$$

One of the implications of Eq. 14 is that a situation in which $\theta < 90°$ tends to be even more wettable than one would predict based on the simple form of the Young equation (Eq. 1). Likewise, when $\theta > 90°$, the roughness will render the solid even less wettable by the liquid under consideration. These relationships are illustrated in Fig. 2. A point that must be emphasized, when viewing this illustration, is that Wenzel's analysis applies only in cases where the probe liquid is able to wet the surface down to the bottom of each valley; situations in which the probe liquid wets only the points of roughness will be considered later.



$$\mathrm{Cos}\,\theta = r_w\;(\gamma_{sv} - \gamma_{sl})\;/\;\gamma_{lv}$$

where r_w = real area/planar area

Fig. 2. Equilibrium effect of surface roughness on the contact angle of a droplet in the case of a material that is slightly "nonwettable" by the probe liquid

Theoretical support for the Wenzel equation

The most frequent complaint made against the Wenzel model is that "of course such a model is irrelevant, because the surfaces are too rough to be at equilibrium". Although such an argument sounds logical, most researchers who have studied the matter closely have tended to back off from such criticism and to join a general chorus in support of the theory (Good 1952; Eick *et al.* 1975; Huh and Mason 1977; Long *et al.* 2005; Wang *et al.* 2014b). For instance Adam and Jessop (1925) noted that even in cases where contact angle hysteresis is observed, one can take the average between an advancing and a receding angle, and then apply the Wenzel equation to the result. Good (1952) pointed out that a random array of bumps on a surface can provide a great many alternative pathways for spreading of a liquid droplet, and such a multitude of possibilities tends to decrease the importance of non-equilibrium "sticking" or "pinning" effects. After a large amount of mathematical derivation, Eick *et al.* (1975) came to the conclusion that the Wenzel equation is pretty accurate when applied to hypothetical surfaces having very regular "bumps". Differences in the slopes of such asperities were found to cause modest deviations from the Wenzel predictions. By contrast, Nakae *et al.* (1998) were able to account for contact angle hysteresis by running simulations with a hemispherical closest-packed model surface and with close-packed hemi-round rods on a hypothetical surface.

Huh and Mason (1977) proposed that if the meniscus is able to jump between neighboring positions having localized minimum energy, then the average of such states will tend to conform to the Wenzel predictions. Such considerations have prompted some researchers to promote the use of vibrations during wettability measurements to hasten the process of equilibration (Johnson and Dettré 1964a; Meiron *et al.* 2004; Kamusewitz and Possart 2006).

Experimental support for the Wenzel equation

Several attempts have been made to verify Wenzel's predictions experimentally. Fabretto *et al.* (2003) observed general agreement with the predictions in the case of glass surfaces that had been made rough by coating with 50 μm glass spheres prior to treatment with fluoropolymer. Tamai and Aratani (1972) found good agreement with the Wenzel equation in the case of mercury on silica surfaces. Liptáková *et al.* (1994), Gindl *et al.* (2001b), Cheng and Sun (2006), and Santoni and Pizzo (2011) observed lower contact angles when wood surfaces were sanded with higher-number (finer grit) sandpapers, which is in agreement with Wenzel's predictions. Sinn *et al.* (2004) also reported that the sanding of wood surfaces made the contact angle test results more repeatable.

Another piece of evidence that tends to support the applicability of the Wenzel equation is to compare predicted surface energies of rough surfaces with those of comparable liquids. Thus, Gindl *et al.* (2001a,b) and Gindl and Tschegg (2002) reported dispersion components in the range of 48 to 50 mJ/m^2 for various wood surfaces. These values are much larger than the dispersion component of surface free energy for liquids having related composition (Table 3). But if Wenzel's roughness coefficient were to have a value of 2, then the cited values would need to be divided by two to estimate the surface free energy based on a nano-scale quantification of surface area, thus resolving the apparent disagreement.

One of the most serious problems encountered in such investigations has been the fact that advancing angles often differ from receding angles (Collett 1972). Most notably, Adam and Jessop (1925) observed contact angle hysteresis of water placed on wax surfaces. Notably, the hysteresis was not observed in the case of very smooth surfaces created by scraping of the wax. Such observations suggested that the measured angles observed in practice are likely to show hysteresis effects. Whether such effects are likely to be superimposed on top of Wenzel's equilibrium effects of roughness, or whether the latter become irrelevant, probably depend on the scale of the roughness, as will be discussed later.

The 90-degree angle rule

According to Wenzel's equation, 90° is a critical value (Wenzel 1936, 1949). As indicated by Eq. 14, if the contact angle measured on a given very smooth surface is different from 90°, then it is predicted to be more different, in the same direction, on a rough surface that is otherwise identical. Such effects tend to amplify the critical nature of the 90 degree contact angle condition as the dividing point between wettable and nonwettable surfaces. Though, as noted above, Fabretto *et al.* (2003) found general agreement with the Wenzel equation, the transition from wetting to nonwetting behavior appeared to take place at 80 degrees rather than 90 degrees. Vogler (1998) used a lower value of 65° as a demarcation between wettable and nonwettable surfaces. Zhang *et al.* (2015) likewise reported a transition from wetting to non-wetting associated with a contact angle of about 67 degrees or lower. Fortes (1981) expressed doubt that Wenzel's 90° rule has been supported by experimental results for values below 90°. Such conditions might be particularly difficult to evaluate in the case of cellulosic surfaces, since one would in particular tend to run into complications with absorption, and possibly also with swelling effects, when low contact angles are being considered.

Minimum roughness dimension

Another critical value to consider is the typical dimension of roughness. In other words, one needs to be concerned about cases in which the scale of roughness may be too large such that the observed contact angles are no longer a true reflection of the equilibrium values envisioned in Eq. 14. It was estimated by de Gennes (1985, see footnote on page 837 of that article) that points or ridges of roughness as high as 100 nm can be readily surmounted by ordinary thermal motions of a meniscus. Huh and Mason (1977) estimated that the critical roughness dimension would be "below micron range". Modaressi and Garnier (2002) observed that asperities larger than 160 nm were sufficient to cause delays in wetting. Zhang *et al.* (2015) observed strong hysteresis effects on surfaces that had been modified at the "micro" level, but the hysteresis effects were much less in the case of modification at both the "micro" and "nano" scales to increase the specific surface area.

Averaging effect of a precursor film

In attempting to explain why bumps and ridges on a surface often fail to block the progress of an advancing or receding meniscus, one important factor to consider is the effects of precursor films. As noted by de Gennes (1985), observations by ellipsometry have shown the presence of very thin films of fluid extending outwards in advance of a wetting meniscus. Thus, it is incorrect to envision the contact line as an abrupt three-phase transition. Rather, there may be an essentially two-dimensional zone on the surface that can be regarded as the site of torsional energy or so-called "line tension". According to de Gennes (1985), most of the energy that gets expended during advancing of a meniscus involves not just the line of contact, but also the precursor film, such that the effects of modest-sized hills and valleys tend to become surmounted and averaged.

Equilibrium effects of open pores on a hydrophobic surface

A different approach needs to be used if the "roughness" is so steep that each depression acts as if it were effectively bottomless, *i.e.* a porous surface. For instance, the depressions of roughness may be sufficiently narrow and deep such that bubbles occupy their lower parts after wetting (de Gennes 1985; Marmur 2006). As was noted earlier, cut surfaces of wood, especially those involving the end grain, are notoriously porous (Bryne and Wålinder 2010). As shown by Gardner *et al.* (1991), the wetting of such surfaces of wood involves very large hysteresis effects. However, before considering such cases, let us first consider what happens in situations where the contact angle is sufficiently high that the probe liquid never enters the pores, *i.e.* the system remains at equilibrium. Thus, as mentioned earlier, the Wenzel equation (Eq. 14) is no longer applicable. For such situations one can apply the model of Cassie and Baxter (1944), which was cited earlier in reference to patches having different chemical composition. However, in this case, the interactive energy is set to zero at all locations where the meniscus encounters the mouth of a pore.

Cassie and Baxter envision the surface as being non-planar, *i.e.* a surface having finite roughness, following a similar approach as had been used by Wenzel. But in addition, the surface is interrupted by pores having sharp edges – a situation that is not conducive to advancing of a fluid on the surface, especially if the contact angle is significantly greater than zero degrees. Equation 15 gives the equilibrium contact angle based on the derivation by Cassie and Baxter (1944),

$$\cos\theta = f_1 \cos\theta_1 - f_2 \qquad (15)$$

where θ is the observed contact angle, θ_1 is what the value of contact angle would have been in the complete absence of porosity, and f_1 and f_2 are fractional amounts of interface corresponding to the land and pore areas. The negative sign in Eq. 15 arises because the contact angle of any liquid on a hypothetical air surface would be 180 degrees, giving rise to a change in sign in Eq. 12 given earlier. The use of Eq. 15 appears to be well justified for use with initially dry cellulosic surfaces, because of the presence of lumen openings, pits, and mesopores in the cell walls. In particular, this approach seems to be well suited for the interpretation of contact angles during initial contact with the fluid, before filling of pores has had time to occur. The Cassie-Baxter model has been supported theoretically by Long *et al.* (2005). When using Eq. 15, it is important to avoid a common mistake that has been perpetuated in a majority of publications dealing with the topic (Milne and Amirfazli 2012). The mistake arises because some researchers have assumed that f_1 plus f_2 equals 1; however, on account of Wenzel's roughness effect, this is not necessarily the case.

A predicable transition from situations governed by the Wenzel equation (Eq. 14) to the Cassie-Baxter equation (Eq. 15) has been proposed, depending on the geometry of roughness, as well as chemical aspects affecting wettability (Ishino and Okumura 2006; Porcheron and Monson 2006; Whyman and Bormashenko 2011; Milne and Amirfazli 2012). Tavana *et al.* (2006) presented direct experimental evidence of such a transition in the case of *n*-hexatriacontane crystals vacuum-deposited on Si surfaces. As has been mentioned, recent work by Zhang *et al.* (2015) revealed that the transition may be sensitive to the scale of roughness. Micro-scale modification of model surfaces yielded strong contact angle hysteresis effects. By contrast, hysteresis effects were strongly subdued in the case of substrates that had been modified with a combination of micro-scaled and nano-scaled roughness features. Such results are consistent with a mechanism in which the random thermally-driven movements of an interface are able to surmount nano-scale morphological barriers (de Gennes 1985; Huh and Mason 1977; Modaressi and Garnier 2002), such that equilibrium values of contact angle can prevail, on average.

Superhydrophobic effects explained

If one applies the predictions of Cassie and Baxter (1944) to systems that resemble extremely porous systems at a nano scale, what emerges is a consistent explanation for super-hydrophobic effects (Song and Rojas 2013). Two requirements must be met to achieve an extremely high resistance to wetting. The first requirement is that the equilibrium contact angle on a hypothetical planar surface of the material should be high enough, usually above 90 degrees. The second requirement is that the surface should be so steeply rough, on a very fine scale, so that the probe liquid just rests on the points of roughness. In other words, when applying the Cassie-Baxter equation, the relative "land area" of the surface is very small in comparison to the "open pore" area. Such a system is illustrated schematically in Fig. 3. There is evidence that the hold-out of water from highly sized paper surfaces can involve the same kind of mechanism (Shen *et al.* 2000). It also has been stated that a multi-scaled roughness, involving both micro-scale and nano-scale features, can be beneficial to achieving superhydrophobic effects (Whyman and Bormashenko 2011).

In anticipation of the mechanism just described, Wenzel (1936) already had suggested the use of granular coatings to amplify the effects of hydrophobization, which turns out to be key to the practical preparation of superhydrophobic surfaces. Also, Cassie and Baxter (1945) envisioned that a complex surface morphology was important for the establishment of very high contact angles of water on various surfaces in nature.

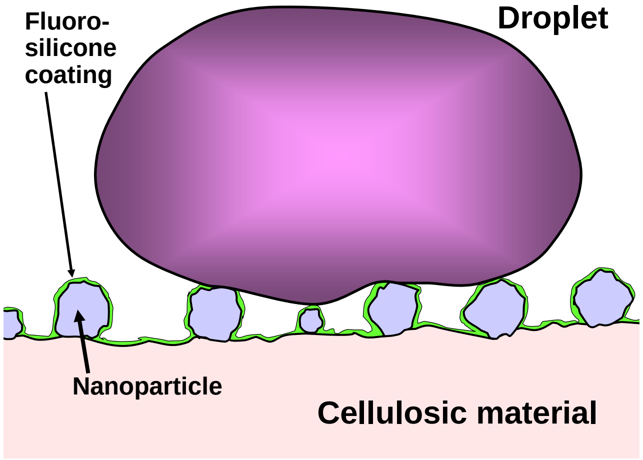


Fig. 3. Schematic illustration of water droplet resting on a superhydrophobic cellulose-based system achieved by coating the substrate with a sparse layer of nanoparticles and then derivatizing the surfaces with a fluoro-substituted trimethoxysilane

Hysteresis Effects Due to Surface Morphology

Evidence of hysteresis on cellulosic surfaces

In situations involving the wetting of cellulosic surfaces, hysteresis effects appear to be the rule rather than the exception, and morphological characteristics appear to be the major contributors to such effects. For example, Bryne and Wålinder (2010) reported differences of 25 to 55 degrees when comparing advancing and receding angles on modified wood specimens. Hodgson and Berg (1988) suggested that especially large hysteresis can be expected when a meniscus has to advance over a cellulosic fiber. Kannangara *et al.* (2006) likewise observed huge hysteresis effects when water droplets landed onto and then, an instant later, attempted to recoil from a paper surface. In contrast, Wistara *et al.* (1999) reported differences of only between 16 and 29 degrees in the course of lengthwise dynamic contact angle measurements on individual wood pulp fibers. Von Bahr *et al.* (2004) observed pronounced wetting hysteresis on paper specimens that had been hydrophobically treated with alkylketene dimer. Though the roughness may have contributed to such effects, the cited authors explained the hysteresis based on there being islands of hydrophobic AKD spread non-uniformly onto the fiber surfaces.

Contact angle hysteresis attributable to roughness

The origin of the effects just mentioned can be visualized by considering the placement of a drop of probe liquid onto an inclined plane that has roughness in the form of a regular staircase. Figure 4 illustrates such a situation.

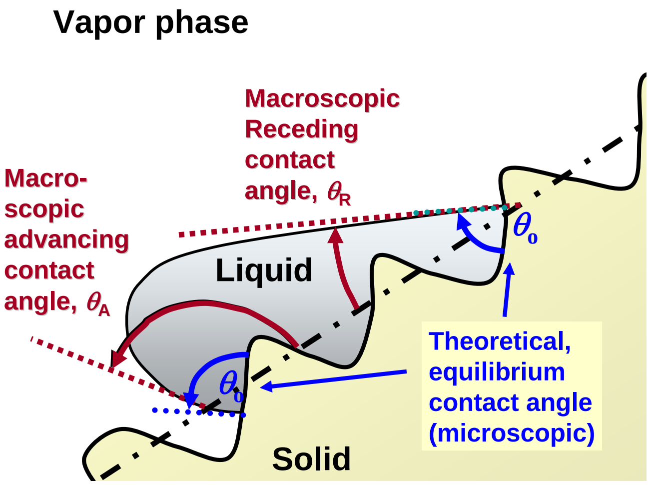


Fig. 4. Schematic illustration to show why the advancing and receding contact angles may appear to be different on a macroscopically rough surface even if the microscopic situation shows a constant value of the equilibrium contact angle

Note in the figure that on a macroscopic scale there can be a pronounced difference between the advancing contact angle θ_A and the receding contact angle θ_R. However, at a microscopic level one can expect that the actual contact angle at equilibrium would still be in agreement with the Young equation (Eq. 1) or the Wenzel equation (Eq. 14). These concepts have been further developed by de Gennes (1985) and Leger and Joanny (1992).

Adam and Jessup (1925) added a term F to the Young equation to account for contact angle hysteresis, as follows:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta + F \qquad \text{(advancing)} \qquad (16)$$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta - F \qquad \text{(receding)} \qquad (17)$$

They assumed a balanced effect in which the equilibrium angle would be the mid-point of $\cos\theta$ for the advancing and receding angle. The justification for such a term is an expected “pinning” of a meniscus on a defect of sufficient size (Fortes 1981; de Gennes 1985; Leger and Joanny 1992; Nakae *et al.* 1998). This kind of interpretation is supported by observations of wavy contact lines of sessile drops (Fortes 1981; Rodríguez-Valverde *et al.* 2002; Samyn 2013). Also, it has been observed that the maximum wetting line tends to remain in place in cases where the liquid either is absorbed into the cellulosic material or evaporates (Modaressi and Garnier 2002). Adam and Jessup (1925) proposed that the cosines of advancing and receding angles ought to be averaged to estimate the value of an equilibrium contact angle. Petrov *et al.* (2003) were able to confirm such an expectation for a well-defined system with various highly purified probe liquids on an amorphous fluoropolymer surface.

Theories related to pinning and groove effects

As has been noted (Shuttleworth and Bailey 1948; Huh and Mason 1977; Rodríguez-Valverde *et al.* 2002), a contact angle cannot be said to be at equilibrium when it is up against an insurmountable barrier, such as a sharp edge. Johnson and Dettré (1964a) simulated such effects by computer, based on an assumed model of a rough surface. On model surfaces having relatively large-scale simulated roughness, sufficient to give a Wenzel roughness factor of two, Johnson and Dettré (1964b) predicted contact angle hysteresis values as high as 70°. When surfaces having a roughness factor of four were assumed, the corresponding hysteresis was a high as 81°. Marmur (1994) predicted that hysteresis effects would depend on the size of a sessile drop and showed that different results could be obtained with different patterns of regular roughness. Ruiz-Cabello *et al.* (2011) considered the behavior or captive bubbles or droplets trapped within repeating round, symmetric sawtooth patterns. Though these studies show what is possible, one needs to keep in mind that real ridges of roughness are unlikely to be as contiguous or as well-aligned as the deterministic models of roughness employed in the cited works. Real systems generally would not show nearly as large hysteresis effects as could be expected for the worst-case models of roughness that have been considered.

Contact Angle Hysteresis on Porous Surfaces

In their original work Cassie and Baxter (1944) had proposed a model suggesting an equilibrium effect, based on the presence of small pores that remained unwetted throughout the interaction. However, it will be proposed here that the same mathematical approach can be applied with a different set of assumptions to account for the relatively large hysteresis effects often observed in the case of cellulosic surfaces. A related mechanism had been proposed by Liptáková and Kúdela (1997).

Suppose that on the first approach of a wetting front of liquid, sharp edges of pores act as a barrier, such that the mouth of each open pores constitutes an area of perfect non-wetting. In other words, one assumes that in the case of an advancing meniscus the system follows the usual interpretation of the Cassie-Baxter relationship expressed by Eq. 12. But then suppose that the situation completely changes once a given area of surface has been completely covered by the probe liquid. After sufficient time has passed, the underlying pores begin to become filled with the probe liquid. Once the pores are at least partly filled with liquid, the corresponding parts of the surface act like perfectly wettable areas, from which the fluid is unlikely to retract. Thus, Eq. 12 might be rewritten as,

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_{\text{self}} \qquad (18)$$

where θ_{self} is zero, since it represent the contact of the probe liquid onto itself. Because the cosine of zero is 1, Eq. 17 can be simplified to,

$$\cos\theta = f_1 \cos\theta_1 + f_2 \qquad (19)$$

which is the same as Eq. (15) except for the sign of the second term. It is proposed here that Eq. 19 might be regarded as a starting point for estimating the effect of porosity on the receding angles of fluids on cellulose surfaces in cases where saturation of the pores has been completed. Figure 5 provides a schematic illustration of this concept, wherein the pores at the advancing edge of a droplet are empty, but the pores at the receding edge of a droplet are filled. Follow-up research is needed to further explore this topic.

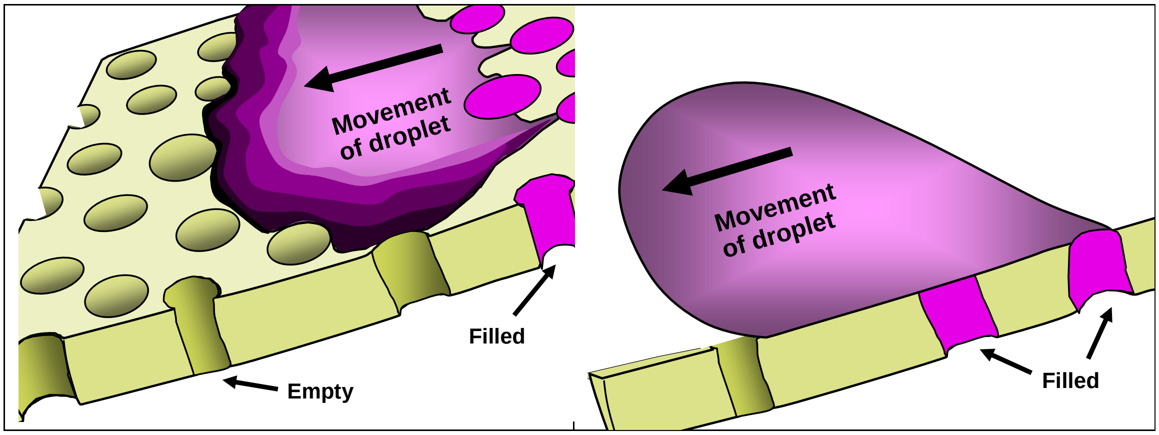


Fig. 5. Top view and side view of an advancing droplet (being pushed toward the left) on a surface having regular porosity and surface area that may be greater than what is represented by a plane or smooth geometric model (Cassie and Baxter 1944)

Confirmation of the mechanism just described, at least when considering cellulosic materials, comes from studies in which the "second advancing contact angle" is markedly lower than the initial advancing contact angle (de Meijer *et al.* 2000). In other words, such effects are consistent with the eventual filling of pores once a given area of the surface has been covered with liquid. Also, such a mechanism may explain why advancing and receding angles sometimes get to be closer together after repeated advancing and retraction across the same test surface (Lam *et al.* 2001). Whang and Gupta (2000) suggested that such outcomes often can be manifested even before an advancing meniscus has reached a certain point on a cellulosic surface due to "hydration" ahead of the contact zone.

The situation just described is especially of interest relative to the observed hysteresis effects when a wood surface, having exposed pores, is gradually withdrawn from water (Gardner *et al.* 1991). There is direct evidence of such an effect in the work of Dankovich and Gray (2011), who studied films composed of cellulose nanocrystals (CNC). Because of the particulate nature of CNC, the spaces between the particles may play the role of pores.

Accounting for Rates of Adsorption

The subject of adsorption of moisture into the bulk of cellulosic material already needed to be introduced above to account for the effects of pores on advancing and receding contact angles. In addition, the spreading of liquids onto cellulosic surfaces can be profoundly affected by its inward movement, *i.e.* absorption (Liptáková *et al.* 1998; Rodríguez-Valverde *et al.* 2002). So the topic of adsorption will be considered next.

The Lucas-Washburn equation

Sometimes the best theoretical models are the simplest. A model of uniform cylindrical capillaries is expected to exactly represent only certain unusual cases of interest, but it is remarkable the extent to which such a model can account for the main effects observed in many practical situations. The model that continues to be used most often to estimate rates of adsorption into porous materials was developed by Lucas (1918) and Washburn (1921). The situation envisioned by these investigators is illustrated in Fig. 6.

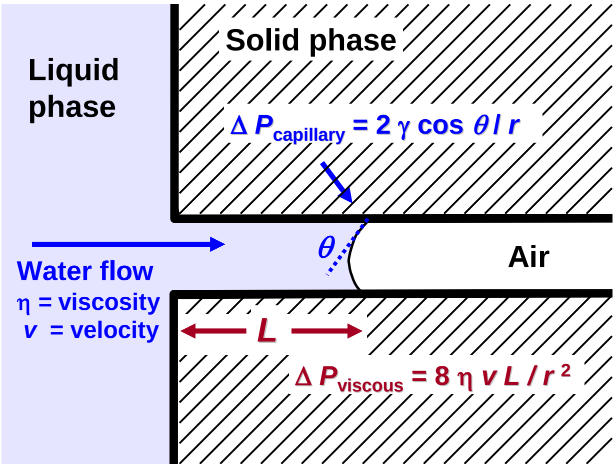


Fig. 6. Factors affecting the rate of permeation of a liquid front into an idealized porous solid, as represented by a single cylindrical pore

Assumptions underlying the Lucas-Washburn equation are as follows: (1) the capillaries are cylindrical and of uniform diameter (2) the walls are perfectly smooth; (3) the contact angle of the liquid with the solid surface is constant, even when the liquid front is moving; (4) the liquid flow is laminar; (5) the liquid is Newtonian; and (6) the capillary is connected to an unlimited reservoir of the pure liquid. Because it is rare that all of these assumptions will be strictly true (especially assumptions 1 and 2), the approach of Lucas and Washburn can be regarded as an approximation in most practical cases.

As shown, a porous solid (one pore shown) is placed in contact (at $t = 0$) with a probe liquid. The flow of liquid into the pore is motivated by capillary pressure, which depends on the contact angle, the liquid-vapor surface tension, and the pore diameter. By this analysis, smaller pores give rise to a greater capillary pressure. The contact angle is assumed to be the same as what would be measurable on a perfectly smooth, flat surface having the same composition. An opposing force, resisting the further passage of liquid into the pore, is attributable to the viscosity of the fluid. These relationships can be expressed by the following equations, which when combined give an estimate of the time required for the fluid to reach a given depth in the porous solid,

Capillary force equation

$$\Delta P_{\mathrm{capillary}} = 2\gamma_{\mathrm{LV}} \cos \theta / r \tag{20}$$

Viscous retarding force equation

$$\Delta P_{\mathrm{viscous}} = 8\eta v L / r^2 \tag{21}$$

Lucas-Washburn equation in differential form

$$\mathrm{d}l/\mathrm{d}t = \gamma_{\mathrm{LV}}\, r \cos \theta / (4\eta L) \tag{22}$$

Lucas-Washburn equation in integrated form

$$\underline{L} = [(2r\, \gamma_{\mathrm{LV}} \cos \theta]\, t / (4\eta)]^{1/2} \tag{23}$$

where r is the equivalent radius of the pores (based on the cylindrical pore model), η is the dynamic viscosity, v is the average velocity of fluid flow into the capillary, L is the distance of permeation at time t, and t is the elapsed time after the initial wetting.

The effects of surface roughness and porosity on wettability, coupled with estimates of the rate of penetration of fluids into porous solids, can account for some general experimental results for cellulosic surfaces; however the fits often show large deviations (Bristow 1967; Aspler *et al.* 1987). Some other effects that have been suggested to account for lack-of-fit relative to the Lucas-Washburn equation are precursor films (de Gennes 1985; Good 1992; Leger and Joanny 1992; Decker *et al.* 1999), the time required to swell cellulosic materials (Shi and Gardner 2000; Masoodi and Pillai 2010), and complex geometries of pores (Kent and Lyne 1989). As noted by Gardner *et al.* (1991) the wetting front within the bulk of the cellulosic material often may wick past the contact line of the meniscus at the surface. Or, in the terminology of Whang and Gupta (2000), the material may become “hydrated”. Indeed, the wettability of cellulosic material is known to be highly influenced by its moisture content before testing (Piao *et al.* 2010). The swelling of the material sometimes can have the effect of constricting the open areas of pore cross-sections (Masoodi *et al.* 2011). Wålinder and Gardner (1999) and Shi and Gardner (2000) supported their theory of the importance of swelling by evaluating the generation of heat during wicking experiments. In contrast to the studies just cited, Lyne (1993) demonstrated that on clean cellophane, as well as various paper types, the wetting delay had nothing to do with the filling of surface pores; rather the effect could be attributed to adsorption of vapor ahead of the advancing front of liquid. In summary, though the situation is complex, the main effects of absorption into cellulosic materials can be estimated based on the equations given above – with heavy emphasis on the importance of contact angles.

When applying the Lucas-Washburn equation to a network of adjoining pore spaces, as in the case of paper, the velocity of liquid following alternate channels into the material will not necessarily be uniform. In fact, a breakthrough study by Roberts *et al.* (2003) revealed that some dry channels within a paper sheet may be entirely bypassed as liquid chooses easier, unblocked pathways. The authors experimentally confirmed that water penetration into paper does not "follow" the Lucas-Washburn equation, which says large pores will allow more liquid penetration (see Eq. 22). In the liquid wicking front, it is the "easy" pores that allow more liquid penetration. Gaps between fibers are the easy channels for liquid to wick, since the channel is continuous. Once another fiber blocks the wicking channel, wicking temporarily stops until the wicking front finds another viable channel to advance again. Possibly this temporary blocking could be linked to the observation of water absorption delay, as previously mentioned.

Molecular alignment

For the sake of completeness, the topic of molecular reorientation within the liquid phase might be expected to have an effect on wettability. In theory it is reasonable to expect some time to be required for molecules to align themselves at a freshly-created or moving interface or contact line. Such an idea was considered by Johnson *et al.* (1977). However, in the case of pure liquids the cited authors found that, if such alignment is required, the process is much faster than practical means of its evaluation. No indication was found that such effects had been considered in relation to the wetting of cellulosic surfaces.

TEST METHODS AND THEIR OUTPUT

Having considered literature related to the chemical and morphological characteristics of cellulosic surfaces, as well as theories related to how such characteristics affect their wettability, the next step is to consider what kinds of experimental procedures can be most appropriate for evaluation of such phenomena in the case of cellulosic surfaces. As noted by Decker *et al.* (1999), "contact angles can be frustrating to measure and complex to interpret". These words seem to be particularly appropriate for the kinds of surfaces being considered here. A recent review article by Petrič and Oven (2015) goes into greater detail regarding experimental aspects of contact angle testing.

General Issues

Probe liquid selection

Before discussing the equipment and procedures used to evaluate contact angles, it makes sense to first consider the selection of probe liquids. It is proposed that such selection ought to be guided, to a large extent, by the expected end-use of the material under evaluation. For instance, if the material is to be bonded by means of an aqueous adhesive, then it follows that one of the probe liquids ought to be water. If one suspects that bonding of a modified cellulosic material to a plastic matrix involves Lewis acid-base interactions, then it will be important to include Lewis acid and base probes in the set of probe liquids.

Since London dispersion forces are always a major factor, some tests also should be run with a non-polar liquid having a very high surface tension, *e.g.* di-iodomethane. Table 3 lists some selected probe liquids, together with information related to their properties. The donor number (DN) and acceptor number (AN) values in the table are defined by Gutmann (1978). The value of AN given by the chemical shift in the phosphorus nuclear magnetic resonance signal when the probe interacts with $(Et)_3PO$ (Mayer *et al.* 1975). By contrast, the value of DN is defined by the heat of formation of an adduct between the probe compound and the Lewis acid $SbCl_5$ (Gutmann *et al.* 1966).

Table 3. Probe Liquid Characteristics

Probe liquid	**Characteristics** (energy units mJm^{-2})	**Citation**
Dispersion force probes		
Di-iodomethane	γ_{LV} = 50.8	Owens and Wendt 1969
α-Bromonaphthalene	γ_{LV} = 44.4	Kudela 2014
Hydrogen bonding probes		
Water	γ_{LV} = 72.8, AN* = 63.4, DN = 75.6	Owens and Wendt 1969
Ethylene glycol	γ_{LV} = 47.7	Paredes *et al.* 2009
Glycerol	γ_{LV} = 64.0	Hosseinaei *et al.* 2011
Lewis acids		
Chloroform	γ_{LV} = 27.5, AN* = 22.7, DN = 0.0	Shi 2007; Rosenholm 2010
Dichloromethane	γ_{LV} = 26.5, AN* = 16.4, DN = 0.0	Shi 2007; Gamelas 2013 IGC
Phenol	γ_{LV} = 40, A hard acid	Fowkes *et al.* 1991
Iodine	A soft acid, solid at room temp.	Fowkes *et al.* 1991
Ethylene glycol (?)	γ_{LV} = 47.7, Status in dispute	Mantanis & Young 1997
Lewis bases		
Dioxane	γ_{LV} = 33.0, AN* = 0.0; DN = 62.2	Shi (2007)
Diethyl ether	γ_{LV} = 17.0, AN* = 5.9; DN = 80.6	Shi 2007; Tze *et al.* 2006
Formamide	γ_{LV} = 58.2, AN* = 39.1. DN = 100.8	Shi 2007; Gindl *et al.* 2001b
Tetrahydrofuran	γ_{LV} = 26.4, AN* = 2.1; DN = 84.0	Shi 2007; Gamelas 2013
Ethylene glycol (?)	γ_{LV} = 47.7, Status in dispute	Wålinder 2002

γ_{LV} = is the liquid's surface tension in equilibrium with its vapor at room temperature (Roosta *et al.* 2012, and http://www.surface-tension.de/); AN is the Lewis acceptor number; DN is the Lewis donor number (Shi 2007). The asterisk in the quantity AN* means that the value has been corrected to remove the dispersion force contribution to a spectral shift (Riddle and Fowkes 1990). Note that the letters "IGC" are listed after certain references. This indicates that the indicated probes were used for inverse gas chromatography, not for contact angles, in the cited cases.

Di-iodomethane is widely regarded as an ideal probe liquid for the assessment of London dispersion capability of a solid surface because of its non-polar nature and its high surface tension (Fowkes *et al.* 1991). A high surface tension of the probe liquid is essential such that the contact angle with a solid surface will be large enough for easy measurement. The high Hamaker constant of this compound, giving it a strong interaction with other entities by means of London dispersion forces, can be attributed to the loosely held electrons in the outer shells of the iodine atoms.

Water has been widely employed as a probe liquid in cases where hydrogen bonding can be expected to play a significant role (Owens and Wendt 1969; Kaelble and Uy 1970; Paredes *et al.* 2009; Kutnar *et al.* 2012; Kudela 2014). Note in Table 3, that although two other possible alternatives to water are listed as possible probes with hydrogen bonding capability, both of them have surface tensions lower than that of water. In addition, the higher viscosity of glycerol may be of concern.

The selection of suitable Lewis acid and Lewis base probes represents a considerably greater challenge, in comparison with the foregoing selections of probes for London dispersion forces and hydrogen bonding/polar interactions. The inherent problem is that every compound containing polar groups is likely to exhibit a variety of both acidic and basic characteristics depending on how it is oriented in relation to the solid surface (Sun and Berg 2003). Only a few compounds are believed to express purely acidic or purely basic Lewis character. Most Lewis probes can be expected to exhibit some interaction with both acidic and basic Lewis sites on a surface under evaluation. To minimize such issues, one can attempt to select probes that are clearly either acidic or clearly basic, to the degree that such selection is possible. At the same time, the probe liquids have to be selected among those that have rather high surface tensions if one hopes to detect measurable contact angles on cellulosic surfaces. If the probe liquid's surface tension is too low, then the contact angle may be near to zero, leading to rapid adsorption into pores.

Based on the entries in Table 3, the status of ethylene glycol as a Lewis acid or base probe needs to be regarded with some suspicion. Mantanis and Young (1997) regarded it as an acidic probe, while Wålinder (2002) regarded it has predominantly Lewis basic. However, attributable to the presence of –OH groups, the compound also could conceivably be employed as a probe for hydrogen bonding capability.

A perceptive reader might have noticed that the descriptions given above about how to select probe liquids were discussed without reference to a recommended model, such as the widely used vOCG model (van Oss *et al.* 1988a), the Kaelble model (Kaelble 1970), or Hansen's approach (Hansen 2007). It is likely that the selection of probe liquids that are relevant to a certain material and industrial process of interest will guide one toward one or more of the existing strategies of analysis, such as those just mentioned. Caution is required, however, given the complexities inherent in cellulosic surfaces, and also because of the theoretical and practical problems associated with interpretation. For instance, Gindl *et al.* (2001a) recommended using a large number of probe liquids for each analysis as a means of achieving more reliable results. Such issues will be considered more fully near the end of this article.

Probe evaluation

The good news about probe evaluation is that, if the liquid is really pure, then its surface tension can be found from tables (*e.g.*, in Roosta *et al.* 2012). Also, perhaps as a back-up, such values can be estimated based on group analysis and regression fitting (Stefanis *et al.* 2005; Gharagheizi *et al.* 2011; Albahri and Alashwak 2013). But the bad news very often may involve ensuring the purity of probe liquids. It has been noted that because of the relatively high surface tensions of the top-candidate probe liquids, they tend to be highly sensitive to the effects of contaminants that would lower their surface tensions (Rosenholm 2010). Also, there is a high probability that contaminants can be released or extracted from various cellulosic materials being evaluated (Wålinder and Gardner 2002b). Such contamination can be expected to distort any interpretation based on measured contact angles (van Oss *et al.* 2001). Surface tensions also can be evaluated by Wilhelmy plate (Wilhelmy 1863), drop mass (Henderson and Micale 1993), and de Nouy ring (Harkins and Jordan 1930) methods, but in each case the values may change during the course of a contact angle experiment as a result of contamination. Only in rare cases has the surface tension of a probe liquid been evaluated again after the contact angle test had been completed (Moghaddam *et al.* 2013).

Static Contact Angles

So-called "static" tests for evaluation of contact angles are those which require at least several seconds of liquid contact with the surface of interest before a value can be obtained. Some widely used test procedures for static contact angles employ sessile drops, captive bubbles, and capillary rise.

Sessile drops

Perhaps because of their simplicity, sessile drop methods have become the most popular way to obtain contact angle data, including evaluation of cellulosic surfaces (Mohammed-Zieger *et al.* 2004; Bryne and Wålinder 2010; Hosseinaie *et al.* 2011; Soumya *et al.* 2011). However, especially when evaluating rough or heterogeneous surfaces such as wood or paper, multiple replicate measurements will be required to detect statistically significant differences among samples treated in different ways.

A negative aspect of the simplest form of a sessile drop test, in which droplets are merely dropped onto the test substrate, is that there is no way to be sure whether the resulting contact angle represents an advancing angle, a receding angle, or something in between, maybe even approaching an equilibrium angle. Results can be highly dependent on the manner in which the droplet is dropped or placed on the surface (Shuttleworth and Bailey 1948). Investigators sometimes have set up their systems so that the advancing and receding of sessile drop volumes can be controlled precisely during the evaluation of contact angles (Gindl *et al.* 2001a; Lam *et al.* 2001; Dankovich and Gray 2011), and such procedures can be selected when using some modern devices. Perhaps the most practical way to evaluate advancing and receding angles of an individual sessile drop is the method already developed by Wenzel (1936); the measurements were carried out on a tilting plate, with measurements done on each side of a droplet until reaching a slope sufficient to make it slide.

Because of local distortions in the shapes of the edges of sessile drops, it has been shown that direct measurements of contact angles, using a goniometer, can lead to relatively large random errors (Uyama *et al.* 1991). Fortunately, this problem can be largely avoided by evaluation of the shapes of droplets based on their height and perimeter when viewed from above (Uyama *et al.* 1991; Kazayawoko *et al.* 1997; Rodríguez-Valverde *et al.* 2002; Marmur 2006). Such systems have been widely implemented on available equipment for evaluation of sessile drops. The contact angle on a relatively flat surface may be obtained from the relationship,

$$\theta = \sin^{-1} (2\, rh) / (r^2 + h^2) \qquad (24)$$

where h is the height of the top of the drop above the plane of the surface and r is its radius when viewed from above (Deshmukh and Bhat 2003). Here it is assumed that the droplet is sufficiently small so that gravitational effects on drop shape can be neglected. Also, the spreading in different directions on the surface needs to be relatively uniform in order to apply Eq. 24 with precision.

Some researchers have advocated the application of vibrations during contact angle assessment, with the aim of achieving values more representative of an equilibrium contact angle (Decker *et al.* 1999; Della Volpe *et al.* 2002; Fabretto *et al.* 2003; Meiron *et al.* 2004; Della Volpe *et al.* 2006). Such vibrations have been shown to "force equilibration" and to cause the advancing and receding branches of data obtained from a dynamic wettability experiment with a Wilhelmy plate (see later) to converge (Della Volpe *et al.* 2002). However, it has not been demonstrated whether or not the use of vibrations would be an appropriate approach in the case of typical cellulosic surfaces.

Droplet time-lapse changes

Microvideographic equipment has become widely available for rapid evaluation of the contact angles of droplets. Rapid data acquisition can be helpful in being able to minimize the effects of absorption on the contact angles measured on cellulosic surfaces (Kalnins *et al.* 1988; Mohammed-Ziegler *et al.* 2004; Kannangara *et al.* 2006). The method can also be used to evaluate rates of absorption into pores.

Kannangara *et al.* (2006) found that droplets impinging onto the surfaces of hydrophobically sized paper surfaces initially exhibited advancing contact angles corresponding to a hydrophobic surface. But upon recoil of the droplet, a fraction of a second later, the receding contact angle was consistent with a hydrophilic surface. Thus, it appears that processes such as absorption and swelling of the solid material happen so rapidly as to interfere with any effort to evaluate a true equilibrium contact angle. If the fluid begins to be wicked into the openings of pores, within the first moments of contact, then it is uncertain whether the contact line would be able to retract from the position of greatest spreading. Lu and Wu (2006) employed dynamic evaluation of sessile drops and characterized wetting rates based on the spreading of the droplets. The ratio of spreading was found to correlate with the surface tensions of the probe liquids.

Captive bubble

Most investigators make the assumption that a droplet freshly placed on a solid surface is more likely to represent an advancing contact angle than a receding angle. In cases where investigators want to investigate receding contact angles, a bubble of air can be placed at the solid-liquid interface (Ruiz-Cabello *et al.* 2011). It has been proposed that results of such captive bubble experiments are more clearly representative of receding angles than some alternative approaches (Rodríquez-Valverde *et al.* 2002).

Capillary rise height

The levels of capillary rise or wicking in a packed bed, paper strip, or porous film can be used as the basis for estimation of contact angles (de Meijer *et al.* 2000). However, in the case of cellulosic materials there are various inherent problems with such an approach. Perhaps the most important is that the pore dimension within a packed bed of fibrous or particulate material does not have a fixed value. The presence of abrupt edges and complex junctions within the pore network can potentially impede progress of capillary rise in a hard-to-predict manner (Kent and Lyne 1989). Also, the tendency of cellulosic materials to swell in the presence of water and certain other liquids can be expected to change the characteristic sizes of pore spaces in the material (Heng *et al.* 2007; Li 2014b). So while the method may seem very relevant for certain applications, one should be cautious regarding the accuracy of values of contact angle that emerge from such an analysis.

Fiber floating

For quick evaluations, van Hazendonk *et al.* (1993) recommended placement of a particulate solid material into a series of liquids, all having a lower density than that of the solid and watching to see whether the material stays on the surface (van Hazendonk *et al.* 1993). The cited work employed various mixtures of 1-methylnaphthaline and octane to achieve surface tensions in the range of 22 to 38 mJm^{-2}. The advantage of the method is that it provides a clear demarcation between “floating” (not wetting) and “sinking” (wetting). However, it needs to be pointed out that the method does not indicate to what extent the observed effects are attributable to physical chemical aspects or morphological aspects of the surfaces. Though the cited authors stated a goal of developing a method insensitive to the effects of morphology, it seems likely that aspects such as particle roughness and their relative tendency to cling together and trap bubbles will affect the results of this kind of tests.

Rivulets

Gajewski (2002) showed that contact angles also can be derived from the widths of “rivulets” of fluids steady flowing down an inclined surface. In particular, it was shown that such measurements can be made reliably even when the flow deviates from a path predicted by gravity.

Dynamic Wetting Tests

Contact angles on cellulosic surfaces are often highly dependent on time. This section will be concerned with methods in which the time-dependency of wetting phenomena is intentionally evaluated. Several review articles have dealt in particular with such issues (de Gennes 1985; Gardner *et al.* 1991; Chibowski 2003; de Meijer *et al.* 2000). Some of the key factors giving rise to the time-dependency of wetting and contact angles on cellulosic surfaces are (a) movement of the line of contact of a meniscus with an outer surface of a solid, *i.e.* spreading, (b) permeation of the liquid into pores, (c) time-dependent changes in the receptivity of the surface resulting from the interaction with the liquid, (d) swelling of the cellulosic material, and (e) evaporation. As described in the subsections that follow, several different practical approaches are available for evaluating the dynamic wettability of cellulosic surfaces, and there are ways that such tools can be used in the future to evaluate such things as the rates of permeation and different components of surface free energy of modified cellulosic surfaces.

Wilhelmy “DCA” method

Figure 7 illustrates the most widely employed means of obtaining both advancing and receding contact angle information, including such samples as strips of paper or relatively long cellulosic fibers, especially in the case of regenerated cellulose fibers

(Miller *et al.* 1983; Gardner *et al.* 1991; Jacob and Berg 1993b; Gunnells *et al.* 1994; Mantanis and Young 1997; Wistara *et al.* 1999; de Meijer *et al.* 2000; Shen *et al.* 2000; Whang and Gupta 2000; Wålinder and Ström 2001; Wålinder and Gardner 2002b; Brugnara *et al.* 2006; Gérardin *et al.* 2007; Wang *et al.* 2007; Bryne and Wålinder 2010; Moghaddam *et al.* 2014; Petrič and Oven 2015). The term "dynamic contact angle" (DCA) has been widely used for experiments of this type, which are based on the Wilhelmy plate principle (Wilhelmy 1863). Such an approach also has been applied to the evaluation of wood pulp fibers, though the short lengths of such fibers tend to make such measurements difficult (Young 1976; Klungness 1981; Hodgson and Berg 1988; Jacob and Berg 1993a; Shen *et al.* 1999). Advancing and receding angles can be readily measured on single textile fibers, as long as one employs a vibration-free environment and a highly sensitive balance (Young 1976; Miller *et al.* 1983). Uyama *et al.* (1991) compared various experimental approaches to obtaining advancing and receding contact angles and concluded that DCA tests using the Wilhelmy method were the most reliable and provided the most information. Hodgson and Berg (1998) found that DCA measurements carried out with single fibers produced results that were well correlated with the wetting behavior of random pads of those fibers. By employing sequences of 10 to 20 repeated cycles of advancing and receding analyses, Mogghaddam *et al.* (2013, 2014) were able to characterize swelling rates in addition to advancing and receding contact angles.

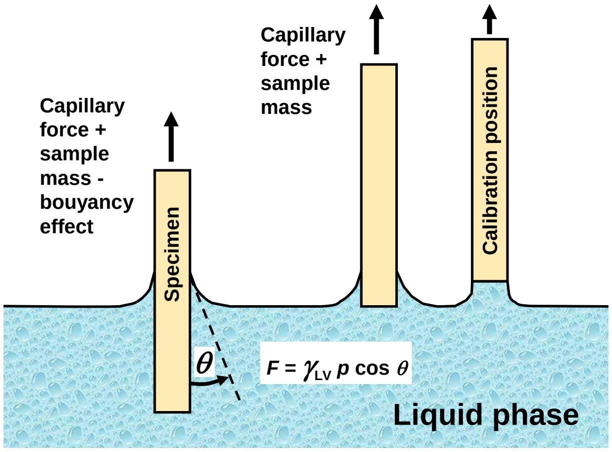


Fig. 7. Schematic illustration of dynamic contact angle measurements by means of the Wilhelmy plate method

By knowing the air-fluid surface tension, one can employ the measured force (using a microbalance) to evaluate the capillary force according to the following equation (Jacob and Berg 1993a),

$$F = \gamma_{LV} p \cos\theta - \rho_L g A h \tag{25}$$

where F is the total force sensed by the microbalance, γ_{LV} is the surface tension of the probe liquid, p is the wetted perimeter, θ is the contact angle, ρ_L is the density of the liquid, g is the gravitational acceleration, A is the cross-sectional area, and h is the depth of immersion of the fiber. Also, it is assumed that the total mass of the specimen in air has been taken into consideration by initially taring the device before the first contact between the specimen and the liquid. Depending on whether the level of the fluid is being raised or lowered at a specific time, the determined values of θ can be either advancing or receding. As noted by Miller *et al.* (1983), a value for the perimeter of a suitably uniform fiber can be obtained by performing a calibration with the specimen at a position illustrated at the far right-hand side of Fig. 7. Under such a condition the effective contact angle will equal zero, giving the largest force exerted on the microbalance, equal to the sample mass plus the product of surface tension and perimeter.

Figure 8 shows replotted results from DCA analysis of a strip of fresh, unmodified wood being wetted by water (Bryne and Wålinder 2010).

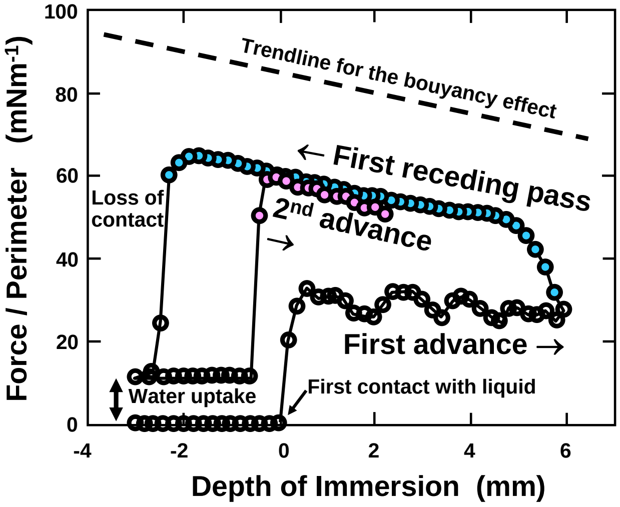


Fig. 8. Dynamic contact angle (DCA) test results replotted from Bryne and Wålinder 2010 for fresh, unmodified Scots pine wood being wetted by water

As shown, there was a sharp increase in measured force when the height of the probe liquid had been raised just far enough to first come into contact with the liquid. However, as is apparent from the graph, the force was markedly uneven during the first advancing pass of liquid to wet the wood specimen. This unevenness is tentatively attributed to the temporary pinning of the contact line on features such as open pores. The subsequent "first receding pass" was much steadier, which suggests that the contact angle remained steady (probably near to zero) during this part of the cycle. At the point where contact was lost between the liquid reservoir and the wood specimen, the force jumped back down, but not all the way to its original tared value. The difference can be attributed to absorption of some water into the lumens or cell walls within the wood. It is notable that the second advancing pass values closely resembled those of the first receding pass. This coincidence suggests that the pores at the surface of the wood were filled with water and therefore did not offer any resistance to wetting. Thus, these results may provide confirmatory evidence to support the mechanism associated with Eq. 19, as described earlier.

As an alternative to carefully measuring each of the terms in Eq. 25, the effect of buoyancy can be accounted for by obtaining the slope of a regression line through the data either during the advancing or the receding part of the cycle. To calculate the instantaneous or average values of the advancing angle θ_A or the receding angle θ_R one must make an estimate of the perimeter, *p*, of the test object. As indicated by the illustration, one of the nice features of this type of analysis is that it can provide an indication of heterogeneity. Although heterogeneity would usually be expressed as a standard deviation of θ_A or θ_R, presumably attributable to roughness, porosity effects, or chemical heterogeneity, it is also possible that the object (such as a cellulosic fiber) has variable cross-section. Only in cases where the perimeter is relatively constant will the observed variations in either θ_A or θ_R provide a reliable measure of contact angle heterogeneity.

A limitation of the Wilhelmy-type DCA analysis, as just described, is that the wetting process has to be quite slow. Thus, in terms of evaluating short-term wetting, the method cannot compete with high-speed observation of drop shapes. Also, in the case of paper strips, the signal often can be dominated by the absorption of fluid, as well as the wicking of fluid within the test strip above the level of the meniscus. Such uptake of water can render the contact angle results difficult to interpret in such cases.

Dynamic advancement and retraction of sessile drops

It is also possible to measure advancing and receding contact angles by means of a modified type of sessile drop evaluation (Lam *et al.* 2001). Such an approach has been applied relatively seldom for testing of cellulosic surfaces (Dankovich and Gray 2011). In principle, liquid can be added to or removed from an existing sessile drop by means of a syringe needle, which either can enter the droplet directly, or it can up from underneath by means of a small hole placed in the surface to be evaluated. Figure 9 illustrates how a receding angle might be obtained by withdrawing liquid from a sessile drop until the point where the line of contract is prompted to retract its position.

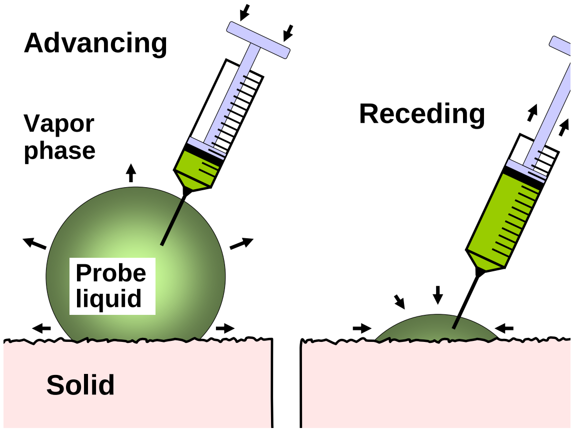


Fig. 9. Schematic illustration of an advancing and receding liquid front, depending on whether liquid has just been injected or withdrawn from the droplet

Based on the relatively few reported measures of receding contact angles in cellulosic surfaces, values of θ_R are often near to zero (Hodgson and Berg 1988). This finding underscores some points made earlier about the nature of typical (uncovered) cellulosic surfaces: They are very rough on a nano-scale and they have various kinds of pores. Also, as predicted by the Lucas-Washburn equation (Eq. 22), many of those pores will have become partly filled with the probe liquid, depending on the time of contact and other factors. There appears to be an opportunity to combine the capability of rapid videography with automated retraction of sessile drop volumes, such that the dynamics of contact angle recession can be evaluated at very short times.

Baptista *et al.* (2012) pioneered the use of simultaneous observation of sessile drops from more than one angle. Such observations revealed that there can be strong deviations from the symmetrical drop shapes assumed in many routine analyses. The three-dimensional method was shown to be effective for the evaluation of the dynamic behavior of wetting fronts.

Microscopic evaluation of the wetted areas of sessile drops has the potential to provide further evidence regarding the wetting of cellulosic surfaces. For instance, a dye can be used so that there is lasting evidence of the drop's perimeter in the contact zone. Feathering phenomena are of particular concern during inkjet printing (Fischer 1999). In other words, an applied droplet of ink may spread preferentially along the edges of fibers. Feathering also can be evaluated by image analysis and by viewing the sharpness of inkjet printed images. Also, by use of a microdensitometer, such as are used in print evaluation, it is possible to evaluate the optical density of a stained or printed area resulting from application of colored fluid. Such optical density measurements can be interpreted in terms of the extent to which the chromophores have permeated into the interior of the material, presumably by passage into a porous network (Kettle *et al.* 2010; Sousa *et al.* 2014).

Absorption Rate Tests

In addition to evaluating advancing contact angles, it is often important to be able to evaluate the rates at which wetting fronts permeate or wick into a porous material. Several test procedures, to be considered in this section, are of particular interest to technologists working with cellulosic materials such as wood and paper. These include capillary rise rate tests, thin-layer wicking rate tests, amounts of fluid transferred during very brief, controlled contact, and various tests to determine the rates of absorption of fluids into paper products.

Rates of capillary rise and wicking

Capillary rise or wicking rate analysis can be used as a tool to study aspects of the wettability of cellulosic materials (Labajos-Broncano *et al.* 1999; Wålinder and Gardner 1999; de Meijer *et al.* 2000; Aranberri-Askargorta *et al.* 2003; Peršin *et al.* 2004; Masoodi *et al.* 2010, 2011; Fan *et al.* 2013; Mei *et al.* 2013). Such methods typically make reference to the Lucas-Washburn equation (Eq. 22; Lucas 1918; Washburn 1921) as the basis for interpretation of the results. The first challenge has been to assign a value to the quantity r, the effective radius of pores. For such a purpose it has been recommended to run comparative tests with a probe liquid having sufficiently low surface tension as to ensure a zero-degree contact angle (Hodgson and Berg 1988). The rate of capillary rise and other values for the calibration liquid are used to solve for r in the equation. Then one repeats the process for a selected liquid of higher surface tension, and the resulting data can be used to solve for the unknown value of θ. The approach seems to be valid as long as the probe liquid's surface tension remains constant and as long as there is no significant swelling of the solids. If geometric parameters of the system shift due to swelling, then the numerical results can be expected to shift relative to the calibration test (Heng *et al.* 2007; Li 2014b).

Edge-wicking tests, which are important for the evaluation of various laminate paperboard products intended for liquid packaging applications, are described by Lyne (2002). Such tests can employ pressurized systems to shorten the time required for testing. Results can be interpreted to show how the porosity of the paperboard changes with time in response to swelling of the cellulosic material during liquid penetration.

Essentially the same physical situation, with the possible exception of the effect of gravity, is involved when investigators employ thin-film wicking as a means to study wetting phenomena (Dourado *et al.* 1998; Simončič *et al.* 2008). However, as long as one focuses on short-term trends, the gravity effects may not yet be significant relative to capillary suction and viscous effects.

Bristow wheel and related methods

The Bristow wheel device, as illustrated in Fig. 10, has been used in several research project aimed at clarifying the mechanisms and rate of wetting of paper products (Bristow 1967; Aspler *et al.* 1984; Yamazaki and Munakata 1993). Related devices and procedures have been described (Sweerman 1961; Bikerman and Whitney 1963; Rosen and Hemstock 1967), which appear to follow the same mechanistic principles.

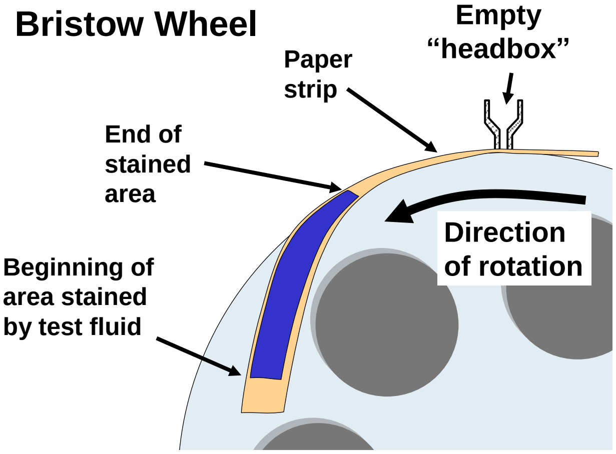


Fig. 10. Schematic illustration of the Bristow wheel apparatus for evaluating the rate of absorption of test fluid into the surface of paper

As shown, the apparatus consists of a slowly rotating wheel, around which is wrapped a narrow strip of paper. A calibrated quantity of colored test fluid (usually 50 μL) is placed in a small metal reservoir ("headbox") having an open top and a 1 mm slot at its base (Bristow 1967). The headbox is lowered into contact with the paper at time equal to zero, and the circumferential velocity of the wheel determines the contact time of the liquid with the surface (*e.g.* 4 to 2000 ms) during which fresh fluid is flowing into the sample.

The headbox becomes empty of fluid at a rate that depends on the wettability of the paper material, as well as its porosity and the roughness of its surface. To evaluate the results, one measures the length of the colored area on the paper strip.

The way that the colored fluid may interact with the paper is shown schematically in Fig. 11.

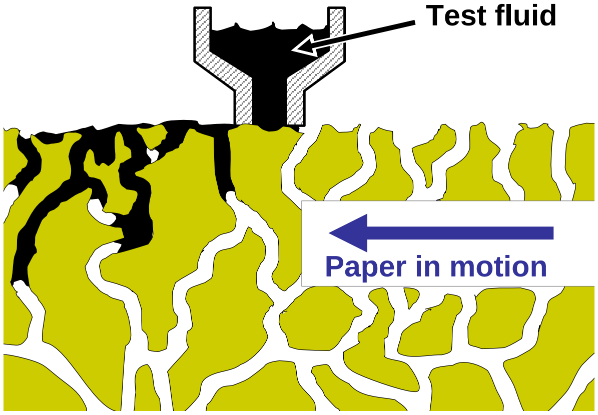


Fig. 11. Schematic illustration representing test fluid flowing from a tiny open-bottomed chamber (headbox) into a paper strip during operation of an experiment with a Bristow wheel

Figure 12 is a schematic illustration based approximately on data reported by Bristow (1967). Several important points can be drawn from these results. First, a certain amount of fluid appeared to be taken up by the paper immediately, and this was the case regardless of the test fluid. This amount was attributed to the surface roughness. Related observations were reported by Labajos-Broncano *et al.* (1999), who studied wicking into silica gel plates. Second, data for the wetting of nonaqueous fluids on the surface generally can be fitted accurately to a constant multiplied by the square-root of the duration of contact time with the reservoir of colored fluid. Such results are a confirmation of the applicability of the Lucas-Washburn equation (Eq. 22) to such systems. Third, in the case of an aqueous fluid, the results generally show that uptake of the liquid was “delayed” (Aspler and Lyne 1984). Thereafter, the results followed a line parallel to that predicted by the Lucas-Washburn equation. It is likely that the delay is related to a rate of adsorption of vapor onto surfaces ahead of a wetting front of liquid. In the case of an aqueous fluid, the speed at which a meniscus advances may also be related to the rate of swelling of the cellulosic material.

It had been shown earlier that by subtracting an adjustable “time of wetting”, it is sometimes possible to line up the data with a linear relationship that passes through the origin, thus matching the Lucas-Washburn equation, within the repeatability of the method (Hubbe *et al.* 2013). The wetting delay has been attributed to the time required for cellulosic material to swell in advance of a front of aqueous liquid (Lepoutre *et al.* 1985). As noted in the cited work, such a mechanism is consistent with the known effect increased wetting rates of cellulosic material with increasing initial moisture content because of equilibration at higher humidity.

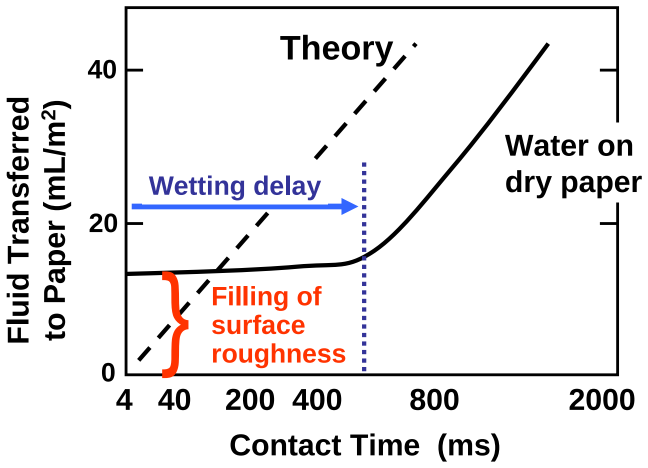


Fig. 12. Schematic illustration of typical absorption rate data obtained from the Bristow wheel test

New insights regarding the mechanism of absorption have been revealed by short-duration absorption tests. For instance, Yamazaki and Munakata (1993) found good agreement of Bristow test data, using a range of solutions of poly-(ethylene glycol) in ethyl alcohol and four typical grades of paper.

Concepts of tortuosity and mean pore radius, as determined by mercury porosimetry, were found to give good fits to the data based on the Lucas-Washburn equation (Eq. 22). Lyne and Huang (1993) used the Bristow wheel apparatus to determine the wettability of paper by probe liquids selected to sense acidic and basic characteristics. Wålinder and Gardner (1999) observed generation of heat ahead of the advance of a meniscus, which is consistent with a mechanism of swelling of the cellulose material from its interior in advance of its actual wetting by an adjacent liquid phase. Modaressi and Garnier (2002) found similar effects in their study based on rates of absorption of water droplets into paper. Liu *et al.* (1995) introduced the concept that microdomains at the surface may be affected by ageing and activation phenomena, depending on their environment. Such concepts merit further examination in future work.

Surfactant effects

A surprising finding by Aspler *et al.* (1987) was that addition of surfactant to the aqueous test fluid did not significantly affect the results of Bristow wheel tests, when compared relative to the results with water used as the test fluid for evaluation of hydrophobically sized sheet of paper. These results are shown replotted in Fig. 13. Such a result may seem odd in light of the fact that the amount of surfactant was sufficient to lower the surface tension to match that of a non-aqueous fluid that gave an excellent fit to the Lucas-Washburn equation, showing no delay in wetting. This apparent disagreement can be attributed to the fact that the dynamic wetting situation does not allow sufficient time for surfactant molecules to reach the interface in sufficient quantity to lower the value of γ_{lv} much below that of pure water (Aspler *et al.* 1987).

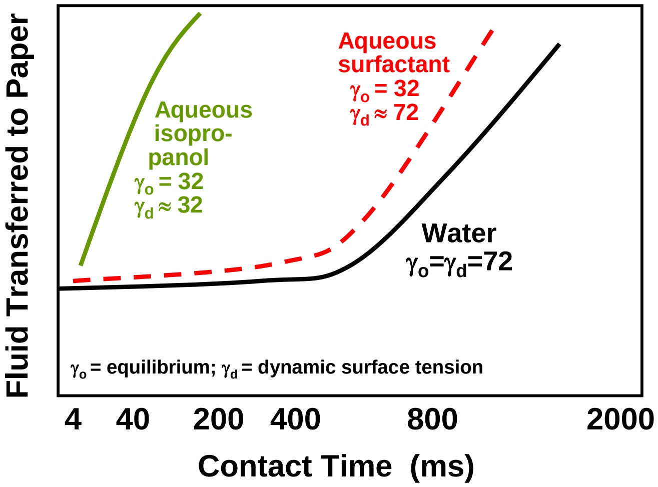


Fig. 13. Replotted data of Aspler *et al.* (1987) comparing three contrasting liquids and their absorption rates into paper

Converging and diverging pores

In certain cases it may be appropriate to replace the assumption of cylindrical pores with other idealized shapes that are closer to the actual situation of interest. For example, Kent and Lyne (1989) suggested that by selection of the shape and size distribution of mineral particles used to coat paper it is possible to engineer the rapid uptake of liquid. Converging "entrance pores" at the external surface of specially prepared paper can be expected to fill very rapidly with applied fluid. By contrast, sharp angles and divergent pores immediately below the entrance pores can have the function of impeding further permeation of the applied fluid into the structure. The suggested mechanism is based on the contrasting effect of convergent *vs.* divergent pores on the capillary forces – especially in the case of liquids exhibiting non-zero contact angles on a smooth, nonporous surface of the same composition. The driving force of a wicking liquid in a capillary is the curvature of the meniscus at the wicking front. In a converging pore, liquid having a given contact angle with the capillary wall will have a much higher curvature than liquid having the same contact angle but in a cylindrical pore (higher curvature corresponds to smaller radius of curvature). In a sufficiently divergent pore, what started out as a positive capillary force favoring wetting of a cylindrical capillary may become neutralized or even reversed. Any discontinuity on the wall of a capillary will deform the curvature of the meniscus of the wicking liquid and change the driving force (therefore the wicking velocity) of the liquid.

When abrupt angularity and frequent changes are present in a network of pores, there will be numerous points where the capillary forces will be either promoted or decreased or even become negative. The complexity of the situation suggests opportunities for computer modeling based on various stochastic models of the pore system. Otherwise, because of the multiple possible paths that liquid can follow within the network of pores, it may be difficult to predict the effect of irregularities in the network of pores.

Applied pressure

The conventional Bristow wheel experiment appears best suited for the study of systems in which fluids are left to absorb into porous material solely by capillary action. For instance, absorption of inkjet ink ordinarily takes place by capillary forces alone, with no applied pressure. But the situation can be quite different in processes where there is a pressure applied to help drive the permeation process. It has been found that capillary forces become less and less important as an applied pressure is increased to force fluid into the porous material (Masoodi *et al.* 2010). Salminen (1988), who applied pressure while running tests analogous to the Bristow wheel tests, found that it was not necessary to consider capillary forces at all when accounting for the observed rates of movement of liquid into paper strips. Thus, there was no effect of changes in the surface tension of the probe liquid on the observed rates of penetration, even with modest applied pressures. This demonstrated that under pressure the liquids wetted the surface instantly and that capillary effects were overcome. Notably, the possible effects of applied pressure and gravity, in addition to capillary force, were already considered by Washburn (1921).

Ultrasonic sensing of absorption dynamics

In cases where it is important to differentiate between effects occurring within very short time periods, it can be advantageous to employ a system based on the amplitude of ultrasound transmission (Bayer *et al.* 1996). As described in the cited work, such measurements allow detection of the onset of penetration of water into paper as early as 40 milliseconds after its rapid immersion. Such measurements rely upon the fact that sound transmission takes place much more readily through a continuous phase of water, in comparison to water that is interrupted by an initially dry sheet of paper. Though the details of responses from the device are also affected by such factors as the change in modulus of elasticity of the paper upon wetting and the likely presence of bubbles, there is almost no other established way to detect such ultra-fast effects associated with wetting.

Sizing tests used by papermakers

As was noted in the introduction to this article, a variety of practical tests are in routine use in production facilities to assess and to be able to adjust the wettability of paper products (TAPPI 1989b, 1990). Although these tests generally had not been designed with the idea of studying the surface free energy or adhesion aspects of the surface, the concepts discussed earlier in this article clearly play major roles in the outcomes of such tests. It is worth noting that the “angle of contact method”, *i.e.* a sessile drop test, is also considered to be an established method for papermaking applications (TAPPI 1989a).

Papermakers have known that the rates of liquid permeation of paper can be greatly affected by one’s choice of test fluid. For instance, the rate of permeation of hot coffee into hydrophobically sized paper is likely to be much more rapid than when using room-temperature water as the test fluid. Likewise, the use of acidic (formic acid) solution can be used as a practical means of speeding up the testing (Chen and Biermann 1995; Sun *et al.* 2014). To proceed further towards revealing aspects described in earlier sections of this article, there is potential to modify some test methods that are widely used in industry by employing test fluids having contrasting hydrogen bonding ability, London/van der Waals capability, Brønsted acidity or basicity, as well as viscosity to gain further evidence of what fundamental factors are the most important for wetting and permeation of liquids for a given cellulose-based product. In general, fluids having lower surface tension can be used to speed up wettability tests and to provide more challenging specifications of hydrophobization of paper products.

In the Bristow wheel test (Bristow 1967), most past work has been done with dyed water, or with various alcohol-water mixtures as a means of adjusting the surface tension and rendering the test more challenging with respect to achieving hold-out of the liquid. But given the relatively small amount of test liquid required for an individual test, there is opportunity to substitute other liquids such as methylene iodide (a neutral, non-polar compounds having a very high Hamaker constant), as well as selected Lewis acids and bases. Also there is a need to follow up on the groundbreaking work of Jacob and Berg (1993b) by use of the Bristow test using aqueous buffer solutions of differing pH. The cited authors observed some interesting dependencies of contact angles on pH, and it would be interesting to see whether such differences also can affect rates of absorption. In such situations it may be advantageous to employ combinations of practical and more fundamental tests of wetting and liquid penetration – allowing a more complete understanding of industrial practices related to the wettability of cellulosic materials.

Alternative Experimental Approaches for Surface Free Energy

Given the practical and theoretical difficulties inherent in contact angle measurements, as already discussed in this article, there is a motivation to consider completely different approaches to gain information about wettability and surface free energy aspects of cellulosic surfaces. The two most important alternative approaches that have been considered in this regard are inverse gas chromatography (IGC) and calorimetry.

Inverse gas chromatography

The inverse gas chromatography (IGC) method, to be reviewed briefly here, provides an alternative means of evaluating surface free energy of materials without the need to deal with a liquid phase (Planinšek and Buckton 2003). In principle, by use of IGC, one can avoid problems associated with contact angles such as pinning on large ridges (Riedl and Kamdem 1992). Application of the IGC method to cellulosic surfaces has been reviewed (Berg 1993; Williams 1994; Gamelas 2013). Also, the method has been employed in several investigations of paper materials (Dorris and Gray 1979, 1980; Kamdem and Riedl 1992; Felix and Gatenholm 1993; Garnier and Glasser 1994; Shen *et al.* 1999; Wålinder and Gardner 2000; Tze and Gardner 2001a; Cantero *et al.* 2003; Tze *et al.* 2006). Tze *et al.* (2006) showed that IGC can be used to predict the adhesion between various modified or unmodified cellulosic surfaces and a polystyrene matrix. Acid-based interactions were shown to play an important role. The IGC method can be regarded as being just like conventional gas chromatography (GC) with the exception that with IGC the probe liquid is presumed to be pure and known, and one aims to characterize the properties of the (unknown) solid materials.

In the cited work related to cellulosic materials, the investigations employ various volatile components mixed very dilutely in inert carrier gases such as nitrogen and argon. The cellulosic material – usually in the form of a dry powder – is placed in a column at controlled temperature. The retention times (and the corresponding retention volumes) are compared between different probe compounds having different known attributes. For example, alkanes of different chain length have been used to evaluate the dispersion component of surface free energy (Dorris and Gray 1980).

Because of its very different mode of operation, one can expect that the IGC method will provide information that is substantially different than what is provided by contact angle measurements. The role of micropore adsorption of probe compounds merits cautious attention, given the known presence of such pores in some cellulose-derived materials (Allan *et al.* 1991; Chowdhury *et al.* 2013). López-Garzón *et al.* (1993) found that the concave curvature of surfaces within micropores was able to account for the higher energy of adsorption of probe molecules within activated carbons. Gun'ko and Bandosz (2003) likewise found that porosity affected the energy of adsorption during inverse gas chromatography experiments. Such behavior may help to explain why some estimates of the dispersion component of surface free energy of cellulosic materials, based on IGC analysis, have tended to be higher than can be explained based on their chemical composition (Luner and Sandell 1969; Felix and Gatenholm 1993; Garnier and Glasser 1994; Heng *et al.* 2007; Gamelas 2013). Peng *et al.* (2013) detected unusually high values of the dispersion component of surface free energy when evaluating cellulosic nanofibrils that had been freeze-dried. Since conventional drying is known to result in closure of small pores, the findings can be interpreted as evidence of interactions within micropores. The usual explanation for the relatively high numbers obtained by IGC analysis is that at very low levels of coverage employed in such work, only the highest energy sites tend to be occupied by probe molecules (Jacob and Berg 1993a; Planinsek and Buckton 2003; Gamelas 2013). Also, there is reason to expect that adsorption of relatively non-polar compounds from the air on cellulosic surface will be strongly influenced by interactions leading to capillary condensation (Zhou *et al.* 2010). Such effects are minimized by working at very low partial pressures of the probe compounds (Dorris and Gray 1980). Adsorption in micropores tends to be anomalously strong and relatively irreversible (Auroux 2008), which calls into question any energy information derived from IGC evaluations on such surfaces.

If IGC data are to be relied upon, it would be reassuring to be able to find relationships between the energy of adsorption and the chemical nature of the solid material. However, the data of Heng *et al.* (2007), if one removes one outlying point, fail to show any significant relationship between the surface energies of different cellulosic materials relative to their chemical composition. So it is not clear than anything useful was being measured. Planinsek and Buckton (2003) also noted concern that polar probe molecules can interact with amorphous regions of cellulosic materials in ways that do not correctly correspond to surface free energy.

It is important to recognize some key differences between a column filled with cellulosic material in comparison to typical packing materials used for conventional gas chromatography. Many GC column materials are in fact gas-liquid chromatography (GLC) packing materials in which there is a thin film of liquid present on the particles (Berezkin 1996). The chromatographic separation of different unknown compounds in a sample of volatile compounds passing through such a column can be attributed to differences in solubility in the prepared liquid films. Nonporous GC packing materials may be selected to avoid uncertainties regarding possible condensation of compounds in micropores (Wu *et al.* 1999). Also, rather than trying to interpret retention times mechanistically, most work that has been carried out with conventional GC and GLC methods is based on comparison of retention times with those of known standard compounds without much concern paid to mechanistic aspects (Heberger 2007).

The situation is more demanding if one's aim is to characterize the solid phase. As a practical matter, given the widespread availability and relatively simple operation of GC equipment, one can regard IGC as a useful tool for probing surface free energy aspects of cellulosic materials. Only tiny quantities of samples or probe compounds are required, and the testing can be rather quick. It would appear that there is opportunity to achieve further gains by employing a range of compounds having known Hamaker constants (for London/van der Waals dispersion interactions) (Visser 1972), acidity and basicity (Drago *et al.* 1977), and hydrogen bonding ability (Tate *et al.* 1996; Thomas 2004).

Attention may be paid also to the effect of different concentrations of the probe compounds in the gas mixture, perhaps to extrapolate to the point where self-association and micropore condensation effects can be ruled out, thus simplifying the interpretation. Thus, there appears to be a need for further study of cellulosic surfaces by means of IGC methods.

Microcalorimetry

Adsorption calorimetry, using probe gases, provides a way to directly measure the heats of interactions of probe molecules with solid materials (Auroux 2008). In view of the strong emphasis on surface free energy as a means of accounting for wettability and adhesion to cellulosic surfaces (Nguyen and Johns 1979; Etzler *et al.* 1995; Dourado *et al.* 1998; Shen *et al.* 2000; Gindl *et al.* 2001a; Mohammed-Ziegler *et al.* 2004; Heng *et al.* 2007; Dankovich and Gray 2011; Rossi *et al.* 2012; Little *et al.* 2013; Li 2014a,b; Qin *et al.* 2014), it is reasonable to consider calorimetry as a potentially useful experimental approach. Such approaches have the potential to avoid the serious concerns mentioned earlier regarding whether the quantities detected by contact angle measurements are directly related to the surface free energy of solid materials (Fowkes *et al.* 1990). Calorimetric measurements leave no such doubts, since they measure heat directly. However, another kind of doubt can arise, especially in the case of cellulosic surfaces. That is, it may be difficult to tell whether a detected heat of interaction can be assigned to an external surface, the area of which can be estimated. In this respect, concerns about micropores and interactions with amorphous regions, as already discussed relative to IGC determinations, will give rise to similar concerns in the case of calorimetric determinations of energies of interaction at cellulosic surfaces. Thus, the generation of heat may be attributable to adsorption of a gaseous probe molecule within pore spaces that would not have had a chance to interact with a spreading meniscus. In other words, rather than sensing aspects of the exposed surface, a calorimetric approach may be more related to evaluation of three-dimensional interactions within a highly porous medium (López-Garzón *et al.* 1993). Such information might be revealing, but it would be inherently difficult to relate the findings to parallel measurements by means of contact angles.

WHAT NEXT FOR SURFACE FREE ENERGY OF CELLULOSIC SURFACES?

As revealed by many studies already cited in this article, there are many serious unresolved problems related to the interpretation of contact angles at cellulosic surfaces. The accuracy and even the validity of much of the published quantitative information related to the surface free energy components of such surfaces remain in doubt in a great many cases. This final section of the article will consider some possible directions of research that might help to resolve parts of this impasse in the coming years.

General goal: Separate chemical issues from morphological issues

Given the fact that serious theoretical and practical issues have been encountered both with respect to the physical chemical aspects of contact angle analysis, and also with morphological issues such as roughness and porosity, it would appear that some innovative approaches are needed. One such approach might involve more scrupulous separation of the physical chemical issues from the morphological issues. Accordingly, the next subsections will consider possible strategies to render cellulosic materials highly flat and nonporous, as well as strategies to render a non-flat and porous cellulosic surface highly uniform in surface chemical content. It will be proposed that the Wenzel and Cassie-Baxter equations become integrated as part of the mathematical structure in future models aiming to understand the wetting interactions of cellulosic surfaces. Then, it will be proposed that a new set of “designer probe liquids” be developed, each of which combines high surface tension in combination with selected Lewis acid or base character. It will be proposed to add an additional term corresponding to hydrogen bonding, in an enhanced model that also includes a London/Lifshitz dispersion term and a pair of terms for Lewis acid-base interactions. It will be proposed to carry out a calculation similar to that employed by Fowkes *et al.* (1990), but this time taking an opposite approach – working to develop a new theory-based model that also happens to fit the available data. New modeling work is also needed in order to account for the effects of three-dimensional porous structures on the contact angles and positions of menisci that involve different degrees of simultaneous penetration into the material. It will then be proposed that more detailed surface chemical characterizations be done to explain observed degrees of wettability based on chemical effects. On a practical side, it will be proposed that there be more systematic study of the wettability characteristics of cellulosic materials that have a wide range of moisture content. And finally, a set of recommendation will be given relative to industrial use of analysis systems involving contact angles and wettability.

Render the Surface Flat and Nonporous

Sample preparation to remove roughness and surface pores

Suppose that your goal is to evaluate the wettability characteristics of a certain cellulosic surface in a way that is not affected by the specimen’s roughness or porosity. A potentially useful way to overcome the effects of roughness and porosity on contact angle measurements would be to apply sufficient pressure against a polished surface in the presence of sufficient moisture and a high enough temperature to plasticize the material and press it into a dense, very smooth format (Fang *et al.* 2012). For example, Zhang *et al.* (2006) densified lactose into the form of a disc before evaluating the forces of surface interaction. Narayan and Hancock (2005) showed that cellulosic surface having roughness less than 2 μm could be achieved by compaction of fine microcrystalline cellulose powders. High-speed contact angle measurements, as described earlier, could be employed to minimize the effects of swelling of the solid, especially when using water as a probe liquid. The smoothness of a pressed surface would be expected to give contact angle data closer to equilibrium values.

In view of the fact that even a partial monolayer of oleophilic material can affect wettability, great care would be required to avoid introduction of contaminants from the pressing equipment. Densification of wood has been found to increase its hydrophobic character (Unsal *et al.* 2011; Kutnar *et al.* 2012), an effect that might be attributable to the migration of oleophilic monomers to the surface. Contamination of surfaces may be hard to avoid during the kind of pressing suggested above. Hot, humid conditions can be expected to accelerate the migration of low-mass oleophilic materials to the surface of a cellulosic material (Swanson and Cordingly 1959). Also, the mechanical processing could be expected to smear waxy substances over cellulosic surfaces, especially if the device is not scrupulously cleaned, down to a molecular level, between specimens. Chemical reactions might be induced as well. Thus, the resulting wettability aspects are likely to be a function of processing conditions such as temperature and moisture content during compression and flattening. In effect, by rendering the surface as flat as possible, one necessarily has to change the material so that it is no longer the original cellulosic material. Such uncertainties may be an unavoidable aspect of tests involving non-purified cellulosic materials.

Nanocellulose thin films

As has been noted earlier, one of the strategies to minimize contact angle hysteresis effects has been to prepare thin films of nanocellulose, thus achieving very low levels of roughness (Edgar and Gray 2003; Dancovich and Gray 2011; Rodionova *et al.* 2012). Also, very low differences between advancing and receding contact angles have been found in some such cases (Dancovich and Gray 2011). Because the component parts of such a structure will have dimensions within a range of about 5 to 100 nm, it is plausible to propose that thermal vibrations will be sufficient to allow wetting fronts to bounce freely between different metastable positions (Johnson and Dettré 1964a,b; de Gennes 1985). Two potential problems to keep in mind, when pursuing such experimentation, concern the discontinuous nature of such films and uncertainties about their adhesion to a support surface.

Research is needed to consider a hypothesis that the meniscus that one detects, by means of contact angle determinations on such a nanocellulose film surface might be associated with a three-dimensional surface zone. The material may be initially dry, but it may become saturated with liquid. Further research may reveal whether such surface zones can fluctuate between a relatively dry and a relatively wet condition, depending on whether the surface zones are adjacent to a liquid phase. Such transformations can be expected to greatly affect wetting. Though the situation is probably analogous to the case of unfilled or filled pores (Cassie and Baxter 1944), further theoretical development appears to be needed to deal with such cases. Whether such zones can be reversibly wetted and de-wetted needs to be experimentally determined.

Rapid three-dimensional imaging of sessile drop interactions

As an alternative to rendering the cellulosic surface very flat, another approach would be to evaluate the wetting interactions in much finer detail. A more complete and nuanced understanding of the wetting of cellulosic surfaces might be achieved by three-dimensional, high speed, microscopic evaluation of the positions and movements of wetting fronts. The confocal microcopy approach has shown great promise for examining small three-dimensional objects of biological origin (Shotton 1989). Shen *et al.* (2000) employed confocal microscopy to detect and quantify air spaces between a drop of water and the surface of a hydrophobically sized paper sheet. With increases in instrumental capabilities, one can envision the possibility of high-speed acquisition of such information immediately after placement of a droplet on a paper surface. Such evidence would go a long way toward showing the practical implications of local convergences, divergences, and abrupt angles of surfaces within networks of pores (Kent and Lyne 1989). On the other hand, other situations might show a dominant influence of viscosity as the factor that limits the rate and extent of the liquid permeation.

Render the Surface Chemically Homogeneous

Suppose that it was possible to uniformize the chemical composition of a cellulosic surface, while maintaining the morphological characteristics exactly the same. Such a transformation could, in principle, provide a way to study just the morphological factors governing wetting. In fact, many of the studies cited in this article have involved extensive treatment with hydrophobizing agents, which work at a molecular level, leaving the morphological features essentially unchanged (Young 1976; Toussaint and Luner 1993; Erbil 1997; Wang and Piao 2011; Li 2014a). It is suggested that future studies could be carried out in which the wettability of different cellulosic surfaces, such as the radial, transverse, and tangential surface of wood, can be studied, focusing on the effects of their morphological differences.

Another approach to achieving the same kind of goal is to employ templating technology. Rather than study the cellulosic material directly, one creates a temporary "cast" of the surface. Then the cast is used as a mold to form a replica of the initial surface, but with an entirely new composition. Steps in such a direction were taken by Persson *et al.* (2004), who created a ceramic cast in order to reveal the internal pore structure of wood fibers. Likewise, Ni *et al.* (2008) prepared porous silica as the inverse-replica of poplar wood. However, a search of the literature did not reveal any complete replication of wood surfaces for purposes of contact angle analysis. Three-dimensional printing (Calvert 2001) may offer a related approach to being able to study the wettability of surfaces having specific morphological features representing cellulosic materials but with uniform chemical composition.

Combine the Chemical & Morphological Tracks of Analysis

Though separate consideration of physical chemical *vs.* morphological aspects of contact angle analysis may continue to be needed to clear up some theoretical aspects, one of the general conclusions that can be drawn from the present review of the literature is that there is an urgent need to simultaneously account for both chemical and morphological aspects during the wetting of cellulosic materials. As a start, it is proposed that the models of Wenzel (1936, see Eq. 14) and Cassie and Baxter (1944, see Eq. 15) become incorporated into future studies aimed at evaluation of different components of free energy associated with cellulosic surfaces. A rare example of such an approach is embodied in the work of Shen *et al.* (2000), who used the Cassie-Baxter equation to achieve a more accurate evaluation of the work of adhesion on sized and unsized paper sheets.

Another practical approach can take advantage of the fact that the pores at a cut surface of wood tend to fill up with a probe liquid – especially in the case of aqueous fluids – after being exposed to a liquid phase. Thus, contrary to the original situation envisioned by Cassie and Baxter (1944), one can have a completely different situation when comparing the first and second times that a given area of surface is being evaluated with an advancing meniscus. This situation is illustrated schematically in Fig. 14.

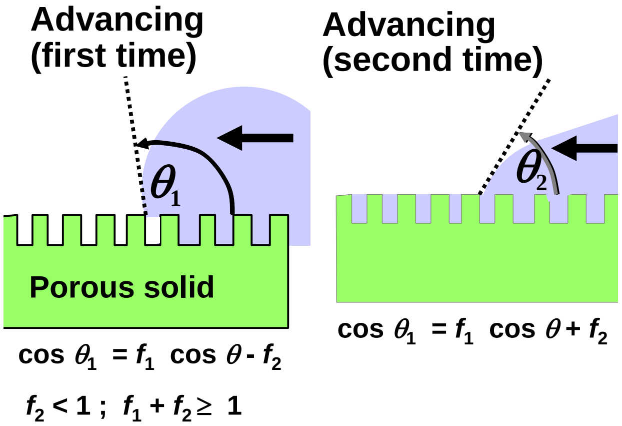


Fig. 14. Schematic illustration contrasting the first and second advancing contact angles on a porous surface, assuming that the pores gradually become filled when the liquid covers the surface

Limited work of this type has shown that the "second advancing contact angle" tends to be lower than the first (de Meijer *et al.* 2000; Bryne and Wålinder 2010). When such information is obtained in the case of cellulosic surfaces, this can provide an alternative means to estimate the energy contributions of the "land areas" of a surface, while being able to treat the "pore areas" as being perfectly wettable. If the relative area of the pores can be estimated, then one can then calculate effects attributable only to the cellulosic material. The initial advancing contact angle provides a contrasting set of input in which the cross-sectional area of open pores provides zero interaction. One would expect that there are many mathematical approaches that could be used for the fitting of contact angle data in a comprehensive manner in such situations.

Develop Better Probes for Lewis Acidity and Basicity

There has been an urgent need for better probes for Lewis acidity and basicity. The word "better," as used here, implies having a monopolar character as well as a relatively high surface tension with air. Probe liquids that have been used in published studies aimed at evaluating Lewis acid and base characteristics of cellulosic materials have been criticized with respect to having insufficient monopolar nature in some cases (Morra 1996; Shen *et al.* 1999; Della Volpe *et al.* 2004). Also, there is a continuing need for probe liquids that have contact angles large enough to be measured on a wide range of surfaces. Liquids having a high surface tension with air are the most likely to be able to develop high contact angles with a range of cellulose-related surfaces. Thus, in order to make progress, it is suggested that some future studies be carried out with designer compounds. For instance, one could start out with di-iodomethane (DIM) as the initial building block, given its high surface tension and widespread usage in contact angle analyses (Owens and Wendt 1969; Kaelble and Uy 1970; Fowkes *et al.* 1991; van Oss *et al.* 2001). Then one could obtain or synthesize derivatives of DIM with selected functional groups representing Lewis basicity or acidity. Alternatively, one could consider a family of such derivatives based on α-bromonaphthalene, which is also used as a nonpolar probe in evaluation of contact angles (Kudela 2014).

As a further goal, it is proposed to go beyond past work based on the donor and acceptor numbers of Gutmann *et al.* (1966) and Mayer *et al.* (1975). Those donor and acceptor numbers do not take into account the hard or soft characteristics of different Lewis acids and bases. So it is proposed that a future study take on the challenge of developing and using designer probe liquids based on the criteria of Drago and coworkers (Drago and Wayland 1965; Drago *et al.* 1971; 1977). Ideally one would then compare contact angles obtained with five related probe compounds – one having a high London dispersion interaction but no significant acidity or basicity, plus a series of four related compounds. The latter four would all share the same high London dispersion attribute (to provide a relatively high surface tension), with one having soft acidity, one having hard acidity, one having soft basicity, and one having hard basicity.

Add a Term or Terms for Hydrogen Bonding

Because of the uniqueness and relatively high strength of hydrogen bonding interactions, it is recommended that a future study or studies make a concerted effort to differentiate between hydrogen bonding contributions and other kinds of polar acid-base interactions affecting wettability. Already some steps in this direction have been taken in published studies. For instance, Kaelble and Uy (1970) used water as a probe compound in combination with separate use of di-iodomethane (DIM). More recently, Hansen (2007) has included a hydrogen bonding term in combination with both London dispersion interactions and generic polar interactions. Because strong hydrogen bonding is limited to certain combinations of elements, especially –OH groups, there ought to be a way, either experimentally or mathematically, to segregate hydrogen bonding effects from other interactions of polar molecules. What remains is to figure out how to do this while simultaneously considering Lewis acid and base interactions, alongside of strictly hydrogen bonding interactions. Presumably an orthogonal analysis could be achieved by avoiding Lewis probe compounds that have any hydrogen bonding capability.

The uniqueness of the contribution of hydrogen bonds, relative to contact angles, is supported by the work of Shi (2007) which seemed to show a disconnect between the interactions sensed by Hansen's approach, emphasizing hydrogen bonding contributions, *vs.* a Lewis acid-base approach. As shown in Fig. 15, which is replotted from that work, one of the systems was able to differentiate between certain of the probe liquids considered, while the other was able to differentiate between another group of compounds. Only by considering both sets of input together was it possible to get a full picture of the differences in wettability characteristics in terms of the degrees of both Lewis acid-base character and the degree of hydrogen bonding character.

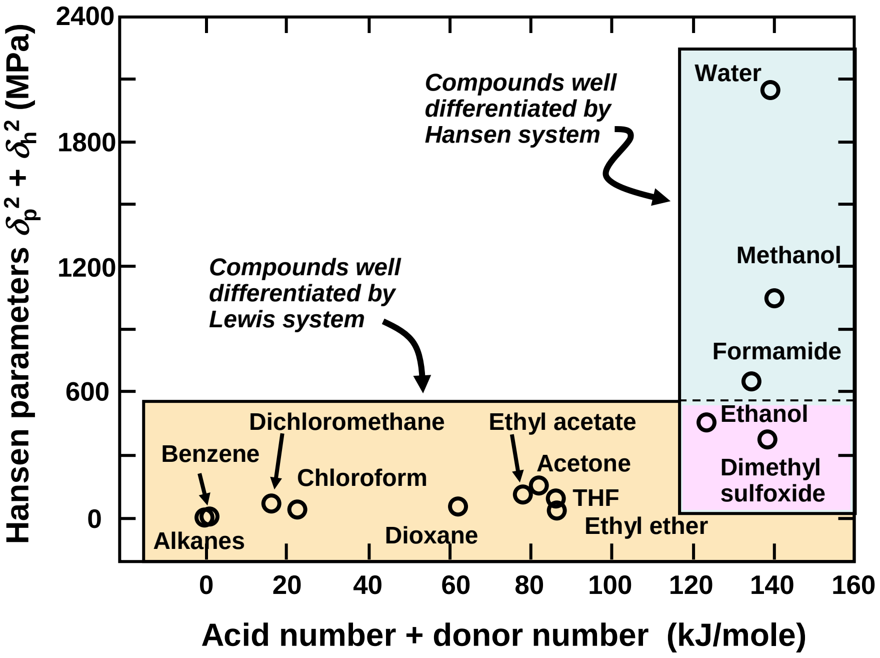


Fig. 15. Replotting of a graph by Shi (2007) contrasting a sum of Hansen parameters *vs.* the sum of Lewis acid and base numbers for some liquids often used in contact angle determinations

Use Immiscible Liquids to Develop Framework for Solids

The work of Fowkes *et al.* (1990), despite its central importance to the whole field covered in this article, seems like the dropping of a single shoe. Readers are waiting for something more. The cited authors used an innovative system of immiscible liquids to directly test the accuracy of some widely used concepts to predict the free energy components of solid surfaces based on contact angles. Not one of the existing approaches was judged to be worthy of further consideration. What remains to be done is to take an opposite approach: Start with a system such as that employed by Fowkes *et al.* (1990) and then attempt to find a completely different mathematical or conceptual model that would fit it. Caution should be employed, however, in applying the results of such work directly in the case of solid surfaces. It remains an open question as to whether the cited authors were correct in concluding that contact angle information is quite unrelated to the free energy of a real solid surface. On the other hand, it makes sense to frame the statement as, "if this solid surface were the surface of an immiscible liquid, then its surface free energy components would likely be as follows…"

Several of the authors cited earlier in this work have emphasized the potential advantages of basing one's analysis on a larger number of probe compounds (Gindl *et al.* 2001b). Presumably, such an approach decreases errors attributable to inaccuracies of estimation of coefficients assumed for individual probe liquids. On the other hand, one might steer away from compounds whose Lewis acid or base character is either not well understood or which is known to be significantly bipolar.

Numerical methods can be used to minimize the overall error of fitting, taking all of data from all of the probes into consideration (Fowkes *et al.* 1990; Della Volpe *et al.* 2004). Though there is nothing particularly original in the approach being suggested here, one gets the impression from the literature that researchers have not adequately grasped the degree to which their painstaking calculations could be found to be so woefully inaccurate (Fowkes *et al.* 1990).

Model 3D Interactions, Analogous to the Wenzel Equation

Much of the theory upon which wetting predictions have relied has been based on a two-dimensional model. Even though roughness involves a third dimension, Wenzel's (1936) equation effectively converts the problem back to an equivalent planar problem by defining a roughness coefficient. The fact that such a model might not be adequate was suggested by Oliver *et al.* (1977), who noted that the energy of wetting of fine granules in a bed might be significantly affected by the presence of sharp edges. But in addition, if one views wood or paper as a system of particles and pores, then it is reasonable to ask whether the energy of wetting within a three-dimensional layer of the solid ought to be incorporated into the analysis of contact angles. Hawker *et al.* (2015) noted the need for a three-dimensional analysis of wettability in the case of plasma-modified porous materials. Just as Wenzel used a coefficient r_w to account for the greater surface area of a rough surface in comparison to an equivalent ideally smooth surface, one could envision a coefficient r_w' to account for the surface areas within a three-dimensional zone of contact in comparison to the ideal flat surface plane. Details regarding the effective depth of such a zone, and whether or not the wetting of such a zone can be governed by the position of an adjacent meniscus, would need to be discovered.

Characterize Surface Composition to Explain Contact Angles

It is reasonable to expect in future years that progress in application of surface-sensitive chemical analyses will shed further light on the wettability of cellulosic surfaces. Analytical methods such as X-ray Photoelectron Spectroscopy (XPS) (van der Heide 2011), and Time of Flight Surface Ionization Mass Spectrometry (TOF-SIMS) (Belu *et al.* 2003) can be used to reveal the extent to which energetic oxygen-containing functionalities are present at cellulosic surfaces. Hydrophobic groups, such as alkyl groups, also can be quantified by such methods. Related information can be obtained by polyelectrolyte titrations (Wågberg *et al.* 1989), or potentiometric titrations (Herrington and Petzold 1992), especially to evaluate the presence of carboxylic acid functions on different cellulosic surfaces. Such information can be potentially helpful in the interpretation of the wettability phenomena observed for the same surfaces (Jacob and Berg 1993b). In summary, one can expect that the influence of chemical groups on the wettability of cellulosic surfaces will remain an intriguing field that will attract the interest of both scientists and engineers for many years into the future.

Compare Dry, Moist, and Wet Samples

Many of the analyses of contact angles considered in this review have involved absolutely dry systems. In addition, tests carried out with inverse gas chromatography are typically done in the absence of moisture (Gamelas 2013). On the other hand, moisture is known to affect water-wettability (Piao *et al.* 2010), and many processes having relevance to cellulosic materials take place in humid or wet environments. As noted by de Gennes (1985), the presence of moisture may be very important in systems where there are very high energy surfaces present; it is known that in a humid environment such surfaces will tend to be quickly leveled to a surface free energy closer to that of water. Dankovich and Gray (2011) observed that contact angles on saturated surfaces, composed of nanocrystalline cellulose films, were quite different from those on dry films of the same type. In view of these issues, it is recommended that some future work examine the wettability characteristics of cellulosic materials that are intentionally prepared with a wide range of moisture content. Since London dispersion and Lewis acid and base interactions will be of interest, a broad range of probe liquids should be considered in such work.

Practical Tests for Industrial Applications

Having just finished making some rather ambitious suggestions for future research work aimed at revealing mechanisms, it might be appropriate to add some comments more suited toward current industrial applications. For purposes of quality control or product development, it is probably fair to say that a reliable and reproducible assessment of wettability and adhesion potential of a surface is likely to be more valuable than a theoretically correct or theoretically complete approach. In that spirit, Table 4 lists some reasonably time-tested approaches that, while not capturing all of the potential information about acid and base contributions to wettability and adhesion, can be expected to reveal trends that could be useful for making adjustments to an industrial process.

Table 4. Wettability Analysis Systems to be Considered for Industrial Applications of Cellulosic Materials

System	Pros and Cons	Citation
Critical surface tensions	**Pros:** Easy experiments; can work well to judge London dispersion interactions. **Cons:** Tends to miss all polar contributions.	Fox and Zisman 1950
Di-iodomethane (DIM) and water	**Pros:** Pretty easy experiments; reliable. **Cons:** May miss some polar contributions.	Kaelble and Uy 1970
Solubility system	**Pros:** Multiple probes used; reliable. **Cons:** Does not sense Lewis contributions.	Hansen 2007

One of the goals of the scientific community, possibly over the next decade, will be to try to develop an improved model involving Lewis acid and base analysis. The goal will be to achieve a degree of internal consistency and explanatory power such that it is justified to place the system on a list such as that of Table 4. In the opinion of the present authors, it is still too early to nominate any of the existing approaches. Given the morphological challenges, as well as the expected swelling of cellulosic materials when in contact with some of the liquids of greatest interest, the point does not seem to have been reached yet where the absolute numbers obtained from analysis with Lewis acid and base probes can be trusted. Also, based on some key studies (Fowkes *et al.* 1990; Della Volpe *et al.* 2004), there appears to be a need to improve the currently available systems of analysis that incorporate Lewis acid and base concepts. The tendency of cellulosic materials to swell in the presence of water and certain other liquids of interest appears inconsistent with the assumptions underlying the Young equation (Eq. 1) and many related concepts. However, given the importance of cellulosic materials – as well as their printing, coating, adhesion, and the preparation of composites – it seems likely that many of the problems highlighted in the present review article will become increasingly well understood in the coming years.

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